Total electron wavefunction is

$$\Psi(\vec{r},\vec{s}) = \psi(\vec{r})\,\chi(\vec{s})$$

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{s}_1,\vec{s}_2) = \psi(\vec{r}_1,\vec{r}_2)\,\chi(\vec{s}_1,\vec{s}_2)$$

this is antisymmetric under particle interchange

If electrons are in singlet state $\chi = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

spatial can be symmetric

(e.g. act like bosons

feel an "exchange force" attraction)

$H_2$

$\oplus$ $e^-$ $e^-$ $\oplus$

$\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

electrons live between protons shielding the proton-proton repulsion

$e^-$ $\oplus$ $\oplus$ $e^-$

electrons in triplet state are thrown apart by "exchange force" & nuclei push each other away: no molecule

Atoms with atomic number $Z$

stationary nucleus with charge $Ze$ & $Z$ electrons

$$H = \sum_{j=1}^{Z}\left[\underbrace{-\frac{\hbar^2}{2m}\nabla_j^2}_{KE} - \underbrace{\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_j}}_{PE}\right] + \underbrace{\frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{\substack{j\\k\neq j}}\frac{e^2}{|\vec{r}_j-\vec{r}_k|}}_{e^- - e^- \text{ interactions}}$$

Want to solve $H\psi = E\psi$ for $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z)$

so that $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z)\,\chi(\vec{s}_1, \vec{s}_2, \dots, \vec{s}_Z)$ is antisymmetric

Can't be solved explicitly except $Z = 1$.

e.g. Helium

$$H = \underbrace{\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1}\right]}_{\text{almost } H_{hydrogen}} + \left[-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2}\right] + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$H_{hydrogen} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r_1}$$

If we ignore $e^- - e^-$ interactions

$H = H_1 + H_2$ $\quad$ $H_1, H_2$ are hydrogen Hamiltonians except $e^2 \to 2e^2$

$\psi(\vec{r}_1, \vec{r}_2) = \psi_{nlm}(\vec{r}_1)\,\psi_{n'l'm'}(\vec{r}_2)$

hydrogen energy eigenstates but $e^2 \to 2e^2$

$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \to \frac{4\pi\epsilon_0\hbar^2}{m\,2e^2}$ $\quad$ half the Bohr radius

$E_n = -\frac{E_1}{n^2}$ $\quad$ $E_1 = \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \to \frac{m}{2\hbar^2}\left(\frac{2e^2}{4\pi\epsilon_0}\right)^2$

four times the energy

e.g. Ground state

$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$

this is symmetric under interchange

so $\chi(\vec{s}_1, \vec{s}_2)$ is antisymmetric : electrons are in singlet state

$E = 4(-13.6\,eV) + 4(-13.6\,eV)$

$= -109\,eV$

actually $E = -79\,eV$ so electron-electron interactions are important

Excited states of helium

$$\frac{1}{\sqrt{2}}\left(\psi_{nlm}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) \pm \psi_{100}(\vec{r}_1)\,\psi_{nlm}(\vec{r}_2)\right)$$

if $+$, then $\chi$ is antisymmetric "parahelium"

if $-$, then $\chi$ is symmetric. "ortho helium"

Ground state is parahelium

Symmetric $\psi$ (parahelium)

Parahelium: electrons tend to be closer together (symmetric spatial wavefunction) and so energy will be higher ($e^-$ are closer together $\ominus\leftrightarrow\ominus$) than orthohelium

If both excited, one will immediately drop to ground state & kick the other electron away - ionization