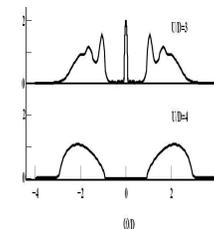
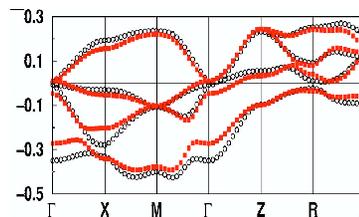
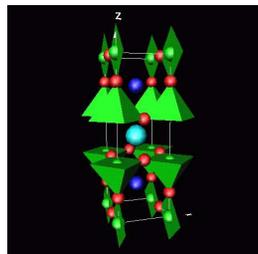
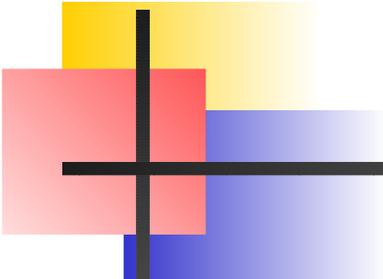


Correlation Effects in Real Material

Tanusri Saha-Dasgupta

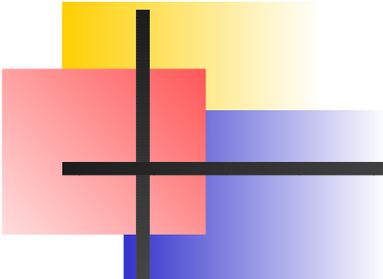
S.N. Bose National Centre for Basic Sciences
Salt Lake, Calcutta, INDIA
tanusri@bose.res.in





Outline

- Introduction: why strong correlations ?
 - Failure of one-electron theories
 - Hesitant electrons: delocalized waves or localized particles ?
 - Examples of strongly correlated materials
 - Different energy scales and MIT in TMO
- Methods to deal with correlations in realistic ways
 - Concepts (LDA+U, LDA+DMFT)
 - Practical details
 - Examples
- Spin-physics out of Correlation
 - t-J and Heisenberg models
 - Super-exchange



Electronic Structure Calculations:

- Good description of many microscopic properties are obtained in terms of -

Born-Oppenheimer Approximation

Nuclei and the electrons to a good approximation may be treated separately.

One-electron Approximation

Each electron behaves as an independent particle moving in the mean field of the other electrons plus the field of the nuclei.

LDA

Most satisfactory foundation of the one electron picture is provided by the local approximation to the Hohenberg-Kohn-Sham density functional formalism

≡ LDA



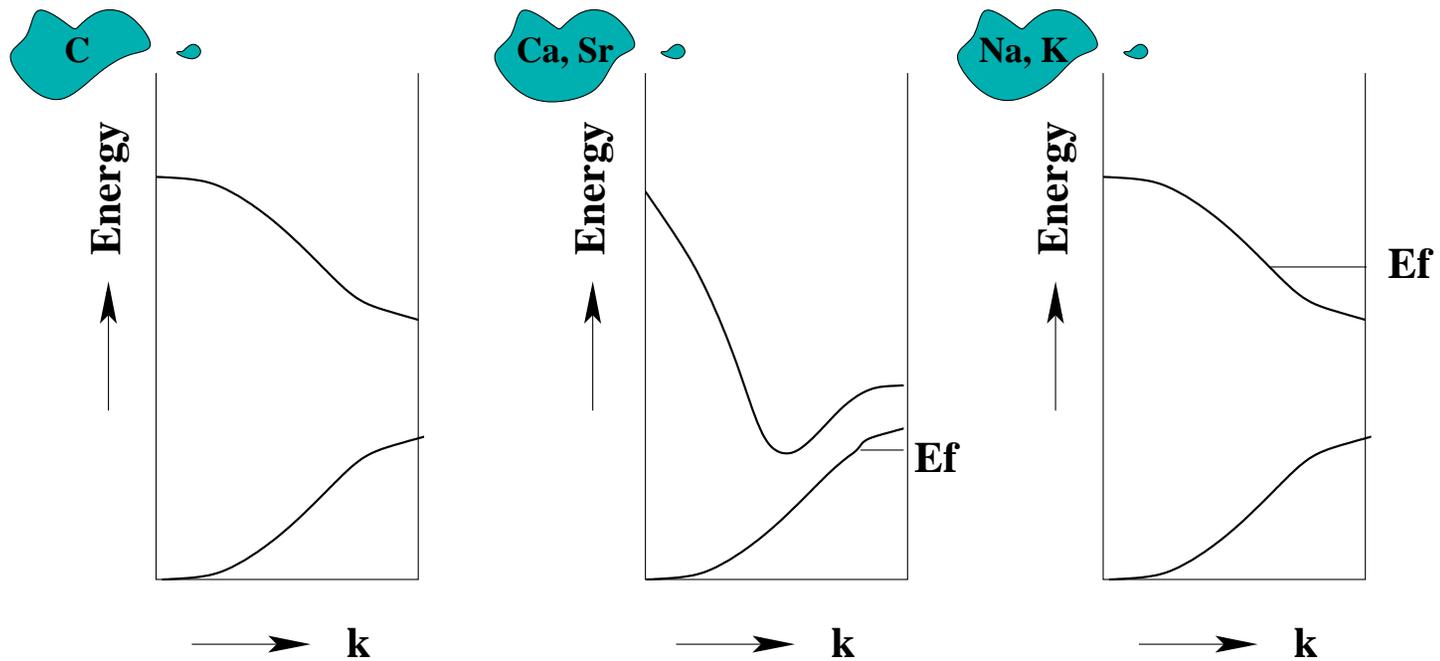
- LDA leads to an effective one electron potential which is a function of local electron density.
- Leads to Self consistent solution to an one electron Schrödinger Eqn.

Strongly correlated electron materials

- * The conventional band-structure calculations within the framework of LDA is **surprising successful** for many materials.
- * However, they **fail** for materials with strong e-e correlation !
 - correlation effect necessarily arise, and
 - the consideration of electron correlation effects provides the natural way to understand the phenomena like the insulating nature of CoO.

Strongly correlated electron materials

Predictions from LDA (Bandstructure)



**Even No. of e's
per unitcell**

$$\rho(\epsilon_F) = 0$$

**Even No. of e's
per unitcell**

+ band overlap
 $\rho(\epsilon_F) \neq 0$

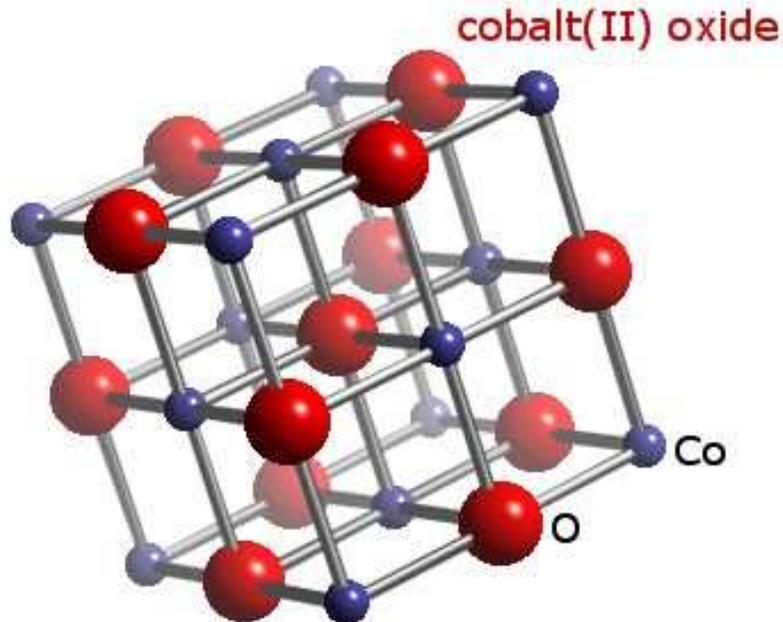
**Odd No. of e's
per unitcell**

$$\rho(\epsilon_F) \neq 0$$

Accordingly to LDA, odd no. of e's per unit cell always give rise to Metal !

Strongly correlated electron materials

Failure of Band Theory

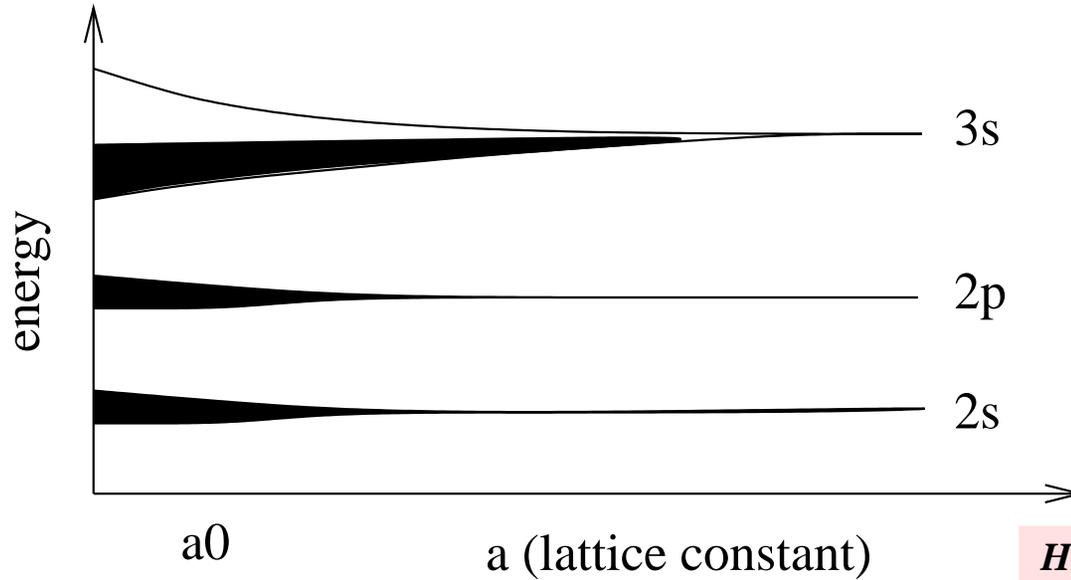


Total No. of electrons = $9 + 6 = 15$

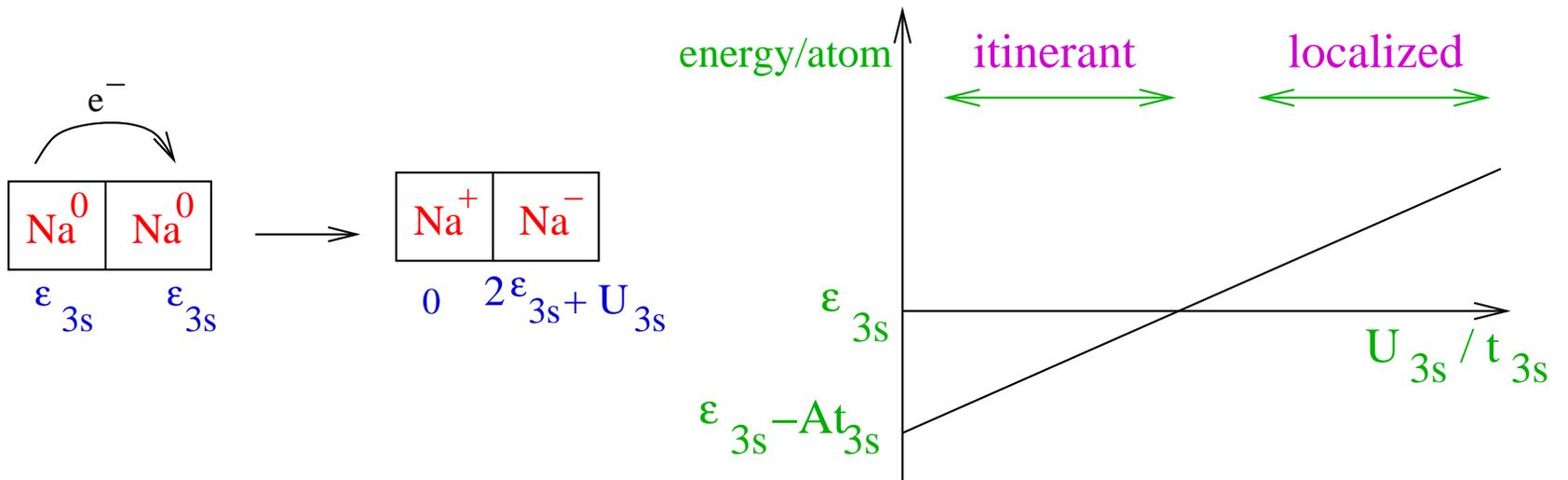
Band theory predicts CoO to be metal, while it is the toughest insulator known

Failure of LDA → Failure of single particle picture
→ Importance of e-e interaction effects (Correlation)

Strongly correlated electron materials



$$H_{3s} = H_{band} + H_{columb}$$



Hesitant e-s: delocalized or localized picture ?

broad energy bands- associated with large KE, highly *itinerant*
→ well described using *wave-like picture*

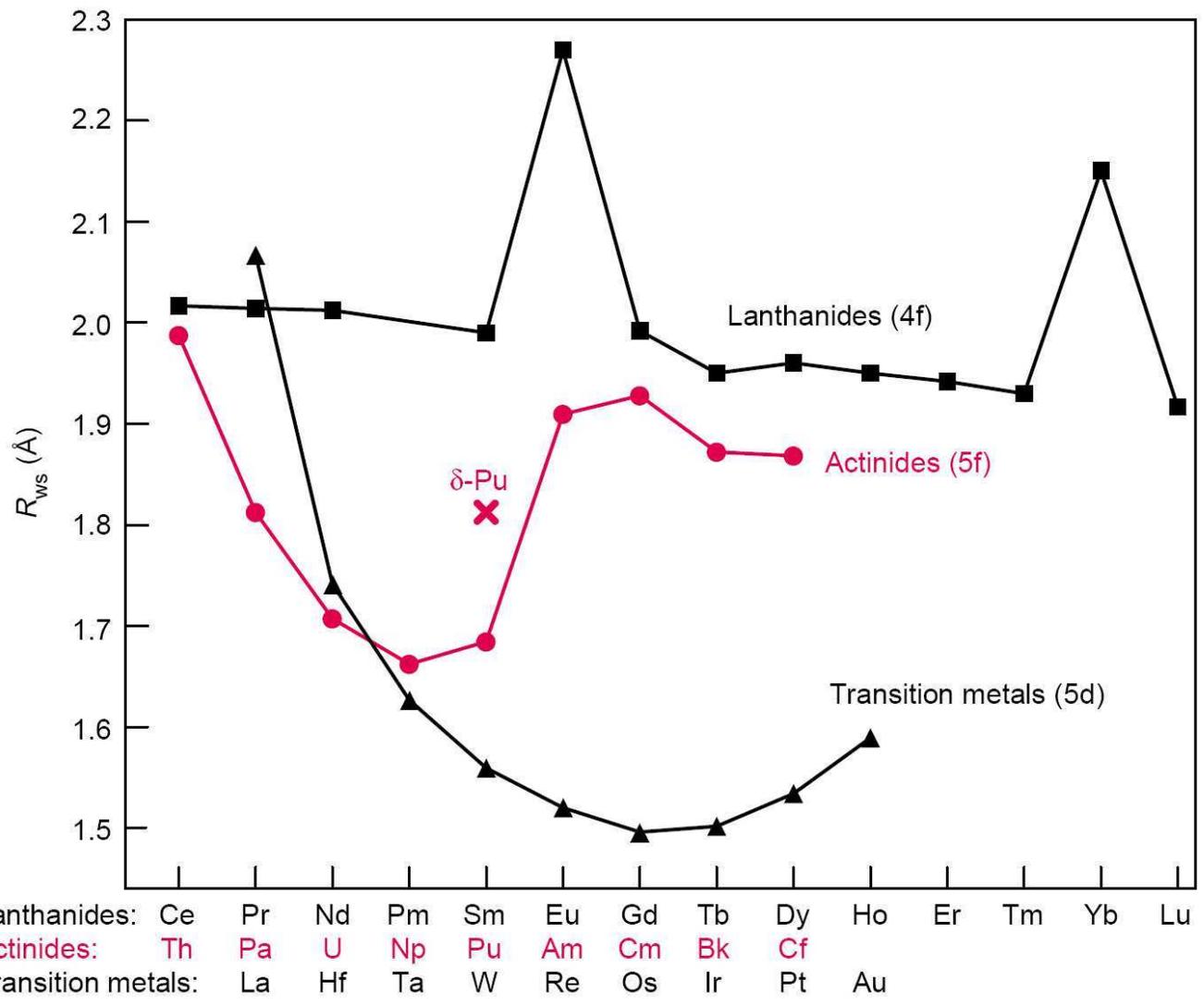
narrow energy bands- e-s spend larger time around a given atom -
tendency towards *localization*, effects of statistical correlations
between the motion of individual electrons become important
→ *particle-like picture* may be more appropriate

Intermediate situation - localized character on short time-scales
and itinerant character on the long time-scale co-exist!
→ e-s *hesitate* between being itinerant and localized.

Examples of strongly correlated materials

Transition metals:

- d-orbitals extend much further from the nucleus than the *core* electrons.
- throughout the 3d series (and even more in 4d series), d-electrons do have an itinerant character, giving rise to quasiparticle bands!
- electron correlations do have important physical effects, but not extreme ones like localization.



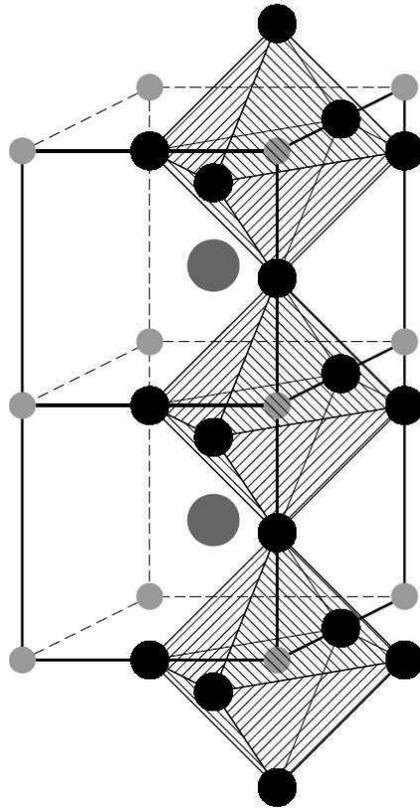
Examples of strongly correlated materials

f-electrons: rare earths, actinides and their compounds:

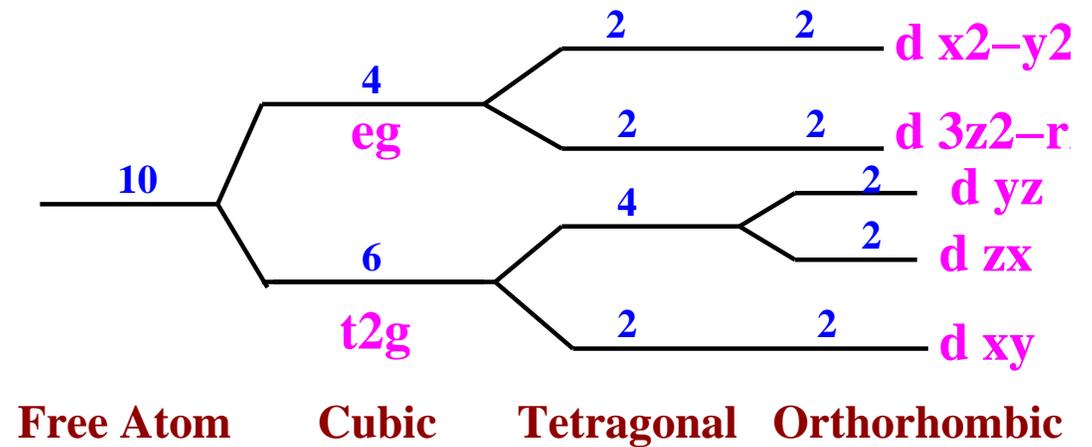
- rare-earth 4f-electrons tend to be localized than itinerant, contribute little to cohesive energy, other e- bands cross E_F , hence the metallic character.
- actinide (5f) display behavior intermediate between TM and rare earths
- e- correlation becomes more apparent in compounds involving rare-earth or actinides.
- extremely large effective mass \rightarrow *heavy fermion behavior*.
- At high temp local mag. mom and Curie law, low-temp screening of the local moment and Pauli form \rightarrow *Kondo effect*

Examples of strongly correlated materials - TMO

- direct overlap between d-orbitals small, can only move through hybridization!

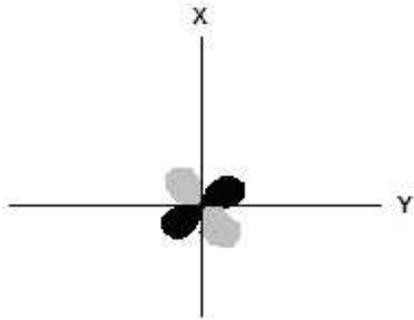


Crystal Field Splitting

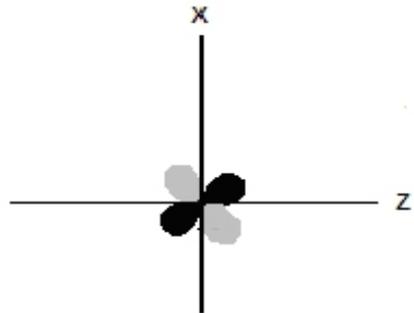


Examples of strongly correlated materials- TMO

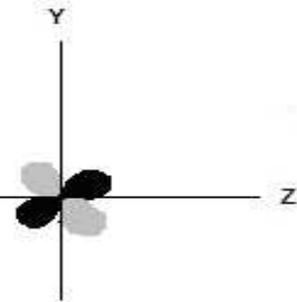
d_{xy}



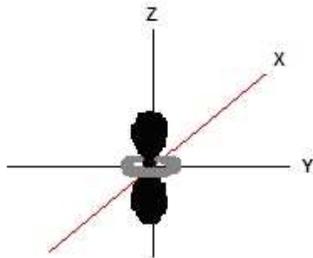
d_{xz}



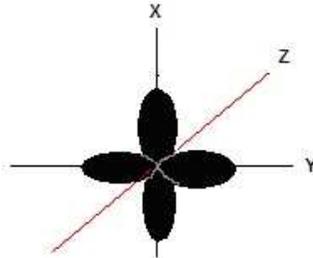
d_{yz}



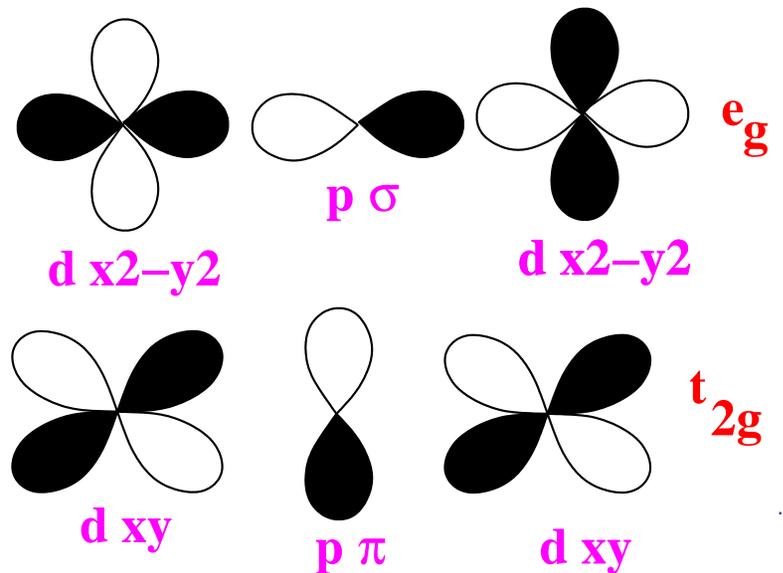
$d_{3z^2-r^2}$



$d_{x^2-y^2}$



Hybridization via the
Ligands (orbitals p/O)



Examples of strongly correlated materials - TMO

Three crucial Energies

t_{pd} Metal-ligand Hybridization

$\Delta = \epsilon_d - \epsilon_p$ Charge Transfer Energy

U On-site Coulomb Repulsion

Band-width is controlled by: $t_{eff} = t_{pd}^2 / \Delta$

Examples of strongly correlated materials - TMO

Minimal model for a TMO

$$H = \epsilon_p \sum_{j\sigma} p_{j\sigma}^\dagger p_{j\sigma} + \epsilon_d \sum_{i\sigma} d_{i\sigma}^\dagger d_{i\sigma} \\ - t_{pd} \sum_{i\sigma} \sum_{\delta} (d_{i\sigma}^\dagger p_{i\pm\delta\sigma} + h.c.) + U_d \sum_i n_{i\uparrow}^d n_{i\downarrow}^d$$

And may be add

$$t_{pp}, U_{pp}, U_{pd}$$

..... orbital degeneracy, etc

Examples of strongly correlated materials - TMO

The infamous Hubbard U

Naively:
$$\int \phi_{i\uparrow}^* \phi_{i\uparrow} \frac{1}{|r-r'|} \phi_{i\downarrow}^* \phi_{i\downarrow}$$

But this is HUGE (10 -20 eV)!

SCREENING plays a key role, in particular by 4s electrons

- *Light TMOs (left of V)*: p-level much below d-level; 4s close by : U

not so big $U < \Delta$

- *Heavy TMOs (right of V)*: p-level much closer; 4s much above

d-level : U is very big $U > \Delta$

Examples of strongly correlated materials - TMO

The Mott phenomenon: turning a half-filled band into an insulator

Consider the simpler case first: $U < \Delta$

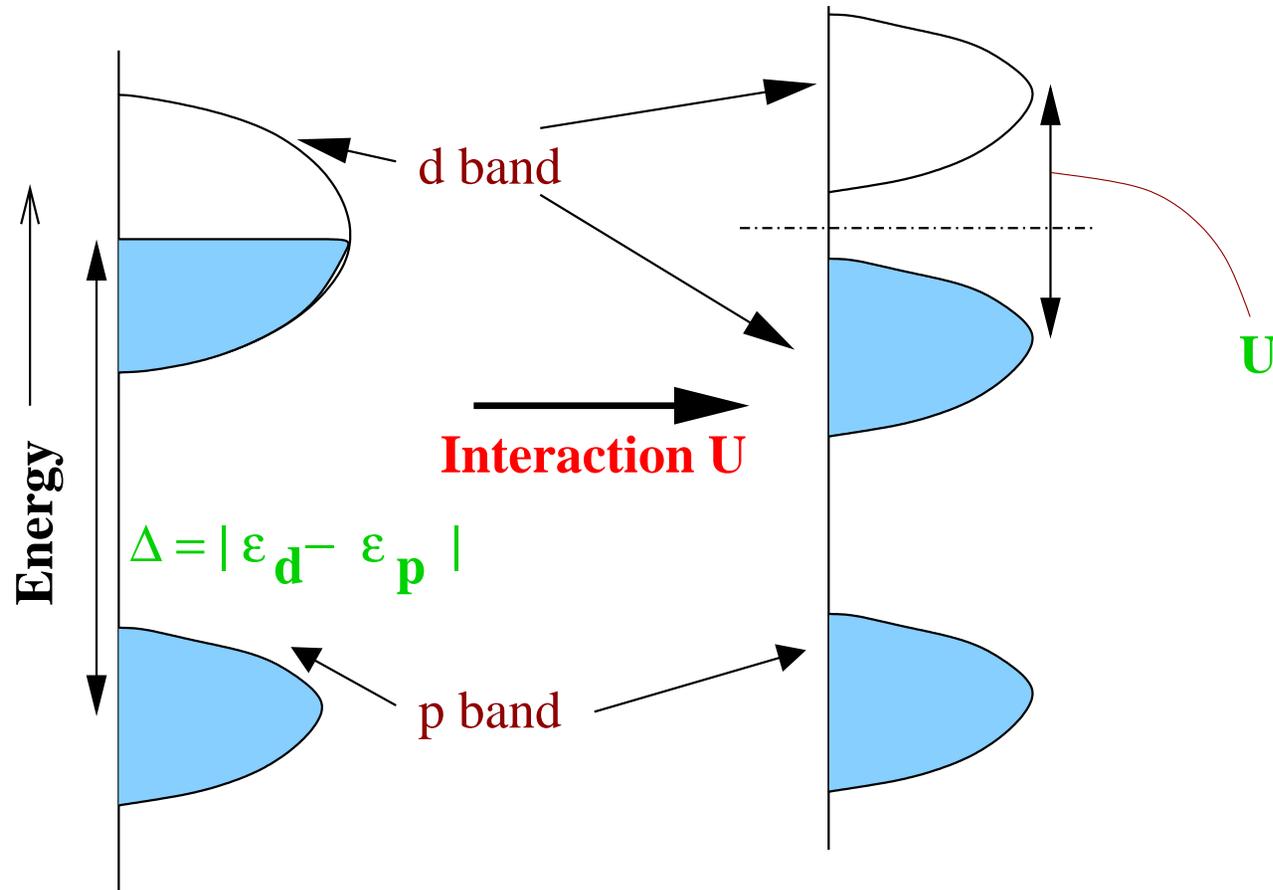
Moving an electron requires creating a hole and a double occupancy: **ENERGY COST U**

This object, once created, can move with a kinetic energy of order of the bandwidth **W**!

$U < W$: A METALLIC STATE IS POSSIBLE

$U > W$: AN INSULATING STATE IS PREFERRED

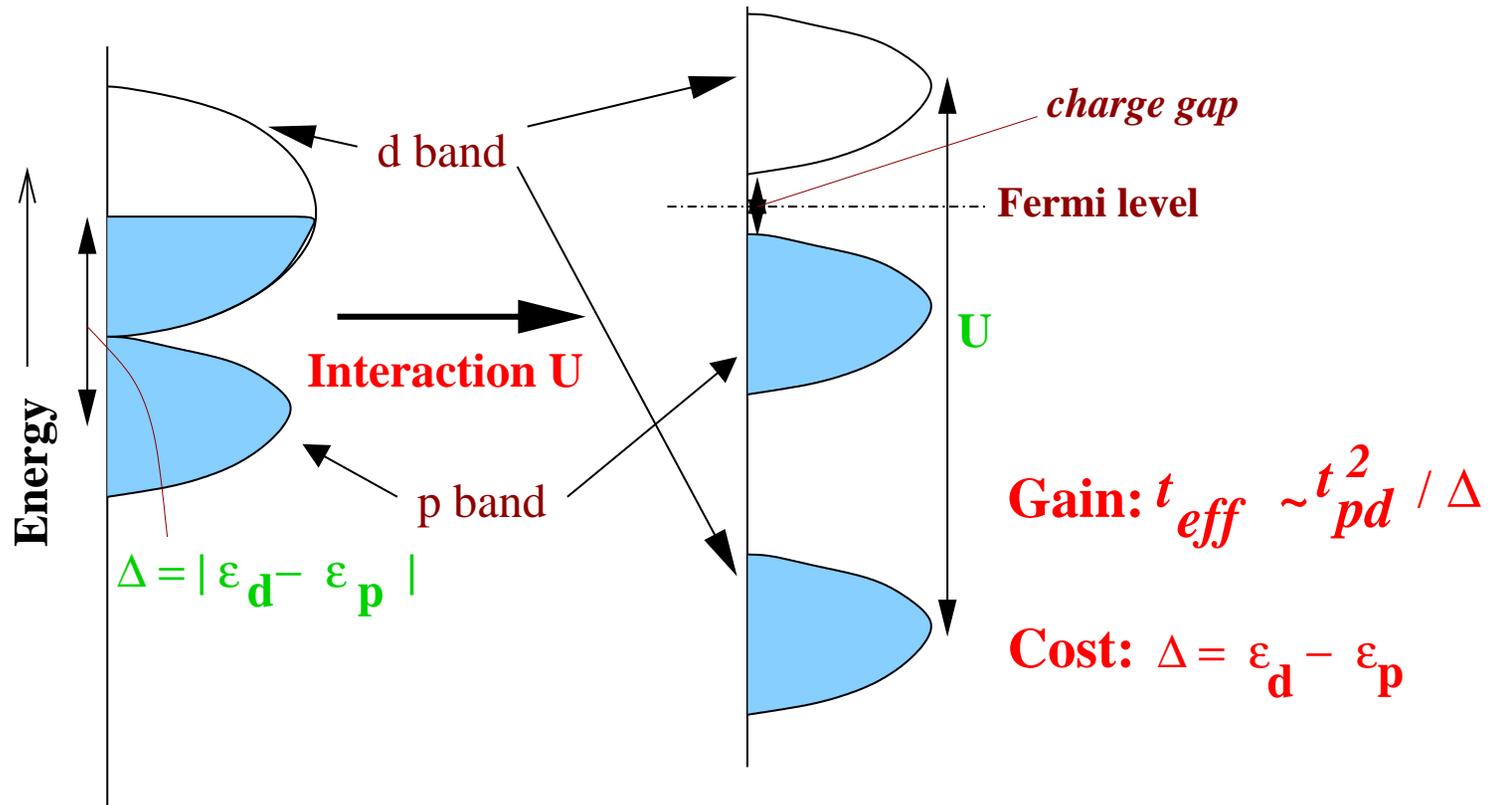
Hubbard bands



The composite excitation hole+double occupancy forms a *band* (cf excitonic band)

Charge transfer insulators

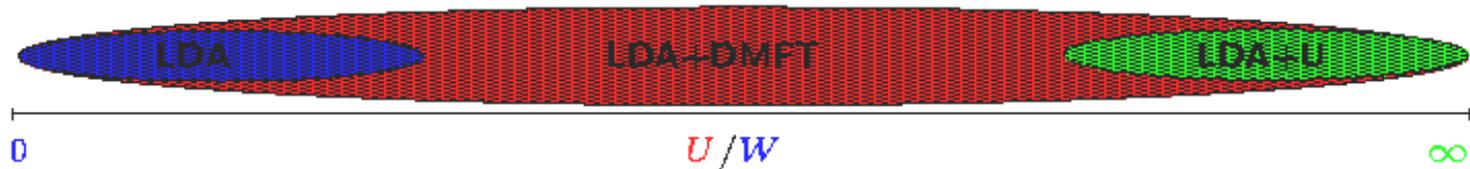
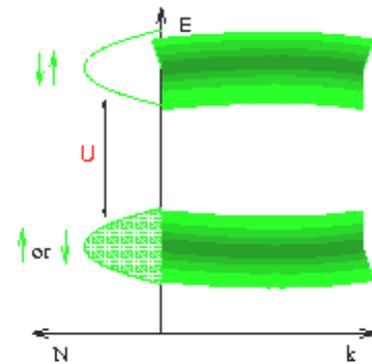
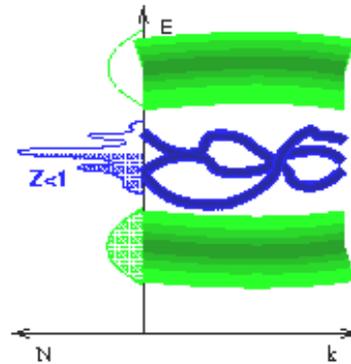
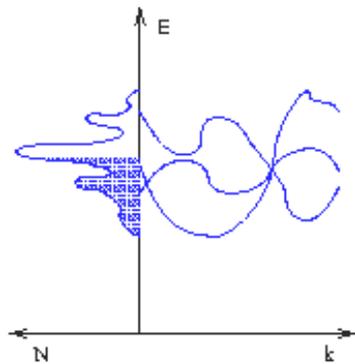
Heavy TMOs



Transition for $\Delta > t_{pd}$

Zaanen, Sawatzky, Allen; Fujimori and Minami

Methods



Weakly correlated Metal

$$U < W$$

LDA gives correct answer

Strongly correlated Metal

**Intermediate regime – Hubbard bands +
QS peak (remainder of LDA metal)**

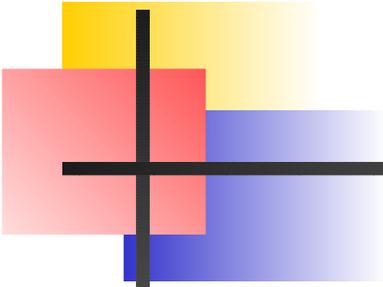
?

Mott insulator

$$U \gg W$$

**Can be described
by "LDA+U" method**

courtesy: K. Held



Basic Idea of LDA+U

PRB 44 (1991) 943, PRB 48 (1993) 169

- Delocalized s and p electrons: LDA

- Localized d or f-electrons: + U

using on-site d-d Coulomb interaction (Hubbard-like term)

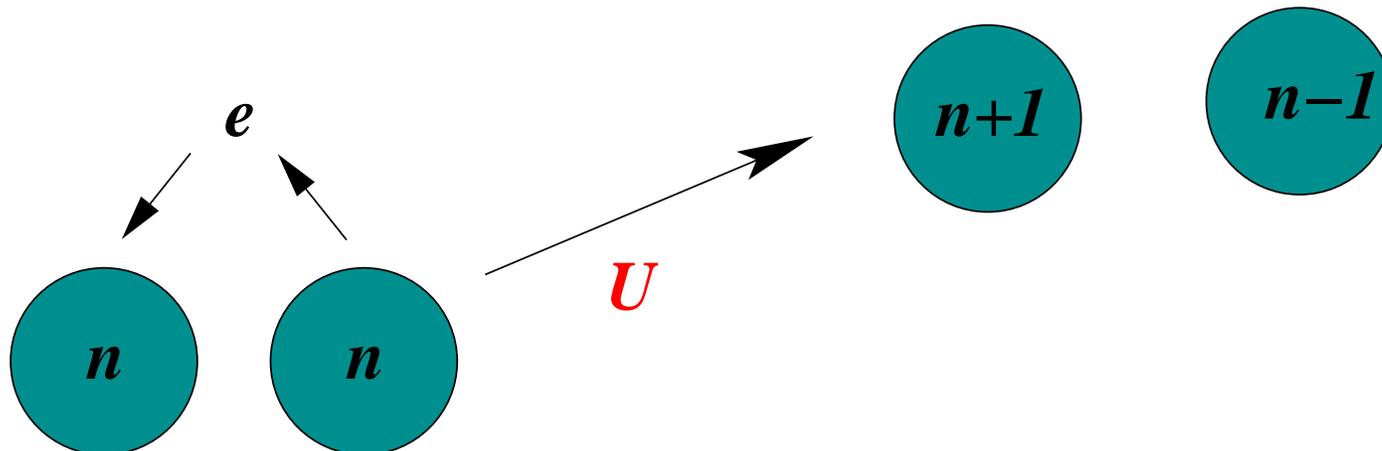
$$U \sum_{i \neq j} n_i n_j$$

instead of averaged Coulomb energy

$$U N(N-1)/2$$

Hubbard U for localized d orbital:

$$U = E(d^{n+1}) + E(d^{n-1}) - 2 E(d^n)$$



LDA+U energy functional (Static Mean Field Theory):

$$E_{local}^{LDA+U} = E^{LDA} - UN(N-1)/2 + \frac{1}{2}U \sum_{i \neq j} n_i n_j$$

LDA+U potential :

$$V_i(\hat{r}) = \frac{\delta E}{\delta n_i(\hat{r})} = V^{LDA}(\hat{r}) + U\left(\frac{1}{2} - n_i\right)$$

LDA+U eigenvalue :

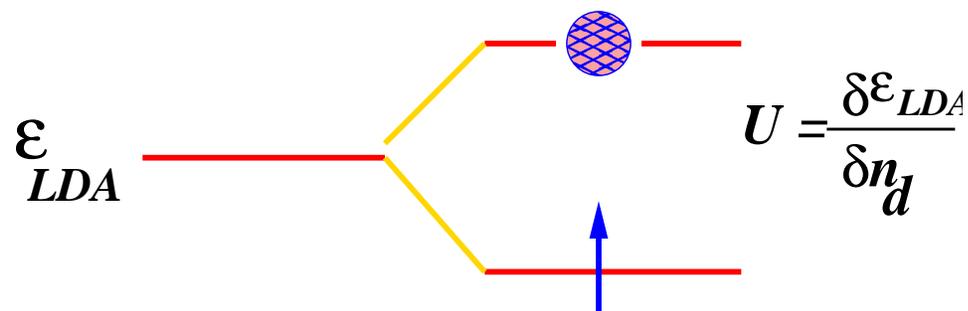
$$\epsilon_i = \frac{\delta E}{\delta n_i} = \epsilon_i^{LDA} + U\left(\frac{1}{2} - n_i\right)$$

For occupied state $n_i = 1 \rightarrow \epsilon_i = \epsilon^{LDA} - U/2$

For unoccupied state $n_i = 0 \rightarrow \epsilon_i = \epsilon^{LDA} + U/2$

⇓

$$\Delta\epsilon_i = U \text{ MOTT-HUBBARD GAP}$$



Rotationally Invariant LDA+U

LDA+U functional:

$$E^{LSDA+U}[\rho^\sigma(r), \{n^\sigma\}] = E^{LSDA}[\rho^\sigma(r)] + E^U[\{n^\sigma\}] - E_{dc}[\{n^\sigma\}]$$

Screened Coulomb Correlations:

$$E^U[\{n^\sigma\}] = \frac{1}{2} \sum_{\{m\}, \sigma} \{ \langle m, m'' | V_{e,e} | m', m''' \rangle n_{mm'}^\sigma n_{m''m'''}^{-\sigma} + \\ (\langle m, m'' | V_{e,e} | m', m''' \rangle - \langle m, m'' | V_{e,e} | m''', m' \rangle) n_{mm'}^\sigma n_{m''m'''}^\sigma \}$$

LDA-double counting term:

$$E_{dc}[\{n^\sigma\}] = \frac{1}{2} U n(n-1) - \frac{1}{2} J [n^\uparrow (n^\uparrow - 1) + n^\downarrow (n^\downarrow - 1)]$$

Slater parametrization of U

Multipole expansion:

$$\frac{1}{|r - r'|} = \sum_{kq} \frac{4\pi}{2k + 1} \frac{r_{<}^k}{r_{>}^{k+1}} Y_{kq}^*(\hat{r}) Y_{kq}(\hat{r}')$$

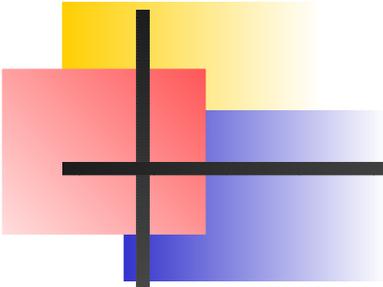
Coulomb Matrix Elements in Y_{lm} basis:

$$\langle mm' || m'' m''' \rangle = \sum_k a_k(m, m'', m', m''') F^k$$

$F^k \rightarrow$ Slater integrals

Average interaction: U and J

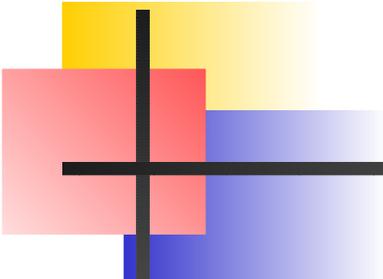
$$U = F^0; J \text{ (for d electrons)} = \frac{1}{14}(F^2 + F^4)$$



How to calculate U and J

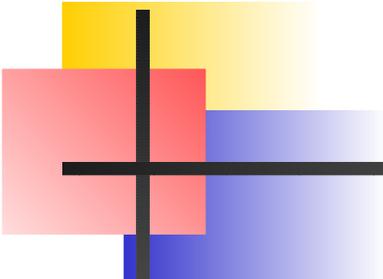
PRB 39 (1989) 9028

- Constrained DFT + Super-cell calculation
- Calculate the energy surface as a function of local charge fluctuations.
- Mapped onto a self-consistent mean-field solution of the Hubbard model.
- Extract U and J from band structure results.



Notes on calculation of U

- Constrained DFT works in the fully localized limit. Therefore often overestimates the magnitude of U .
- For the same element, U depends also on the ionicity in different compounds → higher the ionicity, larger the U .
- One thus varies U in the reasonable range (Comparison with photoemission..).



Where to find U and J

PRB 44 (1991) 943 : 3d atoms

PRB 50 (1994) 16861 : 3d, 4d, 5d atoms

PRB 58 (1998) 1201 : 3d atoms

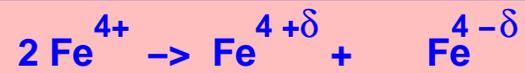
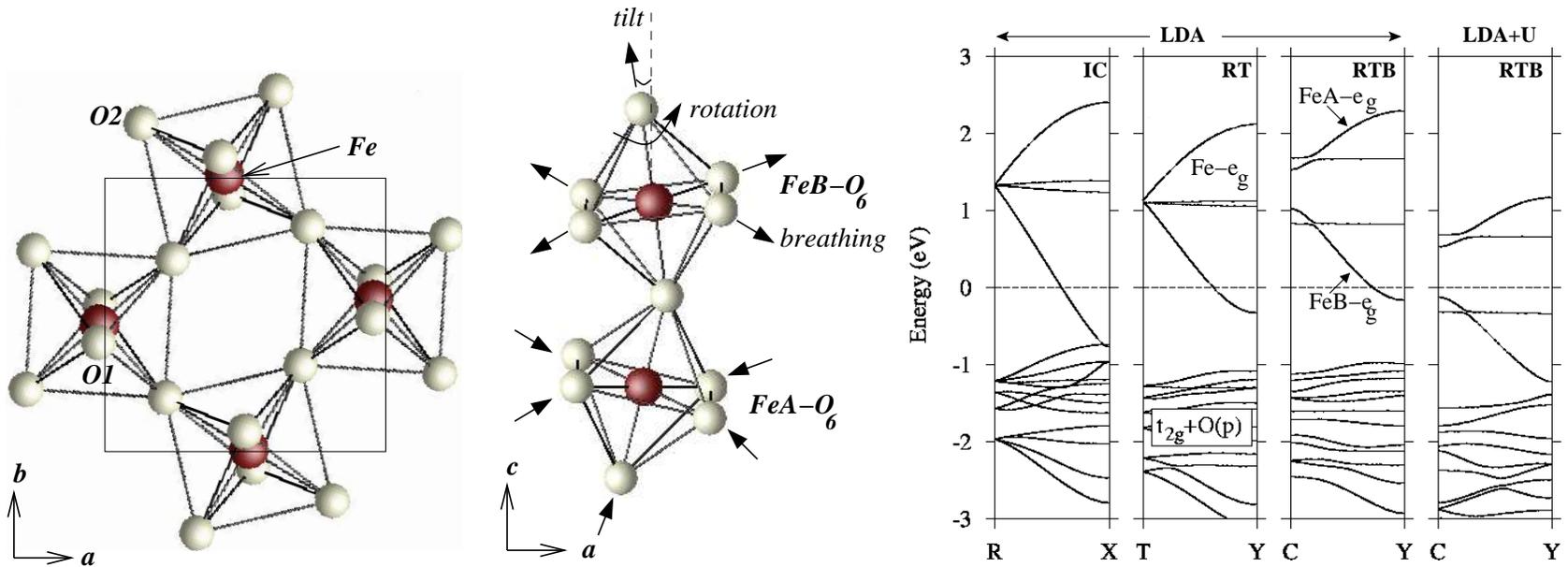
PRB 44 (1991) 13319 : Fe(3d)

PRB 54 (1996) 4387 : Fe(3d)

PRL 80 (1998) 4305 : Cr(3d)

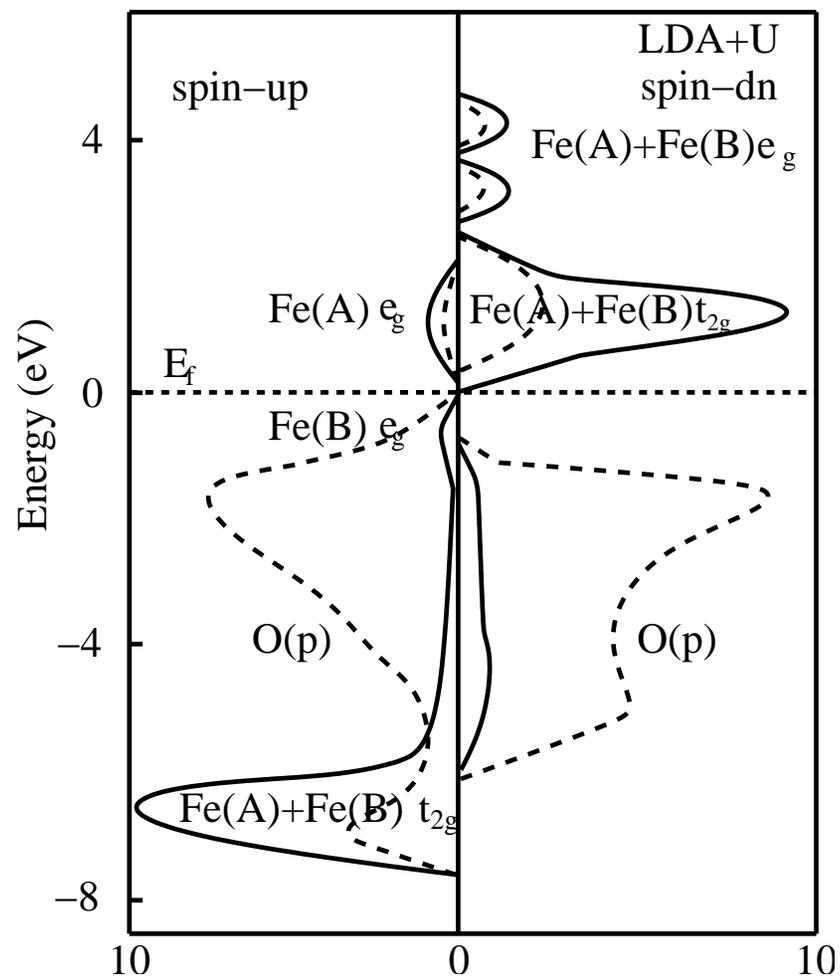
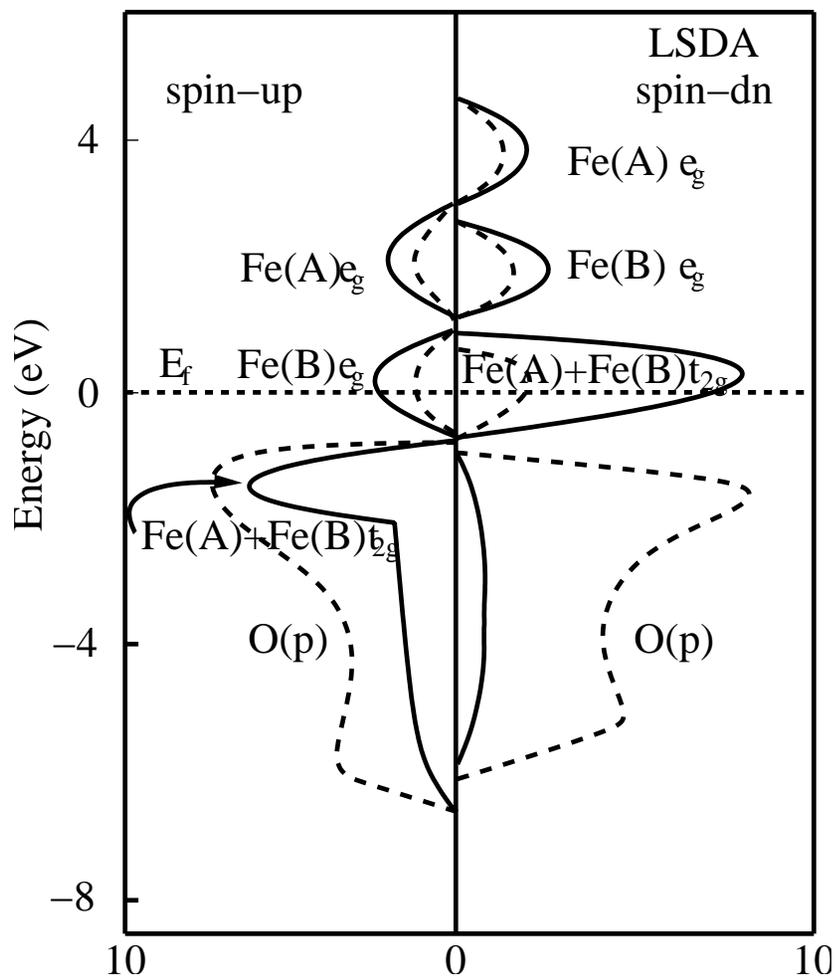
PRB 58 (1998) 9752 : Yb(4f)

CO in CaFeO₃



Phys. Rev. B 72, 045143 (2005)

CO in CaFeO₃



Strongly correlated electron materials

LDA

+Materials-specific

-Fails for strong correln.

Model Approaches

- Input parameters unknown

+ Account for correln. effects

Strongly correlated electron materials

LDA

+Materials-specific

-Fails for strong correln.

Model Approaches

- Input parameters unknown

+ Account for correln. effects

→ Improve the description starting from LDA, by combining *ab-initio* calculations with many-body methods.

→ A major break-through in this respect is **(DMFT)**.

<http://online.kitp.ucsb.edu/online/cem02/>

- Impurity model takes into account of the local dynamics.

- SCF captures the translational invariance and and coherence invariance of the lattice.

Marrying DMFT and DFT-LDA

DMFT emphasizes local correlation → we need a localized basis set, i.e. basis functions which are centered on the atomic positions \mathbf{R} in the crystal lattice



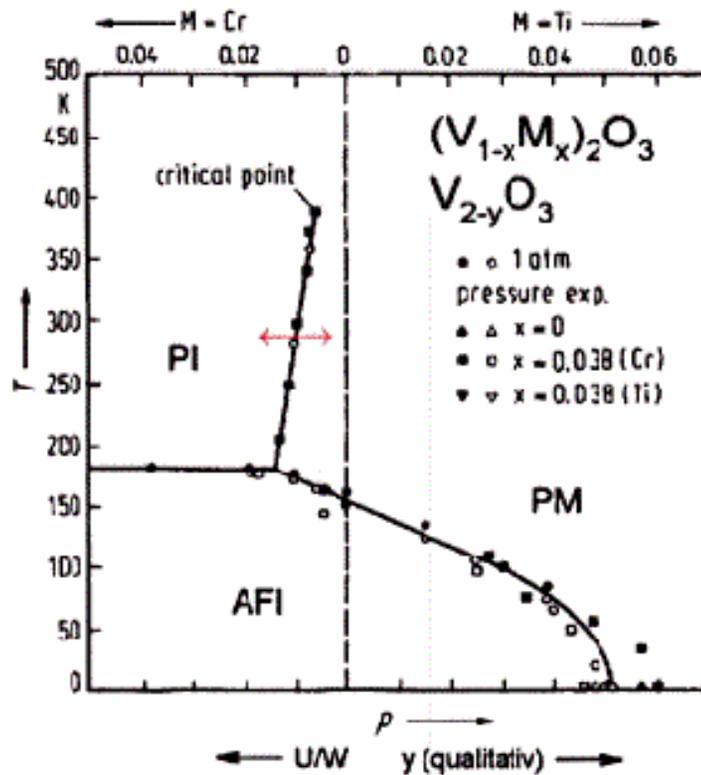
Use Wannier function basis !

NMTO: truly minimal set and Wannier functions

- ♣ A basis set of **localized orbitals** is constructed from the exact scattering solutions of a superposition of short-ranged, spherically-symmetric potential wells (the so-called muffin-tin approximation to the potential) at a mesh of energies, $\epsilon_0, \epsilon_1, \dots, \epsilon_N$
- ♣ The number of energy points, N , defines the order of such muffin-tin orbitals, the NMTO's.
- ♣ Each NMTO satisfies a specific boundary condition which provides it with an orbital character and makes it localized.
- ♣ The NMTO's being energy-selective in nature are flexible and may be chosen to span selected bands \Rightarrow **Downfolding**
- ♣ If these bands are isolated, the NMTO set spans the Hilbert space of the Wannier functions. In other words, the orthonormalized NMTO's are the **localized Wannier functions**.

O. K. Andersen and T. Saha-Dasgupta Phys. Rev. B 62, R16219 (2000)

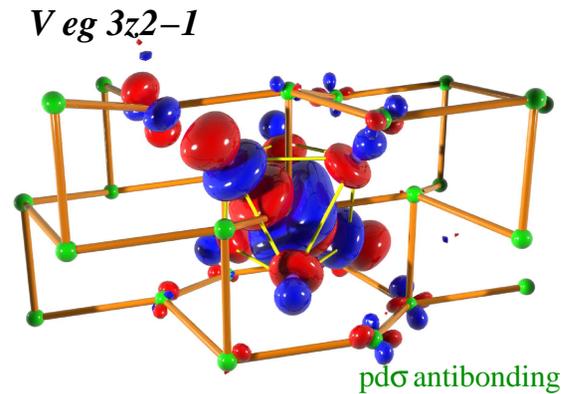
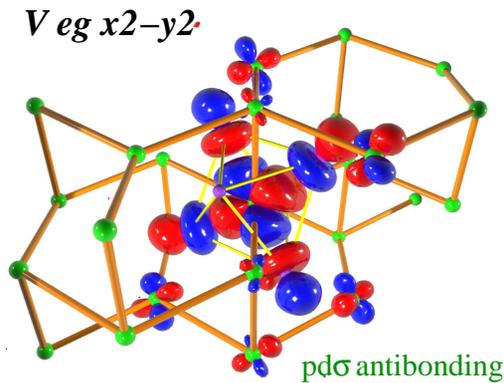
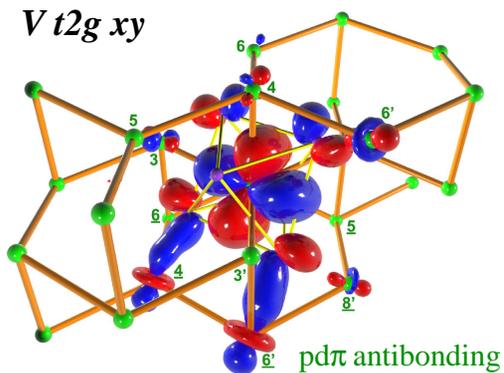
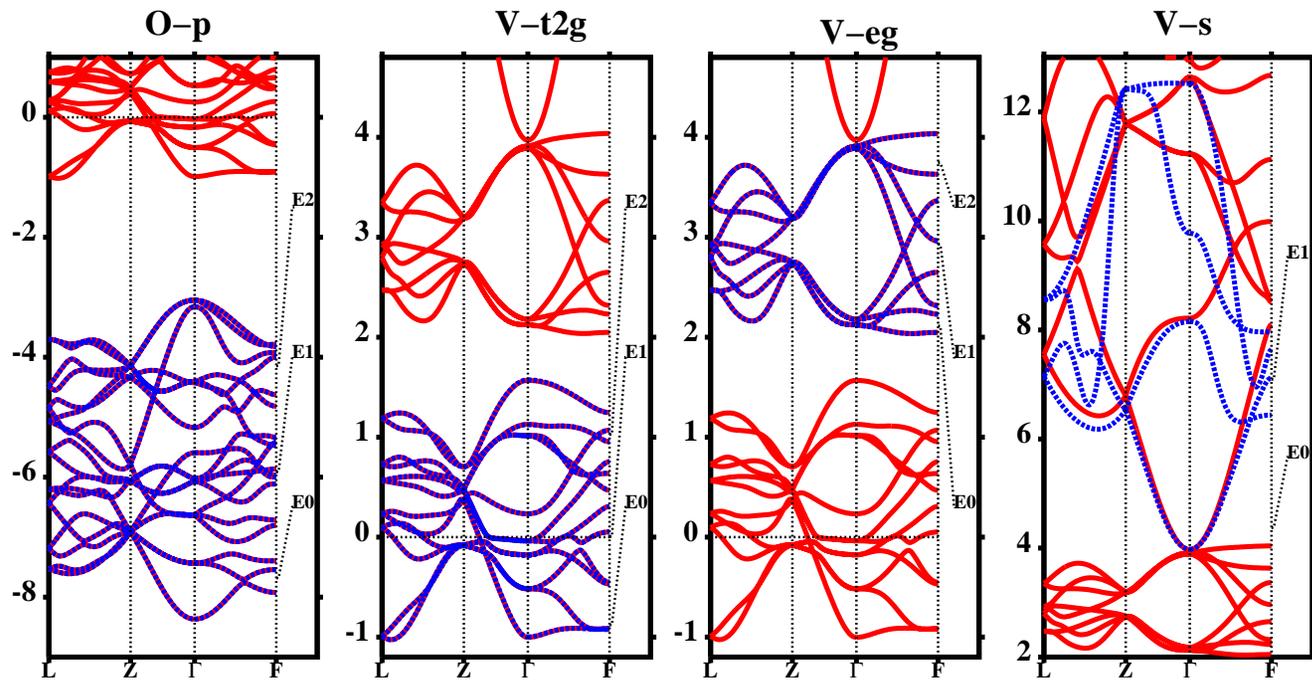
Phase diagram of V_2O_3



McWahn et al.'73

- * undergoes 1st-order M-I transition – can be induced by temp., pressure, alloying
- * PM-PI : same crystal (corundum) & magn. structure
- * only known example among transition-metal oxides to show a PM-PI transition

V2O3: Corundum Structure



NMTO+DMFT

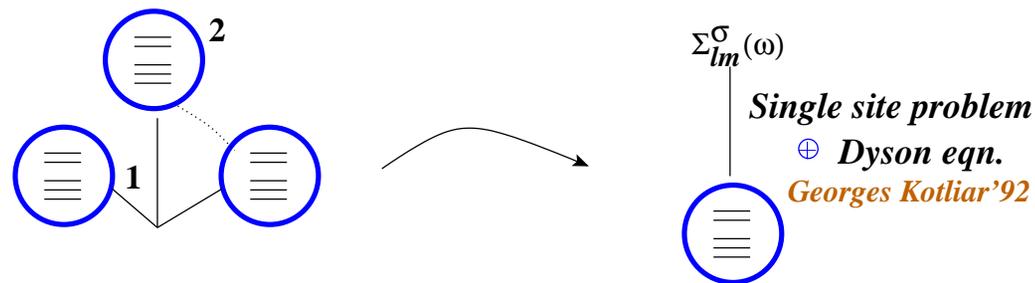
Input Hamiltonian- multi-band Hubbard Hamiltonian:

$$H = H^{lda} + \frac{1}{2} \sum U_{mm'} n_{im\sigma} n_{im'\bar{\sigma}} + \frac{1}{2} \sum_{m \neq m'} [U_{mm'} - J_{mm'}] n_{im\sigma} n_{im'\sigma}$$

- The many-body Hamiltonian depends on the choice of the basis func.– **NMTO's are the ideal candidates!**
- The low-energy Hamiltonian defined above, involves ONLY correlated, localized Wannier orbitals and no other orbitals → **achieved via NMTO-downfolding**
- Assume dc. corrections to be orbital-independent within d-manifold ⇒ **results into simple shift of the chemical potential!**

NMTO+DMFT

⇒ Many-body Hamiltonian solve by DMFT.

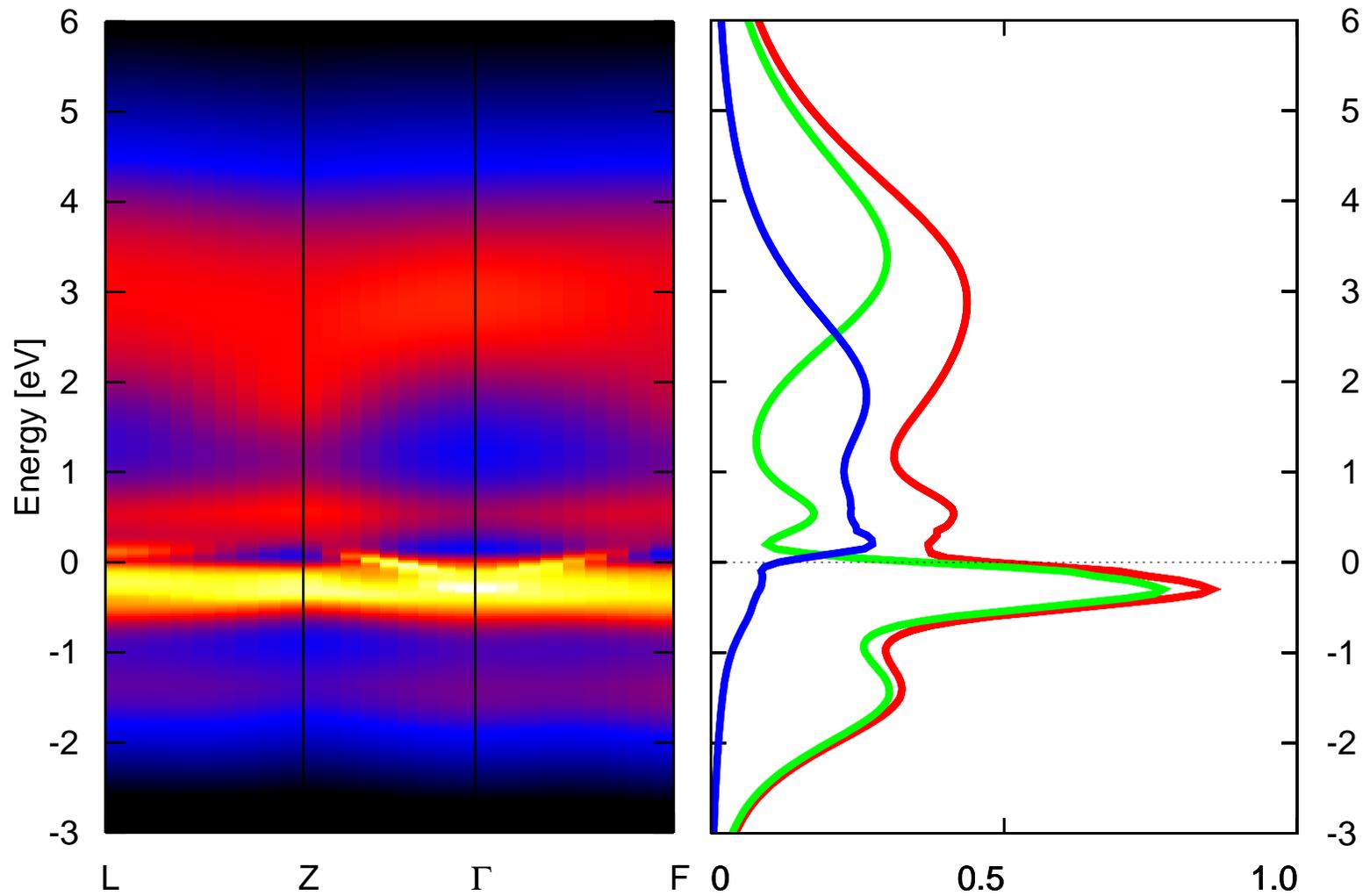


⇒ Multi-orbital quantum impurity problem solve by QMC.

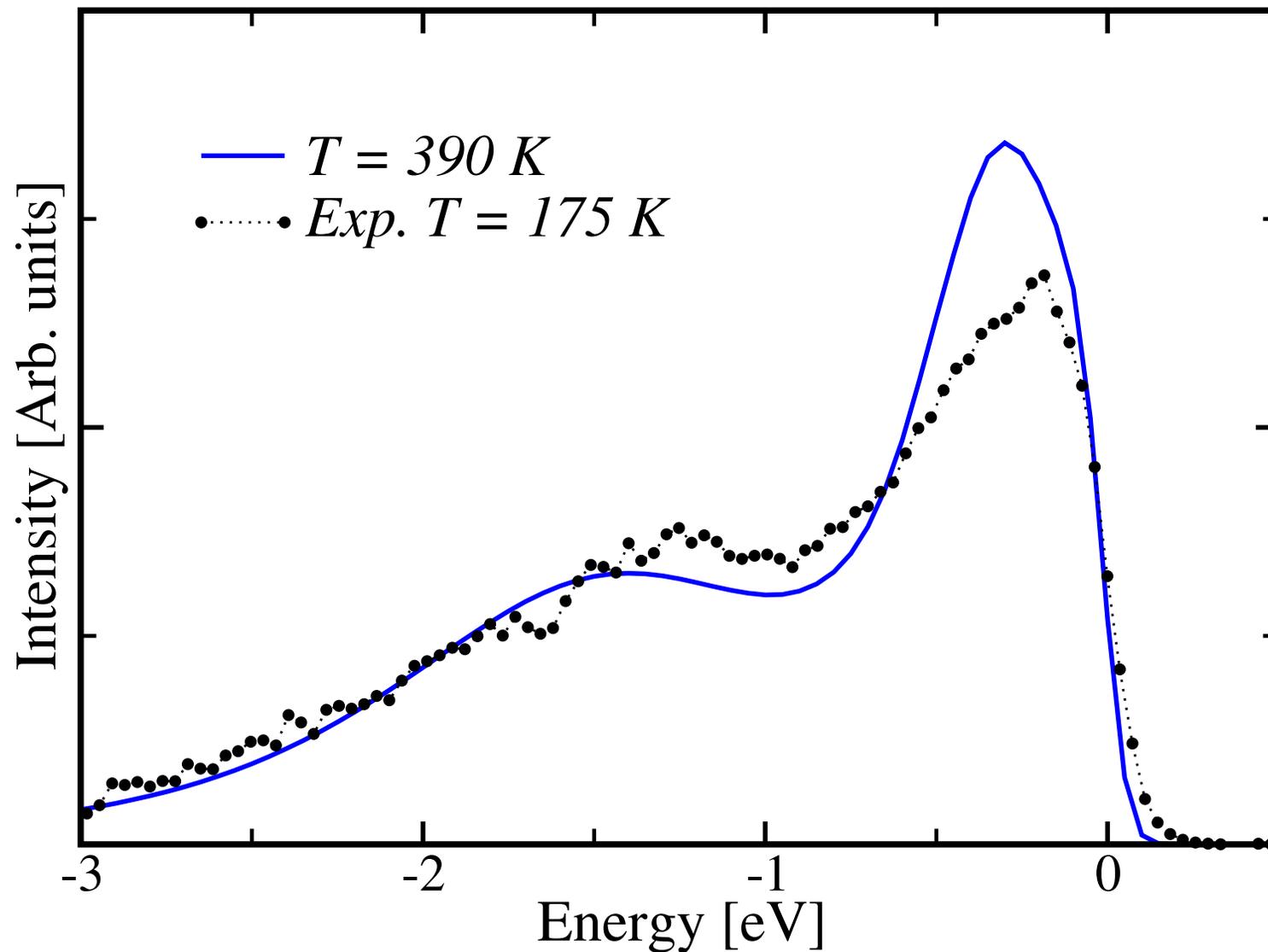


- Maps the interacting electron problem onto a sum of non-interacting problems (*single particle moves in a fluctuating, time-dependent field*)
- Evaluates this sum by Monte Carlo sampling

DMFT results



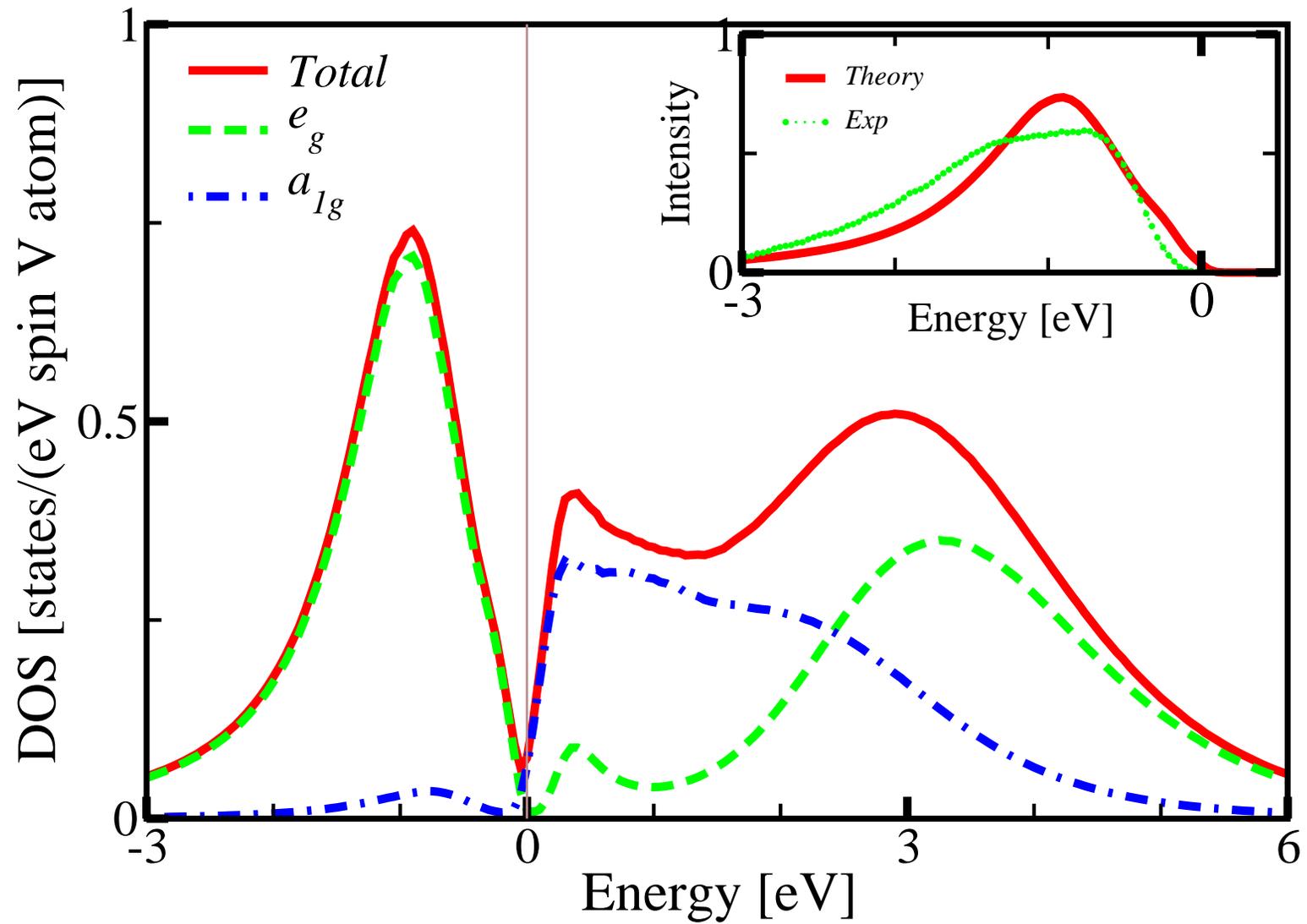
PM spectra - comparison with PES

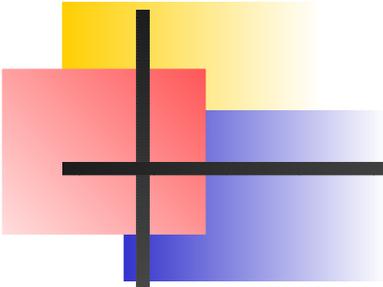


Expt:

Mo *et.al.*

PI spectra - comparison with PES





Hubbard model \implies t-J model

How **spin physics** arises
from

Strong **Electron Correlations** ?

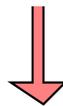
Large U limit of Hubbard Model ($t/U \ll 1$)

————— $\epsilon_{at} + U$

————— ϵ_{at}

- Atomic limit ($t=0$) has huge degeneracy. For L sites occupied by N e⁻'s, singly occupied sites (which is \uparrow or \downarrow spin) can be picked out in $\binom{L}{N} 2^N$ ways !

- Large degeneracy makes the standard perturbation theory inapplicable.
- Treat consecutive orders of t/U systematically \rightarrow *Accomplished by a suitable canonical transformation*
- Motion of e⁻'s are constrained by having to avoid the creation of double occupancy
- Hopping mixes the states!



Rotate to a basis whose states are not mixed in order t

Rotate to a basis whose states are not mixed in order t^2

⋮

Projected Hopping

Local basis:

$$\begin{aligned}
 |0\rangle_j &= \bigcirc \\
 |\uparrow\rangle_j &= \bigcirc \uparrow \\
 |\downarrow\rangle_j &= \bigcirc \downarrow \\
 |d\rangle_j &= \bigcirc \uparrow \downarrow
 \end{aligned}$$

$$\begin{aligned}
 & \underbrace{c_{j\uparrow}^\dagger |0\rangle}_{} \\
 & \underbrace{c_{j\downarrow}^\dagger |0\rangle}_{} \\
 & \underbrace{c_{j\uparrow}^\dagger c_{j\uparrow}^\dagger |0\rangle}_{}
 \end{aligned}$$

PROJECTION OPERATORS:

$$\hat{P}_{j0} = |0\rangle_j \langle 0| = (1 - \hat{n}_{j\uparrow})(1 - \hat{n}_{j\downarrow})$$

$$\hat{P}_{j\uparrow} = |\uparrow\rangle_j \langle \uparrow| = \hat{n}_{j\uparrow}(1 - \hat{n}_{j\downarrow})$$

$$\hat{P}_{j\downarrow} = |\downarrow\rangle_j \langle \downarrow| = (1 - \hat{n}_{j\uparrow})\hat{n}_{j\downarrow}$$

$$\hat{P}_{jd} = |d\rangle_j \langle d| = \hat{n}_{j\uparrow}\hat{n}_{j\downarrow}$$

Ensure there is \uparrow at i

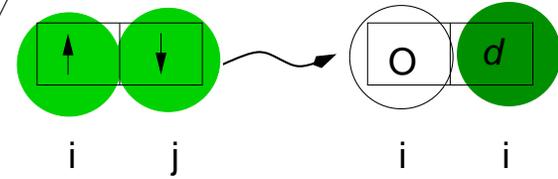
Ensure there is \downarrow at j

Perform the hopping

Ensure site j is $|d\rangle$

Ensure site i is $|0\rangle$

projected hopping



$$\begin{aligned}
 & \hat{P}_{i0} \hat{P}_{jd} c_{j\uparrow}^\dagger c_{i\uparrow} \hat{P}_{i\uparrow} \hat{P}_{i\downarrow} \\
 &= \hat{P}_{jd} c_{j\uparrow}^\dagger c_{i\uparrow} \hat{P}_{i\uparrow} \\
 &= \hat{n}_{j\downarrow} c_{j\uparrow}^\dagger c_{i\uparrow} \hat{n}_{i\downarrow}
 \end{aligned}$$

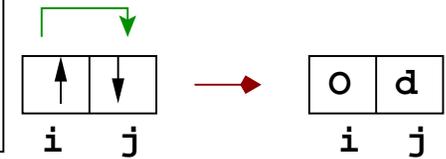
$$B = c c^\dagger c = (1 - c^\dagger c)c = c - c^\dagger c c = c$$

Correlated Hopping

$$H_t = H_t^+ + H_t^- + H_t^0$$

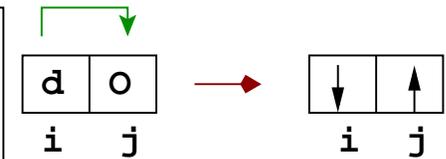
$$H_t^+ = -t \sum_{\langle i,j \rangle, \sigma} \left[\hat{n}_{j\bar{\sigma}} c_{j\sigma}^\dagger c_{i\sigma} (1 - \hat{n}_{i\bar{\sigma}}) + \hat{n}_{i\bar{\sigma}} c_{i\sigma}^\dagger c_{j\sigma} (1 - \hat{n}_{j\bar{\sigma}}) \right]$$

D → D + 1



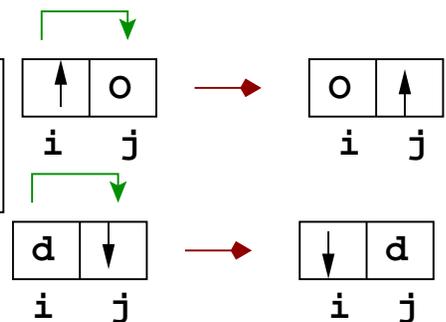
$$H_t^- = -t \sum_{\langle i,j \rangle, \sigma} \left[(1 - \hat{n}_{i\bar{\sigma}}) c_{i\sigma}^\dagger c_{j\sigma} \hat{n}_{j\bar{\sigma}} + (1 - \hat{n}_{j\bar{\sigma}}) c_{j\sigma}^\dagger c_{i\sigma} \hat{n}_{i\bar{\sigma}} \right]$$

D → D - 1



$$H_t^0 = -t \sum_{\langle i,j \rangle, \sigma} \left[(1 - \hat{n}_{i\bar{\sigma}}) c_{i\sigma}^\dagger c_{j\sigma} (1 - \hat{n}_{j\bar{\sigma}}) + \hat{n}_{i\bar{\sigma}} c_{i\sigma}^\dagger c_{j\sigma} \hat{n}_{j\bar{\sigma}} \right]$$

D → D



$$H_t = \sum (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma})$$

Do not care the correlations!

$$H_t = H_t^+ + H_t^- + H_t^0$$

Mind the local correlations!!

→ H_t compared to H_t has acquired a complicated many-body character!

Canonical Transformation

- Intuitive notion: Low energy excitations are propagated in the lower Hubbard subband.
- Pure band motion mixes states from two subbands via H_t^+ and H_t^- .
- *Unmixing* can be achieved via rotation to a new basis.

Define H_{eff} :

$$\begin{aligned} H_{eff} &= e^{iS} H e^{-iS} = H + i[S, H] + \frac{i^2}{2}[S, [S, H]] + \dots + \dots \\ &= H_U + H_t^+ + H_t^- + H_t^o + i[S, H_U] + i[S, H_U + H_t^+ + H_t^- + H_t^o] - \end{aligned}$$

Choose S such that: $H_t^+ + H_t^-$ gets cancelled by $i[S, H_U]$

$$\Rightarrow S = -\frac{i}{U}[H_t^+ - H_t^-]$$

\Downarrow

$$H_{eff} = H_U + H_t^o + \frac{1}{U}[H_t^+, H_t^-] \text{ to order } t^2$$

Hubbard Operators

$$X_j^b = |b\rangle_j \langle a| \quad [\text{Projection Operator: } \hat{P}_a = |a\rangle \langle a| = \sum_j X_j^{a \leftarrow a}]$$

$$C_{j\uparrow}^\dagger = X_j^{\uparrow \leftarrow 0} + X_j^{d \leftarrow \downarrow}$$

$$C_{j\uparrow}^\dagger = X_j^{\downarrow \leftarrow 0} - X_j^{d \leftarrow \uparrow}$$

Convention: $|d\rangle = C_{j\uparrow}^\dagger C_{j\downarrow}^\dagger |0\rangle$

$$\rightarrow C_{j\sigma}^\dagger = X_j^{\sigma \leftarrow 0} + \eta(\sigma) X_j^{d \leftarrow \bar{\sigma}} \quad \left[\eta(\sigma) = \begin{array}{l} +1 \text{ if } \sigma = \uparrow \\ -1 \text{ if } \sigma = \downarrow \end{array} \right]$$

$$H_t^0 = -t \sum_{\langle i,j \rangle \sigma} \left[X_i^\sigma \leftarrow 0 X_j^{0 \leftarrow \bar{\sigma}} + X_i^d \leftarrow \sigma X_j^{d \leftarrow \bar{\sigma}} + \text{H.c.} \right]$$

$$H_t^+ = -t \sum \eta(\sigma) \left[X_i^{d \leftarrow \bar{\sigma}} X_j^{0 \leftarrow \bar{\sigma}} + X_j^{d \leftarrow \bar{\sigma}} X_i^{0 \leftarrow \bar{\sigma}} \right]$$

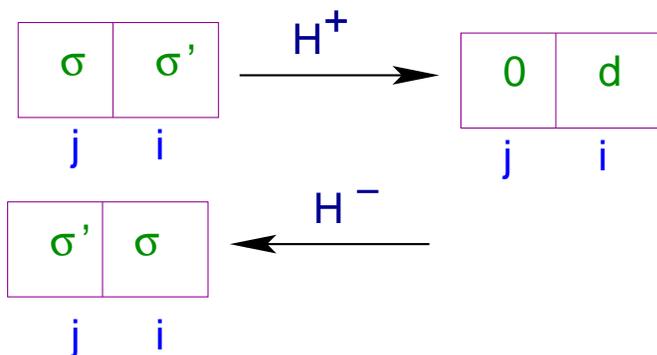
t-J model

- Consider action of H_{eff} on the low energy sub-space

$$H_t^0 \rightsquigarrow -t \sum_{\langle ij \rangle \sigma} \left[X_i^{\sigma \leftarrow 0} X_j^{0 \leftarrow \sigma} + X_j^{\sigma \leftarrow 0} X_i^{0 \leftarrow \sigma} \right]$$

$$\left[H_t^+, H_t^- \right] = \sum_{\langle ij \rangle} \left[H_{tij}^+, H_{tij}^- \right] + \sum_{\langle ijk \rangle} \left[H_{tij}^+, H_{tjk}^- \right]$$

[disjoint pairs commute]



$$\frac{1}{U} \left[H_{tij}^+, H_{tij}^- \right]$$

$$\rightsquigarrow -\frac{1}{U} H_{tij}^- H_{tij}^+$$

$$\rightsquigarrow -\frac{t^2}{U} \sum_{\sigma} \sum_{\sigma'} \eta(\sigma) \eta(\sigma')$$

$\sigma' = \sigma$: original spin arrang.

$\sigma' = -\sigma$: interchange of spin

$$\frac{2t^2}{U} \left(S_i^z S_j^z - \frac{\hat{n}_i \hat{n}_j}{4} \right)$$

$$X_i^{\sigma' \leftarrow -\sigma} X_j^{\sigma \leftarrow \sigma'}$$

Heisenberg model

$$H_{eff} \approx H_{t-J} = -t \sum_{ij} - \sum_{\sigma} (1 - \hat{n}_{i-\sigma}) c_{i\sigma}^{\dagger} C_{j\sigma} (1 - \hat{n}_{i-\sigma}) + h.c. \\ + \frac{4t^2}{U} [S_i S_j - \frac{\hat{n}_i \hat{n}_j}{4}] + 3 - \text{siteterms..}$$

Exact half-filling (n=1):

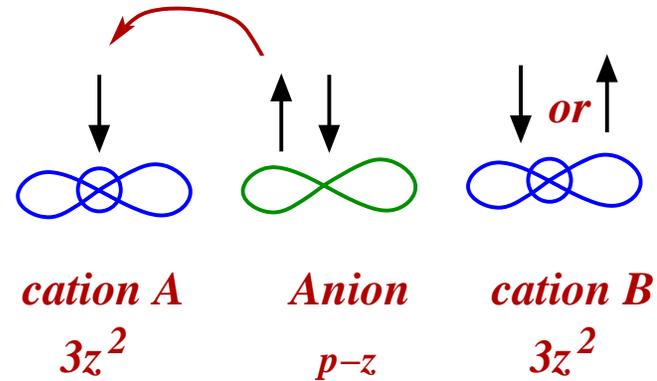
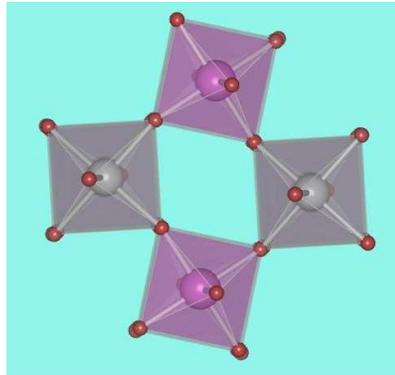
$$H = J \sum_{ij} S_i S_j$$

⇒ AF Heisenberg model [$J = \frac{4t^2}{U}$]

→ if neighboring sites are $\uparrow\downarrow$, a virtual hopping process can create an intermediate 0d pair state with energy U [associated energy gain $\frac{t^2}{U}$.

→ If spins are $\uparrow\uparrow$ or $\downarrow\downarrow$, hopping is prohibited by Pauli principle.

Super-exchange



$$|pz \uparrow \rangle \sim \frac{|pz \uparrow \rangle + b |d_A \uparrow \rangle}{\sqrt{1 + b^2}} \quad [b \sim \frac{\langle pz | H | d_A \rangle}{\epsilon_p - \epsilon_d}]$$

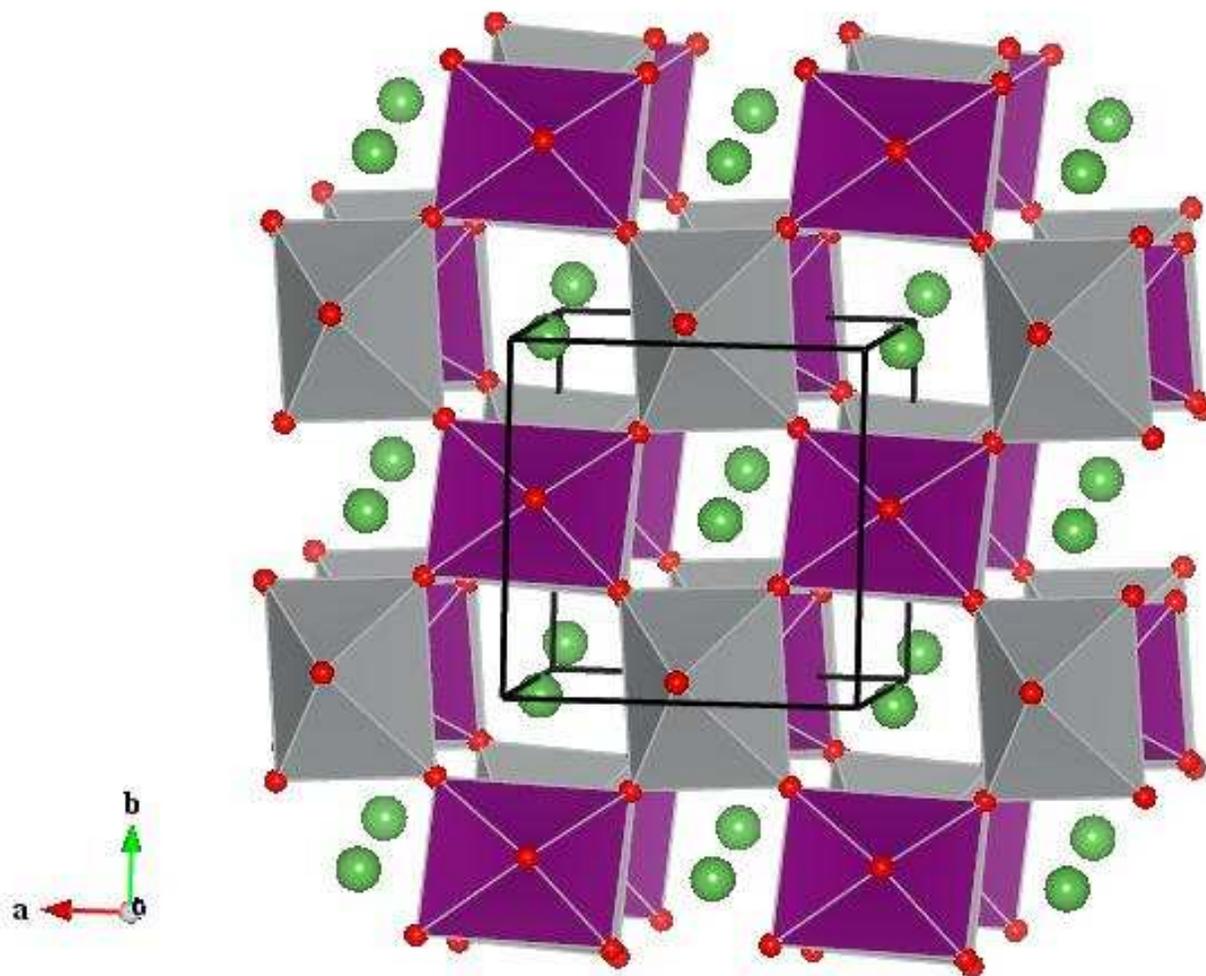
For $\downarrow\downarrow$ *configuration:* $E_{\downarrow\downarrow} \sim \frac{1}{1 + 2b^2} (\langle pz \uparrow | + b \langle d_A \uparrow | + b \langle d_B \uparrow |)$

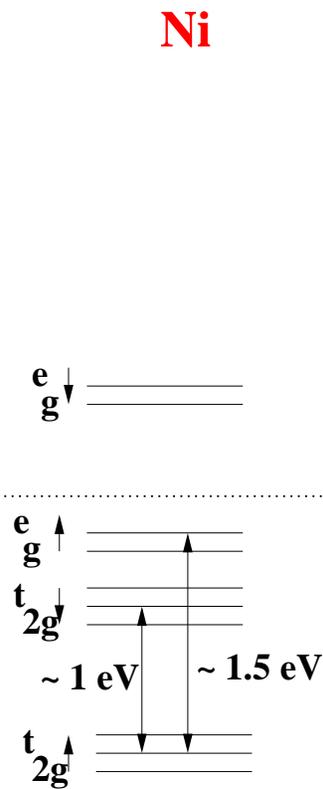
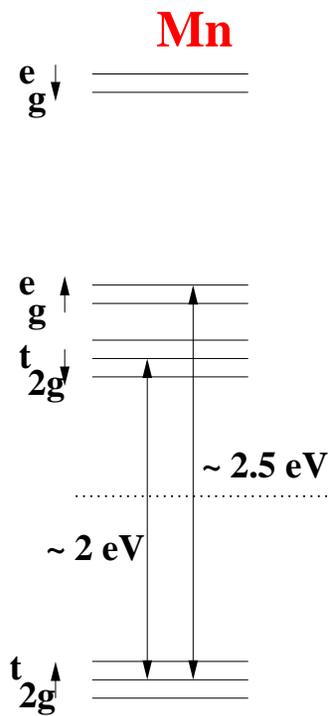
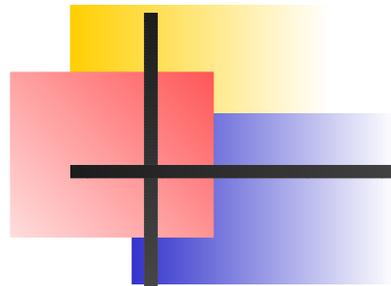
$$\langle pz | H | pz \rangle (|pz \uparrow \rangle + b |d_A \uparrow \rangle + b |d_B \uparrow \rangle)$$

For $\downarrow\uparrow$ *configuration:* $E_{\downarrow\uparrow} \sim 2\epsilon_p + \frac{2b^2}{1 + 2b^2} (\epsilon_p - \epsilon_d)$

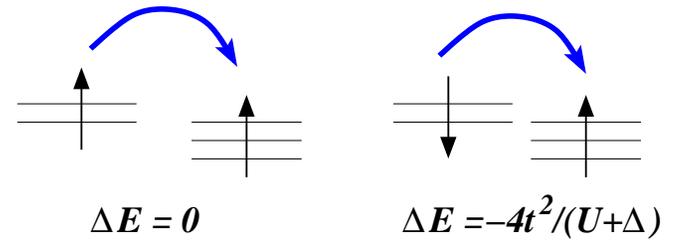
Exchange: $E_{\downarrow\downarrow} - E_{\downarrow\uparrow} \sim 2b^4 (\epsilon_d - \epsilon_p)$ **SUPER-EXCHANGE**

$\text{La}_2\text{NiMnO}_6$ (PRL, 100, 186402)

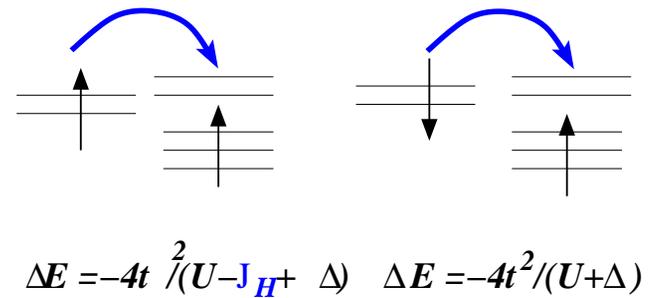




Ni-eg – Mn t2g Superexchange



Ni-eg – Mn eg Superexchange

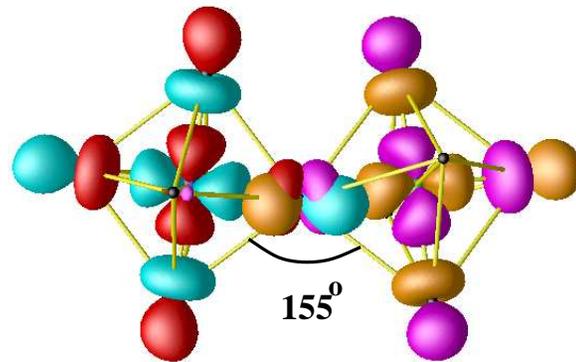


Use NMTO-downfolding to estimate Δ -s and t -s

La₂NiMnO₆ - Magnetism

NMTO-dowfolding study (Effective Ni-Mn model)

NMTO-downfolding Study



$$t_{e-t} = 0.02 \text{ eV}$$

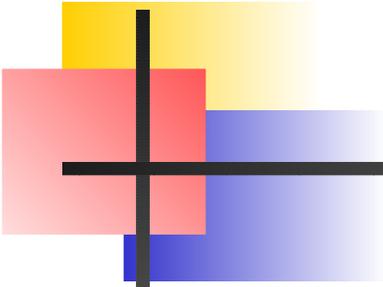
$$\Delta_{e-t} = 0.25 \text{ eV}$$

$$t_{e-e} = 0.20 \text{ eV}$$

$$\Delta_{e-e} = 1.90 \text{ eV}$$

$$\begin{aligned} J_{Ni-Mn} &= J^{AF} + J^{FM} \\ &= 4 \frac{\sum (t_{e,t})^2}{(U + \Delta_{e,t})} - 4 \frac{\sum (t_{e,e})^2 J_H}{(U + \Delta_{e,e} - J_H)(U + \Delta_{e,e})} \end{aligned}$$

$$\Rightarrow J_{Ni-Mn} \approx 4-7 \text{ meV} \quad (U \approx 4-5 \text{ eV}, J_H = 0.9 \text{ eV})$$



Conclusion

♣ Recent technological developments allow for the realistic description of strongly correlated electron system taking into account both the material specific chemical knowledge and the strong correlation aspect.