Electronic structure of correlated electron systems : theory and experiment Lecture 2, 3

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Models are instructive and usefull to demonstrate principles

However

Sometimes we get so involved in the beauty and complexity of the model that we forget what the validating conditions were and use them outside of the range of validity

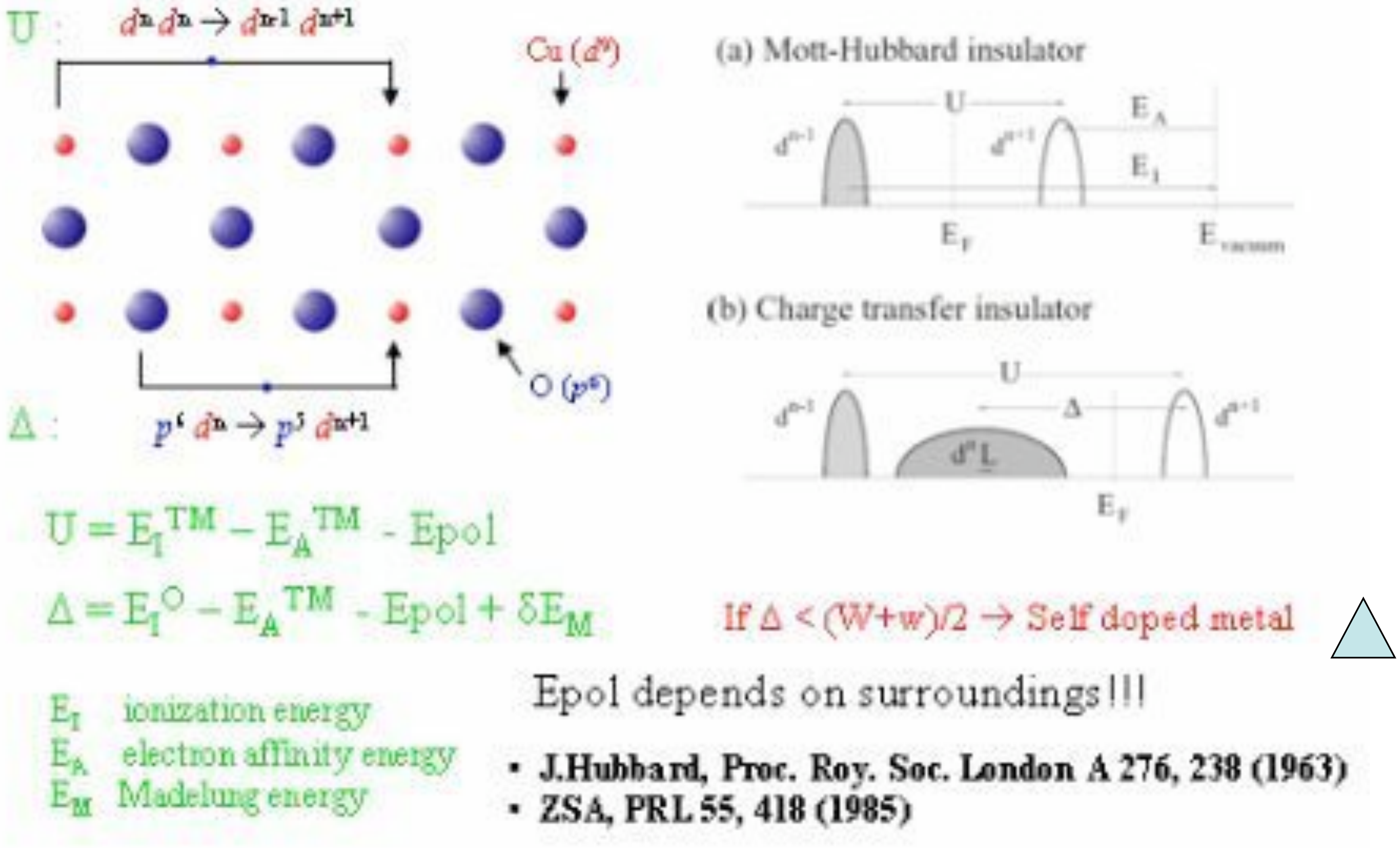
Closer to real systems

Remember that Transition metal and Rare earth compounds

- Consist of real atoms on a lattice with numerous orbitals of importance (unlike H)
- The charge carriers and spins live on atoms
- The atoms or ions can be strongly polarizable
- Polarizability is very non uniform i.e. O2- is highly polarizable Cu2+ is not
- We cannot use conventional screening models based on uniform polarizability
- All of these will play an important role in determining the properties

Correlated Electrons in a Solid

Oxides



(a) Mott-Hubbard insulator

(b) Charge transfer insulator

$$U = E_I^{TM} - E_A^{TM} - Epol$$

$$\Delta = E_I^{O} - E_A^{TM} - Epol + \delta E_M$$

If $\Delta < (W+w)/2 \rightarrow$ Self doped metal

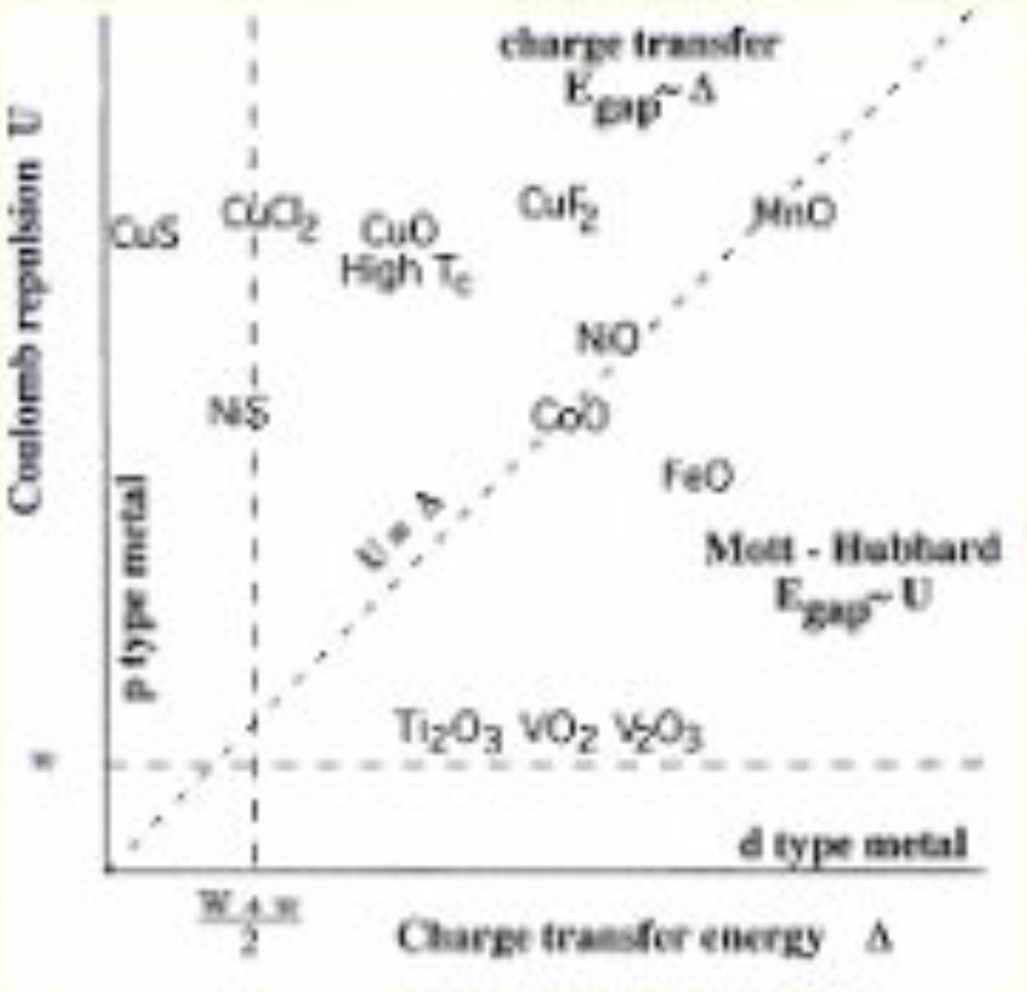
E_I ionization energy
E_A electron affinity energy
E_M Madelung energy

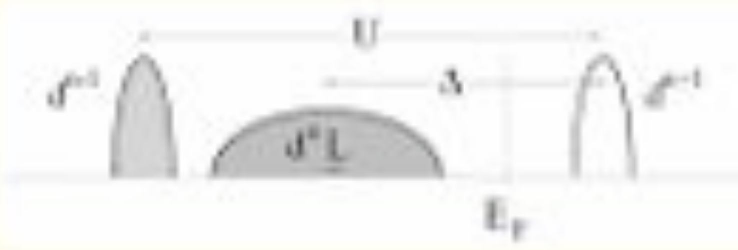
Epol depends on surroundings!!!

- **J.Hubbard, Proc. Roy. Soc. London A 276, 238 (1963)**
- **ZSA, PRL 55, 418 (1985)**

Remember at surfaces U is increased, Madelung is decreased, W is decreased

Zaanen etal





Interesting CuS negative charge transfer superconducting CuI2 would also have negative charge transfer but it is not stable

Phys. Rev. Lett. **55**, 418 (1985)

3 most frequently used theoretical methods

- Anderson like impurity in a semiconducting host consisting of full O 2p bands and empty TM 4s bands including all multiplets

Developed for oxides in early 1980’s, Zaanen, Eskes, Kotani, Gunnarson,-----

- Cluster exact diagonalization methods. O cluster of the correct symmetry with TM in the center. Again include all multiplets crystal fields etc

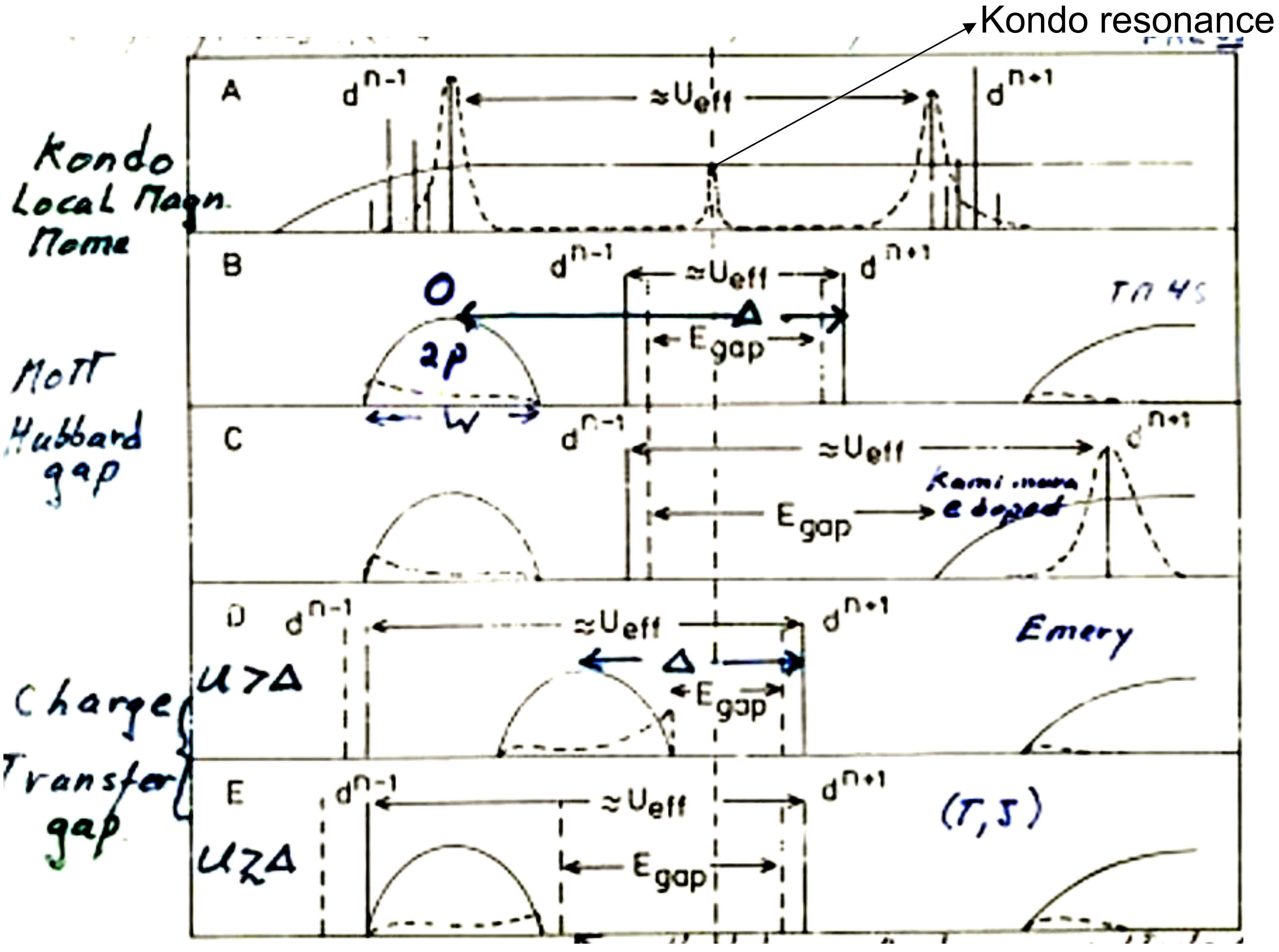
Developed for oxides in early 1980’s Fujimori, Sawatzky, Eskes, ------

- Dynamic Mean Field methods, CDMFT, DCA which to date do not include multiplets

Developed in the late 1990’s: Kotliar, George, Vollhard, Jarrell---

Zaanen et al prl 55 418
(1985)

Anderson impurity ansatz Like DMFT but not self consistant
But also including all multiplet interactions


Kondo resonance

To calculate the gap we calculate the ground state of the system with n,n-1, and n+1 d electrons

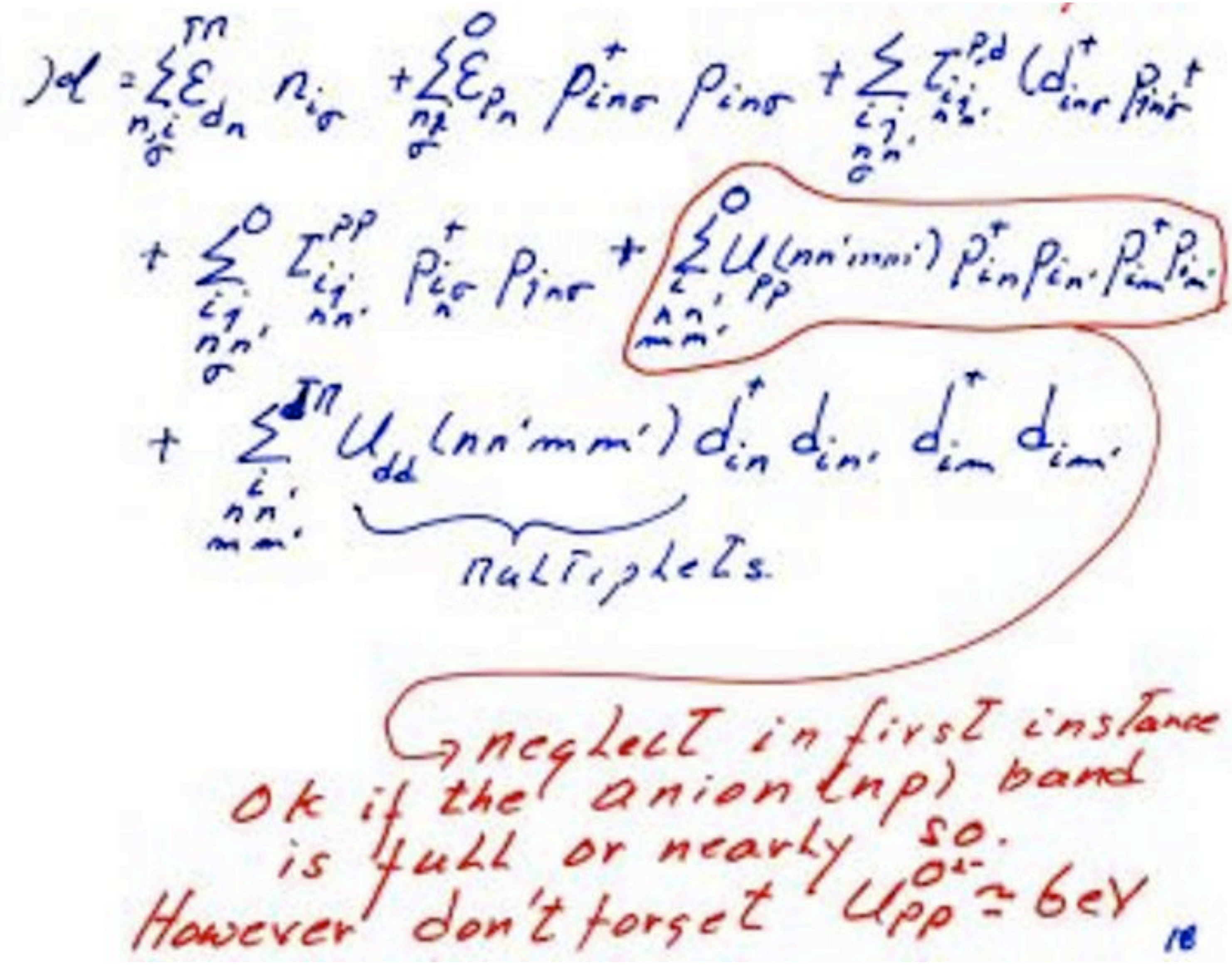
Then the gap is

$$E(\mathrm{Gap}) = E(n-1) + E(n+1) - 2E(n)$$

Two new complications

- d(n) multiplets determined by Slater atomic integrals or Racah parameters A,B,C. These determine Hund’s rules and magnetic moments
- d-O(2p) hybridization (d-p hoping int.) and the O(p)-O(p) hoping (O- 2p band width) determine crystal field splitting, superexchange etc
- These are mostly ionic materials yielding a large Madelung potential energy to the cohesive energy

More general multiband model Hamiltonian



$$\mathcal{H} = \sum_{\substack{n,i\\ \sigma}}^{TM} \varepsilon_{d_n} n_{i\sigma} + \sum_{\substack{n,i\\ \sigma}}^{O} \varepsilon_{p_n} p^{+}_{in\sigma} p_{in\sigma} + \sum_{\substack{ij,\\ nn'\\ \sigma}} T^{pd}_{ij,nn'} (d^{+}_{in\sigma} p_{jn\sigma}^{+}$$

$$+ \sum_{\substack{ij,\\ nn'\\ \sigma}}^{O} T^{pp}_{ij,nn'} p^{+}_{in\sigma} p_{jn\sigma} + \boxed{\sum_{\substack{i,\\ nn'\\ mm'}}^{O} U_{pp}(nn'mm')\, p^{+}_{in} p_{in'} p^{+}_{im} p_{im'}}$$

$$+ \sum_{\substack{i,\\ nn'\\ mm'}}^{TM} \underbrace{U_{dd}(nn'mm')}_{\text{multiplets.}} d^{+}_{in} d_{in'} d^{+}_{im} d_{im'}$$

→ neglect in first instance

Ok if the anion (np) band is full or nearly so.

However don't forget $U_{pp}^{O^{2-}} \simeq 6\text{eV}$

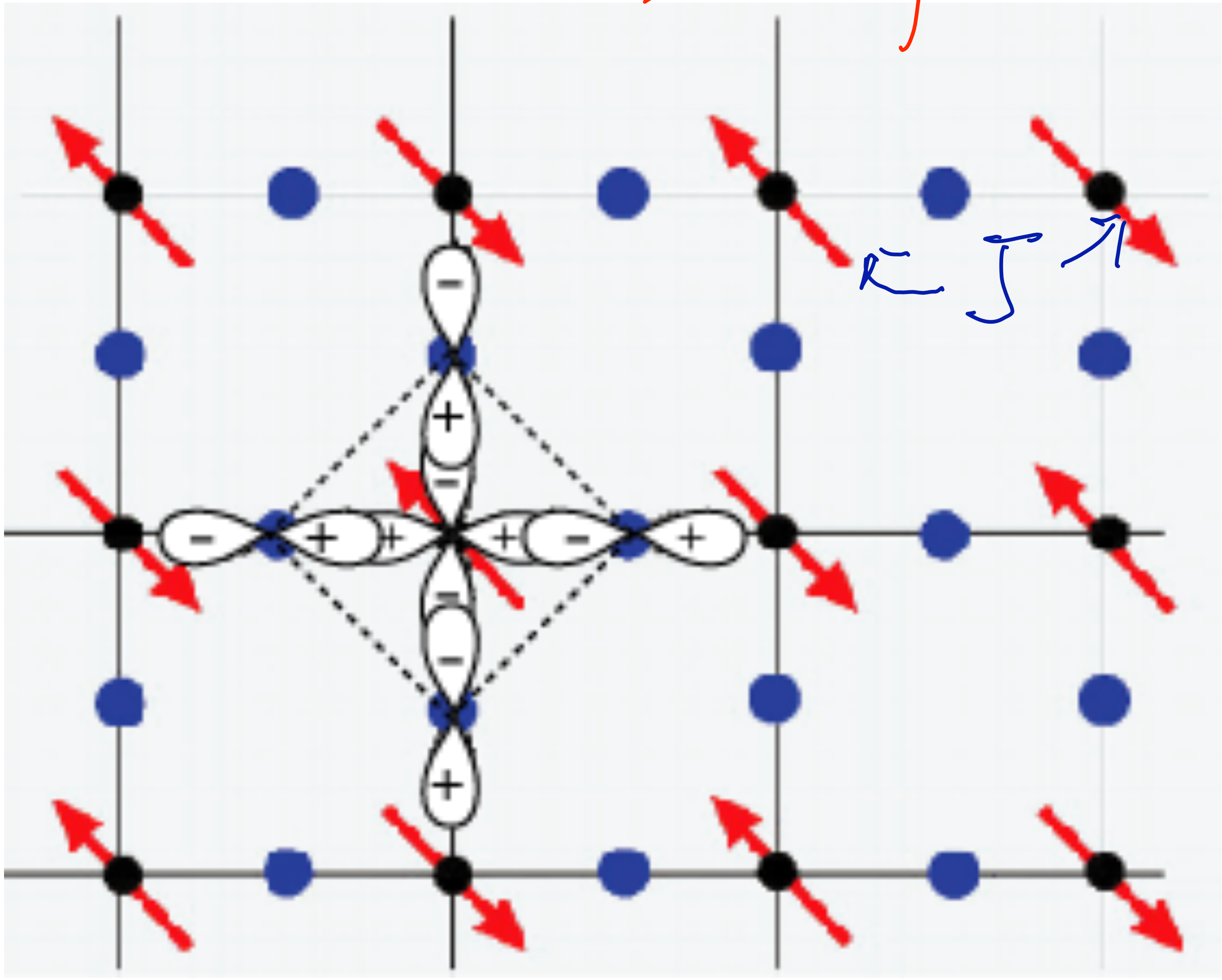
Atomic d-d coulomb interactions

- Note that is a function of up to 4 different quantum numbers U(n,n’,m,m’)This is very important for atomic multiplets who’s eigenstates are often a linear combination of a number of Slater determinants.
- This fact is often neglected in model Hamiltonians
- Take for example the Cu(d8) states in cuprates D4h point group symmetry

Undoped La_2CuO_4

2eV band gap insulator

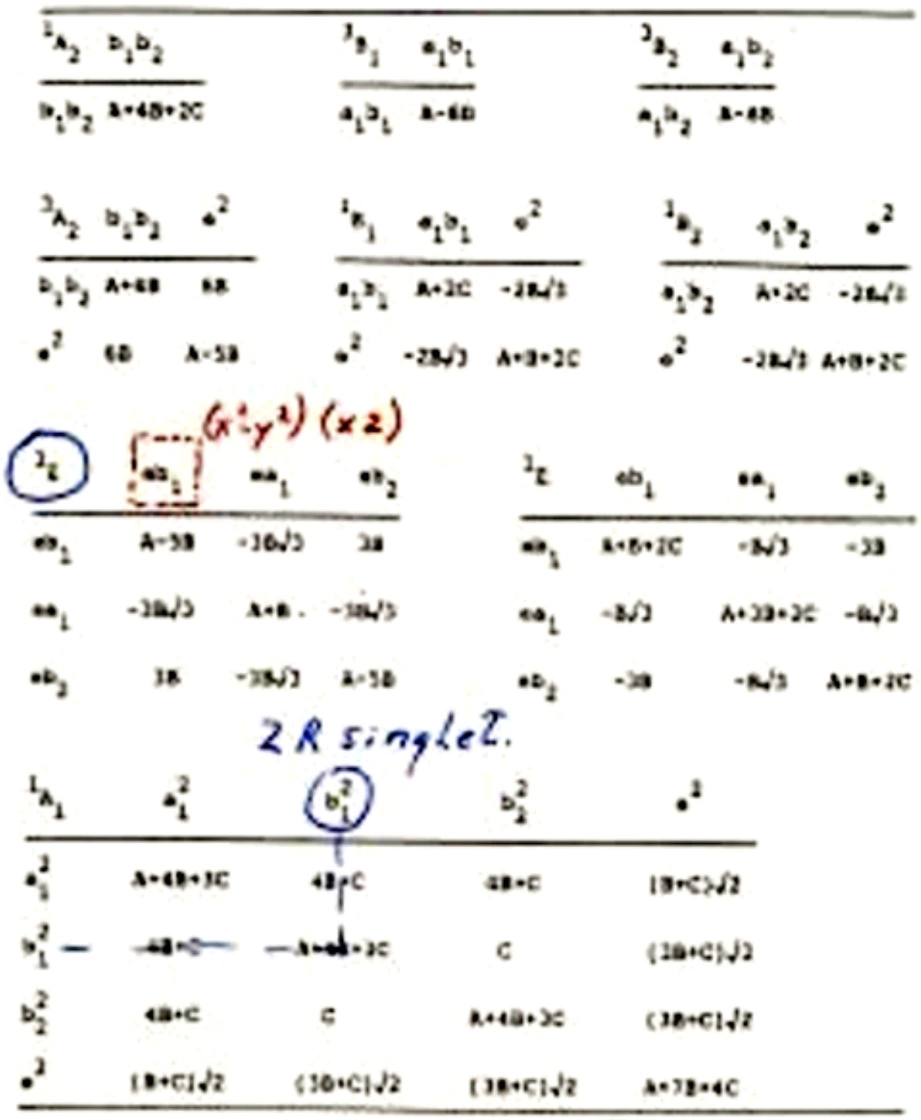
Antiferromagnet



$J \sim 130$ meV

For the N-1 electron states we need d8, d9L, d10L2 where L denotes a hole in O 2p band. The d8 states exhibit multiplets

We will come back to This later



$^1A_2$	b_1b_2
b_1b_2	$A+4B+2C$

$^3B_1$	a_1b_1
a_1b_1	$A-8B$

$^3B_2$	a_1b_2
a_1b_2	$A-8B$

$^3A_2$	b_1b_2	e^2
b_1b_2	$A+4B$	$6B$
e^2	$6B$	$A-5B$

$^1B_1$	a_1b_1	e^2
a_1b_1	$A+2C$	$-2B\sqrt{3}$
e^2	$-2B\sqrt{3}$	$A+B+2C$

$^1B_2$	a_1b_2	e^2
a_1b_2	$A+2C$	$-2B\sqrt{3}$
e^2	$-2B\sqrt{3}$	$A+B+2C$

$(x^2-y^2)\ (x2)$

^3E	eb_1	ea_1	eb_2
eb_1	$A-5B$	$-3B\sqrt{3}$	$3B$
ea_1	$-3B\sqrt{3}$	$A+B$	$-3B\sqrt{3}$
eb_2	$3B$	$-3B\sqrt{3}$	$A-5B$

^1E	eb_1	ea_1	eb_2
eb_1	$A+B+2C$	$-B\sqrt{3}$	$-3B$
ea_1	$-B\sqrt{3}$	$A+3B+2C$	$-B\sqrt{3}$
eb_2	$-3B$	$-B\sqrt{3}$	$A+B+2C$

ZR singlet.

$^1A_1$	a_1^2	b_1^2	b_2^2	e^2
a_1^2	$A+4B+3C$	$4B+C$	$4B+C$	$(B+C)\sqrt{2}$
b_1^2	$4B+C$	$A+4B+3C$	C	$(3B+C)\sqrt{2}$
b_2^2	$4B+C$	C	$A+4B+3C$	$(3B+C)\sqrt{2}$
e^2	$(B+C)\sqrt{2}$	$(3B+C)\sqrt{2}$	$(3B+C)\sqrt{2}$	$A+7B+4C$

- We usually take U(pp) =0 although it is about 5 eV as Measured with Auger but the O 2p band is usuallu fiull or nearly full.

$U_{dd} = E_I(d^n) - E_A(d^n)$ [Hunds Rule]

U_{dd} contains F^0, F^2, F^4

and also some crystal field.

For TM compounds use

Racah parameters instead of Slater:

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

[Again New convention

$F_2 = \frac{1}{49}F^2$, $F_4 = \frac{1}{448}F^4$, $F_0 = F$

B & C from Optical Spectr.

of free ions [or from solid]

↳ Moore's tables

Hunds Rule

First the Physics

Spin parallel electrons must be in different spatial orbitals i.e m_ℓ must be different if they are in the same shell i.e $\ell_1 = \ell_2 \Longrightarrow$ Pauli

$\Downarrow$

Lower Coulomb interaction

$\Downarrow$

Hunds 1st Rule Max. S

Large m_ℓ values means lots of lobes. Two electrons with different m_ℓ have lower Coulomb repulsion because they can avoid each other. The larger m_ℓ the better

Hunds 2nd Rule → Max. L

A Little more formal

From Slater Quantum th. of Atomic st.
chapter 13 + appendix 20

1-electr wavefcn

$$u_{n\ell m_\ell}(r,\theta,\phi)=\frac{(-1)^{(m_\ell+|m_\ell|)/2}}{\sqrt{4\pi}}\sqrt{\frac{(2\ell+1)(\ell-|m_\ell|)!}{(\ell+|m_\ell|)!}}$$

$$\times R_{n\ell}(r)\,P_\ell^{|m_\ell|}(\cos\theta)\,e^{im_\ell\phi}$$

$$\mathcal{H}_{op}=\underbrace{\sum_i f_i}_{\text{one electron}}+\Sigma(\text{pairs } ij)\,g_{ij}$$

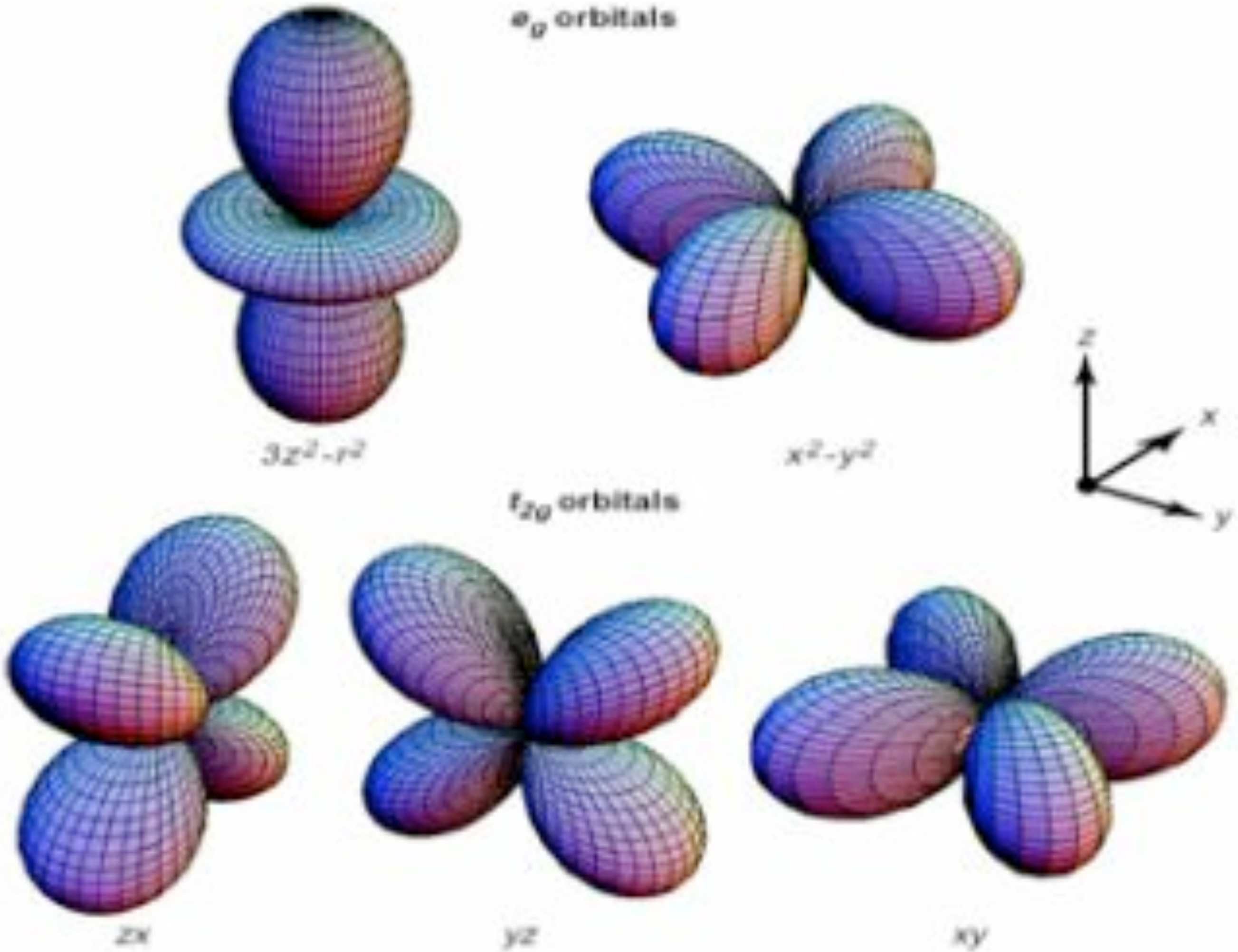
$$\text{one electron} = -\nabla_i^2-\frac{2Z}{r_i}$$

$$g_{ij}=\frac{2}{r_{ij}}$$ → Multiplets → Hunds ru

We need to calculate

$\langle ij|g|rt\rangle$ where i,j,r,t label the q.n's of occupied states

And sum over all ~~pairs~~ $i\,j\,r\,t$ that are occupied in Ψ



e_g orbitals
$3z^2-r^2$
x^2-y^2
z
x
y
t_{2g} orbitals
zx
yz
xy

Two Types of Integrals

$\langle ij|g|ij\rangle$ and $\langle ij|g|ji\rangle$

For 2 electrons in same shell

$$\langle ij|g|ij\rangle = \sum_{k=0}^{\infty} \underbrace{a^k(l_i m_i : l_j m_j)} F^k(n_i l_i : n_j l_j)$$

product of c's

$$F^k = R^k(ij : ij) \rightarrow \text{Direct Coulomb}$$

$$\langle ij|g|ji\rangle = \delta(m_{s_i}\, m_{s_j}) \sum_{k=0}^{\infty} b^k(l_i m_i : l_j m_j)\, G^k(n_i l_i : n_j l_j$$

$$b^k(l_i m_{l_i} : l_j m_{l_j}) = [C^k(l_i m_i : l_j m_j)]^2$$

$$G^k(n_i l_i : n_j l_j) = \iint R^*_{n_i l_i}(r_1)\, R^*_{n_j l_j}(r_2)\, R_{n_j l_j}(r_1)\, R_{n_i l_i}(r_2)\, \overset{\overset{\boxed{r_1^2 r_2^2}}{\downarrow}}{\frac{2 r_<^k}{r_>^{k+1}}}\, dr_1\, dr$$

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-|m|)!}{(k+|m|)!} \frac{r_<^k}{r_>^{k+1}} P_k^{|m|}(\cos\theta_1) P_k^{|m|}(\cos\theta_2)$$

$$\times\ e^{|im(\phi_1-\phi_2)|}$$

$$\langle ij|g|r\tau\rangle = \iint \psi_i^*(\vec{r}_1)\, \psi_j^*(\vec{r}_2) \frac{1}{|r_1-r_2|} \psi_r(\vec{r}_1) \psi_\tau(\vec{r}_2)\, d\tau_1\, d\tau_2$$

$$\therefore\ m_{s_i} = m_{s_r} \qquad m_{s_j} = m_{s_\tau}$$

$$= \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-|m|)!}{(k+|m|)!} (-1)^{m_{\ell_i}+|m_{\ell_i}|+m_{\ell_j}+|m_{\ell_j}|+m_{\ell_r}+|m_{\ell_r}|+\cdots\tau}$$

$$\times \sqrt{\frac{(2\ell_i+1)(\ell_i-|m_{\ell_i}|)!}{(\ell_i+|m_{\ell_i}|)!}} \times \overset{j}{\cdots} \times \overset{r}{\cdots} \times \overset{\tau}{\cdots} \times$$

$$\times \int_0^{\infty}\int_0^{\infty} R^*_{n_i\ell_i}(r_1)\, R^*_{n_j\ell_j}(r_2)\, R_{n_r\ell_r}(r_1)\, R_{n_\tau\ell_\tau}(r_2)\, \frac{2 r_<^k}{r_>^{k+1}}\, r_1^2 r_2^2\, dr_1\, dr_2$$

$$\times \int_0^{\pi} P_{\ell_i}^{|m_i|}(\cos\theta_1)\, P_{\ell_r}^{|m_r|}(\cos\theta_1)\, P_k^{|m|}(\cos\theta_1)\, \frac{\sin\theta_1}{2}\, d\theta_1$$

$$\times \int P_{\ell_j}^{|m_j|}(\cos\theta_2)\, P_{\ell_\tau}^{|m_\tau|}(\cos\theta_2)\, P_k^{|m|}(\cos\theta_2)\, \frac{\sin\theta_2}{2}\, d\theta_2$$

$$\times \int_0^{2\pi} e^{i(-m_{\ell_i}+m_{\ell_r}+m)\phi_1} \frac{d\phi_1}{2\pi} \times \int e^{i(-m_{\ell_j}+m_{\ell_\tau}-m)\phi_2} \frac{d\phi_2}{2\pi}$$

From orthogonality $\int \phi$

$$m = m_{l_i} - m_{l_r} = -m_{l_j} + m_{l_t}$$

$$m_{l_i} + m_{l_j} = m_{l_r} + m_{l_t} \quad (\text{Conserv. } M)$$

$\int \theta$ we use

$$C^k(lm; l'm') = (-1)^{(m+|m|+m'+|m'|+(m-m')+|m-m'|)/2}$$

$$\times \sqrt{\frac{(k-|m-m'|)!}{(k+|m-m'|)!}} \sqrt{\frac{(2l+1)(l-|m|)!}{(l+|m|)!}} \sqrt{\frac{(2l'+1)(l'-|m'|)!}{(l'+|m'|)!}}$$

$$\times \frac{1}{2} \int_{-1}^{1} P_l^{|m|}(u)\, P_{l'}^{|m'|}(u)\, P_k^{|m-m'|}(u\, du$$

Tabulated → Appendix 20

$$\langle ij|g|rt\rangle = \delta(m_{s_i}, m_{s_r})\, \delta(m_{s_j}, m_{s_t})\, \delta(m_{l_i}+m_{l_j}, m_{l_r}+m_{l_t})$$

$$\times \sum_{k=0}^{\infty} C^k(l_i m_{l_i} : l_r m_{l_r})\, C^k(l_t m_{l_t} : l_j m_{l_j})\, R^k(ij;rt)$$

Highest possible value of $\underline{k = l + l'}$

i.e. $l_i + l_r$ or $l_t + l_j$

The coulomb interactions in terms of real space d orbitals

Ballhausen "Intro to Ligand field theory" McGraw-Hill (1962)

Coulomb (J) and exchange (K)

$$J(x2, y2) = \int (x2)^*(1)(y2)^*(2)\, \frac{1}{r_{12}}\, x2(1)\, y2(2)\, d\tau$$

$$K(x2, y2) = \int (x2)^*(1)(y2)^*(2)\, \frac{1}{r_{12}}\, y2(1)\, x2(2)\, d\tau$$

Table 4-5. Coulomb Integrals (J) and Exchange Integrals (K) of the Set $t_{2g}(xz,yz,xy)$ and $e_g(x^2-y^2,z^2)$ (Ref. 19)

$$J(z^2,z^2) = J(x^2-y^2,\, x^2-y^2) = J(xy,xy) = J(xz,xz) = J(yz,yz)$$
$$= F_0 + 4F_2 + 36F_4$$
$$J(x^2-y^2,\, xz) = J(x^2-y^2,\, yz) = J(xy,yz) = J(xy,xz)$$
$$= J(xz,yz) = F_0 - 2F_2 - 4F_4$$
$$J(z^2,xz) = J(z^2,yz) = F_0 + 2F_2 - 24F_4$$
$$J(z^2,xy) = J(z^2,x^2-y^2) = F_0 - 4F_2 + 6F_4$$
$$J(x^2-y^2,\, xy) = F_0 + 4F_2 - 34F_4$$
$$K(xy,yz) = K(xy,xz) = K(xz,yz) = K(x^2-y^2,\, xz) = K(x^2-y^2,\, yz)$$
$$= 3F_2 + 20F_4$$
$$K(z^2,\, x^2-y^2) = K(z^2,xy) = 4F_2 + 15F_4$$
$$K(z^2,xz) = K(z^2,yz) = F_2 + 30F_4$$
$$K(x^2-y^2,\, xy) = 35F_4$$

Table 4-6. Values of the Matrix Elements $(ab|1/r_{12}|cd)$ Different from Zero

a	b	c	d	$(ab\|1/r_{12}\|cd)$
(xz)	(z^2)	(xz)	(x^2-y^2)	$-2\sqrt{3}\,F_2 + 10\sqrt{3}\,F_4$
(yz)	(z^2)	(yz)	(x^2-y^2)	$2\sqrt{3}\,F_2 - 10\sqrt{3}\,F_4$
(xz)	(xz)	(z^2)	(x^2-y^2)	$\sqrt{3}\,F_2 - 5\sqrt{3}\,F_4$
(yz)	(yz)	(z^2)	(x^2-y^2)	$-\sqrt{3}\,F_2 + 5\sqrt{3}\,F_4$
(z^2)	(xy)	(xz)	(yz)	$\sqrt{3}\,F_2 - 5\sqrt{3}\,F_4$
(z^2)	(xy)	(yz)	(xz)	$\sqrt{3}\,F_2 - 5\sqrt{3}\,F_4$
(z^2)	(xz)	(xy)	(yz)	$2\sqrt{3}\,F_2 - 10\sqrt{3}\,F_4$
(x^2-y^2)	(xy)	(xz)	(yz)	$3F_2 - 15F_4$
(x^2-y^2)	(xy)	(yz)	(xz)	$-3F_2 + 15F_4$

Hunds 3rd rule

< half filled $\vec{J} = \vec{L} - \vec{S}$

> half filled $\vec{J} = \vec{L} + \vec{S}$

⇊

Spin - Orbit Coupling

$$\mathcal{H}' = \sum_{i} \frac{1}{2m^2c^2} \left(\vec{\nabla} V_i \times \vec{p}_i \right) \cdot s_i$$

For 1 electron $\vec{j} = \vec{\ell} - \vec{s}$ is lowest

↓

i.e for d^1 electron $\vec{j} = 3/2$

For 1 hole $\vec{j}_{hole} = \vec{\ell} + \vec{s}$

i.e for d^9 $J = 5/2$ (lowest)

Spinorbit results in

- magnetic anisotropy
- g factor different from 2
- orbital contribution to magnetic moment
- $\vec{D} \cdot \vec{S}_1 \times \vec{S}_2$ like interactions

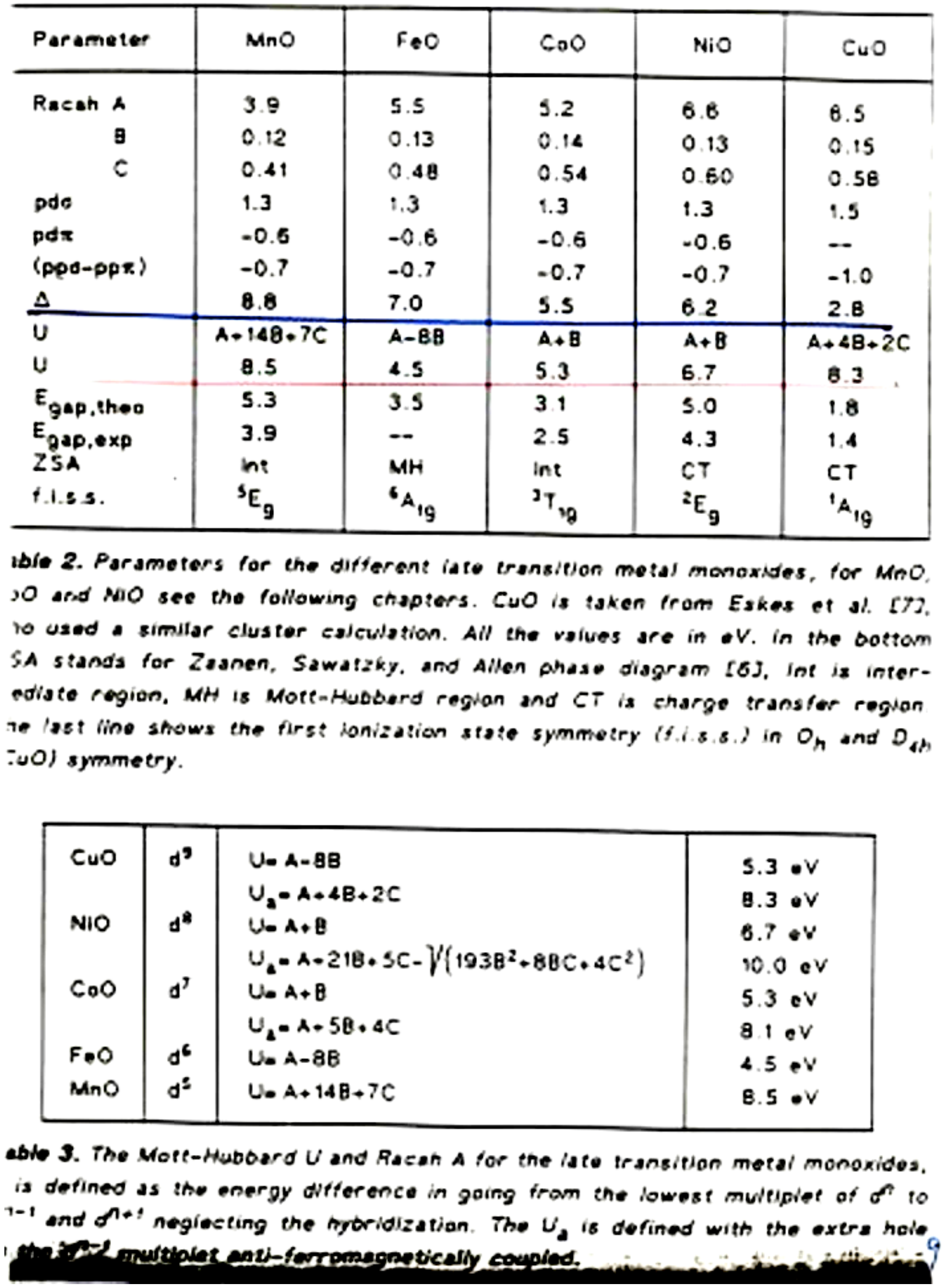
Reduction of coulomb and exchange in solids

- Recall that U or F0 is strongly reduced in the solid. This is the monopole coulomb integral describing the reduction of interaction of two charges on the same atom
- However the other integrals F2 andF4 and G’s do not involve changes of charge but simply changes of the orbital occupations of the electrons so these are not or hardly reduced in solids . The surroundings does not care much if local eg the spin is 1 or zero.
- This makes the multiplet structure all the more important!!!!!

We will talk about screening somewhat latter for now we tabulate some experimentally determined values for some oxides

Note that B and C are only slightly reduced in the solid they do not involve changes in the local charge !!!

Van Elp
Thesis U of
Groningen



Parameter	MnO	FeO	CoO	NiO	CuO
Racah A	3.9	5.5	5.2	6.6	6.5
B	0.12	0.13	0.14	0.13	0.15
C	0.41	0.48	0.54	0.60	0.58
pdσ	1.3	1.3	1.3	1.3	1.5
pdπ	-0.6	-0.6	-0.6	-0.6	--
(ppσ-ppπ)	-0.7	-0.7	-0.7	-0.7	-1.0
Δ	8.8	7.0	5.5	6.2	2.8
U	A+14B+7C	A-8B	A+B	A+B	A+4B+2C
U	8.5	4.5	5.3	6.7	8.3
$E_{gap,theo}$	5.3	3.5	3.1	5.0	1.8
$E_{gap,exp}$	3.9	--	2.5	4.3	1.4
ZSA	Int	MH	Int	CT	CT
f.i.s.s.	^5E_g	$^6A_{1g}$	$^3T_{1g}$	^2E_g	$^1A_{1g}$

ble 2. *Parameters for the different late transition metal monoxides, for MnO, O and NiO see the following chapters. CuO is taken from Eskes et al. [7], o used a similar cluster calculation. All the values are in eV. In the bottom SA stands for Zaanen, Sawatzky, and Allen phase diagram [6], Int is inter- ediate region, MH is Mott-Hubbard region and CT is charge transfer region e last line shows the first ionization state symmetry (f.i.s.s.) in O_h and D_{4h} uO) symmetry.*

CuO	d^9	$U= A-8B$	5.3 eV
		$U_a= A+4B+2C$	8.3 eV
NiO	d^8	$U= A+B$	6.7 eV
		$U_a= A+21B+5C-\sqrt{(193B^2+8BC+4C^2)}$	10.0 eV
CoO	d^7	$U= A+B$	5.3 eV
		$U_a= A+5B+4C$	8.1 eV
FeO	d^6	$U= A-8B$	4.5 eV
MnO	d^5	$U= A+14B+7C$	8.5 eV

able 3. *The Mott-Hubbard U and Racah A for the late transition metal monoxides. is defined as the energy difference in going from the lowest multiplet of d^n to $^{n-1}$ and d^{n+1} neglecting the hybridization. The U_a is defined with the extra hole the d^{n-1} multiplet anti-ferromagnetically coupled.*

Need multiband models to describe TM compounds

However numerous studies have shown that this can sometimes be reduced to an effective single band Hubbard model at least for highTc’s BUT ONLY FOR LOW ENERGY EXCITATIONS E<0.5eV

Macridin et al
Phys. Rev. B 71, 134527 (2005)

Crystal & Ligand fields

ψ_d (Free ion) ~ $Y_\ell^m(\theta,\phi) \to P_\ell(\cos\theta)e^{im\phi}$

$\ell = 2 \qquad m_\ell = \pm 2 \pm 1\, 0$

$\vec{j} = \vec{\ell} + \vec{s}$ or $\vec{\ell} - \vec{s}$ (Hunds rule)

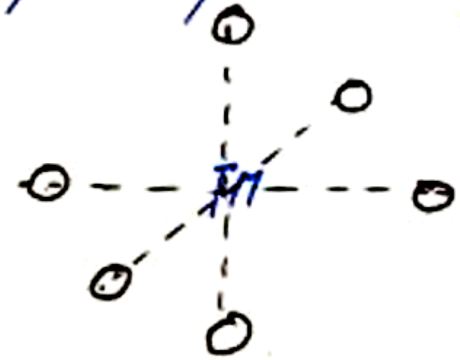
Spin orbit coupling ~ $\lambda\, \vec{\ell}\cdot\vec{s}$

is λ ~ 30 meV often << crystal field

Often Orbital moment is quenched

Construct real orbitals

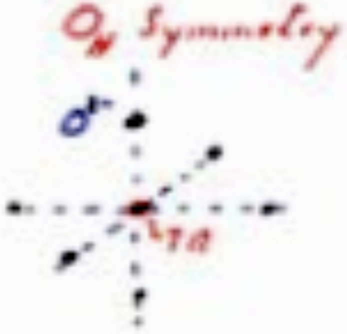
O_h symmetry Octahedral coordination

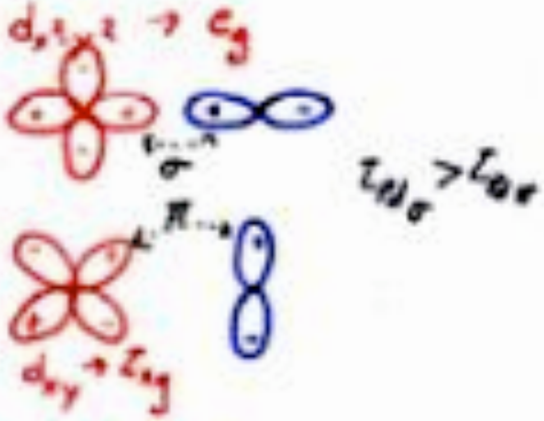


d^n energy levels with
crystal field and Hund's
<u>First</u> rule (Maximize spin)
i.e d-d Coulomb $F^0, \frac{1}{14}(F^2+F^4)$
neglect other contributions
to multiplet splitting.

This is a good starting picture.
For exact go to Tanake -
Sugano diagrams.

Crystal fields / Multiplets / Hunds Rule





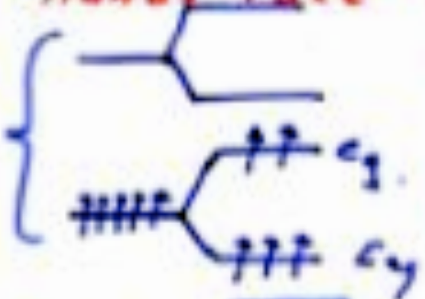
$e_g\ (d_{x^2-y^2},\ d_{3z^2-r^2})$ $t_{2g}\ (d_{xy}, d_{xz}, d_{yz})$

$\Delta e_g - t_{2g} = 10D_q$ For $10D_q > \lambda_{S.O}$ $\langle L_z \rangle = 0$

$10D_q \sim 1\text{-}2\,eV$ $\lambda_{SO} \sim 30\,meV$

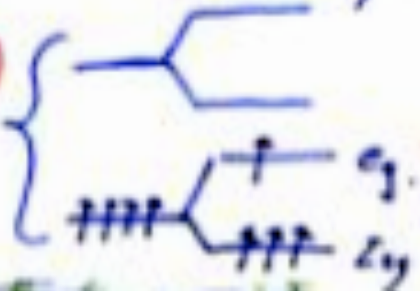
For $\langle L_z \rangle = 0$ Hunds rule spins parall

$d^5 (Mn^{2+}, Fe^{3+})$



Exchange 10J

$d^4 (Mn^{3+}\ Fe^{4+}\ Cr^{2+})$

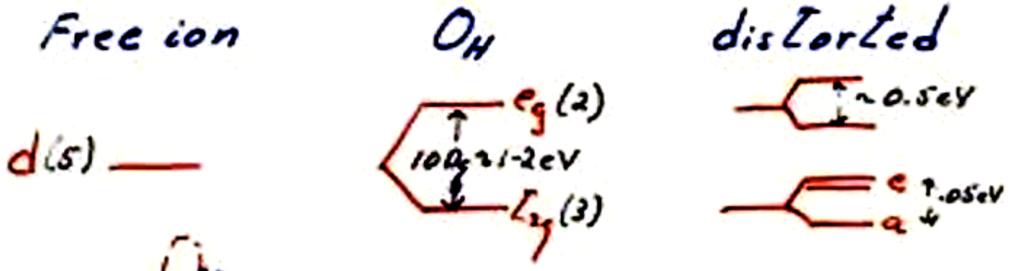


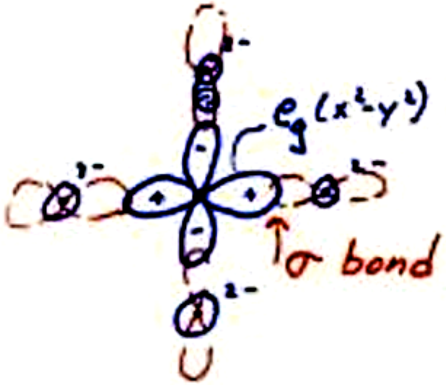
- 2 Fold

Exchange 6J

[illegible]

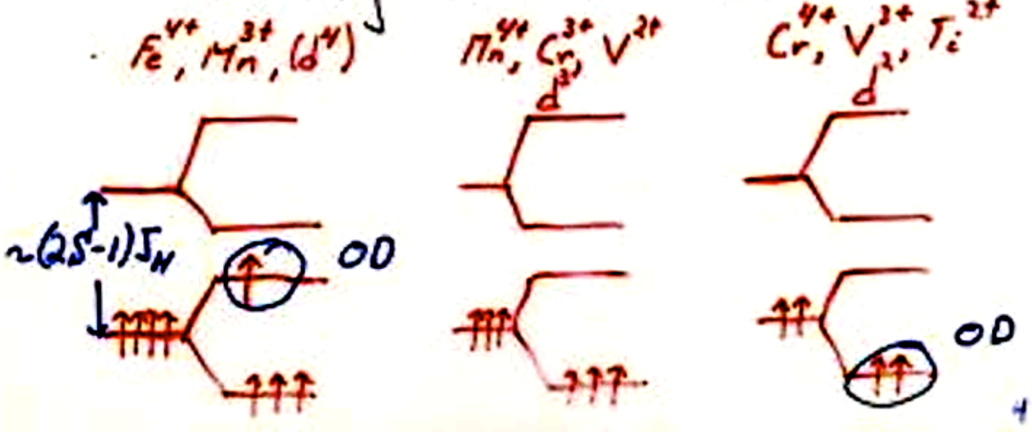
Orbital Degeneracy





S-Orbit ~ 0.05eV (t_{2g}!)

Strong U and J_H (~0.8eV)



Crystal and ligand field splittings

1) Point charge contribution

$$V = \sum_{nm} A_n^m r^n P_n^{|m|}(\cos\theta)\, e^{im\phi}$$

$$\langle d_i \,|\, V \,|\, d_i \rangle = \Delta E$$

Octahedron - Cubic - O_H

Often about 0.5 eV
In Oh symmetry

$i = x^2-y^2,\ 3z^2-r^2 \quad (e_g)$
$\ \ = xy,\ xz,\ yz \quad (t_{2g})$

$n = 0, 4 \quad$ for $\Delta E \neq 0$

$\Delta E \propto \langle d | r^4 | d \rangle \times$ angular part

$$V = A_4^0 r^4 \left[P_4^0(\cos\theta) - \left(\frac{5}{14}\right)^{1/2} \{ P_4^4(\cos\theta) e^{i4\phi} + P_4^{-4}(\cos\theta) e^{-i4\phi} \right]$$

2) Overlap contribution

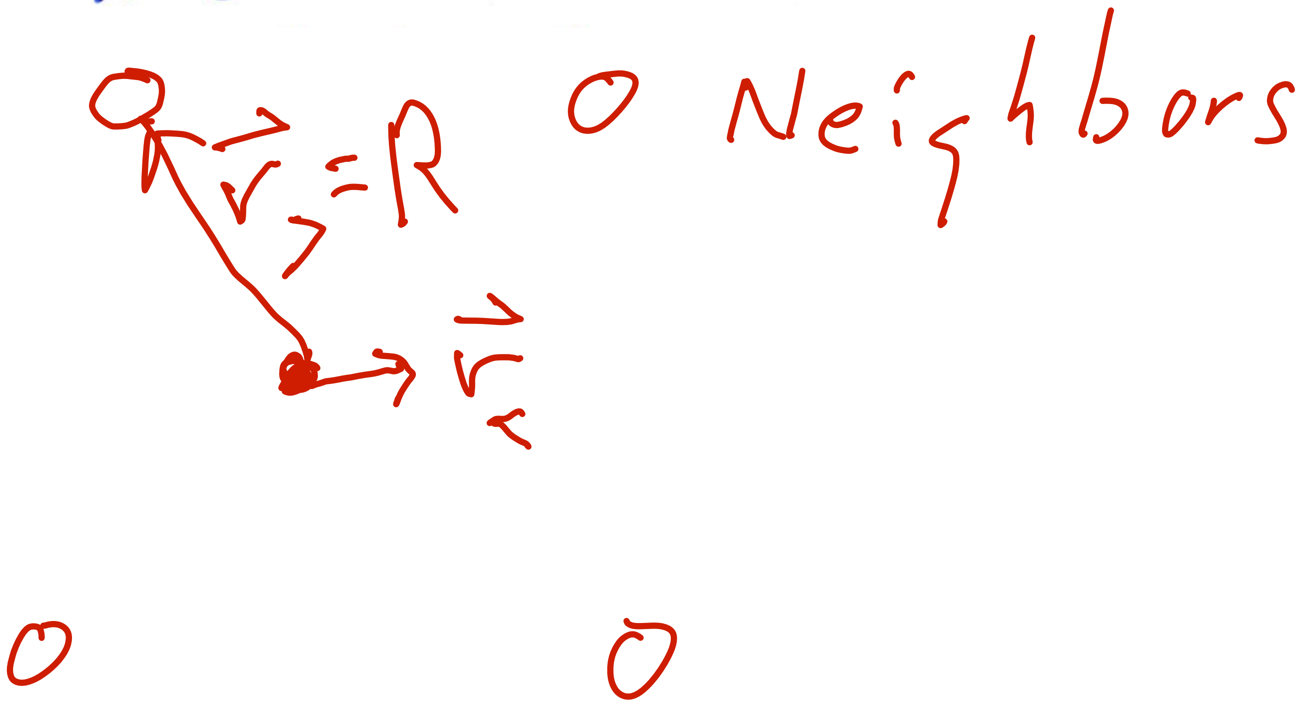

e_g


t_{2g}

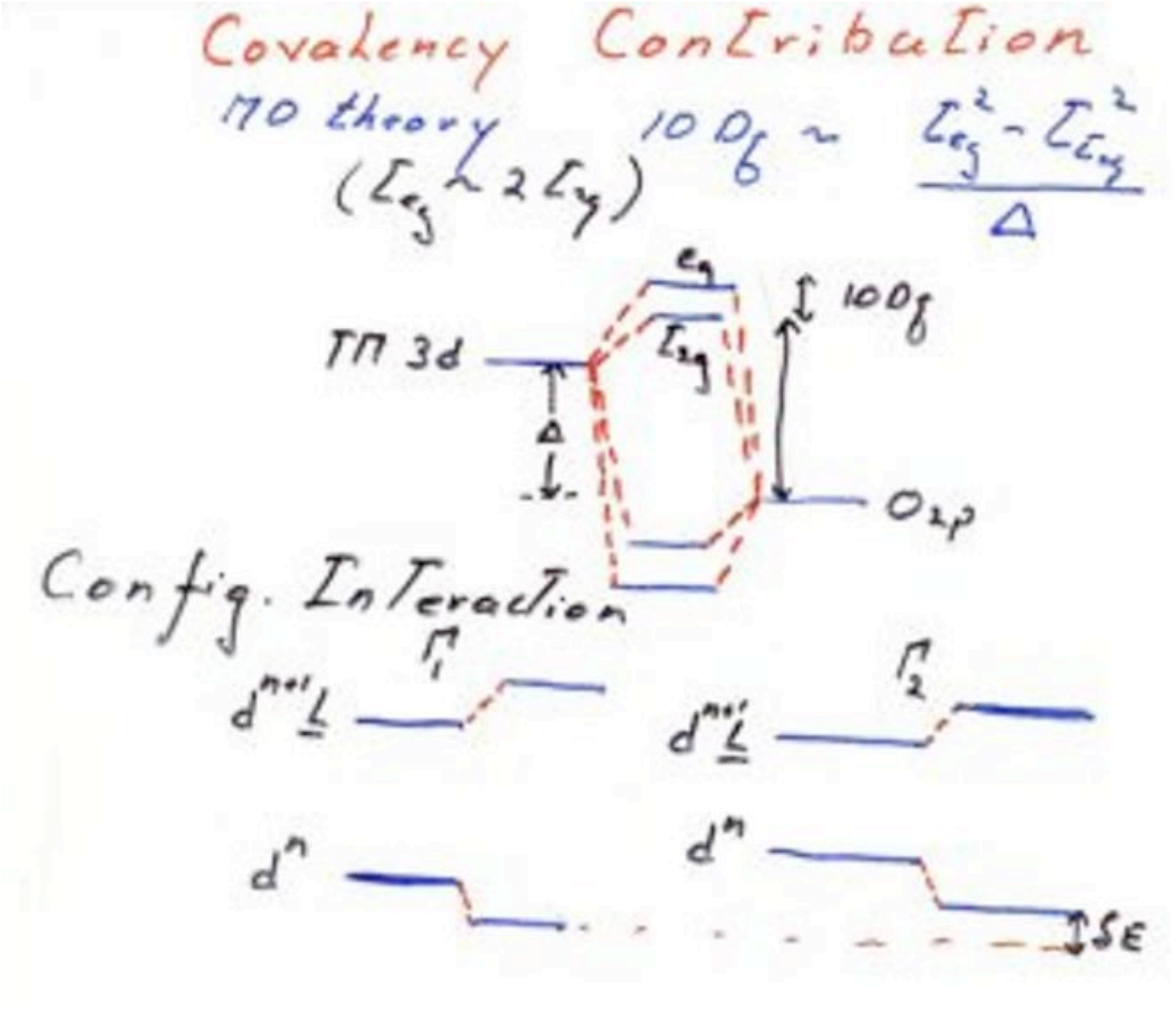
$$\langle d_{e_g} | p_z \rangle > \langle d_{t_{2g}} | p_x \rangle$$

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-|m|)!}{(k+|m|)!} \frac{r_<^k}{r_>^{k+1}} P_k^{|m|}(\cos\theta_1)\, P_k^{|m|}(\cos\theta_2)$$

$$\times \; e^{|im(\phi_1-\phi_2)|}$$



Eg-O2p hoping is 2 times as large as T2g-O-2p hoping



Covalency Contribution

MO theory ($t_{e_g} \sim 2 t_{t_{2g}}$) $10Dq \sim \frac{t_{e_g}^2 - t_{t_{2g}}^2}{\Delta}$

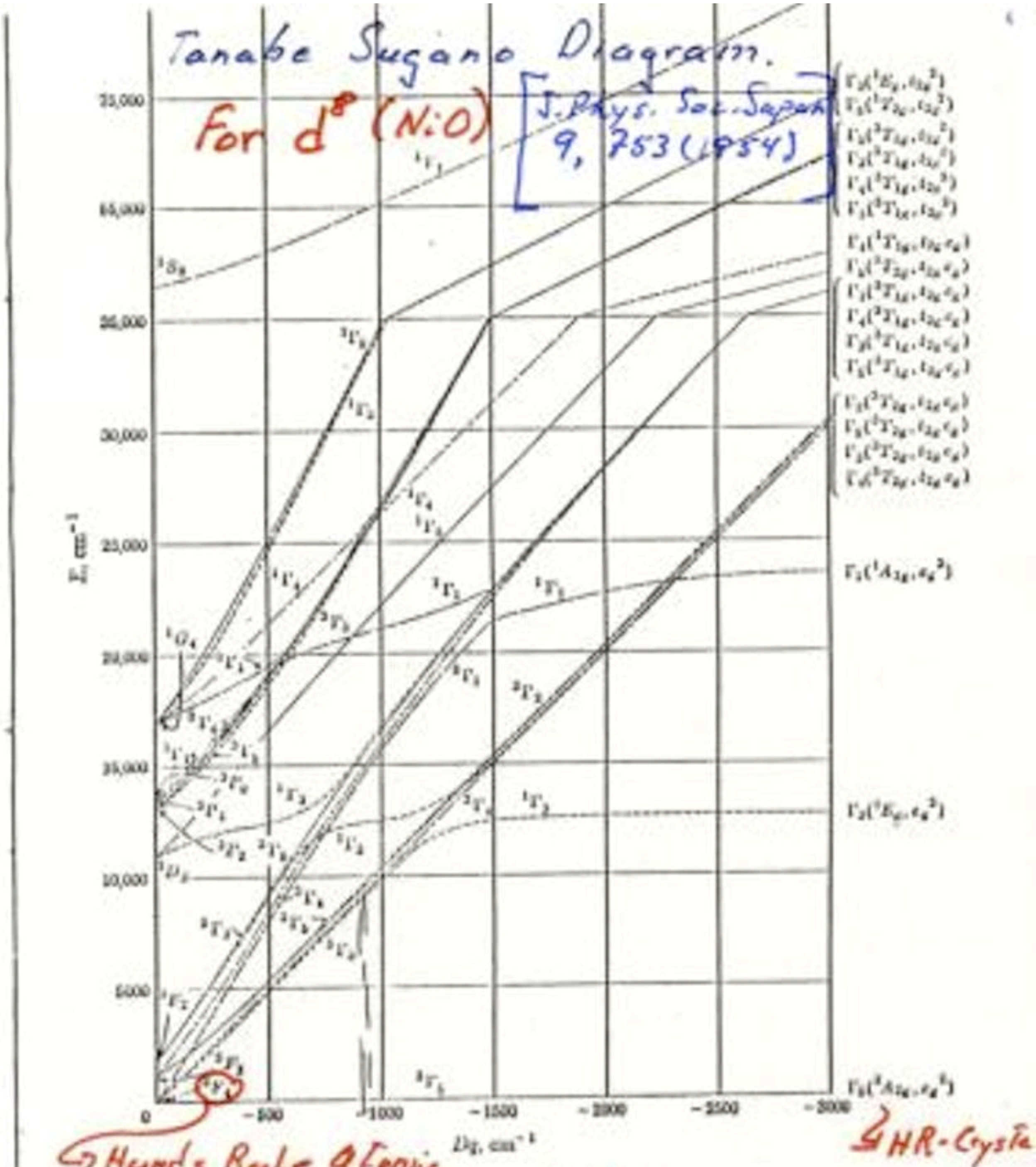
Config. Interaction

Often about 1-2eV
In Oxides

Tanabe Sugano Diagram.

For d^8 (NiO)

[J. Phys. Soc. Japan 9, 753 (1954)]



Hund's Rule Atomic

HR-Crysta

Renormalized Atom

High Spin – Low Spin transition very common in Co(3+)(d6), as in LaCoO3, not so common in Fe(2+)(d6) Because of the smaller hybridization with O(2p)

In some cases also the Spin is quenched [$3d^6$ in O_H]

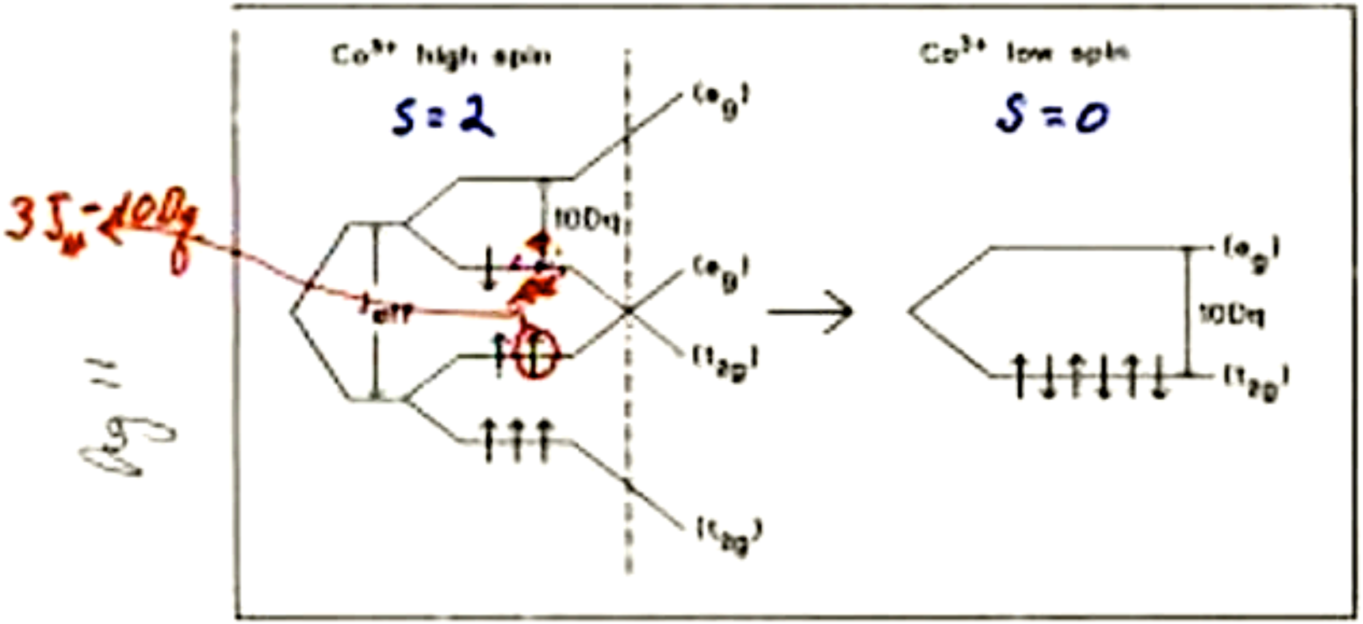
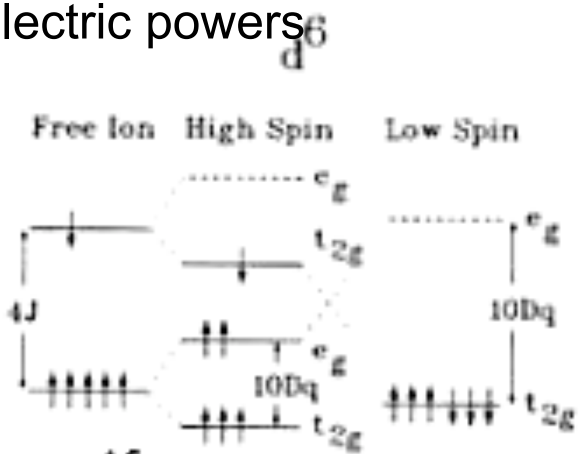


fig 11

Mixed valent system could lead to strange effects
Such as spin blockade for charge transport and high
thermoelectric powers



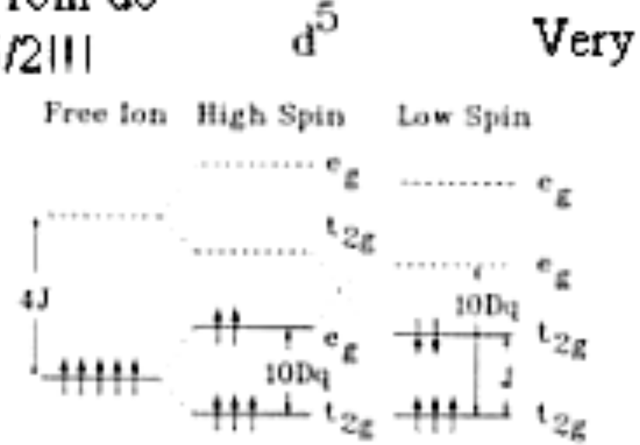
$E(HS)= -10J-4Dq$

$E(LS)=-6J-24Dq$

LS for $10Dq > 2J$

Removing 1 electr. From d6
Could change S by 5/2!!!

Very heavy QP??



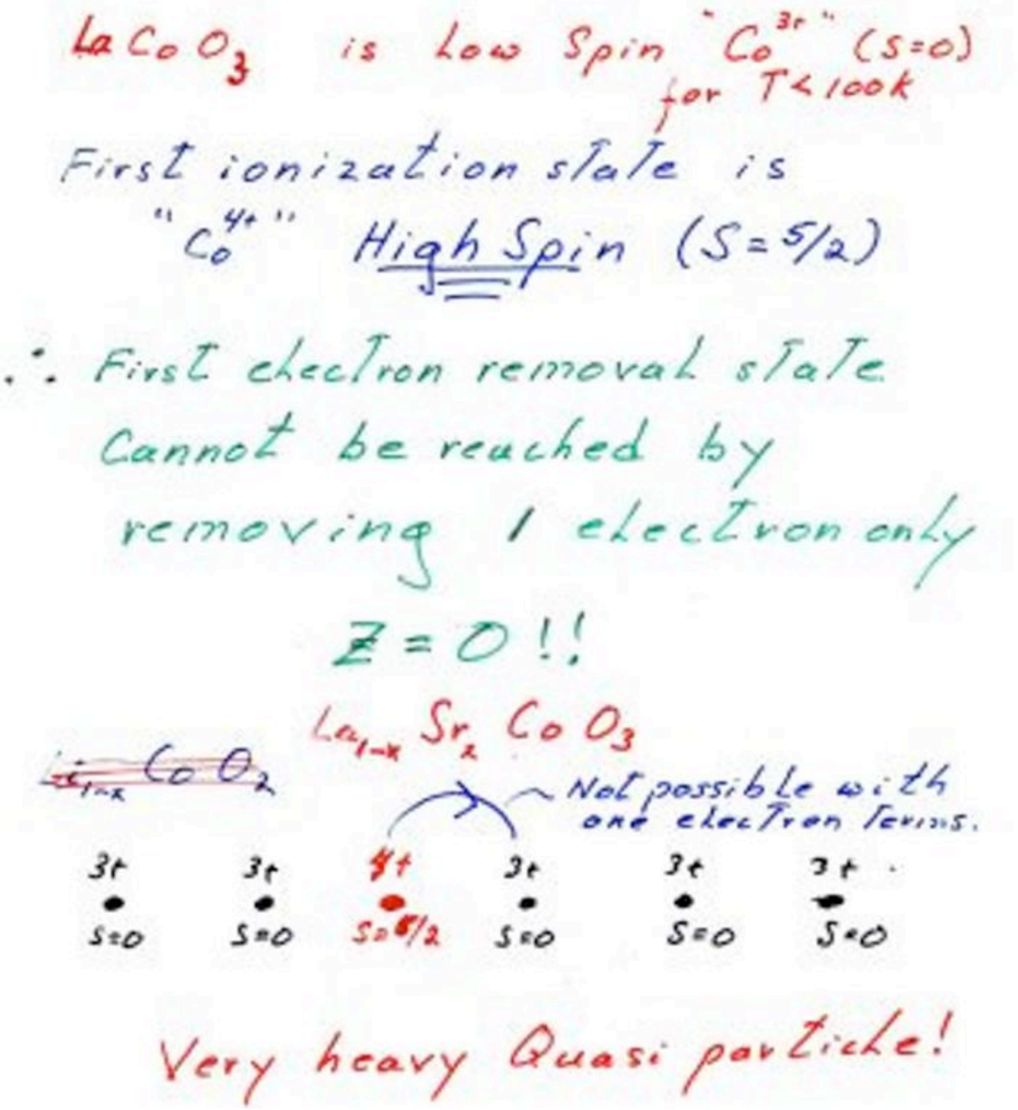
$E(HS) = -10J$

$E(LS)= -4J-20Dq$

LS for $10Dq > 3J$

FIG.8.1. Schematic picture of the electron removal energies (solid lines) and one electron exitation energies (dashed lines) for d^6 and d^5. The left panel represents the free ion and the central panel corresponds to the ion in a weak crystal field, which is further increased in the panel on the right. Note that the exchange splittings of the majority and minority spin states for high spin and low spin are different.

What would happen if 2Jh <10Dq<3Jh
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.



$LaCoO_3$ is Low Spin "Co^{3+}" (S=0) for T<100K

First ionization state is "Co^{4+}" High Spin (S=5/2)

∴ First electron removal state Cannot be reached by removing 1 electron only

Z = 0 !!

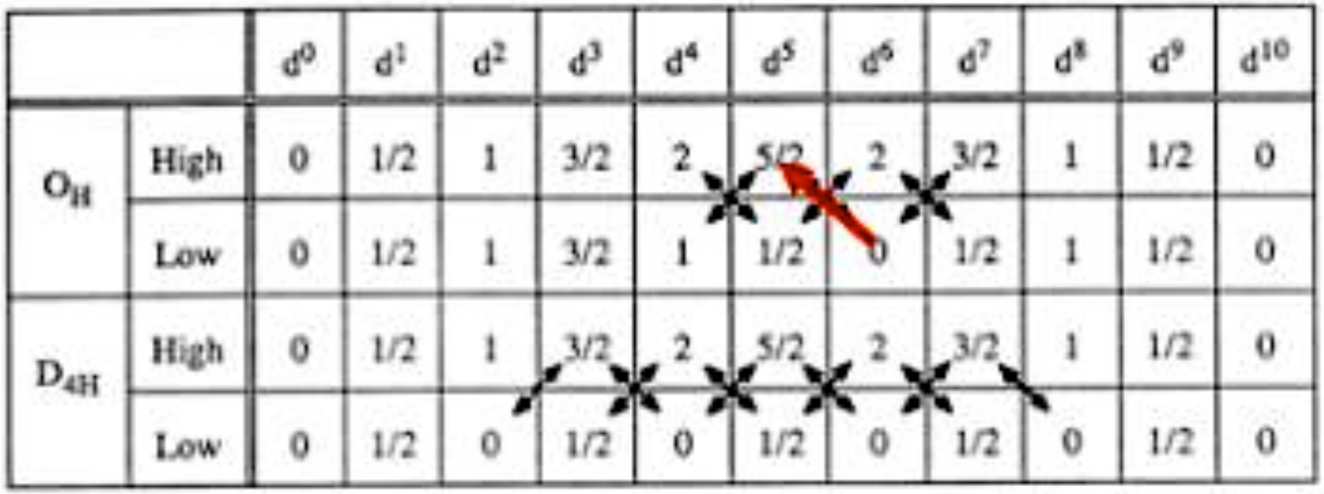
$La_{1-x}Sr_xCoO_3$

~~$Li_{1-x}CoO_2$~~

Not possible with one electron terms.

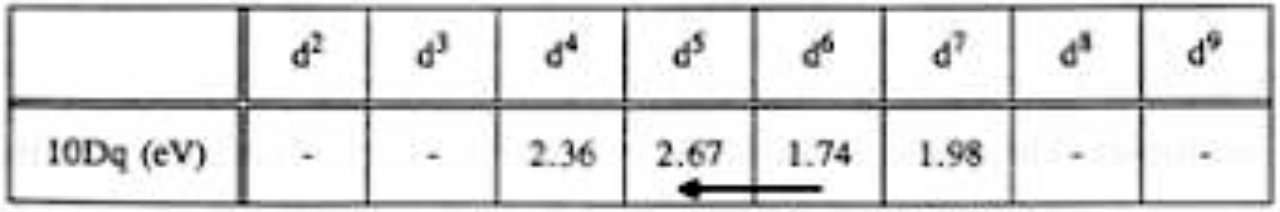
Very heavy Quasi particle!

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 (10*Dq*) 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!!

Orbital degeneracy

$d^4\,(t_{2g}^3\, e_g^1)$ $d^6\,(t_{2g}^4\, e_g^2)$; d^1, d^2, d^7

$d^9\,(t_{2g}^6\, e_g^3)$ $(t_{2g}^{3\uparrow\uparrow}\, t_{2g}^{1}\, e_g^{2\uparrow})$

→ strong JT ion ↳ weak JT

How can we lift degeneracy

1) JT distortion → lower symmetry

$Cu^{2+}(d^9)(t_{2g}^6\, e_g^3)$ $O_h \rightarrow D_{4h}$

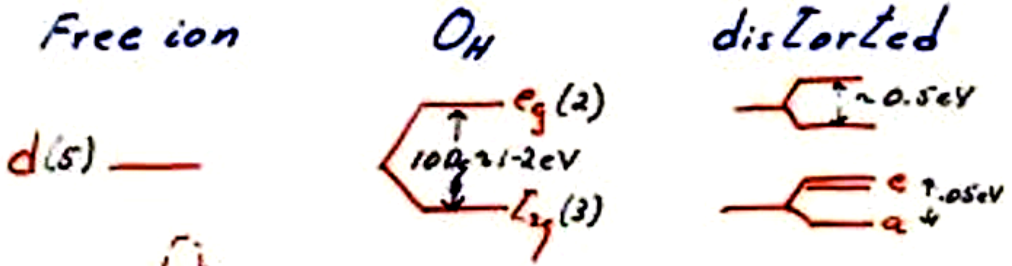
2) Spin orbit (for t_{2g})

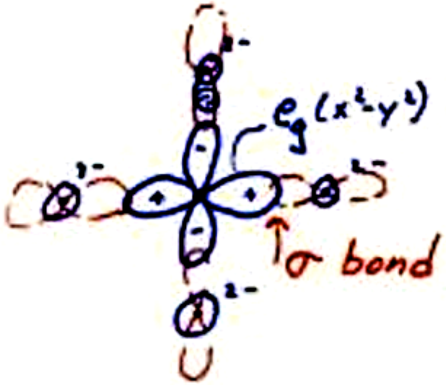
$\lambda \sim 30$ meV for 3d TM's
$\lambda \sim 300$ meV for 4d TM's
(LaSrCoO$_3$ Pellegrin)

→ 3) Orbital ordering

4) charge disproportionation

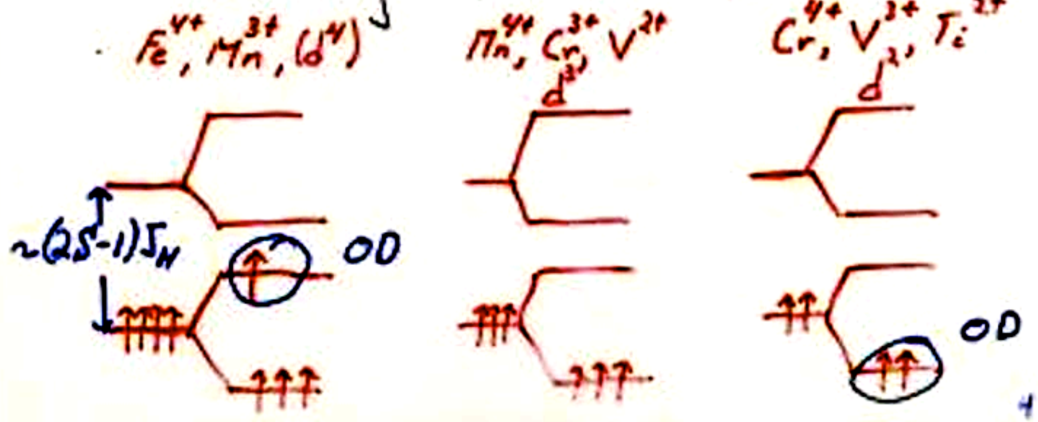
Orbital Degeneracy





S-Orbit ~ 0.05eV (t_{2g}!)

strong U and J_H (~0.8eV)



Kugel Khomskii (1982)

Orbital Ordering

Spin waves Orbital Waves?

Strong Coupling!

$$\mathcal{H} \simeq \sum_{ij} J^{s}_{ij}\, S_i \cdot S_j + \sum_{ij} J^{o}_{ij}\, \hat{O}_i \cdot \hat{O}_j + \sum_{ij} J^{so}_{ij} (\bar{O}_i \cdot \hat{O}_j)(\tilde{S}_i \cdot S_j)$$

in general $\tilde{O} = \tilde{O}$ very complicated

(See Ishihara, Inoue, Maekawa for Mn perveskites)

Orbitons

modified magnon $E(k)$

perhaps even 2 part. bound states [Orbiton - Magnon

$\Downarrow$

Magiton $\leftrightarrow$ Orbinon

Van den Brink et al (1998)

$LaMnO_3$ Murakami et al

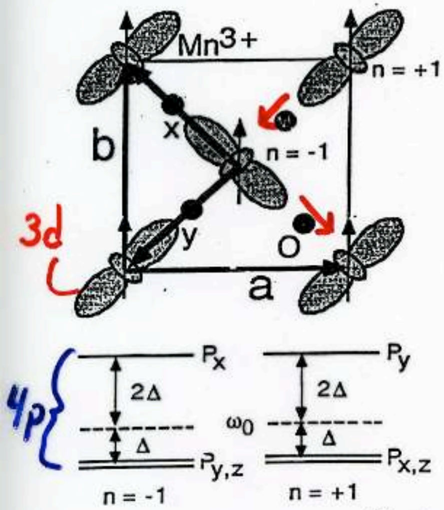


Fig 1

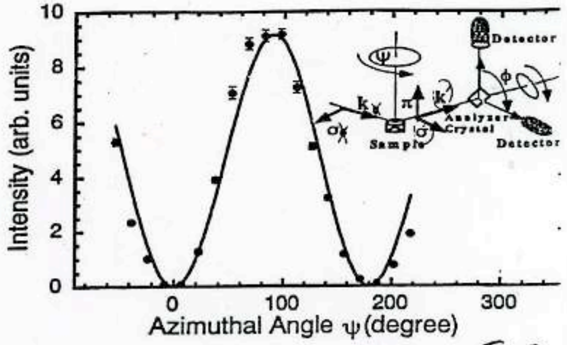


Fig 3

For all Mn identical
(3,0,0) reflection
forbidden

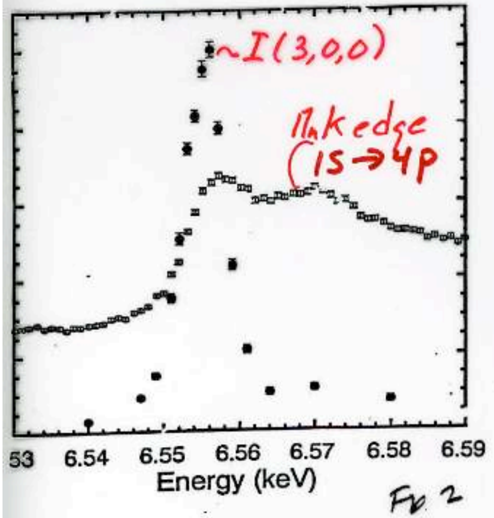


Fig 2

4

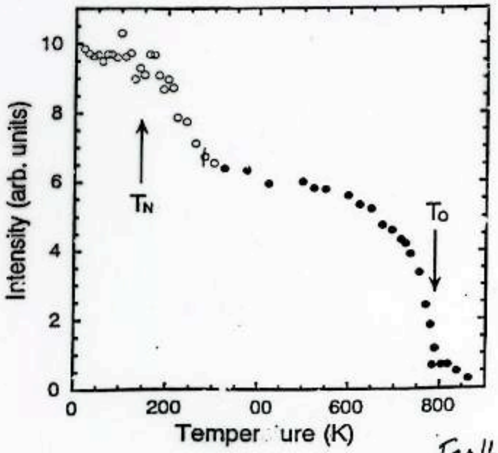


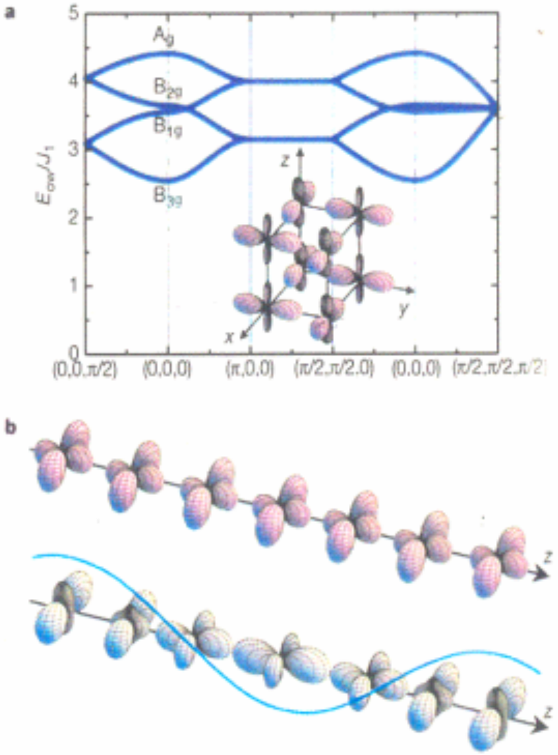
Fig 4

In ab ferro. Spin coupling
antiferro. Orbital Coupling

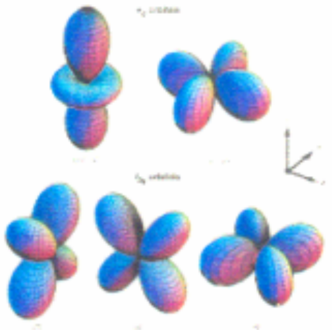
Along c visa versa

Orbital Degrees of Freedom

Ferromagnetic and AFM Mott Insulators



Maekawa et.al. (2001)

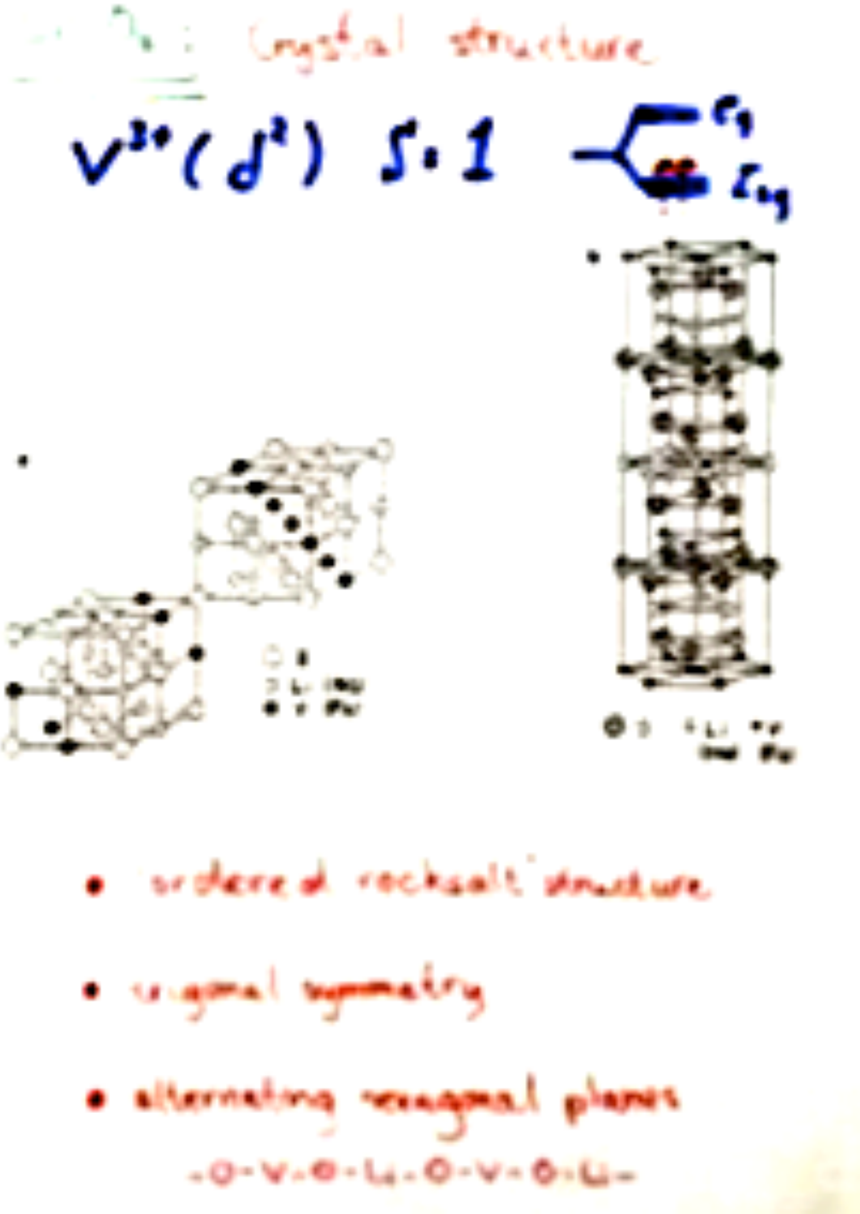


3d-Orbitals

Orbital Excitations fundamentally orgininate from *dd* excitations

Orbital Order

Orbital Excitations/"Orbitons"



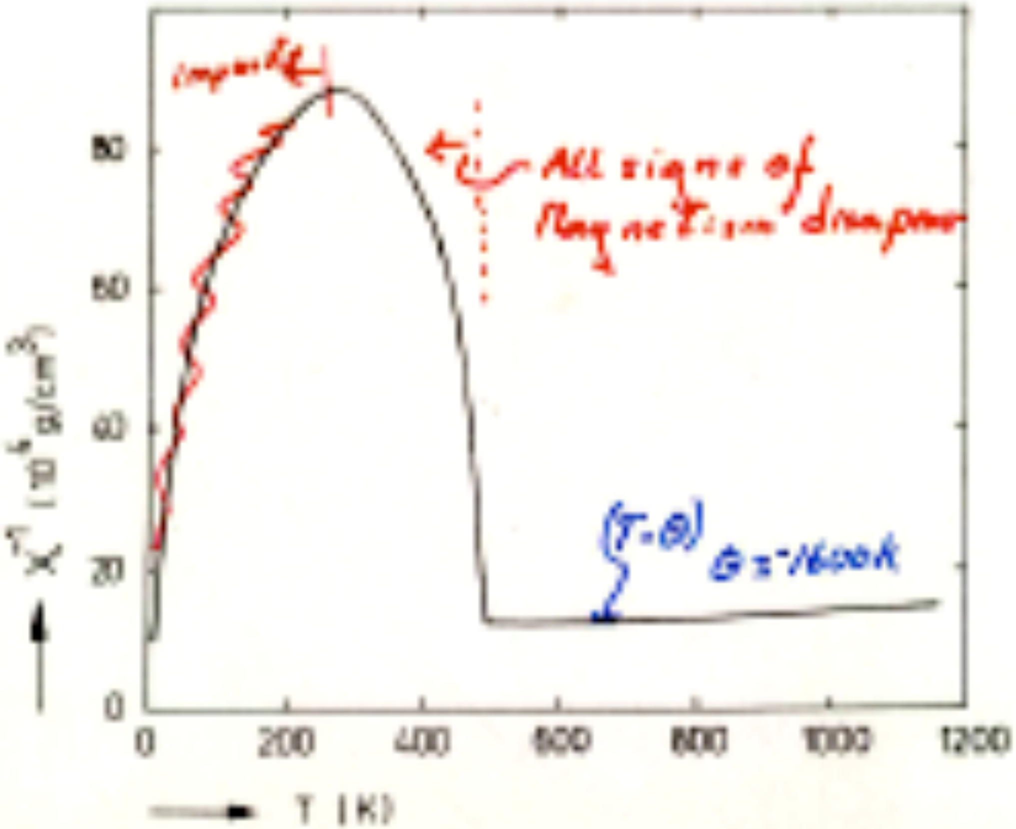
Crystal structure

$V^{3+}(d^2)$ $S=1$

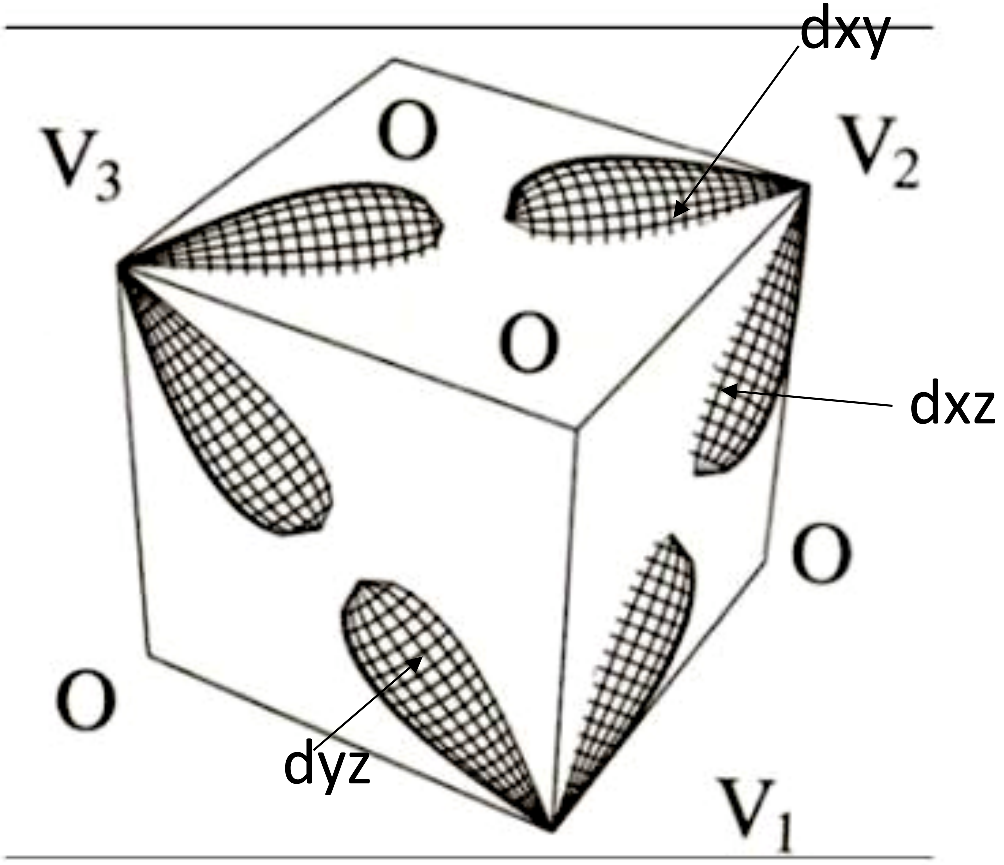
- ordered 'rocksalt' structure
- trigonal symmetry
- alternating hexagonal planes
  -O-V-O-Li-O-V-O-Li-

LiVO2 V(d2—S=1)
Two electrons in a t2g
Orbital

Rock salt strucuture
Alternateing V Li O layers
Each have a triangular lattice

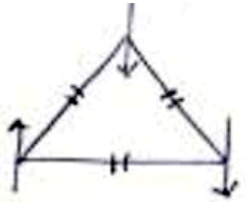

impurity
All signs of Magnetism disappear
(T-θ)
θ≈-1600K
χ^-1 (10^6 g/cm^3)
0
20
40
60
80
0
200
400
600
800
1000
1200
T (K)

This orbital ordering yields a large internal Antiferromagnetic exchange and a weak external ferromagnetic exchange .



Orbital ordering removes frustration

Pen et al PRL 78,1323



$$\mathcal{H} = +\frac{J}{2}\sum_{ij} S_i \cdot S_j$$ (ALL bonds eq)

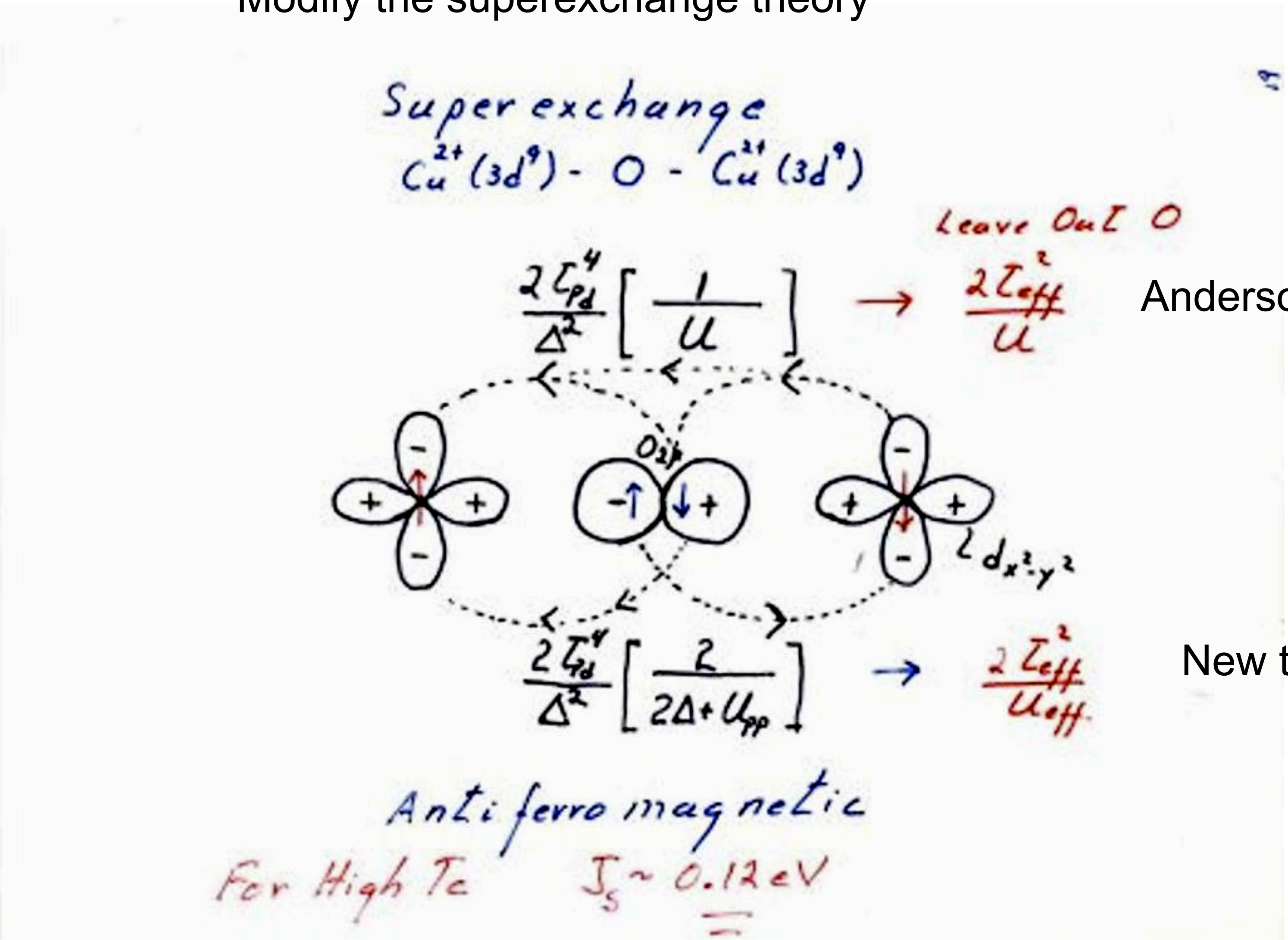
$$S'^2 = (\vec{S}_1 + \vec{S}_2 + \vec{S}_3)^2 = 3S^2 + \sum_{ij} S_i \cdot S_j$$

$$\sum_{ij} S_i \cdot S_j = S'^2 - 3S^2$$
$$= S(S+1) - 3(s)(s+1)$$

$$S = 0, 1, 2, 3$$

$$\sum_{ij} S_i \cdot S_j = -6 \quad (S=0)$$
$$-4 \quad (S=1)$$
$$0 \quad (S=2)$$

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



Superexchange

$Cu^{2+}(3d^9) - O - Cu^{2+}(3d^9)$

Leave Out O

$$\frac{2t_{pd}^4}{\Delta^2}\left[\frac{1}{U}\right] \rightarrow \frac{2t_{eff}^2}{U}$$

Anderson 1961

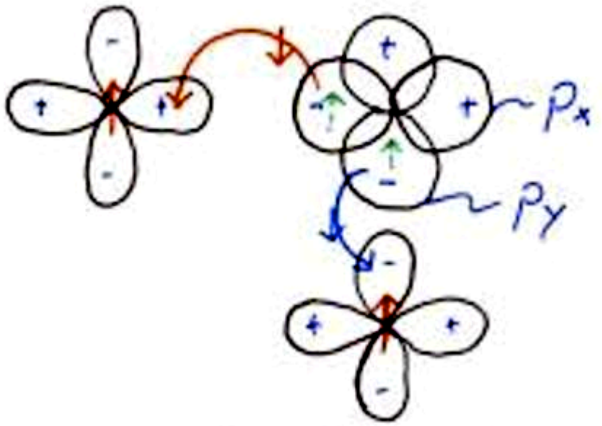
$$\frac{2t_{pd}^4}{\Delta^2}\left[\frac{2}{2\Delta+U_{pp}}\right] \rightarrow \frac{2t_{eff}^2}{U_{eff}}$$

New term

Antiferromagnetic

For High Tc $J_s \sim 0.12\,eV$

90° band Superexchange



Leaves behind in the intermediate state $2p^4$ $S=1$ (Hunds rule)

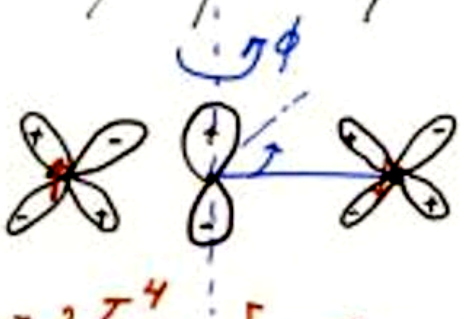
For antiferro - $2p^4$ $S=0$ higher in energy by about 1eV J_H(oxygen)

$$\therefore \quad J = \frac{2t_{pd\sigma}^4}{\Delta^2} \underbrace{\left[\frac{2}{2\Delta} - \frac{2}{2\Delta - J_H(\text{oxygen})} \right]}_{\text{for } U \text{ or } F^0(0) \to 0}$$

This is a <u>small</u> ferro exchange

$$J(\theta) \simeq J_{AF}(180°) \cos^2\theta + J_F(90°) \sin^2\theta$$

Exchange for t_{2g} unpaired Spins



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

by rotating one bond about an axis ⊥ to the bond out of the page J does not change but for rotation in the page it is like e_g orbitals

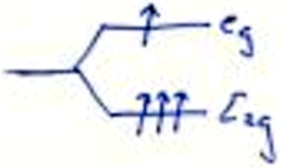
$J(t_{2g}) \sim \frac{1}{8} J(e_g)$ for same angle

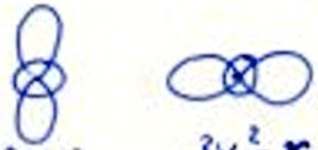
i.e $t_{pd\pi} \sim \frac{1}{2} t_{pd\sigma}$

J (orbital Ordering)

IF We have Spectator Spins

Mn^{3+} d^4

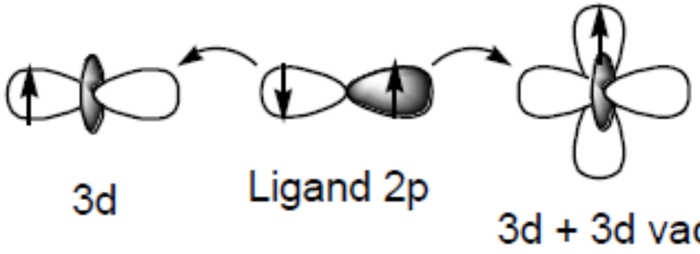




$$J_{ferro} = -2\left[\frac{2t^2}{U-J_H} - \frac{2t^2}{U+3J_H}\right] + \underset{\substack{\downarrow \\ \text{antiferro}}}{\frac{2(t/\sqrt{3})^2}{U}}$$

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

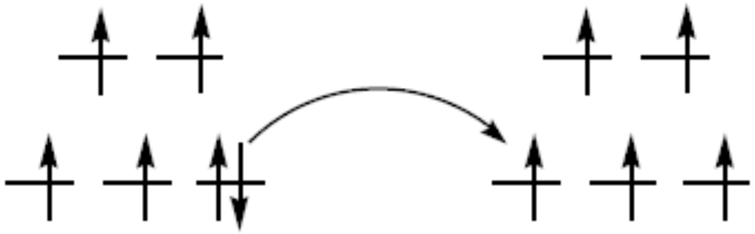
FM



← unfilled orbital orthogonal to filled orbital: FM-coupled metal spins

DOUBLE EXCHANGE

FM



Transfer of the minority spin can occur only if majority spins are aligned parallel

Occurs in Mixed Valent systems

The high Tc cuprates as a more detailed example

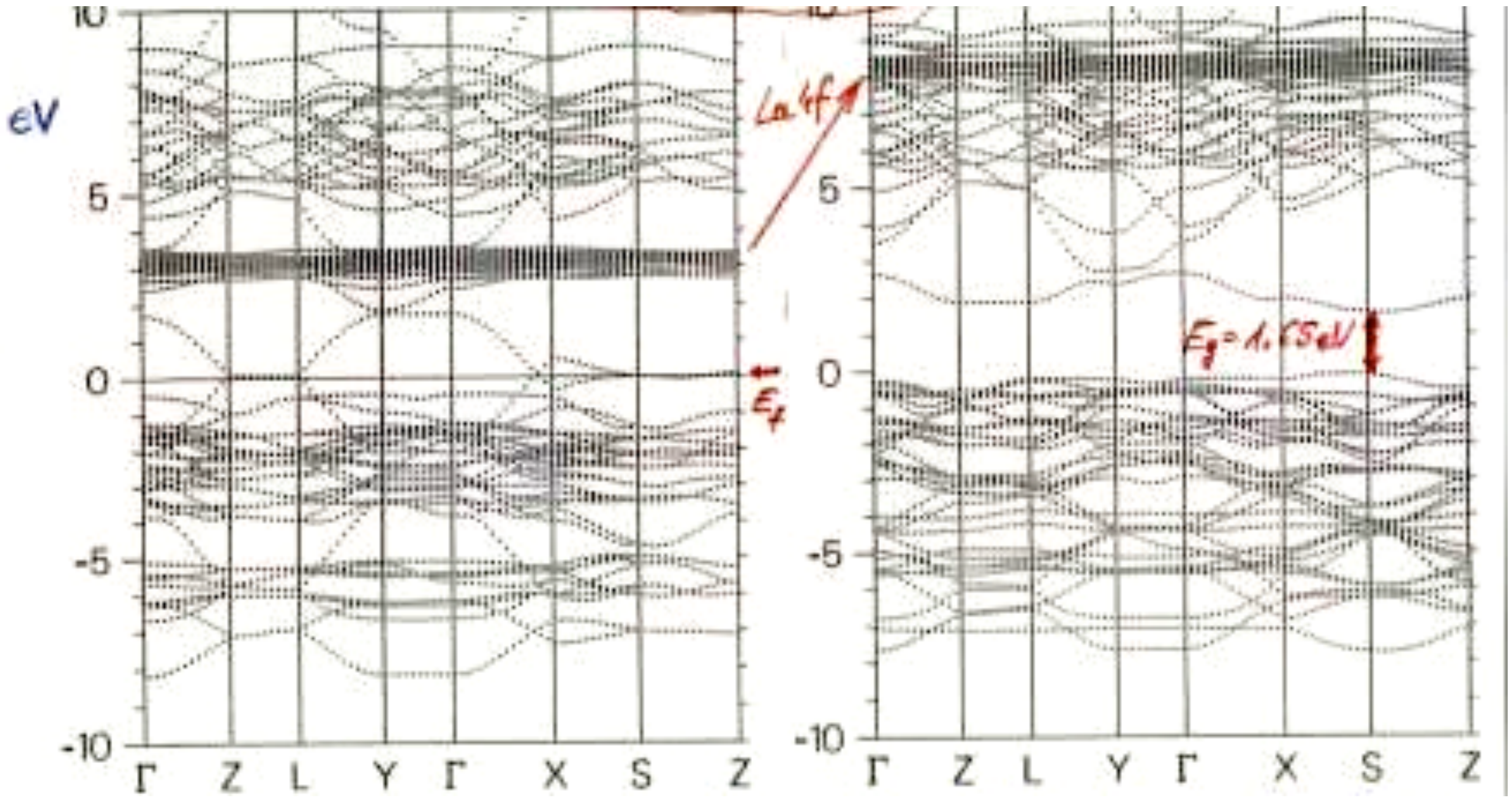
Problems with band gaps or conductivity gaps

- One particle theory like DFT predicts La2CuO4 to be a non magnetic metal while experiment shows it is a strongly antiferromagnetic insulator with a ~2 eV conductivity gap
- This is the case for many transition metal and rare earth compounds and a general problem for correlated electron systems
- Also excitonic states in semiconductors and insulators are not described with conventional DFT methods

Czyzk et l PRB 49,
14211(1994)

La2CuO4

LSDA+U antiferromagnetic   S=.8 Bohr magnetons, E gap = 1.65 eV


LSDA

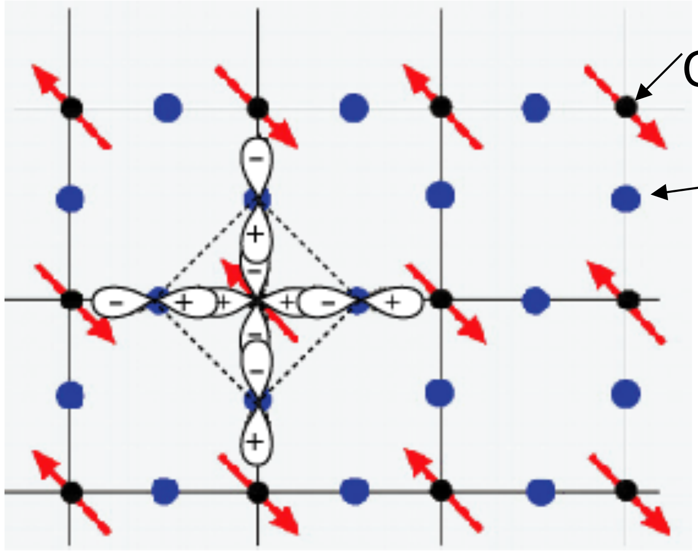
LSDA+U

LSDA+U also has no electron correlation
Single Slater det. of Bloch states. No multiplets.

LDA+U

- Has no correlation in the wave functions
- Single Slater determinants
- Spin is not a good quantum number only the z component
- It can get the gap right and the right spin structure for insulators
- As we saw above it does not get spectral weights right

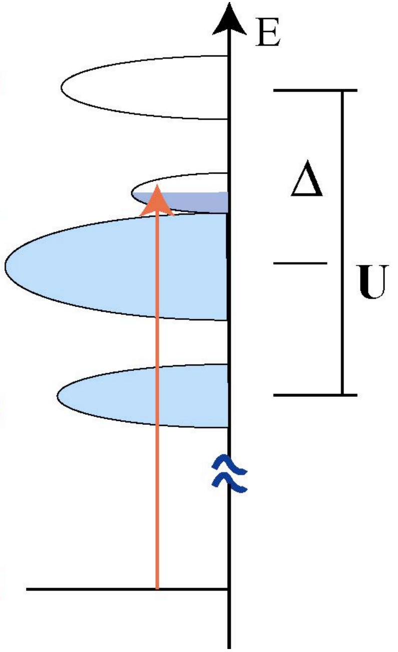
Doped holes in cuprate



Cu2+ d9 S=1/2

O 2- full shell

La2-xSrxCuO4 Sr ---doped holes



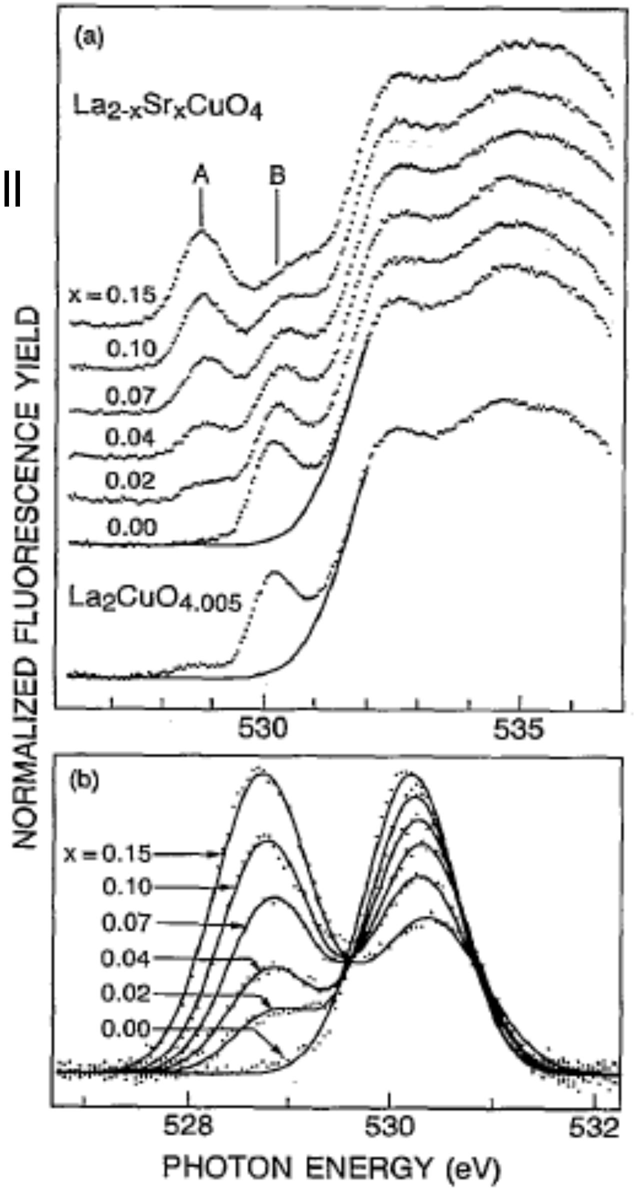
Upper Hubbard band $d^9 \rightarrow d^{10}$

Zhang-Rice singlet band

Charge transfer band $d^9 \rightarrow d^9L^{-1}$

Lower Hubbard band $d^9 \rightarrow d^8$

Oxygen 1s



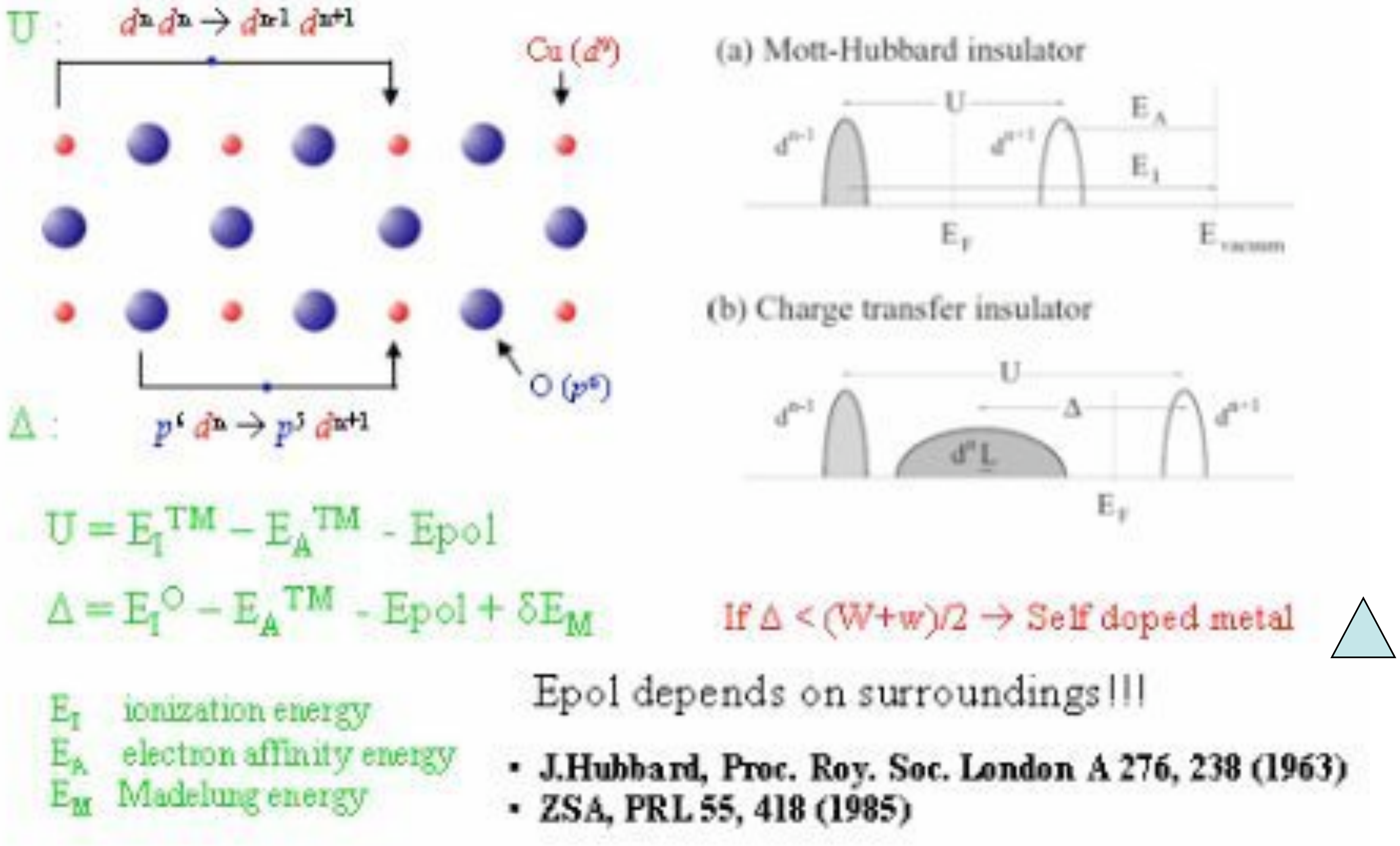
C. T. Chen et al. PRL 66, 104 (1991)

Cuprates belong to the charge transfer class of materials so we must consider both the O 2p bands and the Hubbard U split Cu 3d states in a fully realistic model sometimes called the 3 band Emery model

Emery and Reiter PRB 38,4547 (1988)

Correlated Electrons in a Solid

Oxides



$$U = E_I^{TM} - E_A^{TM} - Epol$$

$$\Delta = E_I^{O} - E_A^{TM} - Epol + \delta E_M$$

If $\Delta < (W+w)/2 \rightarrow$ Self doped metal

E_I ionization energy
E_A electron affinity energy
E_M Madelung energy

Epol depends on surroundings!!!

- **J.Hubbard, Proc. Roy. Soc. London A 276, 238 (1963)**
- **ZSA, PRL 55, 418 (1985)**

Remember at surfaces U is increased, Madelung is decreased, W is decreased

To calculate the spectroscopies and the gap we use the Anderson Impurity model mentioned before with a Cu impurity hybridizing with a initially filled O 2p band

Zaanen and Sawatzky **Progress of Theor. Physics, 101, (1990) 231-270**

To calculate the gap we calculate the ground state of the system with n, $n-1$, and $n+1$ d electrons
Then the gap is

$$E(\text{Gap}) = E(n-1) + E(n+1) - 2E(n)$$

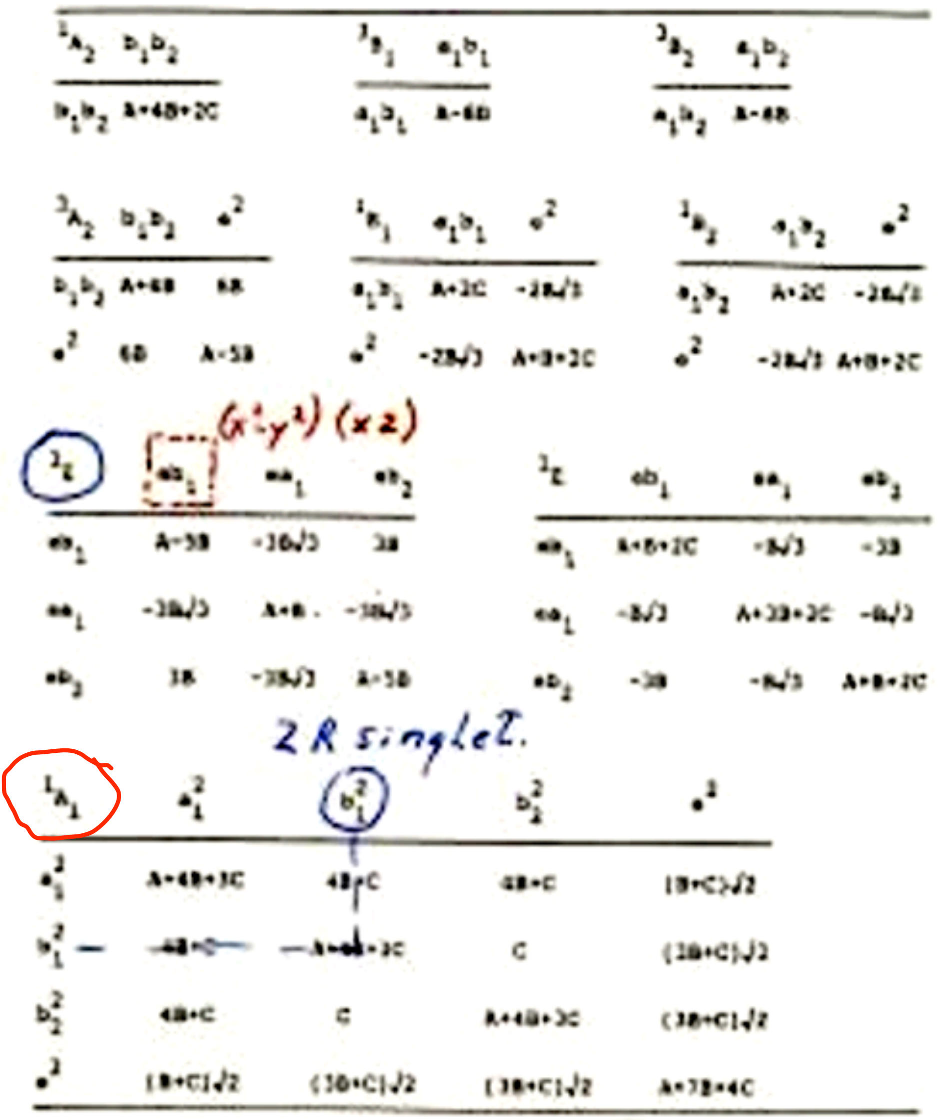
To calculate the ground state i.e. N particle energy and the optical spectrum we need the eigenstates of the N particles system which in the impurity approximation is given by the poles of the one particle greens function for electron removal from the N+1 particle full band state

To calculate the PES spectrum

- Consider a Cu 2+ impurity in a O Lattice
- The ground state and optical spectrum will be given by the one hole Greens function
- The PES spectrum will be given by the two hole Greens function which also includes the lowest energy electron removal state of the various possible symmetries and spins.
- The lowest energy state is the lowest N-1 partical state needed for the gap

Example Cu2+ as in LaCuO4 (d9 s=1/2)
For the N-1 electron states we need d8, d9L, d10L2 where L denotes a hole in O 2p band. The d8 states exhibit multiplets

We need all the two particle states spanned by the irreducible representation of the Cu d8 states. This involves Up to 4x4 Greens function matrices



$^1A_2$	b_1b_2
b_1b_2	$A+4B+2C$

$^3B_1$	a_1b_1
a_1b_1	$A-8B$

$^3B_2$	a_1b_2
a_1b_2	$A-8B$

$^3A_2$	b_1b_2	e^2
b_1b_2	$A+4B$	$6B$
e^2	$6B$	$A-5B$

$^1B_1$	a_1b_1	e^2
a_1b_1	$A+2C$	$-2B\sqrt{3}$
e^2	$-2B\sqrt{3}$	$A+B+2C$

$^1B_2$	a_1b_2	e^2
a_1b_2	$A+2C$	$-2B\sqrt{3}$
e^2	$-2B\sqrt{3}$	$A+B+2C$

(x^2-y^2) (x2)

^3E	eb_1	ea_1	eb_2
eb_1	$A-5B$	$-3B\sqrt{3}$	$3B$
ea_1	$-3B\sqrt{3}$	$A+B$	$-3B\sqrt{3}$
eb_2	$3B$	$-3B\sqrt{3}$	$A-5B$

^1E	eb_1	ea_1	eb_2
eb_1	$A+B+2C$	$-B\sqrt{3}$	$-3B$
ea_1	$-B\sqrt{3}$	$A+3B+2C$	$-B\sqrt{3}$
eb_2	$-3B$	$-B\sqrt{3}$	$A+B+2C$

ZR singleT.

$^1A_1$	a_1^2	b_1^2	b_2^2	e^2
a_1^2	$A+4B+3C$	$4B+C$	$4B+C$	$(B+C)\sqrt{2}$
b_1^2	$4B+C$	$A+4B+3C$	C	$(3B+C)\sqrt{2}$
b_2^2	$4B+C$	C	$A+4B+3C$	$(3B+C)\sqrt{2}$
e^2	$(B+C)\sqrt{2}$	$(3B+C)\sqrt{2}$	$(3B+C)\sqrt{2}$	$A+7B+4C$

To cacluate the inverse photoelectron spectrum is trivial in this model since all states are full for one electron added to the impurity in an otherwise full O 2p band system.

Cu2+ (d9) Impurity in CuO lattice   Eskes et.al PRL 61,1475 (1988)

Parameters
From TB band
structure plus
U and delta fits
Racah parameters
From gas phse
Moores tables
Reduced by 20%

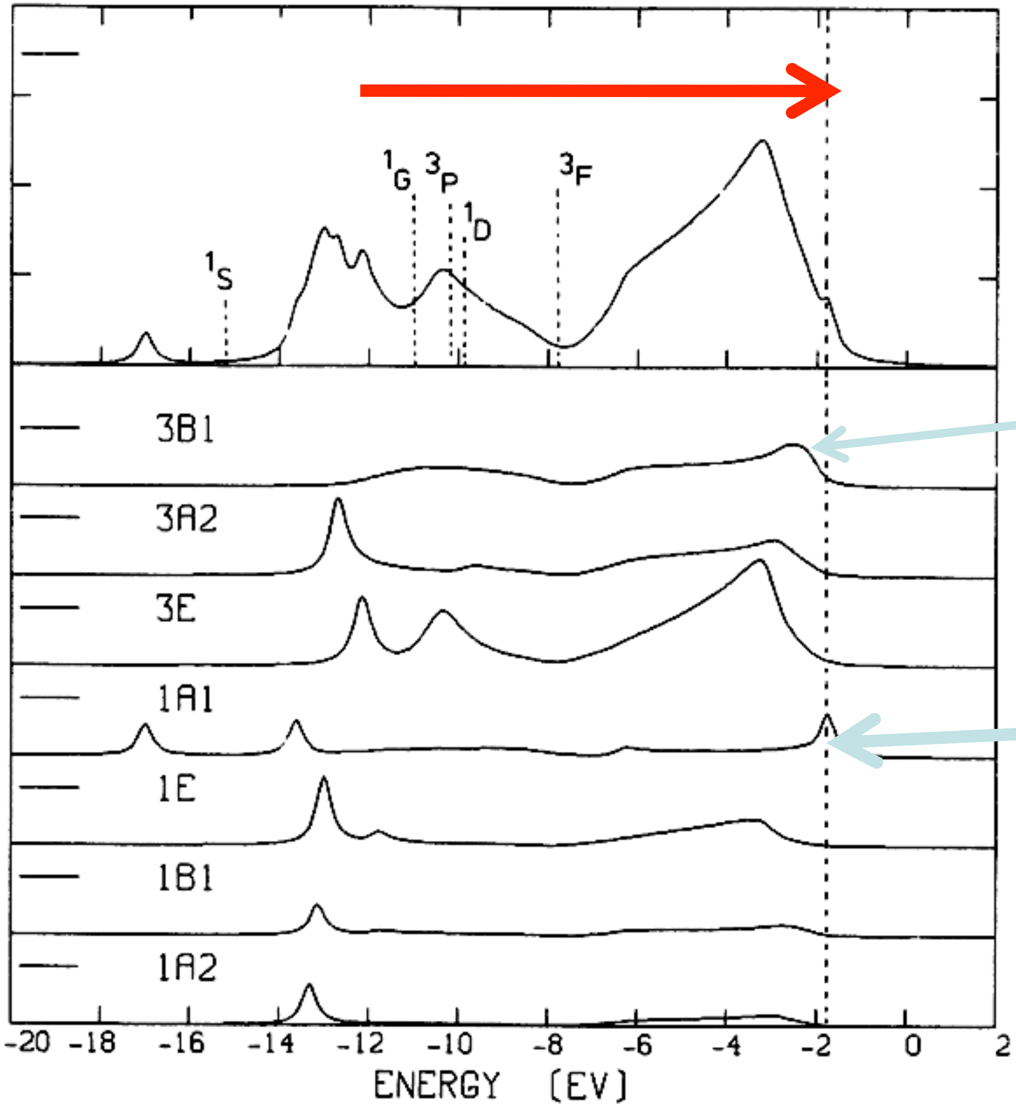


FIG. 1. The *d*-electron–removal spectral weight calculated for $A=7.6$ eV, $\Delta=2.75$ eV, $T(b_{1g})=2.35$ eV, and $W=4.4$ eV. Also shown are the contributions from the various irreducible representations.

Other symmetry
States start at
about ~~0.8~~ eV
Below ZR

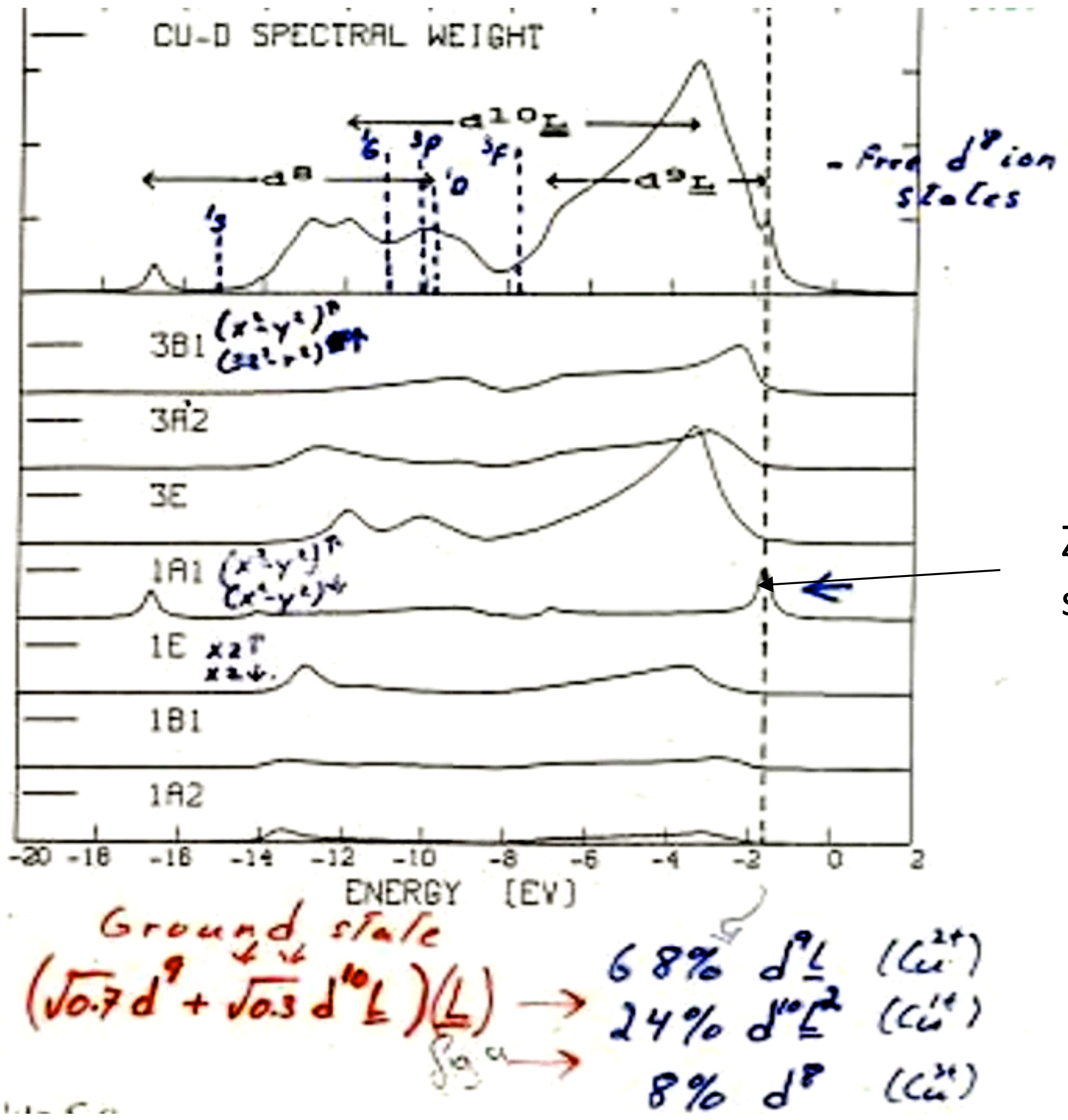
0.5

Zhang rice singlet

H. Eskes and G.A. Sawatzky
PRL 61, 1415 (1988).

Anderson Impurity calculation

Note the large Energy scale Covered by each State!!



Zhang Rice singlet

Ground state

$\left(\sqrt{0.7}\,d^9 + \sqrt{0.3}\,d^{10}\underline{L}\right)(\underline{L}) \rightarrow$

68% $d^9\underline{L}$ (Cu^{2+})

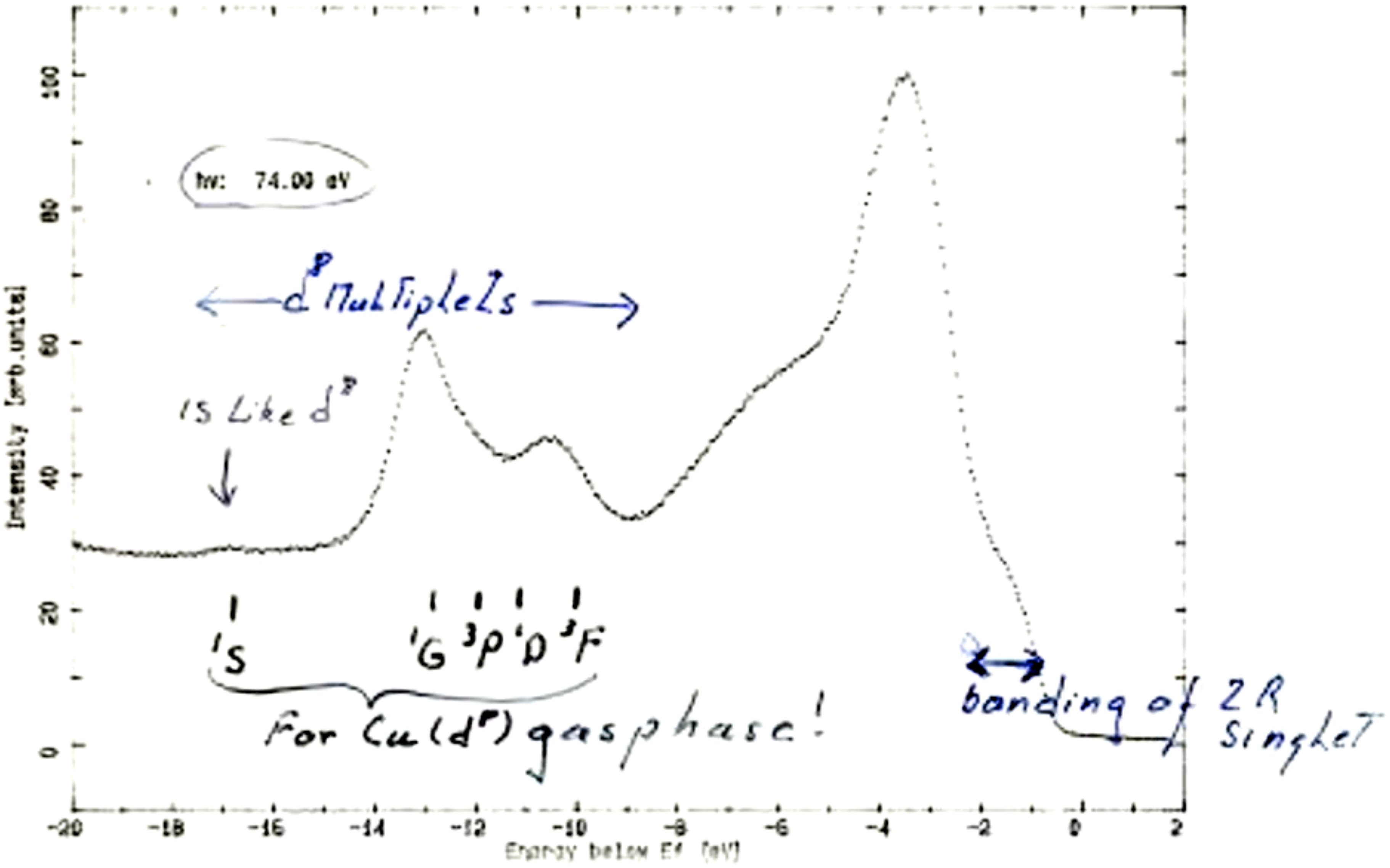
24% $d^{10}\underline{L}^2$ (Cu^{1+})

8% d^8 (Cu^{3+})

J. Ghijsen et al

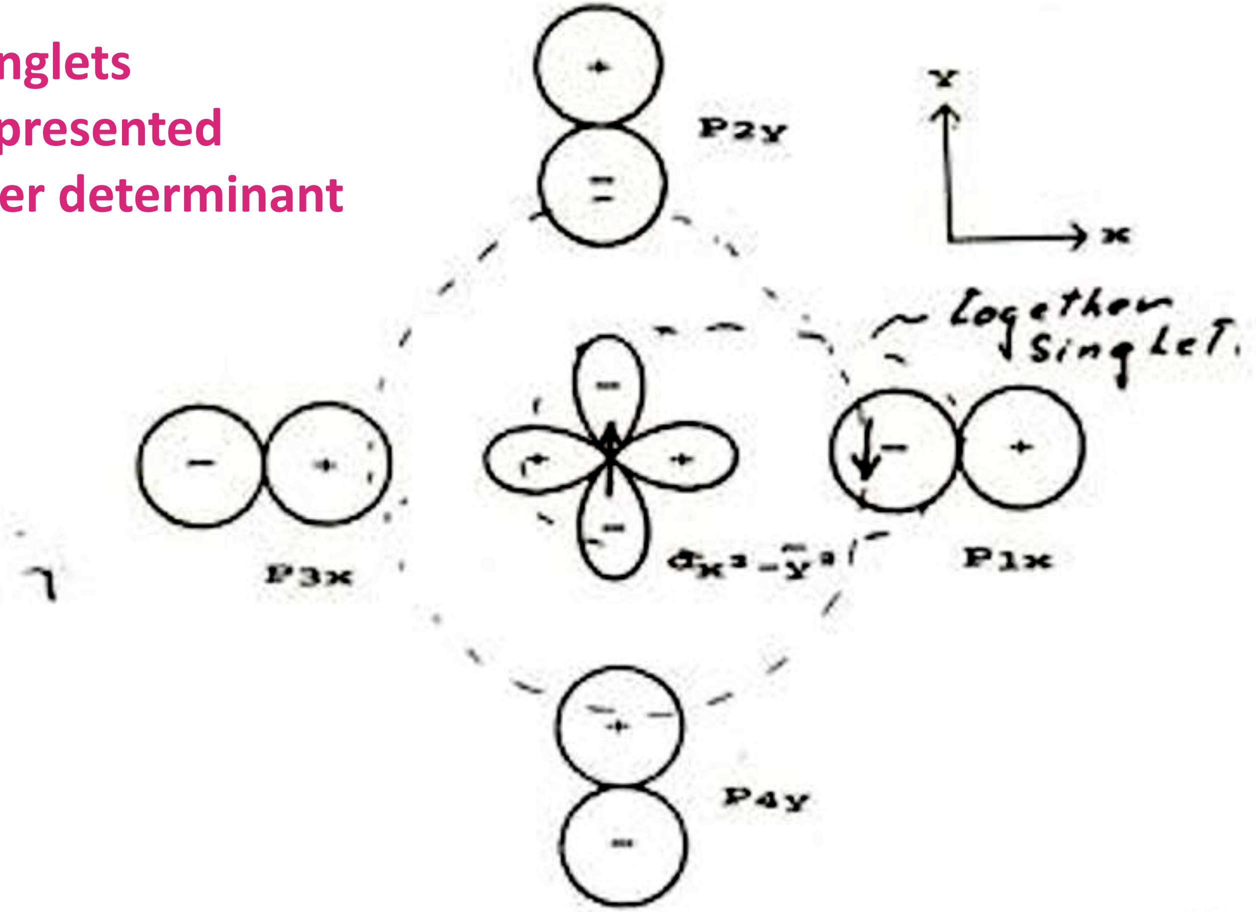
Phys. Rev. B. 42, (1990) 2268.

Resonant Photoemission spectrum of CuO



Energy below Ef in eV

Zhang Rice singlets
Cannot be represented
By single Slater determinant



$$\psi_{\pm}(x^2-y^2) = \frac{1}{\sqrt{4}}\left[-p_{1x} + p_{2y} + p_{3x} - p_{4y}\right]$$

$T^{②} \longrightarrow$ ... bond)

$T_{pd}(b_1) = 2\ T_{pd}$(single bond)

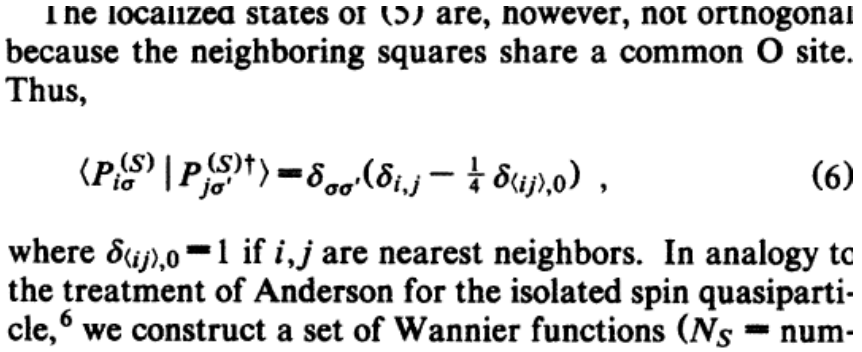
Singlet stabalized by $J \sim \dfrac{4[2T_{pd}]^2}{\Delta_{CT}}$

Is the single band Hubbard model justified?

- For zero or small hole doping the ZR singlet states look much like those of the lower Hubbard band
- So for low doping the low energy scale (<0.5 eV) the Hubbard model could be OK
- However for heavy doping the ZR states start overlapping and loose their integrity and they move away from the pi.2,pi/2 momentum region. So the parameters U and t’s will be doping dependent

Is single band Hubbard justified for Cuprates?

Zhang Rice PRB 1988
37,3759



The localized states of (5) are, however, not orthogonal because the neighboring squares share a common O site. Thus,

$$\langle P_{i\sigma}^{(S)} \,|\, P_{j\sigma'}^{(S)\dagger} \rangle = \delta_{\sigma\sigma'}(\delta_{i,j} - \tfrac{1}{4}\,\delta_{\langle ij\rangle,0}) \ , \qquad (6)$$

where $\delta_{\langle ij\rangle,0} = 1$ if i,j are nearest neighbors. In analogy to the treatment of Anderson for the isolated spin quasiparticle,[6] we construct a set of Wannier functions (N_S = num-

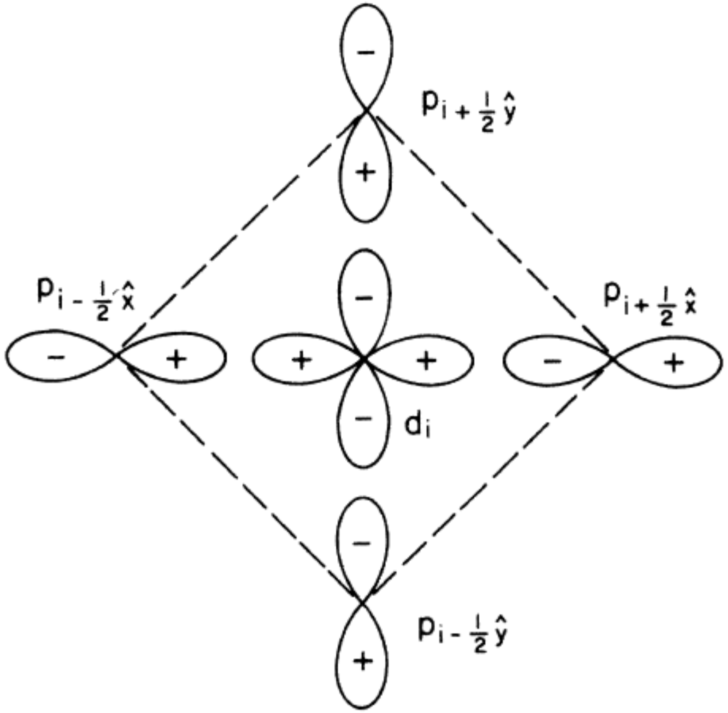


FIG. 1. Schematic diagram of the hybridization of the O hole ($2p^5$) and Cu hole ($3d^9$). The signs + and − represent the phase of the wave functions.

Problem with ZR singlets

- The combination of O 2p states is not compatible with a band structure state
- The wave functions are non orthogonal

$$\phi_{i\sigma} = N_S^{-1/2} \sum_{\mathbf{k}} P_{\mathbf{k}\sigma} \exp(i\mathbf{k}\cdot\mathbf{R}_i) \ , \tag{7}$$

$$P_{\mathbf{k}\sigma} = N_S^{-1/2} \beta_{\mathbf{k}} \sum_{i} P_{i\sigma}^{(S)} \exp(-i\mathbf{k}\cdot\mathbf{R}_i) \ , \tag{8}$$

where $\beta_{\mathbf{k}}$ is a normalization factor

From ZR PRL 37,3759

$$\beta_{\mathbf{k}} = [1 - \tfrac{1}{2}(\cos k_x + \cos k_y)]^{-1/2} \ . \tag{9}$$

Note it goes to infinity at k=0, should we see it at Gamma in ARPES? Luckly it goes to 1 for K= Pi/2,Pi/2 and along the antiferromagnetic zone boundary where the doped holes go at low doping

Problems with ZR singlets

- As we dope the system the integrety of the ZR states disappears
- As we dope the system the ZR states strongly overlap forbidden by Pauli so they must change.

Using a single band model for a doped charge transfer insulator

- At most it can only be used at quite low energies.
- For cuprates there are lots of other states and band for energies above .5 eV
- For cuprates the UHB wave functions are very different from the LHB Therefore parameters can be different
- The ZR like picture is at most valid for only about 200meVor even less. And very low doping

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