Exchange symmetry, spin pairs and Pauli exclusion

GRE undergraduate preparation · local supported objectives

Exchange symmetry, spin pairs and Pauli exclusion

- Apply **exchange symmetry 交换对称性** to the total state, space and spin together.
- Build singlets and triplets.
- Count two-particle states with the **Pauli exclusion principle 泡利不相容原理**.
- Explain exchange correlation: why identical fermions avoid each other.

Exchange symmetry

- With two different orbitals a and b: $\Psi_{\pm} = \frac{1}{\sqrt{2}}\left[a(1)b(2) \pm b(1)a(2)\right]$.
- If $a = b$, only $a(1)a(2)$ exists, and it is symmetric.
- For electrons the total state is **antisymmetric 反对称**, so two electrons can never be in the same complete state.

Singlet and triplet

- Singlet: $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$, total spin $S = 0$, antisymmetric.
- Triplet: $\uparrow\uparrow$, $\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$, $\downarrow\downarrow$, total spin $S = 1$, symmetric.
- For electrons: symmetric space goes with the singlet, antisymmetric space with the triplet.

Counting states

- Two orbitals $\times$ two spins $= 4$ complete states, so two electrons have $\binom{4}{2} = 6$ states: two singlets with both electrons in one orbital, one open-shell singlet, and three triplets.
- Three orbitals: $\binom{6}{2} = 15$ two-electron states.
- Two spinless bosons in two orbitals: 3 states (*aa*, *bb* and the symmetric *ab*).

Exchange correlation

- Particles in Ψ_- keep apart, and those in Ψ_+ bunch together, though no force acts.
- In helium, the triplet ("orthohelium") states have the electrons further apart, so they feel less repulsion and lie lower than the matching singlets.

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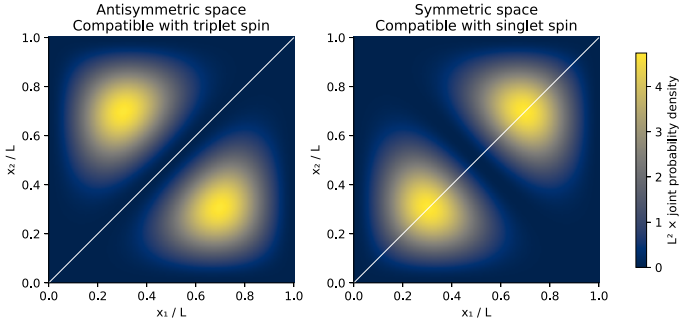
Figure: Exchange correlation



- Identify the axes, units, directions and the stated model.

Worked example: two particles in a well

- $a(L/4) = a(3L/4) = 1/\sqrt{L}$; $b(L/4) = +\sqrt{2/L}$ and $b(3L/4) = -\sqrt{2/L}$.
- $\Psi_- = \frac{1}{\sqrt{2}}\left[-\frac{\sqrt{2}}{L} - \frac{\sqrt{2}}{L}\right] = -\frac{2}{L}$, a density of $4/L^2$.
- $\Psi_+ = 0$ at these points: the symmetric state puts no weight on this pair of positions.

Worked example: counting

- Two electrons in 3 orbitals: 6 complete states, so $\binom{6}{2} = 15$ states. Of these, $3 \times 3 = 9$ are triplets (3 antisymmetric orbital pairs $\times$ 3 spin states) and 6 are singlets (6 symmetric orbital pairs).
- Two electrons in one orbital: only the singlet.
- Two labelled particles in 4 complete states would have $4^2 = 16$ states.

Common errors

- Requiring the spatial part alone to be antisymmetric for electrons.
- Putting two electrons with parallel spins in one orbital.
- Counting **identical particles** as if they were labelled.

Common errors (2)

- Thinking the singlet and triplet differ in energy because of a magnetic force; the main effect is exchange.
- Forgetting that the symmetric *ab* state counts for bosons.

Key terms

- **singlet**: The two-particle spin state with total spin 0, antisymmetric under exchange.
- **triplet**: The three two-particle spin states with total spin 1, symmetric under exchange.
- **identical particles**: Particles that cannot be told apart, even in principle.
- **exchange symmetry**: How a many-particle state behaves when two particles swap labels.

Check yourself

- How many spin states do two spin-½ particles have, and how are they split?
- Two electrons share one spatial orbital. What is their spin state?
- How many states do two spinless bosons have in two orbitals?