Lecture 4
"Magnetic interactions"

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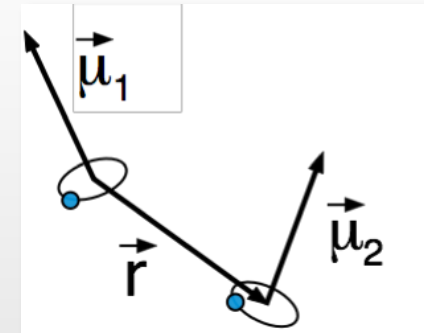paolasini@esrf.fr

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LECTURE 4:
"MAGNETIC INTERACTIONS"

- Dipole vs exchange magnetic interactions.
- Direct and indirect exchange interactions.
- Anisotropic exchange interactions.
- Interplay between orbital and magnetic order.

- Follows directly from Maxwell equations
- Direct interaction between two magnetic moments
- depends on their relative orientation

$$E = \frac{\mu_0}{4\pi r^3}\left[\mu_1 \cdot \mu_2 - \frac{3}{r^2}(\mu_1 \cdot \mathbf{r})(\mu_2 \cdot \mathbf{r})\right]$$

The dipolar interaction is very weak:

$$U \approx \frac{\mu_1\mu_2}{4\pi\, r^3} \qquad r \sim 1\text{Å}, \qquad => U \sim 10^{-23}J = 1K$$
$$\mu_1 = \mu_2 = 1\mu_B$$

Long range interaction, responsible for demagnetizing field and ferro-magnetic domains.
Dipolar interaction are important only when the exchange interactions are small.

- Magnetism is fully quantum mechanical

Competition between the kinetic energy of the electrons squeezed in a small box and the Coulomb repulsion
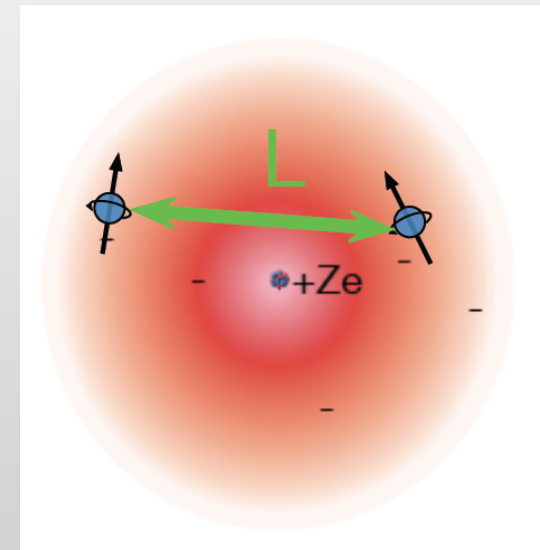
The size of atoms is given by the balance of these two terms:

Kinetic energy $\quad \sim \quad \dfrac{\hbar^2}{2m}\dfrac{\pi^2}{L^2} \quad \approx eV$

Coulomb energy $\quad \sim \quad \dfrac{e^2}{4\pi\varepsilon_0\, L} \quad \approx eV$

Spin-orbit $\qquad\qquad\qquad\quad \approx meV$
Magneto-crystalline anisotropy $\quad \approx \mu eV$

Light atoms:
Z small

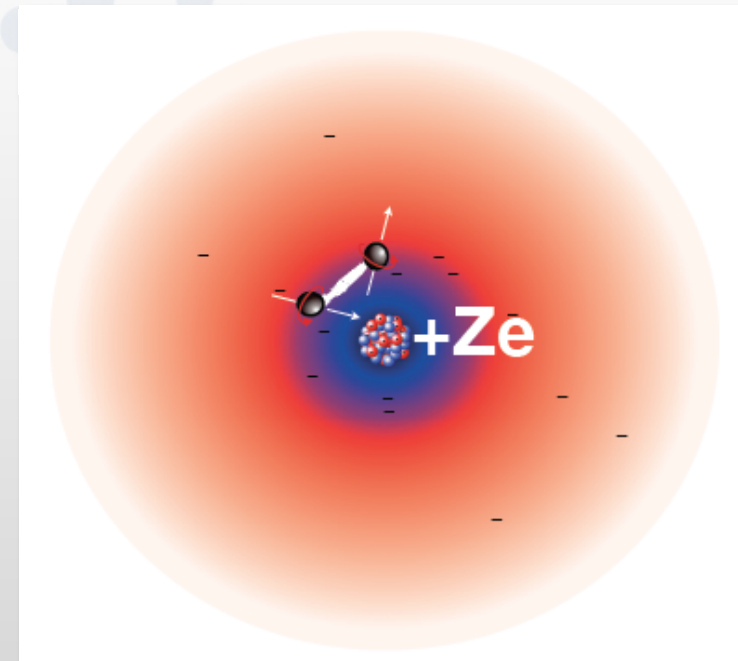Heavy atoms:
Z huge

Electrons far apart:
Weakly interacting

Electrons drawn tightly
together by nucleus:
Strongly interacting and
prone to correlated behavior

Quantum-mechanical description of identical particle

- **Indistinguishable** particles:
  - Bosons: share the same quantum state
    photons, gluons, phonons, helium-4 atoms.
  - Fermions: follows the Pauli exclusion principle

    Electrons, neutrinos, quarks, protons, neutrons, helium-3 atoms

- Symmetry of quantum states
  - Symmetrical (bosons) and anti-symmetrical (fermions) overall wavefunctions

- Statistical properties of identical particles system:
  - Fermions: Fermi-Dirac statistic
  - Bosons: Bose-Einstein statistic

Pauli spin matrices

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

Electron Wavefunction

$$\psi = \begin{pmatrix} \psi\left(\mathbf{x}, +\frac{1}{2}\right) \\ \psi\left(\mathbf{x}, -\frac{1}{2}\right) \end{pmatrix}$$

$$\sigma_x \psi = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \psi\left(\frac{1}{2}\right) \\ \psi\left(-\frac{1}{2}\right) \end{pmatrix}$$

$$\sigma_y \psi = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \psi\left(\frac{1}{2}\right) \\ \psi\left(-\frac{1}{2}\right) \end{pmatrix}$$

$$\sigma_z \psi = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \psi\left(\frac{1}{2}\right) \\ \psi\left(-\frac{1}{2}\right) \end{pmatrix}$$

=>

$$s_x \psi = \begin{pmatrix} \frac{1}{2}\psi\left(-\frac{1}{2}\right) \\ \frac{1}{2}\psi\left(\frac{1}{2}\right) \end{pmatrix}$$

$$s_y \psi = \begin{pmatrix} -\frac{i}{2}\psi\left(-\frac{1}{2}\right) \\ \frac{i}{2}\psi\left(\frac{1}{2}\right) \end{pmatrix}$$

$$s_z \psi = \begin{pmatrix} \frac{1}{2}\psi\left(\frac{1}{2}\right) \\ -\frac{1}{2}\psi\left(-\frac{1}{2}\right) \end{pmatrix}$$

SPINOR: representation of the spin part of electron wavefunction

$$\psi(\mathbf{x},+1/2) => |\uparrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \psi(\mathbf{x},-1/2) => |\downarrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Pauli spin operators

$$\hat{\mathbf{S}} = \frac{1}{2}\hat{\sigma} \qquad \hat{S}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{S}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

We define the eigenstates (spinor states) corresponding to the component along along the z-axis as :

$$|\uparrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |\downarrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

And $\hat{S}_z$ take the eigenvalues $m_s = \pm 1/2$ (units of $\hbar$):

$$\hat{S}_z|\uparrow_z\rangle = \frac{1}{2}|\uparrow_z\rangle, \quad \hat{S}_z|\downarrow_z\rangle = -\frac{1}{2}|\downarrow_z\rangle$$

By analogy, the eigenstates corresponding to the spin pointing along the others cartesian coordinate are:

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad |\downarrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad |\uparrow_y\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} \quad |\downarrow_y\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

A generic quantum state could be represented as can be written as as a linear combination of spinors states:

$$|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix} = a|\uparrow_z\rangle + b|\downarrow_z\rangle$$

with the normaliztion $\quad |a|^2 + |b|^2 = 1$

Notice that the magnitude

$$\hat{\mathbf{S}}^2|\psi\rangle = \left(\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2\right)|\psi\rangle = \left(\frac{1}{4} + \frac{1}{4} + \frac{1}{4}\right)|\psi\rangle = \frac{3}{4}|\psi\rangle$$

The eigenvalues of $\hat{S}^2$ are S(S+1)

- The commutation relations between spin operators are:
$$[\hat{S}_x, \hat{S}_y] = i\ \hat{S}_z \qquad \text{… and cyclic permutation}$$

- The operator $\hat{S}_i$ commutes with the operator $\hat{S}^2$:
$$[\hat{S}^2, \hat{S}_i] = 0$$
… which means that we can simultaneously know both the total spin and one of its components

The coupling of two spins is described by the Heisenberg Hamiltonian:

$$\hat{H} = A\,\hat{S}_1 \cdot \hat{S}_2$$

As we have already see in the previous discussion, the total spin operator for two particle system is a linear combination of the individual spin operators:

$$\hat{S}_{tot} = \hat{S}_1 + \hat{S}_2 \quad => \quad (\hat{S}_{tot})^2 = (\hat{S}_1)^2 + (\hat{S}_2)^2 + 2\hat{S}_1 \cdot \hat{S}_2$$

If the particle are two electrons, i.e. spin-½ particles, the total spin quantum number is S=0 or S=1.

The eigenvalues of $\hat{S}_{tot}^2$ are S(S+1) = 0, 2 for S=0, 1 respectively

Because the eigenvalues of $(\hat{S}_1)^2$ and $(\hat{S}_2)^2$ are both ¾ :

From :
$$(\hat{S}_{tot})^2 = (\hat{S}_1)^2 + (\hat{S}_2)^2 + 2\hat{S}_1 \cdot \hat{S}_2$$

S=0	0	=	¾	+	¾	+2(-¾)
S=1	2	=	¾	+	¾	+2(+¼)

$$\Rightarrow \quad \hat{S}_1 \cdot \hat{S}_2 \quad \nearrow \; -¾ \quad \searrow \; ¼$$

And then the eigenvalues of the Hamiltonian H=$A\,\hat{S}_1 \cdot \hat{S}_2$ are the two energy levels:

$E_T = ¼\,A$ S=1   triplet state degeneracy 2S+1=3

$E_S = -¾\,A$ S=0   singlet state degeneracy 2S+1=1

Notice that A = − (E_S − E_T) is proportional to the exchange integral in the Heisenberg Hamiltonian … as we will see

$$A > 0 \qquad\qquad A < 0$$

Singlet ground state S=0
Anti-ferromagnetic coupling

Triplet ground state S=1
Ferromagnetic coupling

The z-component of the spin m_s along a magnetic field takes the values $m_s=0$ for the singlet and $m_s=-1,0,1$ for the triplet if a magnetic field

The wave function associated to the two states

$$| \uparrow_z \uparrow_z \rangle \quad | \downarrow_z \downarrow_z \rangle$$

is symmetric under exchange of the two spins

But the states $\quad | \downarrow_z \uparrow_z \rangle \quad | \uparrow_z \downarrow_z \rangle$

are not anti- symmetric, or symmetric under the exchange of spin
… just because:

$$| \uparrow_z \downarrow_z \rangle \rightarrow | \downarrow_z \uparrow_z \rangle \neq \pm | \uparrow_z \downarrow_z \rangle$$

Eigenstate	m_s	s	Eigenvalues
$\| \uparrow_z \uparrow_z \rangle$	1	1	$\frac{1}{4}$
$\frac{\|\uparrow_z \downarrow_z\rangle + \|\downarrow_z \uparrow_z\rangle}{\sqrt{2}}$	0	1	$\frac{1}{4}$
$\| \downarrow_z \downarrow_z \rangle$	-1	1	$\frac{1}{4}$
$\frac{\|\uparrow_z \downarrow_z\rangle - \|\downarrow_z \uparrow_z\rangle}{\sqrt{2}}$	0	0	$-\frac{3}{4}$

$$\chi(s_1, s_2) = \boxed{| \uparrow\uparrow \rangle, \; | \downarrow\downarrow \rangle, \; \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}}, \; \boxed{\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}}$$
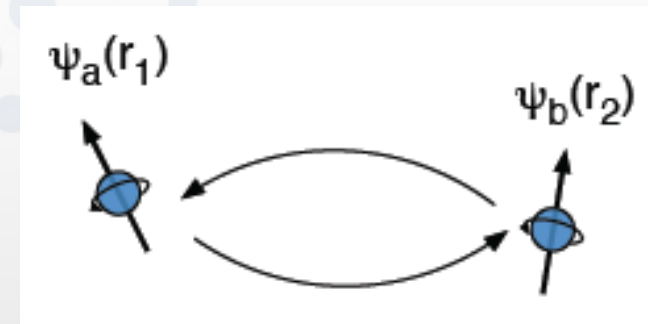
Symmetric (triplet χ_T)   Anti-symmetric (singlet χ_S)

The wave overall functions Ψ_S or Ψ_T must be anti-symmetric (because the electrons are Fermions).

$$\Psi_S = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\,\chi_S$$

$$\Psi_T = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]\,\chi_T$$

Energies of two states:

$$E_S = \int \Psi_S^* \hat{\mathcal{H}} \Psi_S \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

$$E_T = \int \Psi_T^* \hat{\mathcal{H}} \Psi_T \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

Effective Hamiltonian:

$$\hat{\mathcal{H}} = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\mathbf{S}_1 \cdot \mathbf{S}_2$$

Spin part

$$\hat{\mathcal{H}}^{\text{spin}} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$$

J=exchange constant

$$J = \frac{E_S - E_T}{2} = \int \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\hat{\mathcal{H}}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1) \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

We can extend the two electron model to a system of many electrons, and write the Hamiltonian of Heisenberg model as:

$$\hat{\mathcal{H}} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \qquad \text{or} \qquad \hat{\mathcal{H}} = -2\sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Where J_{ij} could be replaced by the exchange constant J between the two first neighbour electrons:

$$J = \frac{E_S - E_T}{2} = \int \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\hat{\mathcal{H}}\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\, d\mathbf{r}_1\, d\mathbf{r}_2.$$

J>0 $E_S > E_T$ Triplet ground state   Ferromagnetic interaction
J<0 $E_T > E_S$ Singlet ground state   Anti-ferromagnetic interaction

Interaction between neighbours atoms due to the overlap of neighbouring magnetic orbitals.

But the exchange interaction is normally short ranged, and cannot explain the long range ordered magnetic structure!

In rare earths the 4f atomic orbitals fall down very rapidly with distance and the exchange integral is very small.

The direct exchange is active in metals, albeit a correct description need to consider both the localized and the band character of the electrons

Competition between the kinetic exchange interaction involving the ligands between two magnetic ions and Coulomb repulsion

$$H = H' + H_0 = \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$
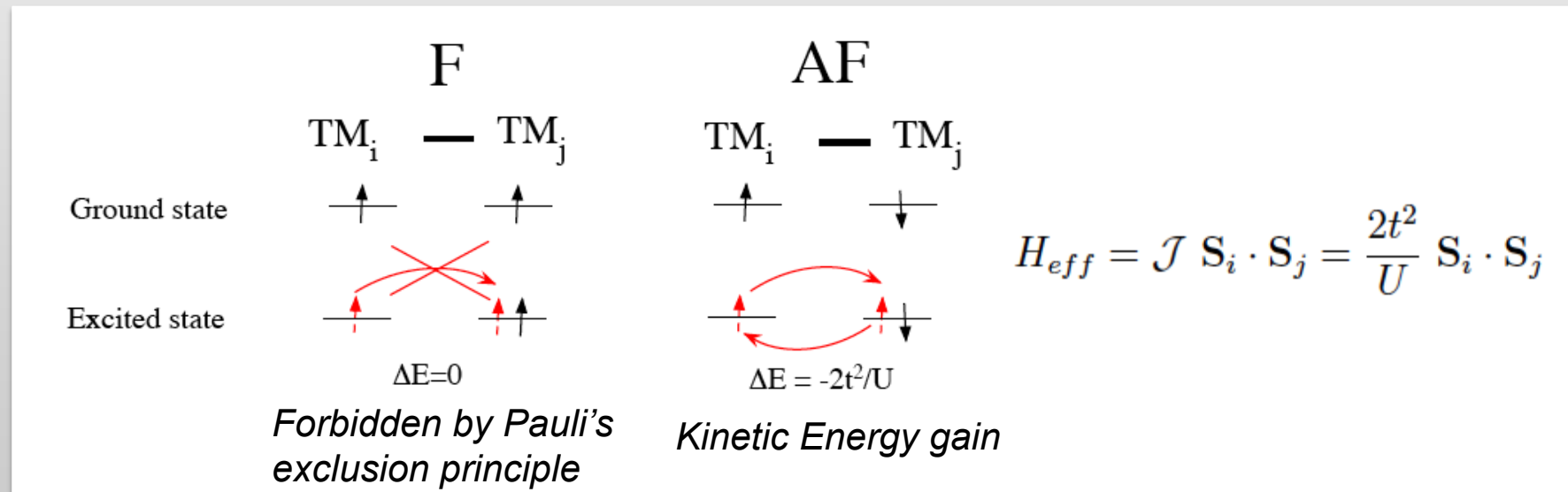
Kinetic term
t_{ij} -> hopping integral

Coulomb inter-atomic repulsion
$n_i = N_{el}/N_{sites}$ -> occupation number
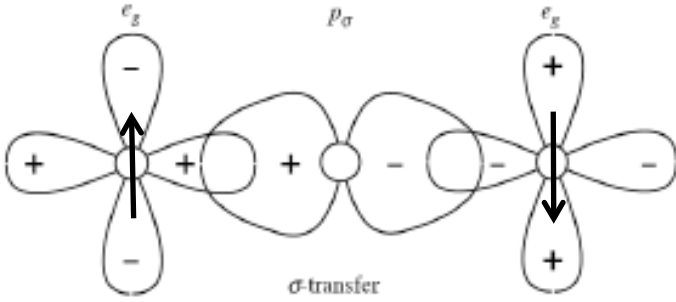
$t_{ij} \gg U$ => itinerant system (metallic state)
$t_{ij} \ll U$ => localized system (insulator)

F

TM$_i$ — TM$_j$

Ground state

Excited state

$\Delta E = 0$

Forbidden by Pauli's exclusion principle

AF

TM$_i$ — TM$_j$

$\Delta E = -2t^2/U$

Kinetic Energy gain

$$H_{eff} = \mathcal{J}\, \mathbf{S}_i \cdot \mathbf{S}_j = \frac{2t^2}{U} \mathbf{S}_i \cdot \mathbf{S}_j$$

If the ligands are take into account, we consider the charge-transfer hopping t_{pd} and the Coulomb repulsion term U_{pp}

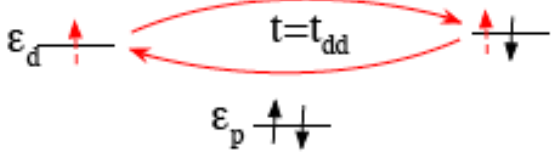$$\Delta = \mathcal{E}_d - \mathcal{E}_p$$

Mott-Hubbard insulator
$$\Delta \gg U$$

$$d^n + d^n \rightarrow d^{n-1} + d^{n+1}$$
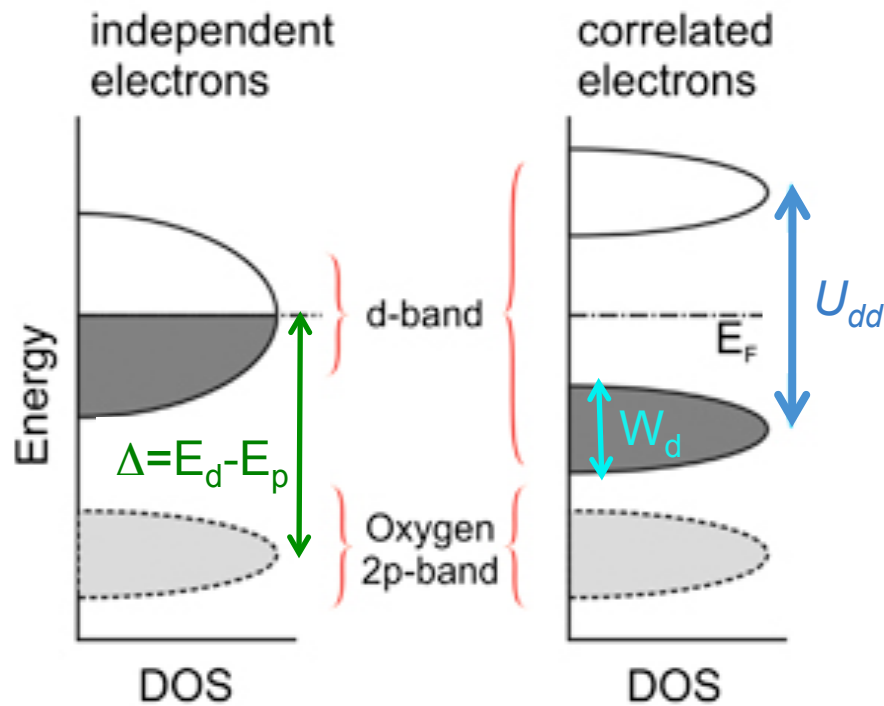
$t = t_{dd}$ $J = 2t_{dd}^2/U$

Charge transfer insulator
$$\Delta \ll U$$

$$d^n + p^6 \rightarrow d^{n+1} p^5 = d^{n+1} L$$

$t = t_{pd}$ $J = 2t_{pd}^4/\Delta^2(2\Delta + U_{pp})$
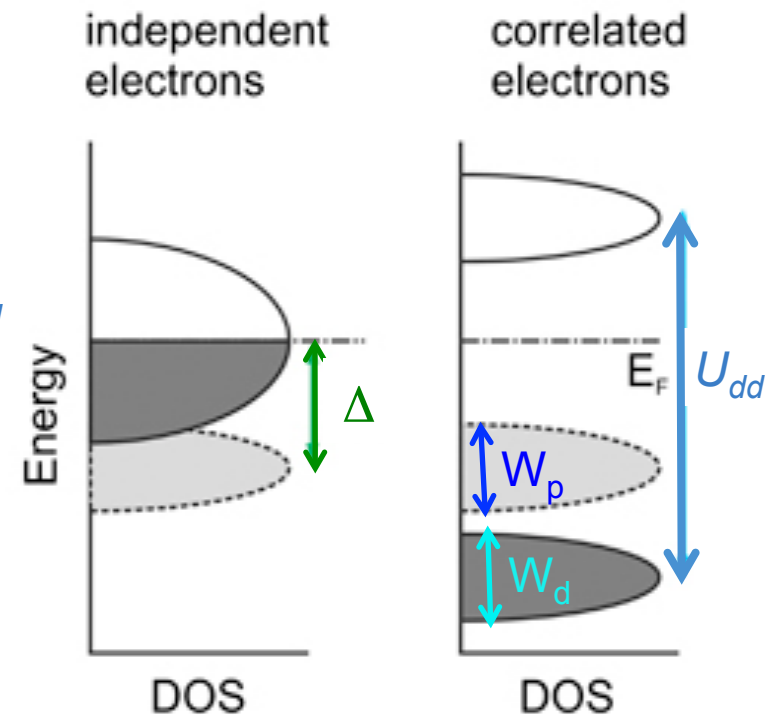
(Biquadratic exchange)

Mott-Hubbard insulator
$\Delta \gg U$

independent electrons | correlated electrons

d-band

Oxygen 2p-band

$\Delta = E_d - E_p$

U_{dd}

W_d

E_F

DOS | DOS

$E_{gap} = U_{dd} - W_d = U - \Delta$

Ex.: V_2O_3, Ti_2O_3, Cr_2O_3.

Charge-transfer insulator
$\Delta \ll U$

independent electrons | correlated electrons
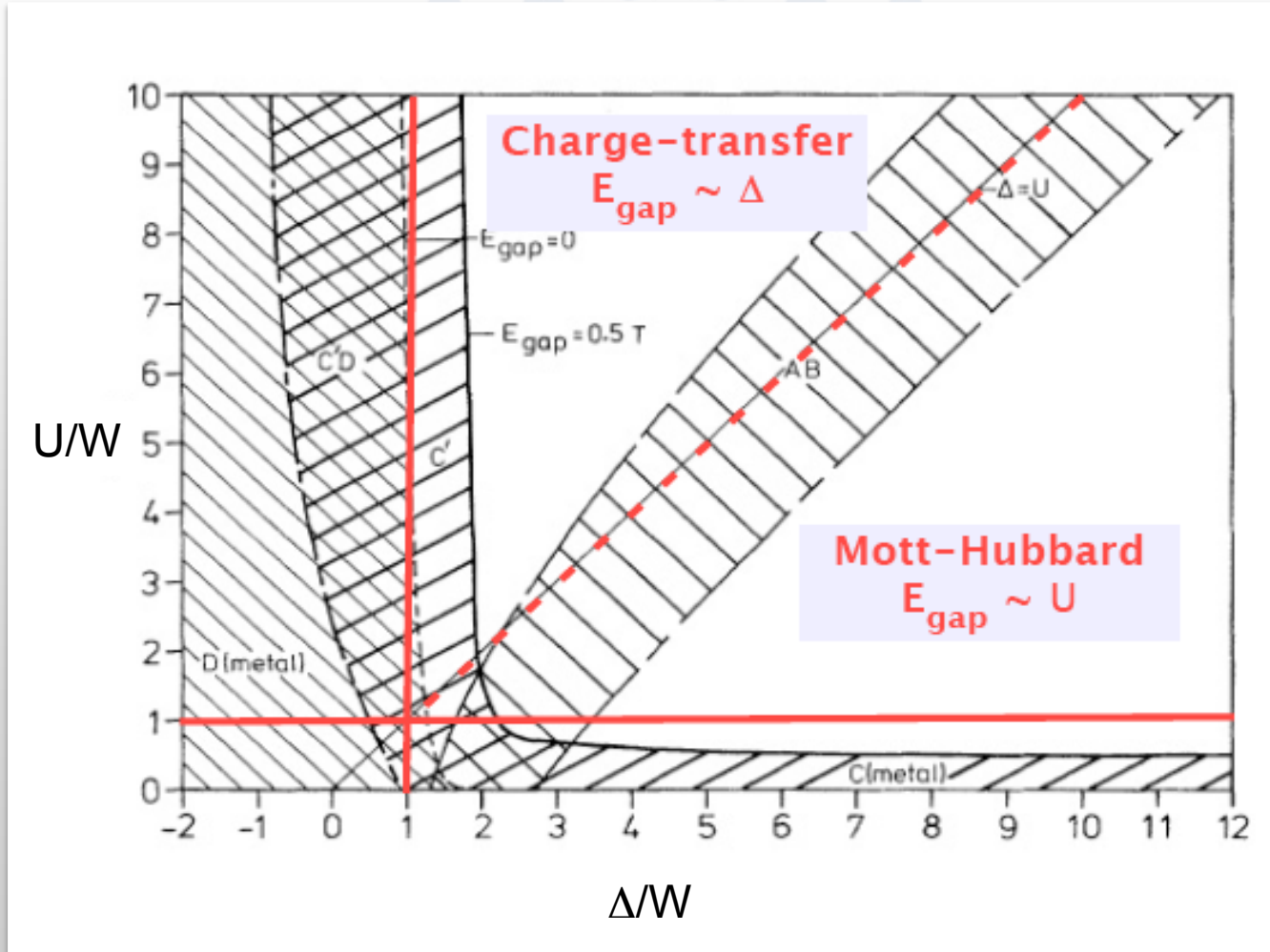
Δ

U_{dd}

W_p

W_d

E_F

Energy

DOS | DOS

$E_{gap} = \Delta - (W_p + W_d/2)$

Ex.: $CuCl_2$, $CuBr_2$, CuO, $NiCl_2$, $NiBr_2$.

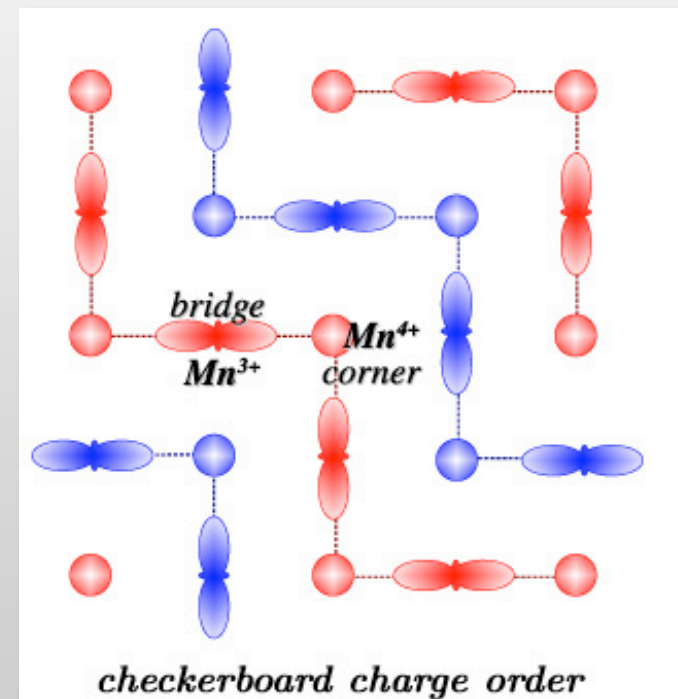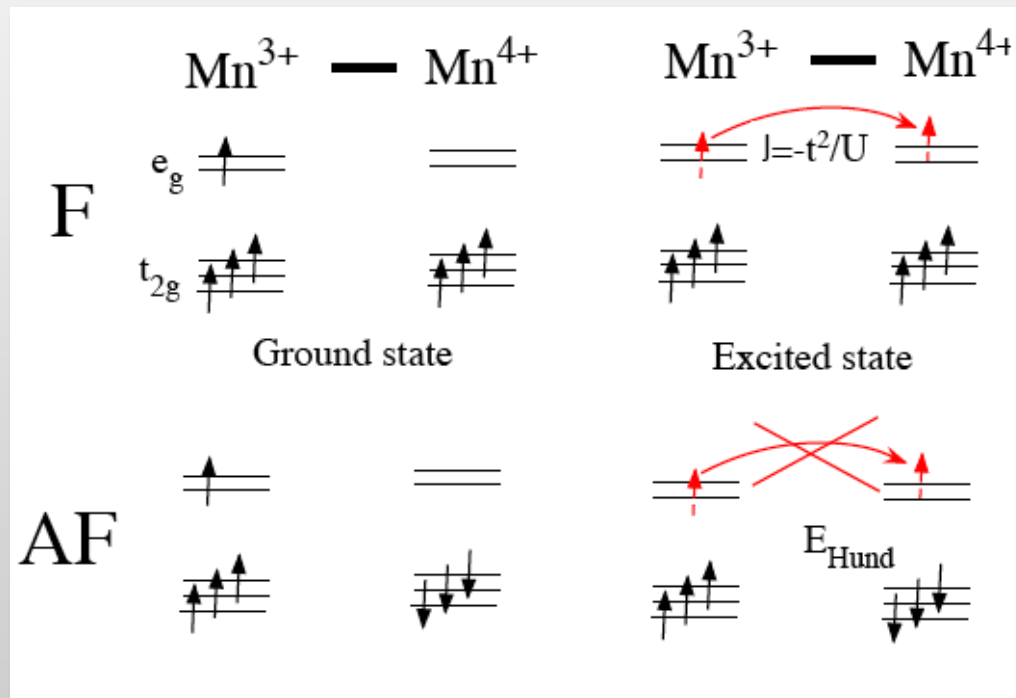$U/W > \Delta/W$ => *Charge transfer and gap is p-d type*
$U/W < \Delta/W$ => *Mott-Hubbard and gap is d-d type*

Occurs in mixed valence ions which display different oxidation states

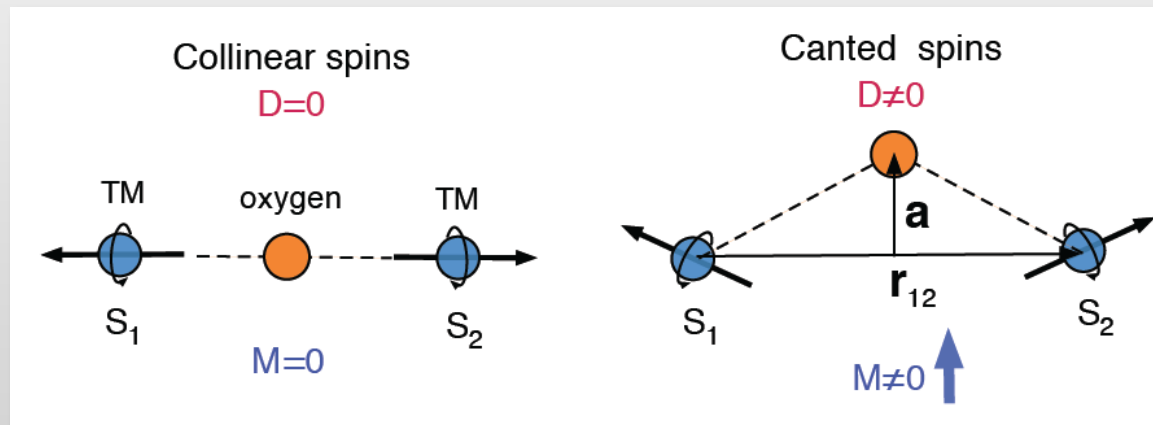*Ex.: LaMnO$_3$: Mn^{3+} (3d^4) and Mn^{4+} (3d^3)*
Hopping between e$_g$ shells allowed for a ferromagnetic alignement of
Mn^{3+} and Mn^{4+} ions (1st Hund's rule satisfied)

The Dzyaloshinskii-Moriya (DM) interaction is an antisymmetric, anisotropic exchange coupling between two spins S_1 and S_2 on a lattice bond r_{12} with no inversion center:

$$H_{DM} = D_{12} \cdot S_1 \times S_2 \qquad D_{12} \sim \lambda \, a \times r_{12}$$

The Dzyaloshinskii-Moriya vector D is proportional spin-orbit coupling constant λ, and depends on the position of the oxygen ion a between two magnetic transition metal ions.
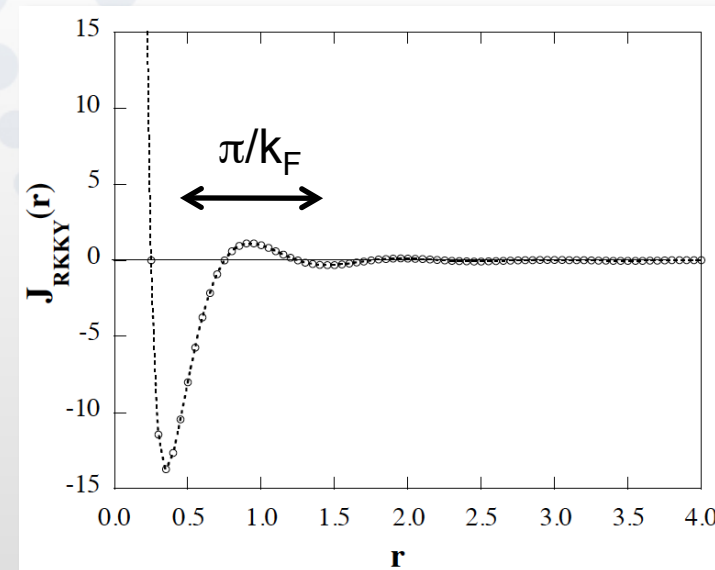

Canting of magnetic moments and a resulting net magnetization M≠0 in an otherwise collinear antiferromagnet (weak ferromagnetism)

Ex.: α-Fe_2O_3, $MnCO_3$, $CoCO_3$, multiferroics.

Indirect exchange interaction mediated by the conduction electrons,
It is called also RKKY (Ruderman, Kittel, Kasuya and Yosida) interaction.

$$\mathcal{J}_{RKKY}(r) \propto \frac{1}{r^3} \cos(2k_F r)$$

k_F=Fermi wavevector

The coupling is oscillatory and could be ferromagnetic or antiferromagnetic, depending on the separation of neighbours atoms.

Important coupling in the case of Rare-earths intermetallic compounds.

- Orbital ordering influence the superexchange interactions because the lowering of local crystal field symmetries affect the spatial part of wavefunctions, and thus the hopping integrals

- The orbital configurations and the resulting ferromagnetic or antiferromagnetic exchange interactions are summarized in the :
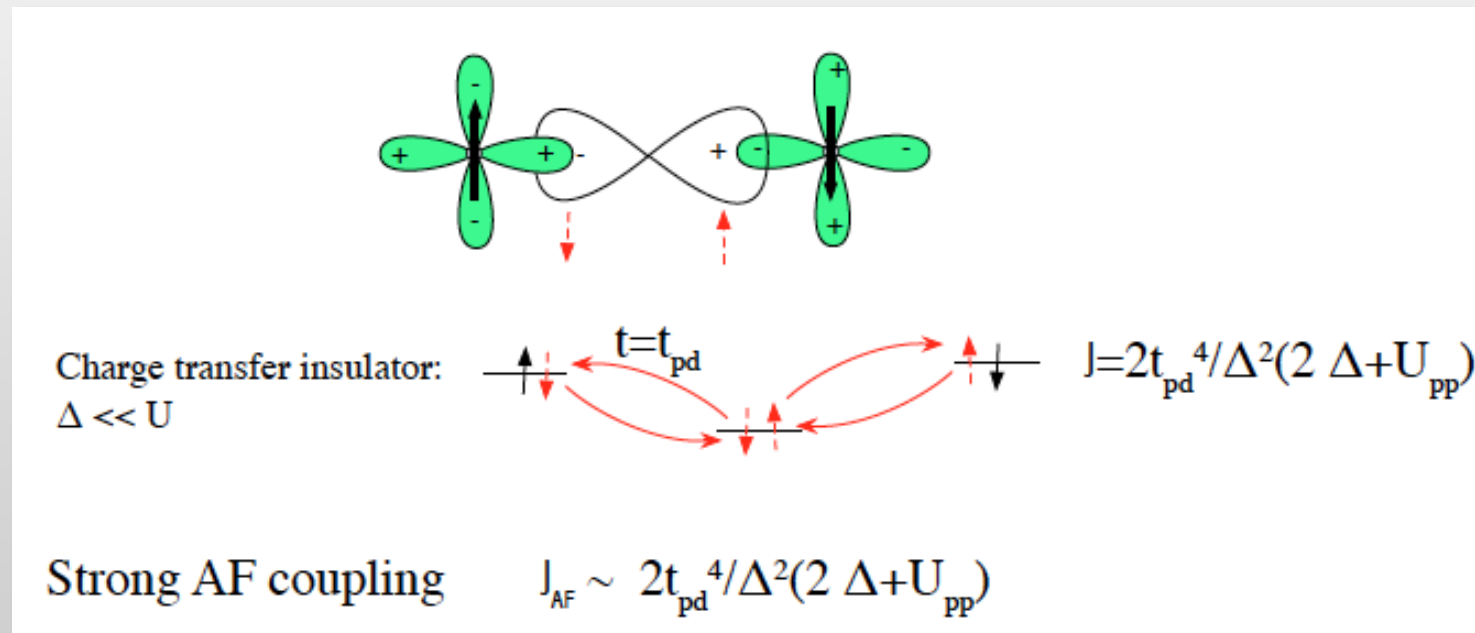
Goodenough-Kanamori-Anderson rules:

RULE 1: Half-filled orbitals: 180º superexchange

RULE 2: Half-filled 90º exchange

RULE 3: Overlap half-filled and empty 180º exchange
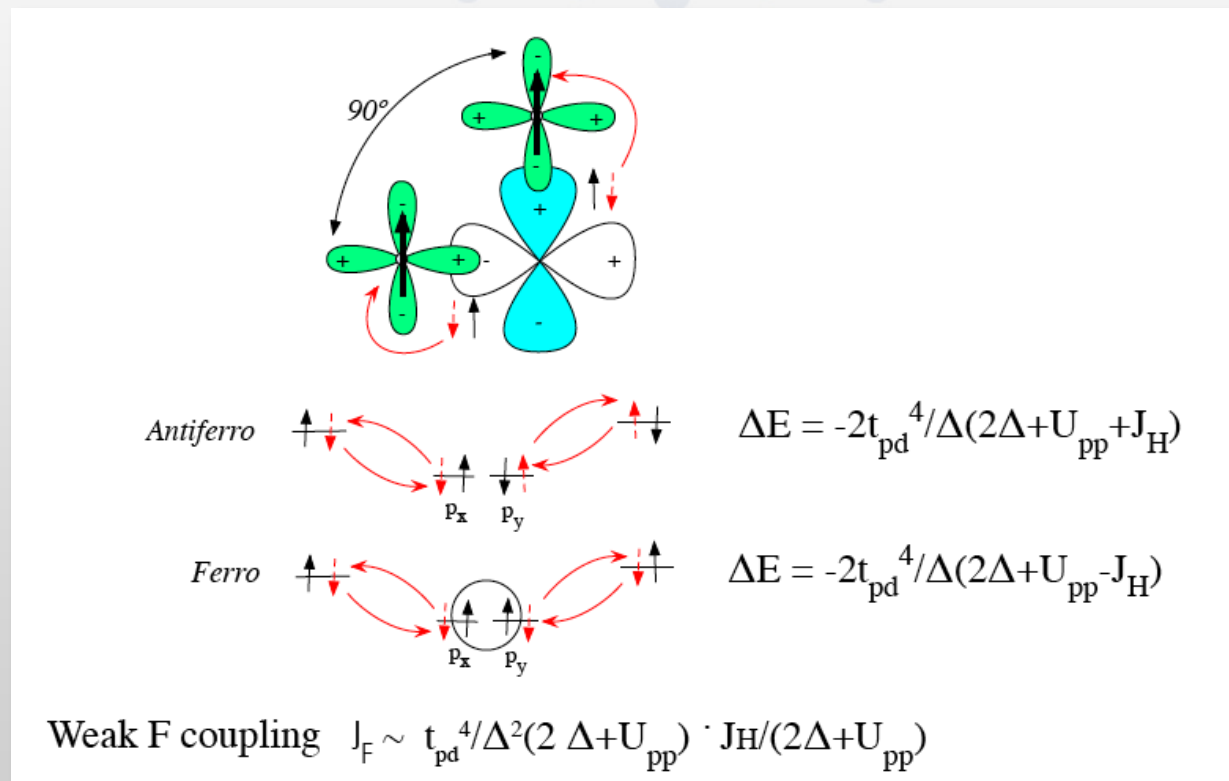
Half-filled orbitals: 180º superexchange

- Already considerend in the case of superexchange
- Can be due to a direct overlap of 3d orbitals (Mott-hubbard) or mediated by ligands (Charge-transfer)
- Is always strong and favours an antiferromagnetic exchange between neighbors ions

Charge transfer insulator: $\Delta \ll U$

$t = t_{pd}$

$J = 2t_{pd}^4 / \Delta^2 (2\Delta + U_{pp})$

Strong AF coupling $\quad J_{AF} \sim 2t_{pd}^4 / \Delta^2 (2\Delta + U_{pp})$

- Ex.: Most of transition-metal oxides, , $LaMnO_3$, $KCuF_3$…
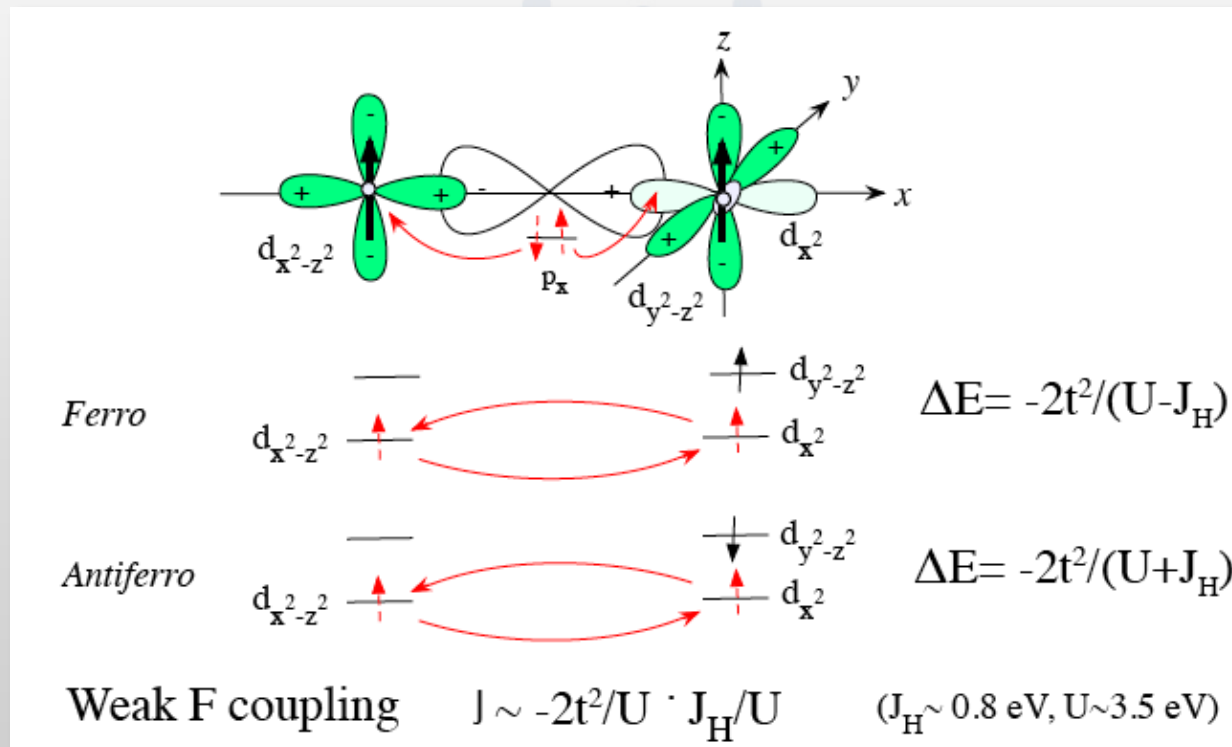
Half-filled orbitals: 90º exchange

- *Electron hopping via different ligand orbitals (ex. 2p oxygen)*
- *1st Hund's rule at oxygen site favours a ferromagnetic exchange*
- *This exchange interaction is weak*

Antiferro $\Delta E = -2t_{pd}^4/\Delta(2\Delta+U_{pp}+J_H)$

Ferro $\Delta E = -2t_{pd}^4/\Delta(2\Delta+U_{pp}-J_H)$

Weak F coupling $J_F \sim t_{pd}^4/\Delta^2(2\Delta+U_{pp}) \cdot J_H/(2\Delta+U_{pp})$

Ex.: Spin ladders, zig-zag spin chains, exotic magnetic structures

Overlap half-filled and empty 180º exchange

- Overlap between an occupied and an unoccupied orbital
- The hopping favour a ferromagnetic alignement of spins in the same unoccupied orbital site
- Weak ferromagnetic intra-site exchange

Ex. : Low dimensional magnetic systems (1D or 2D magnetic structures)

The superexchange Hamiltonian must be generalized to include the ORBITAL degree of freedom among with the spin ones.

$$H' \sim \underline{S}_i \bullet \underline{S}_j \qquad \text{Super-exchange spin}$$

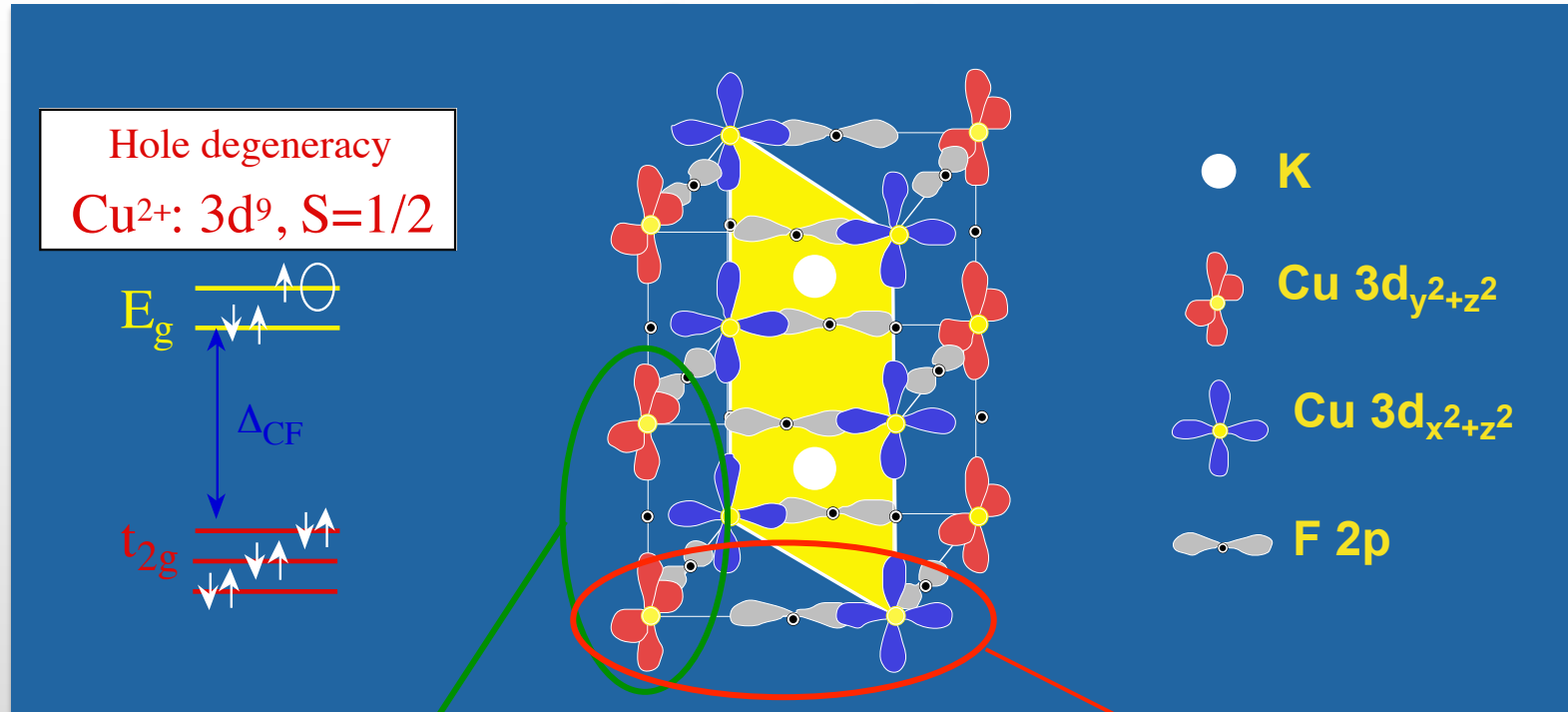$$H'' \sim \underline{\tau}_i \bullet \underline{\tau}_j \qquad \text{Super-exchange orbit (pseudo-spin)}$$

$$H''' \sim \underline{S}_i \bullet \underline{\tau}_j \qquad \text{Mixed term}$$

Close interrelation between the spin and orbital structure

Exemples:
- Colossal magnetoresistence in Manganites
- Low dimensional magnetism
- Spin ladders
- Supraconductivity?

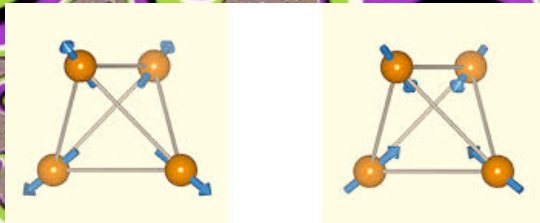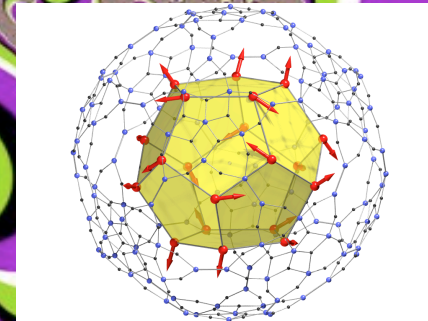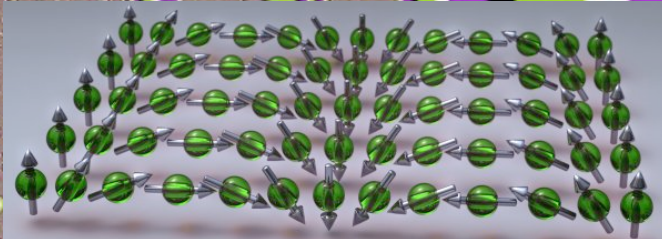(Kugel and Khomskji. Sov. Phys. Usp. 25 (1982) 231)

Hole degeneracy

Cu^{2+}: 3d^9, S=1/2

E$_g$

Δ_{CF}

t$_{2g}$

● K

Cu 3d$_{y^2+z^2}$

Cu 3d$_{x^2+z^2}$

F 2p

1st GKH rule: 180° exchange path
Strong AF exchange

3rd GKH rule: Overlap filled-empty orbitals
Weak F exchange

$$J_{AF} \sim \frac{2t^2}{U}$$

$$J_F \sim -\frac{2t^2}{U-J_H}$$

$$H = J\, S \cdot S$$