Problem 15 (SAGAR DAM)

Polarizability of He atom in ground state :-

First I've calculated the ground state of He ~~with~~ with Variational method.

Let the trial wave fn of for He be given by:

$$\psi_0(r_1, r_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}.$$

(Here I've treated that the electrons are facing effective charge Ze in nucleus due to the screening of one on another. So for each e^-; the ground state is Hydrogen like & I've just taken their product as trial state.)

Now this wave fn is the true G.S (from the solution of H like atom) of an atom with nuclear charge Ze & No electron-electron interaction

i.e
$$H_{true} = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)$$

But here for the ~~true~~ actual system of He the Hamiltonian is given by.

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left\{\left(\frac{2}{r_1} + \frac{2}{r_2}\right) + \frac{-1}{|\vec{r}_1 - \vec{r}_2|}\right\}$$

$$= \underbrace{-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)}_{\longrightarrow H_{true}}$$

$$\underbrace{+ \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)}_{\longrightarrow H'}$$

But we can easily say: $\langle \psi_0 | H_{true} | \psi_0 \rangle = 2Z^2 E_1$

$\therefore \langle \psi_0 | H | \psi_0 \rangle = 2Z^2 E_1 + 2(Z-2) \cdot \frac{e^2}{4\pi\epsilon_0} \cdot \left\langle \frac{1}{r} \right\rangle_{\psi_0}$

$+ \langle V_{ee} \rangle_{\psi_0}$.

but $\left\langle \frac{1}{r} \right\rangle$ is the expectation of $\frac{1}{r}$ in one particle hydrogenic wave function $\psi_{01}(r_1)$.

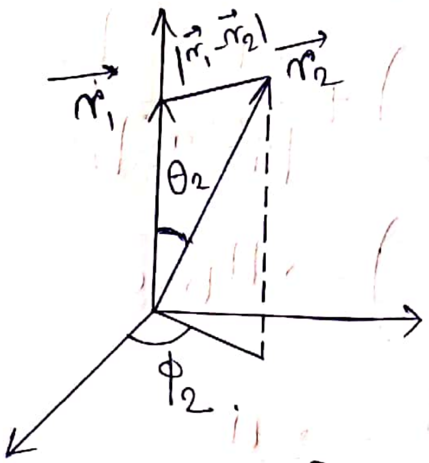
i.e $\left\langle \frac{1}{r_1} \right\rangle = \int_{V_1, V_2} |\psi_0|^2 \cdot \frac{1}{r_1} \, d^3r_1 \cdot d^3r_2$

$$= \underbrace{\int_{V_1} \frac{|\psi_{01}(r_1)|^2}{r_1} d^3r_1}_{\left\langle \frac{1}{r} \right\rangle_{\psi_{01}} \longrightarrow \ = \frac{Z}{a} \text{ (from table)}} \ \underbrace{\int_{V_2} |\psi_0(r_2)|^2 \, d^3r_2}_{1}.$$

& similar for $\left\langle \frac{1}{r_2} \right\rangle$

now for $\langle V_{ee} \rangle$ we get:

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0} \times \left(\frac{Z^3}{\pi a^3} \right)^2 \int \frac{e^{-\frac{2Z(r_1+r_2)}{a}}}{|\vec{r_1} - \vec{r_2}|} d^3r_1 \, d^3r_2$$



If I do the r_2 integral first then:

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

So: r_2 integral gives:

$$I_2 = \int \frac{e^{-\frac{2Zr_2}{a}} \times r_2^2 \sin\theta_2 \, dr_2 \, d\theta_2 \, d\phi_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}.$$

the θ_2 integral gives:

$$\int_0^{\pi} \frac{\sin\theta_2 \, d\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2 \cancel{\sin\theta_2} \cos\theta_2}} = \left. \frac{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}{r_1r_2} \right|_0^{\pi}$$

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

$$= \frac{1}{r_1r_2}\left((r_1+r_2) - |r_1-r_2|\right) = \left.\begin{array}{ll} \frac{2}{r_1} & \text{if } r_1 > r_2 \\ = \frac{2}{r_2} & \text{if } r_1 < r_2 \end{array}\right\}$$

And $\int_0^{2\pi} d\phi = 2\pi$.

So $I_2 = 4\pi \left\{ \int_0^{r_1} \frac{r_2^2}{r_1} e^{-\frac{2Zr_2}{a}} dr_2 + \int_{r_1}^{\infty} r_2 e^{-\frac{2Zr_2}{a}} dr_2 \right\}$

$\Big\downarrow$ Using mathematica.

$$= \frac{\pi a^3}{Z^3 r_1}\left(1 - \left(1+\frac{Zr_1}{a}\right)e^{-\frac{2Zr_1}{a}}\right)$$

$\therefore \langle V_{ee} \rangle$

$$= \frac{e^2}{4\pi\epsilon_0} \times \frac{Z^3}{\pi a^3} \int \left[1 - \left(1+\frac{Zr_1}{a}\right)e^{-\frac{2Zr_1}{a}}\right] e^{-\frac{2Zr_1}{a}} \times r_1 \sin\theta_1 \, dr_1 \, d\theta_1 \, d\phi_1$$

$\Big\downarrow$ Using mathematica.

$$= \frac{5Z}{8a} \times \left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5E_1 Z}{4}.$$

Adding all of them:

$$\langle H\rangle_{\psi_0} = 2Z^2E_1 + \frac{2(Z-2)\cdot Z}{a} \times \frac{e^2}{4\pi\epsilon_0} - \frac{5ZE_1}{4}$$

$$= \left(2Z^2 \cancel{\phi} - 4Z(Z-2) - \frac{5}{4}Z\right)E_1$$

$$= \left(-2Z^2 + \frac{27}{4}Z\right)E_1.$$

∴ for ~~lower~~ upper bound on $\langle H\rangle_0$ we get:

$$\frac{\partial\langle H\rangle}{\partial Z} = 0 \Rightarrow \left(-4Z + \frac{27}{4}\cancel{Z}\right) = 0$$

i.e $Z = \frac{27}{16} = 1.69.$

Imposing external $\vec{E}$ field to calculate Polarizability:-

Now we apply an electric field on the atom along $\hat{z}$ direction with the value $\vec{E} = E_0\hat{z}$. If due to the field the induced dipole moment (which in normal ground state be zero) is $\vec{p}$ then $\vec{p} = \alpha\vec{E}$ & α is polarizability.

Now due to the perturbation $V'_r = -zE_0e$ (for $1e^-$)

i.e $V'(r_1, r_2) = -(z_1 + z_2)E_0e$

We have to calculate $\langle\psi|V'|\psi\rangle$ for perturbation.

According to the selection rule for z i.e
$m' = m$; $l' = l \pm 1$ we get

$\langle \psi_g | H' | \psi_g \rangle = 0$ i.e $\Delta E_g^1 = 0$

as for ψ_g we get only $l = 0$ so $\Delta l = 0$..

(i.e the θ integral here will give $\int_0^\pi \cos\theta \sin\theta \, d\theta = 0$)

So we get first order perturbation gives zero.

for 2nd order perturbation; we get

$$\Delta E^2 = -\sum_{n \neq 1} \frac{|\langle \psi_n | V' | \psi_1 \rangle|^2}{(E_n^0 - E_1^0)} \quad \ldots (1)$$

Here the first contributor to ψ_n will be $|210\rangle$ state.

From the analysis of H like atom; we assume the $|210\rangle$ state of He is approximately (which is again some shifted due to coloumb repulsion correction ~~due to e~~ of electrons.)

$$\psi_{210}(He) \sim \psi_{210}^{Z_H}(r_1) \cdot \psi_{210}^{Z_H}(r_2)$$

So the energy of state $n=2$ is appr

$$E_{|210\rangle} \simeq 2 \times \frac{Z^2 E_H^1}{2^2} \simeq -\frac{Z^2}{2} \times (13.6) \text{ eV} \quad \left(\begin{matrix}\text{This } Z \\ \text{is } 1.69\end{matrix}\right)$$

As higher states are less spaced; so we can assume that $E_n^0 - E_0^0 \simeq E_{|210\rangle}^0 - E_{|100\rangle}^0$

$$\simeq (13.6)\left(\frac{1.69^2}{2} - 1\right) \text{ eV}.$$

$$\simeq -(13.6)\times\left\{\frac{1.69^2}{2} - 1.69^2\times 2\right\}\text{ eV}$$

$$= 58.26 \text{ eV.}$$

So from (1): $\Delta E_g^2 \simeq -\sum_{m=1} \frac{|\langle\psi_{1\circ}|V'|\psi_m\rangle\langle\psi_m|V'|\psi_{1\circ}\rangle|}{E_2^0 - E_1^0}$

$$\simeq -\frac{|\langle\psi_{1\circ}|V'^2|\psi_{1\circ}\rangle|}{E_2^0 - E_1^0} \quad \left(\because \langle\psi_g|V'|\psi_g\rangle = 0\right)$$

$$\simeq -\frac{1}{E_2-E_1}|\langle\psi_{1\circ}|e^2E_0^2(z_1+z_2)^2|\psi_{1\circ}\rangle| \quad \left(\psi_1 \equiv \psi_{ground} \equiv \psi_g\right)$$

$$\simeq -\frac{E_0^2e^2}{E_2-E_1}\left[\langle\psi_1|z_1^2|\psi_1\rangle + \langle\psi_1|z_2^2|\psi_1\rangle + 2\underbrace{\langle\psi_1|z_1z_2|\psi_1\rangle}_{0}\right]$$

$$\simeq -\frac{2e^2E_0^2}{E_2-E_1}\times\underbrace{\langle\psi_1|z_1^2|\psi_1\rangle}_{\text{with mathematica } \to \frac{a^2}{3Z^2}}$$

$Z \to 1.69$

$$\therefore \Delta E_g^2 = -\frac{2e^2E_0^2a^2}{3(E_2-E_1)\times 1.69^2}$$

Now if $\vec{P} = \alpha\vec{E_0}$; then energy of the dipole is:

$|\Delta E| = \frac{\alpha E_0^2}{2}$ (from electrostatics)

$$\therefore \frac{\alpha \cancel{E_0^2}}{2} = \frac{2e^2\cancel{E_0^2}a^2}{3(E_2-E_1)\times 1.69^2} \Rightarrow \alpha = \frac{4e^2a^2}{3\times 1.69^2\cdot(E_2^0-E_1^0)}$$

$$\Rightarrow \alpha = 3.59\times 10^{-42} \text{ (in SI unit)}$$

Answer

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