

Review on Theory of Superexchange

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We follow: General Superexchange, anisotropic superexchange (DM interaction) and Ring exchange

1. Philip Anderson's Superexchange Model (Yan Ru Pei) <https://courses.physics.ucsd.edu/2017/Fall/physics211a/specialtopic/1964.pdf>
2. Erik Koch: Exchange Mechanisms <https://www.cond-mat.de/events/correl12/manuscripts/koch.pdf>
3. Assa's book on Quantum Magnetism
4. Yang Li's notes and video lecture https://www.bilibili.com/video/BV1pZ4y1Y7Fn/?spm_id_from=333.337.search-card.all.click&vd_source=571575ba73b53af612005d06ba562437
5. New Approach to the Theory of Superexchange Interactions (Anderson) <https://journals.aps.org/pr/abstract/10.1103/PhysRev.115.2>
6. Anisotropic Superexchange Interaction and Weak Ferromagnetism (Moriya) <https://journals.aps.org/pr/abstract/10.1103/PhysRev.120.91>
7. Large-U limit of a Hubbard model in a magnetic field: Chiral spin interactions and paramagnetism (Diptiman) <https://journals.aps.org/prb/pdf/10.1103/PhysRevB.51.1922>

1 Background

1.1 The Heitler-London Model

Consider the hydrogen molecule

$$\begin{aligned}
 H &= H_{i-i} + H_1 + H_2 + \Delta H \\
 H_1 &= -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{|r_1 - r_a|} \\
 H_2 &= -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{|r_2 - r_b|} \\
 \Delta H &= e^2 \left(\frac{-1}{|r_1 - r_b|} + \frac{-1}{|r_2 - r_a|} + \frac{1}{|r_1 - r_2|} \right) \\
 H_{ion} &= \frac{e^2}{|r_a - r_b|}
 \end{aligned} \tag{1.1}$$

two hydrogen atom Hamiltonian H_1, H_2 have ground states

$$\begin{aligned}
 H_1 |\psi_a\rangle_1 &= E_0 |\psi_a\rangle_1 \\
 H_2 |\psi_b\rangle_2 &= E_0 |\psi_b\rangle_2
 \end{aligned} \tag{1.2}$$

where $|\rangle_{1/2}$ denote the state of electron 1/2, a/b denote electron at ionic ground state a/b . Denote the composite state as

$$\begin{aligned}
 |ab\rangle &\equiv |\psi_a\rangle_1 |\psi_b\rangle_2 \\
 |ba\rangle &\equiv |\psi_b\rangle_1 |\psi_a\rangle_2
 \end{aligned} \tag{1.3}$$

with $|ab\rangle$ denoting electron 1 at site a and 2 at site b . We should also include the spin degrees of freedom. We can write the state of the wavefunction as a tensor product of the spatial part and the spin part

$$|\psi\rangle = |\psi_s\rangle |\chi\rangle \tag{1.4}$$

we now form singlet and triplet states which are symmetric/antisymmetric

$$\begin{aligned}
 |\psi_+\rangle &= |ab\rangle + |ba\rangle \\
 |\psi_-\rangle &= |ab\rangle - |ba\rangle
 \end{aligned} \tag{1.5}$$

where we have hidden the spin part of the wavefunction. This is because electrons are fermions and must have totally antisymmetric wavefunction, so the spin part of the wavefunction should also be symmetric or antisymmetric:

$$\begin{aligned} |\psi_+\rangle &= [|ab\rangle_s + |ba\rangle_s] \left[\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \right] \\ |\psi_-\rangle &= [|ab\rangle_s - |ba\rangle_s] \{a|\uparrow\uparrow\rangle + b|\downarrow\downarrow\rangle + c\frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}\} \end{aligned} \quad (1.6)$$

it is then clear which spin state we should choose, so we can hide it, since the perturbation ΔH is not spin-dependent.

To normalize the equation, let $\langle\psi_a|\psi_a\rangle = \langle\psi_b|\psi_b\rangle = 1$, $\langle\psi_a|\psi_b\rangle \equiv k$. For simplicity we let k be real. Then we have

$$\begin{aligned} \langle ab|ab\rangle &= \langle ba|ba\rangle = 1 \\ \langle ab|ba\rangle &= \langle ba|ab\rangle = k^2 \end{aligned} \quad (1.7)$$

we can then normalize the two wavefunctions

$$\begin{aligned} |\psi_+\rangle &= \frac{1}{\sqrt{2(1+k^2)}}(|ab\rangle + |ba\rangle) \\ |\psi_-\rangle &= \frac{1}{\sqrt{2(1-k^2)}}(|ab\rangle - |ba\rangle) \end{aligned} \quad (1.8)$$

The energy of these two wavefunctions can be written to first order in perturbation theory

$$\begin{aligned} E_{\pm} &= \frac{1}{2 \pm 2k^2} (b|\pm\langle ba|)(H_0 + \Delta H)(|ab\rangle \pm |ba\rangle) \\ &= \frac{\langle ab|(H_0 + \Delta H)|ab\rangle \pm \langle ba|(H_0 + \Delta H)|ab\rangle}{1 \pm k^2} \end{aligned} \quad (1.9)$$

the zeroth order term is degenerate

$$E_0 = \frac{2E_0 \pm 2k^2 E_0}{1 \pm k^2} + \frac{e}{R_{ab}} = 2E_0 + \frac{e}{R_{ab}} \quad (1.10)$$

To calculate the perturbation, denote the two integrals by

$$\begin{aligned} V_c &= \langle ab|\Delta H|ab\rangle \\ V_{ex} &= \langle ba|\Delta H|ab\rangle \end{aligned} \quad (1.11)$$

which are called **Coulomb integral** and **exchange integral**.

$$E_{\pm} = 2E_0 + \frac{e^2}{R_{ab}} + \frac{V_c \pm V_{ex}}{1 \pm k^2} \quad (1.12)$$

If we assume the overlap $k \ll 1$, we can simplify the expression

$$E_{\pm} = 2E_0 + \frac{e^2}{R_{ab}} + V_c \pm V_{ex} \quad (1.13)$$

for $k = 0$, we can prove that $V_{ex} > 0$ by Fourier transforming the perturbative terms (we will not present here). This means that

$$E_- < E_+ \quad (1.14)$$

with a gap $\Delta = 2V_{ex}$.

$$|\psi_-\rangle = [|ab\rangle_s - |ba\rangle_s] \{a|\uparrow\uparrow\rangle + b|\downarrow\downarrow\rangle + c\frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}\} \quad (1.15)$$

is antisymmetric in space and symmetric in spin. Since the interaction favors this state, and two of the spin states are ferromagnetic, we say that the interaction is **ferromagnetic**.

It is important to note that this model does not capture the full interaction between the two electrons. In the following section, we will present another interacting process known as **charge transfer**. The full interaction between the two electrons is described by the addition of the two.

1.2 Dirac's Spin-exchange Model

The Dirac's spin exchange operator can be written as:

$$P_{12} = \frac{1}{2} \left(1 + \sum_{i=1}^3 \sigma_{1i} \cdot \sigma_{2i} \right) \quad (1.16)$$

we can write it in a more suggestive form

$$\begin{aligned} P_{12} &= \frac{1}{2} + 2\mathbf{S}_1 \cdot \mathbf{S}_2 \\ &= \frac{1}{2} + 2 \left(S_1^z \cdot S_2^z + \frac{1}{4} (S_1^+ + S_1^-) (S_2^+ + S_2^-) - \frac{1}{4} (S_1^+ - S_1^-) (S_2^+ - S_2^-) \right) \\ &= \frac{1}{2} + 2S_1^z \cdot S_2^z + S_1^+ S_2^- + S_1^- S_2^+ \end{aligned} \quad (1.17)$$

$$\begin{aligned} S^+ &= S^x + iS^y, & S^- &= S^x - iS^y \\ S^x &= \frac{1}{2} (S^+ + S^-), & S^y &= \frac{1}{2i} (S^+ - S^-) \end{aligned} \quad (1.18)$$

in this way, we can see that P_{12} clearly does the job of exchanging two spins

$$\begin{aligned} P_{12} |\uparrow_1 \uparrow_2\rangle &= |\uparrow_1 \uparrow_2\rangle \\ P_{12} |\uparrow_1 \downarrow_2\rangle &= |\downarrow_1 \uparrow_2\rangle \end{aligned} \quad (1.19)$$

where σ denotes the Pauli matrix. If we denote the singlet spin wavefunction as $|\chi_-\rangle$, and the triplet state as $|\chi_+\rangle$, then it can be shown that:

$$\begin{aligned} P |\chi_+\rangle &= -|\chi_+\rangle \\ P |\chi_-\rangle &= +|\chi_-\rangle \end{aligned} \quad (1.20)$$

we can write the perturbative Hamiltonian as

$$H = V_c - V_{ex} P \quad (1.21)$$

$$\begin{aligned} H |\chi_+\rangle &= (V_c + V_{ex}) |\chi_+\rangle \\ H |\chi_-\rangle &= (V_c - V_{ex}) |\chi_-\rangle \end{aligned} \quad (1.22)$$

1.3 Direct Exchange with Non-zero Overlap

In the case where the overlap of the electron wavefunctions is non-zero, or $\langle \psi_a | \psi_b \rangle \neq 0$. We can rewrite the energies in the following form:

$$E_{\pm} = 2E_0 + \frac{\left(V_c + \frac{e^2}{R} \right) \pm \left(V_{ex} + k^2 \frac{e^2}{R} \right)}{1 \pm k^2} \quad (1.23)$$

The term $V_c + \frac{e^2}{R}$ is always positive, and the term $V_{ex} + k^2 \frac{e^2}{R}$ is generally **negative**. So in this case, we see that the energy is lower for the singlet $|\chi_+\rangle$, so the direct exchange interaction is anti-ferromagnetic in this case.

1.4 Hubbard Model for Charge Transfer

Consider the Hubbard model

$$H = \sum_{(i,j)\sigma} (t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) + U \sum_i (n_{i\uparrow} n_{i\downarrow}) \quad (1.24)$$

we can separate the Hamiltonian into a static component and an interacting problem

$$\begin{aligned} H_0 &= U \sum_i (n_{i\uparrow} n_{i\downarrow}) \\ \Delta H &= \sum_{(i,j)\sigma} (-t c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) \end{aligned} \quad (1.25)$$

consider the case for two electrons and two sites, there are 6 different states. We denote the states as

$$|1\rangle, |2\rangle, |3\rangle, |6\rangle \quad E_0 = 0, \quad \text{single occupancy per site} \quad (1.26)$$

$$|4\rangle, |5\rangle \quad E_0 = U, \quad \text{double occupancy} \quad (1.27)$$

we have, for all states,

$$\langle i | \Delta H | j \rangle = 0 \quad (1.28)$$

since all states are static and thus must hop to a different static state.

In first order perturbation theory, the transition amplitude $\frac{\langle f | \Delta H | i \rangle}{E_f - E_i}$ must accompany a energy difference of U , since it always map between $(1, 2, 3, 6) \leftrightarrow (4, 5)$.

For the two site model, we can solve it exactly, we use Mathematica package SNEG to write the Hamiltonian and turn it into matrix form

$$H = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -t & -t & 0 \\ 0 & 0 & 0 & -t & -t & 0 \\ 0 & -t & -t & U & 0 & 0 \\ 0 & -t & -t & 0 & U & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (1.29)$$

We can then solve for the eigenenergies and eigenstates:

$$\begin{aligned} E_1 = 0 \quad |\Psi_1\rangle &= |\psi_1\rangle \\ E_2 = 0 \quad |\Psi_2\rangle &= |\psi_6\rangle \\ E_3 = 0 \quad |\Psi_3\rangle &= \frac{1}{\sqrt{2}} (|\psi_2\rangle - |\psi_3\rangle) \\ E_4 = U \quad |\Psi_4\rangle &= \frac{1}{\sqrt{2}} (|\psi_4\rangle - |\psi_5\rangle) \\ E_5 = \frac{1}{2} (U - \sqrt{U^2 + 16t^2}) \quad |\Psi_5\rangle &= \frac{U + \sqrt{U^2 + 16t^2}}{4t} (|\psi_2\rangle + |\psi_3\rangle) + (|\psi_4\rangle + |\psi_5\rangle) \\ E_6 = \frac{1}{2} (U + \sqrt{U^2 + 16t^2}) \quad |\Psi_6\rangle &= \frac{U - \sqrt{U^2 + 16t^2}}{4t} (|\psi_2\rangle + |\psi_3\rangle) + (|\psi_4\rangle + |\psi_5\rangle) \end{aligned} \quad (1.30)$$

Note that the last two eigenstates are not normalized.

In the limit $U/t \gg 1$, the last two terms become, to zeroth order in t/U

$$\begin{aligned} E_5 = 0 \quad |\Psi_5\rangle &= \frac{1}{\sqrt{2}} (|\psi_2\rangle + |\psi_3\rangle) \\ E_6 = U \quad |\Psi_6\rangle &= \frac{1}{\sqrt{2}} (|\psi_4\rangle + |\psi_5\rangle) \end{aligned} \quad (1.31)$$

to non-zero lowest order in t/U

$$\begin{aligned} E_5 = U \left[-\frac{1}{4}(4t/U)^2 \right] \quad |\Psi_5\rangle &= \left(\frac{U}{2t} \right) (|\psi_2\rangle + |\psi_3\rangle) + (|\psi_4\rangle + |\psi_5\rangle) \\ E_6 = U \quad |\Psi_6\rangle &= \left(-\frac{2t}{U} \right) (|\psi_2\rangle + |\psi_3\rangle) + (|\psi_4\rangle + |\psi_5\rangle) \end{aligned} \quad (1.32)$$

In the limit $U/t \ll 1$, the last two terms become

$$\begin{aligned} E_5 = 2t \quad |\Psi_5\rangle &= \frac{1}{2} (|\psi_2\rangle + |\psi_3\rangle + |\psi_4\rangle + |\psi_5\rangle) \\ E_6 = 2t \quad |\Psi_6\rangle &= \frac{1}{2} (-|\psi_2\rangle - |\psi_3\rangle + |\psi_4\rangle + |\psi_5\rangle) \end{aligned} \quad (1.33)$$

In this case, the last two eigenstates are equal mixtures of the “apart” states and the “together” states.

Spin exchange interaction from Hubbard model To derive the effective interaction between the spins, we need to use second order perturbation theory. Since the two subspace in H_0 are degenerate, we will use quasi-degenerate perturbation theory: for a Hamiltonian that is separated into two parts,

$$H = H^0 + H' \quad (1.34)$$

to second order, the interactions are

$$\begin{aligned} H_{mm'}^{(0)} &= H_{mm'}^0 \\ H_{mm'}^{(1)} &= H'_{mm'} \\ H_{mm'}^{(2)} &= \frac{1}{2} \sum_l H'_{ml} H'_{lm'} \left[\frac{1}{E_m - E_l} + \frac{1}{E_{m'} - E_l} \right] \\ H_{mm'}^{(3)} &= -\frac{1}{2} \sum_{l,m''} \left[\frac{H'_{ml} H'_{lm''} H'_{m''m'}}{(E_{m'} - E_l)(E_{m''} - E_l)} + \frac{H'_{mm''} H'_{m''l} H'_{lm'}}{(E_m - E_l)(E_{m''} - E_l)} \right] \\ &\quad + \frac{1}{2} \sum_{l,l'} H'_{ml} H'_{ll'} H'_{l'm'} \left[\frac{1}{(E_m - E_l)(E_m - E_{l'})} + \frac{1}{(E_{m'} - E_l)(E_{m'} - E_{l'})} \right] \end{aligned} \quad (1.35)$$

where the indices m, m', m'' correspond to states in subspace A , the indices l, l', l'' correspond to states in subspace B , and

In our case, the subspace is $\text{span}\{|1\rangle, |2\rangle, |3\rangle, |6\rangle\}$, and we have

$$H^{(0)} = H^{(1)} = 0 \quad (1.36)$$

$$H_{mm'}^{(2)} = -\frac{1}{U} \sum_l \Delta H_{ml} \Delta H_{lm'} \quad (1.37)$$

we obtain

$$H_{eff} = -\frac{2t^2}{U} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (1.38)$$

where $J \equiv -\frac{2t^2}{U} < 0$. We can show that

$$H_{eff} = J(1 - P_{12}) \quad (1.39)$$

compare this with the last section where we had $V_{ex} > 0$ and got a ferromagnetic interaction. This time, J is negative so we have an antiferromagnetic interaction. If we ignore the constant term without P , we can combine the two interactions:

$$H_{total} = -(J + V_{ex})P \quad (1.40)$$

this gives us both ferromagnetic and anti-ferromagnetic terms. There are two things to note here. In the case where the overlap of the two orbitals is zero, the magnitude of the charge transfer interaction J is also zero. This is proven in the later sections. In other words, charge transfer only occurs we have a non-zero overlap of orbitals.

Another thing to note is the J is not negative in general. In this section, all we have shown is that J is negative for the particular model of hydrogen molecule. If we apply the Hubbard model to calculate J for any molecule, the result of J will depend on the valence shells of the atoms involved. The calculation is not always easy. However, as we will see later, there is a shortcut to determining the sign of J , known as the **Hund's rules**.

2 Anderson's approach

At this point, we have discussed the physics behind the **direct exchange** and **electron transfer processes**. Now, we are ready to tackle the physics of superexchange. Superexchange is defined as the interaction between two cations through an intermediate anion. For example, in the simplest case of the $\text{Mn} - \text{O} - \text{Mn}$ structure, superexchange is the interaction between the two Mn^{2+} cations through the O^{2-} anions. This interaction is really just a combination of the direct exchange and electron transfer processes.

In fact, Philip Anderson has formalized the concept of superexchange in his two attempts in 1950 and 1959, and we will be taking a look at the two different approaches he has taken. But before we do so, let's first discuss some preliminary concepts to make our subsequent discussions easier.

2.1 Two States with Weak Coupling

If we consider two states with energies E_1 and E_2 , and the transition energy between much less than the energy difference of the two states $t \ll \Delta E = E_2 - E_1$, then we can write the Hamiltonian as:

$$H = \begin{bmatrix} E_1 & t \\ t & E_2 \end{bmatrix} \quad (2.1)$$

with eigenvalues and eigenstates

$$E_{\pm} = \frac{1}{2} \left(E_1 + E_2 \pm \sqrt{\Delta E^2 + 4t^2} \right) \quad \psi_{\pm} = \begin{bmatrix} E_1 - E_2 \pm \sqrt{\Delta E^2 + 4t^2} \\ 2t \end{bmatrix} \quad (2.2)$$

using the condition $t \ll \Delta E$,

$$\begin{aligned} E_+ &= E_2 + \frac{t^2}{\Delta E}, & \psi_+ &= \begin{bmatrix} t/\Delta E \\ 1 \end{bmatrix}, & \psi_- &= \begin{bmatrix} 1 \\ -t/\Delta E \end{bmatrix} \\ E_- &= E_1 - \frac{t^2}{\Delta E} \end{aligned} \quad (2.3)$$

so we see that the ground state wavefunction is essentially the ground state of the non-interacting Hamiltonian plus a small mixture of the excited state.

2.2 Wavefunction overlap

We say that a wavefunction is symmetric (under **parity exchange**) if $\psi(\mathbf{r}) = \psi(-\mathbf{r})$, and we say that a wavefunction is anti-symmetric if $\psi(\mathbf{r}) = -\psi(-\mathbf{r})$. Assume now that we have two wavefunctions, one is symmetric and the other is anti-symmetric. We can denote $\psi_a(\mathbf{r})$ as the symmetric wavefunction and $\psi_b(\mathbf{r})$ as the anti-symmetric wavefunction. Then it is not hard to prove that the wavefunction overlap is zero, since

$$\langle \psi_b | \psi_a \rangle = \langle \psi_b | P^{-1} P | \psi_a \rangle = -\langle \psi_b | \psi_a \rangle \quad (2.4)$$

In short, the overlap of a symmetric and anti-symmetric wavefunction must be zero. The inverse of this statement is not true, meaning that a zero overlap doesn't necessary mean that one of the wavefunction is symmetric and the other is anti-symmetric. However, for the purpose of our discussion in this paper, we can assume that the inverse statement is true for now. (This is because we are mainly dealing with orbital wavefunctions, and they are either symmetric or anti-symmetric).

Now, let's discuss the process of electron transfer. This is a one particle process, and we can calculate the amplitude of this transfer process to be $\langle \psi_b(r) | U(r) | \psi_a(r) \rangle$, where $U(r)$ is the electron-ion interaction potential, which is a scalar and therefore symmetric under parity exchange. Now, if we assume that ψ_a is symmetric, and ψ_b is anti-symmetric, then it is easy to see that

$$\langle \psi_b | U | \psi_a \rangle = \langle \psi_b | P^{-1} P U P^{-1} P | \psi_a \rangle = -\langle \psi_b | U | \psi_a \rangle \quad (2.5)$$

so it must be zero. Therefore, in a general sense, we see that the process of electron transfer cannot occur if the wavefunction overlap is zero.

This is not the case for direct exchange. The process of direct exchange can occur even if the wavefunction overlap is zero. This is because the direct exchange process involves two particles instead of just one. Let's say initially, electron 1 is at site a , and electron 2 is at site b , and after the exchange, electron 1 is at site b , and electron 2 is at site a , then the amplitude of this exchange process is $\langle \psi_a(2) \psi_b(1) | U(1, 2) | \psi_a(1) \psi_b(2) \rangle$. Again, we are making the assumption that ψ_a is symmetric, ψ_b is antisymmetric, and U is symmetric. The amplitude

$$\langle \psi_a(2) \psi_b(1) | P^{-1} P U(1, 2) P^{-1} P | \psi_a(1) \psi_b(2) \rangle = \langle \psi_a(2) \psi_b(1) | U(1, 2) | \psi_a(1) \psi_b(2) \rangle \quad (2.6)$$

does not acquire a minus sign, since the sign of the two electrons cancel each other to make a symmetric term. So we see that direct exchange can occur even if the wavefunction overlap is zero.

2.3 Anderson's First Attempt

We will only be going over briefly Anderson's first attempt at describing the super-exchange process, since his first approach gives a complicated **third-order perturbative process** and the math is poorly convergent. For the discussion, we will consider the structure $\text{Mn}^{2+} - \text{O}^{2-} - \text{Mn}^{2+}$ as a simple example, suppose they are aligned in the same line. The three ions are bonded by σ bonds so their wavefunction overlaps are non-zero. We label the sites from left to right as A, B, C .

Let's assume that the one of the electron at B site transfers to the C site. Note that the charge transfer interaction is anti-ferromagnetic, so only a down-spin electron can transfer to the C site where the electron is up-spin. Due to Pauli's Exclusion Principle, the remaining un-coupled electron at the B site must have up-spin, so it can only couple to the up-spin electron at A-site through direct exchange, which is a ferromagnetic interaction. Therefore, the net effect is that the electron at site C couples to the electron at site A through a combination of direct exchange and electron transfer, with site B being an intermediate site.

This intuitive picture is useful in visualizing the superexchange process, but it doesn't describe the full picture. To study this more carefully, we will have to treat this quantum mechanically, and write down the full fermionic wavefunction of the electrons involved in the interacting process. This leads us to Anderson's revised approach in describing the superexchange process.

2.4 Anderson's Second Attempt

Let's first begin by carefully studying the d-p σ -bond. Note that the d orbital has a much higher energy than the p orbital, meaning that the transition amplitude is much smaller than the energy difference between the two orbitals. And from the previous sections, we know that we can express the ground state wavefunction as the p orbital wavefunction plus a small mixture of the d orbital wavefunction:

$$\psi_{\text{bond}} = \psi_p + \lambda\psi_d \quad (2.7)$$

where $\lambda \ll 1$. Now, if we assume that the overlap between the two orbitals is $\langle \psi_d | \psi_p \rangle = k$, then we can write the **anti-bonding** wavefunction as:

$$\psi_{\text{anti}} = \psi_d - (\lambda + k)\psi_p \quad (2.8)$$

We can check that the two wavefunctions are in fact orthogonal:

$$\langle \psi_{\text{anti}} | \psi_{\text{bond}} \rangle \approx 0 \quad (2.9)$$

where we have made the assumption that $\lambda \ll 1$ and $k \ll 1$. And as usual, the bonding energy is lower than the anti-bonding energy.

Now, let's return to the study of $\text{Mn}^{2+} - \text{O}^{2-} - \text{Mn}^{2+}$ structure, and extract a three electron wavefunction from it. The three electrons we are interested in is the d electron at the C site and the two p electrons at the B site. Note that in the wavefunction, we also have to consider the electron transfer process, where one electron from the p orbital at B site transfer to the d orbital at C site.

We can write the three-electron wavefunction as a Slater determinant. First, we consider the wavefunction before the electron transfer:

$$\begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ p_{\downarrow}(1) & p_{\downarrow}(2) & p_{\downarrow}(3) \end{vmatrix} \quad (2.10)$$

Note that the d electron has up-spin, and the two p electrons have opposite spins. Now, we write the wavefunction after the electron transfer:

$$\begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ d_{\downarrow}(1) & d_{\downarrow}(2) & d_{\downarrow}(3) \end{vmatrix} \quad (2.11)$$

Recall that we can write the ground state wavefunction as the wavefunction before the transfer plus a small mixture of the wavefunction after the transfer. In other words, we can express the ground state wavefunction as:

$$\begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ p_{\downarrow}(1) & p_{\downarrow}(2) & p_{\downarrow}(3) \end{vmatrix} + \lambda \begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ d_{\downarrow}(1) & d_{\downarrow}(2) & d_{\downarrow}(3) \end{vmatrix} = \begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ p_{\downarrow}(1) + \lambda d_{\downarrow}(1) & p_{\downarrow}(2) + \lambda d_{\downarrow}(2) & p_{\downarrow}(3) + \lambda d_{\downarrow}(3) \end{vmatrix} \quad (2.12)$$

Note that $p_{\uparrow} + \lambda p_{\uparrow} = (1 + \lambda)p_{\uparrow} = p_{\uparrow}$, and $d_{\uparrow} + \lambda d_{\uparrow} = (1 + \lambda)d_{\uparrow} = d_{\uparrow}$. We can rewrite the above equation in the following form

$$\begin{vmatrix} d_{\uparrow}(1) - \gamma p_{\uparrow}(1) & d_{\uparrow}(2) - \gamma p_{\uparrow}(2) & d_{\uparrow}(3) - \gamma p_{\uparrow}(3) \\ p_{\uparrow}(1) + \lambda d_{\uparrow}(1) & p_{\uparrow}(2) + \lambda d_{\uparrow}(2) & p_{\uparrow}(3) + \lambda d_{\uparrow}(3) \\ p_{\downarrow}(1) + \lambda d_{\downarrow}(1) & p_{\downarrow}(2) + \lambda d_{\downarrow}(2) & p_{\downarrow}(3) + \lambda d_{\downarrow}(3) \end{vmatrix} \quad (2.13)$$

with $\lambda = \gamma - k$. The algebra is a bit complicated.

The important thing to note is that $d - \gamma p$ is an anti-bonding state, and $p + \lambda d$ is a bonding state. And from the Slater determinant, we see that two electrons are in the bonding state, and one electron is in the anti-bonding state. The two electrons in the bonding states have opposite spin, so they cancel each other out. Therefore, only the anti-bonding state contributes to the spin of the system, and it extends over the anion (site B). This spin then interacts with the electron at site A, with the energy of the spin coupling governed by the same type of total spin interaction

$$H_{total} = -(J + V_{ex})P \quad (2.14)$$

and this effectively completes our picture of the superexchange interaction between site A and site C, with site B being the intermediate.

2.5 GKA Rules

The GKA rules are a series of semi-empirical rules developed by Goodenough and Kanamori as a refinement to the original model developed by Anderson. The rules are based on the following facts

1. When two orbitals overlap, both direct exchange and charge transfer can occur.
2. When two orbitals have zero overlap, only direct exchange can occur.
3. The greater the wavefunction overlap, the greater the interaction strength.

For example, let's consider bonding between two p orbitals. Let's define the separation of the two atoms to be in the z axis, then:

1. The $p_z - p_z$ bond is a σ bond, meaning that there is a **significant wavefunction overlap**, giving us a strong anti-ferromagnetic interaction.
2. The $p_x - p_x$ and $p_y - p_y$ bonds are π bonds, meaning that there is a smaller wavefunction overlap, giving us an anti-ferromagnetic interaction, though not as strong as that of the σ bond.
3. The $p_x - p_y, p_y - p_z$, and $p_z - p_x$ bonds are not "bonds" in a chemical sense, since they have zero wavefunction overlap. However, they do exhibit weak ferromagnetic interaction through the direct exchange process.

This discussion can easily be generalized to d-p bonds. For example:

1. The $d_{\gamma} - p_{\sigma}$ bond is analogous to σ bonds, meaning that it is strongly anti-ferromagnetic.
2. The $d_{\epsilon} - p_{\pi}$ bond is analogous to π bonds, meaning that it is anti-ferromagnetic, though not as strong as the first case.
3. The $d_{\gamma} - p_{\pi}$ and $d_{\epsilon} - p_{\sigma}$ are not bonds. They have zero wavefunction overlap and are weakly ferromagnetic.

An important thing to note is that although the GKA rules are very general, they are only semi-empirical, meaning that they are not guaranteed to work for all molecular bonds, though the cases where they do not work are very rare.

Applying the GKA Rules In this section, we will use the GKA rules to predict the superexchange interaction of various structures. In doing so, we will evoke **Hund's rule**. Hund's rule, in its simplest form, states that "**every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin**". In other words, if an electron shell is less than half-filled, and it receives another electron, then the received electron will have the same spin as the total spin of the original shell. And if the electron shell is half-filled or more than half-filled, then the received electron will have a spin opposite to the original shell. Using the GKA and Hund's rules, we are ready to look at some superexchange examples:

1. The $\text{Ni}^{2+} - 2p - \text{Ni}^{2+}$ structure. This is in the form of $d_\gamma - p_\sigma - d_\gamma$, meaning that the two bonds are both σ bonds. Furthermore, the valence shells of the Ni^{2+} cations are both more than half filled. For simplicity sake, we still assume the three atoms to be ABC. Let's assume that A and B is bonded by electron transfer. If we assume that site A has spin up, then according to Hund's rule, it must receive a spin down electron from site B. And if site B donates a spin down electron, then it is left with a spin up electron. And since site B and site C has wavefunction overlap, then according to the GKA rules, the interaction between them is anti-ferromagnetic, meaning that site C will have down spin as a result of coupling with the spin up electron of site B. So in the end, we see that the net effect of site A having spin up is to force site C having spin down, so the superexchange interaction is **anti-ferromagnetic**.
2. Now let's look at $\text{V}^{2+} - 2p - \text{Ni}^{2+}$, again in the form $d_\gamma - p_\sigma - d_\gamma$. The difference is that V^{2+} is less than half-filled. In this case, if site A is spin up, then it will also receive a spin up electron from site B. The remaining electron in site B will then have spin down, and it will interact with site C antiferromagnetically, forcing site C to have spin up. So the superexchange interaction is **ferromagnetic** in this case.
3. Let's look at $\text{Ni}^{2+} - 2p - \text{Ni}^{2+}$ again. But this time, the two bonds form a 90 degree angle instead of 180 degree. Even though site A and site B will still have the same wavefunction overlap, the difference now is that site B and site C will have zero wavefunction overlap. The reason is that after "bending" the bonds, site B and site C will form a π bond instead of a σ bond. If site A has spin up, it will still receive a spin down electron from site B, leaving a spin up electron behind. However, this time, the spin up electron will couple with site C ferromagnetically (since they have zero overlap), resulting in a spin up state for site C. So the superexchange interaction is **ferromagnetic**.
4. Again, let's look at $\text{V}^{2+} - 2p - \text{Ni}^{2+}$, this time in the 90 degree form. Following a similar argument, we see that the superexchange interaction is antiferromagnetic.

In summary, we see how the superexchange interaction can be predicted by knowing the **types of bonds** formed, the **degree of the bonds**, and the **electron occupancy** of the shells.

3 Exchange from Downfolding

3.1 DownFolding

We first introduce a method called downfolding, it is somewhat equivalent to degenerate-perturbation theory. Given an eigensystem problem, our goal is to integrate-out high-energy degrees of freedom. We partition the Hilbert space of the full system into states of interest (low-energy states) and 'other' states, which will be integrated out. The Hamiltonian is then written in blocks

$$H = \begin{pmatrix} H_{00} & T_{01} \\ T_{10} & H_{11} \end{pmatrix} \quad (3.1)$$

Our goal is to solve the determinant equation

$$0 = \det(\epsilon I - H) = \det \begin{pmatrix} \epsilon I - H_{00} & -T_{01} \\ -T_{10} & \epsilon I - H_{11} \end{pmatrix} \quad (3.2)$$

We use a formula for the determinant of block matrix, there are two equivalent expressions

$$\begin{aligned} \det \begin{pmatrix} A & B \\ C & D \end{pmatrix} &= \det(A) \det(D - CA^{-1}B) \\ &= \det(A - BD^{-1}C) \det(D) \end{aligned} \quad (3.3)$$

Our goal is to find when the determinant is zero for A. However, notice that

$$Av = \lambda v, \quad A^{-1}v = \lambda^{-1}v \quad (3.4)$$

so when $\det(A) = 0$, $\det(D - CA^{-1}B) = \infty$ and the equation is indeterminant. So we choose the second equation. For our specific case,

$$0 = \det \begin{pmatrix} \epsilon I - H_{00} & -T_{01} \\ -T_{10} & \epsilon I - H_{11} \end{pmatrix} = \det \left(\epsilon I - H_{00} - T_{01} (\epsilon I - H_{11})^{-1} T_{10} \right) \det(\epsilon I - H_{11}) \quad (3.5)$$

Suppose the eigenvalues of H_{00} are in interval I_{00} , that of H_{11} are in I_{11} , I_{00} and I_{11} are well-separated. Also, T_{01}, T_{10} are not very large so the eigenvalues are not change by much, we can then restrict $\epsilon \in I_{00}$, which means we can be sure $\det(\epsilon I - H_{11}) \neq 0$. The problem is thus reduced to

$$0 = \det \left(\epsilon I - H_{00} - T_{01} (\epsilon I - H_{11})^{-1} T_{10} \right) \quad (3.6)$$

This is equivalent to solving an eigenvalue problem

$$H_{eff}(\epsilon) = H_{00} + T_{01} (\epsilon I - H_{11})^{-1} T_{10} \quad (3.7)$$

where ϵ is a parameter to be put into the Hamiltonian, so we have a self-consistent problem. The initial values are easily found by diagonalizing H_{00} first. This identification of determinant, however, only guarantees that the eigenvalues of H_{eff} should match that of H , but does not guarantee that eigenvectors should match also. To do so we will use the resolvent:

$$G(\epsilon) = (\epsilon I - H)^{-1} = \begin{pmatrix} \epsilon I - H_{00} & T_{01} \\ T_{10} & \epsilon I - H_{11} \end{pmatrix}^{-1} \quad (3.8)$$

using the formula for inverse of block matrices

$$\begin{aligned} \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{bmatrix}^{-1} &= \begin{bmatrix} (\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C})^{-1} & -(\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C})^{-1}\mathbf{B}\mathbf{D}^{-1} \\ -\mathbf{D}^{-1}\mathbf{C}(\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C})^{-1} & \mathbf{D}^{-1} + \mathbf{D}^{-1}\mathbf{C}(\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C})^{-1}\mathbf{B}\mathbf{D}^{-1} \end{bmatrix} \\ &\begin{pmatrix} \epsilon I - H_{00} & T_{01} \\ T_{10} & \epsilon I - H_{11} \end{pmatrix}^{-1} \\ &= \begin{bmatrix} G_{00}(\epsilon) & -G_{00}(\epsilon)T_{01}(\epsilon I - H_{11})^{-1} \\ -(\epsilon I - H_{11})^{-1}T_{10}G_{00}(\epsilon) & (\epsilon I - H_{11})^{-1} + (\epsilon I - H_{11})^{-1}T_{10}G_{00}(\epsilon)T_{01}(\epsilon I - H_{11})^{-1} \end{bmatrix} \end{aligned} \quad (3.9)$$

where

$$G_{00}(\epsilon) = \left(\epsilon - [H_{00} + T_{01} (\epsilon I - H_{11})^{-1} T_{10}] \right)^{-1} \quad (3.11)$$

Now the eigenvalue problem $(\epsilon I - H)v = 0$ is mapped to the problem

$$G(\epsilon)v = \begin{pmatrix} G_{00}(\epsilon) & G_{10}(\epsilon) \\ G_{01}(\epsilon) & G_{11}(\epsilon) \end{pmatrix} \begin{pmatrix} v_0 \\ v_1 \end{pmatrix} = \begin{pmatrix} G_{00}v_0 + G_{10}v_1 \\ G_{01}v_1 + G_{11}v_1 \end{pmatrix} = \infty \quad (3.12)$$

focusing on the first row, we want to find $\epsilon \in I_{00}$ such that $0 = G_{00}v_0 + G_{10}v_1$

$$\infty = G_{00}(\epsilon) \left[v_0 - T_{01} (\epsilon I - H_{11})^{-1} v_1 \right] \quad (3.13)$$

clearly, $\epsilon I - H_{11}$ do not have zeros for $\epsilon \in I_{00}$, and all other quantities are finite. Therefore, this is solved only when $G_{00}(\epsilon)$ has a subspace where $G_{00}(\epsilon)v_{eff} = \infty$, where

$$v_{eff} = v_0 - T_{01} (\epsilon I - H_{11})^{-1} v_1 \quad (3.14)$$

notice that v_{eff} is not simply the H_{00} subspace components v_0 , but we must fold the components v_1 outside the subspace into the H_{00} subspace, according to the transition rates back to the low energy subspace of H_{00} , using first order perturbation theory

$$\begin{aligned} H_{eff} &= H_{00} + T_{01} (\epsilon I - H_{11})^{-1} T_{10} \\ &\approx H_{00} + T_{01} (\epsilon_0 I - H_{11})^{-1} T_{10} \end{aligned} \quad (3.15)$$

This effective Hamiltonian describes the physics of the full system, but operates only on the small reduced Hilbert space. Of course, this drastic simplification comes at a price: the effective Hamiltonian is energy dependent. If the hopping matrix elements in T_{01} are small, and/or if the states in the part of the Hilbert space that has been integrated out are energetically well-separated from the states that are explicitly considered, this energy dependence can, to a good approximation, be neglected. We can then replace ϵ by a typical energy ϵ_0 for the states in the reduced Hilbert space to obtain an energy-independent Hamiltonian $H_{eff}(\epsilon_0)$ that gives a good description of the electrons in the reduced Hilbert space, i.e., the states with an energy close to ϵ_0 .

3.2 Direct exchange

Using the technique of downfolding, the effective Hamiltonian for direct exchange between two spins can be easily found. Using basis

$$|\uparrow, \uparrow\rangle, |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |\downarrow, \downarrow\rangle, |\uparrow\downarrow, \emptyset\rangle, |\emptyset, \uparrow\downarrow\rangle \quad (3.16)$$

the full Hamiltonian with Hubbard interaction

$$H = \sum_{(i,j)\sigma} (t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) + U \sum_i (n_{i\uparrow} n_{i\downarrow}) \quad (3.17)$$

is written as

$$H = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -t & -t \\ 0 & 0 & 0 & 0 & t & t \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -t & t & 0 & U & 0 \\ 0 & -t & t & 0 & 0 & U \end{pmatrix} \quad (3.18)$$

with

$$H_{00} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad T_{01} = \begin{pmatrix} 0 & 0 \\ t & t \\ -t & -t \\ 0 & 0 \end{pmatrix}, \quad T_{10} = \begin{pmatrix} 0 & t & -t & 0 \\ 0 & t & -t & 0 \end{pmatrix}, \quad H_{11} = \begin{pmatrix} U & 0 \\ 0 & U \end{pmatrix} \quad (3.19)$$

The effective Hamiltonian

$$H_{eff}(\epsilon) = H_{00} + T_{01} (\epsilon I - H_{11})^{-1} T_{10} \quad (3.20)$$

$$H_{eff}(\epsilon) = -\frac{2t^2}{U - \epsilon} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (3.21)$$

since H_{00} has eigenvalues 0, we can set the initial value $\epsilon = 0$ and recover the same results we obtained before.

In AFM subspace only An even simpler method could be obtained by noticing that the Hubbard interaction H_U conserves the total spin, so the subspace of FM states such as $|\uparrow, \uparrow\rangle$ and that of $|\uparrow, \downarrow\rangle$ can be separately diagonalized. Notice that for FM states, Hubbard interaction is always zero, so

$$\varepsilon_t = 0, \quad |\uparrow, \uparrow\rangle, |\downarrow, \downarrow\rangle \quad (3.22)$$

on the other hands, for states

$$|\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |\uparrow\downarrow, \emptyset\rangle, |\emptyset, \uparrow\downarrow\rangle \quad (3.23)$$

$$H = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & t & t \\ -t & t & U & 0 \\ -t & t & 0 & U \end{pmatrix} \quad (3.24)$$

$$H_{00} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}, \quad T_{01} = \begin{pmatrix} -t & -t \\ t & t \end{pmatrix}, \quad T_{10} = \begin{pmatrix} -t & t \\ -t & t \end{pmatrix}, \quad H_{11} = \begin{pmatrix} U & 0 \\ 0 & U \end{pmatrix} \quad (3.25)$$

$$H_{eff} = \begin{pmatrix} -t & -t \\ t & t \end{pmatrix} \begin{pmatrix} \epsilon - U & 0 \\ 0 & \epsilon - U \end{pmatrix} \begin{pmatrix} -t & t \\ -t & t \end{pmatrix} = \begin{pmatrix} \frac{2t^2}{U - \epsilon} & -\frac{2t^2}{U - \epsilon} \\ -\frac{2t^2}{U - \epsilon} & \frac{2t^2}{U - \epsilon} \end{pmatrix} \quad (3.26)$$

$$\begin{aligned} \varepsilon_1 &= \frac{4t^2}{U}, & |\psi\rangle &= \frac{|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle}{\sqrt{2}} \\ \varepsilon_2 &= 0, & |\psi\rangle &= \frac{|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle}{\sqrt{2}} \end{aligned} \quad (3.27)$$

the singlet splitting is

$$J = \frac{4t^2}{U} \quad (3.28)$$

which is the exchange energy.

This corresponds to the exchange interaction

$$\begin{aligned} J\mathbf{S}_1 \cdot \mathbf{S}_2 &= \frac{J}{2} [(\mathbf{S}_1 + \mathbf{S}_2)^2 - S_1^2 - S_2^2] \\ &= J \left(\frac{1}{2} S_{tot}^2 - \frac{3}{4} \right) \end{aligned} \quad (3.29)$$

with eigenstates

$$\begin{aligned} \varepsilon &= \frac{J}{4}, \quad |\psi\rangle = |\uparrow, \uparrow\rangle, |\downarrow, \downarrow\rangle, \frac{|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle}{\sqrt{2}} \\ \varepsilon &= -\frac{3J}{4}, \quad |\psi\rangle = \frac{|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle}{\sqrt{2}} \end{aligned} \quad (3.30)$$

3.3 Superexchange

For the direct exchange mechanism discussed above, it is crucial that there is hopping between the orbitals. These orbitals are typically localized d -orbitals of transition-metals. However, direct exchange cannot explain the antiferromagnetism of most transition-metal compounds: Since the d -orbitals are so localized, hopping can only occur between orbitals on different atoms that are very close to each other. But most antiferromagnetic insulators are **transition-metal oxides**, so that the transition-metal cations are separated by large oxygen anions. In such a situation, direct hopping between the d -orbitals is very unlikely. The concept of direct exchange can, however, be extended to these cases by taking into account hopping via the intermediate p -orbital. This mechanism is called **superexchange**.

To understand superexchange, we consider two d -orbitals with an oxygen p -orbital in between. We introduce the operator $c_{i\sigma}^\dagger$, which creates a spin- σ electron in the d -orbital at site i , where $i = 1$ denotes the d -orbital on the left and $i = 2$ the one on the right. Likewise $c_{p\sigma}^\dagger$ creates an electron in the p -orbital. The energy of an electron in a d -or p -orbital is ε_d and ε_p , respectively. The Coulomb repulsion between two electrons in a d -orbital is U_d , while we neglect the repulsion between electrons in the p -orbital. Finally, $-t_{pd}$ is the hopping between p and d orbitals. The Hamiltonian for the system is then given by

$$H = \sum_{\sigma} \left(\varepsilon_d \sum_i n_{i\sigma} + \varepsilon_p n_{p\sigma} - t_{pd} \sum_i (c_{i\sigma}^\dagger c_{p\sigma} + c_{p\sigma}^\dagger c_{i\sigma}) \right) + U_d \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3.31)$$

In the absence of hopping, the ground state will have singly occupied d -orbitals, corresponding to a positively charged transition-metal ion, and a doubly occupied p -orbital, corresponding to an O^{2-} ion. To study a possible coupling between the spins on the d -orbitals, we first look at the case where both d -spins point upwards. The Hamiltonian matrix in the corresponding Hilbert space is then given by

$$H = \left(\begin{array}{c|cc} 0 & t_{pd} & t_{pd} \\ \hline t_{pd} & U_d + \Delta_{pd} & 0 \\ t_{pd} & 0 & U_d + \Delta_{pd} \end{array} \right) \begin{array}{l} c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ c_{2\uparrow}^\dagger c_{p\uparrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\uparrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \end{array} \quad (3.32)$$

where we have chosen $2(\varepsilon_p + \varepsilon_d)$ as the zero of our energy scale and defined $\Delta_{pd} = \varepsilon_d - \varepsilon_p$. The basis states of the Hilbert space are given on the right and the lines indicate the partitioning of the Hilbert space for downfolding. The effective Hamiltonian for parallel spins on d -orbitals is then

$$H_{\text{eff}} = (t_{pd}, t_{pd}) \begin{pmatrix} \varepsilon - (U_d + \Delta_{pd}) & 0 \\ 0 & \varepsilon - (U_d + \Delta_{pd}) \end{pmatrix} \begin{pmatrix} t_{pd} \\ t_{pd} \end{pmatrix} \approx -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \quad (3.33)$$

where in the last step we have set $\varepsilon = 0$.

For antiparallel spins the Hilbert space is nine-dimensional. We sort the basis states into groups that are connected by the hopping of one electron. Starting from the two states with singly occupied d -orbitals, the second group has one of the p -electrons transferred to a d -orbital, leading to one doubly occupied d , while the last group has a second electron hopped, leading to either an empty p - or an empty d -orbital. The corresponding Hamiltonian

matrix is

$$\left(\begin{array}{cc|cc|cc|cc} 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 \\ \hline +t_{pd} & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & -t_{pd} & 0 & -t_{pd} \\ +t_{pd} & 0 & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & -t_{pd} & -t_{pd} \\ 0 & +t_{pd} & 0 & 0 & U_d + \Delta_{pd} & 0 & +t_{pd} & 0 & +t_{pd} \\ 0 & +t_{pd} & 0 & 0 & 0 & U_d + \Delta_{pd} & 0 & +t_{pd} & +t_{pd} \\ \hline 0 & 0 & -t_{pd} & 0 & +t_{pd} & 0 & U_d & 0 & 0 \\ 0 & 0 & 0 & -t_{pd} & 0 & +t_{pd} & 0 & U_d & 0 \\ 0 & 0 & -t_{pd} & -t_{pd} & +t_{pd} & +t_{pd} & 0 & 0 & 2(U_d + \Delta_{pd}) \end{array} \right) \quad (3.34)$$

$$\begin{aligned} & c_{2\downarrow}^\dagger c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ & c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger c_{1\downarrow}^\dagger |0\rangle \\ & c_{2\downarrow}^\dagger c_{p\uparrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ & c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ & c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ & c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\uparrow}^\dagger c_{1\downarrow}^\dagger |0\rangle \\ & c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \\ & c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger |0\rangle \\ & c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \end{aligned} \quad (3.35)$$

Downfolding the high energy states with at least one doubly occupied d -orbital, setting $\varepsilon = 0$ and expanding in $1/U_d$ (remembering $(A + \Delta)^{-1} \approx A^{-1} (1 - \Delta A^{-1})$), which is equivalent to second-order perturbation theory, leads to

$$\begin{aligned} H_{\text{eff}} &= H_{00} + T_{01} \left(\varepsilon - \left(H_{11} + T_{12} (\varepsilon - H_{22})^{-1} T_{21} \right) \right)^{-1} T_{10} \\ &\approx H_{00} - T_{01} H_{11}^{-1} T_{10} - T_{01} H_{11}^{-1} T_{12} H_{22}^{-1} T_{21} H_{11}^{-1} T_{10} \\ &= -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{2t_{pd}^4}{(U_d + \Delta_{pd})^2} \left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right) \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \end{aligned} \quad (3.36)$$

The first term is the same as for parallel spins. The additional term is of the same type as that found for the direct exchange mechanism. Again, it can be written in terms of spin operators. In the present case they are the spin operators for the d -orbitals, while the p -orbital does no longer appear in the spin Hamiltonian. The spin coupling is now given by

$$J = \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right) \quad (3.37)$$

which reflects that the superexchange mechanism involves four hopping processes, while direct exchange only involves two hoppings. The hopping process involving only a single doubly occupied d -orbital is a generalization of the simple direct exchange with an effective hopping $t_{\text{eff}} = t_{pd}^2 / (U_d + \Delta_{pd})$ between the d -orbitals and gives the first term, $4t_{\text{eff}}^2 / U_d$, while the hopping process involving two occupied d -orbitals gives the second term $4t_{pd}^4 / (U_d + \Delta_{pd})^3$.

3.4 Ferromagnetic superexchange

In the discussion of superexchange we have, so far, assumed that the oxygen ion lies between the two d -orbitals. The situation is quite different, when the oxygen forms a 90° bridge between the two d -orbitals. By symmetry, there is only hopping between the d - and the p -orbital that point towards each other (see, e.g., the discussion of the Slater-Koster integrals in the lecture of E. Pavarini). As there is also no hopping between the p -orbitals on the same site, the Hamiltonian for the system separates into two parts, one involving only the d orbital on site 1 and the p_x orbital and the other only involving d on site 2 and p_y , e.g.:

$$H_1 = \begin{pmatrix} 0 & +t_{pd} \\ +t_{pd} & U_d + \Delta_{pd} \end{pmatrix} \begin{pmatrix} c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{1\downarrow}^\dagger |0\rangle \\ c_{x\downarrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle \end{pmatrix} \quad (3.38)$$

Since it is not possible for an electron on site 1 to reach site 2, none of the superexchange processes discussed above are operational. Nevertheless, the energy for the system depends on the relative orientation of the electron spins in the two d -orbitals. To see this, we have to remember that Coulomb exchange prefers a triplet for two electrons in different orbitals on the same site (Hund's first rule). Including J_{xy} on the oxygen (but neglecting U_p for simplicity), we get, for the triplet state with two up-electrons, the Hamiltonian

$$\left(\begin{array}{c|cc|c} 0 & t_{pd} & t_{pd} & 0 \\ \hline t_{pd} & U_d + \Delta_{pd} & 0 & t_{pd} \\ t_{pd} & 0 & U_d + \Delta_{pd} & t_{pd} \\ \hline 0 & t_{pd} & t_{pd} & 2(U_d + \Delta_{pd}) - J_{xy} \end{array} \right) \begin{array}{l} c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\uparrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger c_{2\downarrow}^\dagger |0\rangle \end{array} \quad (3.39)$$

The first state has the two up-electrons on the d -orbitals. The second group of states has one d -orbital doubly occupied, while the last state has both d doubly occupied, i.e., two electrons on the two p -orbitals. Calculating the effective Hamiltonian gives the energy of the triplet state

$$H_{\text{eff}} = -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} - \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{1}{2(U_d + \Delta_{pd}) - J_{xy}} \quad (3.40)$$

Starting from singly occupied d -orbitals with opposite spin, we obtain

$$\left(\begin{array}{cc|cc|cc|cc} 0 & 0 & t_{pd} & 0 & t_{pd} & 0 & 0 & 0 \\ 0 & 0 & 0 & t_{pd} & 0 & t_{pd} & 0 & 0 \\ \hline t_{pd} & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & t_{pd} & 0 \\ 0 & t_{pd} & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & t_{pd} \\ \hline t_{pd} & 0 & 0 & 0 & U_d + \Delta_{pd} & 0 & t_{pd} & 0 \\ 0 & t_{pd} & 0 & 0 & 0 & U_d + \Delta_{pd} & 0 & t_{pd} \\ \hline 0 & 0 & t_{pd} & 0 & t_{pd} & 0 & 2(U_d + \Delta_{pd}) & -J_{xy} \\ 0 & 0 & 0 & t_{pd} & 0 & t_{pd} & -J_{xy} & 2(U_d + \Delta_{pd}) \end{array} \right) \quad (3.41)$$

$$P_{12} = \frac{1}{2} + 2\mathbf{S}_1 \cdot \mathbf{S}_2 \quad (3.42)$$

$$\begin{array}{l} 1c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger |0\rangle \\ 2c_{1\downarrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ 3c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger |0\rangle \\ 4c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{y\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ 5c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ 6c_{1\downarrow}^\dagger c_{x\downarrow}^\dagger c_{x\uparrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ 7c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\uparrow}^\dagger c_{y\downarrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \\ 8c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger c_{x\downarrow}^\dagger c_{y\uparrow}^\dagger c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle \end{array} \quad (3.43)$$

giving the effective Hamiltonian

$$H_{\text{eff}} = -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{1}{4(U_d + \Delta_{pd})^2 - J_{xy}^2} \begin{pmatrix} 2(U_d + \Delta_{pd}) + J_{xy} & \\ & 2(U_d + \Delta_{pd}) \end{pmatrix} \quad (3.44)$$

Rearranging the matrices, we can bring this to the canonical form

$$\begin{aligned} H_{\text{eff}} = & -\left(\frac{2t_{pd}^2}{U_d + \Delta_{pd}} + \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{1}{2(U_d + \Delta_{pd}) - J_{xy}} \right) \\ & + \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{J_{xy}}{4(U_d + \Delta_{pd})^2 - J_{xy}^2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \end{aligned} \quad (3.45)$$

The first term is just the energy of the triplet state. The second gives the difference in energy to the singlet. Despite the fact that the electrons cannot be transferred between the d orbitals we thus get a singlet-triplet splitting. This coupling of the spins originates from the states with both d -orbitals doubly occupied: the two remaining electrons, one each on the p_x - and p_y -orbital, respectively, form a triplet of energy $2J_{xy}$ lower than that of the singlet. When the electrons hop back from the d -orbital, the entanglement of the spins is transferred to the remaining electron on the d . Originating from the Coulomb exchange on the oxygen, the exchange coupling is ferromagnetic

$$J = -\frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{2J_{xy}}{4(U_d + \Delta_{pd})^2 - J_{xy}^2} \quad (3.46)$$

It tends to be significantly weaker than the antiferromagnetic 180° superexchange coupling. When the angle of the M-O-M group is larger than 90° , hopping to both p -orbitals becomes possible according to the Slater-Koster rules and the antiferromagnetic superexchange processes start to compete with the ferromagnetic superexchange mediated by the Coulomb exchange on the oxygen. This is one basis of the Goodenough-Kanamori rules.

3.5 t - J Hamiltonian

In this section we will derive the $t - J$ Hamiltonian from Hubbard model. The zeroth-order Hamiltonian is

$$\mathcal{U} = U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3.47)$$

The eigenstates of \mathcal{U} are Fock states in the Wannier representation. \mathcal{U} divides the Fock space into two subspaces:

$$\begin{aligned} S &= [|n_{1\uparrow}, n_{1\downarrow}, n_{2\uparrow} \dots\rangle] & : \forall i, n_{i\uparrow} + n_{i\downarrow} \leq 1 \\ D &= [|n_{1\uparrow}, n_{1\downarrow}, n_{2\uparrow} \dots\rangle] & : \exists i, n_{i\uparrow} + n_{i\downarrow} = 2 \end{aligned} \quad (3.48)$$

D contains at least one doubly occupied site, and S are all configurations with either one or zero electrons per site.

The hopping term

$$\mathcal{T} = - \sum_{ijs} t_{ij} c_{is}^\dagger c_{js} \quad (3.49)$$

is considered as a perturbation. \mathcal{T} couples S to D by hopping an electron into, or out of, a doubly occupied site. \mathcal{U} is diagonal and \mathcal{T} lifts the enormous degeneracy in the two subspaces. \mathcal{H} is partitioned as

$$\mathcal{H} = \begin{pmatrix} P_s \mathcal{T} P_s & P_s \mathcal{T} P_d \\ P_d \mathcal{T} P_s & P_d (\mathcal{T} + \mathcal{U}) P_d \end{pmatrix} \quad (3.50)$$

where $P_{s,d}$ are projection operators onto the subspaces S and D , respectively.

The resolvent operator is

$$\mathcal{G}(E) = (E - \mathcal{H})^{-1} \quad (3.51)$$

The following matrix identity is useful:

$$\left[\begin{pmatrix} A & B \\ C & D \end{pmatrix}^{-1} \right]_{ss} = (A - BD^{-1}C)^{-1} \quad (3.52)$$

where \llbracket_{ss} denotes singly occupied subspace in the upper left quadrant. The projection of \mathcal{G} into the subspace S is as

$$P_s \mathcal{G}(E) P_s = P_s [E - \mathcal{H}]^{-1} P_s = [E - \mathcal{H}^{eff}(E)]^{-1} \quad (3.53)$$

Using the block matrix inverse formula and that $P_s \mathcal{U} = \mathcal{U} P_s = 0$, the effective Hamiltonian is given explicitly by

$$\mathcal{H}^{eff} = P_s \mathcal{T} P_s + P_s \mathcal{T} P_d \{P_d [E - (\mathcal{U} + \mathcal{T})] P_d\}^{-1} P_d \mathcal{T} P_s \quad (3.54)$$

The eigenenergies of \mathcal{H} (which correspond to states with nonzero weights in S) are given by the zeros of the characteristic polynomial

$$\det |E_n - \mathcal{H}^{eff}(E_n)| = 0 \quad (3.55)$$

Note that E_n are not eigenvalues of \mathcal{H}^{eff} , since \mathcal{H}^{eff} depends parametrically on E . If we ignore (for the moment) problems arising from a large number of sites, it is possible to expand $P_d(E - \mathcal{H})^{-1}P_d$, to zeroth order in E/U and to second order in t/U

$$[E - (\mathcal{U} + \mathcal{T})]^{-1} \approx -U^{-1} + \mathcal{O}(E/U) + \mathcal{O}(t/U) \quad (3.56)$$

$$\mathcal{H}^{\text{eff}} \approx P_s \left[\mathcal{T} - \frac{1}{U} \mathcal{T} P_d \mathcal{T} \right] P_s \quad (3.57)$$

to calculate $P_s \mathcal{T} P_d \mathcal{T} P_s$, suppose site k hops to site j and results in double occupancy, site j then hops to site i which recovers the single occupancy. This is then

$$P_s \mathcal{T} P_d \mathcal{T} P_s = \sum_{ijkss'} t_{ij} t_{jk} c_{is}^\dagger c_{js} n_{j\uparrow} n_{j\downarrow} c_{js'}^\dagger c_{ks'} \quad (3.58)$$

where $n_{j\uparrow} n_{j\downarrow}$ in the middle comes from P_d and ensures that we hop to a doubly degenerate site. Therefore, we can write the effective Hamiltonian as

$$\mathcal{H}^{t-J} = P_s \left[\mathcal{T} - \frac{1}{U} \sum_{ijkss'} t_{ij} t_{jk} c_{is}^\dagger c_{js} n_{j\uparrow} n_{j\downarrow} c_{js'}^\dagger c_{ks'} \right] P_s \quad (3.59)$$

\mathcal{H}^{t-J} is commonly called the **t-J model**.

When we are at half-filling, $n_i = 1$, we have $P_s \mathcal{T} P_s = 0$ and $k = i$, let $t_{ij} = t_{ji}$, we can also drop the $n_{j\uparrow} n_{j\downarrow}$ factor, since it is ensured to be 1. We therefore have

$$\begin{aligned} \mathcal{H}^{\text{eff}} &= -P_s \left[\sum_{ijss'} \frac{t_{ij}^2}{U} c_{is}^\dagger c_{js} c_{js'}^\dagger c_{is'} \right] P_s \\ &= -P_s \left[\sum_{ij} \frac{t_{ij}^2}{U} \sum_{ss'} c_{is}^\dagger c_{js} c_{js'}^\dagger c_{is'} \right] P_s \\ &= -P_s \left[\sum_{ij} \frac{t_{ij}^2}{U} \sum_{ss'} c_{is}^\dagger c_{is'} \left(\delta_{ss'} - c_{js'}^\dagger c_{js} \right) \right] P_s \\ &= -P_s \left[\sum_{ij} \frac{t_{ij}^2}{U} \left(n_i - \sum_{ss'} c_{is}^\dagger c_{is'} c_{js'}^\dagger c_{js} \right) \right] P_s \\ &= P_s \left[\sum_{ij} \frac{t_{ij}^2}{U} \sum_{ss'} c_{is}^\dagger c_{is'} c_{js'}^\dagger c_{js} \right] P_s + \text{const} \end{aligned} \quad (3.60)$$

Check that

$$\begin{aligned} H^{QHM} &= \frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \\ &= \frac{1}{8} \sum_{ij} J_{ij} \sum_{ss'} \sum_{ff'} c_{is}^\dagger c_{is'} c_{jf}^\dagger c_{jf'} \vec{\sigma}_{ss'} \cdot \vec{\sigma}_{ff'} \\ &= \frac{1}{8} \sum_{ij} J_{ij} \sum_{ss'} \sum_{ff'} c_{is}^\dagger c_{is'} c_{jf}^\dagger c_{jf'} (2\delta_{sf} \delta_{s'f'} - \delta_{ss'} \delta_{ff'}) \\ &= \frac{1}{2} \sum_{ij} J_{ij} \left(\frac{1}{2} \sum_{ss'} c_{is}^\dagger c_{is'} c_{js'}^\dagger c_{js} - \frac{n_i n_j}{4} \right) \\ &= \sum_{ij} \frac{J_{ij}}{4} \sum_{ss'} c_{is}^\dagger c_{is'} c_{js'}^\dagger c_{js} + \text{const} \end{aligned} \quad (3.61)$$

where $\mathbf{S}_i \equiv \frac{1}{2} \sum_{ss'} c_{is}^\dagger \vec{\sigma}_{ss'} c_{is}$. Comparing this to \mathcal{H}^{eff} , we identify

$$J_{ij} = \frac{4t_{ij}^2}{U} \quad (3.62)$$

4 DM-interaction

4.1 Preparation for the derivation

We will use the Wannier basis

$$\{\omega_{n\uparrow}(\mathbf{r} - \mathbf{R}), \omega_{n\downarrow}(\mathbf{r} - \mathbf{R})\} \quad (4.1)$$

$\hat{\alpha}_{n\uparrow}(\mathbf{R})$ and $\hat{\alpha}_{n\downarrow}^\dagger(\mathbf{R})$ are the annihilation and the creation operators of the electrons in the state $\omega_{n\uparrow}(\mathbf{r} - \mathbf{R})$, etc. The Hamiltonian of the system of electrons, considering SOC can be written as

$$H_1 = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) + H_{SOC} \quad (4.2)$$

where $V(\mathbf{r})$ include the peridic potential

$$H_{SOC} = \frac{\hbar}{2m^2c^2} \mathbf{S} \cdot [\nabla V(\mathbf{r}) \times \mathbf{p}] \quad (4.3)$$

where the H_{SOC} is derived from Dirac equation. For a many-body system

$$H = \sum_i \left[\frac{\hat{\mathbf{p}}_i^2}{2m} + V(\mathbf{r}_i) + \frac{\hbar}{2m^2c^2} \mathbf{S}_i \cdot [\nabla V(\mathbf{r}_i) \times \mathbf{p}_i] \right] \quad (4.4)$$

this is still a one-body interaction, as we have not included the electron-electron Coulomb interaction. Supposing $V(\mathbf{r}) = V(r)$, we can write SOC explicitly as L and S operators

$$\begin{aligned} H_{SOC} &= \frac{\hbar}{2m^2c^2} \mathbf{S} \cdot \left[\frac{dV(r)}{dr} \frac{\mathbf{r}}{r} \times \mathbf{p} \right] \\ &= \lambda \mathbf{L} \cdot \mathbf{S} \\ &= \lambda \left(\hat{L}_z \hat{S}_z + \frac{1}{2} (\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+) \right) \end{aligned} \quad (4.5)$$

where we assumed $\frac{1}{r} \frac{dV(r)}{dr}$ is slow-varying. We now expand the Hamiltonian in the Wannier basis:

$$\langle \omega_{n\sigma}(\mathbf{R}) | H | \omega_{n'\sigma'}(\mathbf{R}') \rangle \quad (4.6)$$

and write the second-quantized form

$$\begin{aligned} \hat{H} &= \hat{H}_0^{\text{all}} + \hat{T}^{\text{all}} \\ &= \sum_{\mathbf{R}} \sum_n \epsilon_n(\mathbf{R}) \left[\hat{\alpha}_{n\uparrow}^\dagger(\mathbf{R}) \hat{\alpha}_{n\uparrow}(\mathbf{R}) + \hat{\alpha}_{n\downarrow}^\dagger(\mathbf{R}) \hat{\alpha}_{n\downarrow}(\mathbf{R}) \right] \\ &+ \sum_{\mathbf{R} \neq \mathbf{R}'} \sum_{n, n'} \left\{ b_{n'n}(\mathbf{R}' - \mathbf{R}) \left[\hat{\alpha}_{n'\uparrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\uparrow}(\mathbf{R}) + \hat{\alpha}_{n'\downarrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\downarrow}(\mathbf{R}) \right] \right. \\ &+ C_{n'n}^z(\mathbf{R}' - \mathbf{R}) \left[\hat{\alpha}_{n'\uparrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\uparrow}(\mathbf{R}) - \hat{\alpha}_{n'\downarrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\downarrow}(\mathbf{R}) \right] \\ &+ C_{n'n}^-(\mathbf{R}' - \mathbf{R}) \hat{\alpha}_{n'\uparrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\downarrow}(\mathbf{R}) \\ &\left. + C_{n'n}^+(\mathbf{R}' - \mathbf{R}) \hat{\alpha}_{n'\downarrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\uparrow}(\mathbf{R}) \right\} \end{aligned} \quad (4.7)$$

where we have defined

$$\begin{aligned} b_{n'n}(\mathbf{R}' - \mathbf{R}) + C_{n'n}^z(\mathbf{R}' - \mathbf{R}) &= \int \omega_{n'\uparrow}^*(\mathbf{r} - \mathbf{R}') H_1 \omega_{n\uparrow}(\mathbf{r} - \mathbf{R}) d\mathbf{r} \\ b_{n'n}(\mathbf{R}' - \mathbf{R}) - C_{n'n}^z(\mathbf{R}' - \mathbf{R}) &= \int \omega_{n'\downarrow}^*(\mathbf{r} - \mathbf{R}') H_1 \omega_{n\downarrow}(\mathbf{r} - \mathbf{R}) d\mathbf{r} \\ C_{n'n}^x(\mathbf{R}' - \mathbf{R}) - iC_{n'n}^y(\mathbf{R}' - \mathbf{R}) &= C_{n'n}^-(\mathbf{R}' - \mathbf{R}) = \int \omega_{n'\uparrow}^*(\mathbf{r} - \mathbf{R}') H_1 \omega_{n\downarrow}(\mathbf{r} - \mathbf{R}) d\mathbf{r} \\ C_{n'n}^x(\mathbf{R}' - \mathbf{R}) + iC_{n'n}^y(\mathbf{R}' - \mathbf{R}) &= C_{n'n}^+(\mathbf{R}' - \mathbf{R}) = \int \omega_{n'\downarrow}^*(\mathbf{r} - \mathbf{R}') H_1 \omega_{n\uparrow}(\mathbf{r} - \mathbf{R}) d\mathbf{r} \end{aligned} \quad (4.8)$$

notice that even without SOC, $b_{n'n}(\mathbf{R}' - \mathbf{R})$ and $C_{n'n}^z(\mathbf{R}' - \mathbf{R})$ should exist and are actually equal, as they involve hopping of spin σ electrons to another site. On the other hand, $C_{n'n}^{+/-}(\mathbf{R}' - \mathbf{R})$ involve an electron hopping to another site and flipping its spin at the same time. This is only possible with spin orbit coupling, where the orbital angular momentum can compensate for the change in spin angular momentum, such that the total angular momentum is conserved.

We will choose the **ground-state-subspace** as states where there are the same number of occupancy at each site $\langle n_i \rangle = \langle n_j \rangle, \forall i, j$. This is specified differently from a one-band Hubbard model, as we now must consider many-bands, as is required by SOC. SOC involve the orbital operator, which clearly maps between different orbitals, say for example $|l=1, m=0\rangle$ and $|l=1, m=1\rangle$. The first excited subspace will be made by transferring one electron from some site i to site j , which comes with a Hubbard energy cost U , whatever orbital are involved between the two sites. According to this division of subspaces, we can write the full Hamiltonian in the form

$$\mathcal{H} = \begin{pmatrix} P_s H_0 P_s & P_s \mathcal{T} P_d \\ P_d \mathcal{T}^\dagger P_s & P_d \mathcal{U} P_d \end{pmatrix} \quad (4.9)$$

where P_s and P_d are projection operators into the ground state subspace and first excited subspace, respectively. We will assume $\mathcal{T} \ll \mathcal{U}$. We will then perform a downfolding technique.

$$\mathcal{H}^{eff}(E) = P_s H_0 P_s + P_s \mathcal{T}^\dagger P_d \{P_d [E - U] P_d\}^{-1} P_d \mathcal{T} P_s \quad (4.10)$$

we choose E in the low energy subspace, which satisfy $E \ll U$, therefore to zeroth order in E/U , we have

$$\mathcal{H}^{eff} \approx P_s H_0 P_s + H_M \quad (4.11)$$

$$H_M \equiv -\frac{P_s \mathcal{T}^\dagger P_d \mathcal{T} P_s}{U} \quad (4.12)$$

where the hopping interaction is

$$\begin{aligned} \mathcal{T} = & \sum_{\mathbf{R} \neq \mathbf{R}'} \sum_{n, n'} b_{n'n}(\mathbf{R}' - \mathbf{R}) \left[\hat{\alpha}_{n'\uparrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\uparrow}(\mathbf{R}) + \hat{\alpha}_{n'\downarrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\downarrow}(\mathbf{R}) \right] \\ & + C_{n'n}^z(\mathbf{R}' - \mathbf{R}) \left[\hat{\alpha}_{n'\uparrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\uparrow}(\mathbf{R}) - \hat{\alpha}_{n'\downarrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\downarrow}(\mathbf{R}) \right] \\ & + C_{n'n}^-(\mathbf{R}' - \mathbf{R}) \hat{\alpha}_{n'\uparrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\downarrow}(\mathbf{R}) \\ & + C_{n'n}^+(\mathbf{R}' - \mathbf{R}) \hat{\alpha}_{n'\downarrow}^\dagger(\mathbf{R}') \hat{\alpha}_{n\uparrow}(\mathbf{R}) + \text{h.c.} \end{aligned} \quad (4.13)$$

it then remains to compute H_M .

4.2 Downfolding the hopping interaction

We will first use a single index $i \equiv (\mathbf{R}_i, n_i)$,

$$\begin{aligned} \mathcal{T} = & \sum_{i,j} b_{ij} \left[\alpha_{i\uparrow}^\dagger \alpha_{j\uparrow} + \alpha_{i\downarrow}^\dagger \alpha_{j\downarrow} \right] + C_{ij}^z \left[\alpha_{i\uparrow}^\dagger \alpha_{j\uparrow} - \alpha_{i\downarrow}^\dagger \alpha_{j\downarrow} \right] \\ & + C_{ij}^- \alpha_{i\uparrow}^\dagger \alpha_{j\downarrow} + C_{ij}^+ \alpha_{i\downarrow}^\dagger \alpha_{j\uparrow} + \text{h.c.} \end{aligned} \quad (4.14)$$

where $\sum'_{i,j}$ has a prime, which means $\mathbf{R}_i \neq \mathbf{R}_j$. We can write

$$\begin{aligned} \mathcal{T} &= \sum_{i,j} \left(T_{ij} + T_{ij}^\dagger \right) \\ T_{ij} &= M_{ij,ab} \alpha_{ia}^\dagger \alpha_{jb} \end{aligned} \quad (4.15)$$

we have that $T_{ij}^\dagger = T_{ji}(\text{coef}^*)$ where all coefficients are complex conjugated. Dropping index i, j for now, we have

$$M \equiv \begin{pmatrix} b + C_z & C_+ \\ C_- & b - C_z \end{pmatrix} = \begin{pmatrix} b + C_z & C_x - iC_y \\ C_x + iC_y & b - C_z \end{pmatrix} = c_\mu \sigma^\mu \equiv c \cdot \sigma \quad (4.16)$$

where $c_{ij,\mu} = (b_{ij}, \mathbf{C}_{ij})$, $\sigma^\mu = (I, \boldsymbol{\sigma})$. Notice that $M^\dagger = c_\mu^* \sigma^\mu$. Now consider the term

$$P_s \mathcal{T}^\dagger P_d \mathcal{T} P_s = \sum_{i,j} \sum_{k,l} P_s T_{ij}^\dagger P_d T_{kl} P_s \quad (4.17)$$

if electron at l hops to k , then the only way to go back to ground state subspace is for an electron at k to hop back to l (these two electrons need not be the same, since in the intermediate state k site will have two electrons). Therefore, we have only one summation

$$P_s \mathcal{T}^\dagger P_d \mathcal{T} P_s = \sum_{i,j} \left(T_{ij} + T_{ij}^\dagger \right) \left(T_{ij} + T_{ij}^\dagger \right) = \sum_{i,j} \left(T_{ij}^\dagger T_{ij} + T_{ij} T_{ij}^\dagger \right) \quad (4.18)$$

where the $(\cdot)_{ji}$ means replacing all the quantities with ji indices. We have $T_{ij} T_{ij}^\dagger = (T_{ij}^\dagger T_{ij}) (i \leftrightarrow j, c_\mu \rightarrow c_\mu^*)$. So we only need to evaluate $T^\dagger T$ for some index pair i, j that we now choose to be 1, 2. From now on let $M = M_{ij}$, we can write

$$\begin{aligned} T^\dagger T &= \left(M_{ab}^* \alpha_{2b}^\dagger \alpha_{1a} \right) \left(M_{cd} \alpha_{1c}^\dagger \alpha_{2d} \right) \\ &= M_{ab}^* M_{cd} \alpha_{2b}^\dagger \alpha_{2d} \left(\delta_{ac} - \alpha_{1c}^\dagger \alpha_{1a} \right) \\ &= M_{ab}^* M_{cd} \alpha_{2b}^\dagger \alpha_{2d} \delta_{ac} - M_{ab}^* M_{cd} \alpha_{1c}^\dagger \alpha_{1a} \alpha_{2b}^\dagger \alpha_{2d} \\ &\equiv h_{1a} + h_{M2} \end{aligned} \quad (4.19)$$

we will not focus on the single-spin operator h_{1a} , now

$$h_{M2} = -M_{ab}^* M_{cd} \alpha_{1c}^\dagger \alpha_{1a} \alpha_{2b}^\dagger \alpha_{2d} \quad (4.20)$$

we now define matrix of quadratic operators

$$\alpha_{ab} \equiv \begin{pmatrix} \alpha_{\uparrow}^\dagger \alpha_{\uparrow} & \alpha_{\uparrow}^\dagger \alpha_{\downarrow} \\ \alpha_{\downarrow}^\dagger \alpha_{\uparrow} & \alpha_{\downarrow}^\dagger \alpha_{\downarrow} \end{pmatrix}_{ab} = \begin{pmatrix} \frac{1}{2}n + S^z & S^x + iS^y \\ S^x - iS^y & \frac{1}{2}n - S^z \end{pmatrix}_{ab} = \left(\frac{1}{2}n + \boldsymbol{\sigma} \cdot \mathbf{S} \right)_{ab} \equiv S_\mu \sigma_{ab}^\mu = \mathbf{S} \cdot \boldsymbol{\sigma}_{ab} \quad (4.21)$$

where $S^\mu = (n/2, \mathbf{S})$ and we used the relations

$$\begin{aligned} \mathbf{S} &= \frac{1}{2} \vec{\alpha}^\dagger \boldsymbol{\sigma} \vec{\alpha} = \frac{1}{2} \begin{pmatrix} \alpha_{\uparrow}^\dagger \alpha_{\downarrow} + \alpha_{\downarrow}^\dagger \alpha_{\uparrow} \\ -i(\alpha_{\uparrow}^\dagger \alpha_{\downarrow} - \alpha_{\downarrow}^\dagger \alpha_{\uparrow}) \\ \alpha_{\uparrow}^\dagger \alpha_{\uparrow} - \alpha_{\downarrow}^\dagger \alpha_{\downarrow} \end{pmatrix} \\ \frac{1}{2}n &= \frac{1}{2} \vec{\alpha}^\dagger \vec{\alpha} = \frac{1}{2} (\alpha_{\uparrow}^\dagger \alpha_{\uparrow} + \alpha_{\downarrow}^\dagger \alpha_{\downarrow}) \end{aligned} \quad (4.22)$$

notice also that $(S_\mu \sigma_{ab}^\mu) = (S_\mu \sigma_{ab}^\mu)^*$ since it is purely real. We can now write h_{M2} in terms of Pauli matrices only

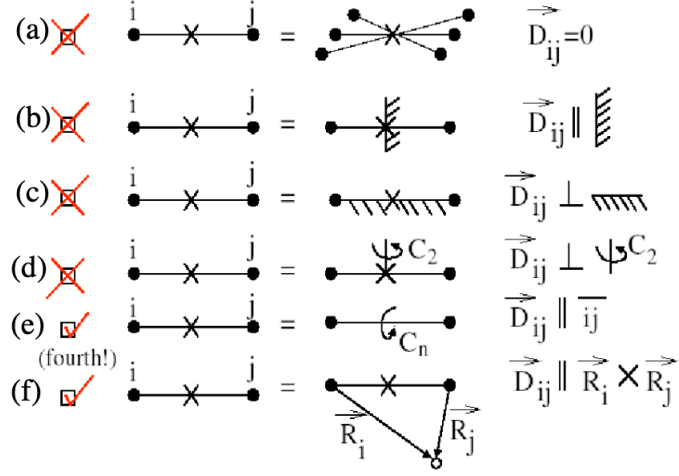
$$\begin{aligned} h_{M2} &= -M_{ab}^* M_{cd} \alpha_{1c}^\dagger \alpha_{1a} \alpha_{2b}^\dagger \alpha_{2d} \\ &= -(c^* \cdot \sigma_{ba}) (c \cdot \sigma_{cd}) (S_1 \cdot \sigma_{ca}) (S_2 \cdot \sigma_{bd}) \\ &= -(c \cdot \sigma_{ab}) (c^* \cdot \sigma_{dc}) (S_1 \cdot \sigma_{ca}) (S_2 \cdot \sigma_{bd}) \\ &= -(c^* \cdot \sigma_{dc}) (S_1 \cdot \sigma_{ca}) (c \cdot \sigma_{ab}) (S_2 \cdot \sigma_{bd}) \\ &= -c^{*\alpha} S_1^\beta c^\gamma S_2^\mu \text{Tr} [\sigma_\alpha \sigma_\beta \sigma_\gamma \sigma_\mu] \end{aligned} \quad (4.23)$$

We can use trace technology

$$\text{Tr} (\sigma_\alpha \sigma_\beta \sigma_\gamma \sigma_\mu) = 2 (\delta_{\alpha\beta} \delta_{\gamma\mu} - \delta_{\alpha\gamma} \delta_{\beta\mu} + \delta_{\alpha\mu} \delta_{\beta\gamma}) + 4 (\delta_{\alpha\gamma} \delta_{0\beta} \delta_{0\mu} + \delta_{\beta\mu} \delta_{0\alpha} \delta_{0\gamma}) - 8 \delta_{0\alpha} \delta_{0\beta} \delta_{0\gamma} \delta_{0\mu} + 2i \sum_{(\alpha\beta\gamma\mu)} \varepsilon_{0\alpha\beta\gamma} \delta_{0\mu} \quad (4.24)$$

substituting this, we have

Figure 4.1: Moriya's Rule



Reference: <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.79.014421>

$$\begin{aligned}
 h_{M2} = & -2 \left((c \cdot S_1) (c^* \cdot S_2) + (c^* \cdot S_1) (c \cdot S_2) - c^2 (S_1 \cdot S_2) \right) \\
 & - 4 \left(c^2 S_1^0 S_2^0 + |c^0|^2 (S_1 \cdot S_2) \right) + 8 |c^0|^2 S_1^0 S_2^0 \\
 & - 2i \left(\sum_{(\alpha\beta\gamma\mu)} \varepsilon_{0\alpha\beta\gamma} \delta_{0\mu} \right) c^\alpha S_1^\beta c^{*\gamma} S_2^\mu
 \end{aligned} \tag{4.25}$$

If we keep all the terms second order in \mathbf{S} ,

$$\begin{aligned}
 h_{M2} = & -2 \left((\mathbf{C} \cdot \mathbf{S}_1) (\mathbf{C}^* \cdot \mathbf{S}_2) + (\mathbf{C}^* \cdot \mathbf{S}_1) (\mathbf{C} \cdot \mathbf{S}_2) - c^2 (\mathbf{S}_1 \cdot \mathbf{S}_2) \right) \\
 & - 4 |c^0|^2 (\mathbf{S}_1 \cdot \mathbf{S}_2) - 2i (\varepsilon_{0\beta\gamma\mu} \delta_{0\alpha} + \varepsilon_{0\mu\alpha\beta} \delta_{0\gamma}) c^\alpha S_1^\beta c^{*\gamma} S_2^\mu \\
 & - 2i (\varepsilon_{0\beta\gamma\mu} \delta_{0\alpha} + \varepsilon_{0\mu\alpha\beta} \delta_{0\gamma}) c^\alpha \mathbf{S}_1^\beta c^{*\gamma} \mathbf{S}_2^\mu \\
 = & -2 |c^0|^2 (\mathbf{S}_1 \cdot \mathbf{S}_2) - 2i (-c^0 \mathbf{C}^* + c^{*0} \mathbf{C}) \cdot (\mathbf{S}_1 \times \mathbf{S}_2) \\
 & - 2 \left((\mathbf{C} \cdot \mathbf{S}_1) (\mathbf{C}^* \cdot \mathbf{S}_2) + (\mathbf{C}^* \cdot \mathbf{S}_1) (\mathbf{C} \cdot \mathbf{S}_2) - \mathbf{C}^2 (\mathbf{S}_1 \cdot \mathbf{S}_2) \right) \\
 = & -2 |b|^2 (\mathbf{S}_1 \cdot \mathbf{S}_2) - 2i (b^* \mathbf{C} - b \mathbf{C}^*) \cdot (\mathbf{S}_1 \times \mathbf{S}_2) \\
 & - 2 \mathbf{S}_1 \cdot (\mathbf{C} \otimes \mathbf{C}^* + \mathbf{C}^* \otimes \mathbf{C} - \mathbb{I} \mathbf{C} \cdot \mathbf{C}^*) \cdot \mathbf{S}_2
 \end{aligned} \tag{4.26}$$

to obtain the final result, we add h_{M2} to $h_{M2}(1 \leftrightarrow 2, b \rightarrow b^*, \mathbf{C} \rightarrow \mathbf{C}^*)$, and multiply by $-1/U$ to get

$$\begin{aligned}
 H = & \frac{4|b|^2}{U} (\mathbf{S}_1 \cdot \mathbf{S}_2) + \frac{4i}{U} (b^* \mathbf{C} - b \mathbf{C}^*) \cdot (\mathbf{S}_1 \times \mathbf{S}_2) + \frac{4}{U} \mathbf{S}_1 \cdot (\mathbf{C} \otimes \mathbf{C}^* + \mathbf{C}^* \otimes \mathbf{C} - \mathbb{I} \mathbf{C} \cdot \mathbf{C}^*) \cdot \mathbf{S}_2 \\
 \equiv & J \mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2) + \mathbf{S}_1 \cdot \Gamma \cdot \mathbf{S}_2
 \end{aligned} \tag{4.27}$$

where

$$\begin{aligned}
 J = & \frac{4|b|^2}{U} \\
 \mathbf{D} = & \frac{4i}{U} (b^* \mathbf{C} - b \mathbf{C}^*) \\
 \Gamma = & \frac{4}{U} (\mathbf{C} \otimes \mathbf{C}^* + \mathbf{C}^* \otimes \mathbf{C} - \mathbb{I} \mathbf{C} \cdot \mathbf{C}^*)
 \end{aligned} \tag{4.28}$$

where Γ is a symmetric matrix representing anisotropic interaction.

4.3 Moriya's Rule

Suppose the two ions contribute to the electron transfer is located at point A and B, the point bisecting AB is denoted by C.

- When a center of inversion is located at C, $D = 0$

This can be proved by noticing that $PSP^{-1} = \mathbf{S}$, and P exchanges 1, 2.

Therefore $P(\mathbf{S}_1 \times \mathbf{S}_2)P^{-1} = -(\mathbf{S}_1 \times \mathbf{S}_2)$, so PHP^{-1} results in $\mathbf{D} = -\mathbf{D}$.

- When a mirror plane perpendicular to AB passes through C, $D \parallel$ (mirror plane)

For example, if we take the mirror plane to be $y - z$ plane, $MSM^{-1} = (-S_x, S_y, S_z)$. On the other hand, it exchanges 1, 2, so

$$M \begin{bmatrix} S_y^1 S_z^2 - S_z^1 S_y^2 \\ S_z^1 S_x^2 - S_x^1 S_z^2 \\ S_x^1 S_y^2 - S_y^1 S_x^2 \end{bmatrix} M^{-1} = - \begin{bmatrix} S_y^1 S_z^2 - S_z^1 S_y^2 \\ - (S_z^1 S_x^2 - S_x^1 S_z^2) \\ - (S_x^1 S_y^2 - S_y^1 S_x^2) \end{bmatrix} \quad (4.29)$$

so $D_x = 0$, D_y, D_z can survive. Therefore $\mathbf{D} \parallel$ (mirror plane).

- When a mirror plane including A B, $D \perp$ (mirror plane)

This is similar to the case above, but without exchanging 1, 2,

$$M \begin{bmatrix} S_y^1 S_z^2 - S_z^1 S_y^2 \\ S_z^1 S_x^2 - S_x^1 S_z^2 \\ S_x^1 S_y^2 - S_y^1 S_x^2 \end{bmatrix} M^{-1} = \begin{bmatrix} S_y^1 S_z^2 - S_z^1 S_y^2 \\ - (S_z^1 S_x^2 - S_x^1 S_z^2) \\ - (S_x^1 S_y^2 - S_y^1 S_x^2) \end{bmatrix} \quad (4.30)$$

so we have the opposite conclusion: $D_y = D_z = 0$ but D_x , can survive. Therefore $\mathbf{D} \perp$ (mirror plane).

- When a C_2 axis perpendicular to AB passes C, $D \perp C_2$ axis

Consider the x-y plane rotation by 180 degrees

$$C_2 = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \quad (4.31)$$

this flips component x and y , so $C_2 \mathbf{S} C_2^{-1} = (-S_x, -S_y, S_z)$. In addition, it swaps 1 and 2, so we have

$$C_2 \begin{bmatrix} S_y^1 S_z^2 - S_z^1 S_y^2 \\ S_z^1 S_x^2 - S_x^1 S_z^2 \\ S_x^1 S_y^2 - S_y^1 S_x^2 \end{bmatrix} C_2^{-1} = - \begin{bmatrix} - (S_y^1 S_z^2 - S_z^1 S_y^2) \\ - (S_z^1 S_x^2 - S_x^1 S_z^2) \\ S_x^1 S_y^2 - S_y^1 S_x^2 \end{bmatrix} \quad (4.32)$$

Therefore, the $D_z = 0$ and D_x, D_y can exist, so $\mathbf{D} \perp C_2$ axis.

- When a $C_{n \geq 2}$ axis along AB passes C, $D \parallel C_2$ axis

This does not swap AB. As for the spin part $C_n \mathbf{S} C_n^{-1} = R_n \mathbf{S}$, we have

$$C_n (\mathbf{S}_1 \times \mathbf{S}_2) C_n^{-1} = (R_n \mathbf{S}_1) \times (R_n \mathbf{S}_2) \quad (4.33)$$

and in general \mathbf{S}_3 is not changed, but $\mathbf{S}_1, \mathbf{S}_2$ are rotated. Therefore $\mathbf{D} \parallel C_2$ axis.

- When there is a $C_{n \geq 2}$ alone A B, $D \parallel AB$.

4.4 La2CuO4

4.4.1 Moriya's Rule

According to Moriya's law, if we

4.4.2 Derivation of the DM vector

We consider an individual Cu – O – Cu bond and the relevant Hamiltonian consists of the crystal-field levels of the 3d hole that forms the Cu^{2+} ions and the antibonding $2p_\sigma$ level of the O and in addition the spin-orbit coupling on the Cu atoms:

We reformulate our problem

$$H = H_0 + H_t + H_{LS} \quad (4.34)$$

with single-site terms

$$\begin{aligned} H_0 = & \sum_{j\sigma} \sum_{\alpha=0,m} \varepsilon_{j\alpha} d_{j\alpha\sigma}^\dagger d_{j\alpha\sigma} + \sum_{k\sigma} \varepsilon_p p_{k\sigma}^\dagger p_{k\sigma} \\ & + U \sum_{j\alpha\alpha'} d_{j\alpha\uparrow}^\dagger d_{j\alpha'\downarrow}^\dagger d_{j\alpha'\downarrow} d_{j\alpha\uparrow} \end{aligned} \quad (4.35)$$

nearest neighbor hybridization term

$$H_t = \sum_{j,\alpha,\sigma} \sum_{k \in \{j\}} \left(t_\alpha d_{j\alpha\sigma}^\dagger p_{k\sigma} + h.c. \right) \quad (4.36)$$

and spin-orbit term

$$H_{LS} = \lambda \sum_j \mathbf{L}_j \cdot \mathbf{S}_j = \frac{\lambda}{2} \sum_j \left(L_j^+ S_j^- + L_j^- S_j^+ + 2L_j^z S_j^z \right). \quad (4.37)$$

The notation is standard and the only new terms involve the **crystal fields** of the 3d hole denoted by $\alpha = 0$ (ground-state energy $\varepsilon_0 = 0$) and $\alpha = m$ (excited-state energy $\varepsilon_m > 0$). The standard Anderson superexchange is obtained in perturbation theory by eliminating the hybridization term to obtain an effective Heisenberg interaction between the Cu^{2+} spins, which is $O(t^4)$.

Moriya considered the lowest-order correction to this process, which involves a single power of the spin-orbit coupling. If we use second-order perturbation theory to eliminate the excited crystal-field levels, we get an additional vector hybridization term

$$H_v = \sum_k \sum_{j \in \{k\}} \mathbf{C}_{kj} \cdot \mathbf{S}_{kj} + H.c. \quad (4.38)$$

where

$$\mathbf{C}_{kj} = -\frac{\lambda}{2} \sum_m \frac{\mathbf{L}_{mo}(j)}{\varepsilon_m} t_m \quad (4.39)$$

and

$$S_{kj}^+ = p_{k\uparrow}^\dagger d_{j0\downarrow}, \quad S_{kj}^- = p_{k\downarrow}^\dagger d_{j0\uparrow}, \quad S_{kj}^z = p_{k\uparrow}^\dagger d_{j0\downarrow} - p_{k\downarrow}^\dagger d_{j0\uparrow} \quad (4.40)$$