

## The Exchange Interaction and The Spin Hamiltonian

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This note derives the final sub-Hamiltonian for the exchange interaction, and then writes the complete spin Hamiltonian  $\mathcal{H}$ .

I use  $\mathcal{H}$  to represent the full spin Hamiltonian. Sub-Hamiltonians are written as hatted  $H$ 's (for example,  $\hat{H}_Z$ ).

### The Exchange Interaction

Quantum mechanics says electrons are indistinguishable fermions. Their combined spatial and spin wavefunction must be antisymmetric. This symmetry links nearby electrons' spins and positions. The exchange interaction is another term that splits energy levels.

Consider two electrons in orbitals  $\varphi_a(\vec{r})$  and  $\varphi_b(\vec{r})$ . The two-electron Hamiltonian is

$$H = \sum_{i=1}^2 \left[ \underbrace{-\frac{\hbar^2}{2m} \nabla_i^2}_{\text{kinetic energy}} + \underbrace{V(\vec{r}_i)}_{\text{potential energy}} \right] + \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}}_{\text{Coulomb repulsion}}.$$

Here,  $V(\vec{r})$  is the one-particle potential. Because electrons are fermions, the total state must be antisymmetric under exchange. We factor it into spatial and spin parts:

$$\Psi_{\text{tot}}(1, 2) = \Psi(\vec{r}_1, \vec{r}_2)\chi(s_1, s_2),$$

where antisymmetry requires

$$\Psi_{\text{tot}}(2, 1) = -\Psi_{\text{tot}}(1, 2).$$

If the spatial  $\Psi$  is symmetric, then the spin state  $\chi$  must be antisymmetric (a singlet). If  $\Psi$  is antisymmetric,  $\chi$  must be symmetric (a triplet).

We build orthonormal spatial orbitals  $\varphi_a, \varphi_b$  and define

$$\Psi_{S(\vec{r}_1, \vec{r}_2)} = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)],$$

$$\Psi_{A(\vec{r}_1, \vec{r}_2)} = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)].$$

The corresponding spin states are

$$\chi_S = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (\text{singlet}),$$

$$\chi_A = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \quad (\text{triplet}).$$

We can diagonalize  $H$  in the two-dimensional subspace spanned by  $\varphi_a\varphi_b$ . Both electrons share the same one-particle energy,

$$E_0 = \langle \varphi_a | \hat{h} | \varphi_a \rangle + \langle \varphi_b | \hat{h} | \varphi_b \rangle, \quad \hat{h} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}).$$

Therefore, any energy splitting arises entirely from the Coulomb term.

### Energy Splitting

Define the direct and exchange integrals:

$$K \equiv \iint d^3 r_1 d^3 r_2 \quad |\varphi_a(1)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} |\varphi_b(2)|^2,$$

$$J \equiv \iint d^3 r_1 d^3 r_2 \quad \varphi_a^*(1)\varphi_b(1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \varphi_b^*(2)\varphi_a(2).$$

Then

$$\langle \Psi_S | H | \Psi_S \rangle = E_0 + K + J, \quad \langle \Psi_A | H | \Psi_A \rangle = E_0 + K - J.$$

Thus the singlet sits at energy  $E_S = E_0 + K + J$ , while each triplet has  $E_T = E_0 + K - J$ . Their energy splitting is

$$\Delta E \equiv E_S - E_T = 2J.$$

The energy splitting due to  $\hat{H}_{\text{ZFS}}$  is analogously  $2D$ . We now want a pure spin Hamiltonian that reproduces the same singlet-triplet shift.

### Exchange Operator

The operator exchanging two spins is

$$\hat{P}_{12}\chi(1, 2) = \chi(2, 1).$$

Its eigenvalues are  $+1$  on the symmetric (triplet) subspace and  $-1$  on the antisymmetric (singlet) subspace.

Define the total spin operator and its square:

$$\hat{S}_{\text{tot}} = \hat{S}_1 + \hat{S}_2,$$

$$\hat{S}_{\text{tot}}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2.$$

For spin- $\frac{1}{2}$  particles,

$$\hat{S}_1^2 = \hat{S}_2^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3\hbar^2}{4}\mathbb{1}.$$

Hence,

$$\hat{S}_{\text{tot}}^2 = \frac{3\hbar^2}{2}\mathbb{1} + 2\hat{S}_1 \cdot \hat{S}_2.$$

For triplet  $S_{\text{tot}} = 1$  and singlet  $S_{\text{tot}} = 0$  states,

$$\hat{S}_{\text{tot}}^2 |10\rangle = 2\hbar^2 |10\rangle, \quad \hat{S}_{\text{tot}}^2 |00\rangle = 0.$$

But we need an exchange operator that satisfies

$$\hat{P}_{12} |10\rangle = +|10\rangle, \quad \hat{P}_{12} |00\rangle = -|00\rangle.$$

Take an ansatz  $\hat{P}_{12} = a\hat{S}_{\text{tot}}^2 + b\mathbb{I}$ . Solving gives the standard result

$$\hat{P}_{12} = \frac{1}{2}(1 + 4\hat{S}_1 \cdot \hat{S}_2).$$

Its eigenvalues are  $-1$  on the singlet and  $+1$  on the triplet manifold. An operator proportional to  $\hat{P}_{12}$  therefore splits singlet and triplet.

### Proportionality Coefficient

Define  $J_{\text{ex}}$  such that

$$\hat{H}_{\text{EX}} = J_{\text{ex}}\hat{P}_{12} = \frac{J_{\text{ex}}}{2}(1 + 4\hat{S}_1 \cdot \hat{S}_2).$$

Acting on the singlet and triplet manifolds:

$$\hat{H}_{\text{EX}}\chi_S = J_{\text{ex}}(-1)\chi_S, \quad \hat{H}_{\text{EX}}\chi_T = J_{\text{ex}}(+1)\chi_T.$$

To reproduce  $\Delta E = 2J$  requires  $J_{\text{ex}} = -J$ . Then

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

$$\Delta E = 2J,$$

as desired. We treat  $J$  as an exchange coupling proportional to orbital overlap. Assuming isotropic exchange, the exchange Hamiltonian can be written as

$$\hat{H}_{\text{EX}} = -J\hat{S}_a \cdot \hat{S}_b.$$

This is the final component of the  $16 \times 16$  spin Hamiltonian. Together, the Zeeman, hyperfine, ZFS, and exchange Hamiltonians describe the core mechanics of spin-dependent recombination.

## Basis States

For a two-electron (carrier + defect) and two-nucleus (silicon and carbon) spin system, there are 16 orthonormal basis states. The full spin Hamiltonian is a  $16 \times 16$  matrix.

To make future calculations easier, we define basis states with the electrons coupled into  $|s, m\rangle$  and the nuclei in their Zeeman basis ( $|\uparrow\rangle, |\downarrow\rangle$ )  $\equiv (|+\frac{1}{2}\rangle, |-\frac{1}{2}\rangle)$ .

### Triplet $|1, +1\rangle$ manifold

$$\begin{aligned} &|1, 1\rangle \otimes |+\frac{1}{2}\rangle_1 \otimes |+\frac{1}{2}\rangle_2 \\ &|1, 1\rangle \otimes |+\frac{1}{2}\rangle_1 \otimes |-\frac{1}{2}\rangle_2 \\ &|1, 1\rangle \otimes |-\frac{1}{2}\rangle_1 \otimes |+\frac{1}{2}\rangle_2 \\ &|1, 1\rangle \otimes |-\frac{1}{2}\rangle_1 \otimes |-\frac{1}{2}\rangle_2 \end{aligned}$$

### Triplet $|1, 0\rangle$ manifold

$$\begin{aligned} &|1, 0\rangle \otimes |+\frac{1}{2}\rangle_1 \otimes |+\frac{1}{2}\rangle_2 \\ &|1, 0\rangle \otimes |+\frac{1}{2}\rangle_1 \otimes |-\frac{1}{2}\rangle_2 \\ &|1, 0\rangle \otimes |-\frac{1}{2}\rangle_1 \otimes |+\frac{1}{2}\rangle_2 \\ &|1, 0\rangle \otimes |-\frac{1}{2}\rangle_1 \otimes |-\frac{1}{2}\rangle_2 \end{aligned}$$

### Singlet $|0, 0\rangle$ manifold

$$\begin{aligned} &|0, 0\rangle \otimes |+\frac{1}{2}\rangle_1 \otimes |+\frac{1}{2}\rangle_2 \\ &|0, 0\rangle \otimes |+\frac{1}{2}\rangle_1 \otimes |-\frac{1}{2}\rangle_2 \\ &|0, 0\rangle \otimes |-\frac{1}{2}\rangle_1 \otimes |+\frac{1}{2}\rangle_2 \\ &|0, 0\rangle \otimes |-\frac{1}{2}\rangle_1 \otimes |-\frac{1}{2}\rangle_2 \end{aligned}$$

### Triplet $|1, -1\rangle$ manifold

$$\begin{aligned} &|1, -1\rangle \otimes |+\frac{1}{2}\rangle_1 \otimes |+\frac{1}{2}\rangle_2 \\ &|1, -1\rangle \otimes |+\frac{1}{2}\rangle_1 \otimes |-\frac{1}{2}\rangle_2 \\ &|1, -1\rangle \otimes |-\frac{1}{2}\rangle_1 \otimes |+\frac{1}{2}\rangle_2 \\ &|1, -1\rangle \otimes |-\frac{1}{2}\rangle_1 \otimes |-\frac{1}{2}\rangle_2 \end{aligned}$$

The first  $|s, m\rangle$  term is the coupled two-electron basis. The  $|\pm\frac{1}{2}\rangle_1 \otimes |\pm\frac{1}{2}\rangle_2$  terms are the two nuclei in their Zeeman basis.

Now we are ready to compute  $\mathcal{H}$  programmatically. We evaluate each sub-Hamiltonian on the basis states above and sum the results.