Magnetic interactions

- Magnetic dipolar interactions
- Exchange interactions: direct exchange, superexchange—indirect exchange in insulators, indirect exchange in metals, double exchange
- Localized moments in dilute magnetic alloys, the Kondo effect

Magnetic dipolar interactions

The energy of two magnetic dipoles $\mathbf{m}_1$ and $\mathbf{m}_2$ separated by distance $\mathbf{r}$ is

$$E = \frac{\mu_0}{4\pi r^3}\left[\mathbf{m}_1 \cdot \mathbf{m}_2 - \frac{3}{r^2}\left(\mathbf{m}_1 \cdot \mathbf{r}\right)\left(\mathbf{m}_2 \cdot \mathbf{r}\right)\right].$$

The magnetic dipolar interaction is very weak.

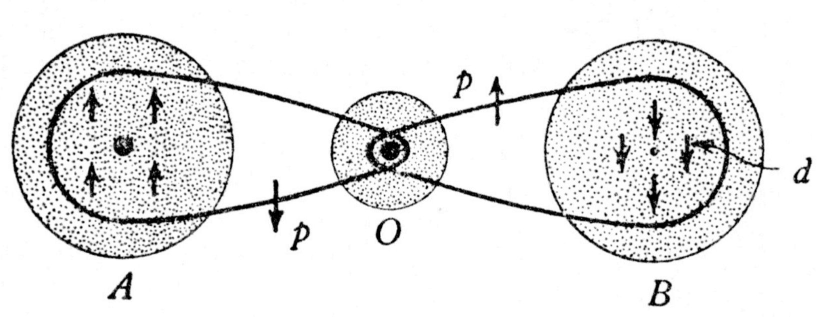
For two moments $m \approx 1\,\mu_B$ separated by $r \approx 1\,\text{Å}$, the interaction energy is about 1 K.

The magnetic dipolar interaction becomes important when the ordering temperature is in the milliKelvin range.

Exchange interactions: direct exchange, superexchange—indirect exchange in insulators, indirect exchange in metals, double exchange

Superexchange—indirect exchange in insulators

Example: MnO. The *d*-electrons in the Mn ion are coupled to electrons in the oxygen; which then interact with the *d*-electrons in a second Mn ion:



[from J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1979)]

Exchange interaction between magnetic moments

1. **Coulomb exchange**
2. **Kinetic exchange (direct exchange & superexchange)**
3. **Double exchange**

1. Coulomb exchange

$$H_U = \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

The Coulomb repulsion between electrons H_U is spin-independent. Nevertheless, because of the antisymmetry of many-electron wave function, the eigenenergies of H_U depend on spin. This gives the multiplet structure in atoms and first two Hund's rules.

Consider two atomic orbitals α= a; b. The two-electron Slater determinants with spins σ and σ' is

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

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

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

Coulomb exchange (2)

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

Coulomb interaction, given by Hamiltonian, $$H_U = \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

results to the first-order energy correction:

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

where $$U_{ab} = e^2 \int d^3r_1 \int d^3r_2\, \frac{|\varphi_a(\vec{r}_1)|^2\, |\varphi_b(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}$$ **(direct Coulomb)**

and $$J_{ab} = e^2 \int d^3r_1 \int d^3r_2\, \frac{\overline{\varphi_a(\vec{r}_1)}\,\varphi_b(\vec{r}_1)\ \overline{\varphi_b(\vec{r}_2)}\,\varphi_a(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\ .$$ **(exchange)**

For the states where the electrons have opposite spin (σ = -σ’) $$\left\langle \Psi_{a,\sigma;\,b,-\sigma} \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi_{a,\sigma;\,b,-\sigma} \right\rangle = U_{ab}$$

The diagonal matrix element for opposite spins has no exchange contribution, as the overlap of the spin functions for the cross terms vanish.

Coulomb exchange (3)

There are however off-diagonal matrix elements

$$\left\langle \Psi_{a\uparrow;\,b\downarrow} \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi_{a\downarrow;\,b\uparrow} \right\rangle = -J_{ab}$$

In the basis of 4 states $\Psi_{\uparrow\uparrow}, \Psi_{\uparrow\downarrow}, \Psi_{\downarrow\uparrow}$ and $\Psi_{\downarrow\downarrow}$ the Coulomb term is

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

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

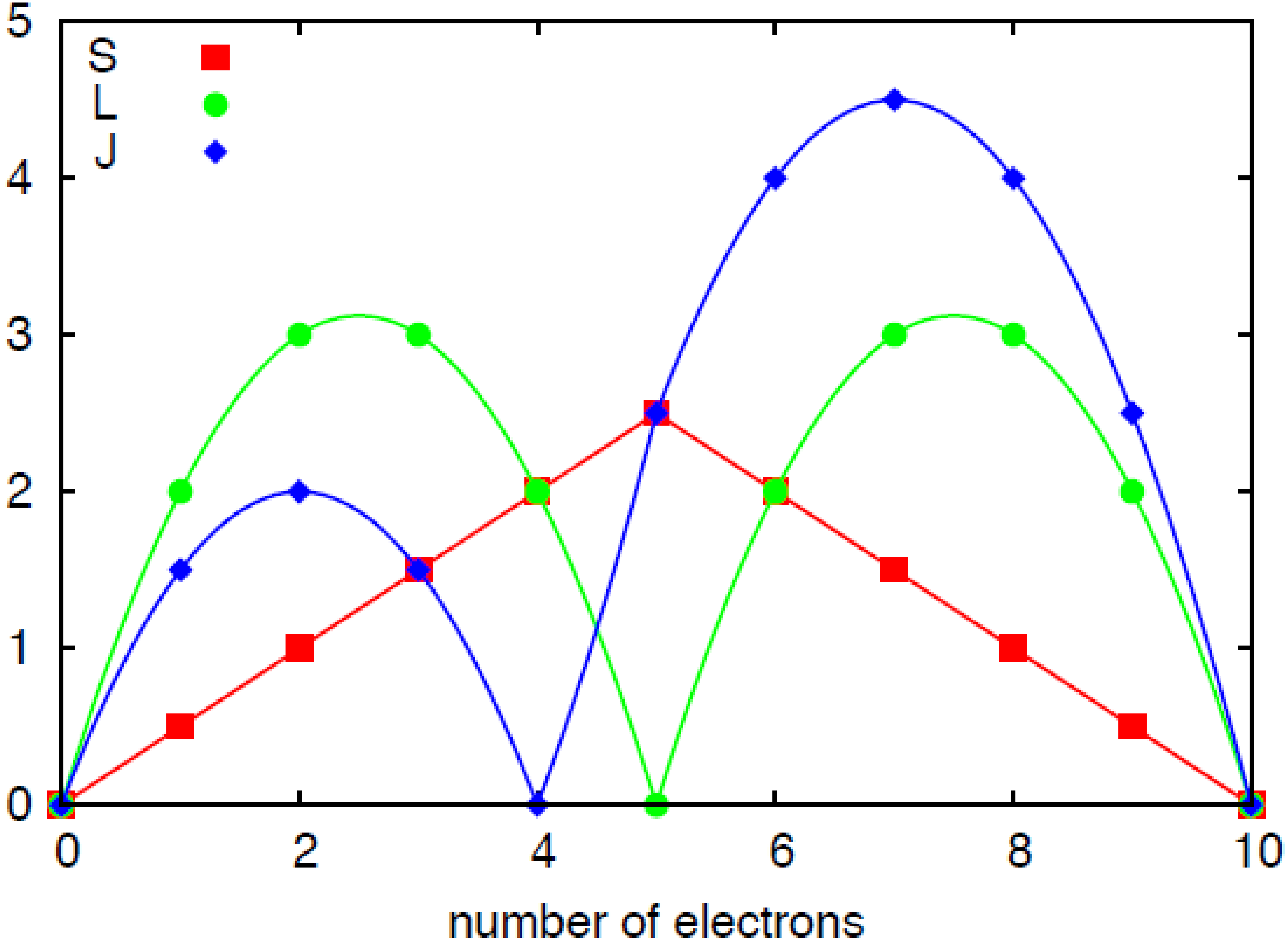
$$\Delta\varepsilon_{\text{triplet}} = U_{ab} - J_{ab}$$

Diagonalizing 2x2 matrix, we obtain third triplet state $(\Psi_{\uparrow\downarrow} + \Psi_{\downarrow\uparrow})/\sqrt{2}$ with energy U_{ab}-J_{ab} and the singlet state $(\Psi_{\uparrow\downarrow} + \Psi_{\downarrow\uparrow})/\sqrt{2}$ with energy U_{ab}+J_{ab}. The exchange matrix element is positive, $J_{ab}>0$:

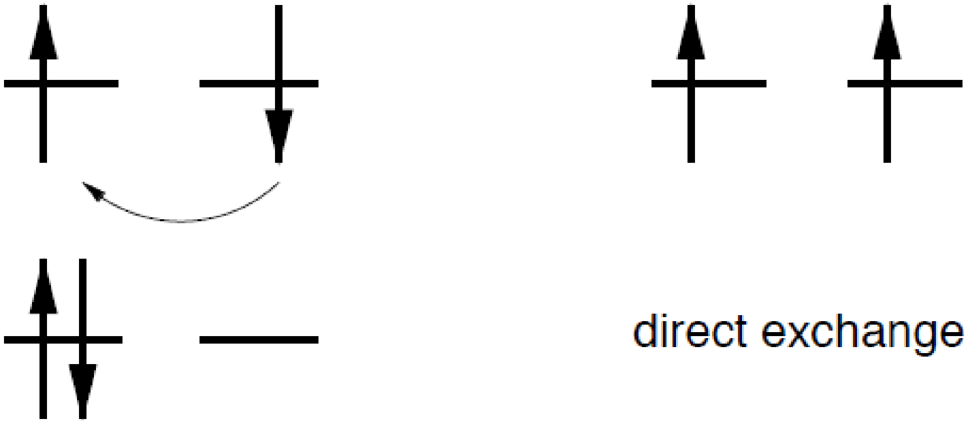
$$J_{ab} = \frac{e^2}{(2\pi)^3} \int d^3k \, |\Phi(\vec{k}\,)|^2 \, \frac{4\pi}{k^2} > 0$$

Hence, the Coulomb energy is lower for triplet spin state, when the coordinate wave function is antisymmetric. This is an example of Hund’s first rule: the lowest state has maximum spin.

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



Kinetic (direct) exchange (qualitative picture)



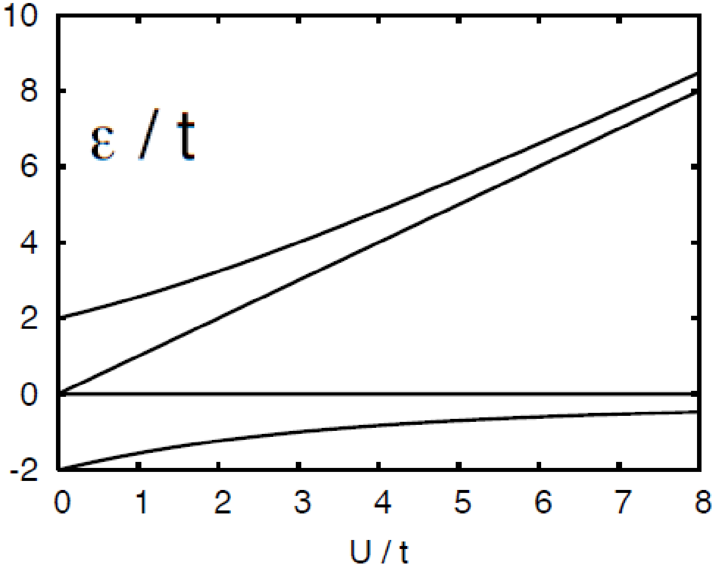
Simple picture of direct kinetic exchange:
the antiparallel alignment of the spins (left) is favored, since it allows the electrons to hop to the neighboring site. For parallel spins (right) hopping is suppressed by the Pauli principle.

If the energy difference between ionic state (two electrons on the same site) $|\uparrow\downarrow,\cdot\rangle$ and the covalent state is U (the Coulomb energy of two electrons being on the same site), and t is the hopping matrix element, then the second-order energy correction is $-t^2/U$.

Kinetic (direct) exchange (example on hydrogen molecule)

The Hamiltonian in 4-state basis contains the Coulomb energy U of two electrons on the same site and hopping term t:

$$H = \begin{array}{cc} \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & +t & +t \\ -t & +t & U & 0 \\ -t & +t & 0 & U \end{pmatrix} & \begin{array}{l} |\uparrow,\downarrow\rangle \\ |\downarrow,\uparrow\rangle \\ |\uparrow\!\downarrow,\cdot\rangle \\ |\cdot,\uparrow\!\downarrow\rangle \end{array} \end{array}$$



Diagonalization of this Hamiltonian gives

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

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

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

ε_- U>>t

The lowest energy state $\varepsilon_s = -\dfrac{4t^2}{U} \quad , \quad \Psi_s = \dfrac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\Big)$

Kinetic 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.

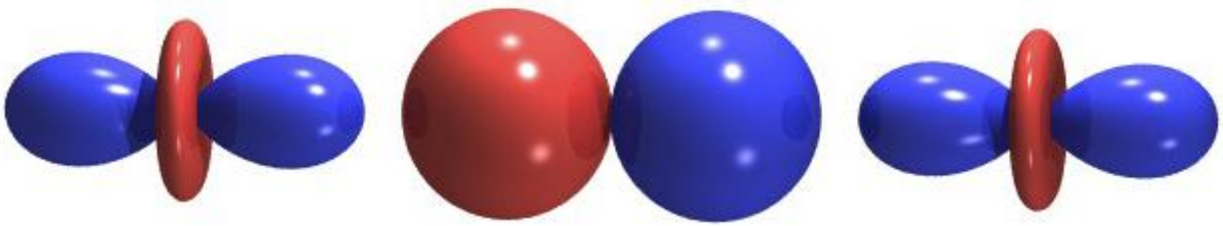
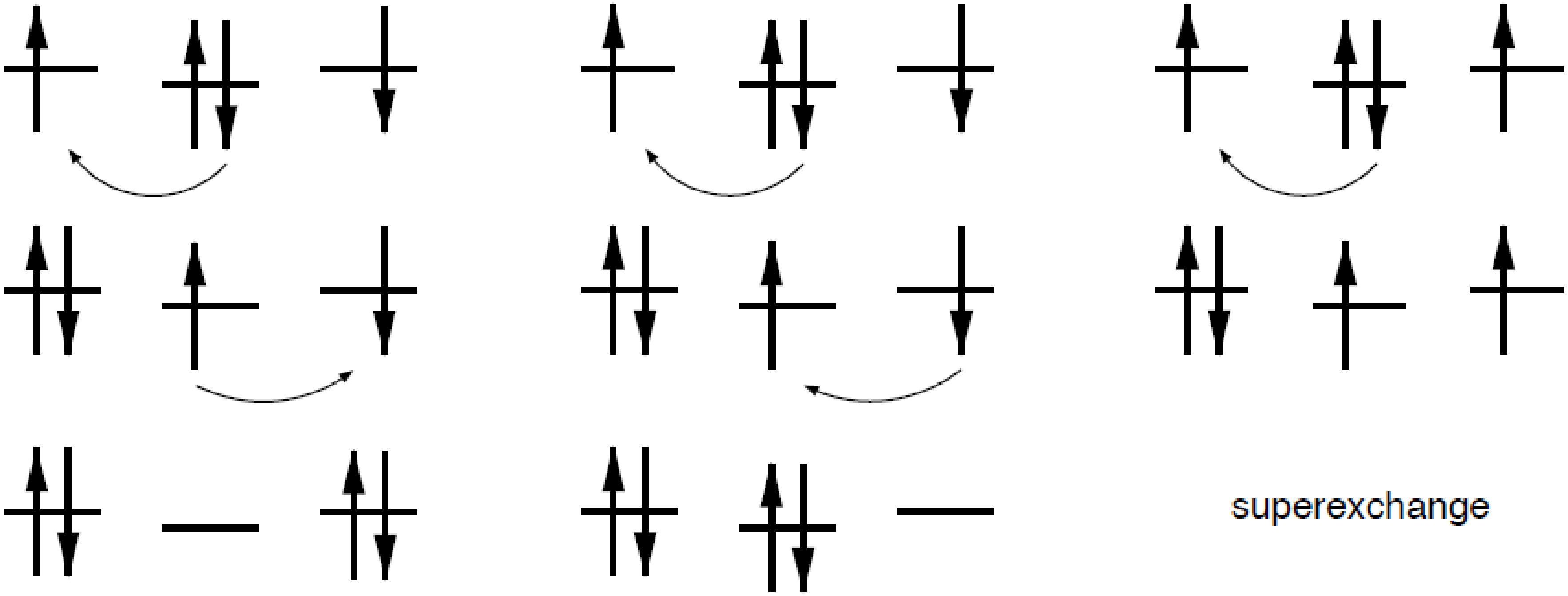


Fig. 5: In superexchange an oxygen p-orbital mediates the exchange interaction between two transition-metal d-orbitals

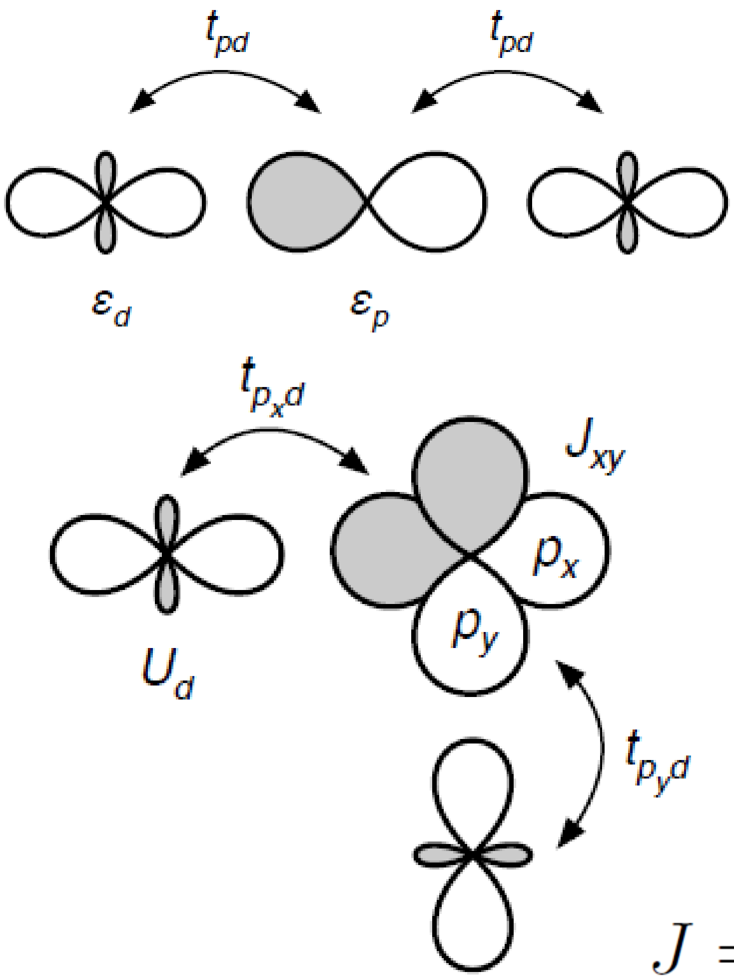
Kinetic superexchange (qualitative picture)



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. 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, making them less favorable energetically.

The energy splitting between ↑↑ and ↑↓ is $J = \frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2}\left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}}\right)$

Ferromagnetic superexchange



Dependence of superexchange on geometry: When the d-orbitals interact via an oxygen in-between (the 180° geometry shown on the top), 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° (bottom), 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, super-exchange is mediated via the Coulomb exchange on the connecting oxygen.

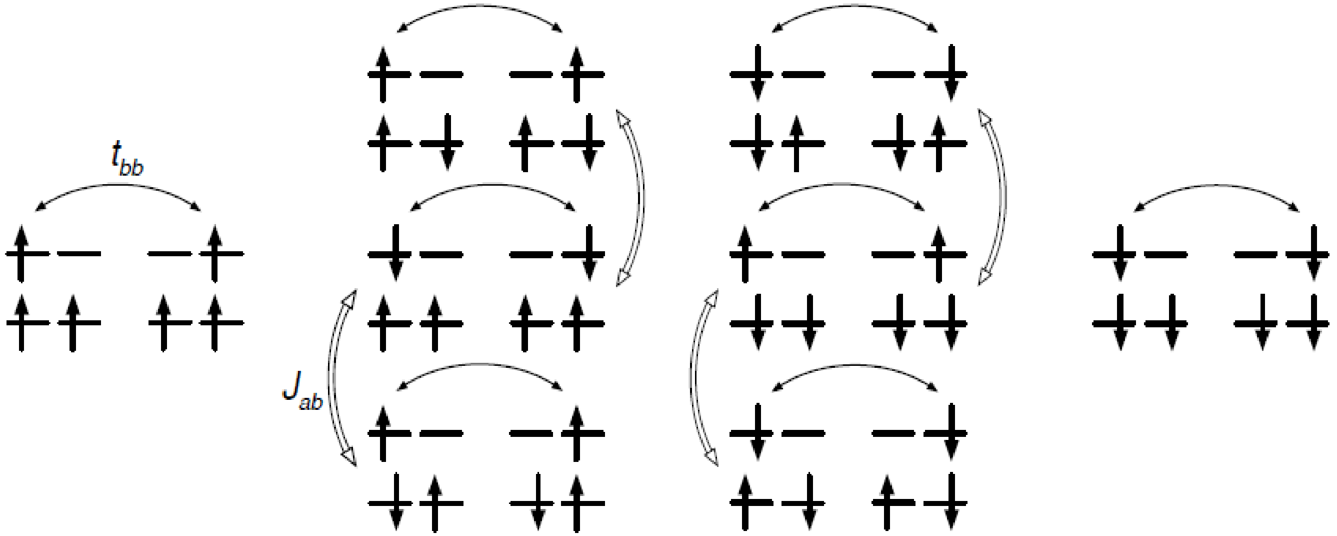
The energy gain from ferromagnetic superexchange

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

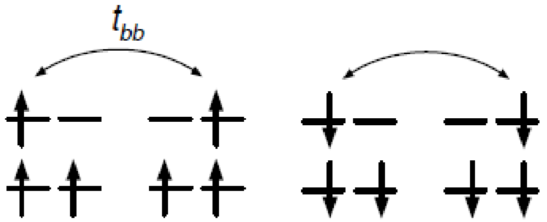
Ferromagnetic superexchange is much [by a factor $J_{xy}/(U_d+\Delta)$] weaker than antiferromagnetic 180° superexchange coupling.

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° 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 cost U. Hence these compounds are usually metallic.



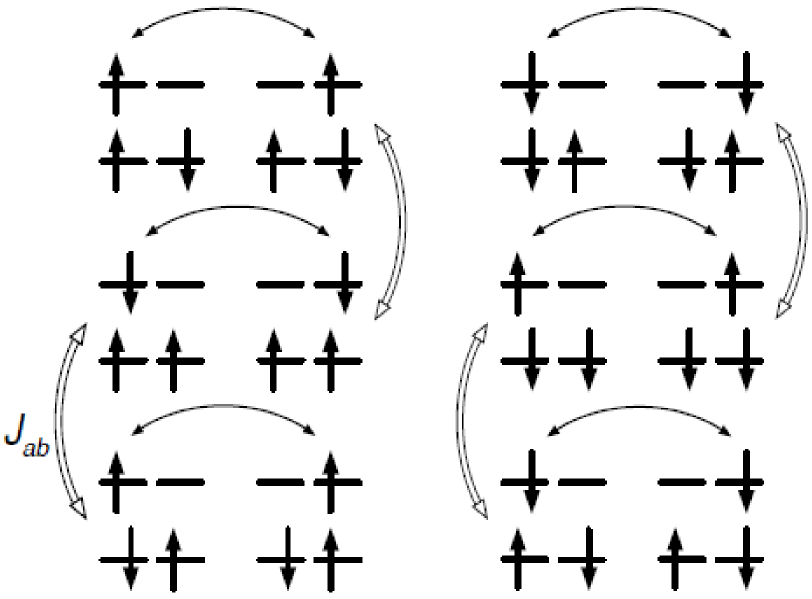
Double exchange (2)



The two S_z=3/2 states have simple 2x2 Hamiltonian

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

The eigenstates are the bonding/antibonding (symmetric/antisymmetric) linear combinations of the Hund's rule triplets. Their dispersion is ±t: $\varepsilon_{\pm} = -J_{ab} \pm t_{bb}$



The six S_z=1/2 states have Hamiltonian

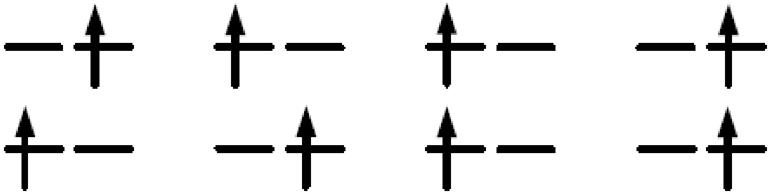
$$H = \begin{pmatrix} -J_{ab} & -t_{bb} & 0 & 0 & 0 & 0 \\ -t_{bb} & 0 & -J_{ab} & 0 & 0 & 0 \\ 0 & -J_{ab} & 0 & -t_{bb} & 0 & 0 \\ 0 & 0 & -t_{bb} & 0 & -J_{ab} & 0 \\ 0 & 0 & 0 & -J_{ab} & 0 & -t_{bb} \\ 0 & 0 & 0 & 0 & -t_{bb} & -J_{ab} \end{pmatrix}$$

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** $S_{\rm tot} = 3/2.$

Orbital ordering

Exchange mechanisms are not restricted to spins. The orbital occupations can also interact (Kugel & Khomskii, 1973). Consider

two sites with two orbitals a and b and the situation when both electrons have the same spin, e.g., spin-up:



Also assume that hopping is possible only between the same orbitals.

The corresponding Hamiltonian is similar to direct kinetic exchange:

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

Hence, by analogy to direct kinetic exchange, the ***antiferro orbital*** ordering is more favorable. The effective Hamiltonian

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

Double exchange (C. Zener, 1951; P.-G. de Gennes, 1960).

(1) Intra-atomic exchange is strong so that the only important configurations are those where the spin of each carrier is parallel to the local ionic spin.

(2) The carriers do not change their spin orientation when moving; accordingly, they can hop from one ion to the next ion if the two ionic spins are not antiparallel.

(3) When hopping is allowed the ground state is lowered, because the carriers are then able to participate in the binding.

This results in a lowered energy for FM configurations.

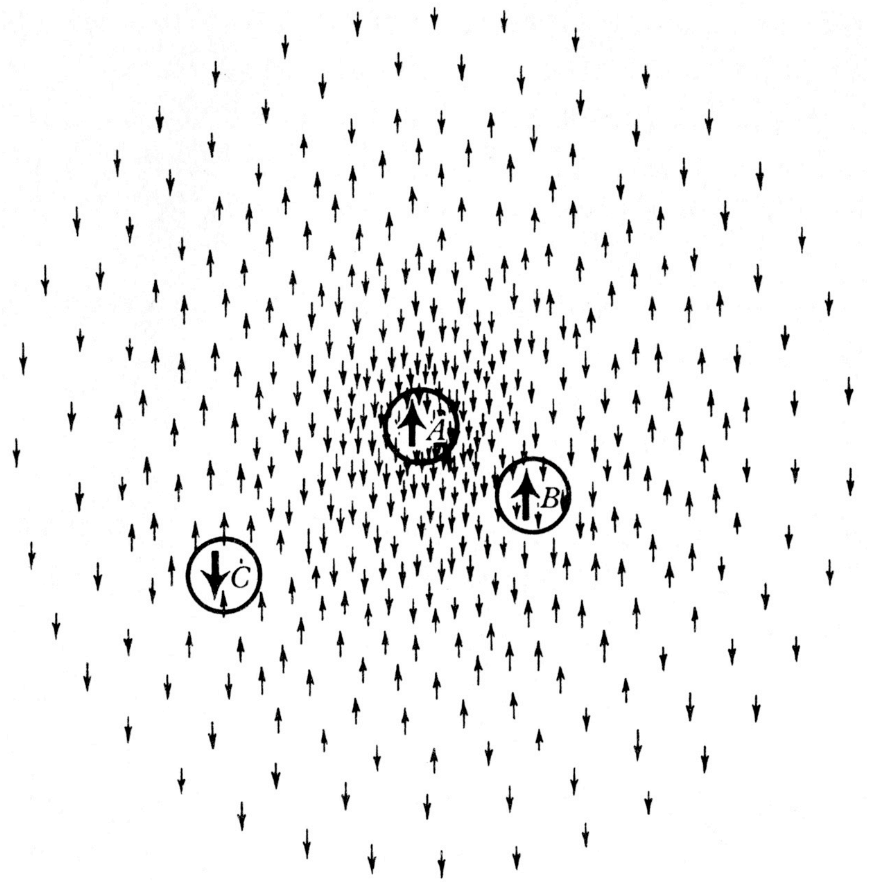
Interaction between localized moments in metals

Indirect exchange in diluted metallic alloys; RKKY interaction

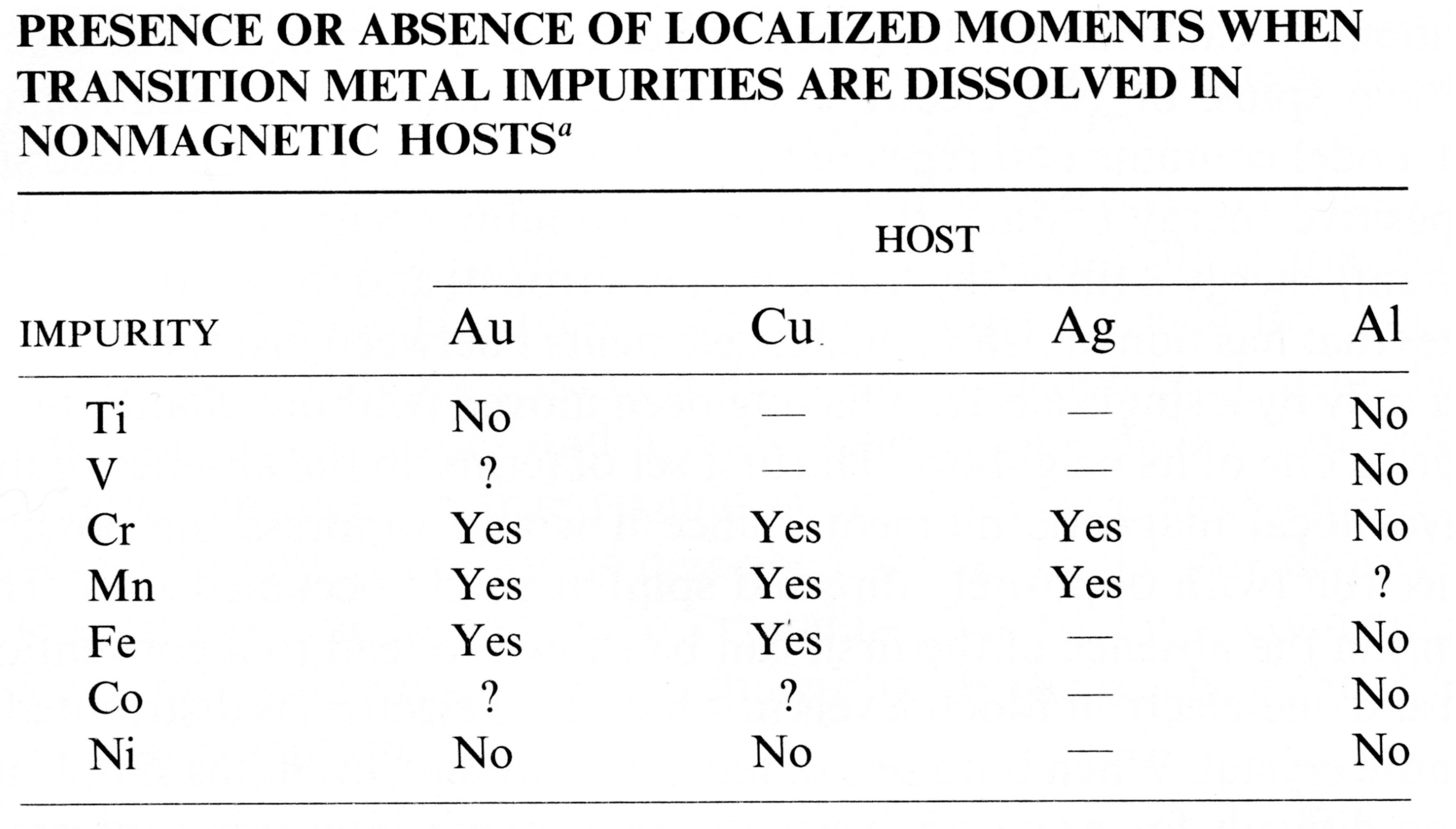
Friedel oscillations of spin polarization of the s-electrons about the impurity A.

Ferromagnetic interaction with the neighbouring impurity B.

Antiferromagnetic interaction with the impurity at a larger distance C.



[from J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1979)]



PRESENCE OR ABSENCE OF LOCALIZED MOMENTS WHEN TRANSITION METAL IMPURITIES ARE DISSOLVED IN NONMAGNETIC HOSTS[a]

	HOST			
IMPURITY	Au	Cu	Ag	Al
Ti	No	—	—	No
V	?	—	—	No
Cr	Yes	Yes	Yes	No
Mn	Yes	Yes	Yes	?
Fe	Yes	Yes	—	No
Co	?	?	—	No
Ni	No	No	—	No

[from N. W. Ashcroft and N. D. Mermin, *Solid State Physics*
(Sounders College Publishing, Fort Worth, 1976)]

The Kondo effect

The resistivity as a function of temperature for dilute CuFe alloys plotted as R/R_0 vs. T ($R_0 = R(0^\circ\mathrm{C})$).

J. Kondo, 1964:

$$T_K \sim \exp\left[-\frac{1}{n(E_F)\,|J|}\right]$$

[from N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Sounders College Publishing, Fort Worth, 1976)]