

Next consider Li. Assume because Li has 3 electrons that its ground state electronic configuration is given by $1s^3$.

Slater Determinant becomes:

$$\psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)\alpha(3) \end{vmatrix} \quad \text{where the 3rd } e^- \text{ has either } \alpha \text{ (or } \beta) \text{ spin}$$

However, the 1st and 3rd columns in this determinant are identical, so $\Psi(1,2,3) = 0$.

Thus, the 3rd e^- must go into the next higher energy orbital with $n = 2$.

\Leftrightarrow Each orbital have a maximum occupancy of two electrons.

= Pauli Exclusion Principle.

Use of Slater Determinants is a course in itself. Will only consider first excited state of He ($N = 2$) to introduce the concepts of exchange and Coulomb energies.

$$\Phi_0 = \frac{1}{\sqrt{2!}} \begin{vmatrix} 1s\alpha(1) & 2s\alpha(1) \\ 1s\alpha(2) & 2s\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [1s\alpha(1)2s\alpha(2) - 1s\alpha(2)2s\alpha(1)]$$

This is one of 3 degenerate possibilities for the excited 3S triplet state (both spins up).

Calculate
 $\langle \Phi_0 | \mathbf{V} | \Phi_0 \rangle$

$$\begin{aligned} \langle \Phi_0 | \hat{V} | \Phi_0 \rangle &= \langle \Phi_0 | \frac{e^2}{r_{12}} | \Phi_0 \rangle \\ &= \frac{1}{2} \left\{ \langle 1s\alpha(1)2s\alpha(2) - 1s\alpha(2)2s\alpha(1) | \frac{e^2}{r_{12}} | 1s\alpha(1)2s\alpha(2) - 1s\alpha(2)2s\alpha(1) \rangle \right\} \\ &= \frac{1}{2} \langle 1s\alpha(1)2s\alpha(2) | \frac{e^2}{r_{12}} | 1s\alpha(1)2s\alpha(2) \rangle \quad (1) \\ &\quad + \frac{1}{2} \langle 1s\alpha(2)2s\alpha(1) | \frac{e^2}{r_{12}} | 1s\alpha(2)2s\alpha(1) \rangle \quad (2) \\ &\quad - \frac{1}{2} \langle 1s\alpha(1)2s\alpha(2) | \frac{e^2}{r_{12}} | 1s\alpha(2)2s\alpha(1) \rangle \quad (3) \\ &\quad - \frac{1}{2} \langle 1s\alpha(2)2s\alpha(1) | \frac{e^2}{r_{12}} | 1s\alpha(1)2s\alpha(2) \rangle \quad (4) \end{aligned}$$

$$= \frac{e^2}{2} \langle |1s\alpha(1)|^2 | \frac{1}{r_{12}} | |2s\alpha(2)|^2 \rangle \quad (1)$$

$$+ \frac{e^2}{2} \langle |1s\alpha(2)|^2 | \frac{1}{r_{12}} | |2s\alpha(1)|^2 \rangle \quad (2)$$

$$- \frac{e^2}{2} \langle 1s\alpha(1)2s\alpha(1) | \frac{1}{r_{12}} | 1s\alpha(2)2s\alpha(2) \rangle \quad (3)$$

$$- \frac{e^2}{2} \langle 1s\alpha(2)2s\alpha(2) | \frac{1}{r_{12}} | 1s\alpha(1)2s\alpha(1) \rangle \quad (4)$$

Integrals (1) and (2) represent the electrostatic Coulomb interaction between the 1s and 2s charge clouds. In (1) electrons 1 and 2 occupy the 1s and 2s orbitals, respectively, while in (2) electrons 1 and 2 occupy the 2s and 1s orbitals, respectively. Both integrals correspond to the same energy because electrons are indistinguishable.

These are “classical” electrostatic interactions since $e|\Psi|^2$ is a charge distribution.

Each integral contributes $\mathbf{J}/2$ to the energy.

Integrals (3) and (4) have a similar form but are not the interactions of two charge clouds since $1s(1)2s(1)$ and $1s(2)2s(2)$ are not probability densities in the usual sense. Instead they arise from an exchange of the two electrons between the 1s and 2s orbitals. As a result the integrals are called exchange integrals, \mathbf{K} . (3) and (4) contribute $\mathbf{K}/2$ to the energy.

The energy of the first excited triplet state in He is therefore $E = \mathbf{E}_0 + \mathbf{J} - \mathbf{K}$ where E_0 is the energy uncorrected for $e^- - e^-$ interactions.

How about the singlet state?

One guess for the Slater determinant is:

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

Another is:

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

The correct form of the excited singlet state of He can be written in Slater Determinant form as:

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

$$\left(= [1s(1)2s(2) + 1s(2)2s(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \right) \text{ as before}$$

Can then show that $E = \mathbf{E}_0 + \mathbf{J} + \mathbf{K}$

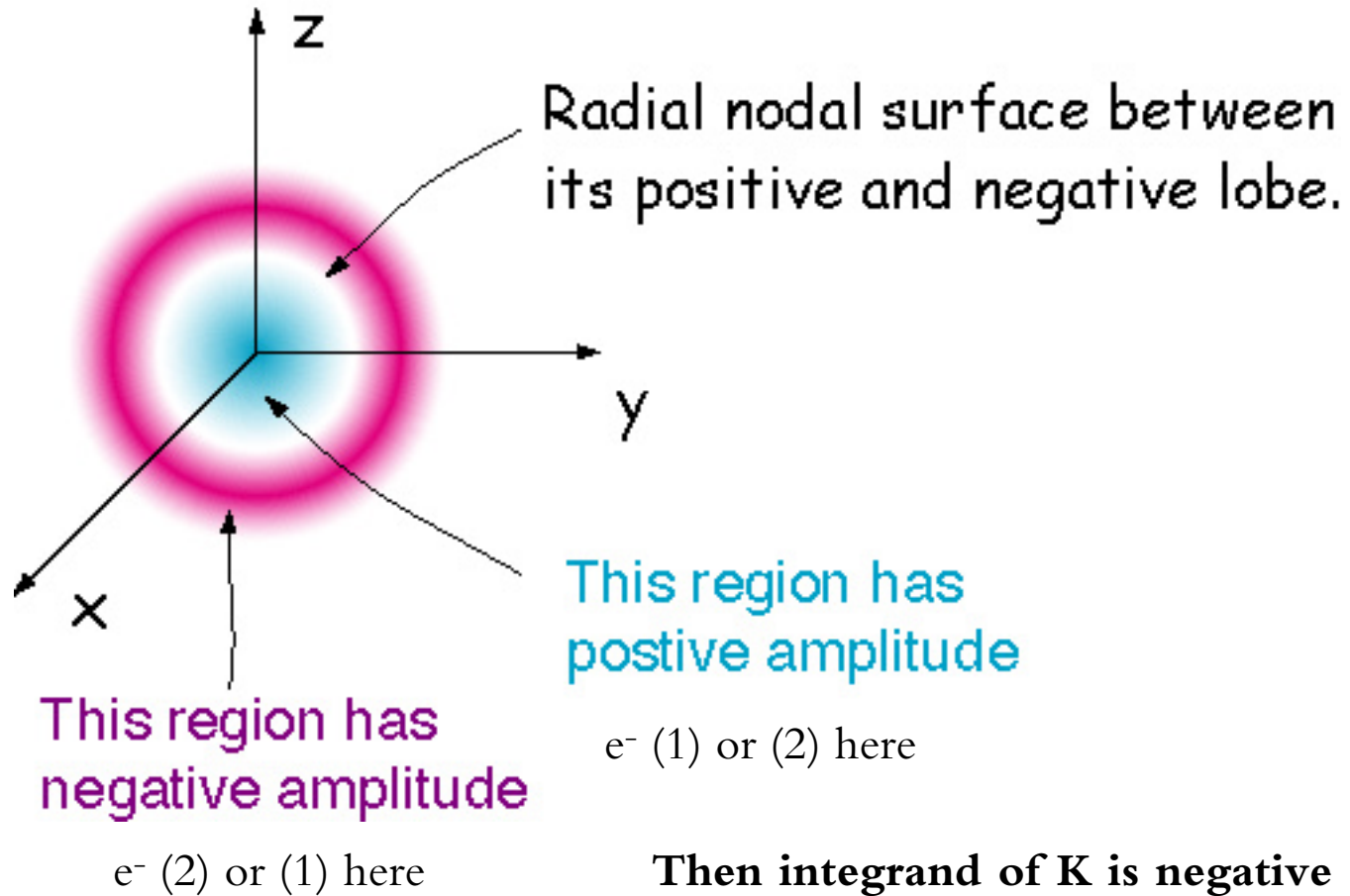
What are the signs of J and K?

The integrand of J is positive everywhere, and so J is positive. Makes sense since the electrostatic interaction between two electron cloud distributions is repulsive.

The integrand of K has both positive and negative contributions. For K to be negative, the electron radius r_1 or r_2 must be inside the 2s orbital nodal surface while the other is outside this distance.

2s orbital

$$n=2, l=0, m_l=0$$

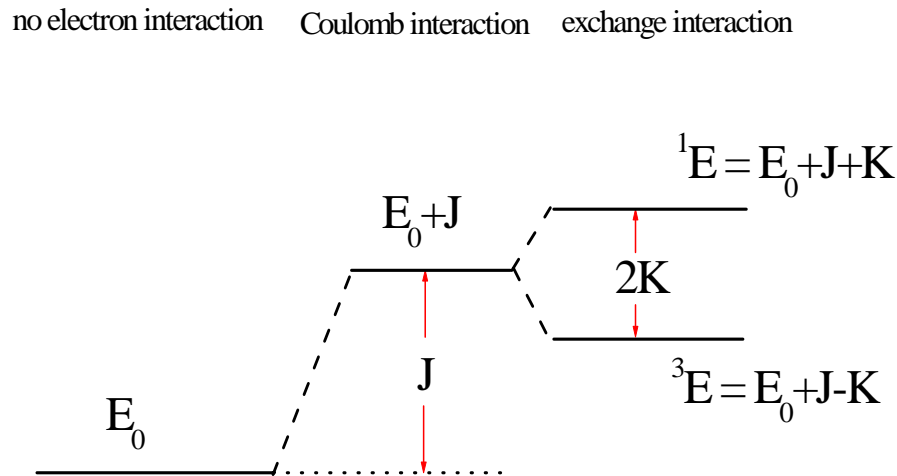


However, the $1/r_{12}$ term weights those regions with smaller r_{12} . Therefore K overall is a positive quantity.

In addition to always being positive the exchange integral, K , always enters with a negative sign. Therefore, it always acts to diminish the electron-electron repulsion energy.

The exchange energy is always much smaller than the associated Coulomb repulsion energy.

In He exchange interaction splits the degeneracy of the singlet and triplet states by an amount $= 2K$



Note: Hund's Rules OK here. The triplet lies lower than the singlet.

8.1: The Hartree-Fock Self-Consistent Field Method

In the many- e^- atom problem we want to find the **single** Slater determinant that gives the lowest energy for the ground-state. The starting point is to use the orbital approximation, the Hartree method, and the Pauli Exclusion Principle.

The Hartree-Fock method assumes the electrons are uncorrelated

A particular e^- feels spatially averaged e^- -charge distribution of the remaining $n-1$ e^- s. \Rightarrow the n -electron Schrodinger Eq. \Rightarrow n 1- e^- Schrodinger Eq.

$$\left[-\frac{\hbar^2}{2m_e} \nabla_{ei}^2 + V_i^{eff}(\vec{r}_i) \right] \cdot \phi_i(\vec{r}_i) = \epsilon_i \cdot \phi_i(\vec{r}_i) \quad i = 1, 2, \dots, n$$

The effective potential V_i^{eff} is spherically symmetric by averaging the total probability density over the angular coordinates – known as the **central field approximation**

The angular part of the wave function is identical to the solution of the H-atom
 \Rightarrow The s, p, d, \dots orbital nomenclature derived for the H-atom remains intact for the 1- e^- orbitals
What remains is to find solutions to the radial part of the Schrodinger Equation. Optimize the radial part using the **variational method**