First order correction to helium gnd st energy

$$E^1 = \langle E_0^0 | V_{int} | E_0^0 \rangle$$ 781

$$u_{100}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$ $Z=2$ for helium

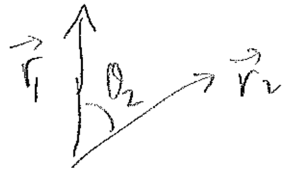
$$V_{int} = \frac{ke^2}{|\vec{r}_1-\vec{r}_2|} = \frac{\alpha\hbar c}{|\vec{r}_1-\vec{r}_2|}$$

$$E^1 = \int d^3\vec{r}_1\, d^3\vec{r}_2\; u_{100}(r_1)^* u_{100}^*(r_2) \frac{\alpha\hbar c}{|\vec{r}_1-\vec{r}_2|} u_{100}(r_1) u_{100}(r_2)$$

$$= \frac{1}{\pi^2}\left(\frac{2}{a_0}\right)^6 \alpha\hbar c \int d^3\vec{r}_1\, e^{-\frac{4r_1}{a_0}} \underbrace{\int d^3\vec{r}_2\, e^{-\frac{4r_2}{a_0}} \frac{1}{|\vec{r}_1-\vec{r}_2|}}_{I_2}$$

Let spherical coord of $\vec{r}_2$ be defined

First do integral over $\vec{r}_2$. relative to $\vec{r}_1$ axis



$$I_2 = \int r_2^2\, dr_2 \sin\theta_2\, d\theta_2\, d\phi_2\, e^{-\frac{4r_2}{a_0}} \frac{1}{u^{1/2}}$$

$u = r_1^2 + r_2^2 - 2r_1r_2\cos\theta$

$du = +2r_1r_2\sin\theta\, d\theta$

$$du = (2r_1r_2\sin\theta_2\, d\theta_2) \Rightarrow \sin\theta_2\, d\theta_2 = \frac{du}{2r_1r_2}$$

$$2\pi \int \frac{r_2}{r_1}\, dr_2\, e^{-\frac{4r_2}{a_0}} \underbrace{\int \frac{du}{2u^{1/2}}}_{u^{1/2}} = \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}\,\Big|_0^\pi = \underbrace{(r_1+r_2)-|r_1-r_2|}$$

$2r_2$ if $r_2 < r_1$

$2r_1$ if $r_2 > r_1$

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

$$= \frac{\pi a_0^3}{8r_1}\left[1 - \left(1+\frac{2r_1}{a_0}\right)e^{-\frac{4r_1}{a_0}}\right]$$

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$$I_1 = \int d^3r_1\, e^{-\frac{4r_1}{a_0}} I_2$$

$$= \int r_1^2 dr_1 \underbrace{\sin\theta_1 d\theta_1 d\phi_1}_{(4\pi)} e^{-\frac{4r_1}{a_0}} \frac{\pi a_0^3}{8r_1}\left[1-\left(1+\frac{2r_1}{a_0}\right)e^{-\frac{4r_1}{a_0}}\right]$$

$$= \frac{\pi^2 a_0^3}{2} \underbrace{\int_0^\infty dr_1 \left[r_1 e^{-\frac{4r_1}{a_0}} - \left(r_1 + \frac{2r_1^2}{a_0}\right) e^{-\frac{8r_1}{a_0}}\right]}_{\frac{5}{128}a_0^2\ \checkmark}$$

so $E' = \frac{1}{\pi^2} \frac{32}{a_0^6} (\alpha\hbar c) \frac{\pi^2 a_0^3}{2} \frac{5}{128} a_0^2 = \frac{\alpha\hbar c}{a_0} \frac{5}{4} = \alpha^2 mc^2 \frac{5}{4}$

But $13.6\,eV = \frac{1}{2}\alpha m c^2$ so $E' = \frac{5}{2}(13.6) = 34\,eV$

$$\left.\begin{aligned} E^0 &= -109\,eV = -4\alpha^2 mc^2 \\ E' &= +34\,eV = \tfrac{5}{4}\alpha^2 mc^2 \end{aligned}\right\} -\tfrac{9}{4}\alpha^2 mc^2$$

so corrected energy is $-75\,eV$ (expt $= -79\,eV$)

$$\left[u_{100}^*(r_1)\, u_{2lm}^*(r_2) \pm u_{2lm}^*(r_1)\, u_{100}^*(r_2)\right] \frac{1}{|r_1 - r_2|} \left[u_{100}(r_1)\, u_{2lm}(r_2) \pm u_{2lm}(r_1)\, u_{100}(r_2)\right]$$

$$= \int |u_{100}(r_1)|^2 \, |u_{2lm}(r_2)|^2 \frac{1}{|r_1 - r_2|} \pm \underbrace{\int u_{100}^*(r_1)\, u_{2lm}(r_1)\, u_{100}(r_2)\, u_{2lm}^*(r_2) \frac{1}{|r_1 - r_2|}}_{\text{exchg term}}$$

NB: anti sym state $\Rightarrow$ lower energy $\Rightarrow$ spin 1 (ortho)
sym stt $\Rightarrow$ higher energy $\Rightarrow$ spin 2 (para)

$\Rightarrow$ ortho < para

(Hund's rule)

<u>Note to self</u>

Space + spin don't <u>have</u> to be separately symm'c or antisym

e.g. could start w/ $[u_{100}(\vec{r}_1)\chi^1_+][u_{2\ell m}(\vec{r}_2)\chi^2_-]$

and antisymmetrize

$\downarrow\uparrow \quad \uparrow\downarrow$

$$u_{100}(r_1)u_{2\ell m}(\vec{r}_2)\chi^1_+\chi^2_- - u_{2\ell m}(r_1)u_{100}(r_2)\chi^1_-\chi^2_+$$

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or could start w/ $[u_{100}(r_1)\chi^1_-][u_{2\ell m}(r_2)\chi^2_+]$

and antisymmetrize

$\uparrow\downarrow \quad \downarrow\uparrow$

$$u_{100}(r_1)u_{2\ell m}(r_2)\chi^1_-\chi^2_+ - u_{2\ell m}(r_1)u_{100}(r_2)\chi^1_+\chi^2_-$$

But then one can form <u>sums</u> + <u>differences</u> of these to get parahelium

$$[u_{100}(r_1)u_{2\ell m}(r_2) + u_{2\ell m}(r_1)u_{100}(r_2)](\chi^1_+\chi^2_- - \chi^1_-\chi^2_+)$$

+ orthohelium

$$[u_{100}(r_1)u_{2\ell m}(r_2) - u_{2\ell m}(r_1)u_{100}(r_2)](\chi^1_+\chi^2_- + \chi^1_-\chi^2_+)$$