what is the spin-Hamiltonian (Heisenberg)

1) It has to be such that $H|\psi_s\rangle = E_s|\psi_s\rangle$

$$H|\psi_t\rangle = E_t|\psi_t\rangle$$

H is the 2-electron Hamiltonian we treated before

$E_s \neq E_t$ because of Coulomb repulsion (e^2/r_{12})

$\psi_s \to$ singlet state with eigenvalue E_s, $S=0$

$\psi_t \to$ triplet state with " E_t, $S=1$

$$S^2 = (S_1+S_2)^2 = S_1^2 + S_2^2 + 2S_1\cdot S_2$$

$$S_1^2 = \tfrac{1}{2}\left(\tfrac{1}{2}+1\right) = S_2^2 = 3/4$$

For $S=0 \Rightarrow 0 = 2\times 3/4 + 2S_1\cdot S_2 \Rightarrow S_1\cdot S_2 = -3/4$

For $S=1 \Rightarrow \underset{S(S+1)}{2} = 2\times 3/4 + 2S_1\cdot S_2 \Rightarrow S_1\cdot S_2 = +1/4$.

So Eigenvalue of $S_1\cdot S_2 = -3/4$ for singlet state

$= +1/4$ for triplet state.

Construct a hamiltonian

$$H = \frac{1}{4}(E_s + 3E_t) - (E_s - E_t)\, S_1\cdot S_2$$

what is $\langle\psi_s|H|\psi_s\rangle = \frac{1}{4}(E_s+3E_t)\langle\psi_s|\psi_s\rangle - (E_s-E_t)\langle\psi_s|S_1\cdot S_2|\psi_s\rangle$

$$= \frac{1}{4}(E_s+3E_t) - \frac{-3}{4}(E_s-E_t) = E_s$$

What is $\langle\psi_t|H|\psi_t\rangle = \frac{1}{4}(E_s+3E_t) - \frac{1}{4}(E_s-E_t) = E_t$.

So H is the spin-Hamiltonian.

Ignoring the constant

$$H_{spin} = -(E_S - E_t)\, S_1 \cdot S_2$$

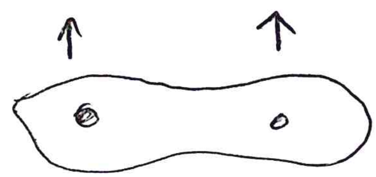
$$\boxed{H_{spin} = -J\, S_1 \cdot S_2} \quad J = (E_S - E_t)$$

when $E_S - E_t > 0$ S_1 is parallel to S_2 (FM) is lower in energy.

when $E_S - E_t < 0$ S_1 is anti parallel to S_2 (AFM)

Wheather $E_S > E_t$ or $E_t > E_S$ depends on the spin-independent Hamiltonian (orbital/space) through pauli exchange and Coulomb interaction

In the case of H_2/O_2 molecule $E_S < E_t$



$S=1$

not low energy

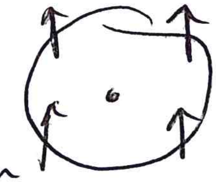
electrons in the middle

$S=0$

low energy.

↳ gain energy through ~~nucleus~~ attraction from both ~~electron~~ nucleus (Singlet state)

But in a single atom



low energy ($S=1$)

Hunds rule

Pauli exclusion does not allow electrons to come close which minimizes coulomb exchange