First order correction to helium grd st. energy

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

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

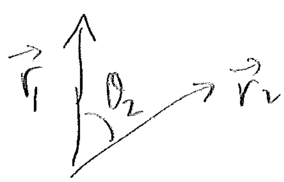
$$V_{int} = \frac{ke^2}{|\vec r_1 - \vec r_2|} = \frac{\alpha\hbar c}{|\vec r_1 - \vec r_2|}$$

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

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

First do integral over $\vec r_2$. Let spherical coords of $\vec r_2$ be defined relative to $\vec r_1$ axis

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



$$I_2 = \int r_2^2\, dr_2 \sin\theta_2\, d\theta_2\, d\phi_2\, e^{-\frac{4r_2}{a_0}} \frac{1}{\sqrt{\underbrace{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}_{u}}}$$

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

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

$2r_2$ if $r_2 < r_1$
$2r_1$ if $r_2 > r_1$

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

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

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

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

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

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

$E^0 = -109\,eV = -4\alpha mc^2$ $\Big\}$ $-\frac{9}{4}\alpha mc^2$

$E' = +34\,eV = \frac{5}{4}\alpha mc^2$ (expt $= -79\,eV$)

so corrected energy is $-75\,eV$

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

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

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

$\Rightarrow$ ortho < para

(Hund's rule)

Note to self

Space + spin don't have to be separately symm'c or antisymm

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

and antisymmetrize

$\downarrow$

$\uparrow$

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

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

and antisymmetrize

$\uparrow$

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

$\downarrow$

But then one can form sums + differences 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

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