4142 HW 6

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Problem 1. *Consider the energy matrix*

$$H = V_0 \begin{pmatrix} 1-\epsilon & 0 & 0 \\ 0 & 1 & \epsilon \\ 0 & \epsilon & 2 \end{pmatrix}$$

where V_0 is constant and ϵ is a small number.

- *Find the exact eigenvalues and eigenvectors of this Hamiltonian.*
- *Use first- and second-order non-degenerate perturbation theory to derive the energy corrections to the unperturbed problem with $\epsilon = 0$.*
- *Use first order degenerate perturbation theory to derive the energy corrections. Compare the results.*

Solution. Clearly, one eigenvector is the first basis state with eigenvalue $V_0(1-\epsilon)$. We can diagonalize the 2×2 matrix pretty easily:

$$\det \begin{vmatrix} 1-\lambda & \epsilon \\ \epsilon & 2-\lambda \end{vmatrix} = 2 - 3\lambda + \lambda^2 - \epsilon^2 \Rightarrow \lambda = \frac{3 \pm \sqrt{1+4\epsilon^2}}{2}$$

The corresponding eigenvectors are

$$\begin{pmatrix} \frac{-1\pm\sqrt{1+4\epsilon^2}}{2\epsilon} \\ 1 \end{pmatrix}$$

The eigenvalues and eigenvectors for the overall problem are then

$$V_0(1-\epsilon) \to \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$V_0 \frac{3-\sqrt{1+4\epsilon^2}}{2} \to \begin{pmatrix} 0 \\ \frac{-1-\sqrt{1+4\epsilon^2}}{2\epsilon} \\ 1 \end{pmatrix}$$

$$V_0 \frac{3+\sqrt{1+4\epsilon^2}}{2} \to \begin{pmatrix} 0 \\ \frac{-1+\sqrt{1+4\epsilon^2}}{2\epsilon} \\ 1 \end{pmatrix}$$

We write the Hamiltonian as

$$H = H_0 + H' = V_0 \left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \epsilon \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \right]$$

We must first compute the 0th-order terms: the solution to the H_0 problem. This is trivial, as the problem is diagonalized: there are two eigenstates with energies V_0 and one with eigenstate $2V_0$ corresponding exactly to the basis states with respect to which the problem is presented. First-order non-degenerate theory gives us

$$E_n^1 = \left\langle \psi_n^0 \right| H' \left| \psi_n^0 \right\rangle .$$

Sticking with the eigenbasis for H_0,

$$E_1^1 = \left\langle \psi_1^0 \right| H' \left| \psi_1^0 \right\rangle = -\epsilon V_0$$

$$E_2^1 = \left\langle \psi_2^0 \right| H' \left| \psi_2^0 \right\rangle = 0$$

$$E_3^1 = \left\langle \psi_3^0 \right| H' \left| \psi_3^0 \right\rangle = 0$$

The second-order non-degenerate theory yields

$$E_1^2 = \frac{\left| \left\langle \psi_2^0 \right| H' \left| \psi_1^0 \right\rangle \right|^2}{E_1^0 - E_2^0} + \frac{\left| \left\langle \psi_3^0 \right| H' \left| \psi_1^0 \right\rangle \right|^2}{E_1^0 - E_3^0} = 0$$

$$E_2^2 = \frac{\left| \left\langle \psi_1^0 \right| H' \left| \psi_2^0 \right\rangle \right|^2}{E_2^0 - E_1^0} + \frac{\left| \left\langle \psi_3^0 \right| H' \left| \psi_2^0 \right\rangle \right|^2}{E_2^0 - E_3^0} = \frac{|\epsilon V_0|^2}{V_0 - 2V_0} = -\epsilon^2 V_0$$

$$E_3^2 = \frac{\left| \left\langle \psi_1^0 \right| H' \left| \psi_3^0 \right\rangle \right|^2}{E_3^0 - E_1^0} + \frac{\left| \left\langle \psi_2^0 \right| H' \left| \psi_3^0 \right\rangle \right|^2}{E_3^0 - E_2^0} = \frac{|\epsilon V_0|^2}{2V_0 - V_0} = \epsilon^2 V_0$$

For the more suitable first-order degenerate correction, we must first find an operator mutually commuting with H_0 and H'. Using the fact that if the product of symmetric matrices is symmetric, then they commute, any diagonal matrix will commute with both. Choose

$$A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3 \end{pmatrix} .$$

Accordingly, the first and second basis eigenstates are suitable to remove their degeneracy in the unperturbed state. The matrix whose eigenvalues are the first-order degenerate corrections is given by

$$W = \epsilon V_0 \begin{pmatrix} -1 & 0 \\ 0 & 0 \end{pmatrix}$$

The eigenvalues are given trivially as $E_\pm^1 = 0, -\epsilon V_0$ These are exactly the non-degenerate first-order corrections to E_1^1 and E_2^1. $\square$

Problem 2. *For the harmonic oscillator with $V(x) = kx^2/2$, the allowed energies are $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$ with $\hbar\omega = \sqrt{k/m}$. Suppose the spring is cooled so that the spring constant rises slightly to $k(1+\epsilon)$.*

1. *Find the exact new energies. Expand in ϵ to second order.*
2. *Instead, treat by perturbation theory to calculate the first order correction to the energy. Compare the results.*

Solution. The new energies are given by $k \mapsto k(\epsilon+1)$, so $E'_n = \left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{k}{m}}\sqrt{1+\epsilon}$. Using the Maclaurin series of $\sqrt{1+x}$, this is to second order

$$E_n^2 = \left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{k}{m}}\left[1+\frac{\epsilon}{2}-\frac{\epsilon^2}{8}\right].$$

Perturbatavely, the perturbation to the Hamiltonian is $H' = \epsilon H_0$, so

$$E_n^1 = \langle\psi_n^0|\, H'\, |\psi_n^0\rangle = \epsilon\left(\frac{1}{2}\hbar\sqrt{\frac{k}{m}}\right)$$

This is precisely the first-order term in the series expansion of the exact solution. □

Problem 3. *Estimate the energy correction to the ground state of the hydrogen atom arising from the finite size of the proton (approx 10^{-13} cm). Assume all the charge of the proton is distributed uniformly on*

1. *the surface of the proton,*
2. *the volume of the proton.*

Solution. With a spherical shell of charge, the electric field inside is zero by Gauss's law, so the potential inside is the potential of a point charge at the boundary: $-\frac{e^2}{4\pi\epsilon_0 r_p}$, where r_p is the radius of the proton. Similarly, for a solid sphere of charge, by Gauss's law the electric field is as a point charge at the center, but the size of that charge is proportional to the volume enclosed by a concentric Gaussian sphere:

$$|E| = \frac{e^2}{4\pi\epsilon_0 r^2}\frac{r^3}{r_p^3} = \frac{e^2}{4\pi\epsilon_0}\frac{r}{r_p^3}$$

Integrating from r_p (whereupon $V = -\frac{e^2}{4\pi\epsilon_0 r_p}$ as before) to r, the potential is

$$V = -\frac{e^2}{8\pi\epsilon_0 r_p^3}(r^2 - r_p^2) - \frac{e^2}{4\pi\epsilon_0 r_p} = -\frac{e^2 r^2}{8\pi\epsilon_0 r_p^3} - \frac{e^2}{8\pi\epsilon_0 r_p}$$

Accordingly, we get new Hamiltonians

$$H = H_0 + H' = \left(\frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}\right) + \Theta(r_p - r)\left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r_p}\right)$$

and

$$H = H_0 + H' = \left(\frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}\right) + \Theta(r_p - r)\left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2 r^2}{8\pi\epsilon_0 r_p^3} - \frac{e^2}{8\pi\epsilon_0 r_p}\right)$$

The first-order correction to the energies can be computed directly:

$$E_n^1 = \langle\psi_n^0|\, H'\, |\psi_n^0\rangle = \langle\psi_n^0|\, \Theta(r_p - r)\left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{8\pi\epsilon_0 r_p}\right) |\psi_n^0\rangle$$

$$= \frac{e^2}{4\pi\epsilon_0} \langle n\ell m| \frac{\Theta(r_p - r)}{r} |n\ell m\rangle - \frac{e^2}{8\pi\epsilon_0 r_p} \langle n\ell m| \Theta(r_p - r) |n\ell m\rangle$$

and

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \langle \psi_n^0 | \Theta(r_p - r) \left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2 r^2}{8\pi\epsilon_0 r_p^3} - \frac{e^2}{8\pi\epsilon_0 r_p} \right) |\psi_n^0\rangle$$

$$= \frac{e^2}{4\pi\epsilon_0} \langle n\ell m| \frac{\Theta(r_p - r)}{r} |n\ell m\rangle - \frac{e^2}{8\pi\epsilon_0 r_p^3} \langle n\ell m| r^2\Theta(r_p - r) |n\ell m\rangle - \frac{e^2}{8\pi\epsilon_0 r_p} \langle n\ell m| \Theta(r_p - r) |n\ell m\rangle$$

To evaluate these, we need to compute several integrals; the angular variables are trivially 1, but the radial integrals are

$$\langle n\ell m| \frac{\Theta(r_p - r)}{r} |n\ell m\rangle = \int_0^{r_p} r|R_{n\ell}(r)|^2 dr$$

$$\langle n\ell m| r^2\Theta(r_p - r) |n\ell m\rangle = \int_0^{r_p} r^3|R_{n\ell}(r)|^2 dr$$

$$\langle n\ell m| \Theta(r_p - r) |n\ell m\rangle = \int_0^{r_p} r^2|R_{n\ell}(r)|^2 dr$$

which, since we're going to first-order anyway, can be estimated by exploiting orthogonality with the approximation

$$\int_0^{r_p} r^2|R_{n\ell}(r)|^2 dr \approx \int_0^{\infty} r^2|R_{n\ell}(r)|^2 dr = 1$$

since $R_{n\ell}(r) \sim e^{-r}$ as $r \to \infty$. This allows us to prove an inductive formula via integration by parts: forms a base case, and

$$\int_0^{r_p} r^3|R_{n\ell}(r)|^2$$

$$\int_0^{r_p} r^n|R_{n\ell}(r)|^2 dr = r_p^{n-2} - \int_0^{r_p}$$

□

Problem 4. *For a two-electron configuration $2p3p$, find the states in $^{2S+1}L_J$ notation.*

Solution. One electron has $n = 2$, $\ell = 2$, and the other $n = 3$, $\ell = 2$. The possible total spin states of the system are the integers from $\frac{1}{2} + \frac{1}{2}$ to $\frac{1}{2} - \frac{1}{2}$, i.e. 1 and 0. The possible L are the integers between 4 and 0, i.e. 0, 1, 2, 3, 4. If the spin is zero, the possible J are 0, 1, 2, 3, 4, and if the spin is one, the possible J are 0, 1, 2, 3, 4, 5. We now list all those states: for spin zero, all of J must come from L, so

$$^1S_0, {}^1P_1, {}^1D_2, {}^1F_3, {}^1G_4,$$

and for spin-1, each L can have total spin $L + 1$, L, or $|L - 1|$, so

$$^3S_0, {}^3S_1, {}^3P_0, {}^3P_1, {}^3P_2, {}^3D_1, {}^3D_2, {}^3D_3, {}^3F_2, {}^3F_3{}^3F_4, {}^3G_3, {}^3G_4, {}^3G_5$$

exhausts the possible states. □

Problem 5. *Consider the Zeeman splitting of the $^2P_{3/2}$ state. What are the spacings of the splitting? Give an estimate for a magnetic field of 0.1 T.*

Solution. To first order, the Zeeman effect corrections are of the form

$$\mu_B g_J B_{ext} m_j$$

where $g_J = 1 + \frac{j(j+1)-\ell(\ell+1)+s(s+1)}{2j(j+1)}$. This is added onto the fine-structure-corrected energy

$$E_{nj} = -\frac{-13.6\,\mathrm{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right];$$

evaluating for our state,

$$E_{n(3/2)} = -\frac{-13.6\,\mathrm{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\frac{2n-3}{4}\right];$$

and

$$g_J = 1 + \frac{(3/2)(5/2) - (1)(2) + (1/2)(3/2)}{3(5/2)} = \frac{4}{3}.$$

The splitting is then

$$E_n = -\frac{-13.6\,\mathrm{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\frac{2n-3}{4}\right] + \frac{4\mu_B}{3}B_{ext}m_j.$$

One has $-j \leq m_j \leq j$ in increments of $1/2$, so $m_j = -3/2, -1, -1/2, 0, 1/2, 1, 3/2$, yielding seven-fold splitting with spacing

$$\frac{2\mu_B}{3}B_{ext}$$

For the given field, the spacing is approximately

$$\frac{2(9.27\times10^{-24}\,\mathrm{J/T})}{3}(0.1\,\mathrm{T}) = 6.18\times10^{-25}\,\mathrm{J} = 3.86\times10^{-6}\,\mathrm{eV}$$

□