SQ21

(a) $$\hat{H}_{\text{helium}} = \underbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}}_{\hat{H}_0} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\hat{H}'}$$

For the given $\hat{H}_0$,

$$\psi(1,2) = \phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2) \qquad \text{with } \phi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Z}{a_0}r}$$

is an eigenfunction of $\hat{H}_0$

$$\hat{H}_0\psi(1,2) = \left[-\frac{\hbar^2}{2m}\nabla_1^2\phi_{1s}(\vec{r}_1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\phi_{1s}(\vec{r}_1)\right]\phi_{1s}(\vec{r}_2)$$

$$+ \left[-\frac{\hbar^2}{2m}\nabla_2^2\phi_{1s}(\vec{r}_2) - \frac{Ze^2}{4\pi\varepsilon_0 r_2}\phi_{1s}(\vec{r}_2)\right]\phi_{1s}(\vec{r}_1)$$

$$= -(2)^2\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\phi_{1s}(\vec{r}_1)\phi_{1s}(\vec{r}_2) - (2)^2\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\phi_{1s}(\vec{r}_2)\phi_{1s}(\vec{r}_1)$$

$$= -8\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\phi_{1s}(\vec{r}_1)\phi_{1s}(\vec{r}_2)$$

$$= -8\underbrace{\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}}_{13.6\,\text{eV}}\psi(1,2)$$

$$\therefore E_{GS}^{(0)} = \int \psi^*(1,2)\,\hat{H}_0\,\psi(1,2)\,d^3r_1\,d^3r_2$$

$$= -8\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\underbrace{\int \phi_{1s}^*(\vec{r}_1)\phi_{1s}(\vec{r}_1)\,d^3r_1}_{1}\underbrace{\int \phi_{1s}^*(\vec{r}_2)\phi_{1s}(\vec{r}_2)\,d^3r_2}_{1}$$

SQ21

(a) $$E_{GS}^{(0)} = -8 \underbrace{\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}}_{13.6\,eV}$$

Zeroth-order energy is -108.8 eV or $-4E_h$ $\left(1\,E_h = \frac{me^4}{16\pi^2\varepsilon_0^2\hbar^2} \approx 27.2\,eV\right)$

It is still very far from the experimental results -78.975 eV

(b) First-order correction to E_{GS} is

$$E_{GS}^{(1)} = \int \psi(1,2)\,\hat{H}'\,\psi(1,2)\,d^3r_1\,d^3r_2$$

$$= \int \phi_{1s}^*(\vec{r}_1)\,\phi_{1s}^*(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)\,d^3r_1\,d^3r_2$$

$$= \frac{e^2}{4\pi\varepsilon_0}\left(\frac{\xi^3}{\pi a_0^3}\right)^2 \int \frac{1}{|\vec{r}_1-\vec{r}_2|}\,e^{-2\xi(r_1+r_2)/a_0}\,d^3r_1\,d^3r_2$$

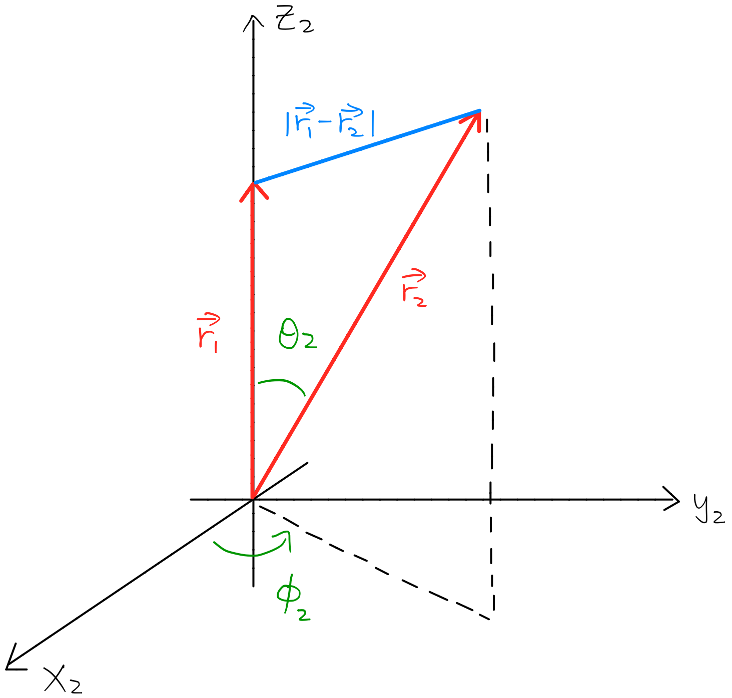
$$= \frac{e^2}{4\pi\varepsilon_0}\left(\frac{\xi^3}{\pi a_0^3}\right)^2 \int e^{-2\xi r_1/a_0}\underbrace{\left(\int \frac{1}{|\vec{r}_1-\vec{r}_2|}\,e^{-2\xi r_2/a_0}\,d^3r_2\right)}\,d^3r_1$$

We denote this integral as I_2, which is a function of $\vec{r}_1$ and inside the integral of $\vec{r}_1$.

Keep in mind that $\xi = 2$ in this question. For the convenience in the next SQ, we keep ξ in the following expressions and substitute its value in the final step.

SQ21

To find $E_{GS}^{(1)}$, we first do the integral I_2 for a fixed $\vec{r}_1$. The coordinate system of $\vec{r}_2$ is chosen according to the figure below, such that the fixed $\vec{r}_1$ lies along the z_2 axis.



By cosine law,

$$|\vec{r}_1-\vec{r}_2| = \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}$$

$$\therefore \quad I_2 = \int_0^\infty\int_0^\pi\int_0^{2\pi} \frac{e^{-2\xi r_2/a_0}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}\, r_2^2\sin\theta_2\, d\phi_2\, d\theta_2\, dr_2$$

$$= \int_0^{2\pi} d\phi_2 \int_0^\infty\int_0^\pi \frac{e^{-2\xi r_2/a_0}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}\, r_2^2\sin\theta_2\, d\theta_2\, dr_2$$

$$= 2\pi \int_0^\infty \underbrace{\left(\int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}\, d\theta_2\right)}_{\theta_2\text{-integral : a function of } r_1 \text{ and } r_2} e^{-2\xi r_2/a_0}\, r_2^2\, dr_2$$

SQ21

The θ_2-integral :

Let $u = \cos\theta_2$

$du = -\sin\theta_2 \, d\theta_2$

$$\int_0^{\pi} \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} \, d\theta_2$$

$$= -\int_1^{-1} \frac{du}{\sqrt{r_1^2+r_2^2-2r_1r_2u}}$$

$$= \left. \frac{\sqrt{r_1^2+r_2^2-2r_1r_2u}}{r_1r_2} \right|_1^{-1}$$

$$= \frac{1}{r_1r_2}\left(\sqrt{r_1^2+r_2^2+2r_1r_2} - \sqrt{r_1^2+r_2^2-2r_1r_2} \right)$$

$$= \frac{1}{r_1r_2}\left(\sqrt{(r_1+r_2)^2} - \sqrt{(r_1-r_2)^2} \right)$$

$$= \frac{1}{r_1r_2}\left(r_1+r_2 - |r_1-r_2| \right)$$

$\sqrt{x^2} = |x| = \begin{cases} x & \text{if } x \geq 0 \\ -x & \text{if } x < 0 \end{cases}$

We don't have absolute sign for r_1+r_2 since $r_1+r_2 \geq 0$

$$= \begin{cases} \frac{1}{r_1r_2}\left[r_1+r_2 - (r_1-r_2) \right] & \text{if } r_2 < r_1 \\ \frac{1}{r_1r_2}\left[r_1+r_2 + (r_1-r_2) \right] & \text{if } r_2 > r_1 \end{cases}$$

$$= \begin{cases} 2/r_1 & \text{if } r_2 < r_1 \\ 2/r_2 & \text{if } r_2 > r_1 \end{cases}$$

It is a piecewise function of r_2 (r_1 is fixed now). Therefore, when calculating the r_2-integral, the integrand is different for different values of r_2.

SQ21

$$I_2 = 2\pi \int_0^\infty \left(\int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} \, d\theta_2 \right) e^{-2\xi r_2/a_0} r_2^2 \, dr_2$$

$$= 2\pi \left[\underbrace{\int_0^{r_1} \frac{2}{r_1} e^{-2\xi r_2/a_0} r_2^2 \, dr_2}_{\text{r_2 is integrated from 0 to r_1, which means $r_2 \le r_1$ and the θ_2-integral equals to $2/r_1$ in this r_2-integral}} + \underbrace{\int_{r_1}^\infty \frac{2}{r_2} e^{-2\xi r_2/a_0} r_2^2 \, dr_2}_{\text{Similarly, $r_2 \ge r_1$ and the θ_2-integral equals to $2/r_2$ in this r_2-integral}} \right]$$

(We get the second line because $\int_a^b f(x)\,dx = \int_a^c f(x)\,dx + \int_c^b f(x)\,dx$ with $a \le c \le b$)

$$I_2 = 4\pi \left[\frac{1}{r_1} \int_0^{r_1} r_2^2 e^{-2\xi r_2/a_0} \, dr_2 + \int_{r_1}^\infty r_2 e^{-2\xi r_2/a_0} \, dr_2 \right]$$

Since $\int_0^{r_1} r_2^2 e^{-2\xi r_2/a_0} \, dr_2 = \frac{a_0^3}{4\xi^3} - e^{-2\xi r_1/a_0} \left[\frac{a_0}{2\xi} r_1^2 + \frac{a_0^2}{2\xi^2} r_1 + \frac{a_0^3}{4\xi^3} \right]$ and

$$\int_{r_1}^\infty r_2 e^{-2\xi r_2/a_0} \, dr_2 = e^{-2\xi r_1/a_0} \left[\frac{a_0}{2\xi} r_1 + \frac{a_0^2}{4\xi^2} \right],$$

$$I_2 = \frac{\pi a_0^3}{\xi^3 r_1} \left[1 - e^{-2\xi r_1/a_0} \left(1 + \frac{\xi r_1}{a_0} \right) \right]$$

Then,

$$E_{GS}^{(1)} = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{\xi^3}{\pi a_0^3} \right)^2 \int e^{-2\xi r_1/a_0} I_2 \, d^3 r_1$$

$$= \frac{e^2}{4\pi\varepsilon_0} \frac{\xi^3}{\pi a_0^3} \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{e^{-2\xi r_1/a_0} \left[1 - e^{-2\xi r_1/a_0} \left(1 + \frac{\xi r_1}{a_0} \right) \right]}{r_1} r_1^2 \sin\theta_1 \, d\phi_1 \, d\theta_1 \, dr_1$$

SQ21

$$E_{GS}^{(1)} = \underbrace{4\pi}_{} \frac{e^2}{4\pi\varepsilon_0} \frac{\xi^3}{\pi a_0^3} \int_0^\infty e^{-2\xi r_1/a_0} \left[1 - e^{-2\xi r_1/a_0} \left(1 + \frac{\xi r_1}{a_0} \right) \right] r_1 \, dr_1$$

$$\int_0^{2\pi} \int_0^{\pi} \sin\theta_1 \, d\theta_1 \, d\phi_1 = 4\pi$$

$$= \frac{e^2 \xi^3}{\varepsilon_0 \pi a_0^3} \int_0^\infty e^{-2\xi r_1/a_0} \left[1 - e^{-2\xi r_1/a_0} \left(1 + \frac{\xi r_1}{a_0} \right) \right] r_1 \, dr_1$$

Since $\int_0^\infty e^{-2\xi r_1/a_0} r_1 \, dr_1 = \frac{a_0^2}{4\xi^2}$, $\int_0^\infty e^{-4\xi r_1/a_0} r_1 dr_1 = \frac{a_0^2}{16\xi^2}$ and

$$\int_0^\infty r_1^2 e^{-4\xi r_1/a_0} dr_1 = \frac{a_0^3}{32\xi^3} ,$$

$$\int_0^\infty e^{-2\xi r_1/a_0} \left[1 - e^{-2\xi r_1/a_0} \left(1 + \frac{\xi r_1}{a_0} \right) \right] r_1 \, dr_1 = \frac{5a_0^2}{32\xi^2}$$

$$\therefore \; E_{GS}^{(1)} = \frac{e^2 \xi^3}{\varepsilon_0 \pi a_0^3} \frac{5a_0^2}{32\xi^2} = \frac{5}{8} \underbrace{\frac{e^2}{4\pi\varepsilon_0 a_0}}_{E_h} \xi = \frac{5\xi}{8} E_h$$

Now, remember that $\xi = 2$ in this question,

$$E_{GS}^{(1)} = \frac{5}{4} E_h \approx 34 \text{ eV}$$

Estimated $E_{GS} \approx E_{GS}^{(0)} + E_{GS}^{(1)} = \left(-4 + \frac{5}{4}\right) E_h = -2.75\, E_h = -74.8 \text{ eV}$

The experimental results : -78.975 eV

(We don't include the antisymmetric spin part : $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ of ψ in the above calculation. It is because we don't have spin operator in the Hamiltonian and the spin part is already normalized so it does not change the inner products $\langle \hat{H}_0 \rangle$ or $\langle \hat{H}' \rangle$)

SQ21

Calculation of some integrals :

1. $\int_0^{r_1} r_2^2 e^{-2\xi r_2/a_0} dr_2$

$= -\frac{a_0}{2\xi} \int_0^{r_1} r_2^2 \, d\left(e^{-2\xi r_2/a_0}\right)$

$= -\frac{a_0}{2\xi}\left[r_2^2 e^{-2\xi r_2/a_0} \Big|_0^{r_1} - 2\int_0^{r_1} r_2 e^{-2\xi r_2/a_0} dr_2 \right]$ (Integration by parts)

$= -\frac{a_0}{2\xi}\left[r_1^2 e^{-2\xi r_1/a_0} + \frac{a_0}{\xi}\int_0^{r_1} r_2 \, d\left(e^{-2\xi r_2/a_0}\right) \right]$

$= -\frac{a_0}{2\xi}\left[r_1^2 e^{-2\xi r_1/a_0} + \frac{a_0}{\xi}\left(r_1 e^{-2\xi r_1/a_0} - \int_0^{r_1} e^{-2\xi r_2/a_0} dr_2 \right) \right]$

$= -\frac{a_0}{2\xi}\left[r_1^2 e^{-2\xi r_1/a_0} + \frac{a_0}{\xi} r_1 e^{-2\xi r_1/a_0} + \frac{a_0^2}{2\xi^2} e^{-2\xi r_2/a_0} \Big|_0^{r_1} \right]$

$= -\frac{a_0}{2\xi}\left[r_1^2 e^{-2\xi r_1/a_0} + \frac{a_0}{\xi} r_1 e^{-2\xi r_1/a_0} + \frac{a_0^2}{2\xi^2} e^{-2\xi r_1/a_0} - \frac{a_0^2}{2\xi^2} \right]$

$= \frac{a_0^3}{4\xi^3} - e^{-2\xi r_1/a_0}\left(\frac{a_0}{2\xi} r_1^2 + \frac{a_0^2}{2\xi^2} r_1 + \frac{a_0^3}{4\xi^3} \right)$

2. $\int_{r_1}^{\infty} r_2 e^{-2\xi r_2/a_0} dr_2$

$= -\frac{a_0}{2\xi}\int_{r_1}^{\infty} r_2 \, d\left(e^{-2\xi r_2/a_0}\right)$

$= -\frac{a_0}{2\xi}\left[r_2 e^{-2\xi r_2/a_0} \Big|_{r_1}^{\infty} - \int_{r_1}^{\infty} e^{-2\xi r_2/a_0} dr_2 \right]$

$= -\frac{a_0}{2\xi}\left[-r_1 e^{-2\xi r_1/a_0} + \frac{a_0}{2\xi} e^{-2\xi r_2/a_0} \Big|_{r_1}^{\infty} \right]$ $\left(\lim_{x\to\infty} x e^{-bx} = 0 \text{ when } b>0 \right)$

$= -\frac{a_0}{2\xi}\left[-r_1 e^{-2\xi r_1/a_0} - \frac{a_0}{2\xi} e^{-2\xi r_1/a_0} \right]$

$= \frac{a_0}{2\xi} r_1 e^{-2\xi r_1/a_0} + \frac{a_0^2}{4\xi^2} e^{-2\xi r_1/a_0}$

SQ21

Calculation of some integrals :

3. $\int_0^\infty r_1 e^{-2\xi r_1/a_0} \, dr_1$

$= -\frac{a_0}{2\xi} \int_0^\infty r_1 \, d(e^{-2\xi r_1/a_0})$

$= -\frac{a_0}{2\xi} \left[\underbrace{r_1 e^{-2\xi r_1/a_0} \Big|_0^\infty}_{0} - \int_0^\infty e^{-2\xi r_1/a_0} \right]$

$= -\frac{a_0}{2\xi} \left[\frac{a_0}{2\xi} e^{-2\xi r_1/a_0} \Big|_0^\infty \right]$

$= -\frac{a_0}{2\xi} \left(-\frac{a_0}{2\xi} \right)$

$= \frac{a_0^2}{4\xi^2}$

4. $\int_0^\infty r_1 e^{-4\xi r_1/a_0} \, dr_1$

$= \frac{a_0^2}{4(2\xi)^2}$ (Replace ξ by 2ξ for the results of last integral)

$= \frac{a_0^2}{16\xi^2}$

SQ21

Calculation of some integrals :

5. $\int_0^\infty r_1^2 e^{-4\xi r_1/a_0} dr_1$

$= -\frac{a_0}{4\xi} \int_0^\infty r_1^2 \, d(e^{-4\xi r_1/a_0})$

$= -\frac{a_0}{4\xi} \left[\underbrace{r_1^2 e^{-4\xi r_1/a_0} \Big|_0^\infty}_{0} - 2\int_0^\infty r_1 e^{-4\xi r_1/a_0} dr_1 \right]$ $\left(\lim_{x\to\infty} x^2 e^{-bx} = 0 \text{ when } b>0 \right)$

$= -\frac{a_0}{4\xi} \left[-2\int_0^\infty r_1 e^{-4\xi r_1/a_0} dr_1 \right]$ $\left(\int_0^\infty r_1 e^{-4\xi r_1/a_0} dr_1 = \frac{a_0^2}{16\xi^2} \right)$

$= \frac{a_0}{4\xi} \, 2 \, \frac{a_0^2}{16\xi^2}$

$= \frac{a_0^3}{32\xi^3}$

SQ22

Taking the trail wavefunction from equation (2):

$$\psi(1,2) = \underbrace{\phi_{1s}(\vec{r_1})\,\phi_{1s}(\vec{r_2})}_{\substack{\text{symmetric} \\ \text{spatial part}}}\ \underbrace{\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)}_{\substack{\text{anti-symmetric} \\ \text{spin part}}}$$

Here, we can focus only on the spatial part,

and put $\phi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{\xi}{a_0}\right)^{\frac{3}{2}} e^{-\frac{\xi}{a_0}r}$, with ξ remains undetermined.

We then have the trail wavefunction to be:

$$\phi_{trail}(\vec{r_1}, \vec{r_2}) = \underbrace{\frac{1}{\sqrt{\pi}}\left(\frac{\xi}{a_0}\right) e^{-\frac{\xi}{a_0}r_1}}_{\phi_{1s}(r_1)}\ \underbrace{\frac{1}{\sqrt{\pi}}\left(\frac{\xi}{a_0}\right) e^{-\frac{\xi}{a_0}r_2}}_{\phi_{1s}(r_2)}$$

To apply variational method, the expectation value of $\hat{H}$ is:

$$\langle \hat{H} \rangle = \iint \phi^*_{trail}(\vec{r_1}, \vec{r_2})\ \hat{H}\ \phi_{trail}(\vec{r_1}, \vec{r_2})\ d^3r_1\, d^3r_2 .$$

where $\hat{H}$ is given in equation (1):

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

The Hamiltonian can be rewrite as:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\xi e^2}{4\pi\epsilon_0 r_1}}_{\hat{H}_1}\ \underbrace{-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{\xi e^2}{4\pi\epsilon_0 r_2}}_{\hat{H}_2} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\hat{H}'} - \underbrace{\frac{(2-\xi)e^2}{4\pi\epsilon_0 r_1}}_{\hat{h}_1} - \underbrace{\frac{(2-\xi)e^2}{4\pi\epsilon_0 r_2}}_{\hat{h}_2}$$

For $\hat{H}_1$ and $\hat{H}_2$, we can think of a single-electron hydrogen-like atom, with nuclear charge ξ,

Remember the fact that the energy level is proportional to ξ^2,

$\therefore$ We can simply write:

$$\langle \hat{H}_1 \rangle = \langle \hat{H}_2 \rangle = \xi^2\,(-13.6\,\text{eV}) = -\frac{1}{2}\xi^2 E_h .$$

In last SQ (SQ21), we also computed the term for $\hat{H}'$,

~~replace Z by ξ,~~

$$\langle \hat{H}' \rangle = \frac{5}{8}\xi E_h$$

So we only left the integrals for $\hat{h}_1$ and $\hat{h}_2$,

$$\langle \hat{h}_1 \rangle = \iint \phi^*_{\text{trail}}(\vec{r}_1, \vec{r}_2)\ \hat{h}_1\ \phi_{\text{trail}}(\vec{r}_1, \vec{r}_2)\, d^3r_1\, d^3r_2$$

$$= \iint \phi^*_{1s}(\vec{r}_1) \left(-\frac{(2-\xi)e^2}{4\pi\epsilon_0 r_1}\right) \phi_{1s}(\vec{r}_1)\quad \phi^*_{1s}(\vec{r}_2)\, \phi_{1s}(\vec{r}_2)\, d^3r_1\, d^3r_2$$

The part with r_2 can be directly integrated out as 1, so we left:

$$\langle \hat{h}_1 \rangle = -\frac{(2-\xi)e^2}{4\pi\epsilon_0} \int \phi^*_{1s}(\vec{r}_1)\, \frac{1}{r_1}\, \phi_{1s}(\vec{r}_1)\, d^3r_1$$

$$= -\frac{(2-\xi)e^2}{4\pi\epsilon_0} \int \frac{1}{\pi}\left(\frac{\xi}{a_0}\right)^3 e^{-\frac{2\xi}{a_0}r_1}\, \frac{1}{r_1}\, d^3r_1$$

$$= -\frac{(2-\xi)e^2}{4\pi\epsilon_0} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{1}{\pi}\left(\frac{\xi}{a_0}\right)^3 e^{-\frac{2\xi}{a_0}r_1}\, \frac{1}{r_1}\, r_1^2 \sin\theta\, dr_1\, d\theta\, d\phi$$

The angular part is simply 4π, then

$$\langle \hat{h}_1 \rangle = -\frac{(2-\xi)e^2}{4\pi\epsilon_0}(4\pi)\int_0^{\infty} \frac{1}{\pi}\left(\frac{\xi}{a_0}\right)^3 e^{-\frac{2\xi}{a_0}r_1}\, r_1\, dr_1$$

$$= -\frac{(2-\xi)e^2}{4\pi\epsilon_0}\, 4\left(\frac{\xi}{a_0}\right)^3\left(\frac{a_0}{2\xi}\right)^2 \qquad \left[\text{Using } \int_0^\infty e^{-\beta x} x^n\, dx = \beta^{-(n+1)}\, n!\right]$$

$$= -\xi(2-\xi)\frac{e^2}{4\pi\epsilon_0 a_0}$$

$$= \xi(\xi-2)E_h,$$

Obviously $\langle \hat{h}_2 \rangle = \langle \hat{h}_1 \rangle$,

$$\therefore \langle \hat{H} \rangle = \langle \hat{H}_1 \rangle + \langle \hat{H}_2 \rangle + \langle \hat{H}' \rangle + \langle \hat{h}_1 \rangle + \langle \hat{h}_2 \rangle$$

$$= -\xi^2 E_h + \frac{5}{8}\xi E_h + 2\xi(\xi-2)E_h$$

$$= \left(-\xi^2 + 2\xi(\xi-2) + \frac{5}{8}\xi\right)E_h.$$

In atomic unit: $\frac{1}{E_h}\langle \hat{H} \rangle = -\xi^2 + 2(\xi - \cancel{\xi}2) + \frac{5}{8}\xi = \xi^2 - \frac{27}{8}\xi.$

To find the minimum, ($\langle \hat{H} \rangle$ is quadratic in ξ with positive coeff in ξ^2)

Set $\frac{\partial \langle \hat{H} \rangle}{\partial \xi} = 0$

$\Rightarrow \quad 2\xi - \frac{27}{8} = 0,$

$\xi = 1.6875$,,

[Note: The value ξ can be thought as the effective charge of an electron "feel" from both the nucleus and the other electron.]

Put this value in $\langle \hat{H} \rangle$, we get:

$\langle \hat{H} \rangle \approx -2.848 \; E_h$,

Comparing to the experimental result $-2.9033 \; E_h$, it is very close (but slightly higher). The variational method works very well here, and better than using the 1st order perturbation method in SQ21.