Helium

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

If we ignore e^2/r_{12}, then we just have

$w_a(x_1)\, w_b(x_2)$ where the w's are

hydrogenic wave functions with $Z = 2$.

For instance we could use

$$\phi(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_{100}(x_1)\,\psi_{n\ell m}(x_2) + (-1)^S \psi_{100}(x_2)\,\psi_{n\ell m}(x_1)\right]$$

to represent the $S=0$ or $S=1$ states with

one e in 100 and the other in $n\ell m$.

The ground state is $(1s)^2$, i.e.,

both are 100. So $\phi(x_1, x_2) = \phi(x_2, x_1)$

and hence $S = 0$. So

$$\begin{aligned}\psi &= \psi_{100}(x_1)\,\psi_{100}(x_2)\,\chi_{S=0} \\ &= \frac{Z^3}{\pi a_0^3}\, e^{-Z(r_1+r_2)/a_0}\, \chi_{S=0} \quad \text{with } Z=2.\end{aligned}$$

This ψ has

$$E = 2 \times 4 \left(-\frac{e^2}{2a_0} \right) = -108.8\,\mathrm{eV}$$

two e's $\quad$ Z^2 $\quad$ $-13.6\,\mathrm{eV}$

This is too low by 30%. But we ignored e^2/r_{12}. So

$$\Delta E_{(1s)^2} = \left\langle \frac{e^2}{r_{12}} \right\rangle_{(1s)^2} = \iint \frac{Z^6}{\pi^2 a_0^6} e^{-2Z(r_1+r_2)/a_0} \frac{e^2}{r_{12}} \, d^3x_1 \, d^3x_2 .$$

Now

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma}} = \sum_{\ell=0}^{\infty} \frac{r_<^\ell}{r_>^{\ell+1}} P_\ell(\cos\gamma)$$

$$\cos\gamma = \frac{x_1 \cdot x_2}{r_1 r_2} .$$ Now

$$P_\ell(\cos\gamma) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\theta_1 \phi_1) \, Y_\ell^m(\theta_2 \phi_2)$$

$$\int Y_\ell^m(\theta_i \phi_i) \, d\Omega_i = \frac{1}{\sqrt{4\pi}} 4\pi \, \delta_{\ell 0} \, \delta_{m 0} .$$ So

$$\Delta E_{(1s)^2} = \frac{Z^6 e^2 (4\pi)^2}{\pi^2 a_0^6} \int_0^\infty r_1^2 dr_1 \left[\int_0^{r_1} r_2^2 dr_2 \frac{e^{-2Z(r_1+r_2)/a_0}}{r_1} + \int_{r_1}^\infty r_2^2 dr_2 \frac{e^{-2Z(r_1+r_2)/a_0}}{r_2} \right]$$

$$\Delta E_{(1s)^2} = 16 \frac{Z^6 e^2}{a_0^6} \frac{5}{128} \frac{a_0^5}{Z^5}$$

$$= \frac{5}{8} \frac{Z e^2}{a_0} = \frac{5}{2} \frac{e^2}{2a_0}$$

So now

$$E_{(1s)^2} = \left(-8 + \frac{5}{2}\right) \frac{e^2}{2a_0} = -\frac{11}{2} \frac{e^2}{2a_0}$$

$$= -\frac{11}{2}\, 13.6\,\text{eV} = -74.8 \text{ eV}.$$

The experimental value is -78.8 eV.

Variational trial function

$$\langle x_1 x_2 | \tilde{0} \rangle = \left(\frac{Z_e^3}{\pi a_0^3}\right) e^{-Z_e (r_1 + r_2)/a_0}$$

where Z_e is the variational parameter.

Now $$\left\langle \frac{p_1^2}{2m} \right\rangle = \frac{Z_e^2 e^2}{2a_0}$$

$$\left\langle -\frac{Z e^2}{r_1} \right\rangle = -Z Z_e \frac{e^2}{a_0}$$

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{5}{8} Z_e \frac{e^2}{a_0}$$

So

$$\bar{H} = \left\langle \frac{p_1^2}{2m} \right\rangle + \left\langle \frac{p_2^2}{2m} \right\rangle - \left\langle \frac{Ze^2}{r_1} \right\rangle - \left\langle \frac{Ze^2}{r_2} \right\rangle + \left\langle \frac{e^2}{r_{12}} \right\rangle$$

$$= \left(Z_e^2 - 2 Z Z_e + \frac{5}{8} Z_e \right) \left(\frac{e^2}{a_0} \right)$$

$$0 = \frac{\partial \bar{H}}{\partial Z_e} = \left(2 Z_e - 2 Z + \frac{5}{8} \right) \left(\frac{e^2}{a_0} \right)$$

$$Z_e = Z - \frac{5}{16} = 2 - \frac{5}{16} = 1.6875$$

$$H(1.6875) = -77.5\,\mathrm{eV}$$

which is pretty close to $-78.8\,\mathrm{eV}$.

This result (A. Unsöld, Ann. Phys. 82 (1927) 355) was an early sign that Schrödinger's wave mechanics was right.

Excited states

(1s) (nl)

$$E = E_{100} + E_{nl m} + \Delta E$$

By first-order perturbation theory,

$$\Delta E = \langle 100, n\ell m, \pm | \frac{e^2}{r_{12}} | 100, n\ell m, \pm \rangle$$

$$= \int d^3x_1 \, d^3x_2 \, \frac{1}{\sqrt{2}} \left[\psi^*_{100}(x_1) \psi^*_{n\ell m}(x_2) \pm \psi^*_{100}(x_2) \psi^*_{n\ell m}(x_1) \right]$$

$$\cdot \frac{e^2}{r_{12}} \frac{1}{\sqrt{2}} \left[\psi_{100}(x_1) \psi_{n\ell m}(x_2) \pm \psi_{100}(x_2) \psi_{n\ell m}(x_1) \right]$$

$$= \underbrace{\int d^3x_1 \, d^3x_2 \, |\psi_{100}(x_1)|^2 \, |\psi_{n\ell m}(x_2)|^2 \, \frac{e^2}{r_{12}}}_{\text{(direct)}}$$

$$\pm \underbrace{\int d^3x_1 \, d^3x_2 \, \psi_{100}(x_1) \psi_{n\ell m}(x_2) \frac{e^2}{r_{12}} \psi^*_{100}(x_2) \psi^*_{n\ell m}(x_1)}_{\text{(exchange)}}$$

$$= I \pm J$$

Now J can be viewed as

$$\int d^3x_1 d^3x_2 \, \psi_{100}(x_1) \psi^*_{n\ell m}(x_1) \, \frac{e^2}{r_{12}} \, \psi^*_{100}(x_2) \psi_{n\ell m}(x_2)$$

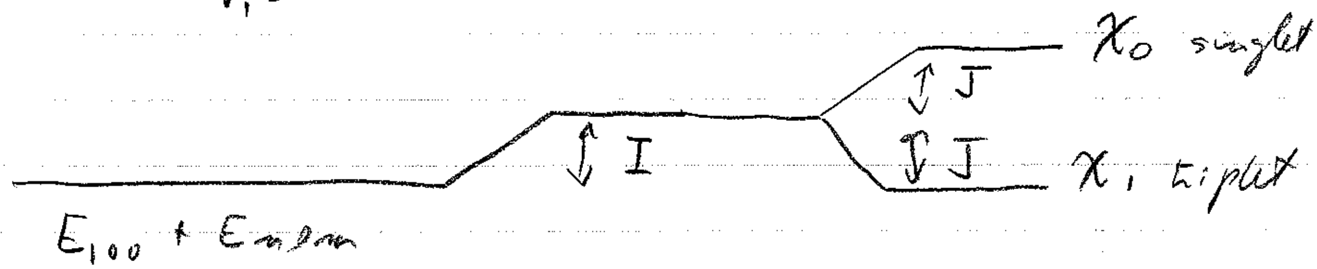
$$= \int d^3x_1 d^3x_2 \, f^*(x_1) \, \frac{e^2}{r_{12}} \, f(x_2) \qquad f(x) = \psi^*_{100}(x) \psi_{n\ell m}(x)$$

$= f^\dagger P f$ where $P = \dfrac{e^2}{r_{12}}$ is positive

so $f^\dagger P f \geq 0$.

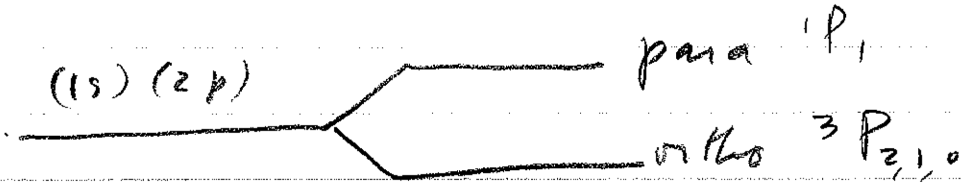
So the lower energy state is the one that is spatially antisymmetric.

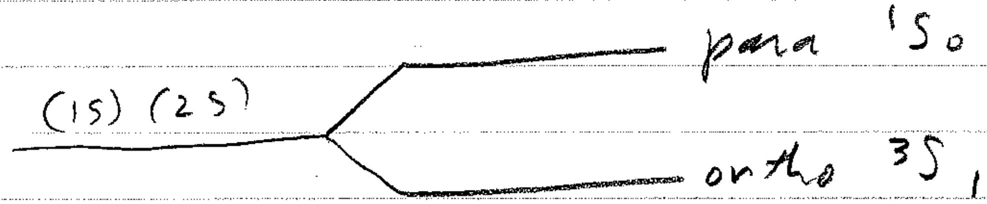
$$\left\langle \frac{e^2}{r_{12}} \right\rangle = I \pm J$$

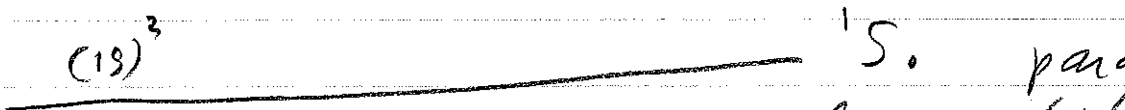


The χ_0 states are parahelium, while the χ_1 states are orthohelium.

The states with less energy are orthohelium.







is only possibility.

Here spin & statistics effects lead to an effective term

$$H_{eff} = H_0 - \gamma \vec{S}_1 \cdot \vec{S}_2 ,$$

where $\gamma > 0$ is some constant, even though the actual H has no spin terms whatsoever.

Ferromagnetism is believed to be similar in its origin.