OXIDE and SEMICONDUCTOR MAGNETISM

J. M. D. Coey

Physics Department, Trinity College, Dublin 2

Ireland.

1. Single-ion effects

2. Collective Effects

3. Examples

Jcoey@tcd.ie

www.tcd.ie/Physics/Magnetism

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The story so far; 3d and 4f localized magnetism in oxides:

Single electron in a spherical atomic potential:

Wave functions $|n,l,m_l\rangle$ $\psi(r,\theta,\phi) = R_{n,l} Y_l^{ml}(\theta,\phi)$ orbitals n,l,m_l can accommodate two electrons, ↑, ↓

Multiple 3d of 4f electrons in a spherical atomic potential:

Multi-electron states - multiplets (L,S,J) $^{2S+1}L_J$ Hund's rules give lowest energy multiplet. Moment of ion is $g\mu_B J$

Single electron in a spherical atomic potential plus crystal field.

New 3d wavefunctions are produced by combining $\psi_{3d,ml}$ with different values of m_l to reflect site symmetry (often octahedral or tetrahedral). Orbltal angular momentum is quenched. The one-electron states, e.g. t_{2g} and e_g are split by the crystal field.

Multiple 3d of 4f electrons in a spherical atomic potential plus crystal field.

The multi-electron states for 3d ions are derived from the orbital terms $|L,S\rangle$ The 2L+1 fold degeneracy of these terms is raised by the crystal field. Spin-orbit coupling is a perturbation, which gives rise to magnetocrystalline anisotropy.

The multielectron states for the 4f ions are the atomic states represented by J. The crystal field in a perturbation which gives rise to magnetocrystalline anisotropy.

2. Collective effects

2.1 Electronic structure of oxides. Mott and change-transfer insulators, ZSA diagram. Metals. Non-integral d-occupancy, hopping conduction, localization, mobility edge.

2.1 Magnetic interactions. Heisenberg Hamiltonian. De Gennes factor. Superexchange interactions. Goodenough-Kannamori rules. Double exchange. Dzialoshinsky-Moriya exchange. Magnetic order in oxides.

2.3 Charge and orbital order. Interatomic orbital interactions. Orbital order. Charge order.

Some references:

Electronic structure, exchange and magnetism in oxides: D. Khomski in Spin Electronics, M. Ziese amd M. J. Thornton, (editors) Springer 2001 pp 89 - 116.

http://link.springer.de/series/lnpp/

2.1 Electronic structure of oxides.

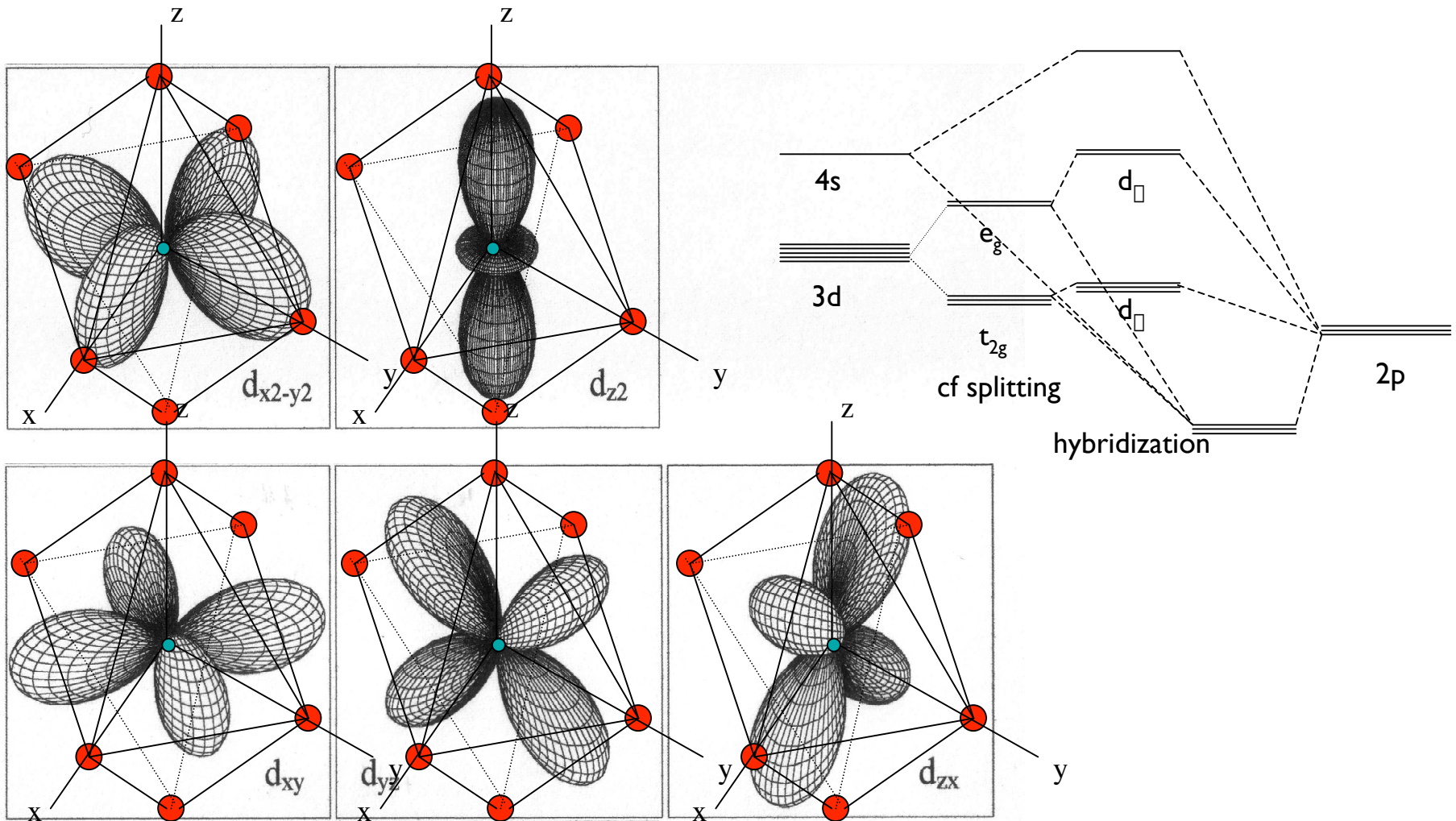Transition metal oxides can exhibit a bewildering variety of electronic states:

➢ Insulators, semiconductors

➢ Hopping conductors (polarons)
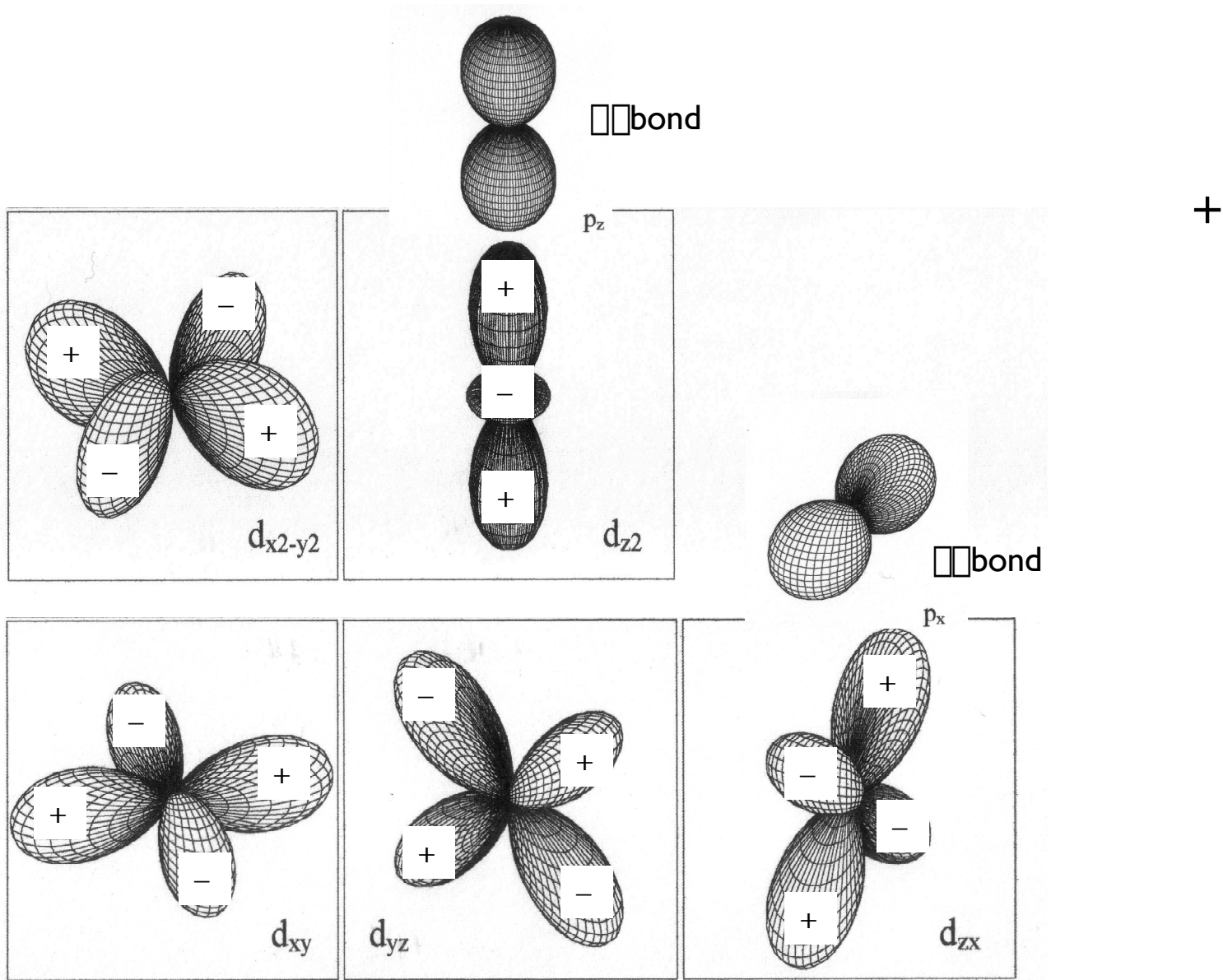
➢ Metals

➢ Superconductors

Transition metal oxides can exhibit a bewildering variety of magnetic properties

➢ Antiferromagnets

➢ Ferrimagnets

➢ Spin glasses

➢ Ferromagnets

➢ Pauli paramagnets

In 3d oxides the same 3d electrons usually determine the electronic and magnetic properties, whereas in 4f oxides, the 4f electons determine the magnetism, and 5d/6s electrons the electronic properties.
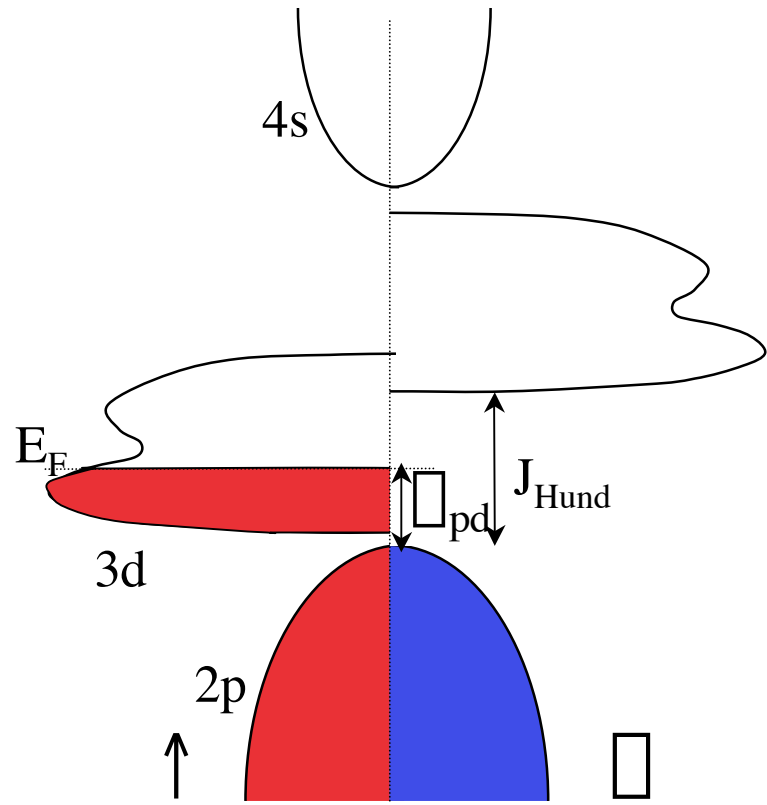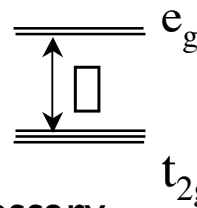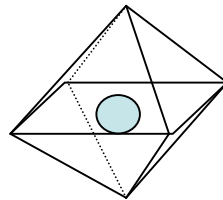
Orbitals in the crystal field

d_{x2-y2}

d_{z2}

d_{xy}

d_{yz}

d_{zx}

4s

3d

e_g

t_{2g}

cf splitting

d_σ

d_π

2p

hybridization

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σ−bond

π−bond

p_z

p_x

d_{x2-y2}

d_{z2}

d_{xy}

d_{yz}

d_{zx}

+

−

+

−

+

−

+

−

+

+

−

+

−

+

+

−

+

−

+

+

−

−

−

+

The 3d shell typically has integral occupancy $3d^n$. The 3d band is narrow, and lies in the 2p(O) - 4s(M) gap 2 – 6 eV. The Fermi level lies in the d-band.

Is the oxide a conductor or an insulator ?

Mott pointed out that for a metal, it is necessary to have some ions in $3d^{n+1}$ and $3d^{n-1}$ states. This is only feasable if the bandwidth W is wide enough. i.e. $W > U_{mott}$ where U_{mott} is (ionization energy - electron affinity). If $W < U_{mott}$ we have a *Mott insulator*
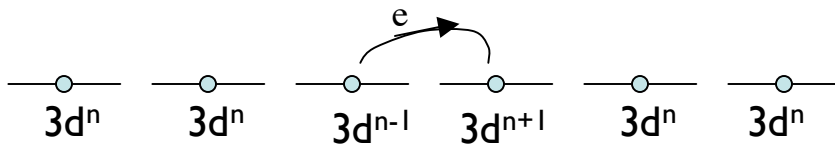
Hubbard Hamiltonian (single, half-filled band}

$$\mathcal{H} = - \Sigma_{ij}\, t_{ij} c^+_{i\sigma} c_{j\sigma} + U\, \Sigma_i n_{i\uparrow} n_{i\downarrow}$$

$$W \approx 2Zt \quad U \approx U_{Mott}$$

Mott insulators and charge-transfer insulators.

In oxides, the charged excited states needed for electrical conduction can also be produced by a different charge-transfer process. The overlap producing the band is between 2p and 3d. Charge transfer from 2p to 3d produces a ligand hole, $2p^5$ ($\underline{L}$).


$$3d^n2p^6 \quad 3d^n2p^6 \quad 3d^n2p^5 \quad 3d^{n+1}2p^6 \quad 3d^n2p^6 \quad 3d^n2p^6$$
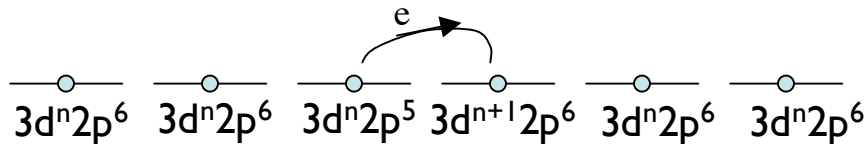
For transition metals at the beginning of the series (Ti, V ...) the $2p \rightarrow 3d$ charge transfer energy $\Delta_{pd} = \varepsilon_d - \varepsilon_p$ is much larger than U. The lowest-energy charged states correspond to $3d^n + 3d^n \rightarrow 3d^{n-1} + 3d^{n+1}$. This costs an energy U, and when $U > t$, gives the Mott insulator. Here $t = t_{dd} = t_{pd}^2 / \Delta_{pd}$

For transition metals at the end of the series (Ni, Cu ...) the charge transfer energy Δ_{pd} may be less than U. The lowest-energy charged states now correspond to $2p^63d^n + 2p^63d^n \rightarrow 2p^53d^n + 2p^63d^{n+1}$. When $\Delta_{pd} > t$, we have a charge-transfer insulator.
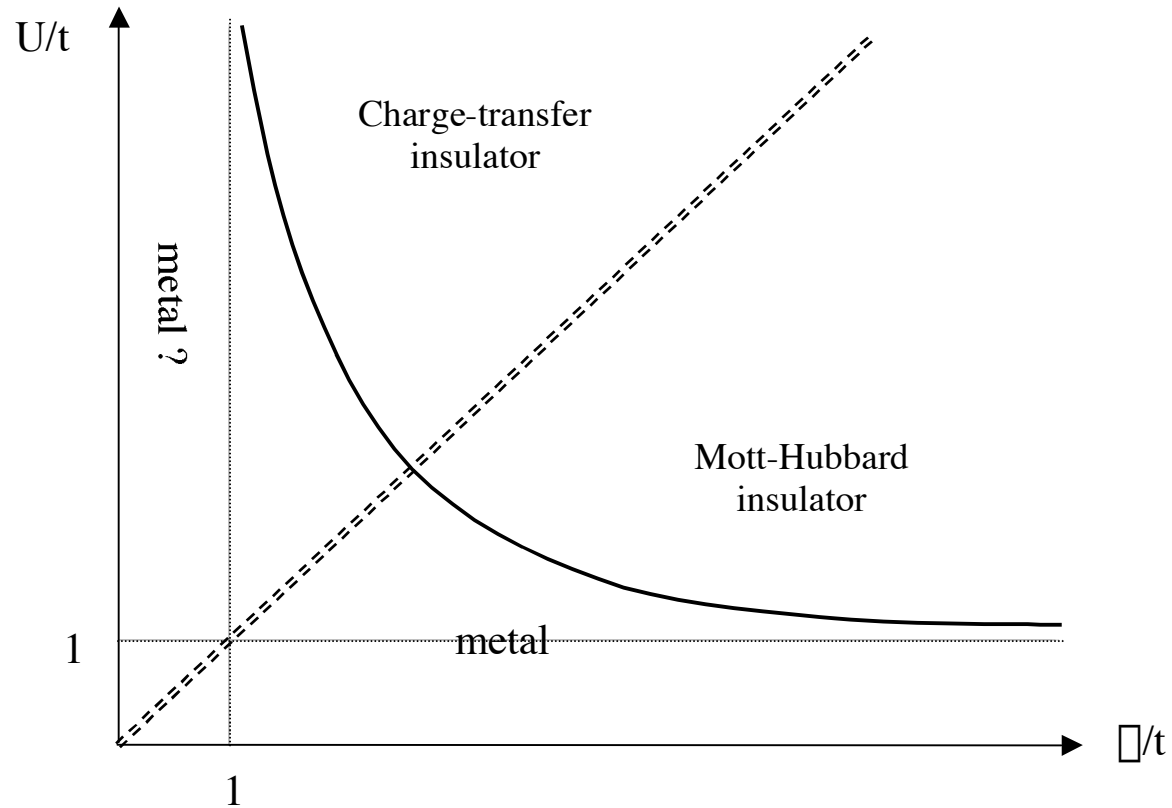
The Hamiltonian is

$$\mathcal{H} = -\sum_{ij} t_{pd} c^+_{i\sigma} c_{j\sigma} + \sum_l \varepsilon_d d^+_{i\sigma} d_{i\sigma} + \varepsilon_p p^+_{j\sigma} p_{j\sigma} + U n_{di\uparrow} n_{di\downarrow}$$
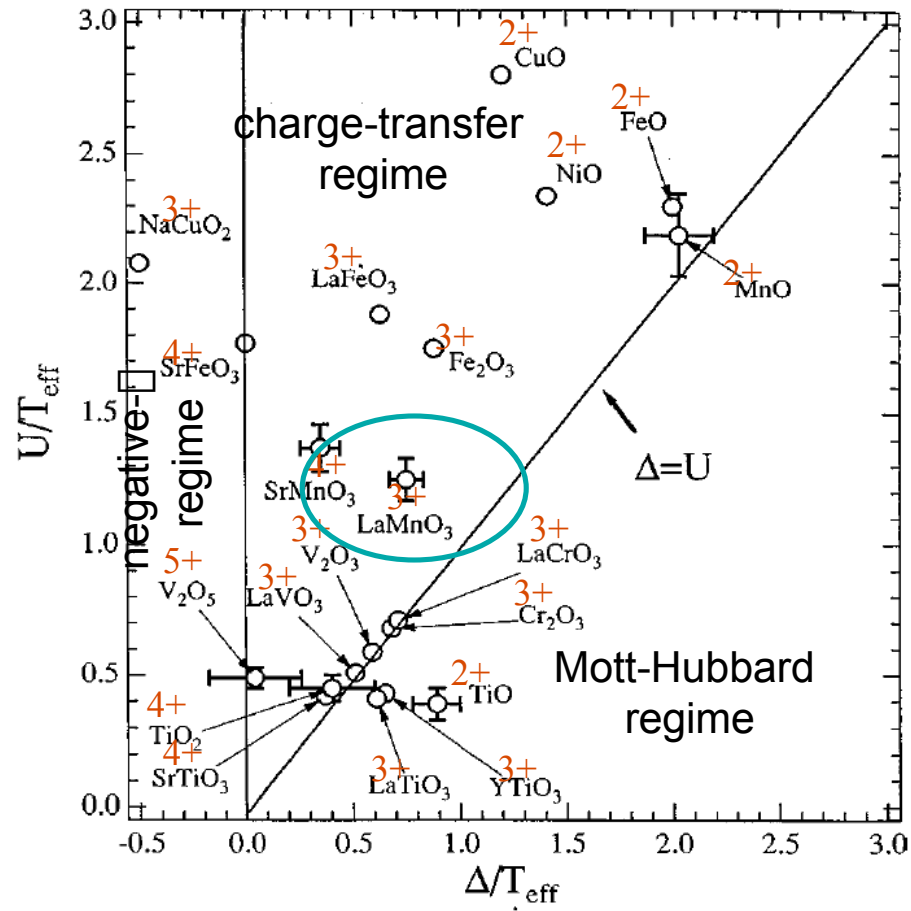
Oxide densities of states
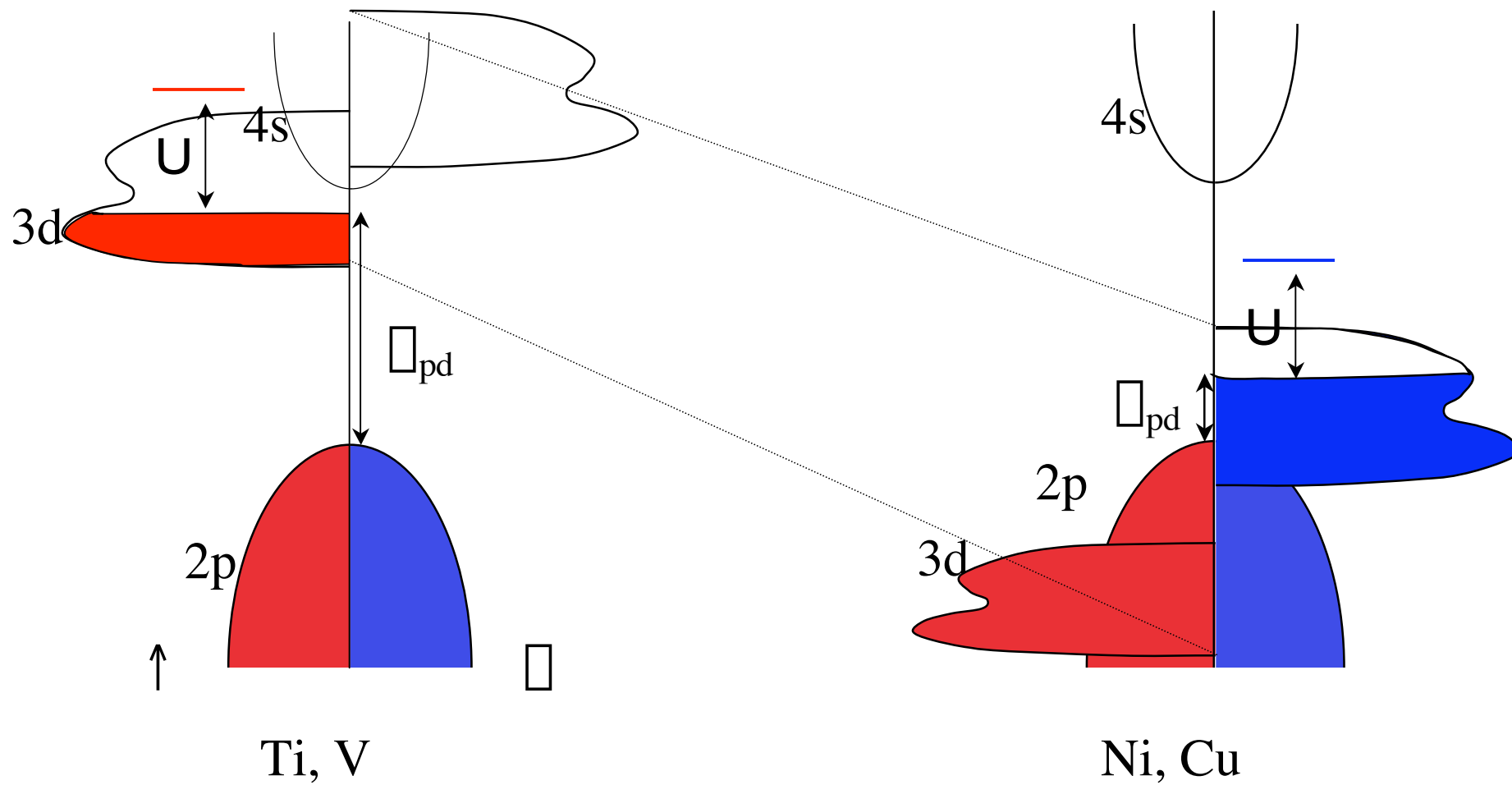
Zaanen-Sawatzky-Allen diagram

The oxides with $\Delta > U > t$ are Mott insulators

The oxides with $U > \Delta > t$ are Charge transfer insulators

Metals appear when $t > U, \Delta$

Bocquet et al., PRB **53**, 1161 (1996)

Non-integral electron occupancy

In theory, the Mott, charge-transfer and crystal-field insulators insulators have a precisely integral 3d occupancy per atom. [A crystal field insulator is one where the Fermi energy falls in a gap in the density of states between crystal-field split levels; eg Cr_2O_3 - Cr^{3+} $3d^3$]

In fact this is unrealistic. Oxides are never perfectly stoichiometric. There are always some excess electrons or holes, which should propagate freely in the conduction band, as in a semiconductor – but they don't. Why not ?

The excess electrons (say) occupy the very bottom of a band where they have a low Fermi velocity. They move so slowly that they distort the surroundings on the ion where they instantaneously reside, creating a *polaron* which has a large effective mass and low mobility. Polarons contribute to the conductivity by thermally-activated hopping.
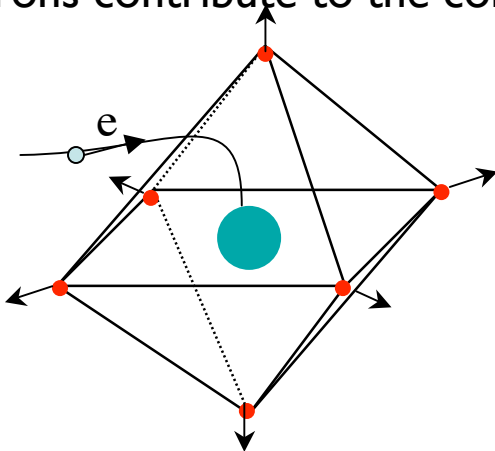
e.g. $v_F \approx 10^4$ m s^{-1} d $\approx$ 0.3 nm   t $\approx$ 3 10^{-14} s

Phonon frequencies $\approx 10^{14}$ Hz

$$\rho = \rho_0 \exp\{E_a/kT\}$$

Polarons do not form in a typical semiconductor like silicon, which is non-polar. Also the electrons there occupy large hydrogenic orbitals some ten or hundreds times bigger than the first Bohr radius (53 pm) on account of the sizable dielectic constant. Mobility μ is high

$$v_{drift} = \mu E$$

MOBILITY of SEMICONDUCTORS (μ in $m^2V^{-1}s^{-1}$)

|	electrons	holes	gap (eV)
Si	0.135	0.048	1.14
GaAs	0.80	0.030	1.43
InSb	3.00	0.045	0.17

(Mobility in metals is much lower, $\mu = 0.1 - 5 \ 10^{-3} \ m^2V^{-1}s^{-1}$ on account of scattering in the conduction band)
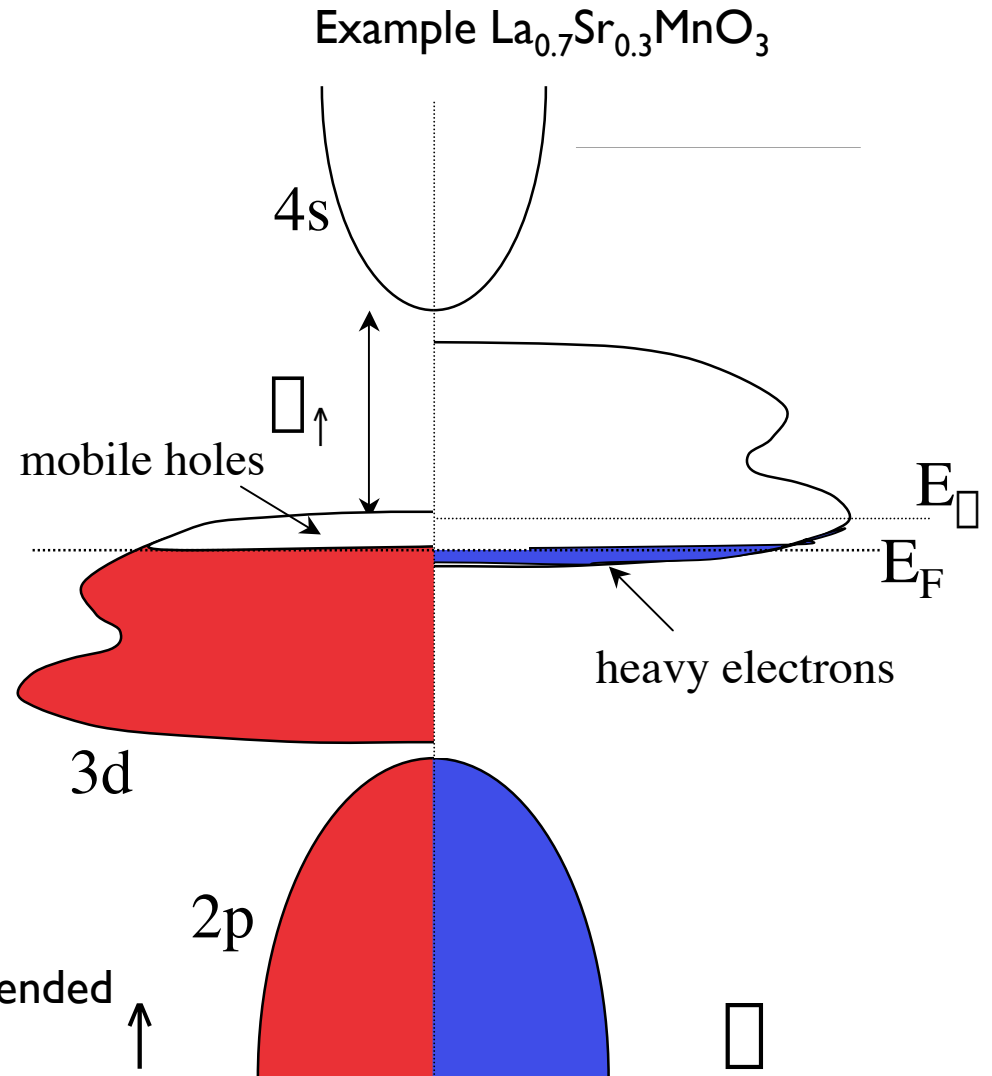
Mobility edge

Whenever there are only a few electrons or holes in a band, they are sensitive to random potential fluctuations caused by imputities or defects. When the occupied bandwidth W is less than the average potential fluctuation U_{av}, Anderson localization occurs.

$$W < U_{av}$$
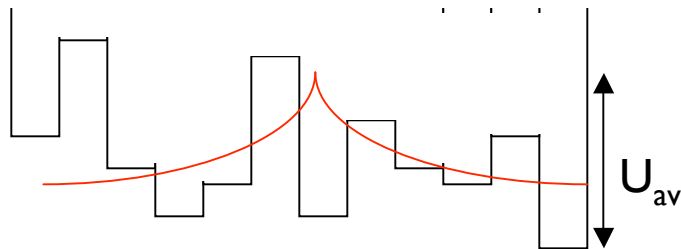
A mobility edge, separating localized and extended states lies about U_{av} from the band edge

Example $La_{0.7}Sr_{0.3}MnO_3$

4s

$\Delta_\uparrow$

mobile holes

E_μ

E_F

heavy electrons

3d

U_{av}

2p

$\uparrow$ $\downarrow$

2.2 Magnetic interactions.

Exchange interactions are often represented by a Heisenberg Hamiltonian

$$\mathcal{H} = -2J \, \Sigma_{i>j} \mathbf{S}_i \cdot \mathbf{S}_j$$

o The interaction couples spins
o The interaction is short-range, depending on the overlap of the interacting orbitals
o J can be positive (ferromagnetic coupling) or negative (antiferromagnetic coupling)

Generally in oxides there are several significant exchange interactions involving ions on different sites. Consider the NaCl-structure monoxides. The cations occupy an fcc lattice (octahedral sites in the close-packed fcc O^{2-} lattice). The two main interactions are: J_1 with 12 nearest neighbour cations (90° M-O-M bond), J_2 with six second-neighbour cations (180° M-O-M bond),
.
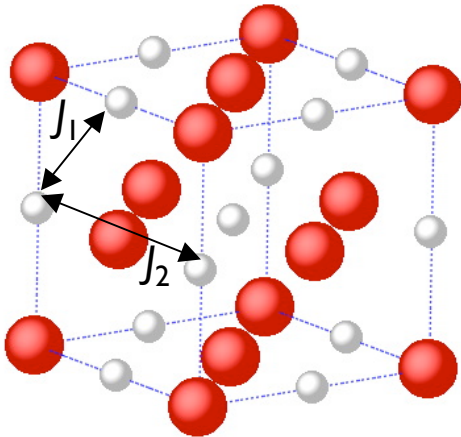
		a_0 (pm)	S	T_N(K)	θ_p (K)	J_1(K)	J_2(K)
MnO	$3d^5$	445	5/2	117	-610	-7.2	-3.5
FeO	$3d^6$	431	2	198	-570	-7.8	-8.2
CoO	$3d^7$	426	3/2	291	-330	-6.9	-21.5
NiO	$3d^8$	418	1	525	-1310	-50	-85

How are the Js actually measured ? (they are virtually impossible to calculate accurately).

In the NaCl structure monoxides, the antiferromagnetic structures partly frustrate the exchange interactions. There are four simple-cubic cation sublattices. The neighbours on an ion on any of them are antiparallel (8) or parallel (4).

$\theta_p = 2S(S+1)\{4J_1 + 8J_1 + 6J_2\}/3k$ $\qquad$ θ_p gives the *weighted average* of the Js

$T_N = 2S(S+1)\{4J_1 - 8J_1 - 6J_2\}/3k$ $\qquad$ T_N gives the sum, taking account of the magnetic structure.

More generally, the complete set of Js are determined by fitting the spin-wave dispersion relations $\omega(q)$ measured by neutron diffraction.

The exchange interaction couples the *spins. What happens for the rate earths*, where J is the good quantum number ?

e.g Eu^{3+} L = 3, S = 3, J = 0.

Since **L**+2**S** = g**J**, **S** = (g-1)**J**.

Hence $T_C = 2(g-1)^2 J(J+1) \{ZJ\}/3k$

The quantity G = $(g-1)^2 J(J+1)$ is known as the de Gennes factor. T_C for an isostructural series of rare earth compounds is proportional to G.
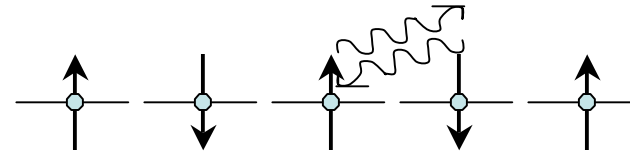
	S	L	J	g(Lande)	G(de Gennes)
La	0	0	0		0
Ce	0.5	3	2.5	0.8571	0.18
Pr	1	5	4	0.8	0.80
Nd	1.5	6	4.5	0.7273	1.84
Pm	2	6	4	0.6	3.20
Sm	2.5	5	2.5	0.2857	4.46
Eu	3	4	0		0
Gd	3.5	0	3.5	2	15.75
Tb	3	3	6	1.5	10.50
Dy	2.5	5	7.5	1.3333	7.08
Ho	2	6	8	1.25	4.50
Er	1.5	6	7.5	1.2	2.55
Tm	1	5	6	1.1667	1.17
Yb	0.5	3	3.5	1.1429	0.32
Lu	0	0	0		0

Exchange in models.

Mott - Hubbard insulator.
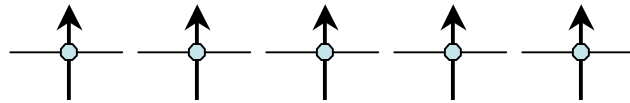
No transfer is possible

Virtual transfer: $\Delta E = -2t^2/U$

$t \approx 0.2$ eV, $U \approx 2$ eV, $\Delta E \approx 0.01$ eV

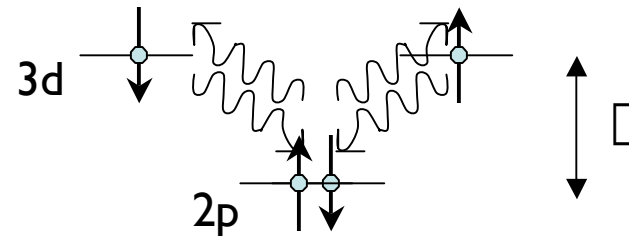1 eV $\equiv$ 11606 K $\Delta E \approx 100$ K

Compare with $-2J\, \mathbf{S}_i \cdot \mathbf{S}_1$

$\uparrow\uparrow$ $- (1/2)J$ $\uparrow\downarrow$ $+(1/2)J$ $\boxed{J = -2t^2/U}$
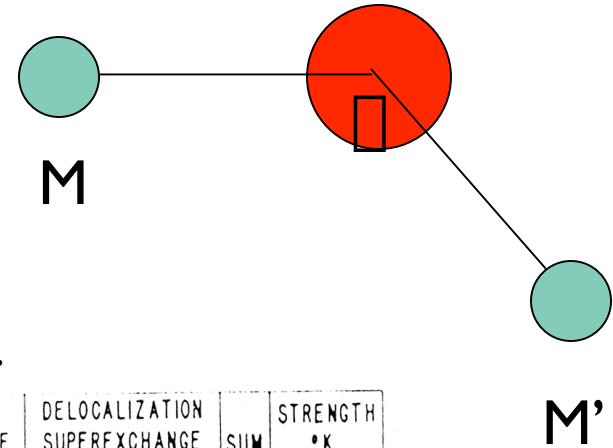
Charge-transfer insulator.

3d

2p

Δ

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

Goodenough-Kanamori rules.

Criginally a complex set of semiempirical rules to describe the superexchange interactions in magnetic insulators with different cations M, M' and bond angles θ, covering both kinetic (1-e transfer) and correlation (2-e, 2-centre) interactions….

M

θ

M'

CASE	OUTER-ELECTRON CONFIGURATION	CORRELATION SUPEREXCHANGE		DELOCALIZATION SUPEREXCHANGE		SUM	STRENGTH °K (OXIDES)
		pσ	pπ	pσ	pπ		
#1	d^5 ... d^5	STRONG ↑↓	WEAK ↑↓	STRONG ↑↓	WEAK ↑↓	↑↓	~750
#2	d^3 ... d^3	WEAK TO MODERATE ↑↓	WEAK ↑↓	—	WEAK ↑↓	↑↓	≲300
#3	d^5 ... d^3	MODERATE ↑↓	WEAK ↑↓	MODERATE ↑↓	WEAK ↑↓	↑↓	~400

A table from '*Magnetism and the Chemical Bond*' by J.B. Goodenough

the rules were subsequently simplified.by Anderson.

case 1. 180° bonds between half-filled orbitals.

3d

2p

Δ
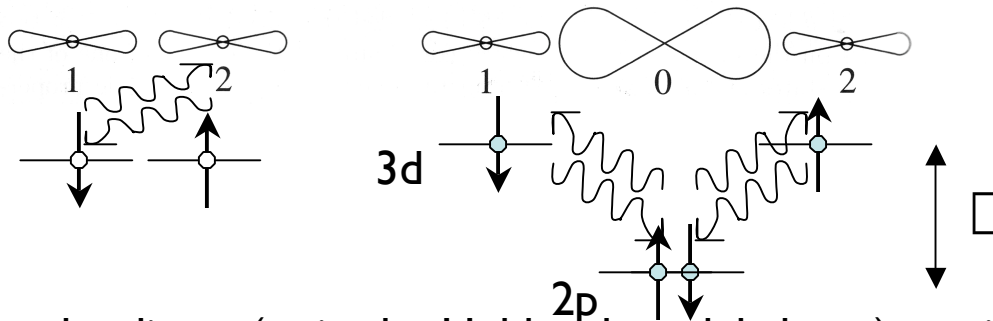
The overlap can be direct (as in the Hubbard model above) or via an intermediate oxygen. In either case the 180° exchange between half-filled orbitals is strong and antiferromagnetic.
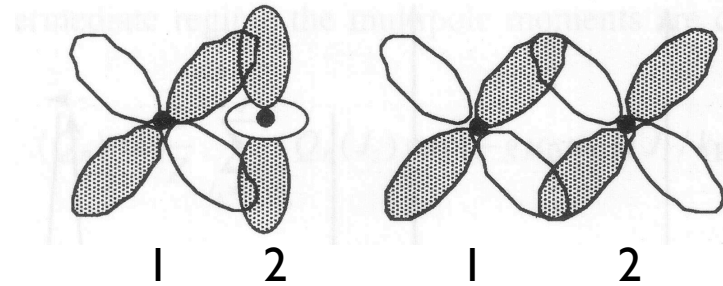
case 2. 90° bonds between half-filled orbitals.

Here the transfer is from different p-orbitals.
The two p-holes are coupled parallel, according
To Hund's first rule. Hence 90° exchange between
 half-filled orbitals is ferromagnetic and rather weak
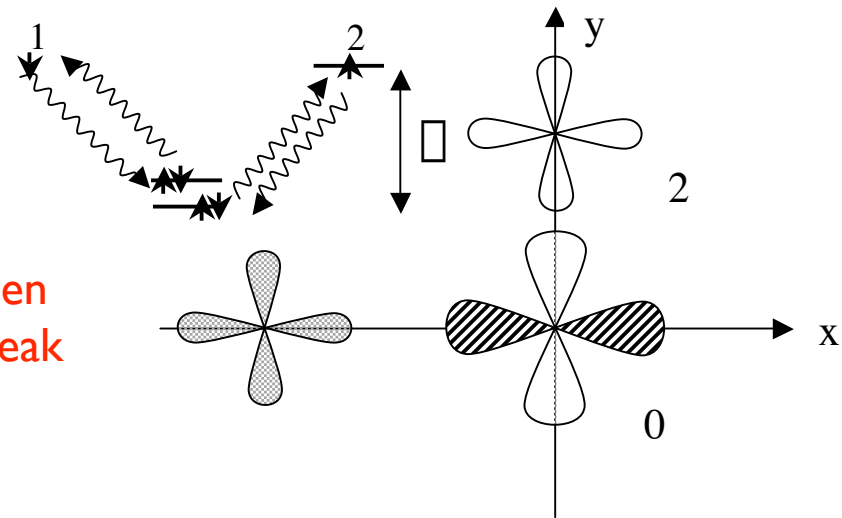
$$J \approx [t_{pd}^4/(\Delta^2(2\Delta + U_{pp})]][J_{hund-2p}/ (2\Delta + U_{pp)}]$$

Examples of d-orbitals with zero overlap integral (left) and nonzero overlap integral (right). The wave function is positive in the shaded areas and negative in the white areas.


1   2   1   2

case 3. bonds between half-filled and empty orbitals

Consider a case with orbital order, where there is no overlap between occupied orbitals, as shown on the left above. Now consider electron transfer between the occupied orbital on site 1 and the orbital on site 2, as shown on the right, which is assumed to be unoccupied. The transfer may proceed via an intermediate oxygen. Transfer is possible, and Hund's rule assures a lower energy when the two electrons in different orbitals on site 2 have parallel spins.

Exchange due to overlap between a half-filled and an empty orbital of different symmetry is ferromagnetic and relatively weak.
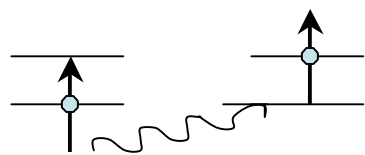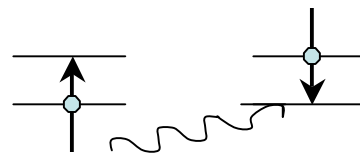

$\Delta E = -2t^2/(U-J_{hund-3d})$ $\Delta E = -2t^2/U$ $J = -(t^2/U)(J_{hund-3d}/U)$

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Other exchange mechanisms: half-filled orbitals.

– Dzialoshinsky-Moria exchange (Antisymmetric exchange)

This can occur whenever the site symmetry of the interacting ions is uniaxial (or lower). A vector exchange constant $\mathbf{D}$ is defined. (Typically $|\mathbf{D}| << |J|$) The D-M interaction is represented by the expression $\boxed{E_{DM} = -\mathbf{D}.\mathbf{S}_1 \wedge \mathbf{S}_2}$ The interaction tends to align the spins perpendicular to each other and to $\mathbf{D}$ which lies along the symmetry axis. Since $|\mathbf{D}| << |J|$ and J is usually antiferromagnetic, the D-M interaction tends to produce canted antiferromagnetic structures.
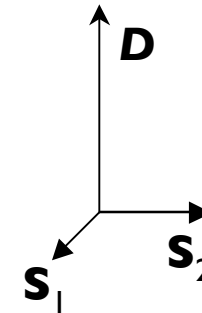
– Biquadratic exchange

This is another weak interaction, represented by

$E_{bq} = -J_{bq}(\mathbf{S}_1 . \mathbf{S}_2)^2$

Exchange mechanisms: partially-filled orbitals.

Partially-filled d-orbitals can be obtained when an oxide is doped to make it 'mixed valence' e.g $(La_{1-x}Sr_x)MnO_3$ or when the d-band overlaps with another band at the Fermi energy. Such materials are usually metals.

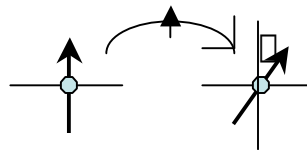– Direct exchange

This is the main interaction in metals
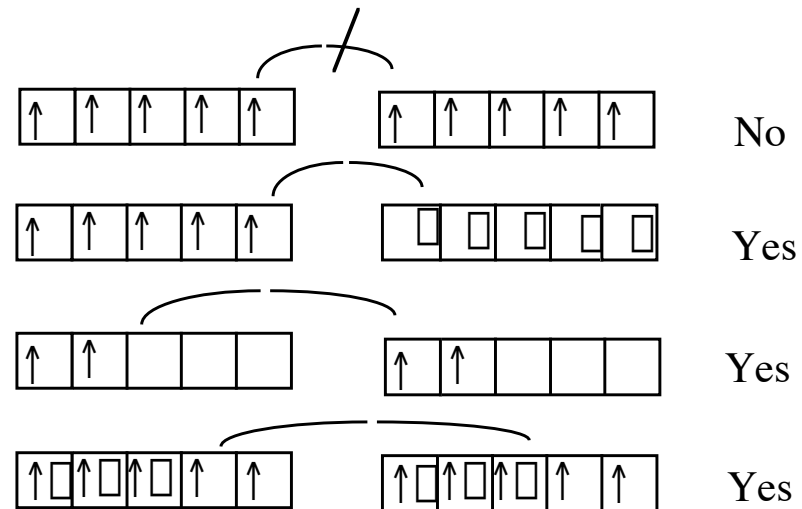
Electron delocalization in bands that are half-full, nearly empty or nearly full.

– Double exchange

Electron transfer from one site to the next in partially (not half) filled orbitals is inhibited by noncollinearity of the core spins. The effective transfer integral for the extra electron is t_{eff}

$$t_{eff} = t \cos(\theta/2)$$

Double exchange in an antiferromagnetically ordered lattice can lead to spin canting.

– Exchange via a spin-polarized valence or conduction band

As in double exchange, there are localized core spins which interact via a delocalized electron in a partly-filled band. These electrons are now in a spin-split valence band (p holes) or a spin-split conduction band (s electrons)
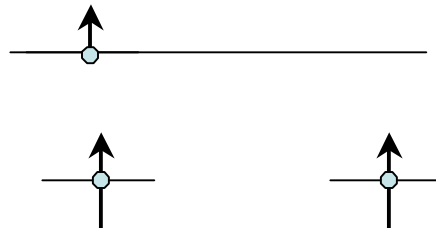
2.3 Charge and orbital order

Charge order

When a d-band is partially filled (not half full), there may be a tendency to charge order (Wigner crystallization) driven by the inter-atomic Coulomb interaction V. This works best when the filling is a simple rational fraction.

e.g Fe^{2+} Fe^{3+} Fe^{2+} Fe^{3+} Fe^{2+} Fe^{3+} filling 1/2 one $t_{2g\downarrow}$ sub-band

  Mn^{3+} Mn^{4+} Mn^{4+} Mn^{3+} Mn^{4+} Mn^{4+} filling 1/3 one $e_{g\uparrow}$ sub-band

Orbital order

Orbital order can be driven by elastic distortion of the environment of an ion with degenerate d-orbitals. e.g. $3d^4$ ions (Cr^{2+}, Mn^{3+}) in octahedral coordination

(Jahn-Teller theorem states that the only degeneracy allowed in the ground state of a quantum system is the Kramers degeneracy due to time reversal – spin reversal). Suppose the system undergoes a deformation ε.
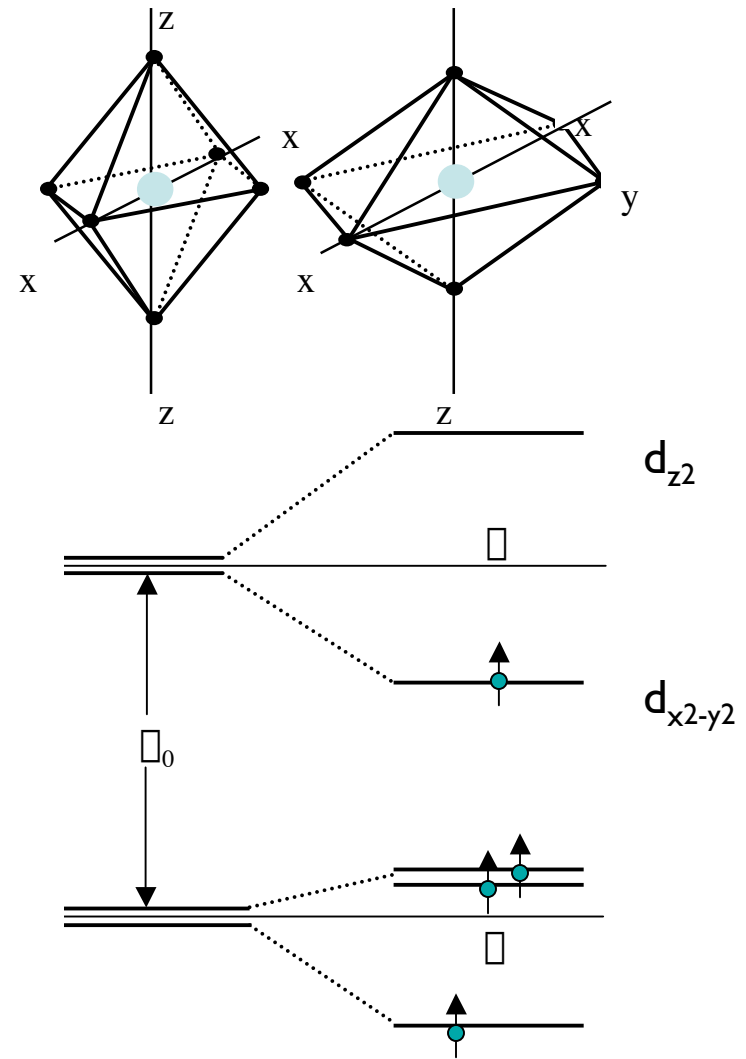
$$E(\varepsilon) = - A\, \varepsilon + B\varepsilon^2$$

cf stabilization   elastic
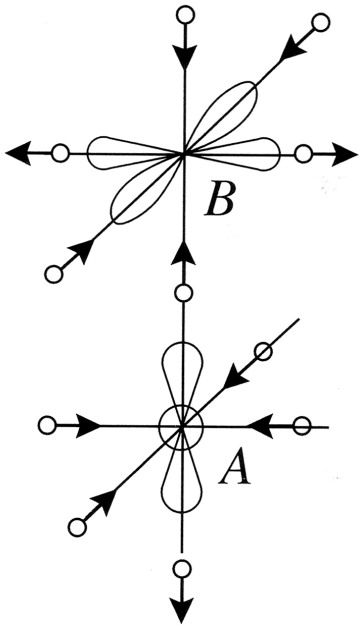
The Jahn-Teller effect produces orbital ordering.

A pseudospin formalism cann be used
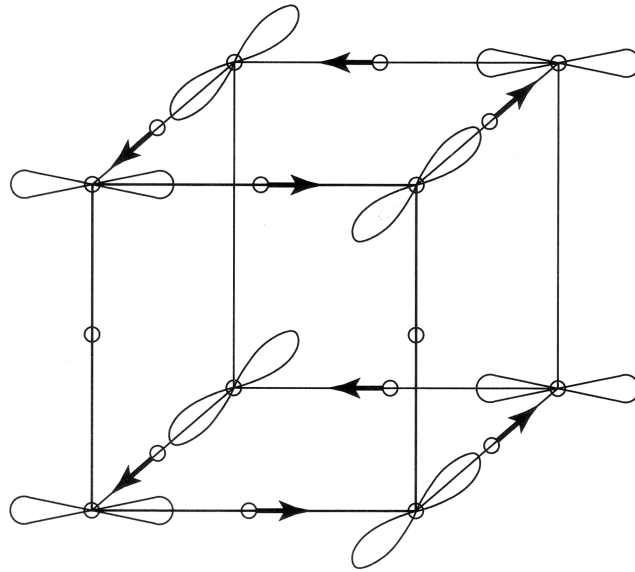
$\tau_z = 1/2$ represents d_{z^2}
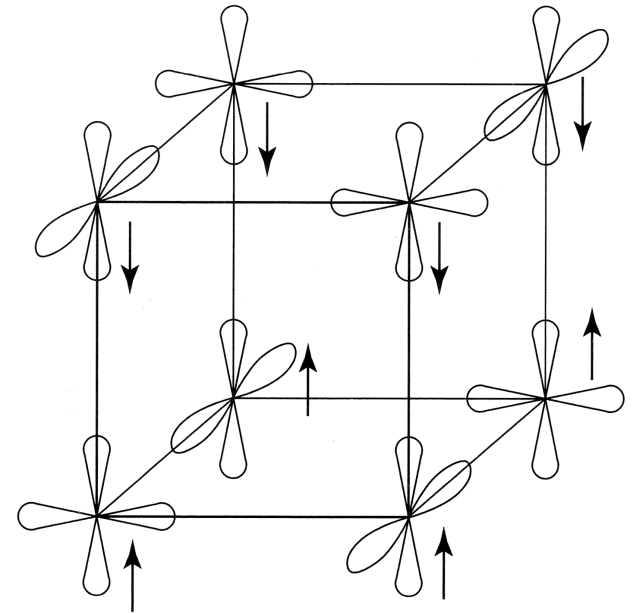
$\tau_z = -1/2$ represents $d_{x^2-y^2}$
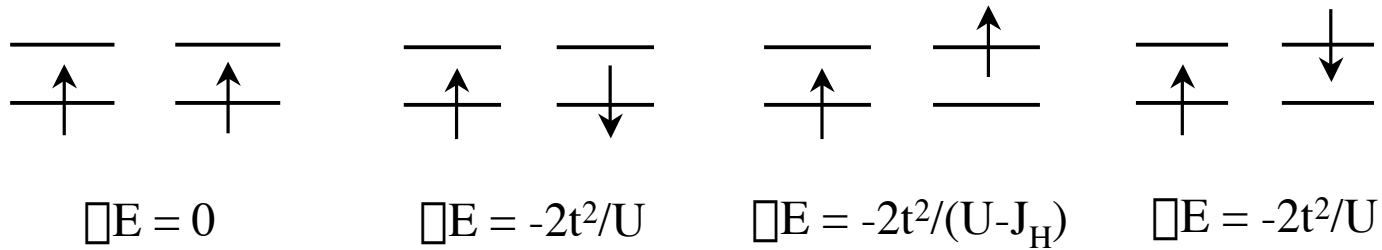
Some examples of orbital order

Shared distortion leads to 'antiferromagnetic' orbital interaction.

Simplified orbital order in $LaMnO_3$. Displacements of oxygen are shown.

Magnetic and orbital order in $KCuF_3$. Cu^{2+} is $3d^9$. There is weak in-plane ferromagnetic coupling, and antiferromagnetic coupling between planes.

$$\Delta E = 0 \qquad \Delta E = -2t^2/U \qquad \Delta E = -2t^2/(U-J_H) \qquad \Delta E = -2t^2/U$$

Exchange favours the occupancy of different orbitals on adjacent sites when the magnetic order is ferromagnetic.

The exchange energy driving orbital order may be as large or larger than the distortive term.