

# Introduction to Magnetic Exchange Mechanisms

(From Heisenberg model to Goodenough-Kanamori rule)

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1 Two Spin Sites Model

$$\begin{array}{cc} \uparrow & \downarrow \\ \hline A & \hat{J} \end{array} \rightarrow \hat{H}.$$

2 Coefficient  $A$  in Heisenberg Model

3 Different Exchange Type

4 Multiple electrons system



$G-k$  rules.

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# Spin space for two spin sites

For a **two equivalent spin- $\frac{1}{2}$  spin sites** (a and b), the complete spin space can be described by 4 states:

CSCC.

$$\{\hat{S}_1, \hat{S}_2, \hat{S}_{1m}, \hat{S}_{2m}\} \quad \begin{array}{l} |\uparrow, \uparrow\rangle, |\downarrow, \downarrow\rangle \\ |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle \end{array} \quad \begin{array}{l} \text{ferromagnetic (FM) states} \\ \text{anti-ferromagnetic (AFM) states} \end{array}$$

$\begin{array}{cc} \downarrow & \downarrow \\ \underline{a} & \underline{b} \end{array}$

The eigenstates for a spin coupling system can be produced by the linear combination of those 4 states.


$S = S_1 + S_2$   $\downarrow m.$   $m = -1 \dots +1$   $S_1, S_2$   $(S_1, S_2)$

$$\left\{ \begin{array}{l} \underline{|1, 1\rangle} = |\uparrow, \uparrow\rangle \\ \underline{|1, -1\rangle} = |\downarrow, \downarrow\rangle \\ \underline{|1, 0\rangle} = \frac{1}{\sqrt{2}} (|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle) \\ \underline{|0, 0\rangle} = \frac{1}{\sqrt{2}} (|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle) \end{array} \right\} \quad \begin{array}{l} \text{triplet states for } \underline{s = 1} \\ \text{singlet state for } \underline{s = 0} \end{array}$$

# The origin of magnetism

Assume the energy of the spin triplet states are degenerated. Use  $E_T$  and  $E_S$  represent the energy of **the spin triplet and spin singlet states**, respectively.

$$\begin{aligned}
 \frac{E_{\text{FM}} - E_{\text{AFM}}}{2\Delta} &= E_{\uparrow,\uparrow} - E_{\downarrow,\uparrow} \\
 &= E_{\uparrow,\uparrow} - E_{\uparrow,\downarrow} \\
 &= E_{1,1} - \frac{1}{2}E_{1,0} - \frac{1}{2}E_{0,0} \\
 &= \frac{1}{2}(E_T - E_S)
 \end{aligned}
 \tag{1}$$


 $\hat{H} = S \cdot S$

## Mark

Obviously, the AFM state and the spin singlet state are different. But, once we express the  $E_T - E_S$  using the spin order, naturally, the  $E_{\text{FM}} - E_{\text{AFM}}$  will also be included.

# Heisenberg Hamiltonian for two spin sites

Let  $E_T - E_S = -2A$ , more specifically,  $E_T = -A, E_S = A$  (If not, just give it an energy shift).

At the same time, for the two spin operators  $\hat{s}_1, \hat{s}_2$ ,

$$\begin{aligned} \underline{2\langle \hat{s}_1 \cdot \hat{s}_2 \rangle + \frac{1}{2}} &= s(s+1) - s_1^2 - s_2^2 + \frac{1}{2} \\ &= \begin{cases} -1, s=0 \\ +1, s=1 \end{cases} \end{aligned}$$

$E_{FM} - E_{AFM} = -A$   
 $E_T - E_S = -2A$   
 $-A(2\hat{S}_1\hat{S}_2 + \frac{1}{2})$   
 $-2A\hat{S}_1\hat{S}_2$   
 $-2A$

Where  $\hat{s} = \hat{s}_1 + \hat{s}_2$ , and the unit  $\hbar$  is not included.

## Important Result

So, the Hamiltonian for  $E_T$  and  $E_S$  can be written as:

$$\underline{\hat{H}_{Ad} = -2A\hat{s}_1 \cdot \hat{s}_2}$$

$\langle FM | H_{Ad} | FM \rangle$   
 $E_{FM} = -\frac{A}{2}$   
 $E_{AFM} = \frac{A}{2}$

This is what we called, Heisenberg Hamiltonian (for two spin sites).

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# A naive idea about the origin of $A$ — MDD

$$\hat{H} = -2A \hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2$$

The only question now is the origin of the coefficient  $A$ .



## Naive idea

Since the Heisenberg Hamiltonian is directly related to spin, it is nature to think that the  $A$  may come from spin-spin interaction. Or more specifically, it comes from the magnetic dipole-dipole(MDD) interaction.

The magnetic dipole generated by spin can be calculated as follow:

$$\mu_S = -g_e \mu_B \langle \hat{S} \rangle \quad (4)$$

Dirac theory gives  $g_e = 2$ , which is changed to  $g_e \approx \underline{2.0023}$  by QED corrections.



# A naive idea about the origin of $A$ — MDD

## Useful energy scales

- $1 \text{ T} \sim 5.8 \times 10^{-2} \text{ meV} \sim 0.67 \text{ K}$  ✓
- $1 \text{ meV} \sim 11.6 \text{ K} \sim 17.2 \text{ T} \sim 8.06 \text{ cm}^{-1}$
- $1 \text{ cm}^{-1} \sim 1.44 \text{ K}$

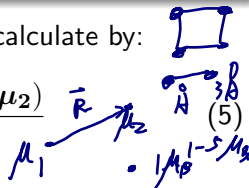
$k_B T$



The energy magnetic dipole-dipole interaction can be calculate by:

$$E_{\text{mdd}} = \frac{\mu_0}{4\pi} \frac{\mu_1 \cdot \mu_2 - 3(e_R \cdot \mu_1)(e_R \cdot \mu_2)}{R^3}$$

Handwritten notes below the equation:  $\mu_B$ ,  $1 \text{ Å}$ .



## Estimate $T_C$ under MDD

For two  $1 \mu_B$  moments at a distance of  $1 \text{ Å}$  the magnetostatic energy is of the order of  $0.05 \text{ meV}$ , corresponding to a temperature of less than  $1 \text{ K}$ .

While, The  $T_C$  for  $\text{Fe}_3\text{O}_4$  is  $858 \text{ K}$ .

$A$  MDD

# Three methods to obtain the coefficient $A$

$$E_T - E_S = -2A$$

The real source of  $A$  is the electron exchange, a quantum many-body interaction.

There are three ways (as I know) to get coefficient  $A$ . Each of them uniquely help us understand the origin of magnetic order.

## Preview for the 3 method

- The first method can help us understand the essence of  $A$ .
- The second method teach us how to determine the sign of  $A$ , and gives a more clear description about  $A$ .
- As for the last one, we can use it in the daily research.

# The 1st method ► Hamiltonian

The first and the directest (also the earliest) method is given by Heitler and London<sup>1</sup> using hydrogen molecule.

In a hydrogen molecule, assume each hydrogen site has one electron without inter-site hopping. Then, the Hamiltonian for this system is,

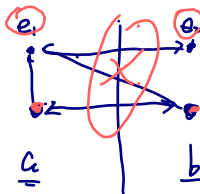
$$\hat{H}_h = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}} \quad (6)$$

$$= \hat{H}_{01} + \hat{H}_{02} + \frac{e^2}{R_{ab}} + \hat{H}_U - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}}$$

Where  $\hat{H}_{01} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r_{a1}},$

$$\hat{H}_{02} = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_{b2}},$$

$$\hat{H}_U = \frac{e^2}{r_{12}}.$$



$$T_1 + V_{h1} + V_{b1} + \frac{V_{12}}{2} + \frac{V_{a2}}{2} + V_{b2} + T_2 + V_{ab}$$

1836

<sup>1</sup>Physik, 1927,44,455

# The 1st method ► Basis

$$\hat{H}_h = \hat{H}_{01} + \hat{H}_{02} + \frac{e^2}{R_{ab}} + \hat{H}_U - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}}$$

Use the eigenstates of  $\hat{H}_{01} + \hat{H}_{02}$  to describe the low energy part of the Hilbert space. After consider the symmetry for fermion,

$$\begin{cases} \psi_S = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] \\ \psi_T = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] \end{cases} \quad \begin{matrix} \uparrow\downarrow - \downarrow\uparrow \\ \uparrow\uparrow \end{matrix} \quad (7)$$

Under this basis, the  $\hat{H}_h$  can be expressed as:

$$\hat{H}_h = 2E_0 + \frac{e^2}{R_{ab}} + \begin{pmatrix} \frac{K+A}{1+I^2} & 0 \\ 0 & \frac{K-A}{1-I^2} \end{pmatrix}, \begin{pmatrix} \psi_S \\ \psi_T \end{pmatrix} \quad (8)$$

$E_S = C + \frac{K+A}{1+I^2} \quad E_T = C + \frac{K-A}{1-I^2}$

# The 1st method ► Energy difference

$$\hat{H}_h = 2E_0 + \frac{e^2}{R_{ab}} + \begin{pmatrix} \frac{K+A}{1+I^2} & 0 \\ 0 & \frac{K-A}{1-I^2} \end{pmatrix} \begin{matrix} |\psi_S\rangle \\ |\psi_T\rangle \end{matrix}$$

$-2A \vec{\Sigma}_1 \cdot \vec{\Sigma}_2$

$S$   
 $I$

$e_1$   
 $e_2$   
 $a$

Where,

$$K = \int \psi_a^*(1) \psi_b^*(2) \left( \frac{e^2}{r_{12}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}} \right) \psi_a(1) \psi_b(2) d^3r_1 d^3r_2 \quad (9a)$$

$$A = \int \psi_a^*(1) \psi_b^*(2) \left( \frac{e^2}{r_{12}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}} \right) \psi_a(2) \psi_b(1) d^3r_1 d^3r_2 \quad (9b)$$

$$I^2 = \int \psi_a^*(1) \psi_b^*(2) \psi_a(2) \psi_b(1) d^3r_1 d^3r_2 \quad (9c)$$

overlap.

Since  $I^2 \ll 1$ ,  $E_T - E_S \approx -2A$



## The 2nd method ► Hamiltonian

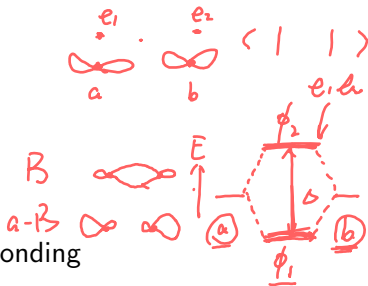
$$\hat{H}_h = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}}$$

$$= \hat{h}_1 + \hat{h}_2 + \frac{e^2}{R_{ab}} + \hat{H}_U$$

Where

$$\hat{h}_1 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{b1}}$$

$$\hat{h}_2 = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b2}}$$



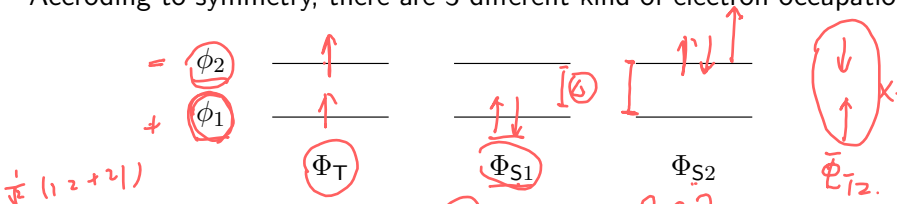
The introduction of  $\hat{h}_1$  (or  $\hat{h}_2$ ) leads us to the bonding state and the anti-bonding state.

$$\phi_1 = \frac{1}{\sqrt{2(1+I^2)}} (\psi_a + \psi_b) \approx \frac{1}{\sqrt{2}} (\underline{\psi_a} + \underline{\psi_b}) \quad (10a)$$

$$\phi_2 = \frac{1}{\sqrt{2(1-I^2)}} (\psi_a - \psi_b) \approx \frac{1}{\sqrt{2}} (\psi_{a\cdot} - \psi_b) \quad (10b)$$

## The 2nd method ► Ground state

The energy difference between  $\phi_1$  and  $\phi_2$  is denoted as:  $\Delta = E_2 - E_1$ .  
According to symmetry, there are 3 different kind of electron occupation.



The ground state for spin triplet:  $\Phi_T$

The ground state for spin singlet:  $\Phi_S = \lambda_1 \Phi_{S1} + \lambda_2 \Phi_{S2}$ .

Use these two state, we can calculate the energy difference between spin triplet and singlet state<sup>2</sup>:

$$-2A = E_T - E_S = -2J_{ab} + \frac{\Delta^2}{U} \quad (11)$$

<sup>2</sup>J. Am. Chem. Soc. 1975, 97, 17, 4884

## The 2nd method ► Energy difference

$$-2A = E_T - E_S = -2J_{ab} + \frac{\Delta^2}{U}$$

Where,

A.  $J_{ab} = \int \psi_a^*(1) \psi_b^*(2) \frac{e^2}{r_{12}} \psi_a(2) \psi_b(1) d^3r_1 d^3r_2$  (12a)

$$U_{ij} = \int \underbrace{\psi_i^*(1)} \underbrace{\psi_j^*(2)} \frac{e^2}{r_{12}} \underbrace{\psi_i(1)} \underbrace{\psi_j(2)} d^3r_1 d^3r_2 \quad (12b)$$

$$U = U_{aa} - U_{ab} \quad (12c)$$

In the first method, we get:

$$A = \int \psi_a^*(1) \psi_b^*(2) \left( \frac{e^2}{r_{12}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}} \right) \psi_a(2) \psi_b(1) d^3r_1 d^3r_2$$



## The 2nd method ► The sign of $J_{ab}$

$$\begin{aligned}
 J_{ab} &= \int \psi_a^*(1) \psi_b^*(2) \frac{e^2}{r_{12}} \psi_a(2) \psi_b(1) d^3r_1 d^3r_2 \\
 &= \int d^3r_1 \underbrace{\psi_a^*(1) \psi_b(1)}_{\Psi^*(1)} \int d^3r_2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \underbrace{\psi_a(2) \psi_b^*(2)}_{\Psi(2)} \\
 &= \int d^3r_1 \Psi^*(1) \frac{1}{(2\pi)^3} \int d^3k e^{i\mathbf{k} \cdot \mathbf{r}_1} \frac{4\pi}{k^2} \tilde{\Psi}(\mathbf{k}) \\
 &= \frac{1}{(2\pi)^3} \int d^3k \underbrace{\int d^3r_1 e^{i\mathbf{k} \cdot \mathbf{r}_1} \Psi^*(1)}_{\tilde{\Psi}^*(-\mathbf{k})} \tilde{\Psi}(\mathbf{k}) \frac{4\pi}{k^2} \\
 &= \frac{1}{(2\pi)^3} \int d^3k \left| \tilde{\Psi}(\mathbf{k}) \right|^2 \frac{4\pi}{k^2} > 0
 \end{aligned}
 \tag{13}$$

$A = \frac{J_{ab}}{FM} - \frac{\Delta^2}{2U}$   
 $A = A_{FM} + A_{AFM}$

## The 2nd method ► Useful observations

$$-2A = E_T - E_S = -2J_{ab} + \frac{\Delta^2}{U}$$

$\frac{4t^2}{U}$

### Observations

- The first term,  $J_{ab}$  is corresponding to the FM state. While, the second term,  $\Delta^2/U$  is corresponding to the AFM state.
- $J_{ab}$  comes from the electron-electron Coulomb exchange.
- $\Delta^2/U$  comes from the electron-ion Coulomb interaction.
- $\Delta^2/U$  can also be regard as the result of electron hopping in different atomic site. And  $\Delta = 2t$ , where  $t$  is the hopping factor.
- The  $\Delta$  here, is the origin of superexchange (or super-superexchange).

# The 3rd method ▶ Starting point

## Starting Point

From the result of 2nd method, we can conclude that, the magnetic state energy difference comes from 2 sources:

- The electron-electron Coulomb exchange. ( $-2J_{ab}$ )
- Electron hopping among different sites. ( $4t^2/U$ )

And that encourage us to introduce the electron hopping in our system.

$$-2A = E_T - E_S = -2J_{ab} + \frac{4t^2}{U}$$

Remember, in the **first method** we declare that, the two electron in different site **cannot hopping** to each other. Although, based on that assumption, we built up a **complete Hilbert space** for ground state, but it is actually **unphysical**. (It is hard to obtain some physical meaning from a Hamiltonian diagonalization.)

## The 3rd method ► Basic idea

Now, Let's open the black box of Hamiltonian diagonalization!

### Basic idea

In the third method, we will still use the single electron state  $\psi_a, \psi_b$ , but permit the electron hopping. That means, the two electrons are now permitted to occupy the same site.

According to the analysis above, the energy different comes from two terms, which we named:

- Coulomb exchange  $(-2J_{ab})$
- Kinetic exchange  $(4t^2/U)$  hopping  $4t^2/U$

The “Coulomb exchange” represent the electron-electron Coulomb exchange. We do not care about the Coulomb exchange when the two electrons occupy the same site, which is also in a independent space. So, when discussing the Coulomb exchange, there is no need to imply the hopping picture.

## The 3rd method ► Coulomb exchange

The Coulomb exchange is related to the electron-electron Coulomb interaction:

$$\hat{H}_U = \frac{e^2}{r_{12}} \quad (14)$$

In the first method, we use the spin singlet and triplet state to symmetrize the real space wavefunction. This work can also be done by one equation:

$$\begin{aligned} \Psi_{a,\sigma;b,\sigma'} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(1)\sigma(1) & \psi_a(2)\sigma(2) \\ \psi_b(1)\sigma'(1) & \psi_b(2)\sigma'(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2)\sigma(1)\sigma'(2) - \psi_b(1)\psi_a(2)\sigma'(1)\sigma(2)] \end{aligned} \quad (15)$$

Where the  $\sigma$  and  $\sigma'$  is the single electron spin.

Instead of using the coupling representation, we express the  $\hat{H}_U$  under the **uncoupling representation**.

## The 3rd method ► Coulomb exchange

$$\frac{e^2}{\gamma_{12}} \hat{H}_U = \begin{pmatrix} U_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & U_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & U_{ab} & 0 \\ 0 & 0 & 0 & U_{ab} - J_{ab} \end{pmatrix} \begin{pmatrix} |\uparrow, \uparrow\rangle \\ |\uparrow, \downarrow\rangle \\ |\downarrow, \uparrow\rangle \\ |\downarrow, \downarrow\rangle \end{pmatrix} \quad \begin{matrix} \text{but } \rightarrow \\ \text{L } \uparrow\downarrow \\ (16) \end{matrix}$$

Check equation (12) to confirm the definition of  $U_{ab}$  and  $J_{ab}$ .

$-2J_{ab}$

### Observations

- Coulomb exchange for spin triplet state:  $E_{CT} = U_{ab} - J_{ab}$
- Coulomb exchange for spin singlet state:  $E_{CS} = U_{ab} + J_{ab}$
- Under the Coulomb exchange, the state  $|\uparrow, \downarrow\rangle$  and  $|\downarrow, \uparrow\rangle$  are coupled. (This is the basis of double exchange.)
- The Coulomb exchange always prefers the spin triplet state, for the  $J_{ab}$  keeps positive.

# The 3rd method ► Kinetic exchange ► Hubbard model

The kinetic exchange is related to the hopping of electrons. To describe this part, we need to use the Hubbard model.

$$\hat{H}_{t-U} = -t \sum_{ij\sigma} \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad (17)$$

The spin parallel state forbids the electron hopping, so their kinetic energy equals to 0.

Under the basis:  $\{ \underbrace{|\uparrow\cdot, \downarrow\cdot\rangle, |\downarrow\cdot, \uparrow\cdot\rangle}_{\text{covalent states}}, \underbrace{|\uparrow\downarrow, \cdot\cdot\rangle, |\cdot\cdot, \uparrow\downarrow\rangle}_{\text{ionic states}} \}$ ,  
The Hamiltonian can be expressed as:

$$\hat{H}_{t-U} = \begin{pmatrix} \underline{0} & 0 & -t & -t \\ 0 & \underline{0} & +t & +t \\ -t & +t & \underline{U} & 0 \\ -t & +t & 0 & \underline{U} \end{pmatrix} \begin{pmatrix} |\uparrow\cdot, \downarrow\cdot\rangle \\ |\downarrow\cdot, \uparrow\cdot\rangle \\ |\uparrow\downarrow, \cdot\cdot\rangle \\ |\cdot\cdot, \uparrow\downarrow\rangle \end{pmatrix} \quad (18)$$

# The 3rd method ► Kinetic exchange ► Energy split

$$\hat{H}_{t-U} = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & +t & +t \\ -t & +t & U & 0 \\ +t & +t & 0 & U \end{pmatrix} \begin{pmatrix} |\uparrow\cdot, \downarrow\cdot\rangle \\ |\downarrow\cdot, \uparrow\cdot\rangle \\ |\uparrow\downarrow, \cdot\cdot\rangle \\ |\cdot\cdot, \uparrow\downarrow\rangle \end{pmatrix}$$

*Handwritten notes:  $t \ll U$  (above matrix),  $2t$  (below matrix), and red circles around the off-diagonal  $t$  terms and the last two basis states.*

After diagonalization, we get:

$$\varepsilon_+ = \frac{U}{2} + \frac{\sqrt{U^2 + 16t^2}}{2}, \quad \Psi_+ = \frac{|\uparrow\cdot, \downarrow\cdot\rangle - |\downarrow\cdot, \uparrow\cdot\rangle - (\varepsilon_+/2t)(|\uparrow\downarrow, \cdot\cdot\rangle + |\cdot\cdot, \uparrow\downarrow\rangle)}{\sqrt{2 + (\varepsilon_+/2t)^2}} \quad (19a)$$

$$\varepsilon_{\text{ion}} = U, \quad \Psi_{\text{ion}} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow, \cdot\cdot\rangle - |\cdot\cdot, \uparrow\downarrow\rangle) \quad (19b)$$

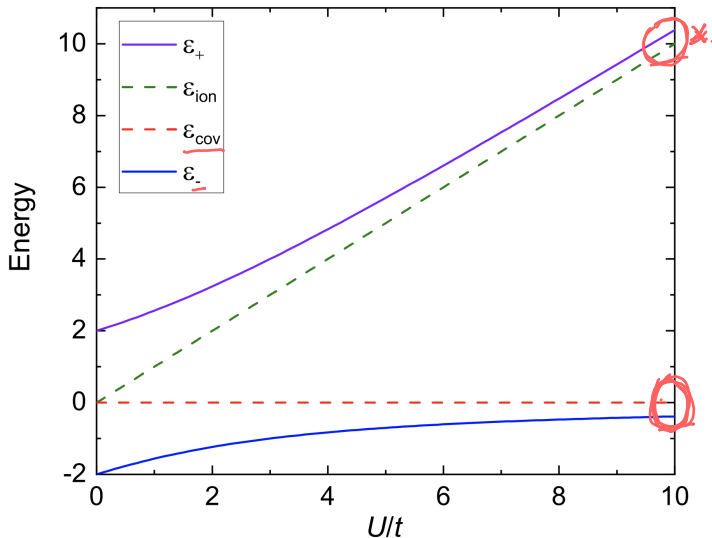
$$\varepsilon_{\text{cov}} = 0, \quad \Psi_{\text{cov}} = \frac{1}{\sqrt{2}}(|\uparrow\cdot, \downarrow\cdot\rangle + |\downarrow\cdot, \uparrow\cdot\rangle) \quad (19c)$$

*Handwritten notes:  $k$  and  $0$  (near  $\Psi_{\text{cov}}$ ), and red arrows pointing to the basis states in  $\Psi_{\text{cov}}$ .*

$$\varepsilon_- = \frac{U}{2} - \frac{\sqrt{U^2 + 16t^2}}{2}, \quad \Psi_- = \frac{|\uparrow\cdot, \downarrow\cdot\rangle - |\downarrow\cdot, \uparrow\cdot\rangle - (\varepsilon_-/2t)(|\uparrow\downarrow, \cdot\cdot\rangle + |\cdot\cdot, \uparrow\downarrow\rangle)}{\sqrt{2 + (\varepsilon_-/2t)^2}} \quad (19d)$$



# The 3rd method ► Kinetic exchange ► Energy plot



# The 3rd method ► Kinetic exchange ► Downfolding

$$\hat{H}_{t-U} = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & +t & +t \\ -t & +t & U & 0 \\ -t & +t & 0 & U \end{pmatrix} \left| \begin{array}{l} |\uparrow\cdot, \downarrow\cdot\rangle \\ |\downarrow\cdot, \uparrow\cdot\rangle \\ |\uparrow\downarrow, \cdot\cdot\rangle \\ |\cdot\cdot, \uparrow\downarrow\rangle \end{array} \right. \quad \xi = \xi_i$$

If  $U \gg t$ , then  $\hat{H}_{11}$  can be regarded as a perturbation for  $\hat{H}_{00}$ .

$$\hat{H}_{t-U} = \begin{pmatrix} \hat{H}_{00} & \hat{T}_{01} \\ \hat{T}_{10} & \hat{H}_{11} \end{pmatrix} \quad (20)$$

Use the downfolding technique<sup>3</sup>:

$$\hat{H}_{00}^{(df)} = \hat{H}_{00} + \hat{T}_{01} (\varepsilon_1 - \hat{H}_{11})^{-1} \hat{T}_{10} \quad \frac{T_{01} T_{10}}{\xi_0 - \xi_1} \quad (21a)$$

$$\approx \hat{H}_{00} + \hat{T}_{01} (\varepsilon_0 - \hat{H}_{11})^{-1} \hat{T}_{10} \quad (21b)$$

Where,  $\varepsilon$  is one eigenvalue of the selected (degenerated) subspace, and  $\varepsilon_0$  is the corresponding eigenvalue of  $\hat{H}_{00}$ .

<sup>3</sup> <https://diglib.tugraz.at/download.php?id=576a8c68b9df4&location=browse>

The 3rd method ► Kinetic exchange ► Perturbation  $\hat{H}_{\text{eff}}$

Use the downfolding technique, we can get the perturbation Hamiltonian:

$$\begin{aligned} \underline{\hat{H}_{\text{eff}}} &= \begin{pmatrix} -t & -t \\ +t & +t \end{pmatrix} \begin{pmatrix} \varepsilon - U & 0 \\ 0 & \varepsilon - U \end{pmatrix}^{-1} \begin{pmatrix} -t & +t \\ -t & +t \end{pmatrix} \\ &\approx -\frac{2t^2}{U} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \end{aligned} \quad (22)$$


Diagonalizing the effective Hamiltonian, we find,

$$E_{\text{KS}} = -\frac{4t^2}{U}, \quad \Psi_{\text{S}} = \frac{1}{\sqrt{2}}(|\uparrow \cdot, \downarrow \cdot\rangle - |\downarrow \cdot, \uparrow \cdot\rangle) \quad (23a)$$

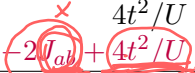
$$E_{\text{KT}} = 0, \quad \Psi_{\text{T}} = \frac{1}{\sqrt{2}}(|\uparrow \cdot, \downarrow \cdot\rangle + |\downarrow \cdot, \uparrow \cdot\rangle) \quad (23b)$$

For the other spin triplet (spin parallel) state, their kinetic energy also equal to 0.


# The 3rd method ► Energy difference



Item	Singlet	Triplet	$E_T - E_S$
Coulomb exchange	$U_{ab} + J_{ab}$	$U_{ab} - J_{ab}$	$-2J_{ab}$
Kinetic exchange	$-4t^2/U$	0	$4t^2/U$
Total	$U_{ab} + J_{ab} - 4t^2/U$	$U_{ab} - J_{ab}$	$-2J_{ab} + 4t^2/U$



## Observations

- $\langle 1 | \dots | \rangle \times \langle T | 0 \rangle \langle 0 | T | 1 \rangle$   
 $\epsilon_1 - \epsilon_2$
- The result agree with what we find in the second method.
  - Spin triplet states are degenerated on the Coulomb exchange term
  - Spin triplet states are degenerated on the kinetic exchange term.
  - Normally, the Coulomb exchange between different atomic site is very weak, for this term is only determined by the direct overlap of orbitals.
  - But, the kinetic exchange may not equally weak, for it can also come from “indirect” overlap.
- 

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$$\begin{array}{c} \uparrow \quad \uparrow \\ \hline \end{array} \quad \begin{array}{l} E_{FM} - E_{AFM} \\ E_T - E_S = -2A \end{array}$$

A. ① C

②  $A = \underline{A_{FM}} + \underline{A_{AFM}}$

③  $\underline{CE} \ll \underline{KE}$

... ..

# Exchange type

Since the Coulomb exchange between different atomic site is weak, when talking about the magnetism of a real material, we usually just focus on the kinetic exchange. Based on that, few difference exchange type is defined.

## Exchange type

- Direct exchange (direct overlap, kinetic energy) ✓
- Superexchange (indirect overlap, kinetic energy) ✓
- Super-superexchange (indirect overlap, kinetic energy) }
- Double exchange (direct overlap, Coulomb energy & kinetic energy)

3d. CE KE.

# Direct exchange

The Hamiltonian for direct exchange can be written as:

$$\hat{H}_{\text{dex}} = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & +t & +t \\ -t & +t & U & 0 \\ -t & +t & 0 & U \end{pmatrix} \begin{matrix} \hat{c}_{2\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\uparrow}^\dagger \hat{c}_{1\downarrow}^\dagger |0\rangle \\ \hat{c}_{1\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\downarrow}^\dagger \hat{c}_{2\uparrow}^\dagger |0\rangle \end{matrix}$$

Direct E:

$\uparrow \leftarrow \downarrow$

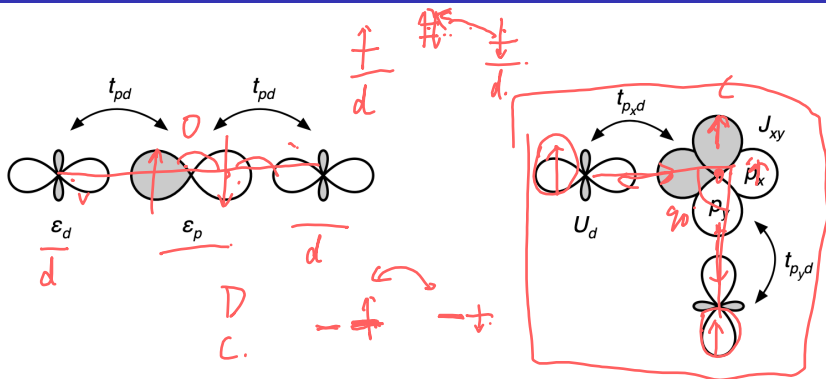
After downfolding,

$$\begin{aligned} \hat{H}_{\text{dex}} &\approx -\frac{2t^2}{U} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{matrix} \hat{c}_{2\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\uparrow}^\dagger \hat{c}_{1\downarrow}^\dagger |0\rangle \end{matrix} \\ &= -\frac{2t^2}{U} \left( \hat{c}_{1\downarrow}^\dagger \hat{c}_{1\downarrow} \hat{c}_{2\uparrow}^\dagger \hat{c}_{2\uparrow} - \hat{c}_{1\uparrow}^\dagger \hat{c}_{1\downarrow} \hat{c}_{2\downarrow}^\dagger \hat{c}_{2\uparrow} - \hat{c}_{1\downarrow}^\dagger \hat{c}_{1\uparrow} \hat{c}_{2\uparrow}^\dagger \hat{c}_{2\downarrow} + \hat{c}_{1\uparrow}^\dagger \hat{c}_{1\uparrow} \hat{c}_{2\downarrow}^\dagger \hat{c}_{2\downarrow} \right) \\ &= \frac{4t^2}{U} \left( \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2 - \frac{\hat{n}_1 \hat{n}_2}{4} \right) \sim \boxed{\frac{4t^2}{U} \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2} \end{aligned} \quad (24)$$

Where, for electron spin  $\hat{\mathbf{s}}_i = (\hat{s}_{ix}, \hat{s}_{iy}, \hat{s}_{iz})$ :

$$\hat{s}_{ix} = \frac{1}{2} \left( \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\downarrow} + \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\uparrow} \right), \quad \hat{s}_{iy} = -\frac{i}{2} \left( \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\downarrow} - \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\uparrow} \right), \quad \hat{s}_{iz} = \frac{1}{2} (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow}) \quad (25)$$

# Superexchange



## Notes

- The 180° superexchange prefer AFM.
- The 90° superexchange prefer FM.

Remember, we are still discussing the “two spin sites model” now.

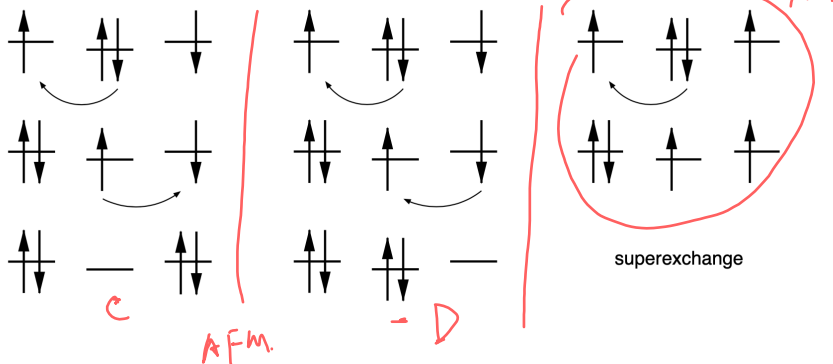


# 180° superexchange ► Hubbard Hamiltonian

The Hamiltonian for 180° superexchange can be written as:

$$\hat{H}_{\text{sup}} = \sum_{\sigma} \left( \varepsilon_d \sum_{i=1,2} \hat{n}_{i\sigma} + \varepsilon_p \hat{n}_{p\sigma} - t_{pd} \sum_{i=1,2} \left( \hat{c}_{i\sigma}^{\dagger} \hat{c}_{p\sigma} + \hat{c}_{p\sigma}^{\dagger} \hat{c}_{i\sigma} \right) \right) + U_d \sum_{i=1,2} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad (26)$$

The figure below will show us how to select the projection basis.



# 180° superexchange ► Spin parallel

For the spin parallel subspace:

$$\hat{H}_{\text{sup}} = \left( \begin{array}{c|cc} 0 & t_{pd} & t_{pd} \\ \hline t_{pd} & U_d + \Delta_{pd} & 0 \\ t_{pd} & 0 & U_d + \Delta_{pd} \end{array} \right) \begin{array}{l} \hat{c}_{2\uparrow}^\dagger \hat{c}_{p\downarrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\uparrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{1\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\downarrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \end{array} \quad (27)$$

Where,  $\Delta_{pd} = \varepsilon_d - \varepsilon_p$ .

Using downfolding technique,

$$\begin{aligned} \hat{H}_{\text{sup}} &= (t_{pd}, t_{pd}) \begin{pmatrix} \varepsilon - (U_d + \Delta_{pd}) & 0 \\ 0 & \varepsilon - (U_d + \Delta_{pd}) \end{pmatrix}^{-1} \begin{pmatrix} t_{pd} \\ t_{pd} \end{pmatrix} \\ &\approx -\frac{2t_{pd}}{U_d} + \Delta_{pd} \end{aligned} \quad (28)$$

# 180° superexchange ► Spin anti-parallel

For the spin anti-parallel subspace:

$$\hat{H}_{\text{sup}} = \begin{pmatrix} \begin{array}{cc|cccc} 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 \\ 0 & 0 & 0 & 0 & +t_{pd} & +t_{pd} \end{array} & \begin{array}{ccc} 0 & 0 & 0 \\ 0 & 0 & 0 \end{array} \\ \hline \begin{array}{cc|cccc} +t_{pd} & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 \\ +t_{pd} & 0 & 0 & U_d + \Delta_{pd} & 0 & 0 \\ 0 & +t_{pd} & 0 & 0 & U_d + \Delta_{pd} & 0 \\ 0 & +t_{pd} & 0 & 0 & 0 & U_d + \Delta_{pd} \end{array} & \begin{array}{ccc} -t_{pd} & 0 & -t_{pd} \\ 0 & -t_{pd} & -t_{pd} \\ +t_{pd} & 0 & +t_{pd} \\ 0 & +t_{pd} & +t_{pd} \end{array} \\ \hline \begin{array}{cc|cccc} 0 & 0 & -t_{pd} & 0 & +t_{pd} & 0 \\ 0 & 0 & 0 & -t_{pd} & 0 & +t_{pd} \\ 0 & 0 & -t_{pd} & -t_{pd} & +t_{pd} & +t_{pd} \end{array} & \begin{array}{ccc} U_d & 0 & 0 \\ 0 & U_d & 0 \\ 0 & 0 & 2(U_d + \Delta_{pd}) \end{array} \end{pmatrix} \begin{matrix} \hat{c}_{2\downarrow}^\dagger \hat{c}_{p\downarrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\uparrow}^\dagger \hat{c}_{p\downarrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{1\downarrow}^\dagger |0\rangle \\ \hat{c}_{2\uparrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{1\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\downarrow}^\dagger \hat{c}_{2\uparrow}^\dagger \hat{c}_{p\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\uparrow}^\dagger \hat{c}_{p\downarrow}^\dagger \hat{c}_{1\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\downarrow}^\dagger \hat{c}_{2\uparrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{1\downarrow}^\dagger |0\rangle \\ \hat{c}_{p\downarrow}^\dagger \hat{c}_{p\uparrow}^\dagger \hat{c}_{1\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\downarrow}^\dagger \hat{c}_{2\uparrow}^\dagger \hat{c}_{p\downarrow}^\dagger \hat{c}_{p\uparrow}^\dagger |0\rangle \\ \hat{c}_{2\downarrow}^\dagger \hat{c}_{2\uparrow}^\dagger \hat{c}_{1\downarrow}^\dagger \hat{c}_{1\uparrow}^\dagger |0\rangle \end{matrix} \quad (29)$$

Using downfolding technique,

$$\begin{aligned} \hat{H}_{\text{sup}} &= \hat{H}_{00} + \hat{T}_{01}(\varepsilon - (\hat{H}_{11} + \hat{T}_{12}(\varepsilon - \hat{H}_{22})^{-1}\hat{T}_{21}))^{-1}\hat{T}_{10} \\ &\approx \hat{H}_{00} - \hat{T}_{01}\hat{H}_{11}^{-1}\hat{T}_{10} - \hat{T}_{01}\hat{H}_{11}^{-1}\hat{T}_{12}\hat{H}_{22}^{-1}\hat{T}_{21}\hat{T}_{10} \\ &= -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{2t_{pd}^4}{(U_d + \Delta_{pd})^2} \left( \frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right) \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad (30) \\ &\stackrel{\text{diag.}}{=} -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \left( \frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right) \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \end{aligned}$$

# 180° superexchange ► Effective Hamiltonian

The spin parallel state Hamiltonian is:

$$\hat{H}_{\text{par}} = -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (31)$$

The spin anti-parallel state Hamiltonian is:

$$\hat{H}_{\text{apar}} = -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \left( \frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right) \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (32)$$

So, the energy difference between spin singlet and triplet state is:

$$E_T - E_S = \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \left( \frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right) \quad (33)$$

Or, we can use the relation between  $\hat{s}_i$  and  $\hat{c}_i$  to get the effective Hamiltonian:

$$\hat{H}_{\text{sup}} = \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \left( \frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right) \hat{s}_1 \cdot \hat{s}_2 \quad (34)$$

*Handwritten notes: -2A > 0, A < 0, Δ<sub>pd</sub> = Δ<sub>d</sub> - ε<sub>p</sub>*

The 180° superexchange prefer AFM.

## Basic step to obtain the effective Hamiltonian

- Write the original Hamiltonian. (Hubbard model)
- Draw all the related spin state.
- Confirm the basis.
- Project the Hamiltonian on the basis.
- Downfolding.
- Use the relation between  $\hat{s}_i$  and  $\hat{c}_i$  to get the effective Hamiltonian

The effective Hamiltonian for 90° superexchange is:  $\underline{p_x} \quad \underline{p_y}$ .

$$\hat{H}_{\text{sup}} = -\frac{4t_4}{(U_d + \Delta_{pd})^2} \frac{2J_{xy}}{4(U_d + \Delta_{pd})^2 - J_{xy}^2} \hat{s}_1 \cdot \hat{s}_2 \quad (35)$$

Where,  $J_{xy}$  is the Coulomb exchange between orbit  $p_x$  and  $p_y$ .  
90° superexchange prefer FM.

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# Heisenberg exchange model for multiple electrons

For spin two sites model, the Heisenberg Hamiltonian is:

$$\hat{H}_{Ad} = -2A \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2$$

*Handwritten notes: Red circles around the 2 and the dot product, and red arrows pointing to the spin vectors.*

When system having more that two sites (still one electron each site), the Heisenberg Hamiltonian is:

$$\hat{H}_A = - \sum_{i \neq j} A_{ij} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j \quad (36)$$

*Handwritten notes: Red circles around the sum and the dot product, and red arrows pointing to the spin vectors. A red 'S' is written above the sum.*

For each pair of sites, the analysis is the same as before.

Further more, the formula is the same, if there are more than one electron on each site, e.g.  $3d^6$ .

$$S = S_1 + S_2 + \dots + S_n \quad 2d \rightarrow J.$$

## Multiple electrons Heisenberg Hamiltonian

$$\hat{H} = - \sum_{i \neq j} A_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j = \left[ \frac{1}{2} \sum_{i \neq j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \right] \quad (37)$$

*Handwritten notes: Red circles around the A\_ij and the dot product, and red arrows pointing to the spin vectors. A red 'S' is written above the sum.*

Where, the  $\hat{\mathbf{S}}_i, \hat{\mathbf{S}}_j$  is determined by the Hund's rule.

# Applications of Heisenberg model

$$\hat{H} = - \sum_{i \neq j} A_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j = \frac{1}{2} \sum_{i \neq j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$

## Application

Using the Hamiltonian above, we can describe:

- Integer magnetic moment below  $T_C$ . (Weiss molecular field)
  - Magnetism in 3d-oxides. (Anderson model, or kinetic exchange)
  - Magnetism in 4f elements or GMR. (RKKY)
- Magnetism near  $T_C$  (Oguchi theory, BPW method).
- Magnetism near 0K, magnon. (Holstein–Primakoff transformation)

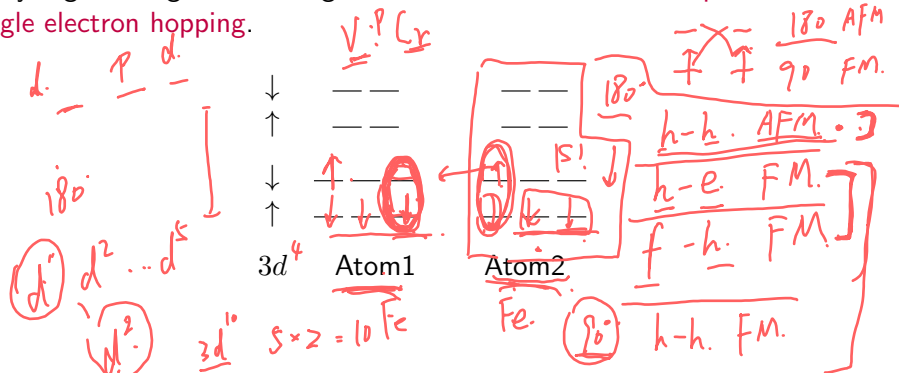
We cannot describe:

- Fractional magnetic moment below  $T_C$ .



# Magnetic analysis of multiple electrons system

When discussing Heisenberg Hamiltonian for multiple electrons, we can (using Hund's rule) **add up all the spin** around the same atom. But when analysing the origin of its magnetic, we still need to use the **picture of single electron hopping**.

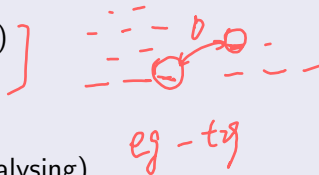


# Magnetic analysis of multiple electrons system

## Basis info.

In order to perform a qualitative analysis about the magnetic of a specific material, we need some basic information:

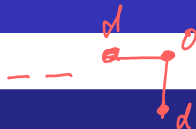
- Crystal field split (symmetry analysing)
- Spin split (band analysing)
- Electrons filling (valence analysing)
- Hopping path (bonding and orbital analysing)
- MAE (not discussed yet...)



-DM  
MOO ?

The Coulomb exchange is usually ignored, if not in a double exchange analysing.

# Goodenough-Kanamori rules



## Goodenough-Kanamori rules

- 1 When two cations have lobes of singly occupied  $3d$ -orbitals which point towards each other giving large overlap and hopping integrals, the exchange is strong and antiferromagnetic ( $J < 0$ ). This is the usual case, for  $120^\circ - 180^\circ$  M-O-M bonds.
- 2 When two cations have a overlap integral between singly occupied  $3d$ -orbitals which is zero by symmetry, the exchange is ferromagnetic and relatively weak. This is the case for  $\sim 90^\circ$  M-O-M bonds.
- 3 When two cations have an overlap between singly occupied  $3d$  orbitals and empty or doubly occupied orbitals of the same type, the exchange is also ferromagnetic, and relatively weak. *FM*

The Goodenough-Kanamori rules are semiempirical rules. It can be derived from the kinetic hopping picture, and works well in practice.

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## Summary

- The magnetic order is related to the spin triplet and singlet state.
- Under the electronic exchange interaction, the 4 degenerated spin state split into 1 spin singlet state and 3 spin triplet state.
- The exchange interaction can be divided into Coulomb exchange and kinetic exchange. The latter is usually more important.
- The Coulomb exchange always prefer FM, while the kinetic exchange depends on the situation.
- Downfolding is an effective technique to carry the energy perturbation.
- Using the hopping picture, we can explain most of the magnetism in insulators.
- Goodenough-Kanamori rules is a handy tool in determine the sign of kinetic exchange.

## Notes

- In DFT calculation, the energy splitting of the up-spin and down-spin can be simulated by DFT+ $U$  or hybrid functional method.
- The orbit magnetization is not counted for it is not appear in the effective Hamiltonian. Only after considering the SOC, will the orbit term show.
- The Heisenberg Hamiltonian is a effective model. Once we find the energy difference between the spin triplet and singlet state (no matter caused by what), we can use the Heisenberg model to describe all of the magnetic properties.

The more general spin Hamiltonian for magnetic.

$$\hat{H}_{\text{mag}} = \underbrace{\frac{1}{2} \sum_{i \neq j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j}_{\text{DM}} + \underbrace{\frac{1}{2} \sum_{i \neq j} D_{ij} \cdot (\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_j)}_{\text{DMI}} + \underbrace{\sum_i A_i \hat{S}_{iz}^2}_{\text{MAE}} + \underbrace{\frac{1}{2} \sum_{i \neq j} K_{ij} (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j)^2}_{\text{4. th La.}} \quad (38)$$