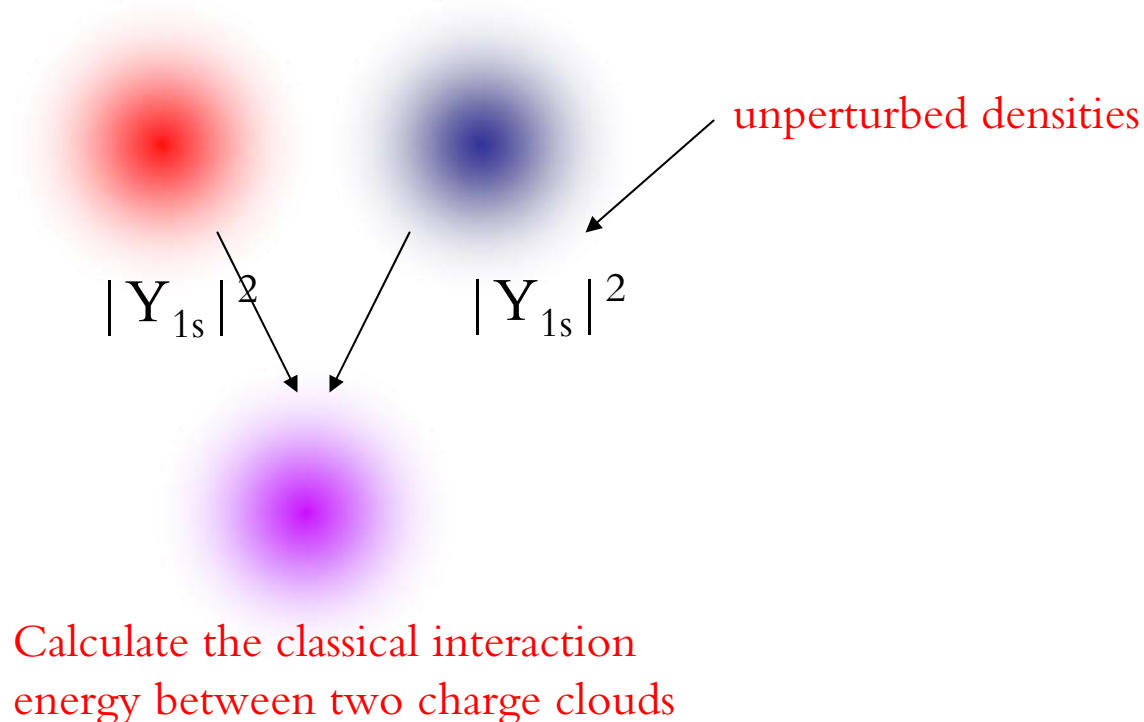


Electron-electron repulsion!

In the previous independent electron approximations the electron-electron repulsion term was completely neglected. Now an approximation for the electron-electron repulsion interaction energy will be obtained.

We still assume the independent electron model, but we try to improve the total energy of the He atom by evaluating the electron-electron interaction energy calculated from the unperturbed wave functions.



$$E = -\frac{Z_{\text{eff}}^2}{n_1^2} \frac{e^2}{2a_0} + -\frac{Z_{\text{eff}}^2}{n_2^2} \frac{e^2}{2a_0} + J_{12}$$

$$= E_1 + E_2 + J_{12}$$

where J_{12} is the estimate for the electron-electron repulsion energy.
 (The symbol J is used out of convention)

How do we calculate J_{12} ?

Let us look at the Hamiltonian for the Helium atom.

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{|\mathbf{r}_1|} - \frac{Ze^2}{|\mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_{12}|}$$

Electron-electron repulsion part of the potential energy

Let's calculate the expectation value using the unperturbed wave functions!

The expectation value is given by: (Assuming normalization)

$$J_{12} = \langle V_{ee} \rangle = \int \Psi_{\text{He}}(1,2)^* \frac{e^2}{|r_1 - r_2|} \Psi_{\text{He}}(1,2) d\tau_1 d\tau_2$$

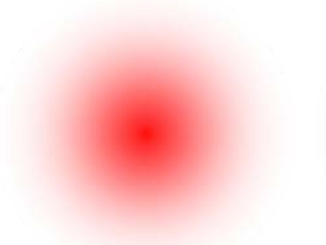
Using our unperturbed product wave function:

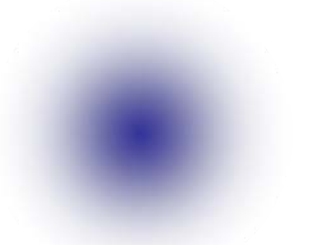
$$J_{12} = \langle V_{ee} \rangle = \int \Psi_{1s}(1)^* \Psi_{1s}(2)^* \frac{e^2}{r_{12}} \Psi_{1s}(1) \Psi_{1s}(2) d\tau_1 d\tau_2$$

$$\langle V_{ee} \rangle = \int \Psi_{1s}(1)^2 \Psi_{1s}(2)^2 \frac{e^2}{r_{12}} d\tau_1 d\tau_2$$

Multiplicative operator so we can rearrange.

electron-electron repulsion energy, using the unperturbed wave functions.

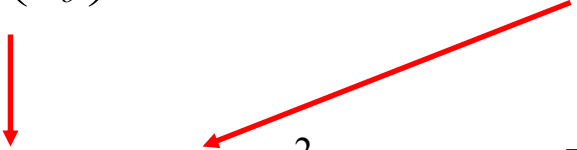

$$|Y_{1s}(1)|^2$$


$$|Y_{1s}(2)|^2$$

$$\langle V_{ee} \rangle = \int \Psi_{1s}(1)^2 \Psi_{1s}(2)^2 \frac{e^2}{r_{12}} d\tau_1 d\tau_2$$

The unperturbed, non-interaction one-electron wave functions are given by the hydrogen-like wave functions with $Z=2$:

$$\psi_{1s}(1) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_o} \right)^{3/2} e^{-Zr_1/a_o} \quad \psi_{1s}(2) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_o} \right)^{3/2} e^{-Zr_2/a_o}$$



$$\langle V_{ee} \rangle = \int \Psi(1)^2 \Psi(2)^2 \frac{e^2}{r_{12}} d\tau_1 d\tau_2 \approx \frac{5}{2} \left(\frac{e^2}{2a_o} \right)$$

We won't go through the work in evaluating this integral. The r_{12}^{-1} terms makes it tricky. You can see why by examining Karplus and Porter, pages 172-178.

Now we have an approximate expression for our total energy

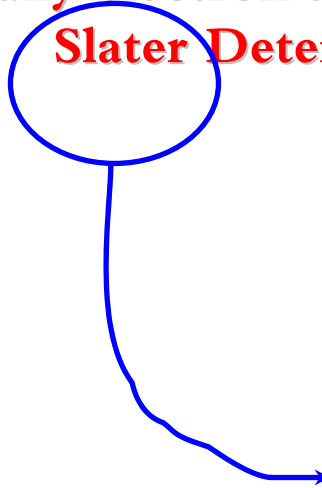
$$\begin{aligned} E &= E_1 + E_2 + \langle V_{ee} \rangle \\ &= -\frac{Z^2 e^2}{2a_o} - \frac{Z^2 e^2}{2a_o} + \frac{5}{2} \left(\frac{e^2}{2a_o} \right) \\ &= -\frac{2e^2}{a_o} - \frac{2e^2}{a_o} + \frac{5 e^2}{4 a_o} = -\frac{11e^2}{4a_o} \\ &= -74.8 \text{ eV} \end{aligned}$$

This compares to the experimental value of -79.0 eV. The electron-electron term accounts for 34 eV. Without the electron-electron repulsion term, the independent electron approximation gives a energy of -108.8 eV.

We are getting there. Now we are only 4.2 eV off or 5% in error!

Electrons has $s = \frac{1}{2}$, and therefore are fermions, and obey the Pauli Exclusion Principle (PEP).

**Proper many electron atoms requires using
Slater Determinants**



This will allow us to calculate energies and properties of many electron systems

Since we are dealing with fermions, the wave function must be antisymmetrical with respect to all transpositions (exchanges) of the N identical particle labels.

For example: if $\Psi(1,2,3,\dots,N) \rightarrow \Psi(2,1,3,\dots,N)$
then $\Psi(2,1,3,\dots,N) = -\Psi(1,2,3,\dots,N)$

This can be assured by writing the wave function as a **Slater Determinant**

Columns: wave functions each electron can occupy

→

$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\rho_1}(1) & \phi_{\rho_2}(1) & \phi_{\rho_3}(1) & \cdots & \phi_{\rho_N}(1) \\ \phi_{\rho_1}(2) & \phi_{\rho_2}(2) & \phi_{\rho_3}(2) & \cdots & \phi_{\rho_N}(2) \\ \phi_{\rho_1}(3) & \phi_{\rho_2}(3) & \phi_{\rho_3}(3) & \cdots & \phi_{\rho_N}(3) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \phi_{\rho_1}(N) & \phi_{\rho_2}(N) & \phi_{\rho_3}(N) & \cdots & \phi_{\rho_N}(N) \end{vmatrix}$$

↓ **Rows: Electrons**

The $\frac{1}{\sqrt{N!}}$ assures that the total wave function is normalized.

Each column is an orbital and the number in brackets is one of the N electrons

Interchange two electron labels (a switch of rows) yields a negative wave function as required for fermions and by the Pauli Exclusion Principle.


The determinant is zero if any row or column are identical.

Consider Helium again

The Slater determinant for the $1s^2$ ground state is:

$$\frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

Note: the electrons are spin-paired in the $1s$ orbital. If $\alpha = \beta$ or vice versa, the determinant = 0

$$= \frac{1}{\sqrt{2}} 1s(1)1s(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$


Spatially symmetric

Spin antisymmetric

What about the excited state configuration $1s2s$? Possible states are 3S and 1S , and Hund's rules state that the 3S lies lower in energy.

Let's explore the stability of the triplet state relative to the singlet state.

The wave functions will be of the form:

$${}^3S = 1s(1)2s(2)\alpha(1)\alpha(2)$$

and

$${}^1S = 1s(1)2s(2)\alpha(1)\beta(2)$$

However the PEP states the wave function must be antisymmetric. Therefore

$${}^3S = [1s(1)2s(2) - 1s(2)2s(1)]\alpha(1)\alpha(2)$$



Spatially antisymmetric

Spin symmetric

and
$${}^1S = [1s(1)2s(2) + 1s(2)2s(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$



Spatially symmetric

Spin antisymmetric

Examine the spatial function carefully:

Let $x_1, y_1, z_1 = x_2, y_2, z_2 = x, y, z$

$${}^3S_{\text{spatial}} = 1s(x, y, z)2s(x, y, z) - 1s(x, y, z)2s(x, y, z) = 0$$

but

$${}^1S_{\text{spatial}} = 1s(x, y, z)2s(x, y, z) + 1s(x, y, z)2s(x, y, z) = 21s(x, y, z)2s(x, y, z)$$

In the first case, there is zero probability that with identical spins, the two electrons will be in the same physical space = **Fermi hole**

In the second case, the probability quadruples [1S]² for finding the electrons in the same physical space = **Fermi heap**

Fermi holes and heaps do not come about because of electron-electron repulsion but because of the exchange symmetry of the wave function. However, Fermi holes and heaps lead to reduced and enhanced electron – electron repulsion energies, respectively.

