Helium and the Exclusion Principle

Pair of electrons with e-e Coulomb interaction neglected ($V_{12}=0$) gives us an antisymmetric total eigenfunction containing products of single electron eigenfunctions.

$$\psi_A(1, 2) = \frac{1}{\sqrt{2}} [\psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2)]$$

$\alpha, \beta$ represent the set of space and spin quantum numbers for each single electron function.

Separate the space and spin part of the total eigenfunction.

$$\psi(1, 2) = \phi(1, 2) \times \chi(1, 2)$$

total eigenfunction

space eigenfunction

spin eigenfunction

Consider the symmetry of this product:

$$\psi_A(1, 2) = \phi_A(1, 2) \times \chi_S(1, 2)$$

For an antisymmetric total eigenfunction, we require one of the two factors to be symmetric, the other must be antisymmetric.

Helium and the Exclusion Principle

Space Eigenfunctions:

$$\phi_A(1, 2) = \frac{1}{\sqrt{2}} [\phi_\alpha(1)\phi_\beta(2) - \phi_\beta(1)\phi_\alpha(2)]$$  (antisymmetric)

$$\phi_S(1, 2) = \frac{1}{\sqrt{2}} [\phi_\alpha(1)\phi_\beta(2) + \phi_\beta(1)\phi_\alpha(2)]$$  (symmetric)

Subscripts lowercase a,b denote the set of space quantum numbers n, l, $m_l$ of a single-electron space function.

Spin Eigenfunctions:

For a single electron the spin-quantum number $m_s$ can take only one of two values, $+1/2$ (spin-up) and $-1/2$ (spin-down). Here we can actually write down all three permutations for two electrons (up-up, up-down, and down-down) and cast them into symmetric and antisymmetric combinations.

$$\chi_A(1, 2) = \frac{1}{\sqrt{2}} \left[ \chi_{+\frac{1}{2}}(1)\chi_{-\frac{1}{2}}(2) - \chi_{-\frac{1}{2}}(1)\chi_{+\frac{1}{2}}(2) \right]$$

$$\chi_S(1, 2) = \frac{1}{\sqrt{2}} \left[ \chi_{+\frac{1}{2}}(1)\chi_{-\frac{1}{2}}(2) + \chi_{-\frac{1}{2}}(1)\chi_{+\frac{1}{2}}(2) \right]$$

$$\chi_A(1, 2) = \chi_{+\frac{1}{2}}(1)\chi_{+\frac{1}{2}}(2)$$  Three symmetric and one antisymmetric combination.

“Triplet” vs. “Singlet”
Spin Angular Momenta

Identify the spin-eigenfunctions with the two spin-angular momentum $S=S_1+S_2$:

$s=1, m_s=+1$:
$$\chi_s(1,2) = \chi_{-\frac{1}{2}} \chi_{-\frac{1}{2}}$$

$s=1, m_s=0$:
$$\chi_s(1,2) = \frac{1}{\sqrt{2}} [\chi_{\frac{1}{2}} \chi_{-\frac{1}{2}} + \chi_{-\frac{1}{2}} \chi_{\frac{1}{2}}]$$

$s=1, m_s=-1$:
$$\chi_s(1,2) = \chi_{\frac{1}{2}} \chi_{\frac{1}{2}}$$

$s=0, m_s=0$:
$$\chi_A(1,2) = \frac{1}{\sqrt{2}} [\chi_{\frac{1}{2}} \chi_{-\frac{1}{2}} - \chi_{-\frac{1}{2}} \chi_{\frac{1}{2}}]$$

**Triplet States** ("parallel spins")

Consider triplet states which have *symmetric* spin-eigenfunctions $\chi_s$:

Need to combine these with *antisymmetric* space-eigenfunction $\phi_A$ in order to get *antisymmetric* total eigenfunction $\psi_A$.

$$\psi_A(1,2) = \phi_A(1,2) \times \chi_S(1,2)$$

Antisymmetric space eigenfunction:

$$\phi_A(1,2) = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)]$$

What happens when the two electrons are in close proximity?

$$\vec{r}_1 \approx \vec{r}_2 \quad \Rightarrow \quad \phi_a(1) \approx \phi_a(2) \quad \phi_b(1) \approx \phi_b(2)$$

$$\phi_a(1)\phi_b(2) \approx \phi_b(1)\phi_a(2)$$

$$\phi_A(1,2) \approx 0$$

Probability density $\phi_A^*\phi_A$ is small when two triplet electrons are close together, i.e. probability of these two electrons being in close proximity is small. Triplet electrons act as if they repel each other.

This called the "Exchange Force"; it creates an "Exchange Hole"
Singlet States ("antiparallel spins")

Consider singlet states which have antisymmetric spin-eigenfunctions $\chi_A$:

Need to combine these with symmetric space-eigenfunction $\phi_S$ in order to get antisymmetric total eigenfunction $\psi_A$: 

$$\psi_A(1, 2) = \phi_S(1, 2) \times \chi_A(1, 2)$$

Symmetric space eigenfunction:

$$\phi_S(1, 2) = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]$$

What happens when the two electrons are in close proximity?

$$\vec{r}_1 \approx \vec{r}_2 \rightarrow \phi_a(1) \approx \phi_a(2) \quad \phi_b(1) \approx \phi_b(2)$$

$$\phi_a(1)\phi_b(2) \approx \phi_b(1)\phi_a(2)$$

$$\phi_S(1, 2) \approx \sqrt{2}\phi_a(1)\phi_b(2)$$

Probability Density: $\phi_S^*\phi_S \approx 2\phi_a^*(1)\phi_b^*(2)\phi_a(1)\phi_b(2)$ (twice the average!)

Increased probability that two singlet electrons are in close proximity to each other. Singlet electrons act as if they attract each other.

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Two Electrons in a 1-D Box Potential

Perspective 2-D plot of the positions of two electrons, with each electron position corresponding to one axis.

$$\phi_1(x) = \sqrt{\frac{2}{a}} \cos \frac{\pi x}{a}$$

$$\phi_2(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$$
Two Electrons in a 1-D Box Potential

\[ \phi_1(x) = \sqrt{\frac{2}{a}} \cos \frac{\pi x}{a} \]
\[ \phi_2(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \]

Perspective 2-D plot of with electron positions as axes

\[ \phi_1(1)\phi_2(2) \]
\[ \phi_2(1)\phi_1(2) \]

Form symmetric and antisymmetric combinations \( \phi_S \) and \( \phi_A \)

\[ \frac{1}{\sqrt{2}} \left[ \phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2) \right] \quad \text{antisymmetric} \]
\[ \frac{1}{\sqrt{2}} \left[ \phi_1(1)\phi_2(2) + \phi_2(1)\phi_1(2) \right] \quad \text{symmetric} \]
Helium - Low Energy Electronic States

With e-e Coulomb interaction, the eigenenergies are no longer degenerate with quantum number $l$ (as in the one-electron atoms).

This is because the average e-e distance change with different $l$ values, leading to different strengths of the Coulomb e-e interaction.

Examine average distance (triangle) in radial distribution function:

- **Electron 1 ($n=1$)**
  - $l=0$
  - Less e-e-repulsion

- **Electron 2 ($n=2$)**
  - $l=1$
  - More e-e-repulsion