

**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

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

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

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

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 can be thought of as behaving like a dipole when subjected to an external electric field. 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  $\langle nlm|Z|n'l'm'\rangle = 0$  unless  $l$  and  $l'$  have opposite parity.

For the nonzero elements, the hydrogen atom wavefunctions 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),

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

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

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

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

$$R_{30}(r) = -\frac{e^{-\rho/2}}{27\sqrt{3}a_0^{3/2}} L_3^1(\rho), \quad R_{31}(r) = -\frac{e^{-\rho/2}\rho}{216\sqrt{6}a_0^{3/2}} L_4^3(\rho), \quad R_{32}(r) = -\frac{e^{-\rho/2}\rho^2}{1080\sqrt{30}a_0^{3/2}} L_5^5(\rho).$$

From (4), the relevant  $L_p^q$  are

$$\begin{aligned} L_3^1(\rho) &= \frac{24 - 36\rho + 12\rho^2 - \rho^3}{6}, \\ L_4^3(\rho) &= \frac{840 - 840\rho + 252\rho^2 - 28\rho^3 + \rho^4}{24}, \\ L_5^5(\rho) &= \frac{30240 - 25200\rho + 7200\rho^2 - 900\rho^3 + 50\rho^4 - \rho^5}{120}. \end{aligned}$$

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

$$\begin{aligned} Y_0^0(\theta, \phi) &= \sqrt{\frac{1}{4\pi}}, \\ Y_1^0(\theta, \phi) &= \sqrt{\frac{3}{4\pi}} \cos \theta, & Y_1^{\pm 1}(\theta, \phi) &= \mp \sqrt{\frac{3}{8\pi}} e^{\pm i\phi} \sin \theta, \\ Y_2^0(\theta, \phi) &= \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1), & Y_2^{\pm 1}(\theta, \phi) &= \mp \sqrt{\frac{15}{8\pi}} e^{\pm i\phi} \cos \theta \sin \theta. \end{aligned}$$

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

$$\begin{aligned} \langle 3lm | V | 3l'm' \rangle &= -e|\mathbf{E}| \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_{3lm}^*(r, \theta, \phi) r \cos \theta \psi_{3l'm'}(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi \\ &= -\frac{81a_0^4 e |\mathbf{E}|}{16} \int_0^{2\pi} \int_{-1}^1 \int_0^\infty \psi_{3lm}^*(r, \theta, \phi) \psi_{3l'm'}(r, \theta, \phi) \rho^3 \cos \theta d\rho d(\cos \theta) d\phi. \end{aligned}$$

For the particular matrix elements, we have

$$\begin{aligned} V_{310}^{300} &= \langle 310 | V | 300 \rangle = -\frac{81a_0^4 e |\mathbf{E}|}{16} \int_0^{2\pi} \int_{-1}^1 \int_0^\infty R_{31}(r) Y_1^{0*}(\theta, \phi) R_{30} Y_0^0(\theta, \phi) \rho^3 \cos \theta d\rho d(\cos \theta) d\phi \\ &= -\frac{a_0 e |\mathbf{E}|}{4608\sqrt{6}\pi} \int_0^{2\pi} \int_{-1}^1 \int_0^\infty L_4^3(\rho) L_3^1(\rho) e^{-\rho} \rho^4 \cos^2 \theta d\rho d(\cos \theta) d\phi \\ &= -\frac{a_0 e |\mathbf{E}|}{2304\sqrt{6}} \int_{-1}^1 \int_0^\infty L_4^3(\rho) L_3^1(\rho) e^{-\rho} \rho^4 \cos^2 \theta d\rho d(\cos \theta) \\ &= -\frac{a_0 e |\mathbf{E}|}{3456\sqrt{6}} \int_{-1}^1 \int_0^\infty L_4^3(\rho) L_3^1(\rho) e^{-\rho} \rho^4 d\rho \end{aligned}$$

$$\begin{aligned}
 &= -\frac{a_0 e |\mathbf{E}|}{497664\sqrt{6}} \int_0^\infty e^{-\rho} \rho^4 (840 - 840\rho + 252\rho^2 - 28\rho^3 + \rho^4) (24 - 36\rho + 12\rho^2 - \rho^3) d\rho \\
 &= -\frac{a_0 e |\mathbf{E}|}{497664\sqrt{6}} \int_0^\infty e^{-\rho} (20160\rho^4 - 50400\rho^5 + 46368\rho^6 - 20664\rho^7 + 4896\rho^8 - 634\rho^9 + 40\rho^{10} - \rho^{11}) d\rho \\
 &= \frac{35}{144\sqrt{6}} a_0 e |\mathbf{E}| = \langle 300 | V | 310 \rangle,
 \end{aligned}$$

$$\begin{aligned}
 V_{32\pm 1}^{31\pm 1} &= \langle 32 \pm 1 | V | 31 \pm 1 \rangle = -\frac{81 a_0^4 e |\mathbf{E}|}{16} \int_0^{2\pi} \int_{-1}^1 \int_0^\infty R_{32}(r) Y_2^{\pm 1*}(\theta, \phi) R_{31}(r) Y_1^{\pm 1}(\theta, \phi) \rho^3 \cos \theta d\rho d(\cos \theta) d\phi \\
 &= -\frac{a_0 e |\mathbf{E}|}{737280\pi} \int_0^{2\pi} \int_{-1}^1 \int_0^\infty L_4^3(\rho) L_5^5(\rho) e^{-\rho} \rho^6 \cos^2 \theta \sin^2 \theta d\rho d(\cos \theta) d\phi \\
 &= -\frac{a_0 e |\mathbf{E}|}{368640} \int_{-1}^1 \int_0^\infty L_4^3(\rho) L_5^5(\rho) e^{-\rho} \rho^6 \cos^2 \theta \sin^2 \theta d\rho d(\cos \theta) \\
 &= -\frac{a_0 e |\mathbf{E}|}{5898250} \int_0^\infty L_4^3(\rho) L_5^5(\rho) e^{-\rho} \rho^6 d\rho \\
 &= -\frac{a_0 e |\mathbf{E}|}{16986931200} \int_0^\infty e^{-\rho} \rho^6 (-\rho^{15} + 78\rho^{14} - 2552\rho^{13} + 45840\rho^{12} - 496440\rho^{11} + 3348240\rho^{10} \\
 &\quad - 14001120\rho^9 + 34836480\rho^8 - 46569600\rho^7 + 25401600\rho^6) d\rho \\
 &= \frac{105}{4096} a_0 e |\mathbf{E}| = \langle 31 \pm 1 | V | 32 \pm 1 \rangle,
 \end{aligned}$$

Therefore,

$nlm$	300	31-1	310	311	32-2	32-1	320	321	322
300	0	0		0	0	0	0	0	0
31-1	0	0	0	0	0		0	0	0
310		0	0	0	0	0		0	0
311	0	0	0	0	0	0	0		0
32-2	0	0	0	0	0	0	0	0	0
32-1	0		0	0	0	0	0	0	0
320	0	0		0	0	0	0	0	0
321	0	0	0		0	0	0	0	0
322	0	0	0	0	0	0	0	0	0

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

**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.