

Philip Anderson's Superexchange Model

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The concept of superexchange was initially introduced by Kramers in 1934[1]. However, the original model did not mention the specific mechanism involved in the superexchange process. In 1950, Philip Anderson attempted to refine Kramer's approach. However, his first attempt resulted in a theory that is complex and poorly convergent[2]. In 1959, Anderson was able to improve on his own theory, achieving a much satisfactory description of superexchange[3]. Later on, his theory was further improved on by Goodenough and Kanamori, culminating in the GKA rules that is essential in describing molecular bonding, Mott insulators, and superconductivity[4][5].

INTRODUCTION

The superexchange interaction is defined as the interaction of two cations over an intermediate anion. For example, consider the structure $\text{Mn}^{2+} - \text{O}^{2-} - \text{Mn}^{2+}$, the two Mn ions are able to interact with each other despite an O^{2-} being "in the way". Although the definition of superexchange is straightforward, the physics behind this process is quite complicated. It took years of trail and error to come up with a satisfactory model for superexchange. The endeavor fortunately paid off, as the superexchange model has proved itself to be of fundamental importance in describing a wide range of phenomena, from Mott insulators to superconductivity.

The process of superexchange is a combination of direct exchange and electron transfer. The models for both have been extensively developed since 30 years before the Anderson's first superexchange paper was published. So to understand the physics behind superexchange, we first have to take a look at the models of direct exchange and electron transfer.

BACKGROUND

The Heitler-London Model

First, let us begin by considering the Hamiltonian for a hydrogen molecule:

$$H = -\frac{\hbar}{2m}(\nabla_1^2 + \nabla_2^2) + e^2\left(-\frac{1}{|r_1 - r_a|} - \frac{1}{|r_2 - r_b|} - \frac{1}{|r_1 - r_b|} - \frac{1}{|r_2 - r_a|} + \frac{1}{|r_1 - r_2|} + \frac{1}{|r_a - r_b|}\right) \quad (1)$$

where r_1 and r_2 are the positions of the two electrons, and r_a and r_b are the positions of the two protons. Electron 1 pairs with proton a , and electron 2 pairs with

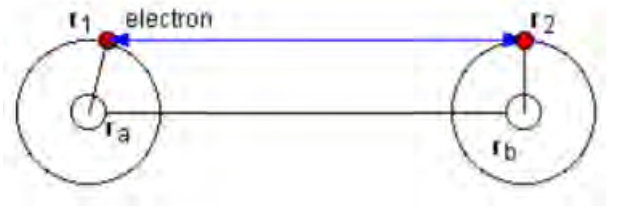


Figure 1: A drawing of a hydrogen molecule. Electron 1 and proton a make up one atom, and electron 2 and proton b make up the other.[6]

proton b . The first two terms are the kinetic terms and the last six terms are the interaction terms.

For the potential terms, the first two terms describe the attraction between the electron and proton within each pair of atoms, the 3rd and 4th term describe the attraction between the electron and the neighboring proton, and the last two terms describe the Coulomb repulsion between two electrons and two atoms respectively.

For the eight total terms, if we treat the first four terms as the zeroth order Hamiltonian, and the last four terms as perturbative terms, then we can write H_0 as:

$$H_0 = -\frac{\hbar}{2m}(\nabla_1^2 + \nabla_2^2) + e^2\left(-\frac{1}{|r_1 - r_a|} - \frac{1}{|r_2 - r_b|}\right) = \left(-\frac{\hbar}{2m}\nabla_1^2 - \frac{e^2}{|r_1 - r_a|}\right) + \left(-\frac{\hbar}{2m}\nabla_2^2 - \frac{e^2}{|r_2 - r_b|}\right) = H_1 + H_2 \quad (2)$$

so we see that the Hamiltonian is separable and we can solve for the eigenstates of the two electrons separately. In other words, we have:

$$H_1\psi_a(r_1) = E_0\psi_a(r_1) \quad (3)$$

$$H_2\psi_b(r_2) = E_0\psi_b(r_2)$$

Note that the eigenstates can be written as a tensor product of the spatial eigenstates and the spin eigenstates, or

$|\psi\rangle = |\psi_s\rangle |\chi\rangle$. Note that the electrons are fermions, so they must have an anti-symmetric total wavefunction. For the singlet state, the spin wavefunction is already anti-symmetric, so we know that the spatial wavefunction must be symmetric, in order to form a anti-symmetric product. On the other hand, the triplet state has a symmetric wavefunction, and therefore must have an anti-symmetric spatial wavefunction. Therefore, we can write the singlet and triplet spatial wavefunctions respectively as follow:

$$\begin{aligned} |\psi_+\rangle &= |\psi_a\rangle_1 |\psi_b\rangle_2 + |\psi_b\rangle_1 |\psi_a\rangle_2 \\ |\psi_-\rangle &= |\psi_a\rangle_1 |\psi_b\rangle_2 - |\psi_b\rangle_1 |\psi_a\rangle_2 \end{aligned} \quad (4)$$

We can easily check that the two above wavefunctions are in fact eigenstates of the free Hamiltonian given in equation 2. We can simplify the expression by denoting $|\psi_a\rangle_1 |\psi_b\rangle_2$ as $|ab\rangle$, which is the total wavefunction for electron 1 being on site a and electron 2 being on site b . Similarly, we denote $|\psi_b\rangle_1 |\psi_a\rangle_2$ as $|ba\rangle$, which is for electron 1 being on site b and electron 2 being on site a .

Note that the wavefunctions are not yet normalized. If we denote the overlap of the wavefunctions of the two electrons as $\langle\psi_a|\psi_b\rangle = k$. For simplicity, if we assume that k is real, then we can derive that $\langle ba|ab\rangle = \langle ab|ba\rangle = k^2$. We can normalize the two eigenstates as follow:

$$\begin{aligned} |\psi_+\rangle &= \frac{1}{\sqrt{2(1+k^2)}}(|ab\rangle + |ba\rangle) \\ |\psi_-\rangle &= \frac{1}{\sqrt{2(1-k^2)}}(|ab\rangle - |ba\rangle) \end{aligned} \quad (5)$$

We can easily verify that $\langle\psi_-|\psi_-\rangle = \langle\psi_+|\psi_+\rangle = 1$ and $\langle\psi_-|\psi_+\rangle = 0$, meaning that the two eigenstates are normalized and orthogonal, as required.

Note that the two states are only eigenstates of the zeroth order Hamiltonian, but not the full Hamiltonian. In fact, we can treat the last four interaction terms as perturbations ΔH , and we can express the full Hamiltonian as $H = H_0 + \Delta H$. We can use first order perturbation theory to calculate the energies of the singlet and triplet states as follow:

$$\begin{aligned} E_{\pm} &= \frac{1}{2 \pm 2k^2} (\langle ab| \pm \langle ba|) (H_0 + \Delta H) (|ab\rangle \pm |ba\rangle) \\ &= \frac{\langle ab|(H_0 + \Delta H)|ab\rangle \pm \langle ba|(H_0 + \Delta H)|ab\rangle}{1 \pm k^2} \end{aligned} \quad (6)$$

where we have used the fact that $\langle ab|H|ab\rangle = \langle ba|H|ba\rangle$ (the Hamiltonian is symmetric under exchange of r_1 and r_2), and also the fact that $\langle ab|H|ab\rangle = \langle ba|H|ab\rangle$ (the Hamiltonian is Hermitian).

It is obvious that $\langle ab|H_0|ab\rangle = 2E_0 \langle ab|ab\rangle = 2E_0$ and $\langle ba|H_0|ab\rangle = 2E_0 \langle ba|ab\rangle = 2k^2 E_0$. Then the zeroth or-

der energy is simply:

$$E_0 = \frac{2E_0 \pm 2k^2 E_0}{1 \pm k^2} = 2E_0 \quad (7)$$

Recall that:

$$\Delta H = e^2 \left(-\frac{1}{|r_1 - r_b|} - \frac{1}{|r_2 - r_a|} + \frac{1}{|r_1 - r_2|} + \frac{1}{|r_a - r_b|} \right) \quad (8)$$

The last term is trivial because it is just the Coulomb repulsion between two protons. It is independent of r_1 and r_2 , so we simply have:

$$\begin{aligned} \langle ab| \frac{e^2}{R_{ab}} |ab\rangle &= \frac{e^2}{R_{ab}} \langle ab|ab\rangle = \frac{e^2}{R_{ab}} \\ \langle ba| \frac{e^2}{R_{ab}} |ab\rangle &= \frac{e^2}{R_{ab}} \langle ba|ab\rangle = k^2 \frac{e^2}{R_{ab}} \end{aligned} \quad (9)$$

where $R_{ab} = |r_a - r_b|$. So we can absorb this term into the zeroth order Hamiltonian and find new energy to be:

$$2E_0 + \frac{e}{R_{ab}} \quad (10)$$

Now, we are only left with three non-trivial terms at the perturbative Hamiltonian, and we can make the following denotation:

$$\begin{aligned} V_c &= \langle ab| e^2 \left(-\frac{1}{|r_1 - r_b|} - \frac{1}{|r_2 - r_a|} + \frac{1}{|r_1 - r_2|} \right) |ab\rangle \\ V_{ex} &= \langle ba| e^2 \left(-\frac{1}{|r_1 - r_b|} - \frac{1}{|r_2 - r_a|} + \frac{1}{|r_1 - r_2|} \right) |ab\rangle \end{aligned} \quad (11)$$

The first term is called the Coulomb integral, and the second term is called the exchange integral.

We can then write the energies in the following form:

$$E_{\pm} = 2E_0 + \frac{e^2}{R_{ab}} + \frac{V_c \pm V_{ex}}{1 \pm k^2} \quad (12)$$

If we make the assumption that the overlap of the two electron wavefunctions is zero, or $\langle\psi_a|\psi_b\rangle = k = 0$, then the expression of the singlet and triplet energies reduces to:

$$E_{\pm} = 2E_0 + \frac{e^2}{R_{ab}} + (V_c \pm V_{ex}) \quad (13)$$

We can prove that the exchange integral V_{ex} is positive if the overlap integral is zero, or $V_{ex} > 0$. This is done by Fourier transforming the perturbative terms (which we will not present here).

Therefore, we see that the triplet energy E_- is lower than the singlet energy E_+ , so the electrons will have a "triplet ground state", meaning that the interaction is ferromagnetic[7].

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.

Dirac's Spin-exchange Model

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

$$P_{12} = \frac{1}{2} \left(1 + \sum_{i=1}^3 \sigma_{1i} \cdot \sigma_{2i} \right) \quad (14)$$

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:

$$\begin{aligned} P|\chi_+\rangle &= -P|\chi_+\rangle \\ P|\chi_-\rangle &= +P|\chi_-\rangle \end{aligned} \quad (15)$$

The signs make intuitive sense since the singlet spin state is anti-ferromagnetic, and the triplet spin state is ferromagnetic. We can then rewrite the perturbative Hamiltonian as:

$$H = V_c - V_{ex}P \quad (16)$$

then we can easily see that:

$$\begin{aligned} H|\chi_+\rangle &= (V_c + V_{ex})|\chi_+\rangle \\ H|\chi_-\rangle &= (V_c - V_{ex})|\chi_-\rangle \end{aligned} \quad (17)$$

confirming equation 13.

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:

$$E_{\pm} = 2E_0 + \frac{(V_c + \frac{e^2}{R}) \pm (V_{ex} + k^2 \frac{e^2}{R})}{1 \pm k^2} \quad (18)$$

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.

Hubbard Model for Charge Transfer

We begin by considering a simple model. Let's imagine that there are some number of atoms and electrons, and each atom can "hold" up to a certain

number of electrons. We can then denote each atom as a "site", and assign it with a label i . Electrons cannot be created or destroyed, but they are free to hop between different atom sites. Within each atom, we can denote the number of up-spin electrons as $n_{i\uparrow}$ and the number of down-spin electrons as $n_{i\downarrow}$, and we have a coulomb potential within each site proportional to the product of these two numbers.

The lengthy description above is called the Hubbard Model, and it can be condensed simply into a Hamiltonian description as[8]:

$$H = \sum_{(i,j)\sigma} (t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + U \sum_i (n_{i\uparrow} n_{i\downarrow}) \quad (19)$$

The first term describes the process of an electron being destroyed at site j and being created at site i . The Hermitian conjugate describes the reverse process (destroyed at site i and created at site j). Intuitively, we can think of this as the electron "hopping" between the two sites, and this is associated with some transition amplitude t_{ij} . In addition, the hopping electron must preserve spin, as denoted by the σ subscript. And the second term is simply the Coulomb interactions between the up-spin state electrons and the down-spin state electrons within each atom site.

As an example, we can consider the simple case of two electrons and two sites. There are six possible states for this configuration, and they are shown schematically at Fig. 2. Note that due to the Pauli Exclusion Principle, two electrons of the same spin cannot be at the same atom site.

If the two electrons are at different sites, then each electron can be in either the up-spin or down-spin state, giving us $2^2 = 4$ possible states. We denote these 4 states as $|\psi_1\rangle$, $|\psi_2\rangle$, $|\psi_3\rangle$, and $|\psi_6\rangle$. The two electrons can also be at the same site. However, this time, the two electrons must have opposite spins, so this give us only 2 possible states, and they are denoted by $|\psi_4\rangle$ and $|\psi_5\rangle$.

Note that we can separate the Hamiltonian into a static component and an interacting component, or $H = H_0 + \Delta H$, where we have:

$$\begin{aligned} H_0 &= U \sum_i (n_{i\uparrow} n_{i\downarrow}) \\ \Delta H &= \sum_{(i,j)\sigma} (-t c_{i\sigma}^\dagger c_{j\sigma} + h.c.) \end{aligned} \quad (20)$$

for simplicity sake, we have assumed that $t_{ij} = -t$ for all i and j . It is obvious that all six states are eigenstates of H_0 , where $H_0|1\rangle = H_0|2\rangle = H_0|3\rangle = H_0|6\rangle = 0$ (since the two electrons are not at the same site) and

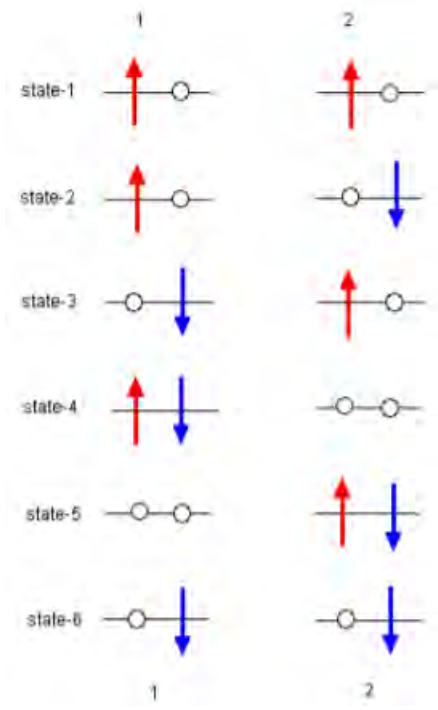


Figure 2: The six possible states for two electrons and two atoms to be in.[6]

$$H_0 |4\rangle = H_0 |5\rangle = U.$$

On the other hand, note that none of the six states are eigenstates of the interacting Hamiltonian. In fact, we have $\langle i|\Delta H|i\rangle = 0$, meaning that the coupling between the same states is zero. This makes intuitive sense because ΔH is the “hopping” term, and an electron must move to a different site. For example, $\langle 4|\Delta H|2\rangle = -t$, describing the down-spin electron hopping from site 2 to site 1. However, not all couplings are nonzero. For example, $\langle 3|\Delta H|2\rangle = 0$, because a transition from state 2 to state 3 requires two hops. First, the down-spin electron must hop from site 2 to site 1, and then the up-spin electron must hop from site 1 to site 2, making this a second-order process.

In first order perturbation theory, the transition amplitude is proportional to the coupling between the two states and inversely proportional to the energy difference, or $\frac{\langle f|\Delta H|i\rangle}{|E_f - E_i|}$. It is important to note that all first order coupling is always associated with an energy difference of U . This is because a first order hopping either brings two electrons together or breaks them apart, giving us an energy change equal to the Coulomb interaction.

Fortunately, we can solve the eigenstates of the full Hamiltonian exactly, so there is really no need to perform perturbative calculations. All we need to do is to simply

calculate the matrix elements and find the eigenstates of the matrix. Note that state 1 and state 6 cannot transition to any other states, nor can they be transitioned to from any other states, as it will violate Pauli Exclusion Principle. States 2 and 3 can transition to states 4 and 5, and the reverse process can also happen. This gives us 8 non-zero matrix elements $-t$. This, in addition to the two U elements for states 4 and 5 gives us a total of 10 non-zero elements. The matrix is as follow:

$$H = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -t & -t & 0 \\ 0 & 0 & 0 & -t & -t & 0 \\ 0 & -t & -t & U & 0 & 0 \\ 0 & -t & -t & 0 & U & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (21)$$

We can then solve for the eigenenergies and eigenstates:

$$\begin{aligned} E_1 &= 0 & |\Psi_1\rangle &= |\psi_1\rangle \\ E_2 &= 0 & |\Psi_2\rangle &= |\psi_6\rangle \\ E_3 &= 0 & |\Psi_3\rangle &= \frac{1}{\sqrt{2}}(|\psi_2\rangle - |\psi_3\rangle) \\ E_4 &= U & |\Psi_4\rangle &= \frac{1}{\sqrt{2}}(|\psi_4\rangle - |\psi_5\rangle) \\ E_5 &= \frac{1}{2}(U - \sqrt{U^2 + 16t^2}) \\ |\Psi_5\rangle &= \frac{U + \sqrt{U^2 + 16t^2}}{4t}(|\psi_2\rangle + |\psi_3\rangle) + (|\psi_4\rangle + |\psi_5\rangle) \\ E_6 &= \frac{1}{2}(U + \sqrt{U^2 + 16t^2}) \\ |\Psi_6\rangle &= \frac{U - \sqrt{U^2 + 16t^2}}{4t}(|\psi_2\rangle + |\psi_3\rangle) + (|\psi_4\rangle + |\psi_5\rangle) \end{aligned} \quad (22)$$

Note that the last two eigenstates are not normalized.

Let us consider two limiting cases. First, let's consider the case where $U \gg t$, then, let's consider the case where $t \gg U$. The first case essentially means that the potential energy is infinitely strong, and it is impossible for the electrons to overcome it. The second case means that there is effectively no potential energy, and the electrons are free to roam around.

In the first case, the last two expressions simply reduce to:

$$\begin{aligned} E_5 &= 0 & |\Psi_5\rangle &= \frac{1}{\sqrt{2}}(|\psi_2\rangle + |\psi_3\rangle) \\ E_6 &= U & |\Psi_6\rangle &= \frac{1}{\sqrt{2}}(|\psi_4\rangle + |\psi_5\rangle) \end{aligned} \quad (23)$$

so we see that in this limiting case, there is no eigenstates that contain a mixture of both the “apart” state and “together” state. This makes intuitive sense because the potential barrier that the electrons have to overcome

to break apart or come together is infinitely high. Therefore, if the electrons start out as an “apart” state, then it can never come together, and vice versa.

Now, let’s look at the other limiting case where $t \gg U$. In this case, the last two expressions then reduce to:

$$\begin{aligned} E_5 = 2t \quad |\Psi_5\rangle &= \frac{1}{2}(|\psi_2\rangle + |\psi_3\rangle + |\psi_4\rangle + |\psi_5\rangle) \\ E_6 = 2t \quad |\Psi_5\rangle &= \frac{1}{2}(-|\psi_2\rangle - |\psi_3\rangle + |\psi_4\rangle + |\psi_5\rangle) \end{aligned} \quad (24)$$

In this case, the last two eigenstates are equal mixtures of the “apart” states and the “together” states. This also makes sense, because the potential barrier is essentially zero in this case, so the electrons are free to roam around. This makes the “apart” states and the “together” states symmetric to each other.

Lastly, let’s derive the spin exchange Hamiltonian from the Hubbard model. To do so, let’s first find the effective Hamiltonian from second order perturbation theory. Note that $\Delta H |2\rangle = -t(|4\rangle + |5\rangle)$, $\Delta H |4\rangle = -t(|2\rangle + |3\rangle)$, and $\Delta H |5\rangle = -t(|2\rangle + |3\rangle)$. Using these and the formula for the effective Hamiltonian, we find:

$$H_{eff} = \frac{\Delta H P \Delta H}{U} |2\rangle = -\frac{2t^2}{U}(|2\rangle - |3\rangle) \quad (25)$$

Note that $|3\rangle$ is just $|2\rangle$ with spin exchanged. In other words, we have $|3\rangle = P|2\rangle$, where P is the Dirac’s spin exchange operator. Therefore, we can write the effective Hamiltonian in terms of the spin exchange operator:

$$H_{eff} = -\frac{2t^2}{U}(1 - P) = J - JP \quad (26)$$

where $J = -\frac{2t^2}{U} < 0$. 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 anti-ferromagnetic interaction. If we ignored the terms without P , we can combine the two interactions (from direct exchange and charge transfe), and write the total Hamiltonian as

$$H_{total} = -(J + V_{ex})P \quad (27)$$

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.

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 Mn – O – 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.

Slater Determinant

This section is going to be mainly math. We will discuss how to construct the total wavefunction of multiple identical fermions. For example, we already know that the wavefunction of two electrons in two states can be written as $\psi = \psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)$, where the subscript denotes the state and the number inside the bracket denotes the electron “label”. Note that this wavefunction is antisymmetric under the exchange of the two electrons.

Now, let’s consider the more complicated case of three electrons in three states. The total wavefunction can be expressed in the form of a Slater determinant, which is just a fancy name for the determinant of a matrix with single particle wavefunctions as elements. In this case, we can express the Slater determinant of three electrons as[9]:

$$\begin{vmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) \\ \psi_2(1) & \psi_2(2) & \psi_2(3) \\ \psi_3(1) & \psi_3(2) & \psi_3(3) \end{vmatrix} \quad (28)$$

which is just:

$$\begin{aligned} & \psi_1(1)\psi_2(2)\psi_3(3) + \psi_1(2)\psi_2(3)\psi_3(1) + \psi_1(3)\psi_2(1)\psi_3(2) \\ & - \psi_1(3)\psi_2(2)\psi_3(1) + \psi_1(1)\psi_2(3)\psi_3(2) + \psi_1(2)\psi_2(1)\psi_3(3) \end{aligned} \quad (29)$$

Note that this wavefunction satisfies the two properties. First, each term of wavefunction bijects to a possible permutation of the electron label, meaning that the wavefunction describes the full picture of each electron occupying the three states with equal possibility. Secondly, the wavefunction is antisymmetric under any pair of electron label exchange, which means that it fully describes three electrons as fermions.

The Slater determinant can be extended to n fermions easily. First, we simply write the matrix with element M_{ij} corresponding to $\psi_i(j)$. Then, we just have to take the determinant of the matrix to obtain the total wavefunction.

To show that this method in fact works, note that the determinant of any square matrix is simply all of possible permutations of the j , and if the permutation is even, then the term has a plus sign, and if the permutation is odd, then the term has a minus sign. So if we perform a pair exchange before we take the determinant, then we are essentially performing an additional transposition, and this makes odd permutations even, and even permutations odd. Therefore, the odd permutations will have a minus sign, and the even permutations will have a plus sign. And the sign of the total wavefunction changes, meaning that it is antisymmetric under any pair of exchange of electron labels.

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:

$$H = \begin{bmatrix} E_1 & t \\ t & E_2 \end{bmatrix} \quad (30)$$

Then we can solve for the eigenenergies:

$$E_{\pm} = \frac{1}{2}(E_1 + E_2 \pm \sqrt{\Delta E^2 + 4t^2}) \quad (31)$$

and the (un-normalized) eigenstates:

$$\psi_{\pm} = \begin{bmatrix} E_1 - E_2 \pm \sqrt{\Delta E^2 + 4t^2} \\ 2t \end{bmatrix} \quad (32)$$

Now, if we bring in the condition that $t \ll \Delta E$, then we can reduce the eigenenergy expressions to:

$$\begin{aligned} E_+ &= E_2 + \frac{t^2}{\Delta E} \\ E_- &= E_1 - \frac{t^2}{\Delta E} \end{aligned} \quad (33)$$

and the eigenstate expressions to:

$$\begin{aligned} \psi_+ &= \psi_2 + \frac{t}{\Delta E} \psi_1 \\ \psi_- &= \psi_1 - \frac{t}{\Delta E} \psi_2 \end{aligned} \quad (34)$$

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.

Wavefunction overlap

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

If we assume that the overlap is non-zero, then we can denote the overlap as:

$$\int \psi_b^*(r) \psi_a(r) dr = k \quad (35)$$

And if we perform a parity operation, then the integral becomes

$$\int \psi_b^*(-r) \psi_a(-r) dr = - \int \psi_b^*(r) \psi_a(r) dr = -k \quad (36)$$

However, the overlap integral should be invariant under parity exchange, so we have $k = -k$, which implies $k = 0$.

In short, the overlap of a symmetric and anti-symmetric wavefunction must be zero. It is important to note that 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 the integral

$$\int \psi_b^*(r)U(r)\psi_a(r)dr = 0 \quad (37)$$

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 anti-symmetric, and U is symmetric. The amplitude of exchange can again be expressed in the following integral form:

$$\int \psi_a^*(r_2)\psi_b^*(r_1)U(r_1,r_2)\psi_a(r_1)\psi_b(r_2) \quad (38)$$

Note that in this case, the integrand is actually symmetric under parity exchange. This is because $\psi_b(r_1)$ and $\psi_b(r_2)$ are both anti-symmetric, and they cancel out to make a symmetric term. Therefore, the direct exchange amplitude is non-zero. So we see that direct exchange can occur even if the wavefunction overlap is zero.

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. The technicality involved in his original paper is far too complicated to be present here, so we will use an intuitive picture to illustrate the main concepts involved in his paper. For this discussion, we will consider the structure $\text{Mn}^{2+} - \text{O}^{2-} - \text{Mn}^{2+}$ as a simple example.

Refer to Fig. 3 for a schematic representation of the $\text{Mn}^{2+} - \text{O}^{2-} - \text{Mn}^{2+}$ structure. We see that the O^{2-} anion is sandwiched between the two Mn^{2+} cations, forming an 180 degree structure. The three ions are bonded by σ bonds, so their wavefunction overlaps are non-zero. We can label the sites from left to right as A, B, and C.

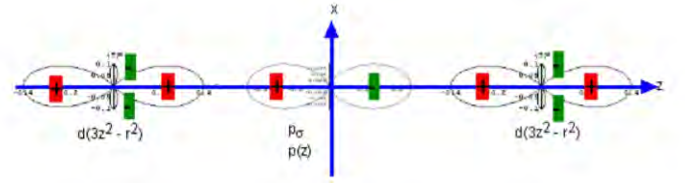


Figure 3: This is a schematic drawing of the $\text{Mn}^{2+} - \text{O}^{2-} - \text{Mn}^{2+}$ structure. The anion in the middle is O^{2-} , and the cations at the two ends are Mn^{2+} . We will label the leftmost ion as A, the intermediate ion as B, and the rightmost ion as C. The + sign denotes an up-spin electron and the - sign denotes the down-spin electron. [6]

WLOG, let's assume that the one of the electron at B site transfers to the C site (the scenario is symmetric if it transfers to the A site instead). 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[2]. 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 super-exchange 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.

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:

$$\psi_{bond} = \psi_p + \lambda\psi_d \quad (39)$$

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 antibonding wavefunction as:

$$\psi_{anti} = \psi_d - (\lambda + k)\psi_p \quad (40)$$

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

$$\begin{aligned} & \langle \psi_{anti} | \psi_{bond} \rangle \\ &= -(\lambda + k) \langle \psi_p | \psi_p \rangle + \lambda \langle \psi_d | \psi_d \rangle + (-\lambda(\lambda + k) + 1) \langle \psi_d | \psi_p \rangle \\ &= -\lambda + k + \lambda - k = 0 \end{aligned} \quad (41)$$

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 $\text{Mn}^{2+} - \text{O}^{2-} - \text{Mn}^{2+}$ 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.

As shown in the previous sections, we can write the three-electron wavefunction as a Slater determinant. First, we consider the wavefunction before the electron transfer:

$$\begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ p_{\downarrow}(1) & p_{\downarrow}(2) & p_{\downarrow}(3) \end{vmatrix} \quad (42)$$

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:

$$\begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ d_{\downarrow}(1) & d_{\downarrow}(2) & d_{\downarrow}(3) \end{vmatrix} \quad (43)$$

Note that after the charge transfer, the original down-spin electron in the p orbital at B site has hopped over to the d orbital at C site, and this is reflected in the last row of the matrix.

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:

$$\begin{aligned} & \begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ p_{\downarrow}(1) & p_{\downarrow}(2) & p_{\downarrow}(3) \end{vmatrix} + \lambda \begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ d_{\downarrow}(1) & d_{\downarrow}(2) & d_{\downarrow}(3) \end{vmatrix} \\ &= \begin{vmatrix} d_{\uparrow}(1) & d_{\uparrow}(2) & d_{\uparrow}(3) \\ p_{\uparrow}(1) & p_{\uparrow}(2) & p_{\uparrow}(3) \\ p_{\downarrow}(1) + \lambda d_{\downarrow}(1) & p_{\downarrow}(2) + \lambda d_{\downarrow}(2) & p_{\downarrow}(3) + \lambda d_{\downarrow}(3) \end{vmatrix} \end{aligned} \quad (44)$$

Note that $p_{\uparrow} + \lambda p_{\uparrow} = (1 + \lambda)p_{\uparrow} = p_{\uparrow}$, and $d_{\uparrow} + \lambda d_{\uparrow} = (1 + \lambda)d_{\uparrow} = d_{\uparrow}$. Note that we can rewrite the above

equation in the following form[6]:

$$\begin{vmatrix} d_{\uparrow}(1) - \gamma p_{\uparrow}(1) & d_{\uparrow}(2) - \gamma p_{\uparrow}(2) & d_{\uparrow}(3) - \gamma p_{\uparrow}(3) \\ p_{\uparrow}(1) + \lambda d_{\uparrow}(1) & p_{\uparrow}(2) + \lambda d_{\uparrow}(2) & p_{\uparrow}(3) + \lambda d_{\uparrow}(3) \\ p_{\downarrow}(1) + \lambda d_{\downarrow}(1) & p_{\downarrow}(2) + \lambda d_{\downarrow}(2) & p_{\downarrow}(3) + \lambda d_{\downarrow}(3) \end{vmatrix} \quad (45)$$

with $\lambda = \gamma - k$. Note that the equality between matrix 44 and matrix 45 is not trivial to show. The derivation involves lengthy algebra and doesn't really provide any illuminating physics insights, so it will be skipped for the time being.

However, 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 equation 27:

$$H_{total} = -(J + V_{ex})P \quad (46)$$

and this effectively completes our picture of the superexchange interaction between site A and site C, with site B being the intermediate[3].

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[4][5]:

- When two orbitals overlap, both direct exchange and charge transfer can occur.
- When two orbitals have zero overlap, only direct exchange can occur.
- 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:

- 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.
- 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.

- 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:

- The $d_\gamma - p_\sigma$ bond is analogous to σ bonds, meaning that it is strongly anti-ferromagnetic.
- 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.
- 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:

- First, let’s look at 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, let’s label the leftmost site as A, the middle site as B, and the rightmost site as C. WLOG, 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.

- 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 anti-ferromagnetically, forcing site C to have spin up. So the superexchange interaction is ferromagnetic in this case.
- 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 an 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.
- 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 anti-ferromagnetic.

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.

EXPERIMENTAL SUPPORT

All of the structures we used in the previous section as examples for superexchange interaction are all real molecular structures. The theoretical predictions of the interaction within the molecules are all verified experimentally through measurements of interaction strengths.

In fact, the superexchange model has successfully predicted the interaction for a wide range of molecules, ranging from the simplest hydrogen molecule to the more complicated structures such as the La_2CuO_4 Mott insulator.

CONCLUSION

The GKA rules are very important in the sense that are very simple, yet they are able to successfully predict the superexchange interaction successfully for a wide range of molecules. It also provides a possible explanation to the high-T superconductive property of certain copper oxide. The superconductivity is due to the condensation of electron pairs via the anti-ferromagnetic superexchange between the Cu^{2+} ions, though this is still a speculation, and whether the superexchange model is fundamental to the superconductivity process is still not established.

Although the GKA rules are simple, we have to remind ourselves that they are established upon the mathematically rigorous model of superexchange. In deriving the GKA rules, certain assumptions and approximations are made. Therefore, the GKA rules should only be viewed as a rule of thumb rather than rules set in stone. For example, the rules break down when the bonding angle deviates from 180 degree, when the electron occupancy is dynamic, or when the spin-orbit coupling becomes non-negligible. Therefore, it is important for us to understand thorough the full picture of superexchange, to ensure that

we do not make any erroneous predictions.

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