Exchange Energy in Two-Electron Systems: A Detailed Derivation from the Pauli Principle

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Abstract

In spin crystals and, in particular, in the context of LLG optimizing machines, the exchange energy plays a crucial role. Mapping any higher-order algorithm to physical spin systems requires precise alignment of the exchange couplings Jij . Here, we derives the mathematical foundations of exchange energy in two-electron systems, demonstrating how fermionic antisymmetry and the Pauli principle lead to the direct (J_C) and exchange (Jex) integrals and how the sign of Jex dictates whether spins align or anti-align. We derive the origin of exchange energy for two electrons by explicitly showing how the fermionic antisymmetry condition imposes constraints on the spin and spatial wavefunctions. We calculate the Coulomb interaction expectation value, define the direct (J_C) and exchange (J_{ex}) integrals, and prove how the sign of J_{ex} determines whether the electrons prefer aligned or anti-aligned spins.

1. Fermionic Antisymmetry and Spin-Space Symmetries

1.1. Total Wavefunction Must Be Antisymmetric

Consider two electrons labeled by coordinates $(\mathbf{r}_1, \sigma_1)$ and $(\mathbf{r}_2, \sigma_2)$, where $\mathbf{r}_i$ denotes spatial coordinates and σ_i denotes spin-$\frac{1}{2}$ variables.Because electron is an spin half particle it obeys fermion statistics thus The Pauli exclusion principle states it is antisymetric for wavefunction:

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) \; = \; -\,\Psi(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1).$$

Hence, **the total wavefunction is antisymmetric under exchange of the two electrons**.

Spin $\times$ Space Factorization. I write for factorization:

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) \; = \; \Phi(\mathbf{r}_1, \mathbf{r}_2)\, \chi(\sigma_1, \sigma_2),$$

where:

- $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is the *spatial* part,

- $\chi(\sigma_1, \sigma_2)$ is the *spin* part.

this is equivalent to bra-ket notation:

$$\langle r_1, \sigma_1; r_2, \sigma_2 \mid \Psi \rangle = \langle r_1, r_2 \mid \Phi \rangle \times \langle \sigma_1, \sigma_2 \mid \chi \rangle.$$

To satisfy antisymmetry, either:

$$\begin{cases} \chi(\sigma_1, \sigma_2) \text{ is symmetric,} \\ \Phi(\mathbf{r}_1, \mathbf{r}_2) \text{ is antisymmetric,} \end{cases} \quad \text{or} \quad \begin{cases} \chi(\sigma_1, \sigma_2) \text{ is antisymmetric,} \\ \Phi(\mathbf{r}_1, \mathbf{r}_2) \text{ is symmetric.} \end{cases}$$

1.2. Spin-$\frac{1}{2}$ Addition: Singlet and Triplet

For two spin-$\frac{1}{2}$ fermions (electrons), the combined spin states split into:

$$\underbrace{S = 1}_{\text{triplet (symmetric spin)}} , \qquad \underbrace{S = 0}_{\text{singlet (antisymmetric spin)}} .$$

Triplet $(S = 1)$ — Symmetric Spin Part.

$$\chi_{T,+1} = \mid \uparrow\uparrow\rangle, \quad \chi_{T,0} = \tfrac{1}{\sqrt{2}}\Big(\mid \uparrow\downarrow\rangle + \mid \downarrow\uparrow\rangle\Big), \quad \chi_{T,-1} = \mid \downarrow\downarrow\rangle.$$

These are all **symmetric under exchange of** $(\sigma_1, \sigma_2) \leftrightarrow (\sigma_2, \sigma_1)$.

Singlet $(S = 0)$ — Antisymmetric Spin Part.

$$\chi_S = \frac{1}{\sqrt{2}}\Big(\mid \uparrow\downarrow\rangle - \mid \downarrow\uparrow\rangle\Big).$$

This state **changes sign** under exchange of the two spins.

Consequences. - If the electrons form a **singlet** spin state, χ_S is antisymmetric; hence $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ must be **symmetric** in $(\mathbf{r}_1, \mathbf{r}_2)$. - If they form a **triplet** spin state, χ_T is symmetric; hence $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ must be **antisymmetric** in $(\mathbf{r}_1, \mathbf{r}_2)$.

2. Constructing Spatial Wavefunctions for Two Orbitals

Let the one-electron orbitals be $\phi_i(\mathbf{r})$ and $\phi_j(\mathbf{r})$, assumed orthonormal. Then two possible two-electron spatial wavefunctions are:

2.1. Symmetric Spatial Combination (for Singlet Spin)

$$\Phi_S(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\Big[\phi_i(\mathbf{r}_1)\,\phi_j(\mathbf{r}_2) + \phi_j(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2)\Big].$$

This is invariant under exchange $(\mathbf{r}_1, \mathbf{r}_2) \leftrightarrow (\mathbf{r}_2, \mathbf{r}_1)$, i.e. *symmetric.*

$$\phi_i(r_1) = \langle r_1 \mid i \rangle$$

is the *position-space wavefunction* of the energy eigenstate $|i\rangle$. In plain English:

> If you prepare an electron in the energy eigenstate $|i\rangle$, then $\phi_i(r_1)$ is the complex amplitude to find that electron at the point r_1.

2.2. Antisymmetric Spatial Combination (for Triplet Spin)

$$\Phi_T(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\Big[\phi_i(\mathbf{r}_1)\,\phi_j(\mathbf{r}_2) - \phi_j(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2)\Big].$$

Now $\Phi_T(\mathbf{r}_1, \mathbf{r}_2) = -\Phi_T(\mathbf{r}_2, \mathbf{r}_1)$, i.e. *antisymmetric*.

3. The Coulomb Hamiltonian and Expectation Values

Let us focus on the operator

$$\hat{H} = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

which describes the electron–electron repulsion. *Note* that this operator is **spin-independent**.

We compute the expectation value

$$E = \langle \Phi \,|\, \hat{H} \,|\, \Phi \rangle = \iint d^3r_1\, d^3r_2\, \Phi^*(\mathbf{r}_1, \mathbf{r}_2)\, \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\, \Phi(\mathbf{r}_1, \mathbf{r}_2).$$

3.1. Detailed Expansion for the Singlet (Symmetric) Case

Set

$$\Phi_S(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\Big[\phi_i(\mathbf{r}_1)\,\phi_j(\mathbf{r}_2) + \phi_j(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2)\Big].$$

Then

$$\Phi_S^* \Phi_S = \frac{1}{2}\Big[\phi_i^*(\mathbf{r}_1)\,\phi_j^*(\mathbf{r}_2) + \phi_j^*(\mathbf{r}_1)\,\phi_i^*(\mathbf{r}_2)\Big] \times \Big[\phi_i(\mathbf{r}_1)\,\phi_j(\mathbf{r}_2) + \phi_j(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2)\Big].$$

When you multiply these terms out and integrate against $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$, you get two *types* of terms:

(1) Direct Term:

$$J_C \equiv \iint d^3r_1\, d^3r_2\, |\phi_i(\mathbf{r}_1)|^2\, \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\, |\phi_j(\mathbf{r}_2)|^2.$$

This arises from multiplying $\phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_1)$ and $\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)$ (or the same with $i \leftrightarrow j$). It represents a "classical-like" repulsion of the charge densities $|\phi_i|^2$ and $|\phi_j|^2$.

(2) Exchange Term:

$$J_{\text{ex}} \equiv \iint \phi_i^*(\mathbf{r}_1)\,\phi_j^*(\mathbf{r}_2)\, \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\, \phi_j(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2)\, d^3r_1\, d^3r_2.$$

This term *only* appears because we have $\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)$ cross-terms. There is no direct classical analog; J_{ex} is a purely quantum-mechanical artifact of *indistinguishability*.

Result for the singlet:

$$E_S = \langle \Phi_S | \hat{H} | \Phi_S \rangle = J_C - J_{\text{ex}}$$

(the minus sign arises from the constructive $+$ signs in Φ_S which lead to "subtracting" certain cross-terms upon full expansion).

3.2. Triplet (Antisymmetric) Case

Similarly, for

$$\Phi_T(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\Big[\phi_i(\mathbf{r}_1)\,\phi_j(\mathbf{r}_2) - \phi_j(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2)\Big],$$

the direct term J_C again appears the *same*, but the cross-term picks up a *plus* sign. Hence:

$$E_T = J_C + J_{\text{ex}}.$$

3.3. Comparison: Singlet vs. Triplet Energies

We therefore get

$$E_S = J_C - J_{\text{ex}}, \quad E_T = J_C + J_{\text{ex}}.$$

All from the same Coulomb operator! The difference is in how the *wavefunction symmetries* redistribute the overlap integrals.

4. Interpreting J_{ex}: Alignment vs. Anti-Alignment

Sign of J_{ex}. we Define

$$\Delta = E_T - E_S = 2\,J_{\text{ex}}.$$

- If $J_{\text{ex}} > 0$, then $E_S < E_T$, so $\Delta > 0$. The *singlet* is lower in energy; **the electrons prefer anti-aligned spins** $(S = 0)$.

- If $J_{\text{ex}} < 0$, then $E_T < E_S$, so $\Delta < 0$. The *triplet* is lower in energy; **the electrons prefer aligned spins** $(S = 1)$.

4.1. Why This Dictates Magnetic Ordering

In extended systems (solids), summing these exchange interactions over many sites yields:

$$\hat{H}_{\text{eff}} \sim -\sum_{\langle i,j \rangle} J_{ij}\,\vec{S}_i \cdot \vec{S}_j,$$

where the *sign* of J_{ij} (related to J_{ex} integrals) determines whether the ground state has *ferromagnetic* order (all spins aligned) or *antiferromagnetic* order (neighboring spins anti-aligned).

5. Summary of the Logic

1. **Pauli Principle:** Two electrons require the total wavefunction to be antisymmetric under exchange. Consequently, if the spin wavefunction is symmetric (triplet), the spatial part is antisymmetric; if the spin wavefunction is antisymmetric (singlet), the spatial part is symmetric.

2. **Coulomb Expectation:** We compute $\langle \Phi | \dfrac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} | \Phi \rangle$, carefully expanding. We identify the *Direct* term J_C and the *Exchange* term J_{ex}.

3. **Energy Formulas:**
$$E_S \;=\; J_C - J_{\text{ex}}, \quad E_T \;=\; J_C + J_{\text{ex}}.$$

4. **Spin Alignment:** If $J_{\text{ex}} > 0$, the system favors the singlet ($S = 0$), i.e. *anti-aligned* spins (antiferromagnetic tendency). If $J_{\text{ex}} < 0$, the system favors the triplet ($S = 1$), i.e. *aligned* spins (ferromagnetic tendency).

Thus, we see how a *spin-independent* Coulomb operator can produce *spin-dependent* physics purely via the requirement of **fermionic antisymmetry** of the total wavefunction. This is the fundamental origin of **exchange energy**.