Physics 472 Lecture 16

The Ground State of Helium

$$H = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

(ignoring fine structure, etc.), $Z = 2$.

Experimentally, $E_{gs} = -78.975\,eV$.

$|E_{gs}|$ is the energy necessary to remove both electrons to "infinity."

Theoretically, this problem cannot be solved exactly. It is an example of the 3-body problem, which generally can only solved approximately.

Let's write $H = H_0 + H_1$, $\lfloor 2$

with $H_0 = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}$

and $H_1 = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$.

We know the ground state of H_0; it is

$$\Psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)$$
$$= \frac{Z^3}{\pi a^3} e^{-\frac{Z(r_1+r_2)}{a}},$$

where $a = \hbar^2/m_e e^2$ = Bohr radius.

Note that since the spatial wave-function is symmetric, the spin wavefunction must be antisymmetric ($S=0$, singlet).

$$H_0 \Psi_0 = -2 \frac{Z^2 m_e e^4}{2\hbar^2} \Psi_0$$

$$= 8 E_1 \Psi_0$$

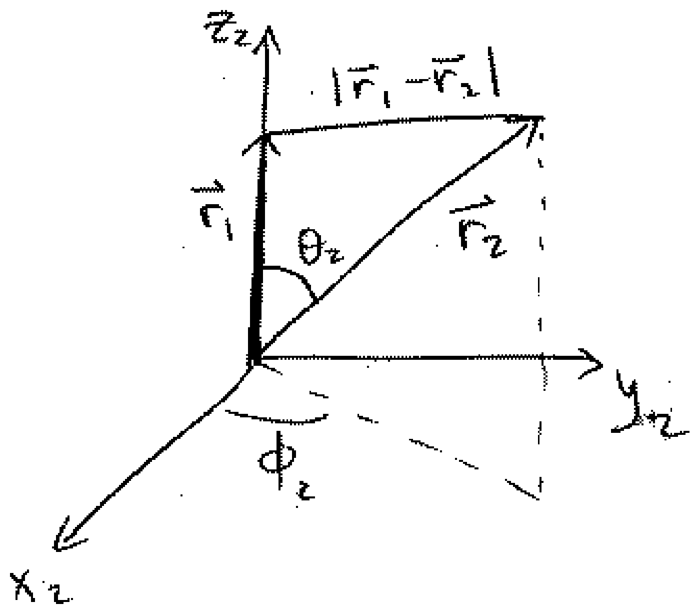
$$8E_1 = -8\,(13.6\,\mathrm{eV}) = -109\,\mathrm{eV}$$

Obviously, this is too low! That is not surprising, since we left out the electron-electron repulsion $H_1 = e^2/|\vec{r}_1 - \vec{r}_2|$. First-order nondegenerate perturbation theory:

$$E_{gs} \cong 8E_1 + \langle H_1 \rangle.$$

$$\langle H_1 \rangle = \left(\frac{8e}{\pi a^3}\right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\vec{r}_1 - \vec{r}_2|}\, d^3r_1\, d^3r_2$$

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



Choosing z_2-axis to lie along $\vec{r}_1$, without loss of generality.

The $\vec{r}_2$-integral is

$$I_2 \equiv \int \frac{e^{-4r_2/a}}{|\vec{r}_1 - \vec{r}_2|} d^3 r_2$$

$$= \int \frac{e^{-4r_2/a} \, r_2^2 \sin\theta_2 \, dr_2 \, d\theta_2 \, d\phi_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}$$

The ϕ_2-integral gives 2π; the θ_2-integral is

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

$$= \left. \frac{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}{r_1 r_2} \right|_0^{\pi}$$

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

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

$$= \begin{cases} \frac{2}{r_1}, & r_2 < r_1 \\ \frac{2}{r_2}, & r_2 > r_1 \end{cases}$$

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

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

Thus

$$\langle H_1 \rangle = \frac{8e^2}{\pi a^3} \int \left[1 - \left(1 + \frac{2r_1}{a}\right) e^{-4r_1/a}\right] e^{-4r_1/a}$$

$$\times\, r_1 \sin\theta_1\, dr_1\, d\theta_1\, d\phi_1$$

$$= 4\pi \left(\frac{8e^2}{\pi a^3}\right) \int_0^\infty \left[r e^{-4r/a} - \left(r - \frac{2r^2}{a}\right) e^{-8r/a}\right] dr$$

$$= \frac{32e^2}{a^3} \frac{5a^2}{128} = \frac{5}{4} \frac{e^2}{a} = 34\,\mathrm{eV}$$

The result of pert. thy is thus

$$E_{gs} \simeq -\left(8 - \frac{5}{2}\right) 13.6\,\mathrm{eV} = -\frac{11}{2}\, 13.6\,\mathrm{eV}$$

$$= -74.8\,\mathrm{eV}$$

Not bad, compared to the exp. value $E_{gs} = -79\,\mathrm{eV}$.

Note that 1st-order pert. thy overestimates E_{gs}. This is because

$$E_{gs}^{(0)} + E_{gs}^{(1)} = \langle \Psi_0 | H_0 | \Psi_0 \rangle + \langle \Psi_0 | H_1 | \Psi_0 \rangle$$

$$= \langle \Psi_0 | H | \Psi_0 \rangle \geq E_{gs}$$

by the variational principle.

Let's use the variational principle to improve our estimate of E_{gs}. Physically, each electron screens the nuclear electric field felt by the other. For example, if $r_2 \gg \frac{a}{2}$, it will see a Coulomb potential with $Z^* = 1$, not 2.

We can take screening into account in the variational wavefunction by replacing Z $(=2)$ with an effective charge $Z^* < 2$: Try

$$\Psi_0(\vec{r}_1,\vec{r}_2) = \frac{Z^*}{\pi a^3} e^{-Z^*\frac{(r_1+r_2)}{a}}.$$

write:

$$H = -\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2)^2 - \frac{Z^* e^2}{r_1} - \frac{Z^* e^2}{r_2}$$

$$+ \frac{Z^*-2}{r_1}e^2 + \frac{Z^*-2}{r_2}e^2 + \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$\langle H \rangle = 2(Z^*)^2 E_1 + 2(Z^*-2)\left\langle \frac{e^2}{r} \right\rangle + \langle H_1 \rangle$$

$$= 2(Z^*)^2 E_1 - 4(Z^*-2)Z^* E_1 + \frac{5Z^*}{8a}$$

$$\langle H \rangle = \left[2(Z^*)^2 - 4(Z^*-2)Z^* - \tfrac{5}{4}Z^*\right]E_1$$

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

minimum:

$$0 = \frac{\partial \langle H \rangle}{\partial Z^*} = \left[-4Z^* + \frac{27}{4}\right]E_1$$

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

our bound is:

$$E_{gs} \geq \frac{729}{128}E_1 = -77.5\,\text{eV}$$

This is 3eV lower than 1st-order pert. thy, and only 1.5eV above the experimental value.