

**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

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

Then

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

The eigenvalues of  $H_0$  are

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

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

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

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  $E_3^{(0)}$ , 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

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

**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

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

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

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

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

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

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  $\mathbf{E}$  field is given by (5.2.17) in Sakurai:

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

$V$  is a dipole interaction because the hydrogen atom has a nonzero dipole moment. Therefore  $V$  obeys the dipole selection rule, which is given by (17.2.21) in Shankar:

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

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  $Z$  is parity odd, so  $\langle nlm|Z|n'l'm'\rangle = 0$  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

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

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

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

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

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

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

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

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

$$\begin{aligned} Y_0^0(\theta, \phi) &= \sqrt{\frac{1}{2^2\pi}}, \\ Y_1^0(\theta, \phi) &= \sqrt{\frac{3}{2^2\pi}} \cos \theta, & Y_1^{\pm 1}(\theta, \phi) &= \mp \sqrt{\frac{3}{2^3\pi}} e^{\pm i\phi} \sin \theta, \\ Y_2^0(\theta, \phi) &= \sqrt{\frac{5}{2^4\pi}} (3 \cos^2 \theta - 1), & Y_2^{\pm 1}(\theta, \phi) &= \mp \sqrt{\frac{3^3 5}{2^3\pi}} e^{\pm i\phi} \cos \theta \sin \theta. \end{aligned}$$

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

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

Firstly,

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

where

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

and

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

where we have used

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

Combining these results, (6) becomes

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

Secondly,

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

where

$$\begin{aligned}
 \int_0^{2\pi} \int_{-1}^1 Y_2^{\pm 1*}(\theta, \phi) Y_1^{\pm 1}(\theta, \phi) \cos \theta d(\cos \theta) d\phi &= \int_0^{2\pi} \int_{-1}^1 \sqrt{\frac{3^{15}}{2^3 \pi}} e^{\mp i\phi} \cos \theta \sin \theta \sqrt{\frac{3}{2^3 \pi}} e^{\pm i\phi} \sin \theta \cos \theta d(\cos \theta) d\phi \\
 &= \frac{3\sqrt{5}}{2^3 \pi} \int_0^{2\pi} d\phi \int_{-1}^1 \cos^2 \theta \sin^2 \theta d(\cos \theta) = \frac{3\sqrt{5}}{2^3 \pi} \int_0^{2\pi} d\phi \int_{-1}^1 \cos^2 \theta (1 - \cos^2 \theta) d(\cos \theta) \\
 &= \frac{3\sqrt{5}}{2^3 \pi} \left[ \phi \right]_0^{2\pi} \left[ \frac{\cos^3 \theta}{3} - \frac{\cos^5 \theta}{5} \right]_{-1}^1 = \frac{3\sqrt{5}}{2^3 \pi} (2\pi) \frac{2^2}{3^{15}} = \frac{1}{\sqrt{5}},
 \end{aligned}$$

and

$$\begin{aligned}
 \int_0^\infty R_{32}(r) R_{31}(r) \rho^3 d\rho &= \int_0^\infty \sqrt{\frac{e^{-\rho}}{2^7 3^7 5^3 a_0^3}} \rho^2 L_5^5(\rho) \sqrt{\frac{e^{-\rho}}{2^7 3^7 a_0^3}} \rho L_4^3(\rho) \rho^3 d\rho = \frac{1}{2^7 3^7 \sqrt{5^3} a_0^3} \int_0^\infty e^{-\rho} L_5^5(\rho) L_4^3(\rho) \rho^6 d\rho \\
 &= -\frac{1}{2^{13} 3^5 \sqrt{5} a_0^3} \int_0^\infty e^{-\rho} (-4 + \rho) \rho^6 d\rho = -\frac{1}{2^{13} 3^5 \sqrt{5} a_0^3} \int_0^\infty e^{-\rho} (-4\rho^6 + \rho^7) d\rho = -\frac{1}{2^{13} 3^5 \sqrt{5} a_0^3} (-4(6!) + 7!) \\
 &= -\frac{2^3 \sqrt{5}}{3^2 a_0^3}.
 \end{aligned}$$

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,

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

where

$$\begin{aligned}
 \int_0^{2\pi} \int_{-1}^1 Y_2^{0*}(\theta, \phi) Y_1^0(\theta, \phi) \cos \theta d(\cos \theta) d\phi &= \int_0^{2\pi} \int_{-1}^1 \sqrt{\frac{5}{2^4 \pi}} (3 \cos^2 \theta - 1) \sqrt{\frac{3}{2^2 \pi}} \cos \theta \cos \theta d(\cos \theta) d\phi \\
 &= \frac{\sqrt{3} \sqrt{5}}{2^3 \pi} \int_0^{2\pi} d\phi \int_{-1}^1 (3 \cos^4 \theta - \cos^2 \theta) d(\cos \theta) = \frac{\sqrt{3} \sqrt{5}}{2^3 \pi} \left[ \phi \right]_0^{2\pi} \left[ \frac{3 \cos^5 \theta}{5} - \frac{\cos^3 \theta}{3} \right]_{-1}^1 = \frac{\sqrt{3} \sqrt{5}}{2^3 \pi} (2\pi) \frac{2^3}{3^{15}} \\
 &= \frac{2}{\sqrt{3} \sqrt{5}},
 \end{aligned}$$

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

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

**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

$$\begin{aligned} 0 &= \det \left( \frac{V}{e|\mathbf{E}|a_0} - \mu I \right) \\ &= \begin{vmatrix} -\mu & 0 & 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\mu & 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & 0 \\ 3\sqrt{6} & 0 & -\mu & 0 & 0 & 0 & 3\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 9/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 0 & 0 \\ 0 & 9/2 & 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 0 \\ 0 & 0 & 3\sqrt{3} & 0 & 0 & 0 & -\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & -\mu & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mu & 0 \end{vmatrix} \\ &= \begin{vmatrix} -\mu & 0 & 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\mu & 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\mu^2-54}{\mu} & 0 & 0 & 0 & 3\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 9/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{81/4-\mu^2}{\mu} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\mu(81-\mu^2)}{\mu^2-54} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{81/4-\mu^2}{\mu} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mu & 0 \end{vmatrix} \\ &= (-\mu)^5 \frac{\mu^2-54}{\mu} \left( \frac{81/4-\mu^2}{\mu} \right)^2 \frac{\mu(81-\mu^2)}{\mu^2-54} = -\mu^3 \left( \frac{81}{4} - \mu^2 \right)^2 (81 - \mu^2) \\ &= \mu^3 \left( \frac{9}{2} - \mu \right)^2 \left( \frac{9}{2} + \mu \right)^2 (9 - \mu)(9 + \mu), \end{aligned}$$

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

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

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

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

From the lecture notes and (5.2.12) in Sakurai, the effective Hamiltonian is given to second order in  $\lambda$  by

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

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. Here,  $P_0$  projects onto the subspace spanned by  $\{|1\rangle, |2\rangle\}$  and  $P_1$  onto that spanned by  $\{|3\rangle\}$ .

Note that

$$P_0 V P_0 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ v_1^* & v_2^* & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

and

$$\begin{aligned} P_0 V P_1 (E_D^{(0)} - H_0)^{-1} P_1 V P_0 &= \frac{1}{E_D^{(0)} - E_3^{(0)}} P_0 V \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} V P_0 \\ &= \frac{1}{E_D^{(0)} - E_3^{(0)}} P_0 \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ v_1^* & v_2^* & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ v_1^* & v_2^* & 0 \end{bmatrix} P_0 = \frac{1}{E_D^{(0)} - E_3^{(0)}} P_0 \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ v_1^* & v_2^* & 0 \end{bmatrix} P_0 \\ &= \frac{1}{E_D^{(0)} - E_3^{(0)}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} |v_1|^2 & v_1 v_2^* & 0 \\ v_1^* v_2 & |v_1|^2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \frac{1}{E_D^{(0)} - E_3^{(0)}} \begin{bmatrix} |v_1|^2 & v_1 v_2^* & 0 \\ v_1^* v_2 & |v_1|^2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \end{aligned}$$

In the degenerate subspace, we have

$$H_{\text{eff}} = \begin{bmatrix} E_D^{(0)} + |v_1|^2 / (E_D^{(0)} - E_3^{(0)}) & v_1 v_2^* / (E_D^{(0)} - E_3^{(0)}) \\ v_1^* v_2 / (E_D^{(0)} - E_3^{(0)}) & E_D^{(0)} + |v_2|^2 / (E_D^{(0)} - E_3^{(0)}) \end{bmatrix}.$$

**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.)

**Solution.** Let  $E$  be the eigenvalues of  $H_{\text{eff}}$ . We need to solve the characteristic equation

$$\begin{aligned}
 0 &= \det(H_{\text{eff}} - EI) = \begin{vmatrix} E_D^{(0)} + |v_1|^2/(E_D^{(0)} - E_3^{(0)}) - E & v_1 v_2^*/(E_D^{(0)} - E_3^{(0)}) \\ v_1^* v_2/(E_D^{(0)} - E_3^{(0)}) & E_D^{(0)} + |v_2|^2/(E_D^{(0)} - E_3^{(0)}) - E \end{vmatrix} \\
 &= \left( E_D^{(0)} + \frac{|v_1|^2}{E_D^{(0)} - E_3^{(0)}} - E \right) \left( E_D^{(0)} + \frac{|v_2|^2}{E_D^{(0)} - E_3^{(0)}} - E \right) - \frac{|v_1|^2 |v_2|^2}{(E_D^{(0)} - E_3^{(0)})^2} \\
 &= E_D^{(0)2} - E_D^{(0)} \frac{|v_2|^2}{E_D^{(0)} - E_3^{(0)}} - E_D^{(0)} E + E_D^{(0)} \frac{|v_1|^2}{E_D^{(0)} - E_3^{(0)}} - E \frac{|v_1|^2}{E_D^{(0)} - E_3^{(0)}} - E_D^{(0)} E - E \frac{|v_2|^2}{E_D^{(0)} - E_3^{(0)}} + E^2 \\
 &= E^2 - E_D^{(0)} E - E \frac{|v_1|^2 + |v_2|^2}{E_D^{(0)} - E_3^{(0)}} - E_D^{(0)} E + E_D^{(0)2} + E_D^{(0)} \frac{|v_1|^2 + |v_2|^2}{E_D^{(0)} - E_3^{(0)}} \\
 &= (E - E_D^{(0)}) \left( E - E_D^{(0)} - \frac{|v_1|^2 |v_2|^2}{(E_D^{(0)} - E_3^{(0)})^2} \right)
 \end{aligned}$$

so the eigenvalues are

$$E_1 = E_D^{(0)}, \quad E_2 = E_D^{(0)} + \frac{|v_1|^2 |v_2|^2}{(E_D^{(0)} - E_3^{(0)})^2}.$$

The eigenvector corresponding to  $E_1$  can be found by

$$\begin{bmatrix} E_D^{(0)} + |v_1|^2/(E_D^{(0)} - E_3^{(0)}) & v_1 v_2^*/(E_D^{(0)} - E_3^{(0)}) \\ v_1^* v_2/(E_D^{(0)} - E_3^{(0)}) & E_D^{(0)} + |v_2|^2/(E_D^{(0)} - E_3^{(0)}) \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = E_D^{(0)} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix}$$

which is equivalent to the system of equations

$$\left( E_D^{(0)} + \frac{|v_1|^2}{E_D^{(0)} - E_3^{(0)}} \right) u_1 + \frac{v_1 v_2^*}{E_D^{(0)} - E_3^{(0)}} u_2 = E_D^{(0)} u_1, \quad \frac{v_1^* v_2}{E_D^{(0)} - E_3^{(0)}} u_1 + \left( E_D^{(0)} + \frac{|v_2|^2}{E_D^{(0)} - E_3^{(0)}} \right) u_2 = E_D^{(0)} u_2.$$

By inspection, these are satisfied when  $u_1 = -v_2^*$  and  $u_2 = v_1^*$ .

For the eigenvector corresponding to  $E_2$ , we have

$$\begin{bmatrix} E_D^{(0)} + |v_1|^2/(E_D^{(0)} - E_3^{(0)}) & v_1 v_2^*/(E_D^{(0)} - E_3^{(0)}) \\ v_1^* v_2/(E_D^{(0)} - E_3^{(0)}) & E_D^{(0)} + |v_2|^2/(E_D^{(0)} - E_3^{(0)}) \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \end{bmatrix} = \left( E_D^{(0)} + \frac{|v_1|^2 + |v_2|^2}{E_D^{(0)} - E_3^{(0)}} \right) \begin{bmatrix} w_1 \\ w_2 \end{bmatrix}$$

which is equivalent to the system of equations

$$\begin{aligned}
 \left( E_D^{(0)} + \frac{|v_1|^2}{E_D^{(0)} - E_3^{(0)}} \right) w_1 + \frac{v_1 v_2^*}{E_D^{(0)} - E_3^{(0)}} w_2 &= \left( E_D^{(0)} + \frac{|v_1|^2 + |v_2|^2}{E_D^{(0)} - E_3^{(0)}} \right) w_1, \\
 \frac{v_1^* v_2}{E_D^{(0)} - E_3^{(0)}} w_1 + \left( E_D^{(0)} + \frac{|v_2|^2}{E_D^{(0)} - E_3^{(0)}} \right) w_2 &= \left( E_D^{(0)} + \frac{|v_1|^2 + |v_2|^2}{E_D^{(0)} - E_3^{(0)}} \right) w_2.
 \end{aligned}$$

By inspection, these are satisfied when  $w_1 = v_1$  and  $w_2 = v_2$ . So we have the eigenvectors

$$|E_1\rangle = \begin{bmatrix} -v_2^* \\ v_1^* \end{bmatrix}, \quad |E_2\rangle = \begin{bmatrix} v_1 \\ v_2 \end{bmatrix}.$$

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