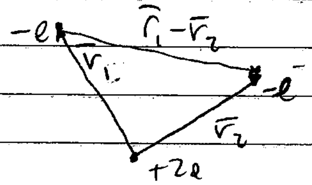
Lecture 12

Helium atom



$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \underbrace{\frac{1}{|\bar r_1 - \bar r_2|}}_{V_{ee}}\right)$$

Calculate E_{gs}

Experimental value $E_{gs} = -78.975\ eV$

Problem: e-e interaction

Assume e-e int $\approx 0 \Rightarrow \psi_0(\bar r_1, \bar r_2) \approx \psi_{100}(\bar r_1)\,\psi_{100}(\bar r_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$

$H = H_1 + H_2$ where $H_i = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{2e^2}{4\pi\varepsilon_0 r_i}$ Hydrogen atom

Ground state energy: $\tilde E_{gs} = -109\ eV$

Use variational principle

trial wave functions? ψ_0 (non-interacting electrons)

$$\langle\psi_0|H|\psi_0\rangle = \tilde{E}_{gs} + \langle\psi_0|V_{ee}|\psi_0\rangle$$

$$\langle\psi_0|V_{ee}|\psi_0\rangle = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{8}{\pi a^3}\right)^2 \int \frac{e^{-\frac{4(r_1+r_2)}{a}}}{|\bar{r}_1-\bar{r}_2|}\, d\bar{r}_1\, d\bar{r}_2$$ [do the integrals separated]

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

$\Downarrow$

$$\langle\psi_0|V_{ee}|\psi_0\rangle = \frac{5}{4a}\left(\frac{e^2}{4\pi\varepsilon_0}\right) = 34\,eV$$

$$\langle\psi_0|H|\psi_0\rangle = -75\,eV$$

Each electron shields the e-ion interaction of the other $\Rightarrow$ each electron sees an effective nuclear charge $Z<2$

$$\psi(\bar{r}_1,\bar{r}_2) \equiv \frac{Z^3}{\pi a^3}\, e^{-Z(r_1+r_2)/a}$$ Z is a parameter

Rewrite $H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) +$

$$+ \frac{e^2}{4\pi\varepsilon_0}\left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

$$\langle\psi|H|\psi\rangle = \frac{Z^2}{4}\hat{E}_{gs} + 2(Z-2)\frac{e^2}{4\pi\varepsilon_0}\underbrace{\langle\psi_{100}|\frac{1}{r}|\psi_{100}\rangle}_{\frac{Z}{e}} + \underbrace{\langle V_{ee}\rangle}_{\frac{5Z}{8e}\left(\frac{e^2}{4\pi\varepsilon_0}\right)}$$

$$\langle\psi|H|\psi\rangle = \left[-2Z^2 + \frac{27}{4}Z\right]\underbrace{(-R_y)}_{-13.6058\,eV}$$

lowest bound $\frac{d}{dZ}\langle H\rangle = -\left[-4Z + \frac{27}{4}\right]R_y = 0$

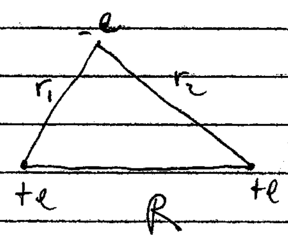
$$\Downarrow$$

$$Z = \frac{27}{16} = 1.69$$

$$\Downarrow$$

$$\langle H\rangle = -77.5\ eV$$

The H_2^+ ion (1 el and 2 protons)



$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

Hydrogen atom in ground state $\psi_0(\bar{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}}$

Electron is equally distributed between the two protons (assume $R \gg a$)

Use $\psi_{trial} = A\left[\psi_0(\bar{r}_1) + \psi_0(\bar{r}_2)\right]$ i.e. a linear combination of atomic orbitals