

Composite systems:

Let us now consider two spin- $\frac{1}{2}$ particles.

Their combined Hilbert space \mathcal{H}^{12} is the tensor product of the individual Hilbert spaces:

$$\mathcal{H}^{12} = \mathcal{H}^1 \otimes \mathcal{H}^2,$$

where \otimes denotes the tensor product.

To see how this works in practice, we can define a basis for \mathcal{H}^{12} using the four states

$$|\uparrow\rangle \otimes |\uparrow\rangle = |\uparrow\rangle|\uparrow\rangle = |\uparrow\uparrow\rangle,$$

$$|\uparrow\rangle \otimes |\downarrow\rangle = \dots$$

$$|\downarrow\rangle \otimes |\uparrow\rangle = \dots$$

$$|\downarrow\rangle \otimes |\downarrow\rangle = \dots = |\downarrow\downarrow\rangle,$$

where we have used the three equivalent notations, $|\alpha\rangle \otimes |\beta\rangle = |\alpha\rangle|\beta\rangle = |\alpha\beta\rangle$

We can now express any state of the two spins using these basis states:

$$|\psi\rangle = C_{\uparrow\uparrow} |\uparrow\uparrow\rangle + C_{\uparrow\downarrow} |\uparrow\downarrow\rangle + C_{\downarrow\uparrow} |\downarrow\uparrow\rangle + C_{\downarrow\downarrow} |\downarrow\downarrow\rangle$$

In the two-particle Hilbert space, the spin operators for the first spin read

$$\hat{\sigma}_z^{(1)} = \hat{\sigma}_z \otimes \mathbb{1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}$$

$$\hat{\sigma}_x^{(1)} = \hat{\sigma}_x \otimes \mathbb{1} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \mathbb{1} \\ \mathbb{1} & 0 \end{pmatrix}$$

$$\hat{\sigma}_y^{(1)} = \hat{\sigma}_y \otimes \mathbb{1} = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & -i\mathbb{1} \\ i\mathbb{1} & 0 \end{pmatrix}$$

The spin operators for the second spin read

$$\hat{\sigma}_z^{(2)} = \mathbb{1} \otimes \hat{\sigma}_z = \begin{pmatrix} \hat{\sigma}_z & 0 \\ 0 & \hat{\sigma}_z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\hat{\sigma}_x^{(2)} = \mathbb{1} \otimes \hat{\sigma}_x = \begin{pmatrix} \hat{\sigma}_x & 0 \\ 0 & \hat{\sigma}_x \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$\hat{\sigma}_y^{(2)} = \mathbb{1} \otimes \hat{\sigma}_y = \begin{pmatrix} \hat{\sigma}_y & 0 \\ 0 & \hat{\sigma}_y \end{pmatrix} = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix}$$

We can also consider the sum of the spin components, for example

$$\begin{aligned} \hat{\sigma}_z^{(1)} + \hat{\sigma}_z^{(2)} &= \hat{\sigma}_z \otimes \mathbb{1} + \mathbb{1} \otimes \hat{\sigma}_z = \begin{pmatrix} \mathbb{1} + \hat{\sigma}_z & 0 \\ 0 & -\mathbb{1} + \hat{\sigma}_z \end{pmatrix} \\ &= \begin{pmatrix} 2 & & 0 \\ & 0 & 0 \\ 0 & & -2 \end{pmatrix} \end{aligned}$$

Recalling that $\hat{S}_z^{(i)} = \frac{\hbar}{2} \hat{\sigma}_z^{(i)}$, we have

$$\hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)} = \hbar \begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix}$$

showing that the four states $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$ have the total z-components $\hbar, 0, 0, -\hbar$ or $m_z = 1, 0, 0, -1$.

We may also consider the total spin squared

$$\begin{aligned} \hat{S}^2 &= (\hat{\sigma}^{(1)} + \hat{\sigma}^{(2)})^2 \\ &= (\hat{\sigma} \otimes \mathbb{1} + \mathbb{1} \otimes \hat{\sigma})^2 \\ &= \hat{\sigma}^2 \otimes \mathbb{1} + \mathbb{1} \otimes \hat{\sigma}^2 + 2 \hat{\sigma} \otimes \hat{\sigma} \\ &= (\hat{\sigma}_x^2 + \hat{\sigma}_y^2 + \hat{\sigma}_z^2) \otimes \mathbb{1} + \mathbb{1} \otimes (\hat{\sigma}_x^2 + \hat{\sigma}_y^2 + \hat{\sigma}_z^2) \\ &\quad + 2(\hat{\sigma}_x \otimes \hat{\sigma}_x + \hat{\sigma}_y \otimes \hat{\sigma}_y + \hat{\sigma}_z \otimes \hat{\sigma}_z) \\ &= 3\mathbb{1} \otimes \mathbb{1} + \mathbb{1} \otimes 3\mathbb{1} + 2(\hat{\sigma}_x \otimes \hat{\sigma}_x + \hat{\sigma}_y \otimes \hat{\sigma}_y + \hat{\sigma}_z \otimes \hat{\sigma}_z) \\ &= 6\mathbb{1} \otimes \mathbb{1} + 2(\hat{\sigma}_x \otimes \hat{\sigma}_x + \hat{\sigma}_y \otimes \hat{\sigma}_y + \hat{\sigma}_z \otimes \hat{\sigma}_z) \end{aligned}$$

Applying this operator to our basis states, we find

$$\begin{aligned}\hat{\underline{\sigma}}^2 |\uparrow\uparrow\rangle &= 6|\uparrow\uparrow\rangle + 2 \left(\underbrace{|\downarrow\downarrow\rangle + i^2 |\downarrow\downarrow\rangle}_0 + |\uparrow\uparrow\rangle \right) \\ &= 8 |\uparrow\uparrow\rangle\end{aligned}$$

$$\begin{aligned}\hat{\underline{\sigma}}^2 |\downarrow\downarrow\rangle &= 6|\downarrow\downarrow\rangle + 2 \left(|\uparrow\uparrow\rangle + (i)^2 |\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle \right) \\ &= 8 |\uparrow\uparrow\rangle\end{aligned}$$

$$\begin{aligned}\hat{\underline{\sigma}}^2 |\uparrow\downarrow\rangle &= 6|\uparrow\downarrow\rangle + 2 \left(|\downarrow\uparrow\rangle + i(-i)|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle \right) \\ &= 4(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)\end{aligned}$$

$$\begin{aligned}\hat{\underline{\sigma}}^2 |\downarrow\uparrow\rangle &= 6|\downarrow\uparrow\rangle + 2 \left(|\uparrow\downarrow\rangle + i(-i)|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) \\ &= 4(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)\end{aligned}$$

We see that $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ are eigenstates of $\hat{\underline{\sigma}}^2$, but $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ are not. However, we can construct the two last eigenstates

as $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle \pm |\downarrow\uparrow\rangle)$, since

$$\begin{aligned}\hat{\underline{\sigma}}^2 \left(|\uparrow\downarrow\rangle \pm |\downarrow\uparrow\rangle \right) &= 4(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \pm 4(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle) \\ &= \begin{cases} 8(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), & (+) \\ 0, & (-) \end{cases}\end{aligned}$$

Recalling that $\hat{S}^2 = \frac{\hbar^2}{4} (\hat{O}^{(1)} + \hat{O}^{(2)})^2$, we find

$$\hat{S}^2 |\uparrow\uparrow\rangle = 2\hbar^2 |\uparrow\uparrow\rangle = s(s+1)\hbar^2 |\uparrow\uparrow\rangle \text{ with } s=1$$

$$\hat{S}^2 |\downarrow\downarrow\rangle = 2\hbar^2 |\downarrow\downarrow\rangle = \dots \dots \dots$$

$$\hat{S}^2 (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) = 2\hbar^2 (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \dots \dots \dots$$

and

$$\hat{S}^2 (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = 0 = s(s+1)\hbar^2 (\dots) \text{ with } s=0.$$

Thus, we have identified the three triplet states

$$|s=1, m_2=1\rangle = |\uparrow\uparrow\rangle$$

$$|s=1, m_2=1\rangle = |\downarrow\downarrow\rangle$$

$$|s=1, m_2=0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

and the singlet state

$$|s=0, m_2=0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$

Identical particles:

We will now consider the construction of many-particle states, in particular systems with several identical particles. To keep the discussion simple, we consider just two particles whose position we denote by x_1 and x_2 .

Since the two particles are identical, their combined state must be unchanged, if we exchange the two particles, i.e.

$$\varphi(x_1, x_2) = e^{i\varphi} \varphi(x_2, x_1),$$

only the overall phase can change, since it has no physical implications. If we interchange the particles twice, we should get back to the original state

$$\varphi(x_1, x_2) = e^{i\varphi} \varphi(x_2, x_1) = (e^{i\varphi})^2 \varphi(x_1, x_2)$$

$$\Rightarrow e^{i\varphi} = \pm 1.$$

Thus, a two-particle state must be either symmetric or anti-symmetric, i.e.

$$\varphi(x_1, x_2) = \pm \varphi(x_2, x_1)$$

Now, particles can be divided into two groups, depending on whether their many-body state is symmetric or anti-symmetric. Particles for which the many-body state is anti-symmetric are called fermions, examples being electrons, protons, and neutrons. The other class is called bosons and includes for example photons, phonons and magnons. It turns out that fermions have half-integer spin, while bosons have integer spin. (This follows from the spin-statistics theorem.)

As an example, we can consider two identical particles that occupy the two single-particle states $\phi_L(x)$ and $\phi_R(x)$. For bosons, the two-particle state read

$$\begin{aligned}\phi_B(x_1, x_2) &= \frac{1}{\sqrt{2}} (\phi_L(x_1)\phi_R(x_2) + \phi_R(x_1)\phi_L(x_2)) \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(x_1) & \phi_L(x_2) \\ \phi_R(x_1) & \phi_R(x_2) \end{vmatrix}_+, \end{aligned}$$

where $\begin{vmatrix} \end{vmatrix}_+$ is a permanent. Here, the $\frac{1}{\sqrt{2}}$ -factor ensures that the state is normalized, and we have assumed that ϕ_L and ϕ_R are orthogonal.

For fermions, the state reads

$$\begin{aligned}\phi_F(x_1, x_2) &= \frac{1}{\sqrt{2}} \left(\phi_L(x_1)\phi_R(x_2) - \phi_R(x_1)\phi_L(x_2) \right) \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_L(x_1) & \phi_L(x_2) \\ \phi_R(x_1) & \phi_R(x_2) \end{vmatrix},\end{aligned}$$

where $\begin{vmatrix} | \\ | \end{vmatrix}$ is a (Slater) determinant.

In the case where $\phi_L(x) = \phi_R(x) = \phi(x)$ is the same state, we have

$$\phi_B(x_1, x_2) = \phi(x_1)\phi(x_2) \text{ for bosons}$$

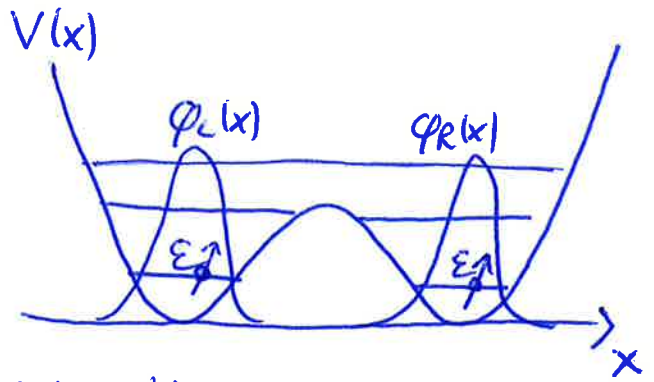
and

$$\phi_F(x_1, x_2) = \phi(x_1)\phi(x_2) - \phi(x_1)\phi(x_2) = 0 \text{ for fermions}$$

Hence, we find that two fermions cannot occupy the same state. This phenomenon is known as the Pauli exclusion principle, which (among other things) can explain the periodic table!

Exchange coupling:

As an example, where the exchange symmetry is important, we now calculate the effective spin-spin interaction between two electrons placed in a double-well potential $V(x)$.



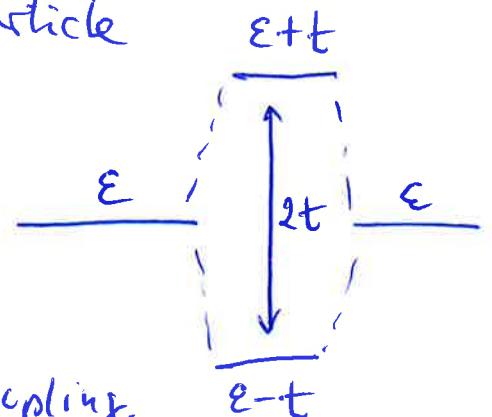
The single-particle Hamiltonian of the problem reads

$$h_i = \begin{pmatrix} \epsilon & -t \\ -t & \epsilon \end{pmatrix},$$

where ϵ is the ground state energy of the left/right potential well, and $-t$ denotes the tunnel coupling between the wells. This is a low-energy description of the problem, where excited states are omitted. (They are assumed to have very large energies). The single-particle

eigenenergies are $\epsilon \pm t$

We now place two electrons in the double-well potential and calculate the effective spin-spin coupling.



First, we impose the exchange symmetry by requiring that the singlet state of the spins must be paired with a symmetric orbital wave function to make the total state antisymmetric:

$$\Psi_{\text{sym}}(x_1, x_2) \propto \underbrace{\frac{1}{\sqrt{2}} (|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2)}_{\text{singlet}}$$

Similarly, the triplet states must be paired with an antisymmetric orbital wave function

$$\Psi_{\text{anti}}(x_1, x_2) \propto \underbrace{\begin{cases} |\uparrow\rangle_1 |\uparrow\rangle_2 \\ (|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2) / \sqrt{2} \\ |\downarrow\rangle_1 |\downarrow\rangle_2 \end{cases}}_{\text{triplets}}$$

We will now evaluate the groundstate energies of the symmetric (E_s) and the antisymmetric (E_t) orbital wave functions. Once we have these groundstate energies, we can write down an effective spin-spin interaction. To see this, we note that

$$\begin{aligned} \hat{S}^2 &= (\hat{S}_1 + \hat{S}_2) \cdot (\hat{S}_1 + \hat{S}_2) = \hat{S}_1^2 + \hat{S}_2^2 + 2 \hat{S}_1 \cdot \hat{S}_2 \\ &= \hbar^2 s_1(s_1+1) + \hbar^2 s_2(s_2+1) + 2 \hat{S}_1 \cdot \hat{S}_2 \\ s_1 = s_2 = \frac{1}{2} \quad \frac{3}{2} \hbar^2 + 2 \hat{S}_1 \cdot \hat{S}_2 &= \hbar^2 s(s+1) = \begin{cases} 0, & \text{singlet } (s=0) \\ 2\hbar^2, & \text{triplet } (s=1) \end{cases} \end{aligned}$$

This implies that

$$\hat{S}_1 \cdot \hat{S}_2 = -\frac{3}{4} \hbar^2 + \frac{S(S+1)}{2} \hbar^2 = \begin{cases} -\frac{3}{4} \hbar^2, & \text{singlet} \\ \frac{1}{4} \hbar^2, & \text{triplet} \end{cases}$$

We can now construct a spin Hamiltonian as

$$\begin{aligned} \hat{H}_{\text{spin}} &\equiv \frac{1}{4}(E_S + 3E_T) - \frac{1}{\hbar^2}(E_S - E_T) \hat{S}_1 \cdot \hat{S}_2 \\ &= \begin{cases} \frac{1}{4}(E_S + 3E_T) - \frac{1}{\hbar^2}(E_S - E_T) \left(-\frac{3}{4}\hbar^2\right) = E_S & (\text{singlet}) \\ \frac{1}{4}(E_S + 3E_T) - \frac{1}{\hbar^2}(E_S - E_T) \left(\frac{1}{4}\hbar^2\right) = E_T & (\text{triplet}) \end{cases} \end{aligned}$$

Thus \hat{H}_{spin} has the eigenenergies E_S for the spin singlet and E_T for the spin triplets.

The constant term $\frac{1}{4}(E_S + 3E_T)$ only gives rise to an overall phase factor and can be omitted.

Thus, we can write the spin Hamiltonian as

$$\hat{H}_{\text{spin}} = -J \hat{S}_1 \cdot \hat{S}_2,$$

where $J \equiv E_T - E_S$ is the singlet-triplet splitting (or exchange coupling) and $\hat{S}_i = \frac{1}{\hbar} \hat{S}_i$.

To calculate the exchange coupling, we need to diagonalize the two-particle Hamiltonian

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{V},$$

where \hat{h}_1, \hat{h}_2 are the single-particle Hamiltonians and \hat{V} accounts for the Coulomb interactions between the electrons.

We start by considering the anti-symmetric orbital part corresponding to the spin triplets:

$$|LR\rangle_T = \frac{1}{\sqrt{2}} (|L\rangle_1 |R\rangle_2 - |R\rangle_1 |L\rangle_2)$$

In the triplet-space, the Hamiltonian reads:

$$\begin{aligned} \hat{H}_T &= \langle LR | \hat{H} | LR \rangle_T \\ &= \frac{1}{2} \left(\langle R | \langle L | + \langle L | \langle R | \right) (\hat{h}_1 + \hat{h}_2 + \hat{V}) (|L\rangle_1 |R\rangle_2 - |R\rangle_1 |L\rangle_2) \\ &= \frac{1}{2} \left(\underbrace{\langle L | \hat{h}_1 | L \rangle_1}_{\epsilon} + \underbrace{\langle R | \hat{h}_1 | R \rangle_1}_{\epsilon} + \underbrace{\langle L | \hat{h}_2 | L \rangle_2}_{\epsilon} + \underbrace{\langle R | \hat{h}_2 | R \rangle_2}_{\epsilon} \right) = 2\epsilon, \end{aligned}$$

where we have used that $\langle LR | R \rangle = 0$ and assumed that $\langle LR | \hat{V} | LR \rangle = 0$, meaning that the Coulomb interactions between electrons in different wells are negligible. Hence, $E_T = 2\epsilon$.

The symmetric orbital parts corresponding to the singlet are

$$|L\rangle_1 |L\rangle_2$$

$$|R\rangle_1 |R\rangle_2$$

$$|LR\rangle_S = \frac{1}{\sqrt{2}} (|L\rangle_1 |R\rangle_2 + |R\rangle_1 |L\rangle_2)$$

In the singlet space, the Hamiltonian is a 3×3 matrix

$$\hat{H}_S = \begin{pmatrix} \langle LL | \hat{H} | LL \rangle & \langle LL | \hat{H} | RR \rangle & \langle LL | \hat{H} | LR \rangle \\ \langle RR | \hat{H} | LL \rangle & \langle RR | \hat{H} | RR \rangle & \langle RR | \hat{H} | LR \rangle \\ \langle LR | \hat{H} | LL \rangle & \langle LR | \hat{H} | RR \rangle & \langle LR | \hat{H} | LR \rangle \end{pmatrix}$$

$$= \begin{pmatrix} h_1 & h_1 & h_1 \\ h_1 & h_1 & h_1 \\ h_1 & h_1 & h_1 \end{pmatrix} + \begin{pmatrix} h_2 & \dots \\ \dots & \dots \\ \dots & \dots \end{pmatrix} + \begin{pmatrix} \hat{V} & & \\ & \hat{V} & \\ & & \hat{V} \end{pmatrix}$$

$$= \begin{pmatrix} \epsilon & 0 & \frac{1}{\sqrt{2}} \langle L | \hat{h}_1 | R \rangle \\ 0 & \epsilon & \frac{1}{\sqrt{2}} \langle R | \hat{h}_1 | L \rangle \\ \frac{1}{\sqrt{2}} \langle R | \hat{h}_1 | L \rangle & \frac{1}{\sqrt{2}} \langle L | \hat{h}_1 | R \rangle & \frac{1}{2} \times 2\epsilon \end{pmatrix} \begin{matrix} \\ \\ \times 2 \\ \text{for } \hat{h}_2 \end{matrix} - t$$

$$+ \begin{pmatrix} U & 0 & 0 \\ 0 & U & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

assuming that $\langle LL | \hat{V} | LL \rangle = \langle RR | \hat{V} | RR \rangle = U$ is the energy cost (Hubbard- U) for double-occupying one of the potential wells. Hence, we obtain

$$\hat{H}_S = \begin{pmatrix} 2\epsilon + U & 0 & 0 \\ 0 & 2\epsilon + U & 0 \\ 0 & 0 & 2\epsilon \end{pmatrix} - t \begin{pmatrix} 0 & 0 & \sqrt{2} \\ 0 & 0 & \sqrt{2} \\ \sqrt{2} & \sqrt{2} & 0 \end{pmatrix}.$$

Without tunneling ($t=0$), the eigenenergies are:

$$|LL\rangle: 2\epsilon + U, |RR\rangle: 2\epsilon + U; |LR\rangle_S: 2\epsilon \leftarrow \text{groundstate}.$$

We now calculate the change of the groundstate energy due to tunneling using perturbation theory, assuming $t \ll U$. There is no first-order correction to the eigenenergy.

To second order, we find

$$\begin{aligned} \Delta E_{gs}^{(2)} &= \sum_{m \neq gs} \frac{|\langle m | \hat{H}' | gs \rangle|^2}{E_{gs} - E_m} \\ &= \frac{|\langle LL | \hat{H}' | gs \rangle|^2}{2\varepsilon - (2\varepsilon + U)} + \frac{|\langle RR | \hat{H}' | gs \rangle|^2}{2\varepsilon - (2\varepsilon + U)} \\ &= \frac{|-\sqrt{2}t|^2}{-U} + \frac{|-\sqrt{2}t|^2}{-U} = -\frac{4t^2}{U} // \end{aligned}$$

We have now found that $E_T = 2\varepsilon$ and

$$E_S = 2\varepsilon - \frac{4t^2}{U} \text{ such that } J = E_T - E_S = \frac{4t^2}{U}$$

$$\text{with } \boxed{\hat{H}_{\text{spin}} = -J \hat{S}_1 \cdot \hat{S}_2 ; J = \frac{4t^2}{U}}$$

This is the Hubbard expression for the exchange coupling between two electronic spins.

Notice that J can be controlled by adjusting the potential $V(\epsilon)$ and thereby the tunnel coupling t .