L73-Helium

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$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + V_{12} \qquad \mathcal{H}_{\frac{1}{2}} = \frac{-\hbar^2}{2m}\nabla^2_{\frac{1}{2}} - \frac{e^2}{4\pi\varepsilon_0 r_{\frac{1}{2}}} \qquad V_{12} = \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

$E_{gs} = -78.95$ exp.

$$\boxed{\begin{array}{l} \text{recall: } E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0^2}\right)^2 \sim Z^2 \\ a = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.529\,\text{Å} \sim \frac{1}{Z} \qquad \psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \end{array}}$$

solution of $\mathcal{H}_1 + \mathcal{H}_2$:

$$\psi_0(r_1, r_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)\,\chi_{sing.}(\vec{s}_1, \vec{s}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} \cdot \chi_{sing}(\vec{s}_1, \vec{s}_2)$$

$$E^{(1)}_{gs} = 8E_1 = -109\,\text{eV}$$

* Apply the variational principle with ψ_0 as our trial wavefunction:

$$\langle \mathcal{H} \rangle = \langle \mathcal{H}_1 + \mathcal{H}_2 \rangle + \langle V_{12} \rangle$$

$$\langle V_{12} \rangle = \int d^3r_1\, d^3r_2\, |\psi_0|^2 \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{8}{\pi a^3}\right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\vec{r}_1 + \vec{r}_2|} d^3r_1\, d^3r_2$$

$\vec{r}_2$ integral: $\quad |\vec{r}_1 - \vec{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta} \quad (r_1 \text{ along } \hat{z}')$

$$I_2 \equiv \int \frac{e^{-4r_2/a}}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_2 = \int_0^\infty\int_0^\pi\int_0^{2\pi} \frac{e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta}} r_2^2\, dr_2 \sin\theta\, d\theta\, d\phi$$

$$\int_0^\pi \frac{\sin\theta\, d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta}} = \left.\frac{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta}}{r_1r_2}\right|_0^\pi = \frac{1}{r_1r_2}\Big[(r_1+r_2) - |r_1 + r_2|\Big] = 2/r_> \qquad r_> = \begin{cases} r_1 & r_1 > r_2 \\ r_2 & r_2 > r_1 \end{cases}$$

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

$$= \frac{\pi a^3}{8r_1}\left[1 - \left(1 + \frac{2r_1}{a}\right)e^{-4r_1/a}\right]$$

$\vec{r}_1$ integral:
$$\langle V_{12} \rangle = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{8}{\pi a^3}\right)^2 \frac{\pi a^3}{8r_1} \underbrace{\int \left[1 - \left(1 + \frac{2r_1}{a}\right)e^{-4r_1/a}\right] r_1^2\, dr_1}_{5a^2/128}\, \underbrace{d\Omega_1}_{4\pi}$$

$$= \frac{5}{4a}\left(\frac{e^2}{4\pi\varepsilon_0}\right) = -5/2\, E_1 = 34\,\text{eV}$$

thus $\langle \mathcal{H} \rangle = -109\,eV + 34\,eV = -75\,eV$ much closer!

note: this was also 1st order perturbation theory!

* what about minimization? (above was a 0-parameter fit)

Assume the mean field of electric charge will modify Z_{eff}.

Dont modify $\mathcal{H}$, just ψ_0!

$$\psi_1 = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$$

Hamiltonian with nuclear charge Z:

$$\mathcal{H}_Z |\psi_1\rangle = 2Z^2 E_1 |\psi_1\rangle$$

$$\mathcal{H} = \mathcal{H}_Z + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|r_1-r_2|}\right)$$

$$\langle \mathcal{H} \rangle = 2Z^2 E_1 + 2(Z-2)\frac{e^2}{4\pi\varepsilon_0}\underbrace{\left\langle \frac{1}{r} \right\rangle}_{Z/a} + \underbrace{V_{ee}}_{a \to a\cdot\frac{2}{Z}}$$

$$= \left[2Z^2 - 4Z(Z-2) - \tfrac{5}{4}Z\right] E_1 = \left[-2Z^2 + \tfrac{27}{4}Z\right] E_1$$

* minimize energy of ground state:

$$\frac{d}{dZ}\langle \mathcal{H} \rangle = \left[-4Z + \tfrac{27}{4}\right] E_1 = 0 \qquad Z = \frac{27}{16} = \frac{3^3}{2^4} \approx 1.69$$

$$\langle \mathcal{H} \rangle = \left(-2Z^2 + \tfrac{27}{4}Z\right) E_1 = -\frac{3^6}{2^7} E_1 = -77.5\,eV$$ 2% off