# Electronic structure of correlated electron systems lecture 9

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Lecture 9 (7 is from Mona Berciu and 8 is from Andrea Damascelli

# Brief review of what we did in lecture 6

# Two new complications

- d(n) multiplets determined by Slater atomic integrals or Racah parameters A,B,C for d electrons. These determine Hund's rules and magnetic moments

-  d-O(2p) hybridization ( d-p hoping int.) and the O(2p)-O(2p) hoping (  O 2p band width) determine crystal field splitting, superexchange , super transferred hyperfine fields etc.

The d-d coulomb interaction terms contain density -density like integrals,
spin dependent exchange integrals  and off diagonal coulomb integrals i.e.
Where  n,n' m,m' are all different. The monopole like coulomb integrals
determine  the average  coulomb interaction between d electrons and basically
are what we often call the Hubbard U.  This monopole integral is strongly reduced
In polarizable surroundings as we discussed above.  Other integrals contribute to
the multiplet structure dependent on exactly which  orbitals and spin states are
 occupied. There are three relevant coulomb integrals  called the Slater integrals;

$F^0$     = monopole integral

$F^2$     = dipole like integral

$F^4$     = quadrupole integral

 For TM compounds one often uses Racah Parameters A,B,C  with ;

$$A = F_0 - 49F_4 ;; B = F_2 - 5F_4 ;; C = 35F_4$$

Where in another convention ;     $$F_2 = \frac{1}{49} F^2 ;; F_4 = \frac{1}{448} F^4 ;; F_0 = F^0$$

The B and C Racah parameters are close to the free ion values and can be carried over
From tabulated gas phase spectroscopy data.  " Moores tables" They are hardly reduced in
A polarizable medium since they do not involve changing the number of electrons on an ion.

# Reduction of coulomb integrals in the solid

- As we noted above the F0 integral or what we called U before is strongly reduced in the presence of a polarizable medium since it involves a change in the local charge i.e. ionization potential minus electron affinity.

- However the other higher order multipole integrals involve simply a dependence on the way the orbitals are occupied keeping the electron count fixed. The surroundings hardly notices such changes and so these integrals remain close to the atomic values.

# Hunds' rules
## First the Physics

- Maximize the total spin—spin parallel electrons must be in different spatial orbitals i.e. m values (Pauli) which reduces the Coulomb repulsion

- 2nd Rule then maximize the total orbital angular momentum L. This involves large m quantum numbers and lots of angular lobes and therefore electrons can avoid each other and lower Coulomb repulsion

# Hunds' third rule

- < half filled shell  J=L-S  > half filled shell J=L+S

- Result of spin orbit coupling

$$\mathrm{H}_{so} = \sum_j \frac{1}{2m^2c^2}(\nabla V(r_j) \times p_j) \bullet s_j$$

- Spin orbit results in magnetic anisotropy, g factors different from 2, orbital contribution to the magnetic moment, ---

# Multiplet structure for free TM atoms rare Earths can be found in the reference

$$E(n, L, S, \lambda) = nI + \frac{1}{2} n(n-1) U_{ave} + U(n, L, S, \lambda)$$

$$U_{ave} = F^0 + \frac{2}{63}\left(F^2 + F^4\right) = F^0 - \frac{2l}{4l+1} J(d, d)$$

$$J(d, d) = \frac{1}{14}(F^2 + F^4)$$

VanderMarel etal PRB 37 , 10674 (1988)

$$C(d, d) = \frac{1}{14}(\frac{9}{7}F^2 - \frac{5}{7}F^4)$$

$$E(n, Hund) = \alpha_I(n)I + \alpha_{F^0}(n)F^0 + \alpha_J(n)J + \alpha_C(n)C$$

$$U^{eff} = E(n+1, Hund) + E(n-1, Hund) - 2E(n, Hund)$$

Where Hund refers to the Hund's rule ground state in each case. That is The lowest energy state for the given number of d electrons

$$\alpha_I(n) = n;; \alpha_{F^0}(n) = \frac{n!}{2};; \alpha_J(n) = No - of - parallel - spin - pairs$$

Table 2.1. *Parameters determining the energies of the Hund's Rule ground states in LS coupling for all d occupations and the expression for the d-d gap for those occupations.*

| state | $\alpha_I$ | $\alpha_{F^0}$ | $\alpha_J$ | $\alpha_C$ | $U^{eff}$ |
|-------|-----------|---------------|-----------|-----------|-----------|
| $d^0(^1S)$ | 0 | 0 | 0 | 0 | |
| $d^1(^2D)$ | 1 | 0 | 0 | 0 | $F^0-J-C$ |
| $d^2(^3F)$ | 2 | 1 | -1 | -1 | $F^0-J+C$ |
| $d^3(^4F)$ | 3 | 3 | -3 | -1 | $F^0-J+C$ |
| $d^4(^5D)$ | 4 | 6 | -6 | 0 | $F^0-J-C$ |
| $d^5(^6S)$ | 5 | 10 | -10 | 0 | $F^0+4J$ |
| $d^6(^5D)$ | 6 | 15 | -10 | 0 | $F^0-J-C'$ |
| $d^7(^4F)$ | 7 | 21 | -11 | -1 | $F^0-J+C$ |
| $d^8(^3F)$ | 8 | 28 | -13 | -1 | $F^0-J+C$ |
| $d^9(^2D)$ | 9 | 36 | -16 | 0 | $F^0-J-C$ |
| $d^{10}(^1S)$ | 10 | 45 | -20 | 0 | |

# Note the strong difference in the effective U for a half filled d shell!!

- The half filled shell is special and has a very large contribution to "U" as we defined it compared to all the other fillings.

- Note that J Hund for the 3d transition metal atoms is about 0.7-0.8 eV and IT IS NOT OR HARDLY REDUCED IN THE SOLID.

- Using the expression for U effective we have

$$U^{eff}(d^5) = E(\uparrow\uparrow\uparrow\uparrow) + E(\uparrow\uparrow\uparrow\uparrow\uparrow\downarrow) - 2E(\uparrow\uparrow\uparrow\uparrow\uparrow) = F^0 + 4J$$

i.e. it costs 4J to remove a parallel spin electron from d5 and you don't gain this back when You add an electron to d5

$$U^{eff}(d^4) = E(\uparrow\uparrow\uparrow) + E(\uparrow\uparrow\uparrow\uparrow\uparrow) - 2E(\uparrow\uparrow\uparrow\uparrow) = F^0 - J - C$$

costs 3J to remove from d4 but win back 4J when you add to d4

# Nultiplet structure of 3d TM free atoms

Note the high energy scale
Note also the lowest energy
state for each case i.e. Hunds'
Rule;

This diagram was made based
on theory and experiment on
TM impurities in Cu,Ag,Au
from which I=-3.2,F0=1.04eV,
F2=8.94 and F4=5.62 as in the
relations for J and C used in the
Hunds rule ground state
energies. The excited states
using relations from Slaters
book. Note that F0 is very
strongly reduced in these nobel
metal hosts.

Combining crystal and ligand fields with the coulomb and exchange interactions in compounds
Use the crystal field and coulomb matrix elements for real orbitals in the tables from Ballhausen and the spin orbit coulpling  and diagonalize

# Angular distribution of "real" d orbitals
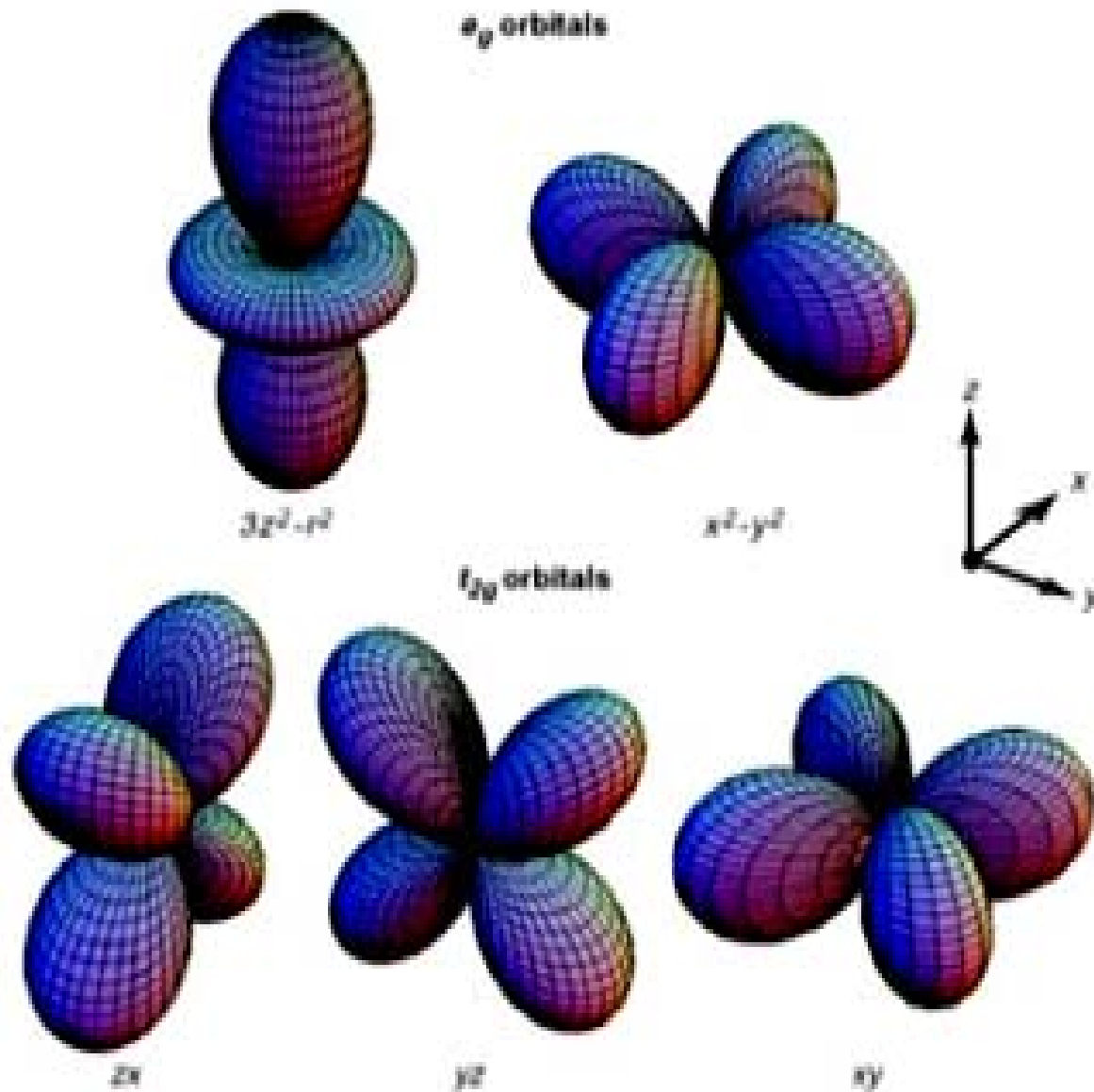
In the next slide is an example of the multiplet structure for Ni 2+ in NiO. NiO has a rock salt structure i.e. NaCl in which Ni 2+is surrounded by 6 O 2- ions in an octahedron. The crystal and ligand fields as described before split the 5 fold degenerate d levels into doubly degenerate eg and triply degenerate t2g levels. These are then occupied by 8 d electrons which according to Hunds rules will have a total spin of 1 and if the crystal field splitting is zero a total orbital angular momentum of 3 and with spin orbit coupling J= 4. The extreme left side gives the free ion results and the extreme right the very strong crystal field limit.
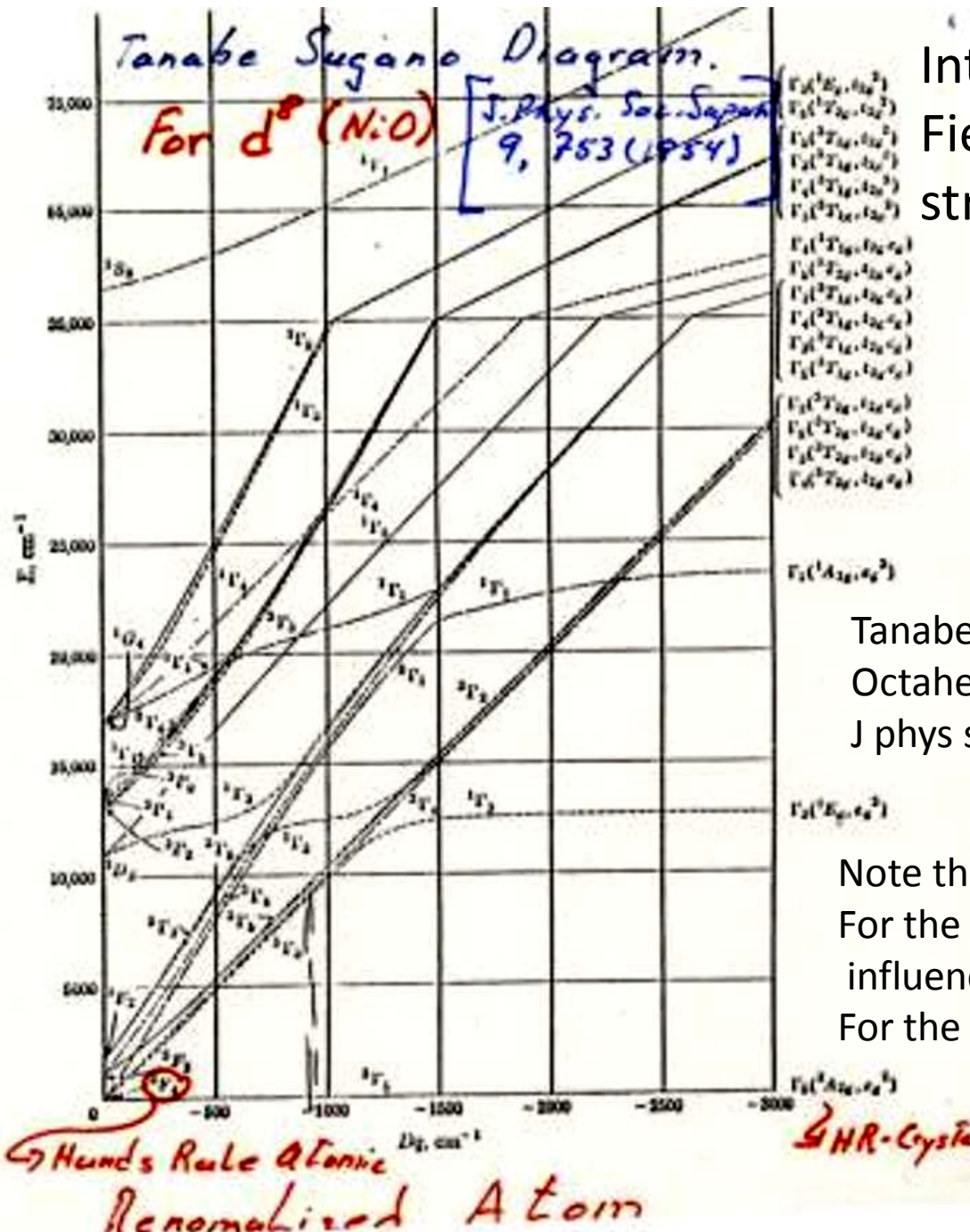
Interplay between crystal Fields and multiplet structure

Tanabe Sugano diagrams for Ni2+ in Octahedral coordination.
J phys soc Jap 9, 753 (1954)

Note the small spin orbit splitting For the free ion and the lack of any influence of the spin orbit coupling For the large crystal field limit.

# Why is the spin orbit coupling not effective for Ni2+ with large crystal field

$$d_{xy} = \frac{1}{i\sqrt{2}}([2,2]-[2,-2])$$

$$d_{xy}, d_{xz}, d_{yz} \rightarrow t_{2g}$$

$$d_{3z^2-r^2} = [2,0]$$

$$d_{x^2-y^2}, d_{3z^2-r^2} \rightarrow e_g$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}([2,-2]+[2,2])$$

$$d_{xz} = \frac{1}{i\sqrt{2}}([2,1]-[2,-1]) \underline{\quad\quad} d_{xz} = \frac{1}{\sqrt{2}}([2,1]+[2,-1])$$

Spin orbit coupling is of the form $\quad H_{so} = \sum \lambda \vec{l_i} \bullet \vec{s_i}$

Where the sum is over the electrons. This couples only states which differ in the ml quantum numbers by 0 or +,- 1. . So eg's are not affected. And for large crystal fields the eg-t2g splitting is much larger than the spin orbit coupling and so this mixing is also suppressed.  So SO coupling will have little effect in a perturbation description for large Crystal field splitting and a d8 configuration

For partially filled t2g orbitals the orbital degeneracy is present as for Ti3+ in OH symmetry SO can at least partially lift this degeneracy and therefore is very important potentially

# How can we experimentally observe the d-d multiplet splittings?

- Optical absorption ( actually d-d transitions are forbidden but somewhat allowed via SO and electron phonon coupling)

- Optical Raman spectroscopy

- Electron Energy Loss spectroscopy

- Resonant soft x ray inelastic scattering which is actually x ray Raman spectroscopy

NiO [$d^8$ $^3A_{2g}$ → $d^8$ $l_i^?$ Transitions]

OPTICAL PROPERTIES OF NiO    1509
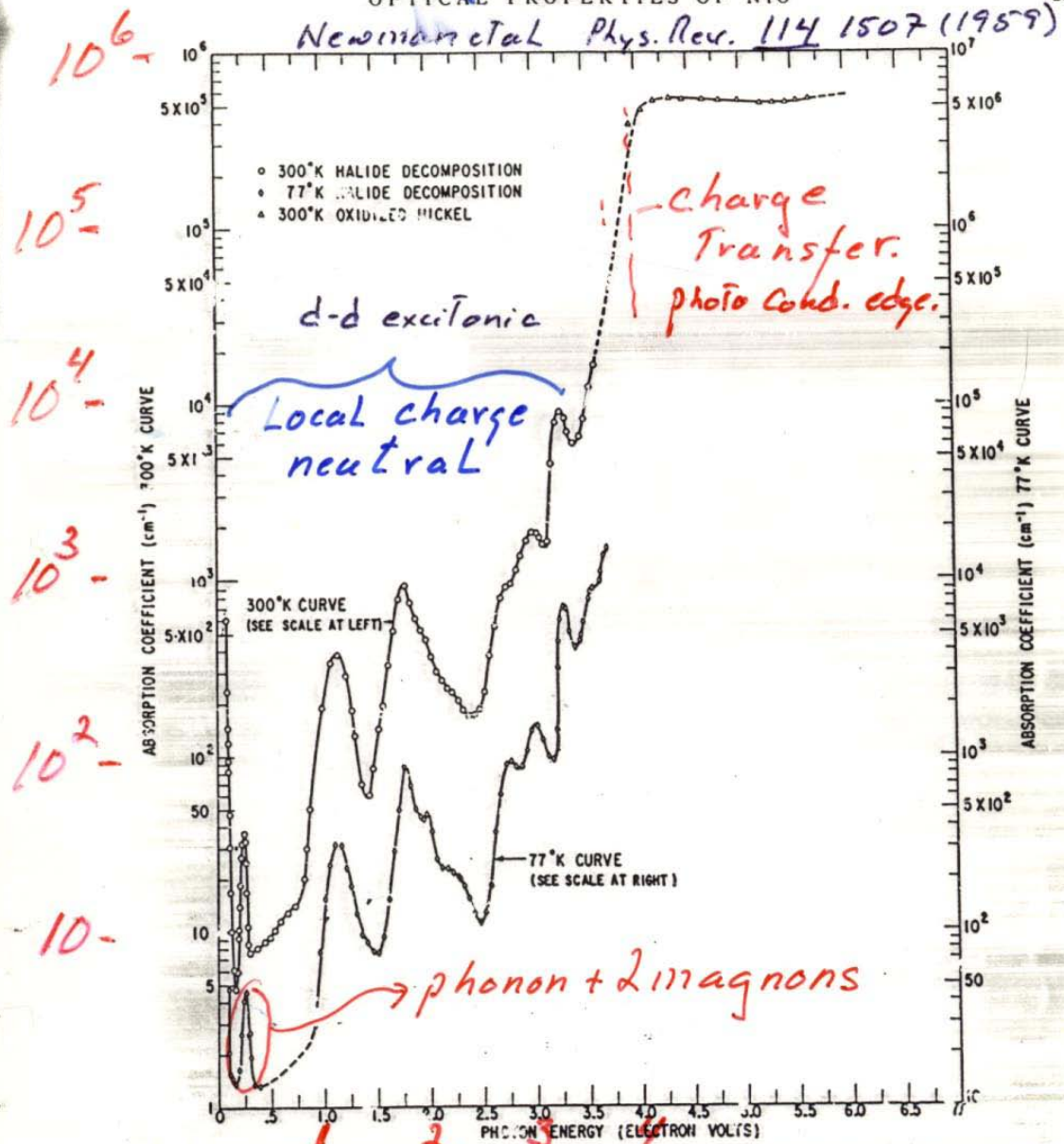
Newman et al. Phys. Rev. 114 1507 (1959)

- charge Transfer.
- photo Cond. edge.

d-d excitonic

Local charge neutral

○ 300°K HALIDE DECOMPOSITION
● 77°K HALIDE DECOMPOSITION
▲ 300°K OXIDIZED NICKEL

300°K CURVE
(SEE SCALE AT LEFT)

77°K CURVE
(SEE SCALE AT RIGHT)

→ phonon + 2 magnons

PHOTON ENERGY (ELECTRON VOLTS)

eV

FIG. 2. Absorption spectrum of NiO at 300°K, 77°K. Dashed lines are interpolations.

The d-d transitions are clearly visible inside the conductivity gap or charge transfer gap of about 4eV. The excitation below 1 eV is a phonon plus two magnons excitations which is sharp and weakly allowed.

# How could we describe this theoretically

- Treat Ni2+ in NiO as an impurity in a lattice of O2- ions. That is neglect the influence of other Ni ions in the lattice because of the very atomic character of the 3d states.

- Then we basically have a two particle problem. i.e. two holes in an otherwise full band system.

- The two holes could both be on Ni i.e. Ni2+ but could be in any of the d8 multiplet states or one hole could be on O and one on Ni or both holes on the same or different O ions.

# Use our Auger theory for two particles

- If we take the vacuum as Ni d10 and all O 2p6 and we determine the two hole eigenstates as in Auger spectroscopy including the crystal fields and Ni3d-O2p hoping integrals plus the full d-d coulomb interactions we should generate the full spectrum of two hole states.

- We can use the two particle Greens function formalism
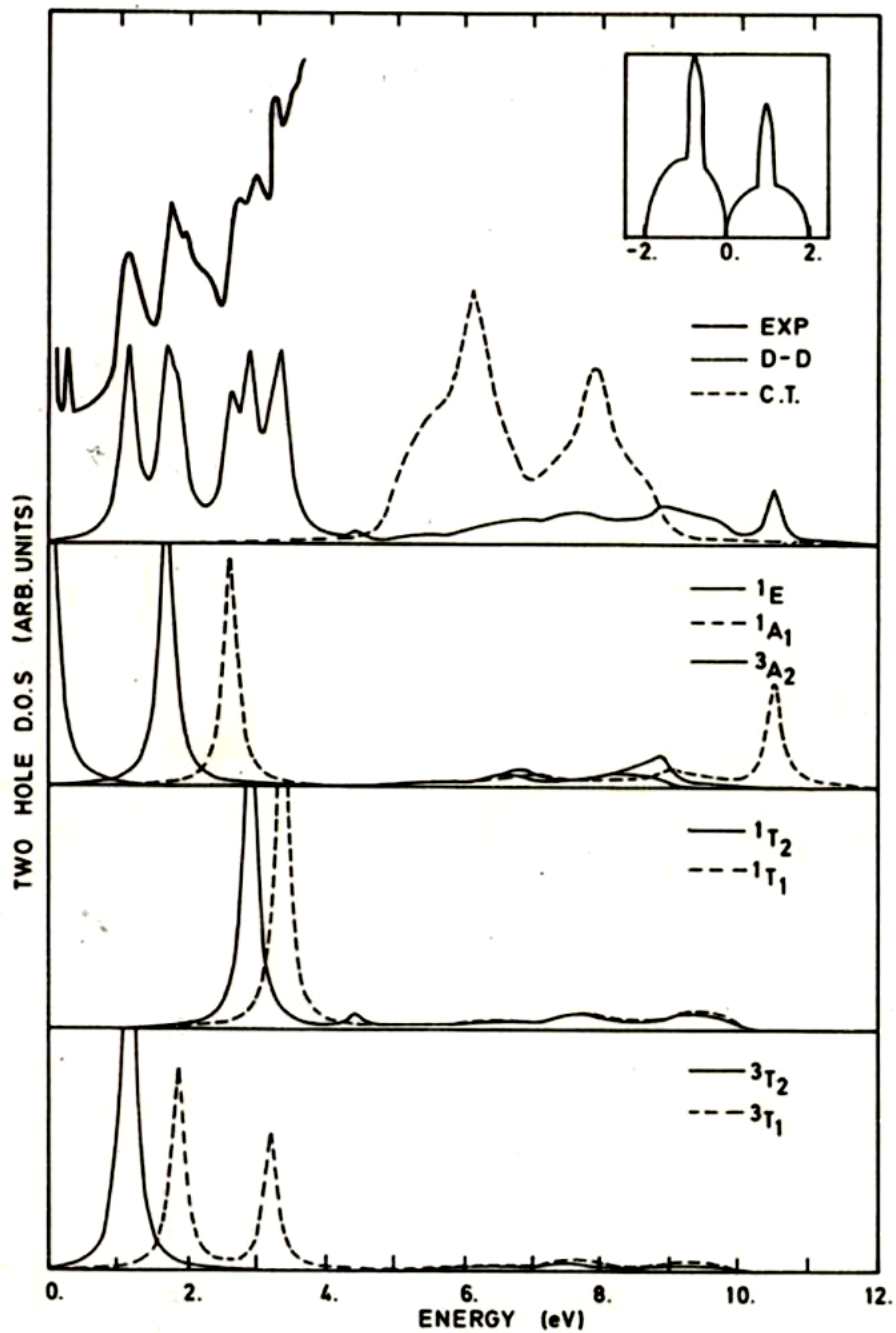
# Model theory for d-d excitations in NiO

- Use the two hole (Auger) theory described before and a vaccum state of d10 for Ni and a full O 2p band

- Add a point charge crystal field and a Ni3d-O2p hybridization for eg and t2g orbitals and an O2p band structure of the form

$$H(hyp) = \sum_{k,n,\sigma} V_{k,n}(c^*_{k,n,\sigma}d_{n,\sigma} + d^*_{n,\sigma}c_{k,n,\sigma})$$ (n lables t2g or eg)

- Add the d-d full coulomb interactions between two d holes $$H(\text{int}) = \sum_{i,j,l,m} U(i,j,l,m)d^*_i d_j d^*_l d_m$$

- Use the two particle Greens function to calculate the energies of all the states corresponding to two holes in Ni 3d

# Ni 3d8 states in OH symmetry

- The irreducible representations spanned by 2 holes in a d level are $\quad ^3A_{1g} \ ^1E_g \ ^1T_{2g} \ ^3T_{1g} \ ^3T_{2g} \ ^3T_{1g} \ ^1A_{1g}$

- Corresponding to the arrangement of two holes in eg and t2g orbitals

- Use the Dyson equation for the two particle Greens function $\quad G_{i,j}^{i',j'}(IR,z) = G_{0,i,j}^{i',j'}(IR,z)\delta_{i,i'}\delta_{j,j'} + \sum_{m,n} G_{0,i,j}^{i,j}(IR,z)U_{i,j}^{m,n}G_{m,n}^{i',j'}(IR,z)$

- In which i,j refer to eg or t2g and spins IR are the various irreducible representations and

- $G_{0,i,j}^{i,j} = g_{eg} \otimes g_{eg}$ or involving two t2g state the small g's are the single hole greens functions involving the hybridization with the O 2p band

- For details see $\qquad$ Zaanen et al CANADIAN J. OF PHYS , 65   1262, 1987

Zaanen et al

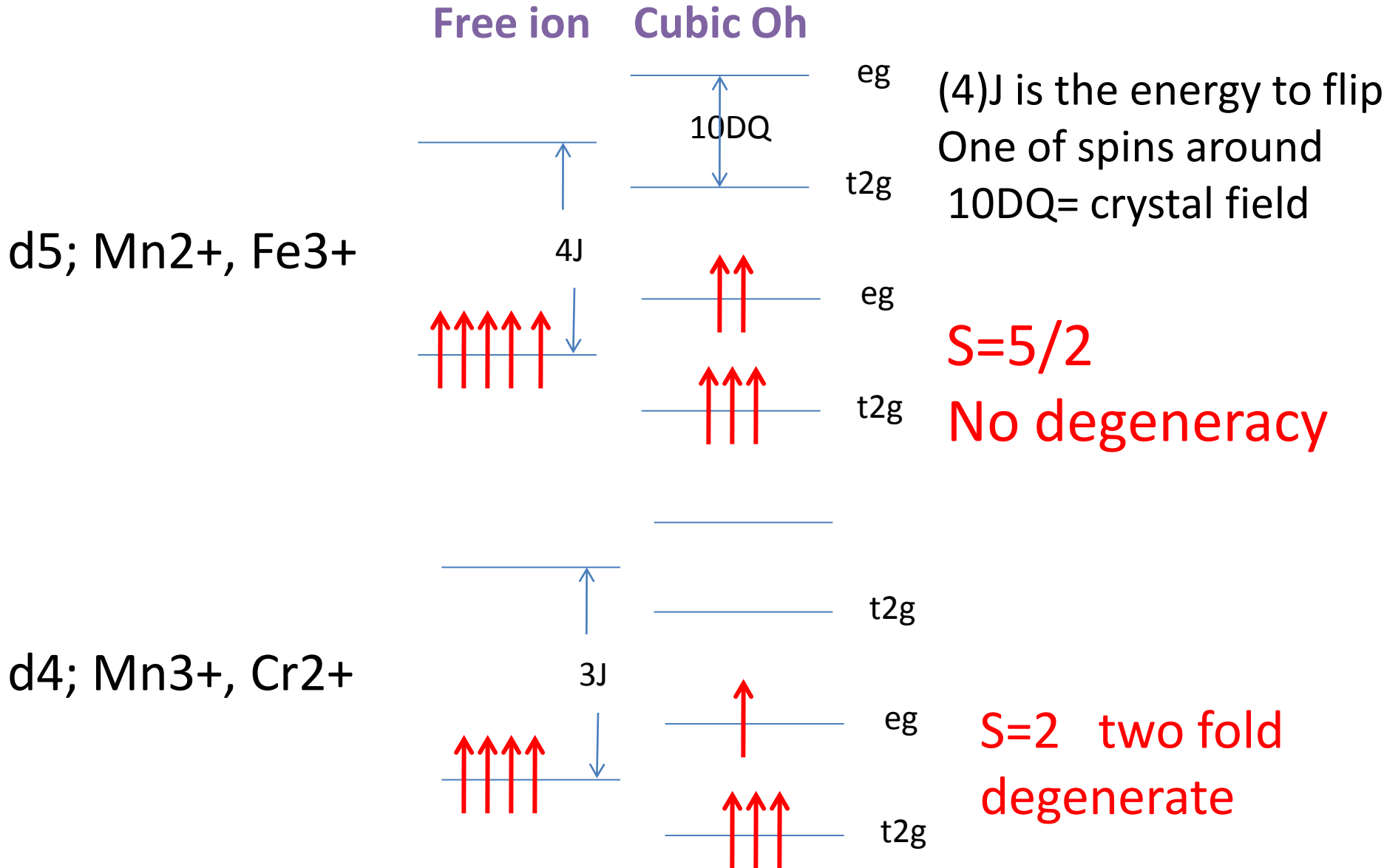Unfortunately this cannot be used
For more than two holes.
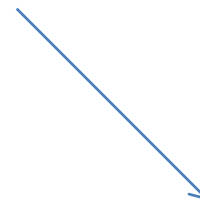
In order to get a picture of the basic physics for various d occupations covering basically the whole 3d series we resort to a simplified but very useful model
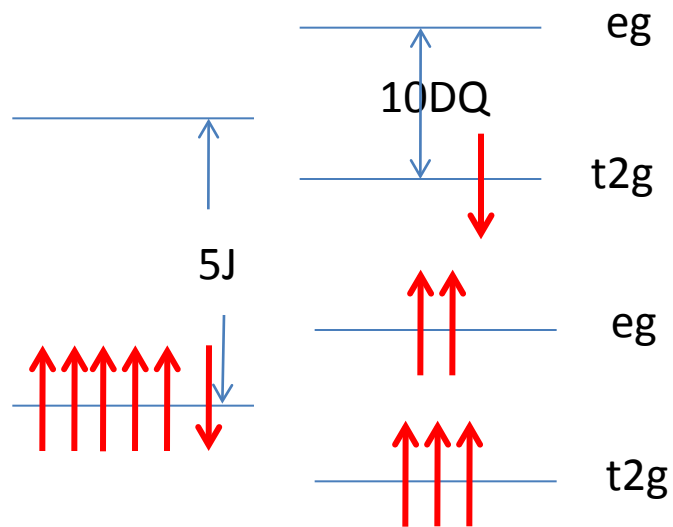
# Simplified picture of Crystal fields and multiplets

- Determine $d^n$ energy levels assuming only crystal and ligand fields and Hunds' first rule i.e. $F^0, and \underline{\quad} J = \dfrac{1}{14}(F^2 + F^4)$

- Neglect other contributions like C in our former slides and the SO coupling

- This is a good starting point to generate a basic understanding . For more exact treatments use Tanabe-Sugano diagrams

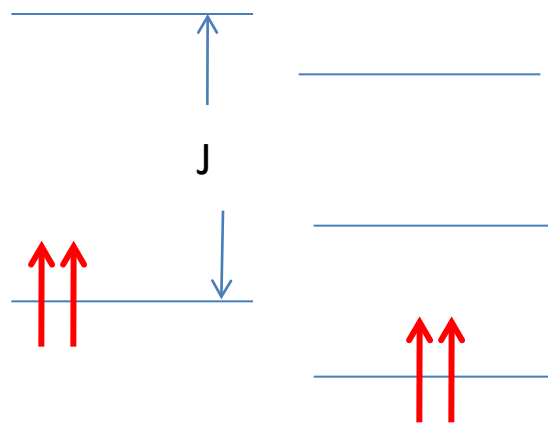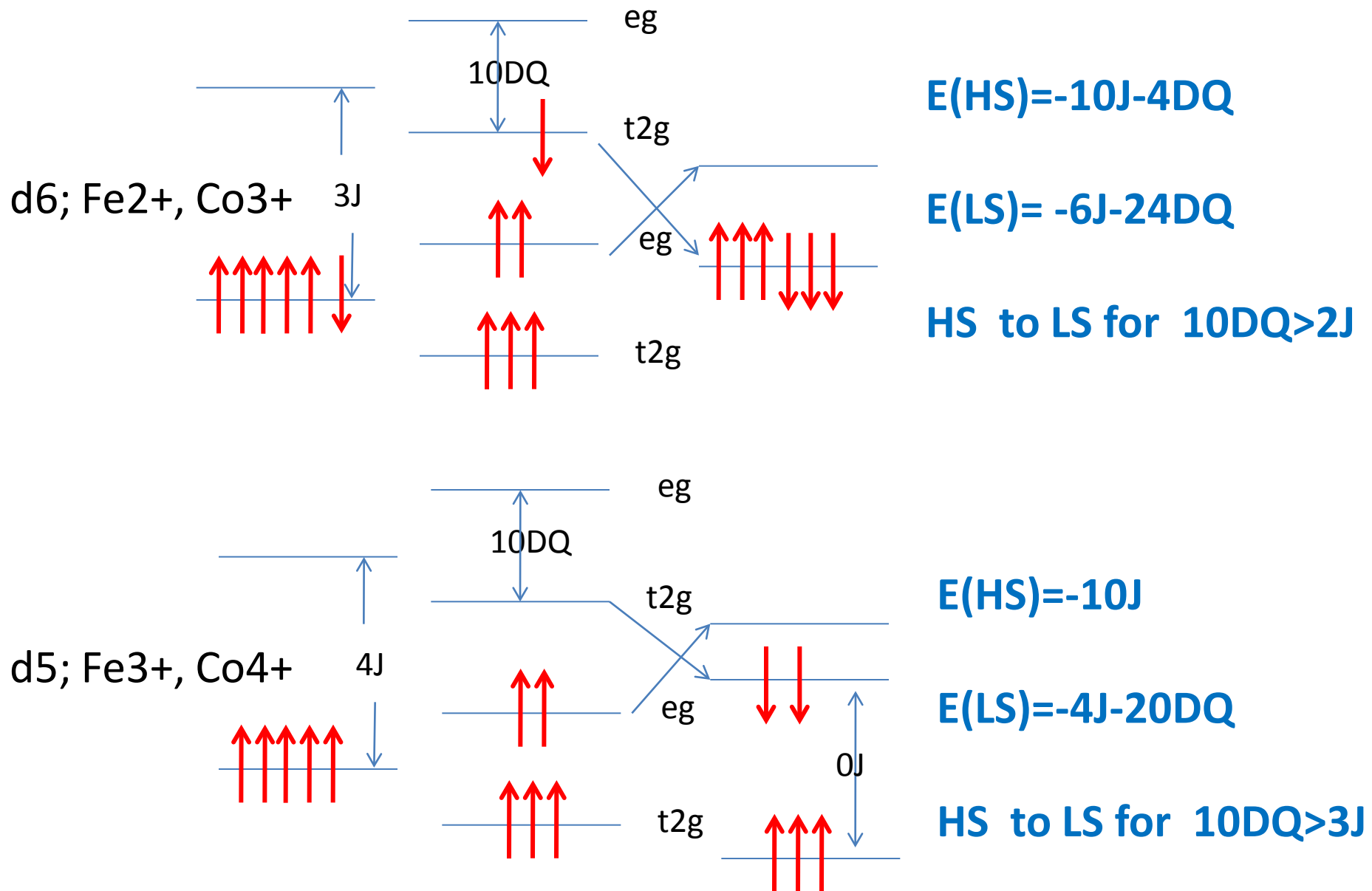# Crystal fields, multiplets, and Hunds rule for cubic (octahedral) point group

**Free ion**     **Cubic Oh**

eg

10DQ

t2g

(4)J is the energy to flip
One of spins around
10DQ= crystal field

**d5; Mn2+, Fe3+**

4J

eg

t2g

S=5/2

No degeneracy

**d4; Mn3+, Cr2+**

3J

t2g

eg

S=2   two fold
degenerate

t2g

d6; Fe2+, Co3+

10DQ

eg

t2g

5J

eg

t2g

**S=2;  3 fold degenerate**

d2; Ti2+, V3+

J

**S=1;  3 fold degenerate**

# Physical picture for high spin to low spin transition



d6; Fe2+, Co3+

3J

10DQ

eg

t2g

eg

t2g

E(HS)=-10J-4DQ

E(LS)= -6J-24DQ

HS to LS for 10DQ>2J

d5; Fe3+, Co4+

4J

10DQ

eg

t2g

eg

t2g

0J

E(HS)=-10J

E(LS)=-4J-20DQ

HS to LS for 10DQ>3J

What would happen if 2J <10Dq<3J and we are in a mixed Valent system? If we remove one electron from d6 we would go from S=0 in d6 to S=5/2 in d5. The "hole " would carry a spin Of 5/2 as it moves in the d6 lattice.

LaCoO3 is in a low spin Co3+ i.e. S=0 state for Temp<100K
The first ionization state would be Co4+ High Spin (S=5/2)
This lowest energy state cannot be reached by removing 1 electron with Spin ½ i.e. invisible to photoemission (from Damascelli notes Z=0
This would correspond to a very heavy quasi particle
In a mixed valent system like La1-xSrxCoO3 the charge carriers would be very heavy. i.e. low electrical conductivity high thermal power

TABLE 8.1. The possible lowest and highest spin states of an 3d ion with n d electrons in a local surrounding of octahedral ($O_h$) or tetrahedral ($D_{4h}$) symmetry. The arrows indicate electron removal or electron addition transitions with $|\Delta S| > 1/2$.

| | | $d^0$ | $d^1$ | $d^2$ | $d^3$ | $d^4$ | $d^5$ | $d^6$ | $d^7$ | $d^8$ | $d^9$ | $d^{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $O_H$ | High | 0 | 1/2 | 1 | 3/2 | 2 | 5/2 | 2 | 3/2 | 1 | 1/2 | 0 |
| | Low | 0 | 1/2 | 1 | 3/2 | 1 | 1/2 | 0 | 1/2 | 1 | 1/2 | 0 |
| $D_{4H}$ | High | 0 | 1/2 | 1 | 3/2 | 2 | 5/2 | 2 | 3/2 | 1 | 1/2 | 0 |
| | Low | 0 | 1/2 | 0 | 1/2 | 0 | 1/2 | 0 | 1/2 | 0 | 1/2 | 0 |

TABLE 8.2. The combined crystal and ligand field splitting ($10Dq$) required for a transition from high spin to low spin.

| | $d^2$ | $d^3$ | $d^4$ | $d^5$ | $d^6$ | $d^7$ | $d^8$ | $d^9$ |
|---|---|---|---|---|---|---|---|---|
| 10Dq (eV) | - | - | 2.36 | 2.67 | 1.74 | 1.98 | - | - |

A window of 1 eV!!

# Goodenough Kanamori Anderson rules
## i.e. interatomic superexchange interactions
## And magnetic structure

For example Cu2+---O----Cu2+ as in La2CuO4 and superconductors
Cu2+ is d9 i.e. 1 eg hole (degenerate in OH) but split in D4H as in a
Strong tetragonal distortion for La2CuO4 structure. The unpaired
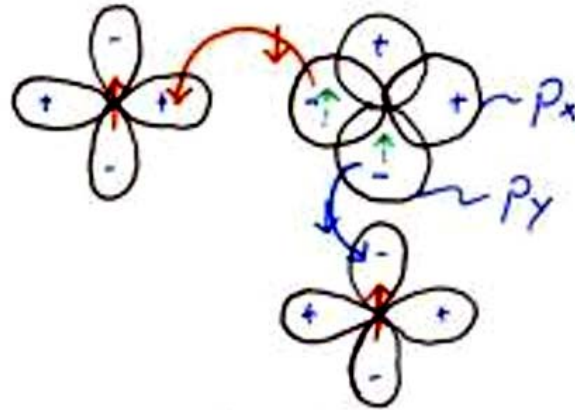electron or hole is in a dx2-y2 orbital with lobes pointing to the 4
Nearest O neighbors.
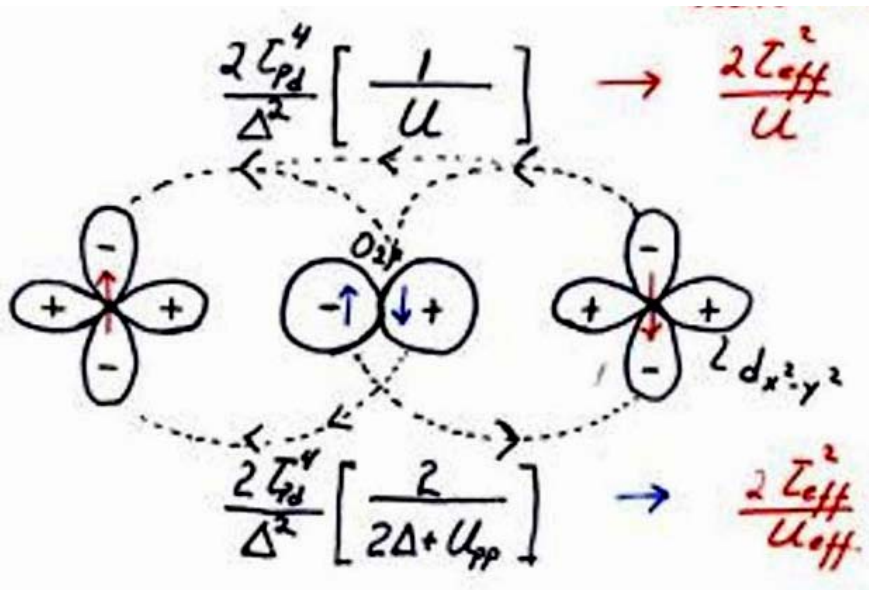


Anderson 1961

If the charge transfer energy $\Delta$ gets small we have to Modify the superexchange theory

New term

**The sum leads to a huge antiferro**
**Interatomic J(sup) =140meV**
**for the Cuprates**

# Superexchange for a 90 degree bond angle

The hoping as in the fig leaves two holes in the intervening
O 2p states i.e. a p4 configuration. The lowest energy state
According to Hund's rule is Spin 1. So this process favours
A ferromagnetic coupling between the Cu spins.

$$J(90) = 2\frac{t_{pd}^4}{\Delta^2}\left[\frac{2}{2\Delta} - \frac{2}{2\Delta - J(hundO2-)}\right]$$

So the net exchange as a function of the
bond angle is:

$$J(\theta) = J(180)\cos^2(\theta) + J(90)\sin^2(\theta)$$

# Superexchange between singly occupied t2g orbitals
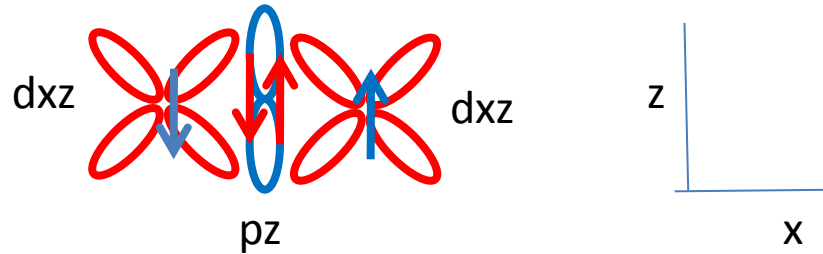


$$J_{anti} = \frac{2t^4_{pd\pi}}{\Delta^2}\left[\frac{2}{2\Delta + U_{pp}} + \frac{1}{U_{dd}}\right]$$

If we now rotate one of the bonds around the z axis the superexchange does not change , but for rotation around the y axis it changes as for eg orbitals. Since

$$t_{pd\pi} \approx \frac{1}{2}t_{pd\sigma} \qquad J_{pd\pi} \approx \frac{1}{16}J_{pd\sigma}$$

# If we have "spectator spins " as in Mn3+ in OH

d4; Mn3+, Cr2+

For ferro orbital ordering we will get a strong antiferromagnetic super exchange since the same intervening O 2p orbital is used in intermediate States as in the example above

$3J$

t2g

eg

t2g

$3x^2 - r^2$      $3y^2 - r^2$
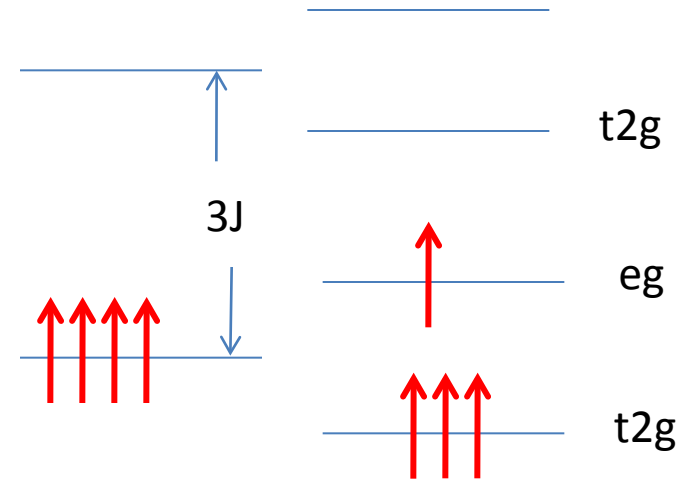
For antiferro orbital ordering The factor of 3 in the Hunds' Rule of Mn is from the "spectator" spins

$$J_{ferro} = -2\left[\frac{2t^2}{u - J_H} - \frac{2t^2}{u + 3J_H}\right] + \frac{2(t/\sqrt{3})^2}{u}$$

antiferro

$$= -\frac{2t^2}{u}\left[\frac{4J_H}{u} - \frac{1}{3}\right]$$

For example in LaMnO3 and  the "Colossal" magneto resistance materials La(1-x)CaxMnO3 and now with "orbital ordering " the extra eg spin has a strong anit ferro superexchange coupling  for ferro orbital ordering i.e. as in the example above for  180 degree bond. But the superexchange is weakly ferromagnetic for antiferro orbital ordering since then both ferro and antiferro terms  compete differing only by the Hunds' rule which now also involves the "spectator " spins in t2g orbitals. We have neglect the wuperexchange involvong the t2g orbitals here.

# Zener Double exchange

- This is important in for example in La(1-x)CaxMnO3 which are colossal magneto resistance materials. Here the extra eg electron pictured in former slides is free to move even if U is large because of the mixed valent nature of the Mn. Some of the Mn3+ (d4) is now Mn3+(d3) which has empty eg orbitals. However the eg electron can only move freely if the spectator t2g spins are ferromagnetically aligned yield a large band width and so a lowering of the kinetic energy.  The ferromagnetic exchange is proportional to the one electron band width