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 3×3 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 σ_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 μ are the roots of the equation

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

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 λ 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 9×9 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 because the hydrogen atom can be thought of as behaving like a dipole when subject to an external electric field. Therefore V 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

$$R_{30}(r) = -\sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(3-1)!}{2(3)3!^3}}e^{-\rho/2}L_3^1(\rho) = -\sqrt{\frac{2^3}{3^3a_0^3}\frac{2}{2^43^4}}e^{-\rho/2}L_3^1(\rho) = -\sqrt{\frac{e^{-\rho}}{3^7a_0^3}}L_3^1(\rho),$$
$$R_{31}(r) = -\sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(3-1-1)!}{2(3)(3+1)!^3}}e^{-\rho/2}\rho L_{3+1}^{2+1}(\rho) = -\sqrt{\frac{2^3}{3^3a_0^3}\frac{1}{2^{10}3^4}}e^{-\rho/2}\rho L_4^3(\rho) = -\sqrt{\frac{e^{-\rho}}{2^73^7a_0^3}}\rho L_4^3(\rho),$$
$$R_{32}(r) = -\sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(3-2-1)!}{2(3)(3+2)!^3}}e^{-\rho/2}\rho^2 L_{3+2}^{4+1}(\rho) = -\sqrt{\frac{2^3}{3^3a_0^3}\frac{1}{2^{10}3^45^3}}e^{-\rho/2}\rho^2 L_5^5(\rho) = -\sqrt{\frac{e^{-\rho}}{2^73^75^3a_0^3}}\rho^2 L_5^5(\rho).$$

From (4), the relevant L_p are

$$L_3(\rho) = e^\rho\frac{d^3}{d\rho^3} = e^\rho\frac{d^2}{d\rho^2} = e^\rho\frac{d}{d\rho} = 6 - 18\rho + 9\rho^2 - \rho^3,$$

$$\begin{aligned} L_4(\rho) &= e^\rho\frac{d^4}{d\rho^4} = e^\rho\frac{d^3}{d\rho^3} = e^\rho\frac{d^2}{d\rho^2} \\ &= e^\rho\frac{d}{d\rho} = 24 - 96\rho + 72\rho^2 - 16\rho^3 + \rho^4, \end{aligned}$$

$$\begin{aligned} L_5(\rho) &= e^\rho\frac{d^5}{d\rho^5} = e^\rho\frac{d^4}{d\rho^4} = e^\rho\frac{d^3}{d\rho^3} \\ &= e^\rho\frac{d^2}{d\rho^2} \\ &= e^\rho\frac{d}{d\rho} = 120 - 600\rho + 600\rho^2 - 200\rho^3 + 25\rho^4 - \rho^5 \end{aligned}$$

and then the relevant L_p^q are

$$\begin{aligned} L_3^1(\rho) &= \frac{dL_3(\rho)}{d\rho} = -18 + 18\rho - 3\rho^2 = -3(6 - 6\rho + \rho^2), \\ L_4^3(\rho) &= \frac{d^3L_4(\rho)}{d\rho^3} = -(3!)16 + \left(\frac{4!}{1!}\right)\rho = 24(-4+\rho) = 2^33(-4+\rho), \\ L_5^5(\rho) &= \frac{d^5L_5(\rho)}{d\rho^5} = -5! = -120 = -2^33^15. \end{aligned}$$

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

$$
\begin{aligned}
Y_0^0(\theta,\phi) &= \sqrt{\frac{1}{2^2\pi}}, \\
Y_1^0(\theta,\phi) &= \sqrt{\frac{3}{2^2\pi}}\cos\theta, & Y_1^{\pm1}(\theta,\phi) &= \mp\sqrt{\frac{3}{2^3\pi}}e^{\pm i\phi}\sin\theta, \\
Y_2^0(\theta,\phi) &= \sqrt{\frac{5}{2^4\pi}}(3\cos^2\theta-1), & Y_2^{\pm1}(\theta,\phi) &= \mp\sqrt{\frac{3^1 5}{2^3\pi}}e^{\pm i\phi}\cos\theta\sin\theta.
\end{aligned}
$$

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

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

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

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

and

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

where we have used

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

Combining these results, (6) becomes

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

Secondly,

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

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

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

For the hydrogen atom, H_0 is ninefold degenerate, so we need to find the eigenvalues of the full matrix V given by (**??**). Let $\Delta_i^{(1)} = e|\mathbf{E}|a_0\mu_i$ denote the eigenvalues of V, where μ are the roots of the equation

$$0 = \det(V - \mu I) =$$

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, E_2, E_3. Assume $E_1 = E_2 = E$. 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 $\{|1\rangle, |2\rangle\}$.

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 Shankar's *Principles of Quantum Mechanics* in addition to Sakurai's *Modern Quantum Mechanics* while writing up these solutions.