Helium

\[ U = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \]

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

\[ \psi_{a_1}(x_1) \psi_{a_2}(x_2) \] where the \( \psi \)'s are a

hydrogenic wave functions with \( Z = 2 \).

For instance we could use

\[ \phi(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \psi_{100}(x_1) \psi_{010}(x_2) + (-1)^5 \psi_{100}(x_2) \psi_{010}(x_1) \right] \]

to represent the \( S = 0 \) or \( S = 1 \) states with

one \( e \) in \( 110 \) and the other in \( 010 \).

The ground state is \((15)^2\), i.e.,

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

and hence \( S = 0 \). So

\[ \psi = \psi_{100}(x_1) \psi_{100}(x_2) \chi_{S=0} = \frac{Z^2}{\pi \alpha_0^3} \epsilon \]

\[ \chi_{S=0} \text{ with } Z = 2. \]
This has

\[ E = 2 \times 4 \left( -\frac{e^2}{2a_0} \right) = -108.8 \text{ eV} \]

two e's

This is \( V_{100} \) lower by 30\%o. But we ignored \( e^2/r_{12} \) so

\[ \Delta E_{(15)^2} = \left\langle \frac{e^2}{r_{12}} \right\rangle_{(15)^2} = \int \frac{\pi^2 e^6}{n^2 a_0} e \frac{e^2}{r_{12}} \, d^3x_1 \, d^3x_2 \]

Now

\[ \frac{1}{r_{12}} = \frac{1}{\sqrt{r_{12}^2 + r_{21}^2 - 2 r_{12} r_{21} \cos \gamma}} = \sum_{l=0}^{\infty} \frac{r_{12}^l}{l^{2l+1}} P_l (\cos \gamma) \]

Now

\[ \cos \gamma = \frac{x_1 \cdot x_2}{r_{12} r_{21}} \]

\[ P_l (\cos \gamma) = \frac{4\pi}{l^{2l+1}} \sum_{m=-l}^{l} \mathcal{Y}^m_l (\theta_1, \phi_1) \mathcal{Y}^{*m}_{-l} (\theta_2, \phi_2) \]

\[ \int \mathcal{Y}^m_l (\theta, \phi) \, d\Omega_i = \frac{1}{\sqrt{4\pi}} 4\pi \delta_{m0} \delta_{l0} \text{ for } 5\% \]

\[ \Delta E_{(15)^2} = \frac{\pi^2 e^6}{n^2 a_0^2} \int_0^\infty \int_0^{n_1} \frac{e^{2l} \, dv_1}{n_1^{2l+1}} \left[ \int_0^{n_1} \frac{e^2}{r_1} \, dv_2 + \int_0^{n_2} \frac{e^2}{r_2} \, dv_2 \right] \]
$$\Delta E = \frac{16}{15^2} \frac{Z e^2}{a_o^6} \frac{5}{128} \frac{a_o}{2^{2.5}}$$

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

So now

$$E_{(15)^2} = \left(-8 + \frac{5}{2}\right) \frac{e^2}{2a_o} = -\frac{11}{2} \frac{e^2}{2a_o}$$

$$= -\frac{11}{2} \times 13.6 \text{ eV} = -74.8 \text{ eV}.$$
\[ H = < \frac{p_i^2}{2m} > + < \frac{p_e^2}{2m_e} > - < \frac{2e^2}{\alpha} > - < \frac{2e^2}{\alpha_e} > + < \frac{e^2}{\alpha_e} > \]

\[ = \left( \frac{2e^2}{\alpha} - 2 \frac{2e}{\alpha} \right) \left( \frac{e^2}{\alpha_0} \right) \]

\[ 0 = \frac{\partial H}{\partial \frac{2e}{\alpha}} = \left( 2 \frac{2e}{\alpha} - 2 \frac{2}{\alpha} + \frac{5}{8} \right) \left( \frac{e^2}{\alpha_0} \right) \]

\[ 2e = 2 - \frac{5}{16} = 2 - \frac{5}{16} = 1.6875 \]

\[ H(1.6875) = -77.5 \text{ eV} \]

which is pretty close to \(-78.8 \text{ eV}\).

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

**Excited States**

\[ (1s) (n \ell) \]

\[ E = E_{100} + E_{n \ell m} + \Delta E \]
By first order perturbation theory,

\[ \Delta E = \langle 100, n\sigma m \rangle + \frac{e^2}{\hbar} \langle 100, n\sigma m, \sigma \rangle \]

\[ = \int d^3x_1 d^3x_2 \frac{1}{\hbar} \left[ \Phi_{100}^*(x_1) \Phi_{n\sigma m}^*(x_2) \pm \Phi_{100}(x_2) \Phi_{n\sigma m}(x_1) \right] \]

\[ \cdot \frac{e^2}{\hbar} \left[ \Phi_{100}(x_1) \Phi_{n\sigma m}(x_2) \pm \Phi_{100}(x_2) \Phi_{n\sigma m}(x_1) \right] \]

\[ = \int d^3x_1 d^3x_2 \left| \Phi_{100}(x_1) \right|^2 \left| \Phi_{n\sigma m}(x_2) \right|^2 \frac{e^2}{\hbar} \frac{1}{\hbar} \text{(direct)} \]

\[ \pm \int d^3x_1 d^3x_2 \Phi_{100}(x_1) \Phi_{n\sigma m}(x_2) \frac{e^2}{\hbar} \Phi_{100}^*(x_2) \Phi_{n\sigma m}^*(x_1) \text{ (exchange)} \]

\[ = I \pm J \]

Now \( J \) can be viewed as

\[ \left( \int d^3x_1 d^3x_2 \Phi_{100}(x_1) \Phi_{n\sigma m}(x_2) \frac{e^2}{\hbar} \Phi_{100}^*(x_2) \Phi_{n\sigma m}^*(x_1) \right) \]

\[ = \int d^3x_1 d^3x_2 f(x_1) \frac{e^2}{\hbar} f(x_2) \quad f(x_1) = \Phi_{100}^*(x_1) \Phi_{n\sigma m}(x_1) \]

\[ = \frac{e^2}{\hbar} \text{ where } P = \frac{e^2}{\hbar} \text{ is positive} \]

So \( f^+ P f \geq 0 \).
So the lower energy state is the one that is spatially antisymmetric.

\[ \langle \frac{e^2}{r_{12}} \rangle = \pm J \]

The \( \chi_0 \) states are para-helium, while the \( \chi_1 \) states are orthohelium.

The states with less energy are orthohelium.

\( (1s)(2p) \) \( \rightarrow \) para \( ^1P_1 \) \( \rightarrow \) ortho \( ^3P_2 \). \n
\( (1s)(2s) \) \( \rightarrow \) para \( ^1S_0 \) \( \rightarrow \) ortho \( ^3S_1 \).

\( (1s)^3 \) \( \rightarrow \) \( ^3S_0 \) para is only possibility.
Here spin & statistics effects lead to an effective term:

\[ H_{\text{eff}} = H_0 - \gamma \hat{S}_1 \cdot \hat{S}_2, \]

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

Ferro magnetism is believed to be associated with it.