Problem Set 4

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Problem 1:
Solution:

(a)
Here, we can look at the Stark effect for the $2S_{1/2}$ and $2P_{1/2}$ Hydrogen states, such that a field $\mathcal{E}$ is applied. We consider the response in two regimes: (1) $e\mathcal{E}a_0 << \delta$ and (2) $e\mathcal{E}a_0 >> \delta$ with δ as the Lamb shift. We will consider the set of states $\{|nljm_j\rangle\} = \{|21\frac{1}{2} \pm \frac{1}{2}\rangle, |20\frac{1}{2} \pm \frac{1}{2}\rangle\} = \{|1\frac{1}{2} \pm \frac{1}{2}\rangle, |0\frac{1}{2} \pm \frac{1}{2}\rangle\}$. We will start with case (1).

Case 1: $e\mathcal{E}a_0 << \delta$.

Since in this weak field regime, the effects of the external electric field are small compared to the spin-orbit splitting. Hence, we must not approximate the s and p states to be degenerate. Instead, we will separate into two degenerate subspaces, one corresponding to the s and p spaces. These two subspaces are spanned by the set of vectors $\{|ljm_j\rangle\}_0 = \{|0\frac{1}{2} \pm \frac{1}{2}\rangle\}$ and $\{|ljm_j\rangle\}_1 = \{|1\frac{1}{2} \pm \frac{1}{2}\rangle\}$. From the degenerate subspaces spanned by the sets $\{|ljm_j\rangle\}_0$ and $\{|ljm_j\rangle\}_1$, we can construct the perturbation Hamiltonia corresponding to each splitting: V_0 and V_1. The matrix elements we seek are $\langle 0\frac{1}{2}m_j|V|0\frac{1}{2}m_j'\rangle$ and $\langle 1\frac{1}{2}m_j|V|1\frac{1}{2}m_j'\rangle$. We can evaluate the first,

$$V_0 = \begin{pmatrix} \langle\frac{1}{2}\frac{1}{2}0|V|0\frac{1}{2}\frac{1}{2}\rangle & \langle\frac{1}{2}\frac{1}{2}0|V|0\frac{1}{2}-\frac{1}{2}\rangle \\ \langle\frac{1}{2}\frac{1}{2}0|V|0\frac{1}{2}-\frac{1}{2}\rangle & \langle\frac{1}{2}-\frac{1}{2}0|V|0-\frac{1}{2}\frac{1}{2}\rangle \end{pmatrix}$$

This invites us to evaluate the matrix elements: $\langle 0\frac{1}{2}\frac{1}{2}|V|0\frac{1}{2}\frac{1}{2}\rangle$, $\langle 0\frac{1}{2}-\frac{1}{2}|V|0\frac{1}{2}-\frac{1}{2}\rangle$, and $\langle 0\frac{1}{2}\frac{1}{2}|V|0\frac{1}{2}-\frac{1}{2}\rangle$. To do this, we must convert from the $|ljm_j\rangle$ basis to the $|lm_lm_s\rangle$. We must this for the two states: $|ljm_j\rangle = |0\frac{1}{2}\frac{1}{2}\rangle, |0\frac{1}{2}-\frac{1}{2}\rangle$. This can be done using the transforms ,

$$|0\frac{1}{2}\frac{1}{2}\rangle = \sum_{m_s=-1/2}^{1/2} |0m_s\rangle\langle 0m_s|0\frac{1}{2}\rangle = |0-\frac{1}{2}\rangle\langle 0-\frac{1}{2}|0\frac{1}{2}\rangle + |0\frac{1}{2}\rangle\langle 0\frac{1}{2}|0\frac{1}{2}\rangle$$

$$= \sqrt{\frac{1}{2}-\frac{1}{2}}|0-\frac{1}{2}\rangle + \sqrt{\frac{1}{2}+\frac{1}{2}}|0\frac{1}{2}\rangle = |0\frac{1}{2}\rangle$$

$$|0\frac{1}{2}-\frac{1}{2}\rangle = \sum_{m_s=-1/2}^{1/2} |0m_s\rangle\langle 0m_s|0-\frac{1}{2}\rangle = |0-\frac{1}{2}\rangle\langle 0-\frac{1}{2}|0-\frac{1}{2}\rangle + |0\frac{1}{2}\rangle\langle 0\frac{1}{2}|0-\frac{1}{2}\rangle$$

$$= |0-\frac{1}{2}\rangle$$

Hence, we have

$$\langle\frac{1}{2}\frac{1}{2}0|V|0\frac{1}{2}\frac{1}{2}\rangle = \langle\frac{1}{2}0|V|0\frac{1}{2}\rangle = e\mathcal{E}\langle\frac{1}{2}0|z|0\frac{1}{2}\rangle = e\mathcal{E}\langle\frac{1}{2}0|T_0^{(1)}|0\frac{1}{2}\rangle = 0$$

$$\langle\frac{1}{2}-\frac{1}{2}0|V|0-\frac{1}{2}\frac{1}{2}\rangle = \langle-\frac{1}{2}0|V|0-\frac{1}{2}\rangle = e\mathcal{E}\langle-\frac{1}{2}0|z|0-\frac{1}{2}\rangle = e\mathcal{E}\langle-\frac{1}{2}0|T_0^{(1)}|0-\frac{1}{2}\rangle = 0$$

$$\langle\frac{1}{2}\frac{1}{2}0|V|0-\frac{1}{2}\frac{1}{2}\rangle = \langle\frac{1}{2}0|V|0-\frac{1}{2}\rangle = e\mathcal{E}\langle-\frac{1}{2}0|z|0\frac{1}{2}\rangle = e\mathcal{E}\langle-\frac{1}{2}0|T_0^{(1)}|0\frac{1}{2}\rangle = 0$$

Since all these matrix elements vanish, we shouldn't expect any shifts in energy for the $2S_{1/2}$ under low fields. Likewise, we can evaluate the matrix elements for V_1.

$$V_1 = \begin{pmatrix} \langle 1\frac{1}{2}\frac{1}{2}|V|1\frac{1}{2}\frac{1}{2}\rangle & \langle 1\frac{1}{2}\frac{1}{2}|V|1\frac{1}{2}-\frac{1}{2}\rangle \\ \langle 1\frac{1}{2}\frac{1}{2}|V|1\frac{1}{2}-\frac{1}{2}\rangle & \langle 1\frac{1}{2}-\frac{1}{2}|V|1\frac{1}{2}-\frac{1}{2}\rangle \end{pmatrix}$$

We can write these states in the $|lm_lm_s\rangle$ basis.

$$|1\frac{1}{2}\frac{1}{2}\rangle = \sum_{m_l=-1}^{1}\sum_{m_s=-1/2}^{1/2} |m_lm_s\rangle\langle m_lm_s|\frac{1}{2}\frac{1}{2}\rangle$$

$$= |-1-\frac{1}{2}\rangle\langle -1-\frac{1}{2}|\frac{1}{2}\frac{1}{2}\rangle + |0-\frac{1}{2}\rangle\langle 0-\frac{1}{2}|\frac{1}{2}\frac{1}{2}\rangle + |1-\frac{1}{2}\rangle\langle 1-\frac{1}{2}|\frac{1}{2}\frac{1}{2}\rangle$$
$$+|-1\frac{1}{2}\rangle\langle -1\frac{1}{2}|\frac{1}{2}\frac{1}{2}\rangle + |0\frac{1}{2}\rangle\langle 0\frac{1}{2}|\frac{1}{2}\frac{1}{2}\rangle + |1-\frac{1}{2}\rangle\langle 1\frac{1}{2}|\frac{1}{2}\frac{1}{2}\rangle$$
$$= \sqrt{\frac{2}{3}}|1-\frac{1}{2}\rangle - \sqrt{\frac{1}{3}}|0\frac{1}{2}\rangle$$

$$|1\frac{1}{2}-\frac{1}{2}\rangle = \sum_{m_l=-1}^{1}\sum_{m_s=-1/2}^{1/2} |m_lm_s\rangle\langle m_lm_s|\frac{1}{2}-\frac{1}{2}\rangle$$

$$= |-1-\frac{1}{2}\rangle\langle -1-\frac{1}{2}|\frac{1}{2}-\frac{1}{2}\rangle + |0-\frac{1}{2}\rangle\langle 0-\frac{1}{2}|\frac{1}{2}-\frac{1}{2}\rangle + |1-\frac{1}{2}\rangle\langle 1-\frac{1}{2}|\frac{1}{2}-\frac{1}{2}\rangle$$
$$+|-1\frac{1}{2}\rangle\langle -1\frac{1}{2}|\frac{1}{2}-\frac{1}{2}\rangle + |0\frac{1}{2}\rangle\langle 0\frac{1}{2}|\frac{1}{2}-\frac{1}{2}\rangle + |1-\frac{1}{2}\rangle\langle 1\frac{1}{2}|\frac{1}{2}-\frac{1}{2}\rangle$$
$$\sqrt{\frac{1}{3}}|0-\frac{1}{2}\rangle - \sqrt{\frac{2}{3}}|-1\frac{1}{2}\rangle$$

Since all these matrix elements in first order go to zero, we can proceed to use second order perturbation theory. This gives us the following expression for the energy shift of each state,

$$\Delta E_n = \sum_{m\neq n} \frac{|\langle m|V|n\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

where we sum over all states that don't have the same ground state energy. Hence, we only consider mixing between the p and s states. This gives us,

$$\Delta E_{S+} = -\frac{e\mathcal{E}}{\delta}[|\langle\frac{1}{2}\frac{1}{2}0|V|1\frac{1}{2}\frac{1}{2}\rangle|^2 + |\langle\frac{1}{2}\frac{1}{2}0|V|1\frac{1}{2}-\frac{1}{2}\rangle|^2] = -\frac{e\mathcal{E}}{\delta}[9a_0^2+36a_0^2] = -\frac{45e\mathcal{E}a_0^2}{\delta}$$

$$\Delta E_{S-} = -\frac{e\mathcal{E}}{\delta}[|\langle -\frac{1}{2}\frac{1}{2}0|V|1\frac{1}{2}\frac{1}{2}\rangle|^2 + |\langle -\frac{1}{2}\frac{1}{2}0|V|1\frac{1}{2}-\frac{1}{2}\rangle|^2] = -\frac{e\mathcal{E}}{\delta}[36a_0^2+9a_0^2] = -\frac{45e\mathcal{E}a_0^2}{\delta}$$

$$\Delta E_{P+} = \frac{e\mathcal{E}}{\delta}[|\langle\frac{1}{2}\frac{1}{2}1|V|0\frac{1}{2}\frac{1}{2}\rangle|^2 + |\langle\frac{1}{2}\frac{1}{2}1|V|0\frac{1}{2}-\frac{1}{2}\rangle|^2] = \frac{e\mathcal{E}}{\delta}[9a_0^2+36a_0^2] = \frac{45e\mathcal{E}a_0^2}{\delta}$$

$$\Delta E_{P-} = \frac{e\mathcal{E}}{\delta}[|\langle -\frac{1}{2}\frac{1}{2}1|V|0\frac{1}{2}\frac{1}{2}\rangle|^2 + |\langle -\frac{1}{2}\frac{1}{2}1|V|0\frac{1}{2}-\frac{1}{2}\rangle|^2] = \frac{e\mathcal{E}}{\delta}[[36a_0^2+9a_0^2] = \frac{45e\mathcal{E}a_0^2}{\delta}$$

Hence, we have obtained these second order energy shifts for the low-field regime.

Case 2: $e\mathcal{E}a_0 >> \delta$.

For very large fields, we can assume that the S and P states are degenerate. Hence, we form a degenerate subspace spanned by the set of vectors $\{|ljm_j\rangle\} = \{|0\frac{1}{2} \pm \frac{1}{2}\rangle, |1\frac{1}{2} \pm \frac{1}{2}\rangle\}$. This will give us a 4x4 perturbation Hamiltonian V. Hence,

$$V = e\mathcal{E}\begin{pmatrix} \langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|0\frac{1}{2}\frac{1}{2}\rangle & \langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|0\frac{1}{2}-\frac{1}{2}\rangle & \langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle & \langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle \\ H.C. & \langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|0\frac{1}{2}-\frac{1}{2}\rangle & \langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle & \langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle \\ H.C. & H.C. & \langle\frac{1}{2}\frac{1}{2}1|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle & \langle\frac{1}{2}\frac{1}{2}1|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle \\ H.C. & H.C. & H.C. & \langle -\frac{1}{2}\frac{1}{2}1|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle \end{pmatrix}$$

We can first attempt to evaluate the diagonal elements. This simplifies to,

$$V = e\mathcal{E}\begin{pmatrix} 0 & 0 & \langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle & \langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle \\ H.C. & 0 & \langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle & \langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle \\ H.C. & H.C. & 0 & 0 \\ H.C. & H.C. & H.C. & 0 \end{pmatrix}$$

This requires us to compute 4 matrix elements: $\langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle, \langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle, \langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle, \langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle$.

We can refer to the CG transformations we did in the first part of the problem. This provides us with the following,

$$\langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle = \langle\frac{1}{2}0|T_0^{(1)}|[\sqrt{\frac{2}{3}}|1-\frac{1}{2}\rangle - \sqrt{\frac{1}{3}}|0\frac{1}{2}\rangle] = -\sqrt{\frac{1}{3}}\langle\frac{1}{2}00|T_0^{(1)}|10\frac{1}{2}\rangle = -\sqrt{\frac{1}{3}}3\sqrt{3}a_0 = -3a_0$$

$$\langle\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle = \langle\frac{1}{2}0|T_0^{(1)}|[\sqrt{\frac{1}{3}}|0-\frac{1}{2}\rangle - \sqrt{\frac{2}{3}}|-1\frac{1}{2}\rangle] = -\sqrt{\frac{2}{3}}\langle\frac{1}{2}0|T_0^{(1)}|-1\frac{1}{2}\rangle = -6a_0$$

$$\langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}\frac{1}{2}\rangle = -6a_0$$

$$\langle -\frac{1}{2}\frac{1}{2}0|T_0^{(1)}|1\frac{1}{2}-\frac{1}{2}\rangle = -3a_0$$

This gives a form for V.

$$V = -e3a_0\mathcal{E}\begin{pmatrix} 0 & 0 & 1 & 2 \\ H.C. & 0 & 2 & 1 \\ H.C. & H.C. & 0 & 0 \\ H.C. & H.C. & H.C. & 0 \end{pmatrix}$$

We can diagnolize this matrix to obtain the energy shifts corresponding to the eigenvalues of each state.

$$\Delta E_{S+} = -3e\mathcal{E}a_0$$

$$\Delta E_{S-} = 3e\mathcal{E}a_0$$

$$\Delta E_{P+} = -9e\mathcal{E}a_0$$

$$\Delta E_{P-} = 9e\mathcal{E}a_0$$

Using our perturbation expression for each state $E_n = E_n^0 + \Delta E_n$. Hence,

$$E_{S+} = -\delta/2 - 3e\mathcal{E}a_0$$

$$E_{S-} = -\delta/2 + 3e\mathcal{E}a_0$$

$$E_{P+} = \delta/2 - 9e\mathcal{E}a_0$$

$$E_{P-} = \delta/2 + 9e\mathcal{E}a_0$$

Problem 2:
Solution:

Here we consider a 1D potential $V(x) = \lambda|x|$. We can use a Gaussian variational wavefunction to estimate an upper bound on the energy. Considering a wavefunction of the form, $\psi_0(x) = \exp(-\frac{x^2}{a})$ with a as a variational parameter. We want to solve,

$$\min_a \frac{\langle\psi_0|\mathcal{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle}$$

We can first evaluate the expectation value $\langle\psi_0|\mathcal{H}|\psi_0\rangle$ given by,

$$\langle\psi_0|\mathcal{H}|\psi_0\rangle = \int_{-\infty}^{\infty} dx(\frac{\hbar^2}{2m}|\frac{d\psi}{dx}|^2 + \lambda|x||\psi|^2)$$

$$= \int_{-\infty}^{\infty} dx(\frac{4\hbar^2 x^2}{2ma^2} e^{-2x^2/a} + \lambda|x|e^{-2x^2/a})$$

Evaluating this integral in Mathematica gives us,

$$\langle\psi_0|\mathcal{H}|\psi_0\rangle = \frac{1}{4}a^{3/2}\frac{4\hbar^2}{2ma^2} + \frac{\lambda a}{2}$$

For the demoninator, we have

$$\langle\psi_0|\psi_0\rangle = \int_{-\infty}^{\infty} e^{-2x^2/a}dx = \sqrt{\frac{\pi a}{2}}$$

This brings us to solving the optimization problem,

$$\min_a \frac{\frac{1}{4}a^{3/2}\frac{4\hbar^2}{2ma^2} + \frac{\lambda a}{2}}{\sqrt{\frac{\pi a}{2}}}$$

Finding the derivative and setting it to 0 gives,

$$\frac{a^{3/2}\lambda m - 2\hbar^2}{2a^2 m\sqrt{2\pi}} = 0$$

Solving this gives us the optimal a,

$$a = 2^{3/2}(\frac{\hbar^2}{\lambda m})^{2/3}$$

Hence, our optimal variational wave function will be

$$\psi_0(x) = \exp(-\frac{(2\lambda m)^{2/3}x^2}{\hbar^2})$$

Hence, the bound on the ground state energy is given by

$$E_0 = \langle\psi_0|\mathcal{H}|\psi_0\rangle = \int_{-\infty}^{\infty}(\frac{\hbar^2}{2m}(\frac{(4\lambda m)^{2/3}x}{\hbar^2})^2)\exp(-\frac{(4\lambda m)^{2/3}x^2}{\hbar^2})dx$$

$$-\lambda\int_{-\infty}^{0} x\exp(-\frac{(4\lambda m)^{2/3}x^2}{\hbar^2}) + \lambda\int_{0}^{\infty} x\exp(-\frac{(4\lambda m)^{2/3}x^2}{\hbar^2})$$

$$= \frac{\sqrt{\pi}m(\lambda m)^{4/3}}{2(2^{1/3}\hbar^2(\frac{(\lambda m)^{2/3}}{\hbar^2})^{3/2}}$$

From this we can say that the Gaussian is a worse variational wave function (energy is further off from using the approximation in class). We can attribute this to the fact that the gaussian will drop off more sharply, for it has an x^2 factor, rather than an x in the argument of the exponential.

Problem 3:
Solution:

Here we have the Hamiltonian

$$\mathcal{H} = \frac{|\mathbf{p}_1|^2}{2m} + \frac{|\mathbf{p}_2|^2}{2m} - \frac{2e^2}{|\mathbf{r}_1|} - \frac{2e^2}{|\mathbf{2}_1|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

(a) If we ignore the last term of $\mathcal{H}$, we would have the Hamiltonian corresponding to twice the energy of the Hydrogen atom. Hence, we would have eigenvalues

$$E_n = -2(13.6 \text{ eV})\frac{Z^2}{n^2} = -(27.2 \text{ eV})\frac{Z^2}{n^2}$$

This will serve as our lower bound for the actual ground state energy.
(b) We can now employ first order perturbation theory to obtain an approximate correction to the ground state energy. If we take the ground state wave function to be

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) = \frac{1}{\pi a_0^3} \exp(-\frac{2}{a_0}(|\mathbf{r}_1| + |\mathbf{r}_2|))$$

our approximation for the perturbed ground state energy is,

$$E_0^{(1)} = E_0 + \langle \psi_0(\mathbf{r}_1, \mathbf{r}_2)| \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_0(\mathbf{r}_1, \mathbf{r}_2)\rangle$$

To evaluate. the integral corresponding to the expected value of the perturbation, we can first re-write the perturbation as a multipole expansion

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l,m} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}(\hat{\Omega}_1)^\star Y_{lm}(\hat{\Omega}_2)$$

We can now attempt to evaluate the integral using this form of the perturbation,

$$\langle \psi_0(\mathbf{r}_1, \mathbf{r}_2)| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_0(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\pi^2 a_0^6} \sum_{l,m} \frac{4\pi}{2l+1} \int_{\mathbf{r}_1} d^3\mathbf{r}_1 \int_{\mathbf{r}_1} d^3\mathbf{r}_2 \frac{r_<^l}{r_>^{l+1}} Y_{lm}(\hat{\Omega}_1)^\star Y_{lm}(\hat{\Omega}_2)$$

$$\times \exp(-\frac{4}{a_0}(|\mathbf{r}_1| + |\mathbf{r}_2|))$$

Due to the symmetry of the potential, it will be sufficient to only consider terms corresponding to $m = l = 0$. Hence, the expansion becomes

$$\frac{4\pi}{\pi^2 a_0^6} \int_{\mathbf{r}_1} d^3\mathbf{r}_1 \int_{\mathbf{r}_1} d^3\mathbf{r}_2 \frac{r_<^l}{r_>^{l+1}} Y_{00}(\hat{\Omega}_1)^\star Y_{00}(\hat{\Omega}_2) \times \exp(-\frac{4}{a_0}(|\mathbf{r}_1| + |\mathbf{r}_2|))$$

$$= \frac{4}{\pi a_0^6} \int_{\Omega_1} Y_{00}(\hat{\Omega}_1)^\star d\Omega_1 \int_{\Omega_2} Y_{00}(\hat{\Omega}_2) d\Omega_2 \int_{r_1} r_1^2 dr_1 \int_{r_2} r_2^2 dr_2 \frac{1}{r_>} e^{-\frac{4}{a_0}(r_1+r_2)}$$

$$= (\frac{8}{\pi a_0^3})^2 (4\pi)^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{1}{r_>} e^{-\frac{4}{a_0}(r_1+r_2)}$$

$$= (\frac{8}{\pi a_0^3})^2 (4\pi)^2 [\int_0^\infty r_1^2 dr_1 \int_0^{r_1} r_2^2 dr_2 \frac{1}{r_>} e^{-\frac{4}{a_0}(r_1+r_2)} + \int_0^\infty r_2^2 dr_2 \int_0^{r_1} r_1^2 dr_2 \frac{1}{r_>} e^{-\frac{4}{a_0}(r_1+r_2)}]$$

$$= 2(\frac{8}{\pi a_0^3})^2 (4\pi)^2 \int_0^\infty r_1^2 dr_1 \int_0^{r_1} r_2^2 (\frac{1}{r_1} e^{-\frac{4}{a_0}(r_1+r_2)}) dr_2$$

$$= 2(\frac{8}{\pi a_0^3})^2 (4\pi)^2 \frac{a_0}{32} \int_0^\infty r_1 [e^{-8r_1/a_0}(a_0^2(e^{4r_1/a_0} - 1) - 4a_0 r_1 - 8r_1^2)] dr_1$$

$$= \frac{1}{4a_0}$$

(*above integral computed in Mathematica*). Hence, we get that our perturbed energy comes out to

$$E_0^{(1)} = -(27.2 \text{ eV})Z^2 + \frac{e^2}{4a_0}$$

The accuracy of this energy correction is hard to probe. The fact that perturbation theory is employed here for an interaction that is strong relative to the unperturbed Hamiltonian suggests that PT may not be the best approach here.

(c) Now we consider the variational wave function of the form,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z_{eff}}{\pi a_0^3} \exp(-\frac{Z_{eff}}{a_0}(|\mathbf{r}_1| + |\mathbf{r}_2|))$$

This invites us to solve the following optimization problem,

$$\min_{Z_{eff}} \frac{\langle\psi(\mathbf{r}_1,\mathbf{r}_2)|\mathcal{H}|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle}{\langle\psi(\mathbf{r}_1,\mathbf{r}_2)|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle}$$

We can first consider evaluating the numerator, given by

$$\langle\psi(\mathbf{r}_1,\mathbf{r}_2)|\mathcal{H}|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$$

$$= \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 [\frac{|\mathbf{p}_1|^2}{2m} + \frac{|\mathbf{p}_2|^2}{2m} - \frac{2e^2}{|\mathbf{r}_1|} - \frac{2e^2}{|\mathbf{r}_1|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}]|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2$$

$$= \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 [\frac{\hbar^2}{2m}(|\nabla_{\mathbf{r}_1}\psi|^2 + |\nabla_{\mathbf{r}_2}\psi|^2) - 2e^2(\frac{1}{|\mathbf{r}_1|} + \frac{1}{|\mathbf{r}_2|})|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2 + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}]|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2]$$

$$= \frac{Z_{eff}^2}{\pi^2 a_0^6}[\int d\Omega_1 \int d\Omega_2 [\int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 [(\frac{\hbar^2 Z_{eff}^2}{m a_0^2}) e^{-\frac{2Z_{eff}}{a_0}(r_1+r_2)} - 2e^2(r_1^{-1} + r_2^{-1}) e^{-\frac{2Z_{eff}}{a_0}(r_1+r_2)}$$

$$+ \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-\frac{2Z_{eff}}{a_0}(r_1+r_2)}]]]$$

$$= \frac{16 Z_{eff}^2}{a_0^6}[\int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 [(\frac{\hbar^2 Z_{eff}^2}{m a_0^2}) e^{-\frac{2Z_{eff}}{a_0}(r_1+r_2)} - 2e^2(r_1^{-1} + r_2^{-1}) e^{-\frac{2Z_{eff}}{a_0}(r_1+r_2)}$$

$$+ \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-\frac{2Z_{eff}}{a_0}(r_1+r_2)}]]]$$

$$= \frac{16 Z_{eff}^2}{a_0^6}[(\frac{\hbar^2 Z_{eff}^2}{m a_0^2}) \int_0^\infty dr_1 r_1^2 e^{-\frac{2Z_{eff}}{a_0} r_1} \int_0^\infty dr_2 r_2^2 e^{-\frac{2Z_{eff}}{a_0} r_2}$$

$$-2e^2 \int_0^\infty \int_0^\infty dr_1 dr_2 (r_1^{-1} + r_2^{-1}) r_1^2 r_2^2 e^{-\frac{2Z_{eff}}{a_0}(r_1+r_2)}$$

$$+ \int_0^\infty \int_0^\infty dr_1 dr_2 r_1^2 r_2^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-\frac{2Z_{eff}}{a_0}(r_1+r_2)}]$$

$$= \frac{16 Z_{eff}^2}{a_0^6}[\frac{\hbar^2 Z_{eff}^2}{m a_0^2} \frac{a_0^6}{16 Z_{eff}^6} - \frac{e^2 a_0^5}{4 Z_{eff}^5} + \frac{e^2}{Z_{eff} a_0}]$$

The denominator comes out to,

$$\langle\psi_0|\psi\rangle = \frac{a_0^6}{16 Z_{eff}^6}$$

We can obtain the derivative,

$$\frac{\partial}{\partial Z_{eff}}(\frac{16Z_{eff}^6}{a_0^6}\frac{16Z_{eff}^2}{a_0^6})[\frac{\hbar^2 Z_{eff}^2}{ma_0^2}\frac{a_0^6}{16Z_{eff}^6}-\frac{e^2a_0^5}{4Z_{eff}^5}+\frac{e^2}{Z_{eff}a_0}]=0$$

Solving this in Mathematica gives us, $Z_{eff}=2-5/16$. If we plug this into our expression,

$$E_0=\frac{16Z_{eff}^2}{a_0^6}[\frac{\hbar^2 Z_{eff}^2}{ma_0^2}\frac{a_0^6}{16Z_{eff}^6}-\frac{e^2a_0^5}{4Z_{eff}^5}+\frac{e^2}{Z_{eff}a_0}]$$

we get an energy of -75 eV. This is in close agreement with experiment.