Physics 633 Homework 2

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1) We can write the Hamiltonian for the helium atom as the sum of two hydrogen atom Hamiltonians plus a perturbation due to the repulsive force between the two electrons. The sum of two hydrogen atom Hamiltonians is

$$H_0 = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} - \frac{2\hbar c\alpha}{r_1} - \frac{2\hbar c\alpha}{r_2} \tag{1}$$

Ignoring any exchange-symmetry effects, the eigenfunctions of this Hamiltonian are just products of eigenfunctions of the hydrogen atom Hamiltonian. For justification, let A_1 and A_2 be operators and let x_1 and x_2 be eigenvectors, with eigenvalues λ_1 and λ_2, of A_1 and A_2 respectively. Then $(A_1 + A_2)x_1x_2 = \lambda_1 x_1 x_2 + \lambda_2 x_1 x_2 = (\lambda_1 + \lambda_2)x_1x_2$. Therefore, eigenfunctions of (1) are

$$\psi^{(0)}_{n_1,l_1,m_1,n_2,l_2,m_2}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{n_1,l_1,m_1}(\boldsymbol{r}_1)\psi_{n_2,l_2,m_2}(\boldsymbol{r}_2) \tag{2}$$

with corresponding eigenvalues

$$E_{n_1,n_2} = -2\alpha^2 c^2 m_e \left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) \tag{3}$$

The full perturbed Hamiltonian is then given by

$$H = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} - \frac{2\hbar c\alpha}{r_1} - \frac{2\hbar c\alpha}{r_2} + \frac{\hbar c\alpha}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{4}$$

From the reading on nondegenerate perturbation theory, we know that the first order energy shift is given by

$$\begin{aligned}
\delta E_1 &= \left\langle \psi^{(0)} \middle| V \middle| \psi^{(0)} \right\rangle \\
\delta E_1 &= \int d\boldsymbol{r}_2 d\boldsymbol{r}_1 \frac{\hbar c\alpha}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \psi_{1,0,0}(\boldsymbol{r}_1)^2 \psi_{1,0,0}(\boldsymbol{r}_2)^2 \\
\delta E_1 &= \hbar c\alpha \left(\frac{1}{\pi a^3}\right)^2 \int d\boldsymbol{r}_2 d\boldsymbol{r}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} e^{-2r_1/a} e^{-2r_2/a}
\end{aligned} \tag{5}$$

where $a = \frac{\hbar}{2\alpha m_e c}$. We can write both integrals in spherical coordinates in which the polar angle measures the angle from $\boldsymbol{r}_1$ to $\boldsymbol{r}_2$ and expand the potential as

$$\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \frac{1}{r_>} \sum_{\ell=0}^{\infty} P_\ell(\cos\theta) \left(\frac{r_<}{r_>}\right)^\ell \tag{6}$$

If we substitute this for $\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$, then the integral over $\boldsymbol{r}_2$ in (5) will eliminate all but the $\ell = 0$ term in the sum, since $\int_{-1}^{1} dx P_\ell(x) = 0$ for $\ell \neq 0$. Therefore, (5) becomes

$$\begin{aligned}
\delta E_1 &= \hbar c\alpha \left(\frac{4\pi}{\pi a^3}\right)^2 \int_0^\infty \int_0^\infty r_1^2 r_2^2 dr_2 dr_1 \frac{1}{r_>} e^{-2r_1/a} e^{-2r_2/a} \\
\delta E_1 &= \hbar c\alpha \left(\frac{4\pi}{\pi a^3}\right)^2 \int_0^\infty dr_1 \left[\int_0^\infty dr_2 r_1^2 r_2^2 \frac{1}{\max(r_1, r_2)} e^{-2r_1/a} e^{-2r_2/a}\right] \\
\delta E_1 &= \hbar c\alpha \left(\frac{4\pi}{\pi a^3}\right)^2 \int_0^\infty dr_1 \left[\int_0^{r_1} dr_2 r_1^2 r_2^2 \frac{1}{r_1} e^{-2r_1/a} e^{-2r_2/a} + \int_{r_1}^\infty dr_2 \frac{1}{r_2} e^{-2r_1/a} e^{-2r_2/a}\right] \\
\delta E_1 &= 2\hbar c\alpha \left(\frac{4\pi}{\pi a^3}\right)^2 \int_0^\infty dr_1 \int_0^{r_1} dr_2 r_1^2 r_2^2 \frac{1}{r_1} e^{-2r_1/a} e^{-2r_2/a} \\
\delta E_1 &= 2\hbar c\alpha \left(\frac{4}{a^3}\right)^2 \frac{5a^5}{256} \\
\delta E_1 &= \frac{5\hbar c\alpha}{8a} \\
\delta E_1 &= \frac{5\hbar c\alpha}{8} \frac{2\alpha m_e c}{\hbar} \\
\delta E_1 &= \frac{5c^2\alpha^2 m_e}{4} \\
\delta E_1 &\approx 34.01 \text{ eV}
\end{aligned} \tag{7}$$

Therefore, the ground-state energy of helium is

$$E_1 + \delta E_1 \approx -74.79 \text{ eV} \tag{8}$$

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2) We start with the relativistic perturbation to the Hamiltonian, given by

$$H_{\text{rel}} := -\frac{p^4}{8m_e^3 c^2} \tag{9}$$

We can rewrite this in terms of the "vanilla" Hydrogen atom Hamiltonian as follows

$$
\begin{aligned}
H_{\text{rel}} &= -\frac{1}{2m_e c^2}\left(\frac{p^2}{2m_e}\right)^2 \\
H_{\text{rel}} &= -\frac{1}{2m_e c^2}\left(H + \frac{\hbar c\alpha}{r}\right)^2
\end{aligned}
\tag{10}
$$

a) First we must argue that H_{rel} commutes with H. Since we may write H_{rel} according to (9), we need only show that H commutes with $H\frac{1}{r}$. Let $|n\rangle$ be an energy eigenstate, then

$$
\begin{aligned}
\langle n| \left[H, H\frac{1}{r}\right] |n\rangle &= \langle n| HH\frac{1}{r} - H\frac{1}{r}H |n\rangle \\
\langle n| \left[H, H\frac{1}{r}\right] |n\rangle &= E_n \langle n| H\frac{1}{r} - H\frac{1}{r} |n\rangle \\
\langle n| \left[H, H\frac{1}{r}\right] |n\rangle &= 0
\end{aligned}
\tag{11}
$$

Similarly, $\left[H, \frac{1}{r}H\right] = 0$. So, H_{rel} is diagonal in the basis of eigenstates of H. Therefore, the energy shifts, to first order, are given by

$$
\begin{aligned}
\langle n| H_{\text{rel}} |n\rangle &= -\frac{1}{2m_e c^2} \langle n| H^2 + \frac{\hbar c\alpha}{r}H + H\frac{\hbar c\alpha}{r} + \frac{\hbar^2 c^2\alpha^2}{r^2} |n\rangle \\
\langle n| H_{\text{rel}} |n\rangle &= -\frac{1}{2m_e c^2}\left(E_n^2 + 2\hbar c\alpha E_n \left\langle \frac{1}{r}\right\rangle + \hbar^2 c^2\alpha^2 \left\langle \frac{1}{r^2}\right\rangle\right) \\
\langle n| H_{\text{rel}} |n\rangle &= \frac{1}{2m_e c^2}\left(-E_n^2 - 2\hbar c\alpha E_n\left(\frac{m_e c\alpha}{\hbar n^2}\right) - \hbar^2 c^2\alpha^2\left(\frac{m_e^2 c^2 n\alpha^2}{\hbar^2 (L+1/2)n^4}\right)\right) \\
\langle n| H_{\text{rel}} |n\rangle &= \frac{1}{2m_e c^2}\left(-E_n^2 + 4E_n^2 - 4E_n^2\left(\frac{n}{L+1/2}\right)\right) \\
\Delta E_{\text{rel}} &= \frac{E_n^2}{2m_e c^2}\left(3 - \frac{4n}{L+1/2}\right)
\end{aligned}
\tag{12}
$$

b) With $g_S - 1 \approx 1$, the fine structure shift is

$$
\Delta E_{\text{fs}} = \frac{(E_n^2)n}{m_e c^2}\frac{J(J+1) - L(L+1) - \frac{1}{2}(\frac{1}{2}+1)}{L(L+1/2)(L+1)}
\tag{13}
$$

So, with $L = J \pm \frac{1}{2}$, we have

$$
\Delta E_{\text{fs}} + \Delta E_{\text{rel}} = \frac{(E_n^2)}{m_e c^2}\left(\frac{J(J+1) - (J\pm\frac{1}{2})(J\pm\frac{1}{2}+1) - \frac{3}{4}}{(J\pm\frac{1}{2})(J\pm\frac{1}{2}+1/2)(J\pm\frac{1}{2}+1)}n + \frac{1}{2}\left(3 - \frac{4n}{J\pm\frac{1}{2}+1/2}\right)\right)
\tag{14}
$$

Using Mathematica to simplify this gives

$$\Delta E_{\text{fs}} + \Delta E_{\text{rel}} = \frac{(E_n^2)}{m_e c^2}\left(\frac{3}{2} - \frac{4n}{2J+1}\right)$$
$$\Delta E_{\text{fs}} + \Delta E_{\text{rel}} = \frac{(E_n^2)}{2m_e c^2}\left(3 - \frac{4n}{J+1/2}\right) \tag{15}$$

which is surprisingly independent of whether or $\pm$ is $+$ or $-$.

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3) The perturbation due to the Darwin term is given by

$$H_D = \frac{\hbar^2 \pi}{2m_e^2 c^2}\frac{e^2}{4\pi\epsilon_0}\delta^3(\boldsymbol{r}) \tag{16}$$

a) Since this commutes with the regular hydrogen atom Hamiltonian, we can use first order, non-degenerate perturbation theory. The first order energy corrections are then given by $\delta E_1 = \langle\psi_0| H_D |\psi_0\rangle$. Let $|n, l, m\rangle$ be an energy eigenstate of the hydrogen atom. Then we have

$$
\begin{aligned}
\delta E_1 &= \langle n,l,m|\, H_D\, |n,l,m\rangle \\
\delta E_1 &= \frac{\hbar^2\pi}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\int d\Omega\int_0^\infty r^2dr\ \psi_{nlm}(r,\Omega)^*\delta^3(\boldsymbol{r})\psi_{nlm}(r,\Omega) \\
\delta E_1 &= \frac{\hbar^2\pi}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\int d\Omega\int_0^\infty r^2dr\ \delta^3(\boldsymbol{r})|\psi_{nlm}(r,\Omega)|^2 \\
\delta E_1 &= \frac{\hbar^2\pi}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\int d\Omega\int_0^\infty r^2dr\ \delta^3(\boldsymbol{r})R_{nl}(r)^2|Y_l^m(\Omega)|^2 \\
\delta E_1 &= \frac{\hbar^2\pi}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\int_0^{2\pi}\int_0^{\pi}\sin(\theta)d\theta\phi\int_0^\infty r^2dr\ \frac{\delta(r)\delta(\theta)\delta(\phi)}{r^2\sin(\theta)}R_{nl}(r)^2|Y_l^m(\Omega)|^2 \\
\delta E_1 &= \frac{\hbar^2\pi}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{na_0}\right)^3|Y_l^m(0,0)|^2\left(\frac{(n-l-1)!}{2n(n+l)!}e^{-\rho}\rho^{2l}L_{n-l-1}^{2l+1}(\rho)^2\right)\Bigg|_{\rho=0} \\
\delta E_1 &= \frac{\hbar^2\pi}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{na_0}\right)^3|Y_l^m(0,0)|^2\left(\frac{(n-l-1)!}{2n(n+l)!}\binom{n+l}{n-l-1}^2\right)\delta_{l,0} \\
\delta E_1 &= \frac{\hbar^2\pi}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{na_0}\right)^3|Y_0^0(0,0)|^2\left(\frac{(n-1)!}{2n(n!)}\binom{n}{n-1}^2\right)\delta_{l,0} \\
\delta E_1 &= \frac{\hbar^2\pi}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{na_0}\right)^3\frac{1}{8\pi}\delta_{l,0} \\
\delta E_1 &= \frac{1}{2}\frac{\hbar^4}{m_e^3c^2}\frac{1}{n^3a_0^4}\delta_{l,0} \\
\delta E_1 &= \frac{m_ec^2\alpha^4}{2n^3}\delta_{l,0}
\end{aligned}
\tag{17}
$$

b) Adding ΔE_D to $\Delta E_{\rm rel}$ and evaluating the $L=0$ case gives

$$
\begin{aligned}
\Delta E_{\rm rel}+\Delta E_D &= \frac{E_n^2}{2m_ec^2}\left(3-\frac{4n}{1/2}\right)+\frac{m_ec^2\alpha^4}{2n^3} \\
\Delta E_{\rm rel}+\Delta E_D &= \frac{E_n^2}{2m_ec^2}(3-8n)+4\frac{E_n^2n}{2m_ec^2} \\
\Delta E_{\rm rel}+\Delta E_D &= \frac{E_n^2}{2m_ec^2}(3-4n)
\end{aligned}
\tag{18}
$$

which is equivalent to (15) with $J=1/2$.

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4) Starting with $H_{\rm hfs}=A_{\rm hfs}\frac{\boldsymbol{I}\cdot\boldsymbol{J}}{\hbar^2}$ and $H_B^{(\rm hfs)}=\frac{\mu_B}{\hbar}(g_JJ_z+g_II_z)B_z$ we compute matrix elements of $H_{\rm hfs}+H_B^{(\rm hfs)}$ in the "strong-field basis", $|J\ m_J;I\ m_I\rangle$. We first rewrite $H_{\rm hfs}$ as $H_{\rm hfs}=$

$\frac{A_{\text{hfs}}}{\hbar^2}\left(I_z J_z + \frac{1}{2}\left(I_+ J_- + I_- J_+\right)\right)$. We know the matrix will be block diagonal (and symmetric) with 2×2 blocks since the raising an lowering operators will annihilate terms that are farther from 1 entry from the diagonal, while the z component operators ensure that diagonal elements remain non-zero. Additionally, the products of raising and lowering operators will only yield terms for which m_I and m_J are offset by 1 on either side of the braket.

Given m_I, and with $H = H_{\text{hfs}} + H_B^{(\text{hfs})}$, the matrix elements for a block are given by

$$\begin{aligned}
\langle {}^1\!/_2\ {}^1\!/_2; I\ m_I |\, H \,| {}^1\!/_2\ {}^1\!/_2; I\ m_I \rangle & \\
&= A_{\text{hfs}} \frac{m_I}{2} + \mu_B \left(\frac{g_J}{2} + g_I m_I \right) B \\
\langle {}^1\!/_2\ \ {-}{}^1\!/_2; I\ m_I + 1 |\, H \,| {}^1\!/_2\ \ {-}{}^1\!/_2; I\ m_I + 1 \rangle & \\
&= -A_{\text{hfs}} \frac{(m_I + 1)}{2} + \mu_B \left(-\frac{g_J}{2} + g_I (m_I + 1) \right) B \\
\langle {}^1\!/_2\ \ {-}{}^1\!/_2; I\ m_I + 1 |\, H \,| {}^1\!/_2\ {}^1\!/_2; I\ m_I \rangle & \\
&= \frac{A_{\text{hfs}}}{2} \sqrt{({}^1\!/_2 + {}^1\!/_2)({}^1\!/_2 - {}^1\!/_2 + 1)} \sqrt{(I + m_I + 1)(I - m_I)} \\
&= \frac{A_{\text{hfs}}}{2} \sqrt{(I + m_I + 1)(I - m_I)} \\
&= \langle {}^1\!/_2\ {}^1\!/_2; I\ m_I |\, H \,| {}^1\!/_2\ \ {-}{}^1\!/_2; I\ m_I + 1 \rangle
\end{aligned} \tag{19}$$

Since eigenvalues of a block in a block diagonal matrix are eigenvalues of the original matrix, we need only find the eigenvalues of

$$\begin{bmatrix} A_{\text{hfs}} \frac{m_I}{2} + \mu_B \left(\frac{g_J}{2} + g_I m_I \right) B & \frac{A_{\text{hfs}}}{2} \sqrt{(I + m_I + 1)(I - m_I)} \\ \frac{A_{\text{hfs}}}{2} \sqrt{(I + m_I + 1)(I - m_I)} & -A_{\text{hfs}} \frac{(m_I + 1)}{2} + \mu_B \left(-\frac{g_J}{2} + g_I (m_I + 1) \right) B \end{bmatrix} \tag{20}$$

Using Mathematica, we find that the eigenvalues are

$$
\begin{aligned}
\Delta E &= \frac{1}{4}\left(-A_{\text{hfs}} + 2\mu_B B g_I (1+2m_I)\right. \\
&\quad \left. \pm \sqrt{A_{\text{hfs}}^2 (1+2I)^2 - 4A_{\text{hfs}}\mu_B B(g_I - g_J)(1+2m_I) + 4\mu_B^2 B^2 (g_I - g_J)^2}\right) \\
\Delta E &= -\frac{\Delta E_{\text{hfs}}}{2(2I+1)} + \mu_B B g_I (m_I + {}^1\!/\!_2) \\
&\quad \pm \frac{A_{\text{hfs}}}{4}(1+2I)\sqrt{1 - \frac{4\mu_B B(g_I - g_J)(1+2m_I)}{A_{\text{hfs}}(1+2I)^2} + \frac{4\mu_B^2 B^2 (g_I - g_J)^2}{A_{\text{hfs}}(1+2I)^2}} \\
\Delta E &= -\frac{\Delta E_{\text{hfs}}}{2(2I+1)} + \mu_B B g_I (m_I + {}^1\!/\!_2) \\
&\quad \pm \frac{A_{\text{hfs}}}{4}(1+2I)\sqrt{1 + \frac{4\mu_B B(g_J - g_I)(1+2m_I)}{A_{\text{hfs}}(I+{}^1\!/\!_2)^2} + \frac{\mu_B^2 B^2 (g_I - g_J)^2}{A_{\text{hfs}}(I+{}^1\!/\!_2)^2}} \\
\Delta E &= -\frac{\Delta E_{\text{hfs}}}{2(2I+1)} + \mu_B B g_I m \pm \frac{\Delta E_{\text{hfs}}}{2}\sqrt{1 + \frac{4mx}{2I+1} + x^2}
\end{aligned}
\tag{21}
$$

where

$$
\begin{aligned}
\Delta E_{\text{hfs}} &= A_{\text{hfs}}\left(I + \frac{1}{2}\right) \\
x &= \frac{\mu_B (g_J - g_I) B}{\Delta E_{\text{hfs}}} \\
m &= m_I \pm m_J
\end{aligned}
\tag{22}
$$

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