7 Exchange Mechanisms

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Contents

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1 Introduction

One of the profound *Surprises in Theoretical Physics* [1] is that magnetism is an inherently quantum mechanical effect. Classically, magnetic moments originate from electric currents: A current density $\vec{j}(\vec{r})$ generates a magnetic moment

$$\vec{\mu} = \frac{1}{2}\int \vec{r}\times\vec{j}\,d^3r\,. \tag{1}$$

These moments interact via the dipole-dipole interaction. The magnetostatic interaction energy between two dipoles at a distance R, $\hat{R}$ being the unit-vector from the position of the first to that of the second dipole,

$$\Delta E = \frac{\mu_0}{4\pi}\,\frac{\vec{\mu}_1\cdot\vec{\mu}_2 - 3(\hat{R}\cdot\vec{\mu}_1)(\hat{R}\cdot\vec{\mu_2})}{R^3} = \frac{\vec{\mu}_1\cdot\vec{\mu}_2 - 3(\hat{R}\cdot\vec{\mu}_1)(\hat{R}\cdot\vec{\mu_2})}{4\pi\varepsilon_0 c^2\;R^3} \tag{2}$$

depends on their distance and relative orientation. This can, however, not be the origin of the magnetism found in actual materials: In a classical system charges cannot flow in thermodynamic equilibrium, the celebrated Bohr-van Leuween theorem, and hence there are no magnetic moments to begin with [2].
In quantum mechanics, however, non-vanishing charge currents in the ground state are not uncommon: An electron in state $\Psi(\vec{r})$ corresponds to a current density

$$\vec{j}(\vec{r}) = -\frac{e\hbar}{2im_e}\left(\overline{\Psi(\vec{r})}\nabla\Psi(\vec{r}) - \Psi(\vec{r})\nabla\overline{\Psi(\vec{r})}\right) \tag{3}$$

which, for complex wave function $\Psi(\vec{r})$, is usually non-vanishing. According to (1) it produces a magnetic moment proportional to the expectation value of the angular momentum

$$\vec{\mu}_L = -\frac{e\hbar}{2m_e}\,\langle\vec{L}\,\rangle = -\mu_B\,\langle\vec{L}\,\rangle\,. \tag{4}$$

The constant of proportionality is the Bohr magneton μ_B. In particular, an atomic orbital $|n,l,m\rangle$ has a magnetic moment proportional to the magnetic quantum number $\vec{\mu} = -\mu_B\,m\,\hat{z}$. Also the electron spin $\vec{S}$ carries a magnetic moment

$$\vec{\mu}_S = -g_e\mu_B\,\langle\vec{S}\,\rangle\,. \tag{5}$$

The constant of proportionality between spin and magnetic moment differs from that between orbital momentum and moment by the gyromagnetic ratio g_0. Dirac theory gives $g_e = 2$, which is changed to $g_e \approx 2.0023\ldots$ by QED corrections.
Atomic moments are thus of the order of μ_B. For two such moments at a distance of 1 Å the magnetostatic energy (2) is of the order of 0.05 meV, corresponding to a temperature of less than 1 K. Therefore, magnetic ordering which, e.g., in magnetite (Fe_3O_4), persists till about 860 K, must originate from an interaction other that the magnetostatic interaction of dipoles. Indeed, it is the interplay of electronic properties which are apparently unrelated to magnetism, the Pauli principle in combination with the Coulomb repulsion (Coulomb exchange) as well

as the hopping of electrons (kinetic exchange) that leads to an effective coupling between the magnetic moments in a solid.

The basic mechanisms of the exchange coupling are quite simple: Since many-body wave functions must change sign under the permutation of Fermions, electrons of the same spin cannot be at the same position. Electrons of like spin thus tend to avoid each other, i.e., the probability of finding them close to each other tends to be lower than for electrons of opposite spin (exchange hole). In that sense the Coulomb energy between two electrons depends on their relative spins. By this argument, aligning electron spins tends be energetically favorable. This *Coulomb exchange* is the basis of Hund's first rule. When more than one atom is involved, electrons can hop from one site to the neighbor. This kinetic term is, again, modified by the Pauli principle, as the hopping to an orbital on the neighboring atom will only be possible, if there is not already an electron of the same spin occupying that orbital and by the Coulomb repulsion among the electrons. This is the idea of *kinetic exchange*. When Coulomb exchange and kinetic terms work together we speak of *double exchange*. In that case the electron-hopping serves to mediate the spin-correlation created on an atom to its neighbors.

Exchange mechanisms are idealizations of characteristic situations found in real materials. As such they are merely approximations, but they afford a simplification of the complicated realistic description, which provides a good basis for thinking about the relevant effects in a real material. We will start by discussing the effect of Coulomb exchange matrix elements (Sec. 2). To keep things simple, we will discuss a two-orbital model and only mention atomic multiplets and Hund's rule, while the full Coulomb vertex is discussed in the lecture of R. Eder. Next we turn to exchange mechanisms involving also hopping (Sec. 3). We start by looking at the a simple two-site model with two electrons. Focussing on the limit of strong electronic correlations (Coulomb repulsion dominating electron hopping), we introduce the method of downfolding to derive an effective Hamiltonian in which an explicit coupling of the electron spins appears. While conceptually simple, this direct exchange mechanism is rarely found in real materials. There hopping between correlated orbitals is usually mediated by a weakly correlated orbital. This is the superexchange mechanism. The derivation is very similar to that of kinetic exchange. However, the number of states involved, makes explicit book-keeping tedious. To simplify our work, we introduce second quantization as a simple notation of many-electron states. This also enables us to easily discuss double exchange, which combines direct exchange on an atom with coupling to the neighbors via electron hopping. Examples are the superexchange between transition metal atoms bridged by an oxygen at a right angle, which arises from the Coulomb exchange on the oxygen, as well as the exchange in mixed-valence compounds (Sec. 4). The competition between kinetic and double exchange is described by the Goodenough-Kanamori rules. Finally we show that exchange is not restricted to coupling spins, but can also produce interactions between orbital occupations (Sec. 5).

How exchange gives rise to an effective coupling of momenta is most easily shown for single- or two-site models. To see how these results carry over to solids, we consider the case of direct exchange (Sec. 6). Starting from the Hubbard model we show how taking the limit of strong correlations leads to the t-J-model, which, for half-filling, simplifies to the Heisenberg model.

2 Coulomb exchange

The Coulomb repulsion between electrons,

$$H_U = \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}\,, \tag{6}$$

is manifestly spin-independent. Nevertheless, because of the antisymmetry of the many-electron wave function, the eigenenergies of H_U depend on the spin. This is the basis of the multiplet structure in atoms and of Hund's first two rules.

To understand the mechanism of this Coulomb exchange we consider a simple two-electron model. In the spirit of tight-binding (see the lecture of E. Pavarini), we assume that we have solved the two-electron Hamiltonian H_0, replacing the interaction term H_U, e.g. as a self-consistent potential $\sum_i U(\vec{r}_i)$, obtaining an orthonormal set of one-electron eigenstates $\varphi_\alpha(\vec{r})$ with eigenvalues ε_α. We now ask for the effect of re-introducing the interaction $H_U - \sum_i U(\vec{r}_i)$. The largest effect we will find for states that are degenerate.

Let us consider two orbitals $\alpha = a,\, b$. Then the two-electron Slater determinants with spins σ and σ'

$$\begin{aligned} \Psi_{a,\sigma;\,b\sigma'}(\vec{r}_1, s_1;\, \vec{r}_2, s_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(\vec{r}_1)\,\sigma(s_1) & \varphi_a(\vec{r}_2)\,\sigma(s_2) \\ \varphi_b(\vec{r}_1)\,\sigma'(s_1) & \varphi_b(\vec{r}_2)\,\sigma'(s_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \Big(\varphi_a(\vec{r}_1)\,\varphi_a(\vec{r}_2)\;\sigma(s_1)\,\sigma'(s_2) - \varphi_b(\vec{r}_1)\,\varphi_a(\vec{r}_2)\;\sigma'(s_1)\,\sigma(s_2) \Big) \end{aligned} \tag{7}$$

are degenerate eigenstates of H_0 with eigenvalue $\varepsilon_a + \varepsilon_b$, independent of the spin orientations. To see how this degeneracy is lifted, we calculate the matrix elements of H_U in the basis of the Slater determinants $\Psi_{a,\sigma;\,b\sigma'}$.

When both electrons have the same spin ($\sigma = \sigma'$), we can factor out the spin functions

$$\Psi_{a,\sigma;\,b\sigma} = \frac{1}{\sqrt{2}} \Big(\varphi_a(\vec{r}_1)\varphi_b(\vec{r}_2) - \varphi_b(\vec{r}_1)\varphi_a(\vec{r}_2) \Big)\; \sigma(s_1)\sigma(s_2) \tag{8}$$

and obtain

$$\left\langle \Psi_{a,\sigma;\,b,\sigma} \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi_{a,\sigma;\,b,\sigma} \right\rangle = \frac{1}{2}\,(U_{ab} - J_{ab} - J_{ba} + U_{ba}) = U_{ab} - J_{ab} \tag{9}$$

where the direct terms are the Coulomb integral

$$U_{ab} = \int d^3r_1 \int d^3r_2\, \frac{|\varphi_a(\vec{r}_1)|^2\;|\varphi_b(\vec{r}_1)|^2}{|\vec{r}_1 - \vec{r}_2|} \tag{10}$$

while the cross terms give the exchange integral

$$J_{ab} = \int d^3r_1 \int d^3r_2\, \frac{\overline{\varphi_a(\vec{r}_1)}\,\varphi_b(\vec{r}_1)\;\overline{\varphi_b(\vec{r}_2)}\,\varphi_a(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\,. \tag{11}$$

For the states where the electrons have opposite spin ($\sigma' = -\sigma$)

$$\left\langle \Psi_{a,\sigma;\,b,-\sigma} \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi_{a,\sigma;\,b,-\sigma} \right\rangle = U_{ab} \tag{12}$$

the diagonal matrix element has no exchange contribution, as the overlap of the spin functions for the cross terms vanish. There are however off-diagonal matrix elements

$$\left\langle \Psi_{a\uparrow;\,b\downarrow} \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi_{a\downarrow;\,b\uparrow} \right\rangle = -J_{ab} \ . \tag{13}$$

Since H_U does not change the spins, these are the only non-zero matrix elements. In the basis of the states $\Psi_{\uparrow\uparrow}$, $\Psi_{\uparrow\downarrow}$, $\Psi_{\downarrow\uparrow}$ and $\Psi_{\downarrow\downarrow}$ the Coulomb term is thus given by

$$H_U = \begin{pmatrix} U_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & U_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & U_{ab} & 0 \\ 0 & 0 & 0 & U_{ab} - J_{ab} \end{pmatrix} . \tag{14}$$

The triplet states $\Psi_{\uparrow\uparrow}$ and $\Psi_{\downarrow\downarrow}$ are obviously eigenstates of H_U with eigenenergy

$$\Delta\varepsilon_{\text{triplet}} = U_{ab} - J_{ab} \ . \tag{15}$$

Diagonalizing the 2×2 submatrix, we obtain the third triplet state $(\Psi_{\uparrow\downarrow} + \Psi_{\downarrow\uparrow})/\sqrt{2}$ and the singlet state $(\Psi_{\uparrow\downarrow} - \Psi_{\downarrow\uparrow})/\sqrt{2}$

$$\frac{1}{\sqrt{2}}\left(\Psi_{\uparrow\downarrow} - \Psi_{\downarrow\uparrow}\right) = \frac{1}{\sqrt{2}}\Big(\varphi_a(\vec{r}_1)\varphi_b(\vec{r}_2) + \varphi_b(\vec{r}_1)\varphi_a(\vec{r}_2)\Big)\ \frac{1}{\sqrt{2}}\Big(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle\Big) \tag{16}$$

with energy

$$\Delta\varepsilon_{\text{singlet}} = U_{ab} + J_{ab} \ . \tag{17}$$

To see whether the triplet or the singlet is lower in energy, we need to know the sign of the exchange matrix element. While the Coulomb integral U_{ab}, having a positive integrand, is obviously positive, it is less obvious that also $J_{ab} > 0$. Introducing $\Phi(\vec{r}) = \overline{\varphi_a(\vec{r})}\varphi_b(\vec{r})$ and rewriting the integral using the convolution theorem as well as the Fourier transform of $1/r$, we obtain [3, 4]:

$$\begin{aligned} J_{ab} &= \int d^3r_1\, \overline{\Phi(\vec{r}_1)} \underbrace{\int d^3r_2\, \frac{1}{|\vec{r}_1 - \vec{r}_2|}\, \Phi(\vec{r}_2)}_{=\int dk\, e^{ikr_1} 4\pi/k^2 \Phi(k)\,/(2\pi)^3} && (18) \\ &= \frac{1}{(2\pi)^3} \int d^3k \underbrace{\int d^3r_1\ e^{i\vec{k}\cdot\vec{r}_1} \overline{\Phi(\vec{r}_1)}}_{=\overline{\Phi(-k)}}\, \Phi(\vec{k}\,)\, \frac{4\pi}{k^2} && (19) \\ &= \frac{1}{(2\pi)^3} \int d^3k\ |\Phi(\vec{k}\,)|^2\, \frac{4\pi}{k^2} > 0 && (20) \end{aligned}$$

Thus the triplet states are below the singlet state by an energy $2J_{ab}$. If the φ_α are degenerate atomic orbitals, this is an example of Hund's first rule: For an atomic shell, the lowest state will have maximum spin.

Since H_U only contains interactions within the system of electrons, it commutes with the total orbital momentum $[H_U, \vec{L}_{\text{tot}}] = 0$. Obviously it also commutes with the total spin $\vec{S}_{\text{tot}}$. The

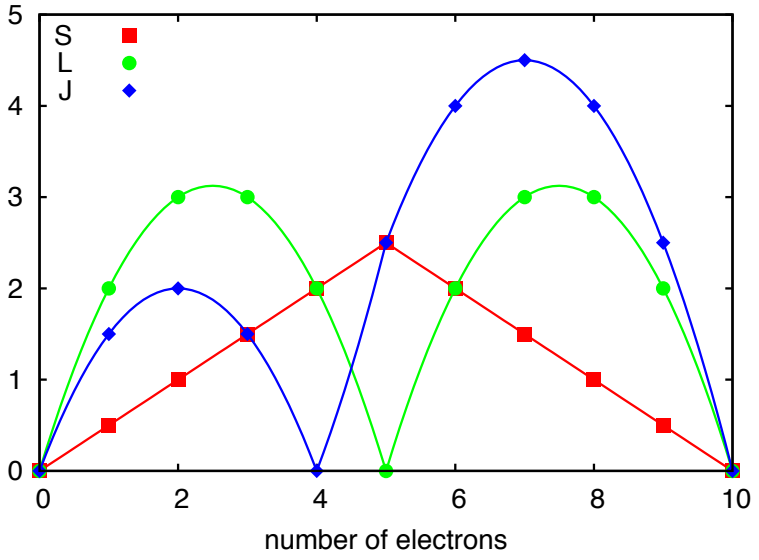


Fig. 1: *Angular momenta of the Hund's rules ground state* $^{2S+1}L_J$ *for* d*-shells.*

eigenstates of $H_0 + H_U$ can thus be classified by their quantum numbers L and S. These terms are written as ^{2S+1}L. For p- and d-shells they are listed in table 1. Hund's rules give the multiplet term with the lowest energy: For a given shell, this lowest state has the largest possible spin (Hund's first rule). If there are several terms of maximum multiplicity, the one with lowest energy has the largest total orbital momentum (Hund's second rule). There is a third Hund's rule, which, however, is not related with the electron-electron repulsion but with spin-orbit coupling: Within L-S coupling H_{SO} splits the atomic orbitals into eigenstates of the total angular momentum $\vec{J} = \vec{L}_{\text{tot}} + \vec{S}_{\text{tot}}$. The multiplets ^{2S+1}L thus split into $^{2S+1}L_J$. The term with the lowest energy is the one with smallest J if the shell is less than half-filled and largest J if it is more than half-filled (Hund's third rule). These rules are illustrated for d-shells in Fig. 2. A more detailed discussion of multiplet effects and the Coulomb interaction in atomic-like systems is given in the lecture of R. Eder and in [5,6]

s				^{2}**S**						
p^1 or p^5				^{2}**P**						
p^2 or p^4		^1S	^1D				^{3}**P**			
p^3				^2P	^2D			^{4}**S**		
d^1 or d^9				^{2}**D**						
d^2 or d^8		^1S	^1D	^1G			^3P	^{3}**F**		
d^3 or d^7				^2P	$^{2\times}{}^2D$	^2F	^2G	^2H	^4P	^{4}**F**
d^4 or d^6	$^{2\times}{}^1S$	$^{2\times}{}^1D$	^1F	$^{2\times}{}^1G$	^1I	$^{2\times}{}^3P$	^3D	$^{2\times}{}^3F$	^3G	^3H	^{5}**D**
d^5			^2S	^2P	$^{3\times}{}^2D$	$^{2\times}{}^2F$	$^{2\times}{}^2G$	^2H	^2I	^4P ^4D ^4F ^4G ^{6}**S**

Table 1: *Atomic multiplets for open* s*-,* p*-, and* d*-shells. For terms that appear multiple times the number of distinct terms is indicated. The Hund's rules ground state is indicated in bold.*

3 Kinetic exchange

When electron-hopping plays the main role in the exchange mechanism, we speak of kinetic exchange. In contrast to Coulomb exchange the resulting interactions are usually antiferromagnetic, i.e., they prefer antiparallel spins. The physical principle of kinetic exchange can be understood in a simple two-site system. We discuss this problem in some detail and introduce two key concept along the way: downfolding and second quantization. More realistic exchange mechanisms are then natural generalizations of this simple mechanism [7–9].

3.1 A toy model

As a toy model, we consider the minimal model of an H_2 molecule. We restrict ourselves to two (orthogonal) orbitals, φ_1 and φ_2, separated by some distance. If we add an electron to the system, that electron will be able to move between the two orbitals, with a matrix element $-t$. Because we allow the electron to only occupy two s-orbitals, the Hamiltonian is a 2×2 matrix

$$H = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix} . \tag{21}$$

This tight-binding Hamiltonian is easily diagonalized giving the linear combinations

$$\varphi_\pm = \frac{1}{\sqrt{2}} \Big(\varphi_1 \pm \varphi_2 \Big) \tag{22}$$

as eigenstates with eigenenergies $\varepsilon_\pm = \mp t$. We have written the hopping matrix element as $-t$, so that for $t > 0$ the state without a node, φ_+, is the ground state.
Pictorially we can write the basis states by specifying which orbital the electron occupies. For a spin-up electron we then write

$$\varphi_1 = |\uparrow , \cdot \rangle \qquad \text{and} \qquad \varphi_2 = | \cdot , \uparrow \rangle \tag{23}$$

where we now represent the basis states by where the electron is located.
If there are two electrons in the system, i.e., one electron per orbital, we can again use basis states which just specify, which orbitals the electrons occupy. For two electrons of opposite spin we then find two states where the electrons are in different orbitals

$$|\uparrow , \downarrow \rangle \qquad |\downarrow , \uparrow \rangle \qquad \text{“covalent states”}$$

and two states where the electrons are in the same orbital

$$|\updownarrow , \cdot \rangle \qquad | \cdot , \updownarrow \rangle \qquad \text{“ionic states”.}$$

In this basis the Hamiltonian matrix for our simple model of the H_2 molecule has the form

$$H = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & +t & +t \\ -t & +t & U & 0 \\ -t & +t & 0 & U \end{pmatrix} \qquad \begin{matrix} |\uparrow , \downarrow \rangle \\ |\downarrow , \uparrow \rangle \\ |\updownarrow , \cdot \rangle \\ | \cdot , \updownarrow \rangle \end{matrix} \tag{24}$$

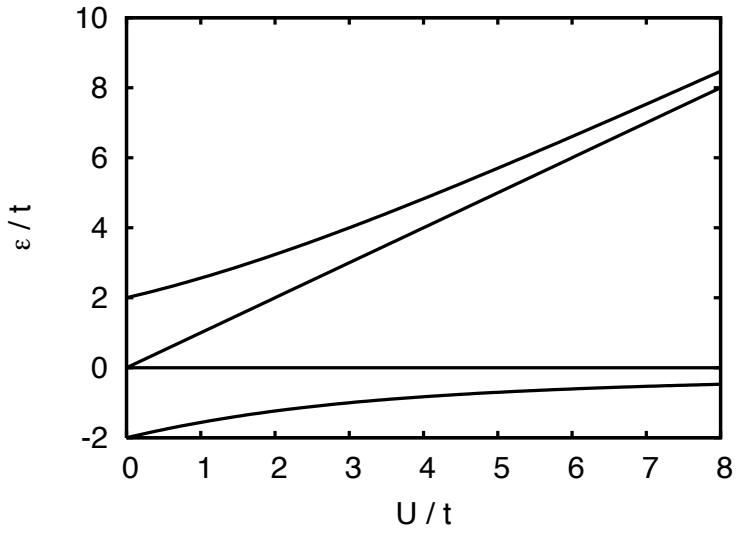


Fig. 2: *Spectrum of the two-site Hubbard model as a function of U. For large U there are two levels with energy close to zero. Their energy difference corresponds to the exchange energy. The remaining two states with ionic character have an energy roughly proportional to U.*

As before, moving an electron to a neighboring orbital gives a matrix element $-t$, with an additional sign when the order of the electrons is changed (Fermi statistics!). For the ionic states, where both electrons are in the same orbital, we have the Coulomb matrix element U. Coulomb matrix elements involving electrons on different sites are, for reasonably large distance between the sites, negligible. So there is no Coulomb exchange, just the local Coulomb repulsion in our model. Diagonalizing H we find the energy spectrum and the corresponding eigenstates:

$$\varepsilon_\pm = \frac{U}{2} \pm \frac{\sqrt{U^2+16\,t^2}}{2} \quad , \quad \Psi_\pm = \frac{\Big(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle - \frac{\varepsilon_\pm}{2t}\big[\,|\!\updownarrow,\cdot\,\rangle + |\,\cdot,\!\updownarrow\rangle\,\big]\Big)}{\sqrt{2+\varepsilon_\pm^2/(2t^2)}}$$

$$\varepsilon_{\rm cov} = 0 \quad , \quad \Psi_{\rm cov} = \frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\Big)$$

$$\varepsilon_{\rm ion} = U \quad , \quad \Psi_{\rm ion} = \frac{1}{\sqrt{2}}\Big(|\!\updownarrow,\cdot\,\rangle - |\,\cdot,\!\updownarrow\rangle\Big)$$

The eigenenergies as a function of U are shown in figure 2.

3.2 Direct exchange

Again, we have found that the energy of two-electron states depends on the relative spin of the electrons. To understand this more clearly we analyze the limit when U is much larger than t. From Fig. 2 we see that there are two states with energies that increase with U. They are the states $\Psi_{\rm ion}$ and Ψ_+ that have considerable contributions of the ionic states. Then there are two states whose energy is close to zero. They are the states that have mainly covalent character. To find the energy and the character of these levels in the limit $U \to \infty$ we can just expand $\varepsilon_- \to -4t^2/U$ and $\varepsilon_+ \to U + 4t^2/U$. We thus see that while the purely covalent state, the spin-triplet state $\Psi_{\rm cov}$, is independent of U, Ψ_- has a slightly lower energy due to some small

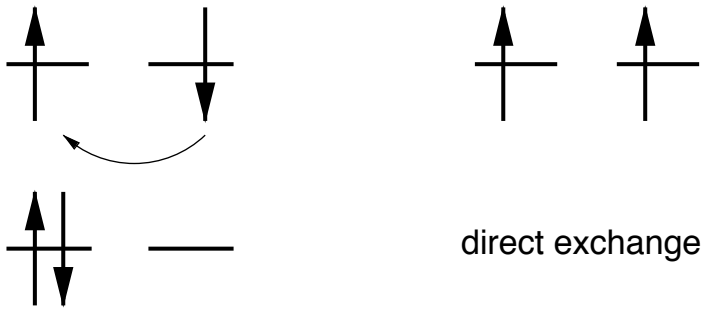


Fig. 3: *Simple picture of direct exchange: The antiparallel alignment of the spins (left) is favored, since it allows the electrons to hop to the neighboring site. For parallel spins (right) hopping is suppressed by the Pauli principle.*

admixture of the ionic states. In the limit $U \to \infty$ it becomes the maximally entangled state $(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle)/\sqrt{2}$. We see that for large U, Ψ_- cannot be expressed, even approximately, as a Slater determinant, see also Sec. 3.4. This is the reason why strongly correlated systems are so difficult to describe.

A more instructive method to analyze the large-U limit, which can readily be generalized to more complex situations, where we can no longer diagonalize the full Hamiltonian, is the downfolding technique. The mathematical background is explained in the appendix. The idea of downfolding is to partition the Hilbert space into parts that are of interest, here the low-energy convalent type states, and states that should be projected out, here the high-energy ionic states. With this partitioning we can view the Hamitonian matrix (24) as built of 2×2 submatrices. Calculating the inverse on the space of covalent states (see Eqn. (84) in the appendix) we find an *effective Hamiltonian* which now operates on the covalent states only:

$$H_{\text{eff}}(\varepsilon) = \begin{pmatrix} -t & -t \\ +t & +t \end{pmatrix} \begin{pmatrix} \varepsilon - U & 0 \\ 0 & \varepsilon - U \end{pmatrix}^{-1} \begin{pmatrix} -t & +t \\ -t & +t \end{pmatrix} \approx -\frac{2t^2}{U} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \qquad (25)$$

In the last step we have made an approximation by setting ε to zero, which is roughly the energy of the states with covalent character.

The process of eliminating the ionic states thus gives rise to an effective interaction between the covalent states, which was not present in the original Hamiltonian (24). Diagonalizing the effective Hamiltonian, we find

$$\varepsilon_s = -\frac{4t^2}{U} \quad , \qquad \Psi_s = \frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\Big)$$
$$\varepsilon_t = 0 \qquad , \qquad \Psi_t = \frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\Big)$$

These states correspond to the singlet and triplet states in the hydrogen molecule. Here the singlet-triplett splitting is $J = -4t^2/U$. The other states in the triplet are those with two electrons of parallel spin: $|\uparrow,\uparrow\rangle$ and $|\downarrow,\downarrow\rangle$. They, of course, also have energy zero, as hopping is impossible due to the Pauli principle.

To understand the nature of the effective interaction in the low-energy Hamiltonian we observe that the off-diagonal matrix elements in (25) correspond to flipping the spin of both electrons ("exchange"). Remembering that

$$\vec{S}_1 \cdot \vec{S}_2 = S_1^z S_2^z + \frac{1}{2}\Big(S_1^+ S_2^- + S_1^- S_2^+\Big) \tag{26}$$

we see that the effective interaction will contain a spin-spin coupling term.

3.3 Second quantization for pedestrians

A more systematic way for obtaining the form of the effective interaction is by using second quantization, which will also help us simplify our notation. In second quantization we use operators to specify in which orbital an electron is located. As an example, $c^\dagger_{1,\uparrow}$ puts a spin-up electron in orbital φ_1. Denoting the system with no electrons by $|0\rangle$, the basis states that we have considered so far are written as

$$\begin{aligned} |\uparrow,\cdot\rangle &= c^\dagger_{1\uparrow}|0\rangle \\ |\cdot,\uparrow\rangle &= c^\dagger_{2\uparrow}|0\rangle \end{aligned}$$

for the single-electron states, and

$$\begin{aligned} |\uparrow,\downarrow\rangle &= c^\dagger_{2\downarrow}c^\dagger_{1\uparrow}|0\rangle \\ |\downarrow,\uparrow\rangle &= c^\dagger_{2\uparrow}c^\dagger_{1\downarrow}|0\rangle \\ |\updownarrow,\cdot\rangle &= c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}|0\rangle \\ |\cdot,\updownarrow\rangle &= c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}|0\rangle \end{aligned} \tag{27}$$

for the two-electron states. In order to describe the hopping of an electron from one orbital to another, we introduce operators that annihilate an electron. For example $c_{1\uparrow}$ removes a spin-up electron from orbital φ_1. The hopping of an up electron from φ_1 to φ_2 is thus described by the operator $c^\dagger_{2\uparrow}c_{1\uparrow}$ that first takes an electron out of orbital 1 and then creates one in orbital 2. The Hamiltonian for a spin-up electron hopping between two orbitals can thus be written as

$$H = -t\Big(c^\dagger_{1\uparrow}c_{2\uparrow} + c^\dagger_{2\uparrow}c_{1\uparrow}\Big)\,. \tag{28}$$

Calculating the matrix elements with the single-electron basis states, we recover the matrix (21). For the calculation we need to know that the operators that describe the electrons *anticommute*. This reflects the fact that a many-electron wave function changes sign when two electrons are exchanged. Using the notation $\{a,b\} = ab + ba$ we have

$$\Big\{c_{i\sigma},\, c_{j\sigma'}\Big\} = 0 \qquad \Big\{c^\dagger_{i\sigma},\, c^\dagger_{j\sigma'}\Big\} = 0 \qquad \Big\{c_{i\sigma},\, c^\dagger_{j\sigma'}\Big\} = \delta_{i,j}\delta_{\sigma,\sigma'}$$

Moreover, trying to annihilate an electron in a state where there is no electron, results in zero: $c_{i\sigma}|0\rangle = 0$. Finally, as the notation implies, $c^\dagger_{i\sigma}$ is the adjoint of $c_{i\sigma}$ and $\langle 0|0\rangle = 1$.

To describe the Coulomb repulsion between two electrons in the same orbital we use that $n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}$ returns 0 when operating on a basis state with no spin-σ electron in orbital φ_i, and has eigenvalue 1 for a basis state with a spin-σ electron in orbital φ_i. It is thus called the occupation-number operator. The Coulomb repulsion in orbital φ_1 is then described by the operator $U n_{1\uparrow} n_{1\downarrow}$, which is non-zero only when there is a spin-up *and* a spin-down electron in φ_1. The Hamiltonian for our two-orbital model, where both up- and down-spin electrons can hop, and including the Coulomb repulsion for two electrons in the same orbital, is thus given by

$$\begin{aligned} H &= -t\left(c^\dagger_{1\uparrow}c_{2\uparrow} + c^\dagger_{2\uparrow}c_{1\uparrow} + c^\dagger_{1\downarrow}c_{2\downarrow} + c^\dagger_{2\downarrow}c_{1\downarrow}\right) + U\left(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow}\right) \\ &= -t\sum_{i,j,\sigma} c^\dagger_{j\sigma}c_{i\sigma} + U\sum_i n_{i\uparrow}n_{i\downarrow}\ . \end{aligned} \tag{29}$$

You should convince yourself that when you calculate the matrix elements for the two-electron states, you recover the matrix (24). The great advantage of writing the Hamiltonian in second-quantized form is that it is valid for any number of electrons, while the matrix form is restricted to a particular number of electrons.

Coming back to the effective Hamiltonian (25), we can rewrite H_{eff} in second quantized form:

$$\begin{aligned} H_{\text{eff}} &= -\frac{2t^2}{U}\left(c^\dagger_{2\uparrow}c^\dagger_{1\downarrow}c_{1\downarrow}c_{2\uparrow} - c^\dagger_{2\downarrow}c^\dagger_{1\uparrow}c_{1\downarrow}c_{2\uparrow} - c^\dagger_{2\uparrow}c^\dagger_{1\downarrow}c_{1\uparrow}c_{2\downarrow} + c^\dagger_{2\downarrow}c^\dagger_{1\uparrow}c_{1\uparrow}c_{2\downarrow}\right) \\ &= -\frac{2t^2}{U}\left(c^\dagger_{1\downarrow}c_{1\downarrow}c^\dagger_{2\uparrow}c_{2\uparrow} - c^\dagger_{1\uparrow}c_{1\downarrow}c^\dagger_{2\downarrow}c_{2\uparrow} - c^\dagger_{1\downarrow}c_{1\uparrow}c^\dagger_{2\uparrow}c_{2\downarrow} + c^\dagger_{1\uparrow}c_{1\uparrow}c^\dagger_{2\downarrow}c_{2\downarrow}\right) \end{aligned} \tag{30}$$

Looking at equation (89) in the appendix we see that the spin operators are given in second quantization by

$$S^x_i = \frac{1}{2}\left(c^\dagger_{i\uparrow}c_{i\downarrow} + c^\dagger_{i\downarrow}c_{i\uparrow}\right) \qquad S^y_i = -\frac{i}{2}\left(c^\dagger_{i\uparrow}c_{i\downarrow} - c^\dagger_{i\downarrow}c_{i\uparrow}\right) \qquad S^z_i = \frac{1}{2}\left(n_{i\uparrow} - n_{i\downarrow}\right). \tag{31}$$

From this we find (after some calculation) that the effective Hamiltonian can be written in terms of the spin operators

$$H_{\text{eff}} = \frac{4t^2}{U}\left(\vec{S}_1 \cdot \vec{S}_2 - \frac{n_1\, n_2}{4}\right). \tag{32}$$

To conclude, we again find that the completely spin-independent Hamiltonian (29), in the limit of large U, gives rise to a spin-spin interaction. Since the exchange coupling $J = 4t^2/U$ is positive, states with antiparallel spins have lower energy. Thus direct exchange leads to *antiferromagnetism*.

It is important to realize that the singlet-triplet splitting for the effective Hamiltonian really arises from the admixture of ionic states into the singlet. By downfolding we eliminate the high-energy ionic states, i.e., charge fluctuations, from our Hilbert space. The eliminated states then give rise to an effective spin-spin interaction on the new reduced low-energy Hilbert space. We must therefore keep in mind that, when working with the effective Hamiltonian (32), we are considering slightly different states than when working with the original Hamiltonian (29).

3.4 Mean-field treatment

To conclude our discussion of the simplest kinetic exchange mechanism, it is instructive to consider the results of a mean-field treatment. For the two-electron Hamiltonian (24) it is straightforward to find the Hartree-Fock solution by directly minimizing the energy expectation value for a two-electron Slater determinant. The most general ansatz is a Slater determinant constructed from an orbital $\varphi(\theta_\uparrow) = \sin(\theta_\uparrow)\,\varphi_1 + \cos(\theta_\uparrow)\,\varphi_2$ for the spin-up, and $\varphi(\theta_\downarrow) = \sin(\theta_\downarrow)\,\varphi_1 + \cos(\theta_\downarrow)\,\varphi_2$ for the spin-down electron:

$$|\Psi(\theta_\uparrow,\theta_\downarrow)\rangle = \left(\sin(\theta_\downarrow)\,c^\dagger_{1\downarrow} + \cos(\theta_\downarrow)\,c^\dagger_{2\downarrow}\right)\,\left(\sin(\theta_\uparrow)\,c^\dagger_{1\uparrow} + \cos(\theta_\uparrow)\,c^\dagger_{2\uparrow}\right)\,|0\rangle\ . \tag{33}$$

Translating the second quantized states via (27) into the basis used for writing the Hamiltonian matrix (24), we find the expectation value

$$\begin{aligned}\langle\Psi(\theta_\uparrow,\theta_\downarrow)|H|\Psi(\theta_\uparrow,\theta_\downarrow)\rangle \;=\;& -2t\,(\sin\theta_\uparrow\sin\theta_\downarrow + \cos\theta_\uparrow\cos\theta_\downarrow)\,(\cos\theta_\uparrow\sin\theta_\downarrow + \sin\theta_\uparrow\cos\theta_\downarrow)\\ & +U\left(\sin^2\theta_\uparrow\sin^2\theta_\downarrow + \cos^2\theta_\uparrow\cos^2\theta_\downarrow\right)\ .\end{aligned} \tag{34}$$

If the Slater determinant respects the symmetry of the molecule under the exchange of sites (mirror symmetry of the H_2 molecule), it follows that the Hartree-Fock orbitals for both spins are the bonding state φ_+ ($\theta = \pi/4$). This is the *restricted Hartree-Fock* solution. The corresponding energy is $E(\pi/4,\pi/4) = -2t + U/2$. The excited states are obtained by replacing occupied orbitals φ_+ with φ_-. Alltogether we obtain the restricted Hartree-Fock spectrum

$$\begin{aligned} E(\ \ \pi/4,\ \ \pi/4) &= -2t + U/2\\ E(\ \ \pi/4,-\pi/4) &= \qquad U/2\\ E(-\pi/4,\ \ \pi/4) &= \qquad U/2\\ E(-\pi/4,-\pi/4) &= \ \ 2t + U/2 \end{aligned} \tag{35}$$

Comparing to the energy for a state with both electrons of the same spin ($E = 0$), we see that there is no spin-triplet, i.e., Hartree-Fock breaks the spin symmetry. The states (35) are *spin-contaminated* [10]. Even worse, the Hartree-Fock ground state, and consequently all the states, are independent of U. The weight of the ionic states is always $1/2$, leading to an increase of the energy with $U/2$.

To avoid this, we can allow the Hartree-Fock solution to break the symmetry of the molecule (*unrestricted Hartree-Fock*), putting, e.g., more of the up-spin electron in the orbital on site 1 and more of the down-spin electron in orbital 2. For $U < 2t$ this does not lead to a state of lower energy. For larger U there is a symmetry-broken ground state

$$\Psi_{UHF} = \Psi(\theta,\pi/2-\theta)\ \text{ with }\quad \theta(U) = \frac{\pi}{4} \pm \frac{1}{2}\arccos\left(\frac{2t}{U}\right)\ . \tag{36}$$

Its energy is $E_{UHF} = -2t^2/U$. This looks similar to the singlet energy ε_s, however, with a different prefactor. Still there is no triplet state (spin contamination) and, for $U \to \infty$, the overlap with the true singlet ground state goes to $|\langle\Psi_{UHF}|\Psi_-\rangle|^2 = 1/2$. In an extended system the breaking of the symmetry implies long-range order.

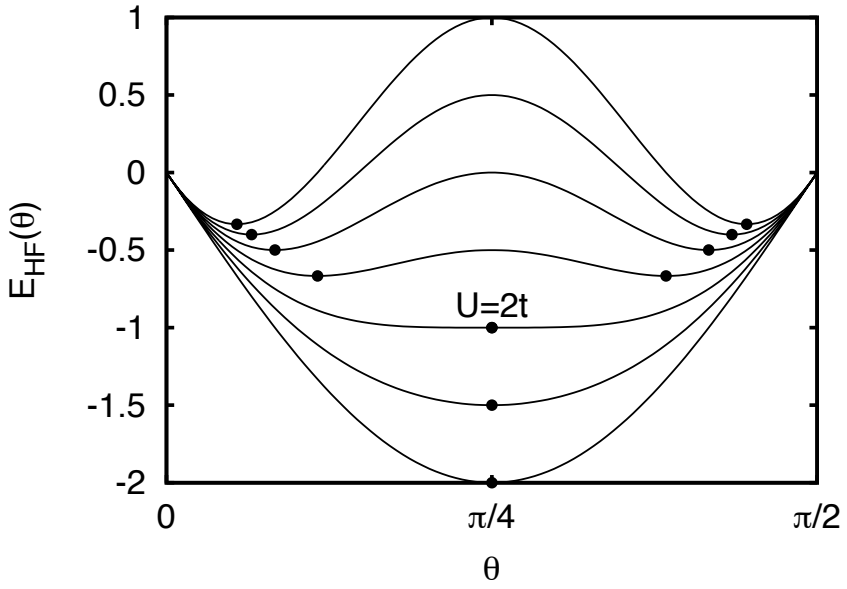


Fig. 4: *Energy expectation value for a Slater determinant $\Psi(\theta, \pi/2-\theta)$ for $U=0,\ t,\ 2t,\ \ldots,\ 6t$. When $U \leq 2t$ the minimum is at $\theta = \pi/4$. This is the Hartree-Fock solution with the bonding orbitals φ_+ occupied. For $U \geq 2t$, $\theta = \pi/4$ is still an extremal point (restricted Hartree-Fock solution), but an energy minimum is only attained when the symmetry is broken (unrestricted Hartree-Fock solution).*

3.5 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, shown in figure 5, 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 $c^\dagger_{i\sigma}$, 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 (see figure 5). Likewise $c^\dagger_{p\sigma}$ 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 of figure 5 is then given by

$$H = \sum_\sigma \left(\varepsilon_d \sum_i n_{i\sigma} + \varepsilon_p \, n_{p\sigma} - t_{pd} \sum_i \left(c^\dagger_{i\sigma} c_{p\sigma} + c^\dagger_{p\sigma} c_{i\sigma} \right) \right) + U_d \sum_i n_{i\uparrow} n_{i\downarrow} \, . \qquad (37)$$

In the absence of hopping, the ground state will have singly occupied d-orbitals, corresponding

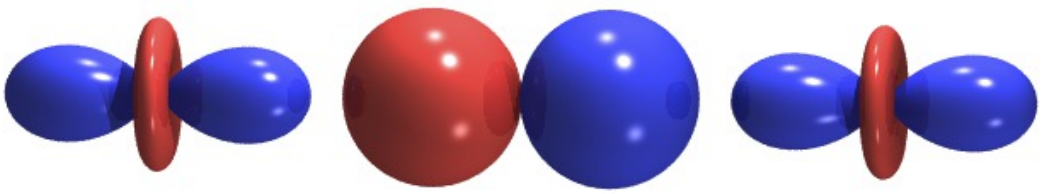


Fig. 5: *In superexchange an oxygen p-orbital mediates the exchange interaction between two transition-metal d-orbitals.*

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 (see the far right of Fig. 6). The Hamiltonian matrix in the corresponding Hilbert space is then given by

$$H = \left(\begin{array}{c|cc} 0 & t_{pd} & t_{pd} \\ \hline t_{pd} & U_d + \Delta_{pd} & 0 \\ t_{pd} & 0 & U_d + \Delta_{pd} \end{array}\right) \begin{array}{l} c^\dagger_{2\uparrow} c^\dagger_{p\downarrow} c^\dagger_{p\uparrow} c^\dagger_{1\uparrow} |0\rangle \\ c^\dagger_{2\uparrow} c^\dagger_{p\uparrow} c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} |0\rangle \\ c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} c^\dagger_{p\uparrow} c^\dagger_{1\uparrow} |0\rangle \end{array} \tag{38}$$

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

$$H_{\text{eff}} = (t_{pd}, t_{pd}) \begin{pmatrix} \varepsilon - (U_d + \Delta_{pd}) & 0 \\ 0 & \varepsilon - (U_d + \Delta_{pd}) \end{pmatrix} \begin{pmatrix} t_{pd} \\ t_{pd} \end{pmatrix} \approx -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} \tag{39}$$

where in the last step we have set ε to zero.

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 transfered 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

$$\left(\begin{array}{cc|cccc|ccc} 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & +t_{pd} & +t_{pd} & 0 & 0 & 0 \\ \hline +t_{pd} & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & -t_{pd} & 0 & -t_{pd} \\ +t_{pd} & 0 & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & -t_{pd} & -t_{pd} \\ 0 & +t_{pd} & 0 & 0 & U_d + \Delta_{pd} & 0 & +t_{pd} & 0 & +t_{pd} \\ 0 & +t_{pd} & 0 & 0 & 0 & U_d + \Delta_{pd} & 0 & +t_{pd} & +t_{pd} \\ \hline 0 & 0 & -t_{pd} & 0 & +t_{pd} & 0 & U_d & 0 & 0 \\ 0 & 0 & 0 & -t_{pd} & 0 & +t_{pd} & 0 & U_d & 0 \\ 0 & 0 & -t_{pd} & -t_{pd} & +t_{pd} & +t_{pd} & 0 & 0 & 2(U_d + \Delta_{pd}) \end{array}\right) \begin{array}{l} c^\dagger_{2\downarrow} c^\dagger_{p\downarrow} c^\dagger_{p\uparrow} c^\dagger_{1\uparrow} |0\rangle \\ c^\dagger_{2\uparrow} c^\dagger_{p\downarrow} c^\dagger_{p\uparrow} c^\dagger_{1\downarrow} |0\rangle \\ c^\dagger_{2\downarrow} c^\dagger_{p\uparrow} c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} |0\rangle \\ c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} c^\dagger_{p\downarrow} c^\dagger_{1\uparrow} |0\rangle \\ c^\dagger_{2\uparrow} c^\dagger_{p\downarrow} c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} |0\rangle \\ c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} c^\dagger_{p\uparrow} c^\dagger_{1\downarrow} |0\rangle \\ c^\dagger_{p\downarrow} c^\dagger_{p\uparrow} c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} |0\rangle \\ c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} c^\dagger_{p\downarrow} c^\dagger_{p\uparrow} |0\rangle \\ c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} |0\rangle \end{array}$$

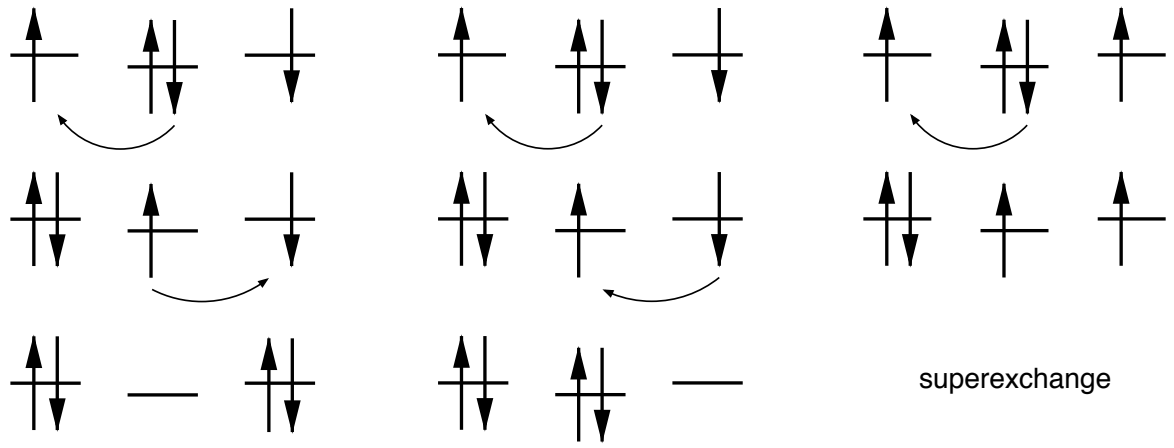


Fig. 6: *Simple picture of superexchange. Here the orbital on the central site is different from the orbitals on the sides. Typically, in the center there is a oxygen p-orbital coupling two d-orbitals. This situation is illustrated in Fig. 5. For antiparallel spins on the d-orbitals there are two ways that two consecutive hopping processes are possible. For parallel spins the Pauli principle suppresses the second hopping process.*

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

$$\begin{aligned} H_{\text{eff}} &= H_{00} + T_{01}\left(\varepsilon - \left(H_{11} + T_{12}\left(\varepsilon - H_{22}\right)^{-1} T_{21}\right)\right)^{-1} T_{10} \\ &\approx H_{00} - T_{01}H_{11}^{-1}T_{10} - T_{01}H_{11}^{-1}T_{12}H_{22}^{-1}T_{21}H_{11}^{-1}T_{10} \qquad (40) \\ &= -\frac{2t_{pd}^2}{U_d + \Delta_{pd}}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{2t_{pd}^4}{(U_d + \Delta_{pd})^2}\left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}}\right)\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \qquad (41) \end{aligned}$$

The first term is the same as for parallel spins (39). 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

$$J = \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2}\left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}}\right), \qquad (42)$$

which reflects that the superexchange mechanism involves four hopping processes (see Fig. 6), while direct exchange only involves two hoppings (see Fig. 3). The hopping process involving only a single doubly occupied d-orbital (middle of Fig. 6) 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, $4t_{\text{eff}}^2/U_d$, in (42), while the hopping process involving two occupied d-orbitals (left in Fig. 6) gives the second term $4t_{pd}^4/(U_d + \Delta_{pd})^3$.

3.6 Ferromagnetic superexchange

In the discussion of superexchange we have, so far, assumed that the oxygen ion lies between the two d-orbitals. This 180^o geometry is shown on the left of Fig. 7. The situation is quite different, when the oxygen forms a 90^o bridge between the two d-orbitals, see the right of Fig. 7. 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.:

$$H_1 = \begin{pmatrix} 0 & +t_{pd} \\ +t_{pd} & U_d + \Delta_{pd} \end{pmatrix} \qquad \begin{matrix} c^\dagger_{x\downarrow} c^\dagger_{x\uparrow} c^\dagger_{1\downarrow} |0\rangle \\ c^\dagger_{x\downarrow} c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} |0\rangle \end{matrix} \tag{43}$$

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

$$\left(\begin{array}{c|cc|c} 0 & t_{pd} & t_{pd} & 0 \\ \hline t_{pd} & U_d + \Delta_{pd} & 0 & t_{pd} \\ t_{pd} & 0 & U_d + \Delta_{pd} & t_{pd} \\ \hline 0 & t_{pd} & t_{pd} & 2(U_d + \Delta_{pd}) - J_{xy} \end{array}\right) \qquad \begin{matrix} c^\dagger_{1\uparrow} c^\dagger_{x\downarrow} c^\dagger_{x\uparrow} c^\dagger_{y\downarrow} c^\dagger_{y\uparrow} c^\dagger_{2\uparrow} |0\rangle \\ c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} c^\dagger_{x\uparrow} c^\dagger_{y\downarrow} c^\dagger_{y\uparrow} c^\dagger_{2\uparrow} |0\rangle \\ c^\dagger_{1\uparrow} c^\dagger_{x\downarrow} c^\dagger_{x\uparrow} c^\dagger_{y\uparrow} c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} |0\rangle \\ c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} c^\dagger_{x\uparrow} c^\dagger_{y\uparrow} c^\dagger_{2\downarrow} c^\dagger_{2\downarrow} |0\rangle \end{matrix} . \tag{44}$$

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 – the situation discussed in Sec. 2. Calculating the effective Hamiltonian as in (40) gives the energy of the triplet state

$$H_{\text{eff}} = -\frac{2t_{pd}^2}{U_d + \Delta_{pd}} - \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \frac{1}{2(U_d + \Delta_{pd}) - J_{xy}} . \tag{45}$$

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

$$\left(\begin{array}{cc|cccc|cc} 0 & 0 & t_{pd} & 0 & t_{pd} & 0 & 0 & 0 \\ 0 & 0 & 0 & t_{pd} & 0 & t_{pd} & 0 & 0 \\ \hline t_{pd} & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & t_{pd} & 0 \\ 0 & t_{pd} & 0 & U_d + \Delta_{pd} & 0 & 0 & 0 & t_{pd} \\ t_{pd} & 0 & 0 & 0 & U_d + \Delta_{pd} & 0 & t_{pd} & 0 \\ 0 & t_{pd} & 0 & 0 & 0 & U_d + \Delta_{pd} & 0 & t_{pd} \\ \hline 0 & 0 & t_{pd} & 0 & t_{pd} & 0 & 2(U_d + \Delta_{pd}) & -J_{xy} \\ 0 & 0 & 0 & t_{pd} & 0 & t_{pd} & -J_{xy} & 2(U_d + \Delta_{pd}) \end{array}\right) \qquad \begin{matrix} c^\dagger_{1\uparrow} c^\dagger_{x\downarrow} c^\dagger_{x\uparrow} c^\dagger_{y\downarrow} c^\dagger_{y\uparrow} c^\dagger_{2\downarrow} |0\rangle \\ c^\dagger_{1\downarrow} c^\dagger_{x\downarrow} c^\dagger_{x\uparrow} c^\dagger_{y\downarrow} c^\dagger_{y\uparrow} c^\dagger_{2\uparrow} |0\rangle \\ c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} c^\dagger_{x\uparrow} c^\dagger_{y\downarrow} c^\dagger_{y\uparrow} c^\dagger_{2\downarrow} |0\rangle \\ c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} c^\dagger_{x\downarrow} c^\dagger_{y\downarrow} c^\dagger_{y\uparrow} c^\dagger_{2\uparrow} |0\rangle \\ c^\dagger_{1\uparrow} c^\dagger_{x\downarrow} c^\dagger_{x\uparrow} c^\dagger_{y\downarrow} c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} |0\rangle \\ c^\dagger_{1\downarrow} c^\dagger_{x\downarrow} c^\dagger_{x\uparrow} c^\dagger_{y\uparrow} c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} |0\rangle \\ c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} c^\dagger_{x\uparrow} c^\dagger_{y\downarrow} c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} |0\rangle \\ c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} c^\dagger_{x\downarrow} c^\dagger_{y\uparrow} c^\dagger_{2\downarrow} c^\dagger_{2\uparrow} |0\rangle \end{matrix}$$

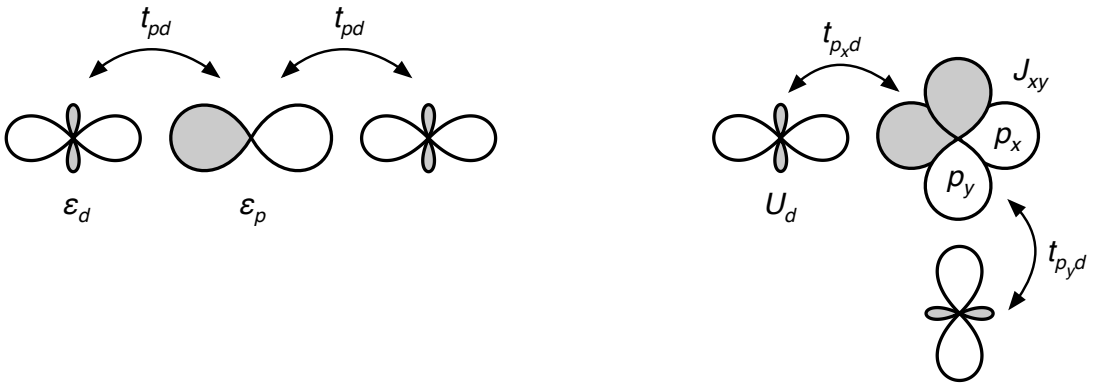


Fig. 7: *Dependence of superexchange on geometry: When the d-orbitals interact via an oxygen in-between (the 180^o geometry shown on the left), both d-orbitals couple to the same p-orbital, while the hopping to the two other p-orbitals vanishes by symmetry. The result is antiferromagnetic superexchange. When the angle of the M-O-M group is 90^o (right), the d-orbitals couple to orthogonal p-orbitals, making it impossible for an electron on one d-orbital to reach the d-orbital on the other site. In this case, superexchange is mediated via the Coulomb exchange on the connecting oxygen.*

giving the effective Hamiltonian

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

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

$$\begin{aligned} H_{\text{eff}} = &-\left(\frac{2t_{pd}^2}{U_d+\Delta_{pd}} + \frac{4t_{pd}^4}{(U_d+\Delta_{pd})^2}\frac{1}{2(U_d+\Delta_{pd})-J_{xy}}\right) \\ &+ \frac{4t_{pd}^4}{(U_d+\Delta_{pd})^2}\frac{J_{xy}}{4(U_d+\Delta_{pd})^2-J_{xy}^2}\begin{pmatrix}1&-1\\-1&1\end{pmatrix}. \end{aligned} \tag{46}$$

The first term is just the energy of the triplet state (45). 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 (see Eqn. (15)). 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

$$J = -\frac{4t_{pd}^4}{(U_d+\Delta_{pd})^2}\frac{2J_{xy}}{4(U_d+\Delta_{pd})^2-J_{xy}^2}. \tag{47}$$

It tends to be significantly weaker than the antiferromagnetic 180^o superexchange coupling (42). When the angle of the M-O-M group is larger than 90^o, hopping to both p-orbitals becomes possible according to the Slater-Koster rules and the antiferromagnetic superexchange processes of Fig. 6 start to compete with the ferromagnetic superexchange mediated by the Coulomb exchange on the oxygen. This is one basis of the Goodenough-Kanamori rules [7, 11].

4 Double exchange

Double exchange takes its name from the fact that it results from a combination of Coulomb- and kinetic-exchange. In that sense the 90^o superexchange mechanism discussed above is a double exchange mechanism. More commonly, double exchange is encountered in mixed-valence compounds. So far we have considered systems with an integer number of electrons per site. When correlations are strong the lowest energy state will essentially have the same number of electrons on every site and hopping will be strongly suppressed by the Coulomb repulsion energy U as we have seen for the simple two-site model of kinetic exchange. In a mixed valence system the number of electrons per site is non-integer, so even for large U some site will have more electrons than others. Thus electrons can hop between such sites without incurring a cost U. Hence these compounds are usually metallic.
As a simple example we consider two sites with two orbitals of the type discussed in Sec. 2. We assume that each site has one electron in orbital a, and that there is only a single electron in the b-orbitals. This electron can hop between the sites via a hopping matrix element t_{bb}. The situation is illustrated in Fig. 8.
When all three spins are up, $S^z_{\rm tot} = 3/2$, we have a simple 2×2 Hamiltonian, taking U_{ab} as our zero of energy

$$H = \begin{pmatrix} -J_{ab} & -t_{bb} \\ -t_{bb} & -J_{ab} \end{pmatrix} . \tag{48}$$

The eigenstates are the bonding/antibonding linear combinations of the Hund's rule triplets. Their dispersion is $\pm t$:

$$\varepsilon_\pm = -J_{ab} \pm t_{bb} . \tag{49}$$

We see that the hopping couples the two sites into a state with the electrons in the a-orbital in a triplet state:

$$\Psi_\pm = \frac{1}{\sqrt{2}}\Big(|\uparrow,\uparrow\rangle_1 \,|\cdot,\uparrow\rangle_2 \pm |\cdot,\uparrow\rangle_1 \,|\uparrow,\uparrow\rangle_2\Big) = \frac{1}{\sqrt{2}}\Big(|\uparrow,\cdot\rangle_b \pm |\cdot,\uparrow\rangle_b\Big)\,|\uparrow,\uparrow\rangle_a \tag{50}$$

In the language of quantum information (see the lecture of D. DiVincenzo), the hopping electron teleports the local triplet from the sites to the a-orbitals.
To obtain the Hamiltonian for the $S^z_{\rm tot} = 1/2$ states, we arrange the basis states in the order they are connected by matrix elements, see Fig. 8. We obtain the tridiagonal Hamiltonian

$$H = \begin{pmatrix} -J_{ab} & -t_{bb} & 0 & 0 & 0 & 0 \\ -t_{bb} & 0 & -J_{ab} & 0 & 0 & 0 \\ 0 & -J_{ab} & 0 & -t_{bb} & 0 & 0 \\ 0 & 0 & -t_{bb} & 0 & -J_{ab} & 0 \\ 0 & 0 & 0 & -J_{ab} & 0 & -t_{bb} \\ 0 & 0 & 0 & 0 & -t_{bb} & -J_{ab} \end{pmatrix} \tag{51}$$

The ground-state is the equally weighted linear combination of all basis states. It has energy $\varepsilon = -J_{ab} - t_{bb}$ and belongs to the sector with $S_{\rm tot} = 3/2$. Again, the hopping electron teleports

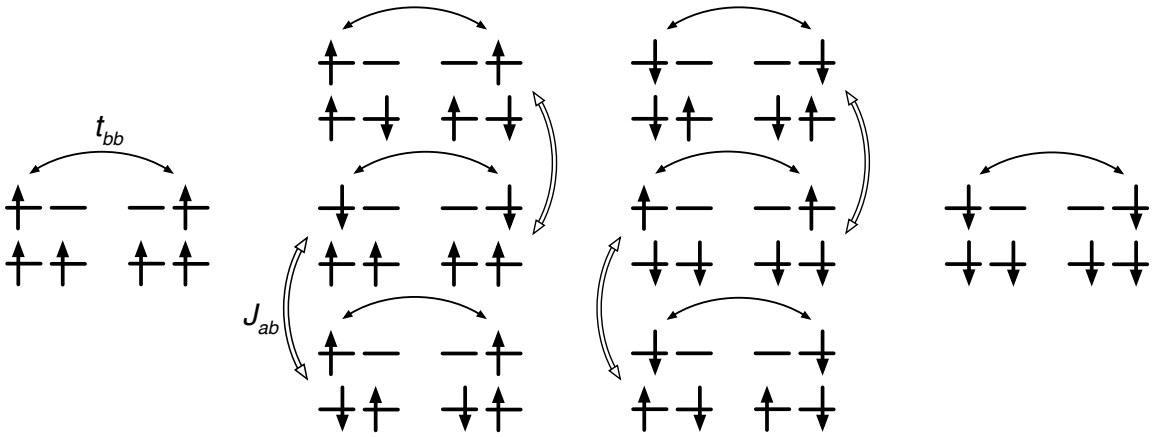


Fig. 8: *Matrix elements entering the double-exchange Hamiltonian. Hopping matrix elements t_{bb} are indicated as double arrows, Coulomb-exchange matrix elements J_{ab} as double lines. Note that the right half of the states are obtained from the left by flipping all spins.*

the triplets from the sites into a triplet state of the spins in the a-orbitals:

$$\begin{aligned}\frac{1}{\sqrt{6}}\Big(&|\uparrow,\uparrow\rangle_1|\cdot,\downarrow\rangle_2+|\cdot,\uparrow\rangle_1|\uparrow,\downarrow\rangle_2+|\cdot,\uparrow\rangle_1|\downarrow,\uparrow\rangle_2+|\downarrow,\uparrow\rangle_1|\cdot,\uparrow\rangle_2+|\uparrow,\downarrow\rangle_1|\cdot,\uparrow\rangle_2+|\cdot,\downarrow\rangle_1|\uparrow,\uparrow\rangle_2\Big)\\ &= \frac{1}{\sqrt{2}}\Big(|\uparrow,\cdot\rangle_b+|\cdot,\uparrow\rangle_b\Big)\,\frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle_a+|\downarrow,\uparrow\rangle_a\Big)+\frac{1}{\sqrt{2}}\Big(|\downarrow,\cdot\rangle_b+|\cdot,\downarrow\rangle_b\Big)\,|\uparrow,\uparrow\rangle_a\end{aligned}$$

As in the $S^z_{\rm tot}=3/2$-sector, there is a corresponding eigenstate of energy $\varepsilon=-J_{ab}+t_{bb}$ with the b-electron antibonding. Again, we find that the triplet state is centered at $-J_{ab}$ with dispersion $\pm t_{bb}$. Thus the hopping electron in orbital b tends to align the spins in orbital a.
While the total spin is conserved, this is not true for the spin on site i, $\vec{S}_{i,a}+\vec{S}_{i,b}$ or for the spin in the a-orbitals $\vec{S}_{1a}+\vec{S}_{2a}$. Consequently the hopping mixes the Hund's rule singlets and triplets and therefore does not produce a singlet state of the a electrons. Instead, for $t_{bb}\ll J_{ab}$, we find in first order perturbation theory

$$\begin{array}{ll}
-J_{ab}-t_{bb} & \big(\ 1,\ \ 1,\ \ 1,\ \ 1,\ \ 1,\ \ 1\big)^T/\sqrt{6}\\
-J_{ab}-t_{bb}/2 & \big(\ 2,\ \ 1,\ \ 1,-1,-1,-2\big)^T/\sqrt{12}\\
-J_{ab}+t_{bb}/2 & \big(\ 2,-1,-1,-1,-1,\ \ 2\big)^T/\sqrt{12}\\
-J_{ab}+t_{bb} & \big(\ 1,-1,-1,\ \ 1,\ \ 1,-1\big)^T/\sqrt{6}\\
\\
+J_{ab}-t_{bb}/2 & \big(\ 0,\ \ 1,-1,-1,\ \ 1,\ \ 0\big)^T/2\\
+J_{ab}+t_{bb}/2 & \big(\ 0,\ \ 1,-1,\ \ 1,-1,\ \ 0\big)^T/2
\end{array}\qquad (52)$$

While the triplet states, $S_{\rm tot}=3/2$, are centered around $-J_{ab}$ with dispersion $\pm t_{bb}$, states with singlet character are centered at the same energy, but have smaller dispersion, $\pm t_{bb}/2$.
We can look at the situation from a different perspective, focusing on the effect of the spins in the a-orbitals on the hopping electron. This is another source of Goodenough-Kanamori rules [11]. We choose the quantization-axis on site 2 rotated relative to that on site 1 by an angle ϑ. Taking the original quantization axis as $\hat{z}$ and the direction from site 1 to site 2 as $\hat{x}$,

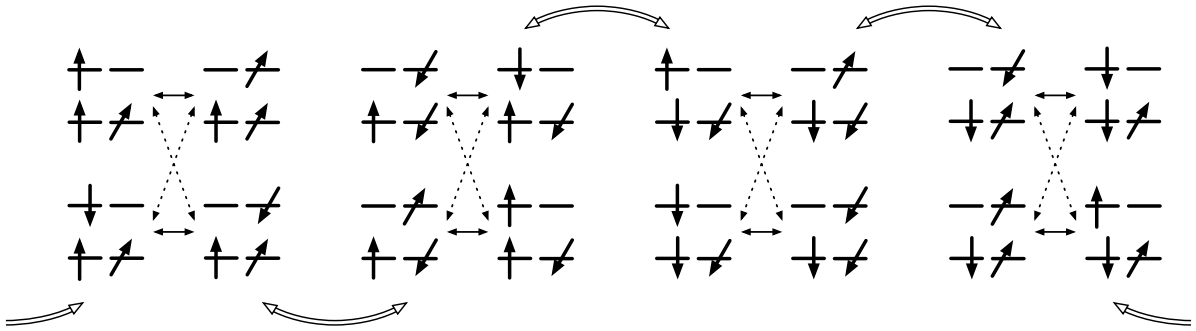


Fig. 9: *With quantization axes tilted between the sites, all states couple. Matrix elements are indicated by arrows: Hopping only couples sites with the same occupation of the a-orbitals. Full lines stand for $t_{bb}\cos(\vartheta/2)$, dotted lines for matrix elements proportional to $t_{bb}\sin(\vartheta/2)$. These states are coupled by off-diagonal Coulomb exchange matrix elements J_{ab}, shown as double lines.*

the rotation in spin space is given by $exp(-i\sigma_y\,\vartheta/2)$ (see appendix C). Introducing operators $d_{2b\sigma}$ in the rotated basis, we have, in terms of the original operators,

$$d_{2b\uparrow} = \cos(\vartheta/2)\,c_{2b\uparrow} - \sin(\vartheta/2)\,c_{2b\downarrow} \tag{53}$$

$$d_{2b\downarrow} = \sin(\vartheta/2)\,c_{2b\uparrow} + \cos(\vartheta/2)\,c_{2b\downarrow} \tag{54}$$

so the hopping becomes

$$-t_{bb}\,c^\dagger_{2b\uparrow}c_{1b\uparrow} = -t_{bb}\left(+\cos(\vartheta/2)\,d^\dagger_{2b\uparrow} + \sin(\vartheta/2)\,d^\dagger_{2b\downarrow}\right)c_{1b\uparrow} \tag{55}$$

$$-t_{bb}\,c^\dagger_{2b\downarrow}c_{1b\downarrow} = -t_{bb}\left(-\sin(\vartheta/2)\,d^\dagger_{2b\uparrow} + \cos(\vartheta/2)\,d^\dagger_{2b\downarrow}\right)c_{1b\downarrow}\,. \tag{56}$$

Obviously, such a change of basis does not change the spectrum of the resulting Hamiltonian. We do get a new situation, however, when we assume that the spin on orbital a is *fixed*. This is, e.g., a good approximation when the spin in the a-orbital arises actually not a from a single electron, but from many electrons coupled by Hund's rule, e.g., in a half-filled t_{2g}-level, like in the manganites. Then there are no off-diagonal exchange terms (double lines in Fig. 9) and the Hamiltonian splits into 4×4 blocks with only hopping (solid and dotted lines in Fig. 9) and on-site Coulomb exchange J_{ab}. The Hamiltonian then becomes

$$H = \left(\begin{array}{cc|cc} -J_{ab} & +t_{bb}\,\cos(\vartheta/2) & +t_{bb}\,\sin(\vartheta/2) & 0 \\ +t_{bb}\,\cos(\vartheta/2) & -J_{ab} & 0 & -t_{bb}\,\sin(\vartheta/2) \\ \hline +t_{bb}\,\sin(\vartheta/2) & 0 & 0 & +t_{bb}\,\cos(\vartheta/2) \\ 0 & -t_{bb}\,\sin(\vartheta/2) & +t_{bb}\,\cos(\vartheta/2) & 0 \end{array}\right), \tag{57}$$

where the a-spin simply produces a Zeeman splitting of orbital b, proportional to the exchange coupling J_{ab}. In the limit $t_{bb} \ll J_{ab}$ we can neglect the states with misaligned spins and obtain

$$\varepsilon = -J_{ab} \pm t_{bb}\,\cos(\vartheta/2)\,, \tag{58}$$

i.e., for parallel spins, $\vartheta = 0$, the gain in kinetic energy is maximized, giving the ground-state energy of the full Hamiltonian, while for anti-parallel spins, $\vartheta = \pi$ the dispersion vanishes.

5 Orbital-ordering

Exchange mechanisms are not restricted to the coupling of spins. As pointed out by Kugel and Khomskii [12], also orbital occupations can interact. Such a coupling leads, besides an ordering of the spins, to an ordering of the orbitals.

To understand the mechanism of orbital-ordering, we consider an e_g-molecule, i.e., two sites with two orbitals a and b, as discussed in Sec. 2. The Hamiltonian on the sites is thus given by (14). In addition, the two sites are coupled by hopping matrix elements t_{aa} and t_{bb}, i.e., hopping does not change the type, a or b, of the occupied orbital. We now consider the case of one electron in orbital a and the other in orbital b.

First, we consider the situation when both electrons have the same spin, e.g., spin-up. The basis states are shown in Fig. 10. Setting up the Hamiltonian is analogous to setting up (24)

$$H = \left(\begin{array}{cc|cc} 0 & 0 & -t_{bb} & -t_{aa} \\ 0 & 0 & +t_{aa} & +t_{bb} \\ \hline -t_{bb} & +t_{aa} & U_{ab}-J_{ab} & 0 \\ -t_{aa} & +t_{bb} & 0 & U_{ab}-J_{ab} \end{array}\right). \tag{59}$$

Downfolding to the states without doubly occupied sites, we obtain

$$H_{\text{eff}} \approx -\frac{1}{U_{ab}-J_{ab}} \begin{pmatrix} t_{aa}^2+t_{bb}^2 & -2t_{aa}t_{bb} \\ -2t_{aa}t_{bb} & t_{aa}^2+t_{bb}^2 \end{pmatrix} = -\frac{(t_{aa}-t_{bb})^2}{U_{ab}-J_{ab}} - \frac{2t_{aa}t_{bb}}{U_{ab}-J_{ab}} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \tag{60}$$

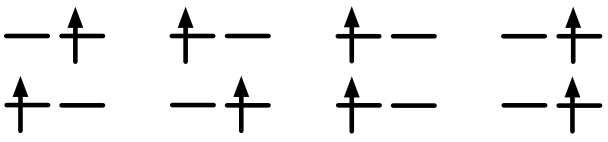
Thus we find that there is an interaction between the states with exchanged orbital-occupation, i.e., an orbital-exchange. For the present case of ferromagnetically aligned spins, the exchange coupling favors the orbital singlet, when the hopping matrix elements are of the same sign. In analogy with the situation in kinetic exchange, this is called antiferro orbital exchange. To make the relation with kinetic exchange even more explicit, we can introduce, in analogy to (31), pseudo-spin operators $\vec{T}_{i\sigma}$

$$T_{i\sigma}^x = \frac{1}{2}\left(c_{ai\sigma}^\dagger c_{bi\sigma} + c_{bi\sigma}^\dagger c_{ai\sigma}\right),\ T_{i\sigma}^y = -\frac{i}{2}\left(c_{ai\sigma}^\dagger c_{bi\sigma} - c_{bi\sigma}^\dagger c_{ai\sigma}\right),\ T_{i\sigma}^z = \frac{1}{2}\left(n_{ai\sigma} - n_{bi\sigma}\right) \tag{61}$$

so that we can write

$$H_{\text{eff}} = -\frac{(t_{aa}-t_{bb})^2}{U_{ab}-J_{ab}} + \frac{4t_{aa}t_{bb}}{U_{ab}-J_{ab}}\left(\vec{T}_{1\uparrow}\cdot\vec{T}_{2\uparrow} - \frac{1}{4}\right). \tag{62}$$

Fig. 10: *Basis states for an up-electron in orbital a and another up-electron in orbital b. Note that the states are ordered as in Eqn. (24).*



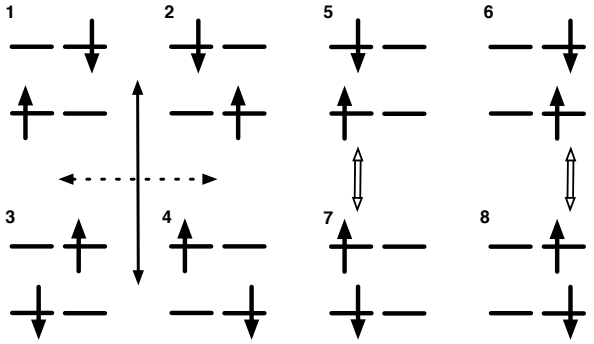


Fig. 11: *Basis states for electrons of opposite spin. The numbering used for the matrix (63) is indicated. Spin exchange is indicated by the full, orbital exchange by the dotted arrow. The states with both electrons on the same site are coupled via Coulomb exchange (double arrows).*

When the two electrons have opposite spin, we can study the interplay of spin- and orbital-exchange. The basis states shown in Fig. 11. We expect orbital exchange to operate between the first two states in each row and spin exchange between the states between the rows. The Hamiltonian is

$$H = \left(\begin{array}{cccc|cccc} 0 & 0 & 0 & 0 & -t_{bb} & -t_{aa} & 0 & 0 \\ 0 & 0 & 0 & 0 & +t_{aa} & +t_{bb} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -t_{bb} & -t_{aa} \\ 0 & 0 & 0 & 0 & 0 & 0 & +t_{aa} & +t_{bb} \\ \hline -t_{bb} & +t_{aa} & 0 & 0 & U_{ab} & 0 & -J_{ab} & 0 \\ -t_{aa} & +t_{bb} & 0 & 0 & 0 & U_{ab} & 0 & -J_{ab} \\ 0 & 0 & -t_{bb} & +t_{aa} & -J_{ab} & 0 & U_{ab} & 0 \\ 0 & 0 & -t_{aa} & +t_{bb} & 0 & -J_{ab} & 0 & U_{ab} \end{array}\right) \tag{63}$$

from which we obtain

$$\begin{aligned} H_{\text{eff}} &\approx -\frac{1}{U_{ab}^2 - J_{ab}^2} \begin{pmatrix} (t_{aa}^2+t_{bb}^2)U_{ab} & -2t_{aa}t_{bb}\,U_{ab} & (t_{aa}^2+t_{bb}^2)J_{ab} & -2t_{aa}t_{bb}\,J_{ab} \\ -2t_{aa}t_{bb}\,U_{ab} & (t_{aa}^2+t_{bb}^2)U_{ab} & -2t_{aa}t_{bb}\,J_{ab} & (t_{aa}^2+t_{bb}^2)J_{ab} \\ (t_{aa}^2+t_{bb}^2)J_{ab} & -2t_{aa}t_{bb}\,J_{ab} & (t_{aa}^2+t_{bb}^2)U_{ab} & -2t_{aa}t_{bb}\,U_{ab} \\ -2t_{aa}t_{bb}\,J_{ab} & (t_{aa}^2+t_{bb}^2)J_{ab} & -2t_{aa}t_{bb}\,U_{ab} & (t_{aa}^2+t_{bb}^2)J_{ab} \end{pmatrix} \\ &= -\frac{1}{U_{ab}^2 - J_{ab}^2} \begin{pmatrix} U_{ab} & J_{ab} \\ J_{ab} & U_{ab} \end{pmatrix} \otimes \begin{pmatrix} t_{aa}^2+t_{bb}^2 & -2t_{aa}t_{bb} \\ -2t_{aa}t_{bb} & t_{aa}^2+t_{bb}^2 \end{pmatrix} \\ &= -\frac{1}{U_{ab}^2 - J_{ab}^2} \left[U_{ab} + J_{ab} - J_{ab} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}\right] \otimes \left[(t_{aa}-t_{bb})^2 + 2t_{aa}t_{bb} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}\right]. \end{aligned} \tag{64}$$

I.e., we get a simultaneous coupling of the spin- and orbital degrees of freedom. The first term describes the coupling of the spins, which is antiferromagnetic, while the coupling of the orbitals is, for hopping matrix elements of the same sign, ferro, i.e., orbital triplet. In terms of the spin and pseudo-spin operators we can write, with $\vec{T}_i = \sum_\sigma \vec{T}_{i\sigma}$ and $\vec{S}_i = \sum_{\alpha\in\{a,b\}} \vec{S}_{\alpha,i}$

$$H_{\text{eff}} = -\frac{1}{U_{ab}^2 - J_{ab}^2} \left[(U_{ab}+J_{ab}) + 2J_{ab}\left(\vec{S}_1\cdot\vec{S}_2 - \frac{1}{4}\right)\right] \left[(t_{aa}-t_{bb})^2 - 4t_{aa}t_{bb}\left(\vec{T}_1\cdot\vec{T}_2 - \frac{1}{4}\right)\right].$$

There will be additional terms when we allow states with both electrons in the same orbital.

6 Extended systems

6.1 Hubbard model

We now turn to *extended* systems. For this we consider the Hubbard model [13] on an infinite lattice. Note that now the Hilbert space is infinitely dimensional, so we can no longer write down the Hamiltonian in its matrix form but have to rely on the second quantized form (29)

$$H = -t \sum_{i,j,\sigma} c^\dagger_{j\sigma} c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \,. \tag{65}$$

As in our toy model we still assume that each atom has only a single relevant orbital. There are links between the neighboring atoms with matrix elements t, which can be intuitively interpreted as hopping from site to site. In the absence of other terms the hopping gives rise to a band. A second energy scale is given by the Coulomb repulsion U between two electrons on the same atom. If this on-site Coulomb repulsion is comparable to or even larger than the band width, the electrons can no longer be considered independent; since the double occupation of an atom is energetically very costly, the movement of an electron will be hindered by the Coulomb repulsion. One says that the electrons move in a *correlated* way. We should note that also the Pauli principle hinders the movement of an electron. This effect can, however, be efficiently described by constructing a Slater determinant of independent-electron wave functions. Correlations, on the other hand, are notoriously difficult to describe since no simple wave functions for such systems are available. In the case of strong correlations, i.e., for $U \gg t$, we will treat the hopping as a perturbation. This is called the *atomic limit*, since the sites are almost independent atoms. Thus it is most appropriate to describe strongly correlated electrons in a local picture, i.e., in terms of electron configurations, which are the states that diagonalize the Coulomb term.

6.2 Mott transition

The physics described by the Hubbard model is the interplay between kinetic energy and Coulomb repulsion. Writing the Hubbard-Hamiltonian either in real or in k-space

$$\begin{aligned} H = \;& -t \sum_{i,j,\sigma} c^\dagger_{j\sigma} c_{i\sigma} \qquad + U \sum_i n_{i\uparrow} n_{i\downarrow} \\ = \;& \sum_{k\sigma} \varepsilon_k \, c^\dagger_{k\sigma} c_{k\sigma} \;\; + \frac{U}{M} \sum_{k,k',q} c^\dagger_{k\uparrow} c_{k-q\uparrow} c^\dagger_{k'\downarrow} c_{k'+q\downarrow} \,, \end{aligned}$$

where M is the number of lattice sites, we see that there are obviously two limiting cases: There is the non-interacting- or band-limit, when $t \gg U$. In that case, only the hopping term survives, i.e., there are no interactions, and the Hamiltonian can be solved easily in k-space. The energy levels then form a band and the system is metallic, except when the band is completely filled. In the opposite case, the atomic limit, the interaction term dominates. In that limit, to minimize the Coulomb energy, the electrons will be distributed over the lattice sites as uniformly

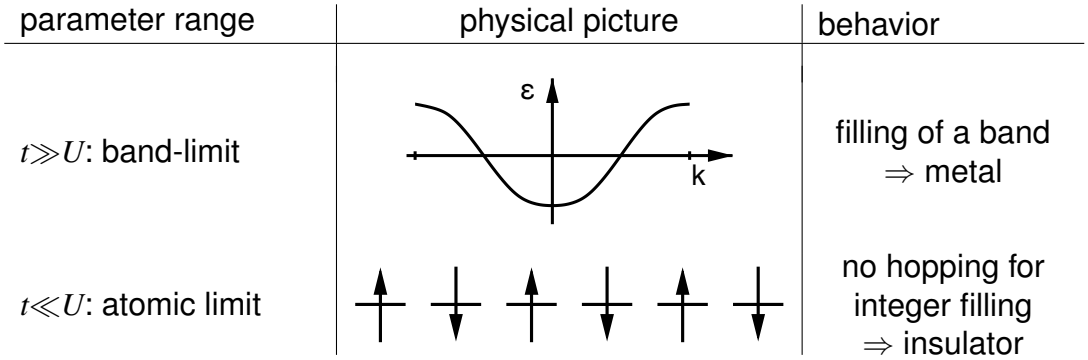


Fig. 12: *Metal-insulator transition for half-filling, i.e., one electron per site.*

as possible. For a non-degenerate, half-filled system this means, that every site carries exactly one electron, and hopping is suppressed, because it would create a doubly occupied site, which would increase the energy by $U \gg t$. Thus in the atomic limit the half-filled system will be an insulator. Clearly, in-between these two limiting cases there must be, at some value U_c, the so-called *critical* U, a transition from a metallic to an insulating state — the Mott transition [14]. Usually this transition is expected when U becomes of the order of the (non-interacting) band width W.

As the criterion for determining the metal-insulator transition we can use the opening of the gap for charge-carrying single-electron excitations

$$E_g = E(N+1) - 2E(N) + E(N-1)\,, \tag{66}$$

where $E(N)$ denotes the total energy of a cluster of M atoms with N electrons. For the half-filled system we have $N = M$. It is instructive to again consider the two limiting cases. In the non-interacting limit the total energy is given by the sum over the eigenvalues of the hopping Hamiltonian $\sum_{n:\mathrm{occ}} \varepsilon_n$. Thus, in the non-interacting limit $E_g^{\mathrm{band}} = \varepsilon_{N+1} - \varepsilon_N$, which, for a partly filled band, will vanish in the limit of infinite system size. On the other hand, in the atomic limit, the Coulomb energy for a single site with n electrons is $Un(n-1)/2$. Thus, for half-filling of we have

$$E_g^{\mathrm{atml}} = U\,, \tag{67}$$

i.e., the insulating state in the atomic limit is characterized by a finite gap.

For an infinite system the gap E_g can be rewritten in terms of the chemical potential. In the thermodynamic limit ($M \to \infty$ with N/M constant) we have to distinguish two types: the energy needed to add an electron to the system (electron affinity)

$$\mu^+ = \lim(E(N+1) - E(N)) = \left.\frac{d\varepsilon(n)}{dn}\right|_{n\searrow 1}\,, \tag{68}$$

and the energy required to extract an electron from the system (ionization energy)

$$\mu^- = \lim(E(N) - E(N-1)) = \left.\frac{d\varepsilon(n)}{dn}\right|_{n\nearrow 1}\,. \tag{69}$$

The gap is then given by the discontinuity in the left- and right-derivative of the energy per site $\varepsilon(n) = \lim E(N)/M$: $E_g = \mu^+ - \mu^-$.

6.3 Heisenberg model

We now consider the Hubbard model in the limit of large U. This is the generalization of the discussion of direct kinetic exchange in Sec. 3.2 to an extended system. For large U we work with the electron configurations, in which the interaction term is diagonal. Configurations with doubly occupied sites will have energies of the order of U or larger, so these are the configurations that we would like to project out. For downfolding we thus partition the configuration basis, and hence the Hilbert space, into the set of low-energy states which have no doubly occupied sites

$$S = \left\{ |n_{1\uparrow}, n_{1\downarrow}, n_{2\uparrow}, n_{2\downarrow}, \ldots\rangle \,\middle|\, \forall i : \, n_{i\uparrow} + n_{i\downarrow} \leq 1 \right\} \tag{70}$$

and the set of high-energy states with one or more doubly occupied sites

$$D = \left\{ |n_{1\uparrow}, n_{1\downarrow}, n_{2\uparrow}, n_{2\downarrow}, \ldots\rangle \,\middle|\, \exists i : \, n_{i\uparrow} + n_{i\downarrow} = 2 \right\} \, . \tag{71}$$

The hopping term T, which for large U is a perturbation to the interaction term I, couples the subspaces by hopping an electron into or out of a doubly occupied site. In addition it lifts the degeneracies within the subspaces. Hence the Hamiltonian can be partitioned as (note that $I \equiv 0$ on subspace S)

$$\hat{H} = \begin{pmatrix} P_S \, T \, P_S & P_S \, T \, P_D \\ P_D \, T \, P_S & P_D \, (T + I) \, P_D \end{pmatrix} \, , \tag{72}$$

Since we are dealing with an extended system, the subspaces are infinite, so we cannot write the Hamiltonian on the subspaces as matrices. Instead we restrict the operators to the appropriate subspace by using projection operators, P_S projecting on the low-energy configurations S, P_D projecting on D. Just like in 3.2 we can then write down an effective Hamiltonian operating on the low-energy configurations only:

$$H_{\text{eff}} = P_S \, T \, P_S + P_S \, T \, P_D \, \left[P_D \, (\varepsilon - (I + T)) \, P_D \right]^{-1} P_D \, T \, P_S \, , \tag{73}$$

Unlike in the derivation of direct exchange, for the extended system we have no way of calculating the inverse in the second term explicitly. We can, however, expand in powers of t/U. This is Kato's method for perturbation theory (see, e.g., section 16.3 of [15]). Essentially we only need to consider configurations with a *single* double-occupancy – these correspond to the states of lowest energy in D. On this subspace the interaction term is diagonal with eigenvalue U and can thus be easily inverted. We then obtain the Hamiltonian

$$H_{t-J} = P_S \left[T - \frac{t^2}{U} \sum_{\langle ij \rangle \langle jk \rangle \sigma\sigma'} c^\dagger_{k\sigma'} c_{j\sigma'} \, n_{j\uparrow} n_{j\downarrow} \, c^\dagger_{j\sigma} c_{i\sigma} \right] P_S \, , \tag{74}$$

which is called the t-J Hamiltonian. The first term describes the hopping, constrained to configurations with no doubly occupied sites. Thus it essentially describes the hopping of empty sites (holes). To understand what the second term does, we observe that, because of the operators $n_{j\uparrow} n_{j\downarrow}$, there are only contributions for states with a singly occupied site j: $n_{j\sigma} = 0$ and $n_{j,-\sigma} = 1$. After applying the second term, site j will again be singly occupied with $n_{j\sigma'} = 0$

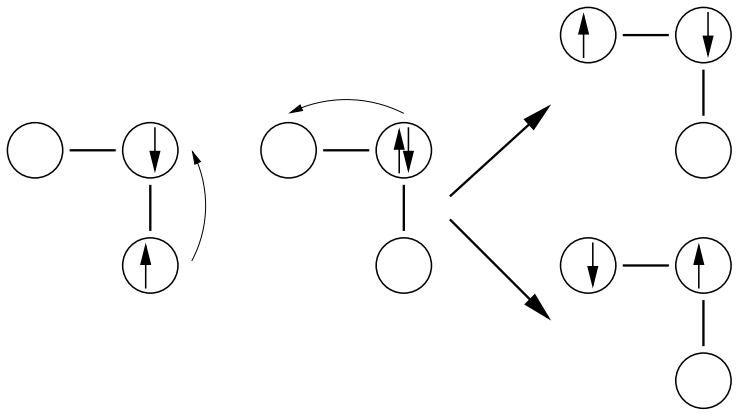


Fig. 13: *Processes contained in the three-site term T': indirect hopping processes to a second-nearest neighbor site with an intermediate (virtual) doubly occupied state. In the first process the two hopping processes are performed by the same electron, in the second process each electron hops once and thus the spin on the intermediate site is flipped.*

and $n_{j,-\sigma'} = 1$. Hence, for $\sigma \neq \sigma'$ the spin on site j will be flipped. Moreover, we distinguish the contributions where only two different sites are involved ($k = i$) from the three-site terms ($k \neq i$). The terms for $k = i$ are just the ones we already know from the kinetic exchange mechanism. The three-site terms describe a second-nearest neighbor hopping of an electron from site i to site k via a singly occupied intermediate site j. For $\sigma = \sigma'$ the spin of the hopping electron is opposite to that on the intermediate site. For $\sigma \neq \sigma'$ the spin of the intermediate site is flipped – as is that of the hopping electron. This is shown in Fig. 13. The t-J Hamiltonian is

$$H_{t-J} = P_S \left[T + H_H + T'\right] P_S \tag{75}$$

with

$$T = -t \sum_{\langle ij\rangle,\sigma} c^\dagger_{j\sigma} c_{i\sigma} \tag{76}$$

$$H_H = \frac{4t^2}{U} \sum_{\langle ij\rangle} \left(\vec{S}_j \cdot \vec{S}_i - \frac{n_i n_j}{4}\right) \tag{77}$$

$$T' = -\frac{t^2}{U} \sum_{\substack{\langle ij\rangle\langle jk\rangle \\ i\neq k}} \sum_{\sigma} \left(c^\dagger_{k\sigma}(1-n_{j\sigma})c_{i\sigma} - c^\dagger_{k,-\sigma}c^\dagger_{j\sigma}c_{j,-\sigma}c_{i\sigma}\right) n_{j,-\sigma} \tag{78}$$

In the case of half-filling, when $n_i = 1$, all hopping processes are suppressed, i.e., the projection P_S annihilates T and T'. Thus for a Mott insulator the t-J model reduces to the spin $1/2$ Heisenberg model

$$H_H = J \sum_{\langle ij\rangle} \vec{S}_j \cdot \vec{S}_i + \text{const.} \tag{79}$$

with the exchange coupling $J = 4t^2/U$ given by the direct kinetic exchange mechanism. We again stress that the spin-spin interaction is a result of projecting out the states with double occupancies.

7 Conclusion

We have seen that magnetic interactions in matter arise from the interplay of the Pauli principle and Coulomb interaction, kinetic energy, or both. The resulting effective couplings between magnetic moments are thus not fundamental interactions and, usually, take quite complex forms. However, in limiting cases they can become quite simple and transparent. These scenarios are called exchange mechanisms, of which we have discussed here a small selection. They give an idea of what magnetic interactions can be expected in real materials. Thus, despite their simplicity, exchange mechanisms provide vital guides for understanding the physics of complex ordering phenomena, of spins and orbital-occupations, from simple concepts.

Acknowledgment

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Appendices

A Atomic units

Practical electronic structure calculations are usually done in atomic units, a. u. for short. While the idea behind the atomic units is remarkably simple, in practice there is often some confusion when trying to convert to SI units. We therefore give a brief explanation.
The motivation for introducing atomic units is to simplify the equations. For example, in SI units the Hamiltonian of a hydrogen atom is

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0\, r}\ . \tag{80}$$

To avoid having to keep track of the constants, we would like to simplify this to

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}\ . \tag{81}$$

To this end we invent units in which the *numerical values* of the electron mass m_e, the elementary charge e, the Planck-constant $\hbar$, and the dielectric constant $4\pi\epsilon_0$ are all equal to one. This immediately tells us: 1 a.u. mass $= m_e$ and 1 a.u. charge $= e$. To complete the set of basis units we still need the atomic unit of length, which we call a_0, and of time, t_0. To find the values of a_0 and t_0 we write $\hbar$ and $4\pi\epsilon_0$ (using simple dimensional analysis) in atomic units: $\hbar = 1\, m_e a_0^2/t_0$ and $4\pi\epsilon_0 = 1\, t_0^2 e^2/(m_e a_0^3)$. Solving this system of equations, we find

1 a.u. length	$= a_0 =$	$4\pi\epsilon_0\hbar^2/m_e e^2$	$\approx 5.2918\cdot 10^{-11}$	m
1 a.u. mass	$= m_e =$		$\approx 9.1095\cdot 10^{-31}$	kg
1 a.u. time	$= t_0 =$	$(4\pi\epsilon_0)^2\hbar^3/m_e e^4$	$\approx 2.4189\cdot 10^{-17}$	s
1 a.u. charge	$= e =$		$\approx 1.6022\cdot 10^{-19}$	C

The atomic unit of length, a_0, is the Bohr radius. As the dimension of energy is mass times length squared divided by time squared, its atomic unit is $m_e a_0^2/t_0^2 = m_e e^4/(4\pi\epsilon_0)^2\hbar^2$. Because of its importance the atomic unit of energy has a name, the Hartree. One Hartree is minus twice the ground-state energy of the hydrogen atom (80), about 27.211 eV. The speed of light c in atomic units is given by $c\ t_0/a_0 = 4\pi\varepsilon_0\hbar c/e^2 = 1/\alpha$, where α is the fine structure constant. Thus $c = \alpha^{-1}$ a.u. ≈ 137 a.u. The Bohr magneton is $\mu_B = 1/2$ a.u.

B Downfolding

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

$$H = \begin{pmatrix} H_{00} & T_{01} \\ T_{10} & H_{11} \end{pmatrix} , \tag{82}$$

where H_{00} is the Hamiltonian restricted to the states of interest (reduced Hilbert space), H_{11} the Hamiltonian for the 'other' states, and the T matrices describe transitions between the two subspaces. The resolvent is partitioned likewise

$$G(\varepsilon) = (\varepsilon - H)^{-1} = \begin{pmatrix} \varepsilon - H_{00} & T_{01} \\ T_{10} & \varepsilon - H_{11} \end{pmatrix}^{-1} . \tag{83}$$

Calculating the inverse of the 2×2 matrix, taking into account that the entries are matrices themselves and thus do not commute, we obtain

$$G_{00}(\varepsilon) = \left(\varepsilon - [H_{00} + \underbrace{T_{01}(\varepsilon - H_{11})^{-1} T_{10}}_{=H_{\text{eff}}}] \right)^{-1} . \tag{84}$$

This expression looks just like the resolvent for a Hamiltonian

$$\begin{aligned} H_{\text{eff}} &= H_{00} + T_{01}(\varepsilon - H_{11})^{-1} T_{10} && (85) \\ &\approx H_{00} + T_{01}(\varepsilon_0 - H_{11})^{-1} T_{10} && (86) \end{aligned}$$

on the reduced Hilbert space. 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 $H_{\text{eff}}(\varepsilon_0)$ that gives a good description of the electrons in the reduced Hilbert space, i.e., the states with an energy close to ε_0.

C Pauli matrices

Here we collect the most important properties of the Pauli matrices. The Pauli or spin matrices are defined as

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{87}$$

They are hermitean, i.e. $\sigma_i^\dagger = \sigma_i$, and $\sigma_i^2 = 1$. Therefore their eigenvalues are ± 1. The eigenvectors of σ_z are $|m_z\rangle$, $m_z = \pm 1$:

$$|+1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |-1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{88}$$

For these vectors we find

$$\sigma_x|\,m_z\rangle = |\,-m_z\rangle \quad \sigma_y|\,m_z\rangle = i m_z|\,-m_z\rangle \quad \sigma_z|\,m_z\rangle = m_z|\,m_z\rangle \tag{89}$$

The products of the Pauli matrices are $\sigma_x\,\sigma_y = i\sigma_z$, where the indices can be permuted cyclically. From this follows for the commutator

$$[\sigma_x, \sigma_y] = 2i\sigma_z \tag{90}$$

while the anticommutator vanishes:

$$\{\sigma_x, \sigma_y\} = 0 \tag{91}$$

Finally a rotation by an angle φ about the axis $\hat{n}$ changes the spin matrices

$$R_{\hat{n}}(\varphi) = e^{-i\hat{n}\cdot\vec{\sigma}\,\varphi/2} = cos(\varphi/2) - i\sin(\varphi/2)\,\hat{n}\cdot\vec{\sigma} \tag{92}$$

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