Materials Modeling from First-principles Electronic Structure Calculations

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Research Activity in the group

- First principles study of complex crystalline solids.
- Electronic structure of strongly correlated systems.
- First-principle calculation of electronic structure and phase stability of alloys.
- Electronic structure and quantum transmittance through nano-materials.

Funding: Dept of Sc. & Tech, India, Board of Res on Nuclear Sc., Indo-Dutch, Indo-Russian, Indo-Austrian

Motivation

$\longrightarrow$ Novel materials are key to new technologies.

$\longrightarrow$ Materials-specific theory, specially computational theory are being used for microscopic understanding.

$\longrightarrow$ System sizes are often large, $\&$ materials are often complex and complicated in their behavior.

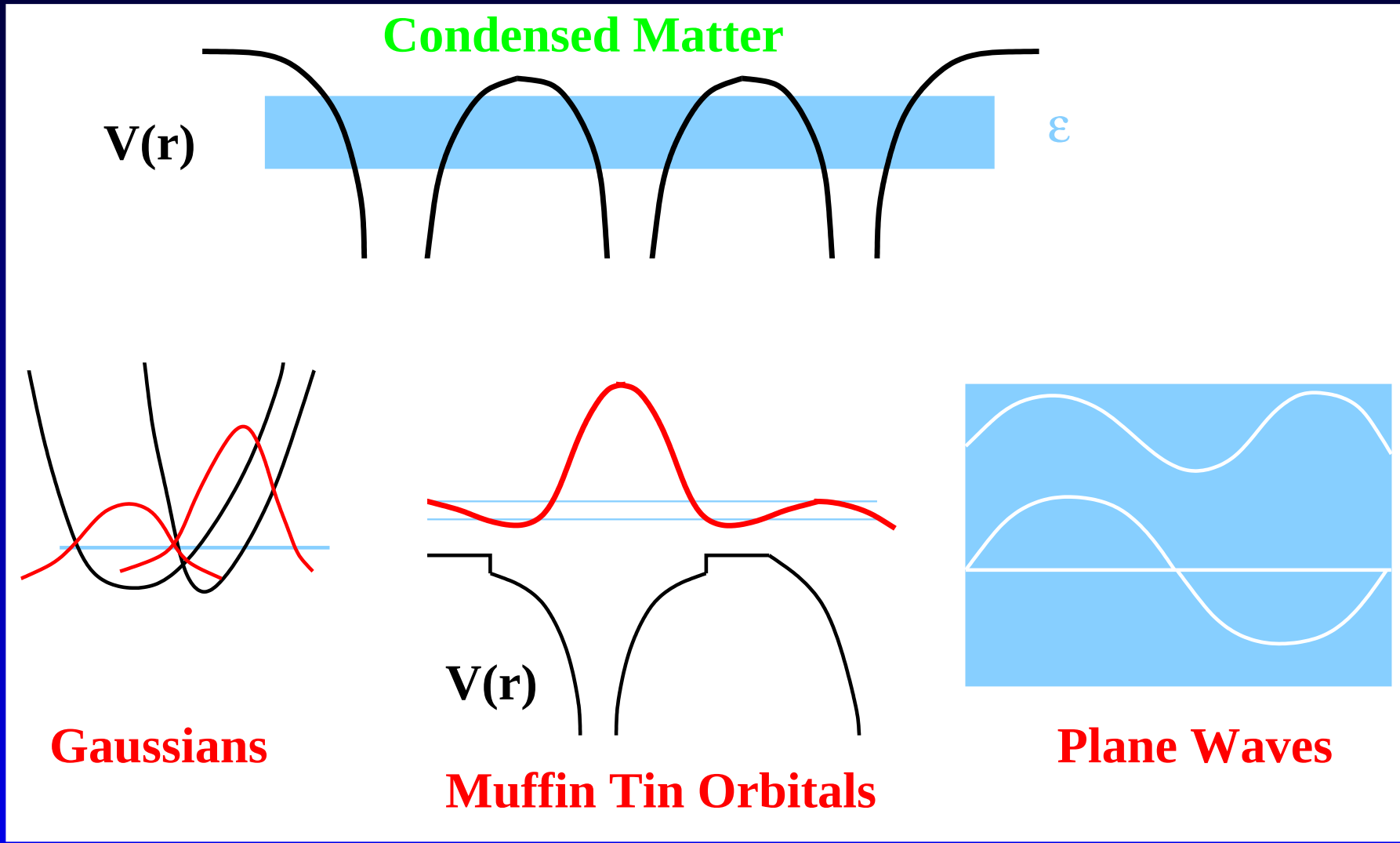
$\longrightarrow$ Modeling is playing an ever increasing role in search for new materials.

$\longrightarrow$ The chemistry controls the physical (electrical, magnetic, optical) properties.

At the root of all are the Electrons!

Motivation

Ab initio Electronic Structure Calculations



Motivation

Our goal is to find a generally applicable **electronic structure method**, which is *intelligible, fast and accurate.*

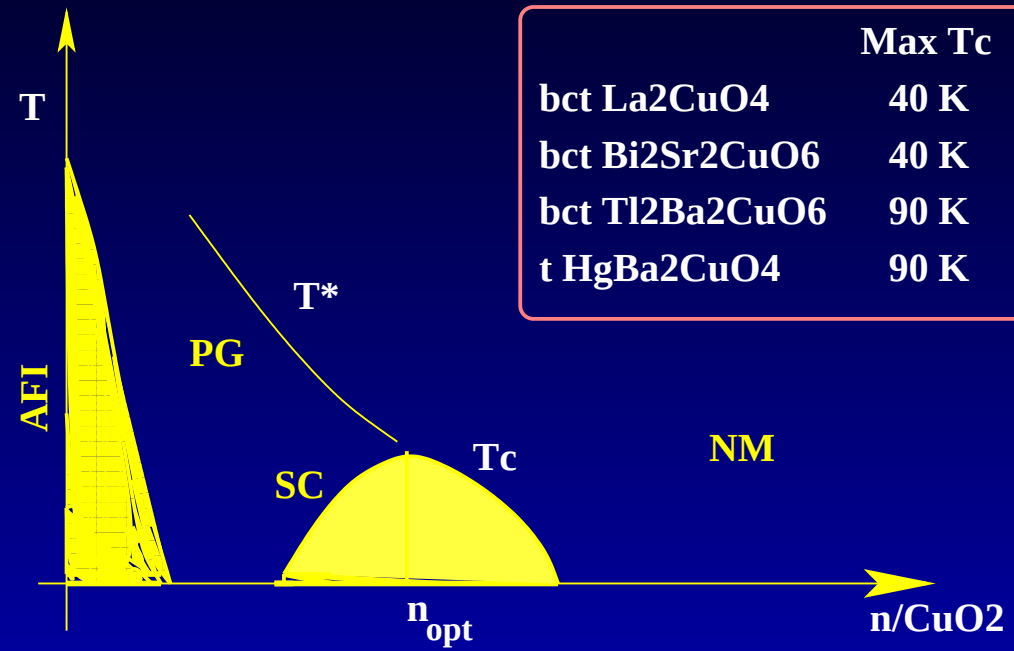
$\Downarrow$

Muffin-Tin Orbitals of N-th order (NMTO)

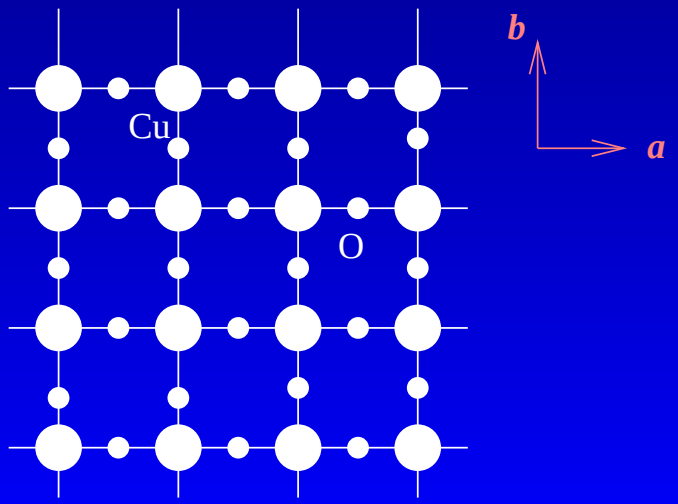
- Provides an useful way of deriving the few-band Hamiltonians starting from complicated LDA band-structure.
- NMTO's being *energy-selective* by nature, produce *truly minimal basis sets* $\Rightarrow$ the Wannier-like functions
- Adds *Chemical Reality* to Physicists Models

(PRB 62, R16219)

HTSC



	Max Tc
bct La2CuO4	40 K
bct Bi2Sr2CuO6	40 K
bct Tl2Ba2CuO6	90 K
t HgBa2CuO4	90 K



Material dependence→

Electronic structure

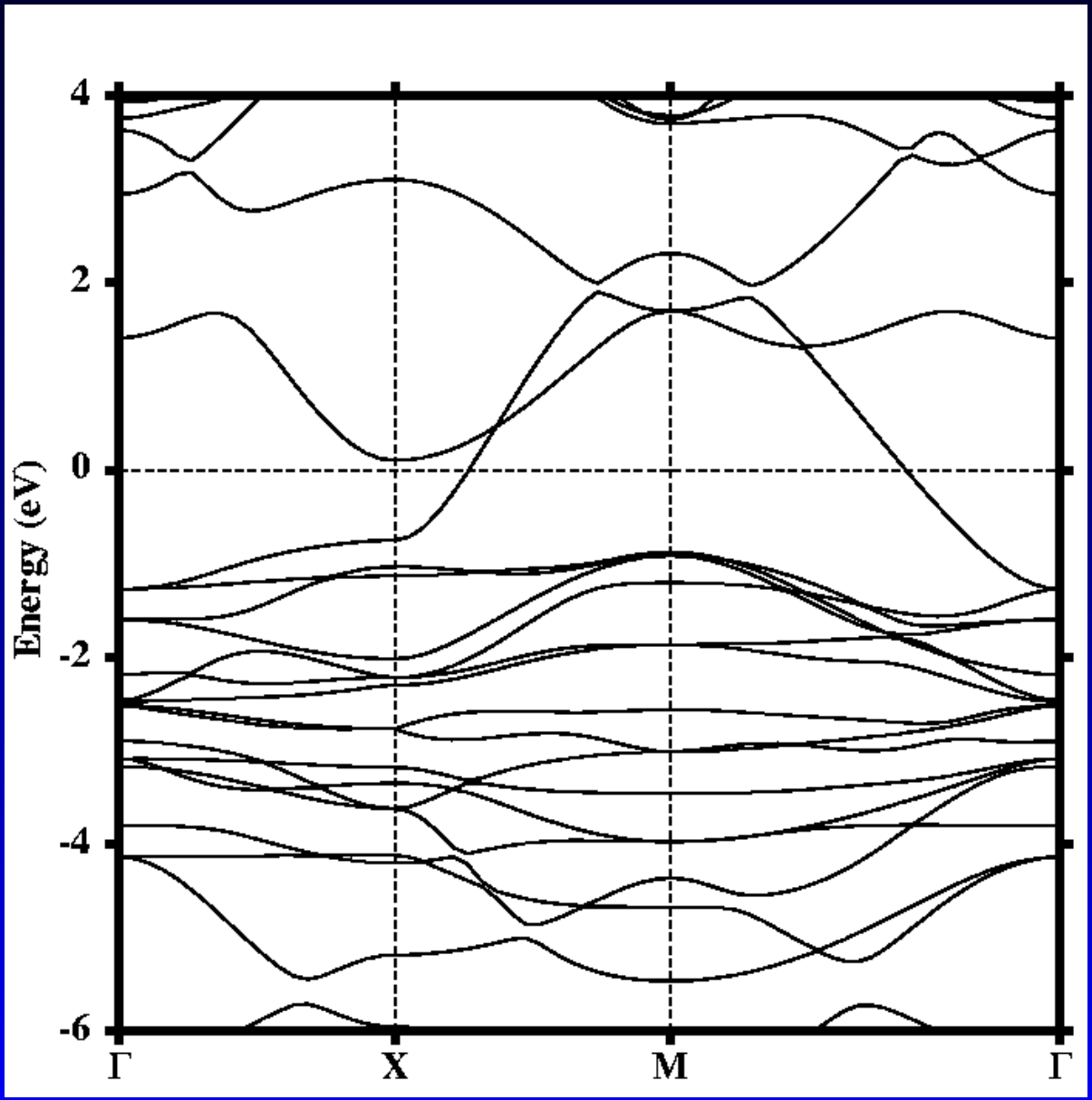
Hopping integrals→

$$H_0 = \Sigma\, t_{ij}\, c_i^{\dagger}\, c_j$$

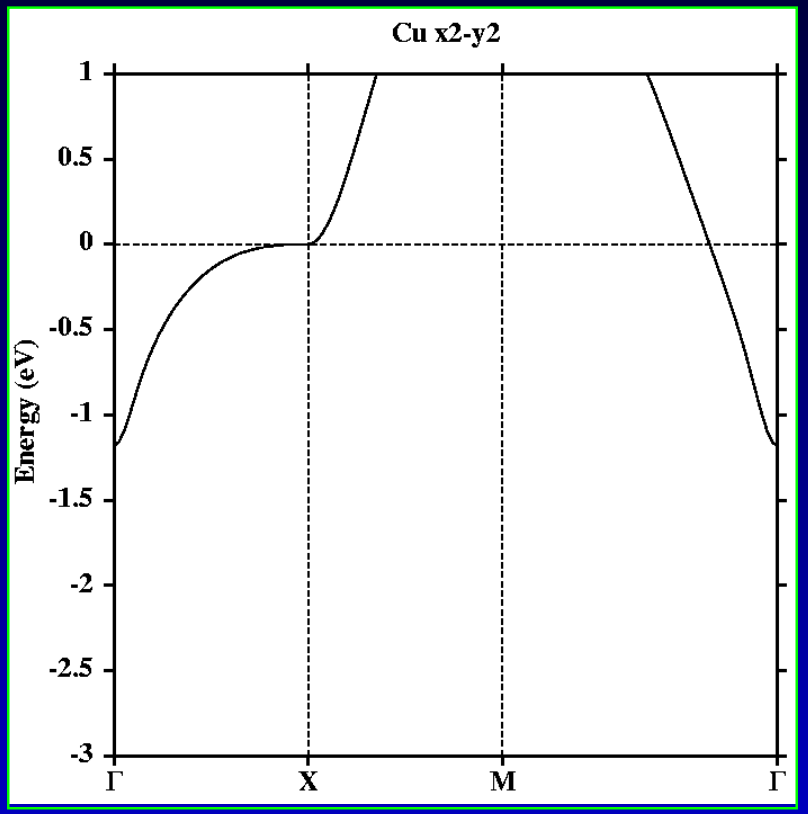
Model Hamiltonian→

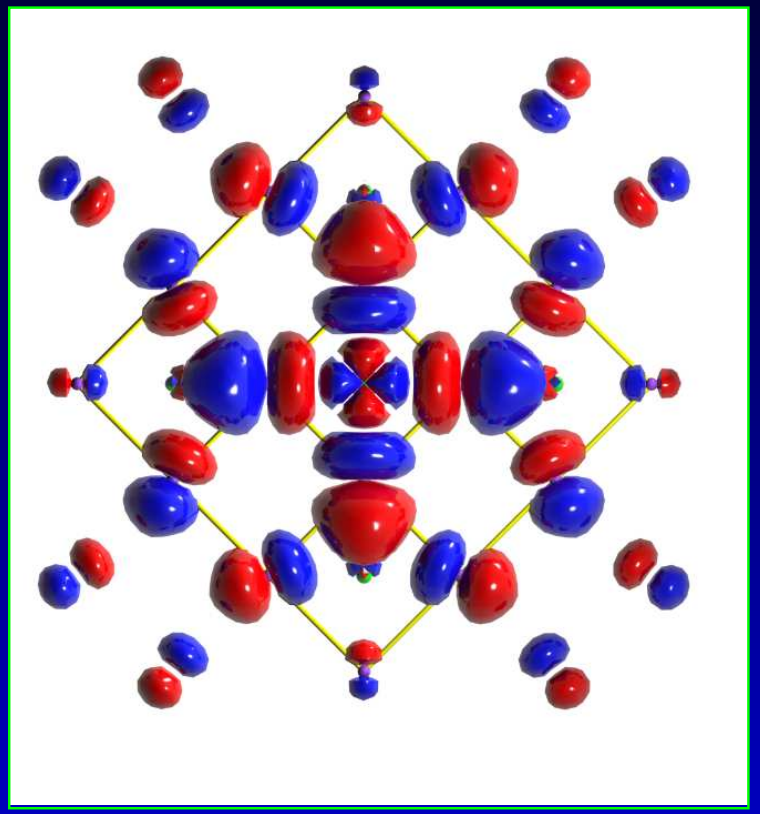
$$H = H_0 + \text{Correln.} + \ldots$$

HTSC Bands



NMTO downfolding

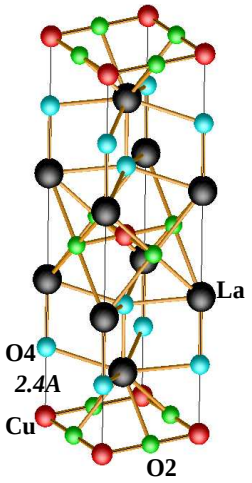


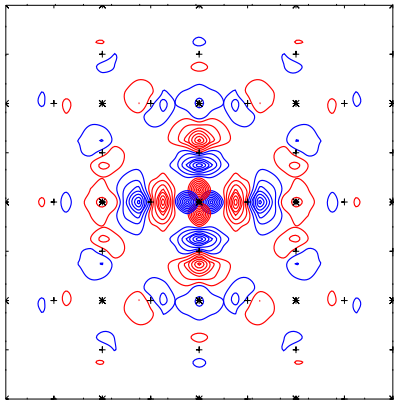


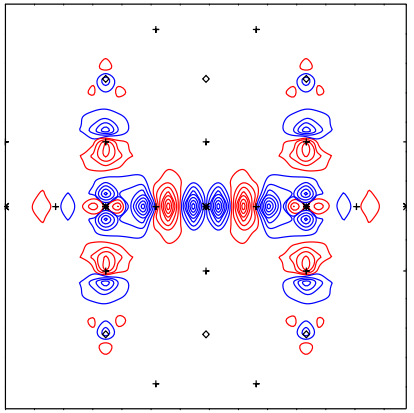
NMTO Wannier-like functions

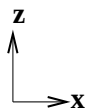
La_2CuO_4

(Tc = 40°K)



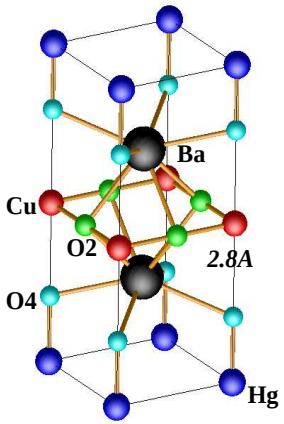


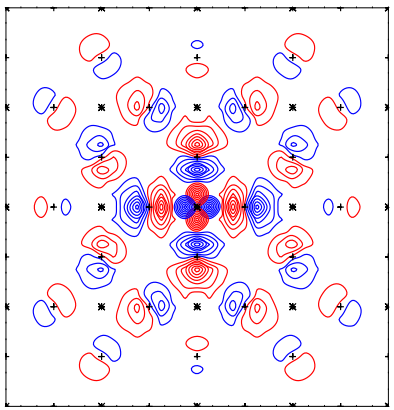


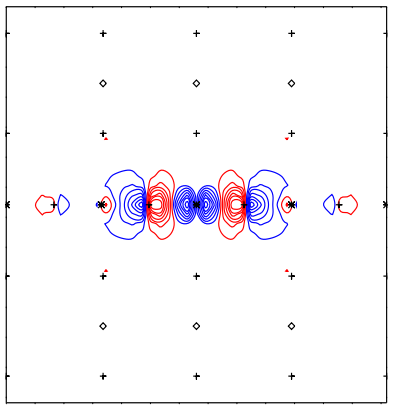


$HgBa_2CuO_4$

(Tc = 90°K)





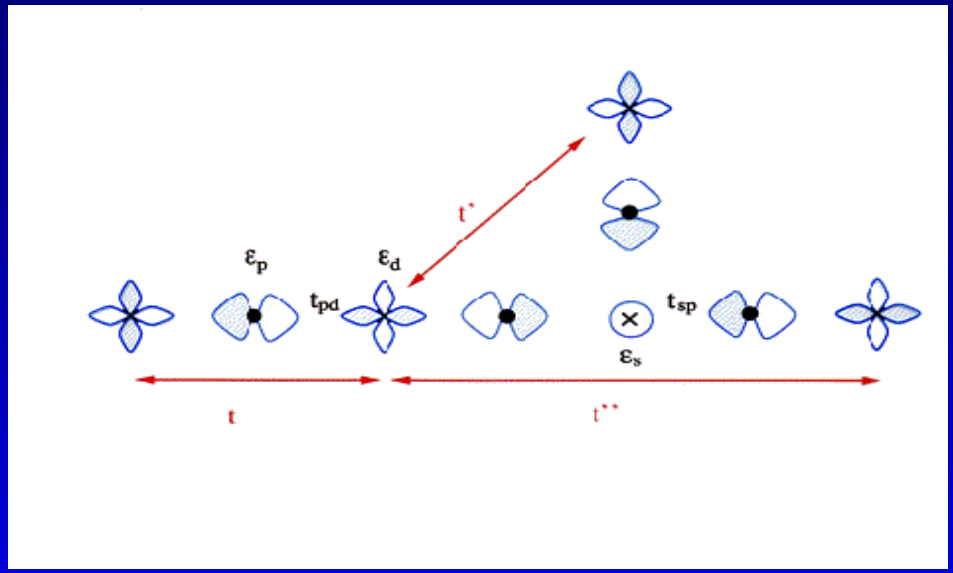


Cu $d_{x^2-y^2}$ only model

$$\begin{aligned}\epsilon(k) &= -2t(cosk_x + cosk_y) + 4t^{'}cosk_x cosk_y \\ &\quad -2t^{''}(cos2k_x + cos2k_y) + \ldots\end{aligned}$$

Cu $d_{x^2-y^2}$ only model

$$\epsilon(k) = -2t(cosk_x + cosk_y) + 4t^{'}cosk_x cosk_y$$
$$-2t^{''}(cos2k_x + cos2k_y) + \ldots$$

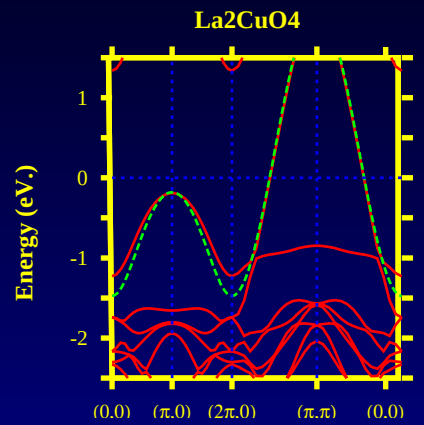


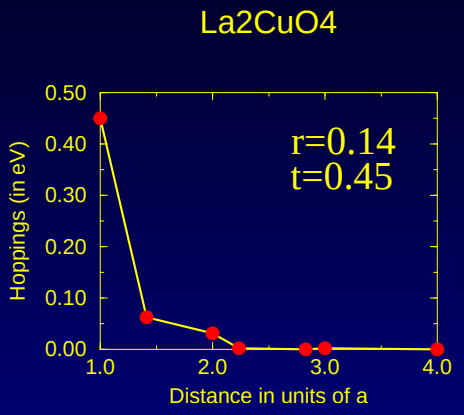
Cu $d_{x^2-y^2}$ only model

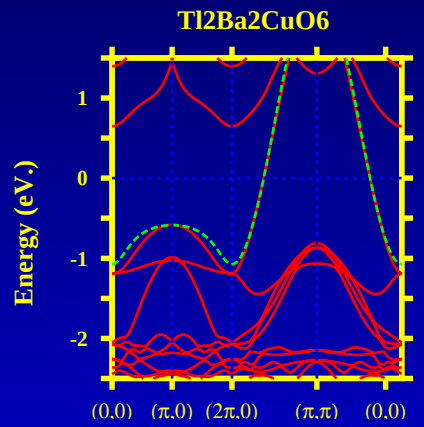
$$\begin{aligned}\epsilon(k) &= -2t(cosk_x + cosk_y) + 4t^{'}cosk_x cosk_y \\ &\quad -2t^{''}(cos2k_x + cos2k_y) + \ldots\end{aligned}$$

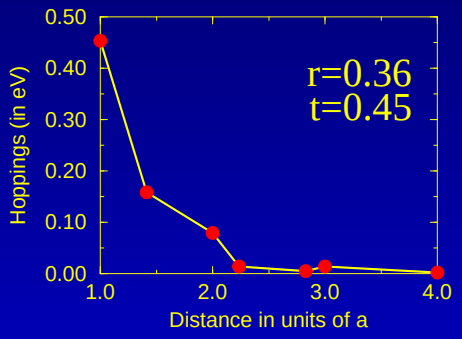
with $t^{'}/t = r + o(r)$ [range parameter]

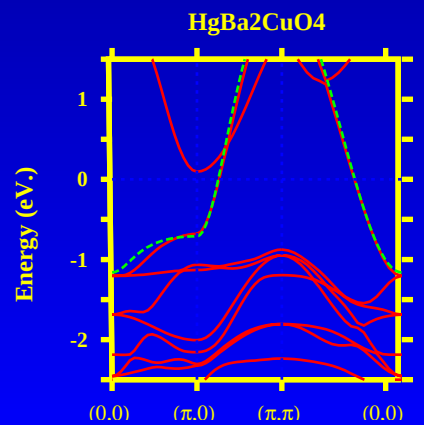
$t^{''}/t^{'} \approx 1/2$

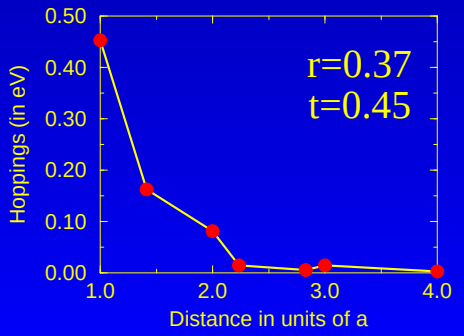

La2CuO4
Energy (eV.)
1
0
-1
-2
(0.0)
(π.0)
(2π.0)
(π.π)
(0.0)


La2CuO4
r=0.14
t=0.45
Hoppings (in eV)
0.50
0.40
0.30
0.20
0.10
0.00
1.0
2.0
3.0
4.0
Distance in units of a


Tl2Ba2CuO6
Energy (eV.)
1
0
-1
-2
(0.0)
(π.0)
(2π.0)
(π.π)
(0.0)

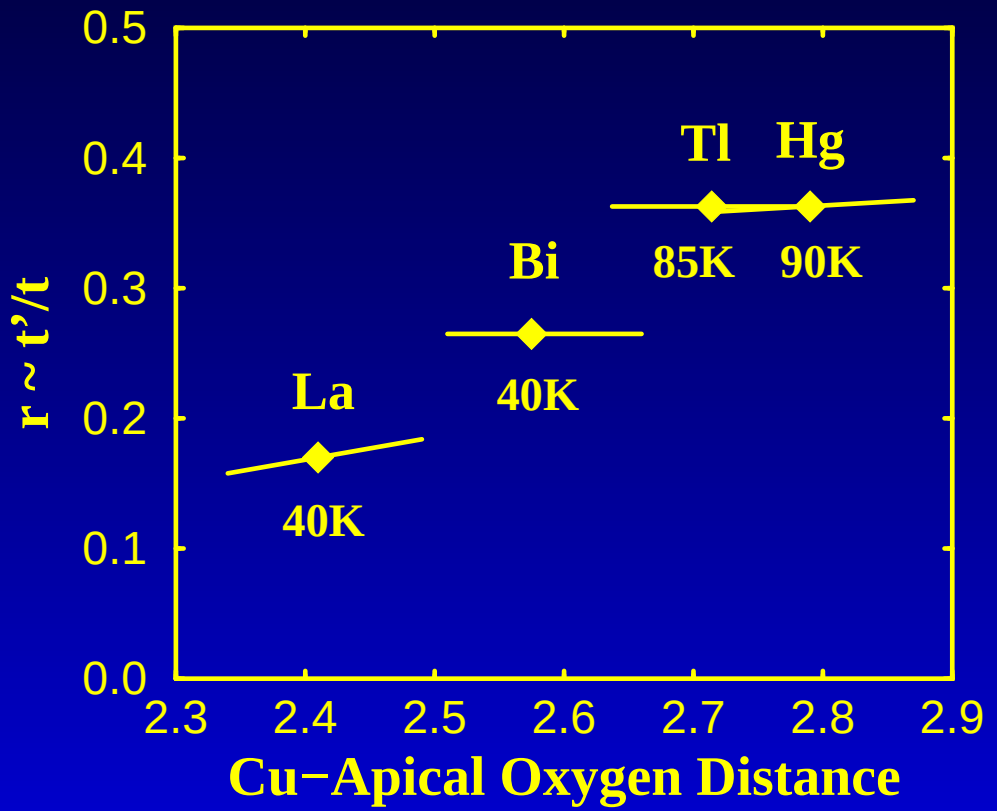

Tl2Ba2CuO6
r=0.36
t=0.45
Hoppings (in eV)
0.50
0.40
0.30
0.20
0.10
0.00
1.0
2.0
3.0
4.0
Distance in units of a


HgBa2CuO4
Energy (eV.)
1
0
-1
-2
(0.0)
(π.0)
(π.π)
(0.0)


HgBa2CuO4
r=0.37
t=0.45
Hoppings (in eV)
0.50
0.40
0.30
0.20
0.10
0.00
1.0
2.0
3.0
4.0
Distance in units of a

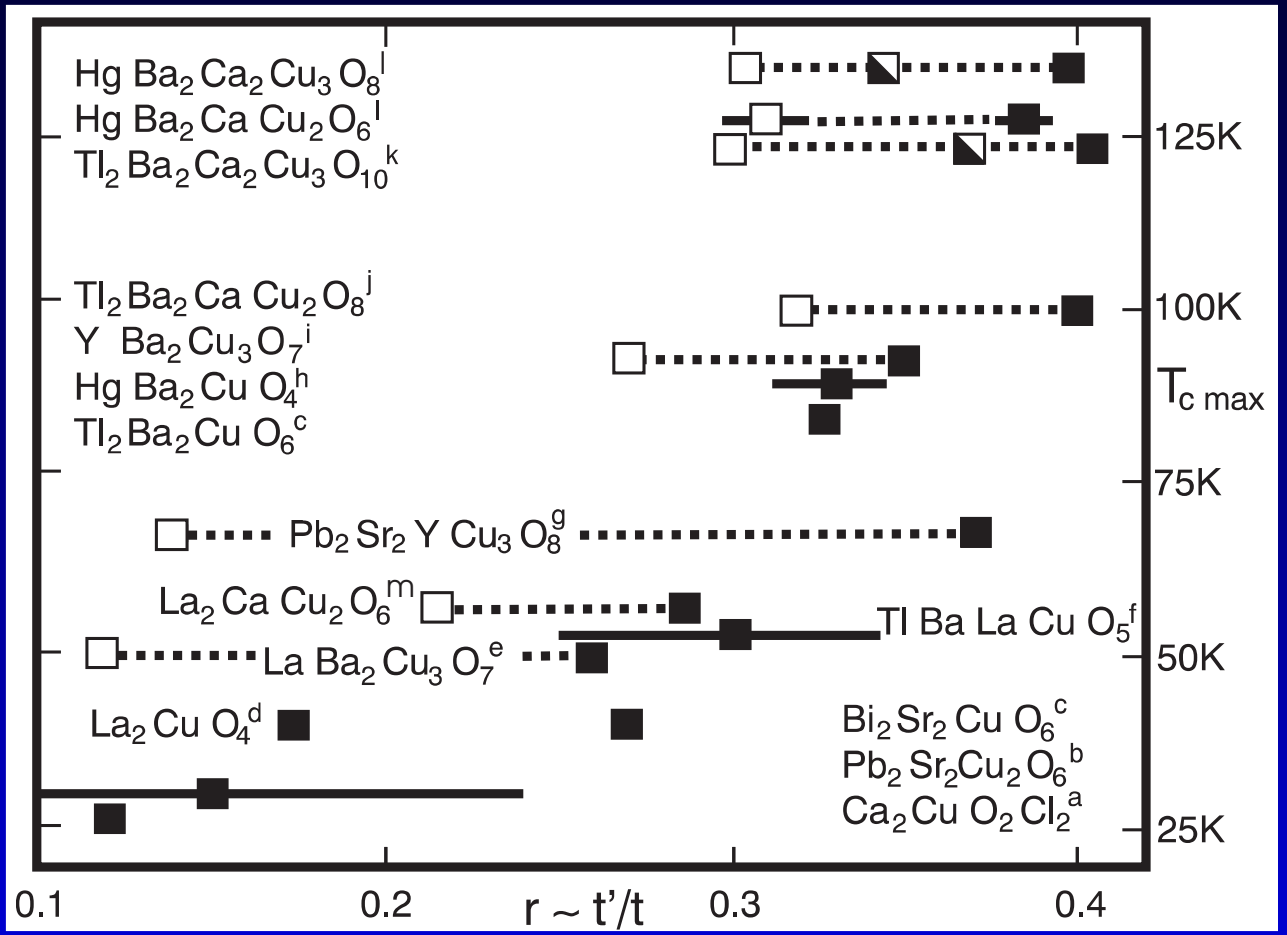
Parameters of one-band model

single-layer materials



r is controlled by the distance from Cu to apical O and the bonding of apical O to La, Bi, Tl or Hg

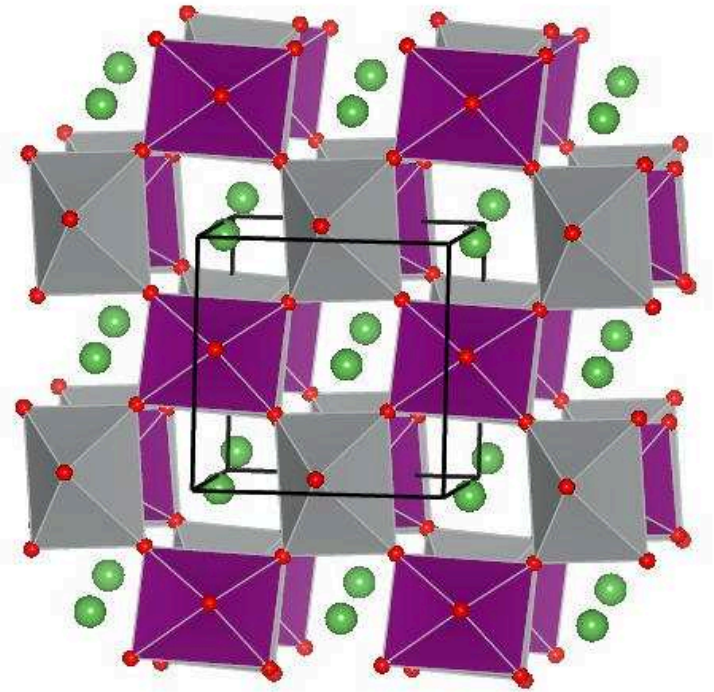
Material dependence

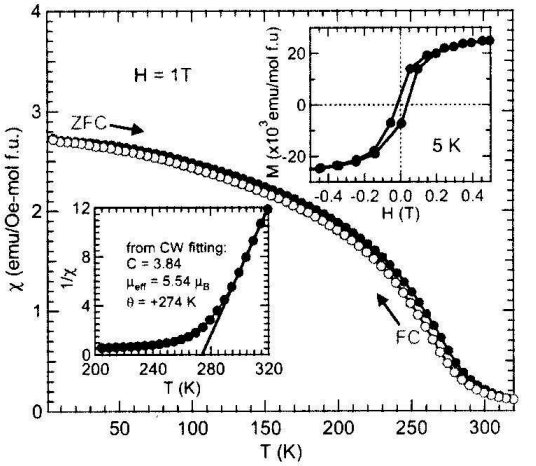


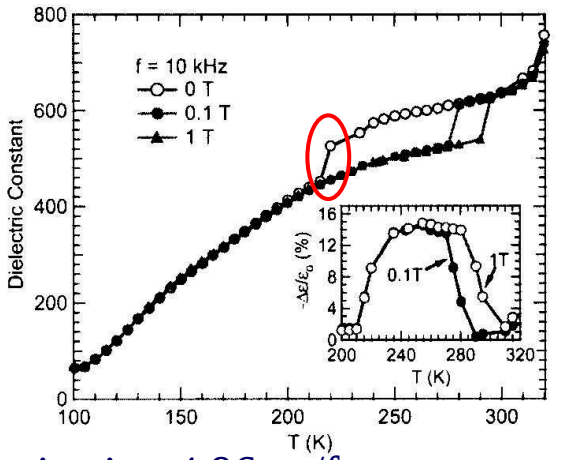
PRL 87 047003; PRB 80, 014510; PRB 79, 134522; PRB 78, 035132

La_2NiMnO_6

A FM insulating double-perovskite with magnetocapacitance at room temperature



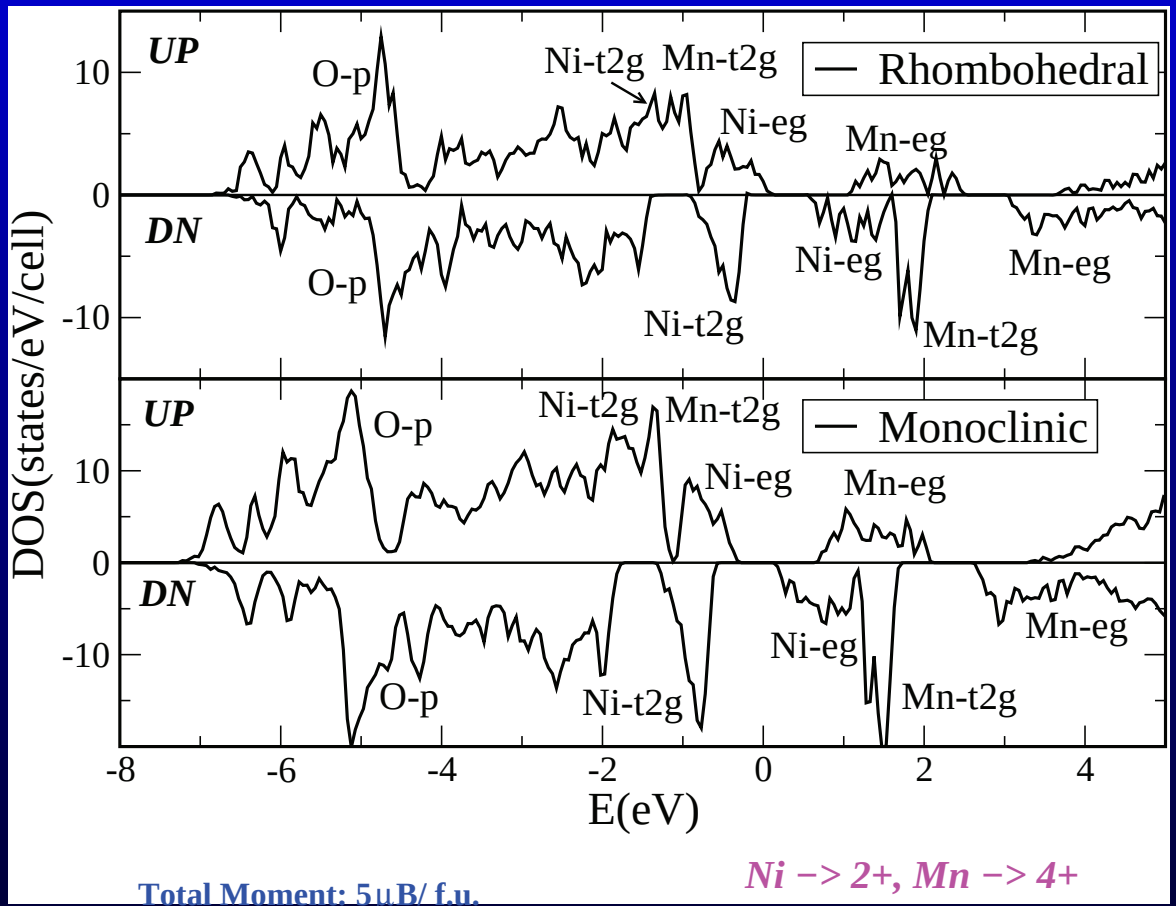




FM Tc ~ 280 K , Saturation Magnetization 4.96 μ_B/f.u.

Adv. Mater. ***17****, 2225 (2005)*

La_2NiMnO_6 - GGA electronic structure



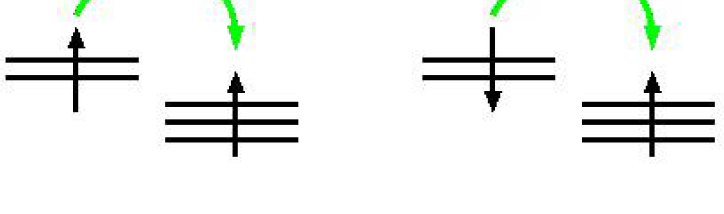
Ni −> 2+, Mn −> 4+

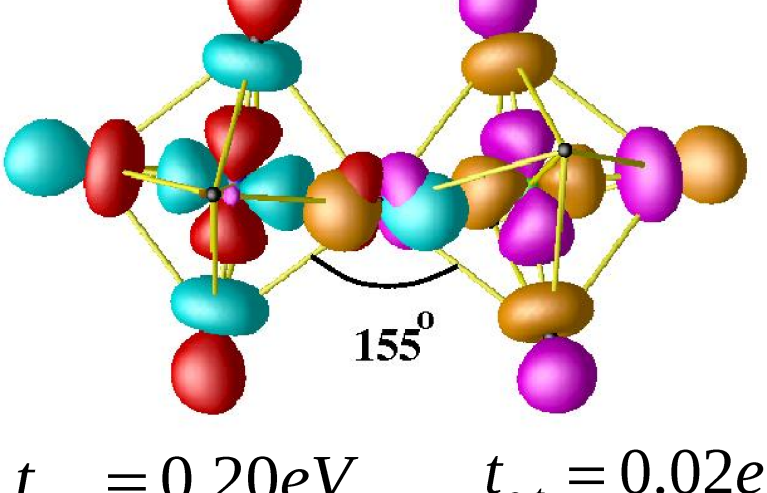
Total Moment: 5μB/ f.u.

Moment at Ni: ~ 1.5μB **Moment at Mn: 3μB**

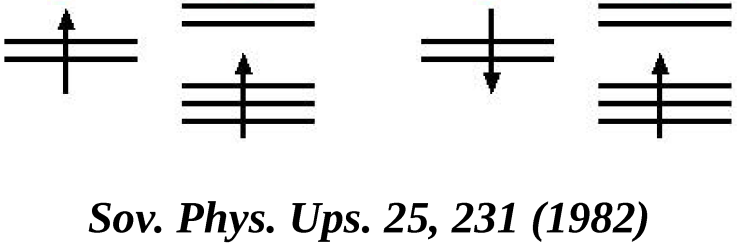
Magnetism: Extended Kugel-Khomski model

Ni eg – Mn t2g Superexchange





Ni eg – Mn eg Superexchange



$t_{e,e} = 0.20eV \qquad t_{e,t} = 0.02eV$

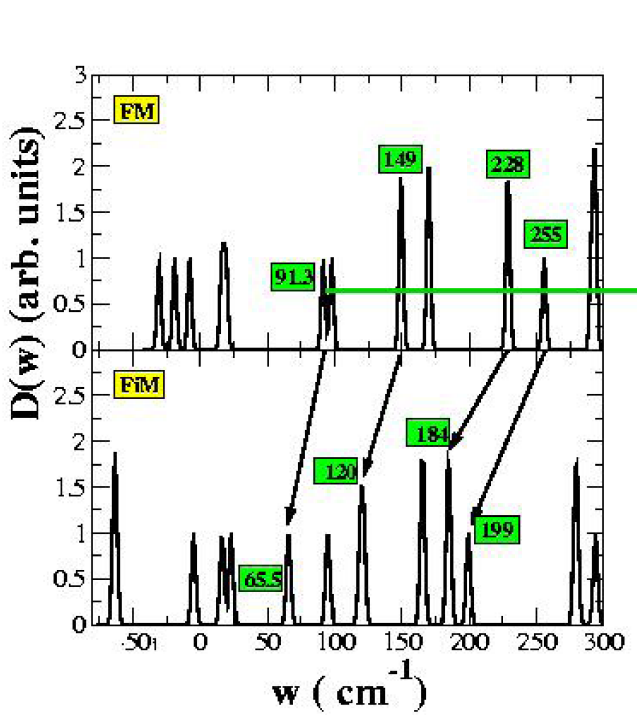
$\Delta_{e,e} = 1.90eV \qquad \Delta_{e,t} = 0.25eV$

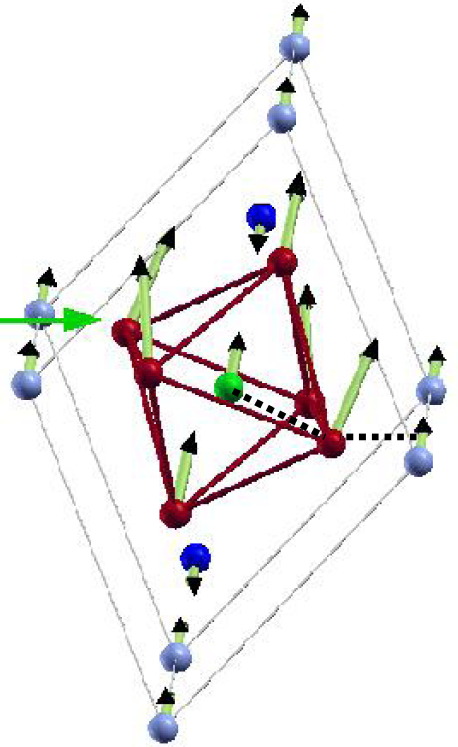
Sov. Phys. Ups. 25, 231 (1982)

$$J_{Ni-Mn} = 4\frac{\sum_{m,m'}(t_{e^m,t^{m'}})^2}{(U+\Delta_{e,t})} - 4\frac{\sum_{m,m'}(t_{e^m,e^{m'}})^2 J_H}{(U+\Delta_{e,e}-J_H)(U+\Delta_{e,e})}$$

$J_{\text{Ni-Mn}}$≈4-7 meV
(U≈4-5 eV, J_{H}=0.9 eV)

Analysis of Γ-Point Phonons and calculated dielectric constant





- Presence of soft IR-active phonon modes exhibiting strong coupling with spin.
- The lowest energy IR-active mode soften in FiM phase, in which atomic displacements make the Ni-O-Mn angles closer to 180º, indication of exchange striction.

Calculated Dielectric Constants

Static Dielectric Response : $\varepsilon_0 = \varepsilon_\infty + \varepsilon_{ph} = \varepsilon_\infty + \sum_m \frac{\sum^2_{p,m}}{\omega^2_m}$

$\varepsilon_\infty \rightarrow$ Electronic Dielectric Constant : 22 (FM) ; 20 (FiM)

$\varepsilon_{ph} \rightarrow$ Sum of contribution from each IR-active phonon.

$\sum_{p,m}$: Effective plasma frequency, calculated from Born effective charge tensor and the eigendisplacements of the phonons.

ω_m : Phonon frequency.

Calculated values : $\varepsilon_0 \rightarrow$ 119 (FM)
221 (FiM)
Dominated by the softest IR-active mode : 77 (FM)
185(FiM)

PRL 100, 186402; PRB 79, 144403

Strongly correlated electrons

LDA	Model Approaches
+ Materials−specific	− Input parameters unknown
− Fails for strong correln.	+ Account for correln. effects

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

Effective Models

- Hubbard Hamiltonian

$$H_{Hu} = -\sum_{<i,j>,\sigma} t_{ij}[\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{j,\sigma} + \hat{c}^{\dagger}_{j,\sigma}\hat{c}_{i,\sigma}] + U\sum_{i}\hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow}$$

- t-J Hamiltonian $U \gg t$ $J \approx t^2/U$

$$H_{t-J} = -\sum_{<i,j>,\sigma} t_{ij}[\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{j,\sigma} + \hat{c}^{\dagger}_{j,\sigma}\hat{c}_{i,\sigma}] + \sum_{<i,j>} J_{ij}\hat{S}_i\hat{S}_j$$

- Heisenberg Hamiltonian 1 electron/site

$$H_{Heis} = \sum_{<i,j>} J_{ij}\hat{S}_i\hat{S}_j$$

Methods

- Density Functional Theory.- Electronic structure

$$\Downarrow \; downfolding + e - e \;\; correln$$

Effective Model

$$\Downarrow$$

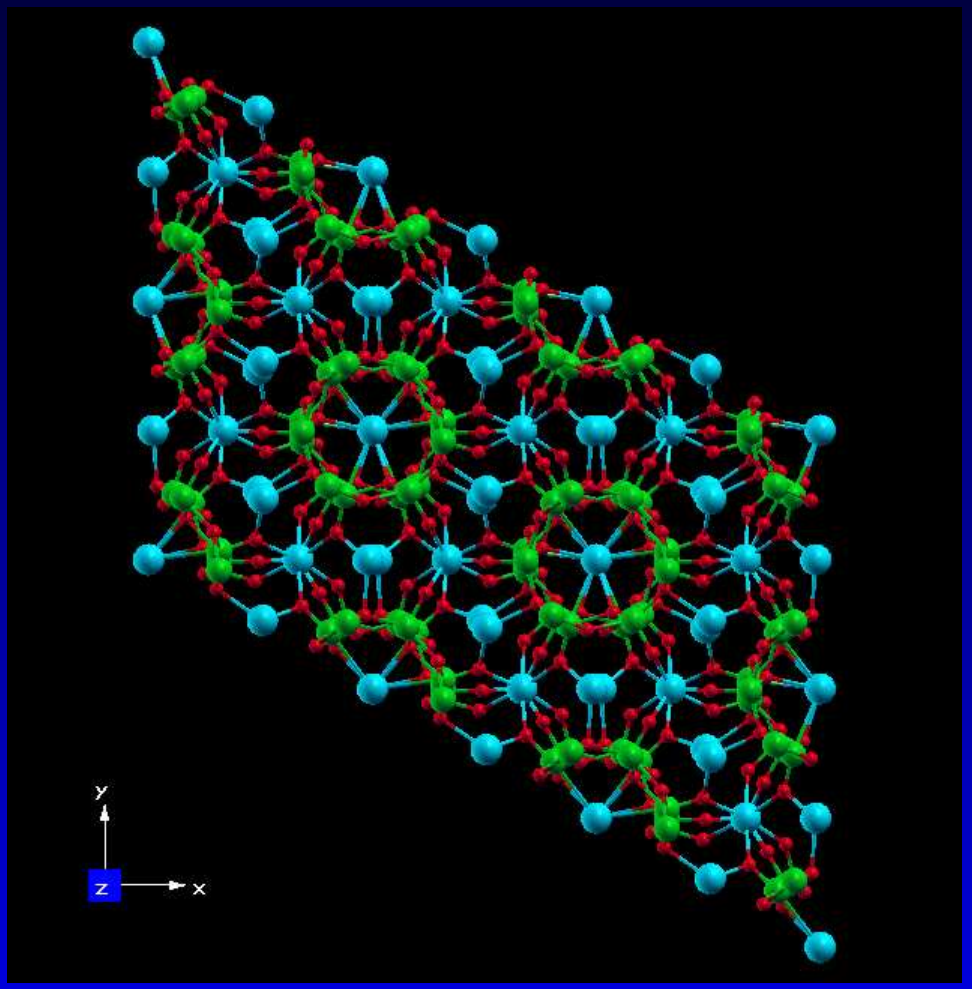
- Many-body methods.- Exact diagonalization, QMC, DMRG, Bond-Operator Theory, variational Ansätze, ...

$$\Downarrow$$

Physical Picture

QSS: Ex. Na2V3O7

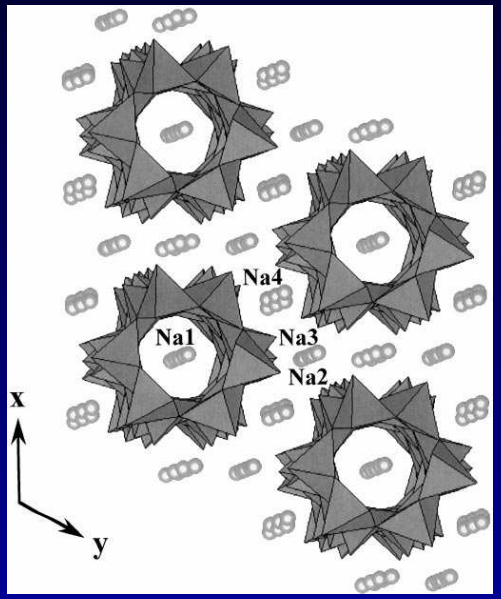
First transition-metal based nanotubular system!



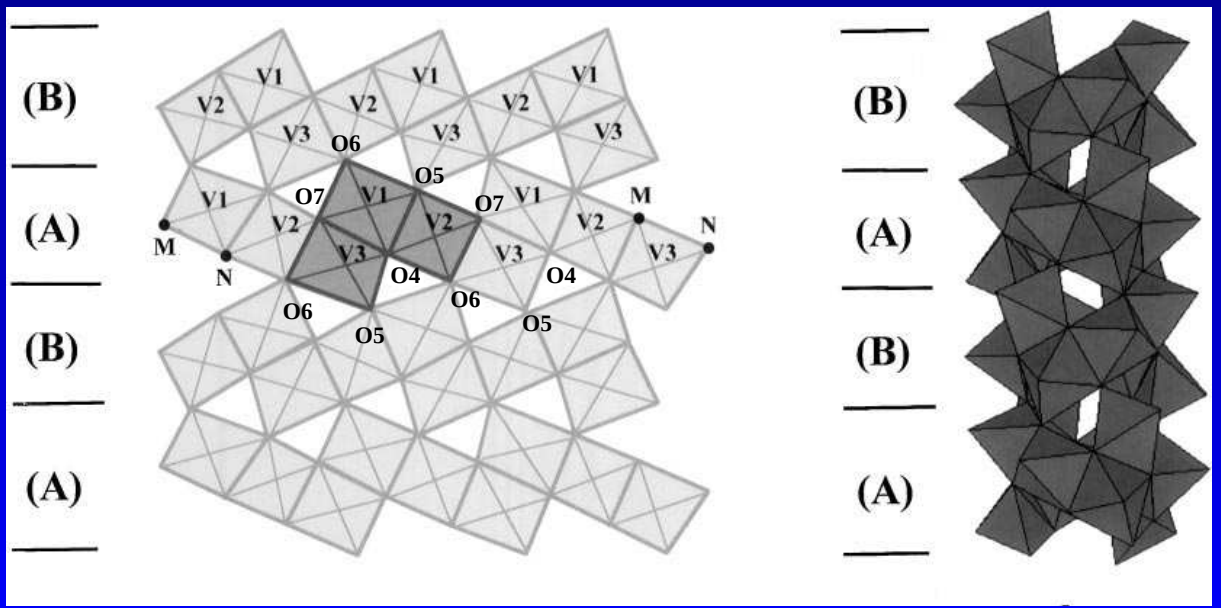
- *Na*
- *V*
- *O*

- Distorted VO_5 pyramids. V^{4+} - $3d^1$, spin-1/2 system

$Na_2V_3O_7$: Crystal Structure



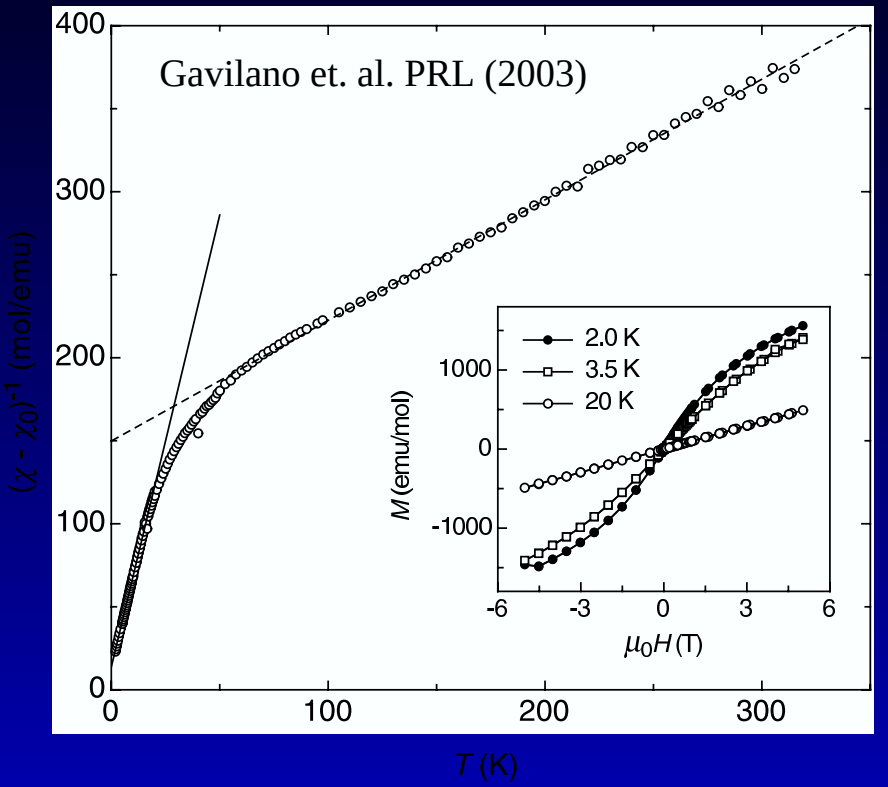
- Distorted VO5 square−pyramids
- Interaction paths:
  corner− and edge−shared pyramids
- V4+ : $3d^1$
- spin−1/2 system



Description of the underlying low-energy spin model?

- Nine-leg spin-tubes
  Millet et. al. Jour. Solid St. Chem. (1999)
- Mutually intersecting helical spin chains
  Whangbo et. al. Solid St. Comm. (2000)
- Effective three-leg spin tubes with inter-ring frustration
  Lüscher et. al. PRB (2004)
- Dimerized vanadium moments
  Gavilano et. al. cond-mat/0501756

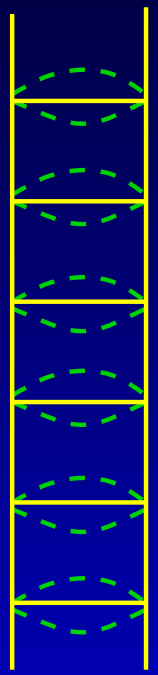
$Na_2V_3O_7$: Magnetic Susceptibility



- Curie-Weiss at high and low T: $\chi(T) = \chi_{dia} + \frac{C}{T-\theta}$
- AFM interactions
- *reduction* in effective magnetic moment high T $\longrightarrow$ low T

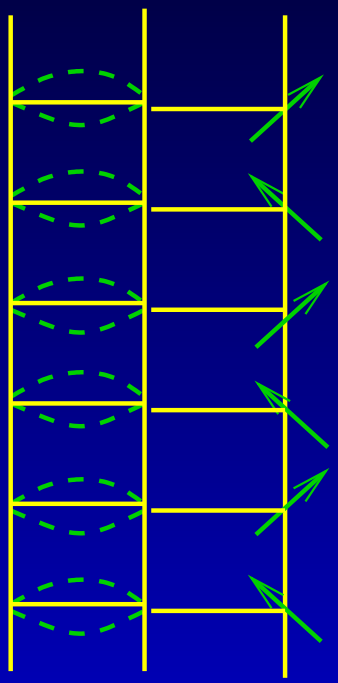
AFM spin-1/2 Ladder Systems

- **Even−leg ladders**

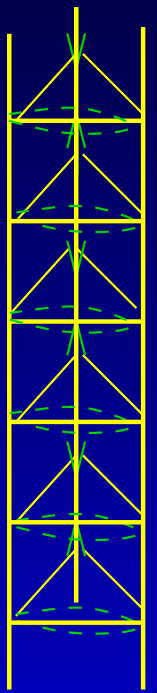


- **Odd−leg ladders**

O.B.C



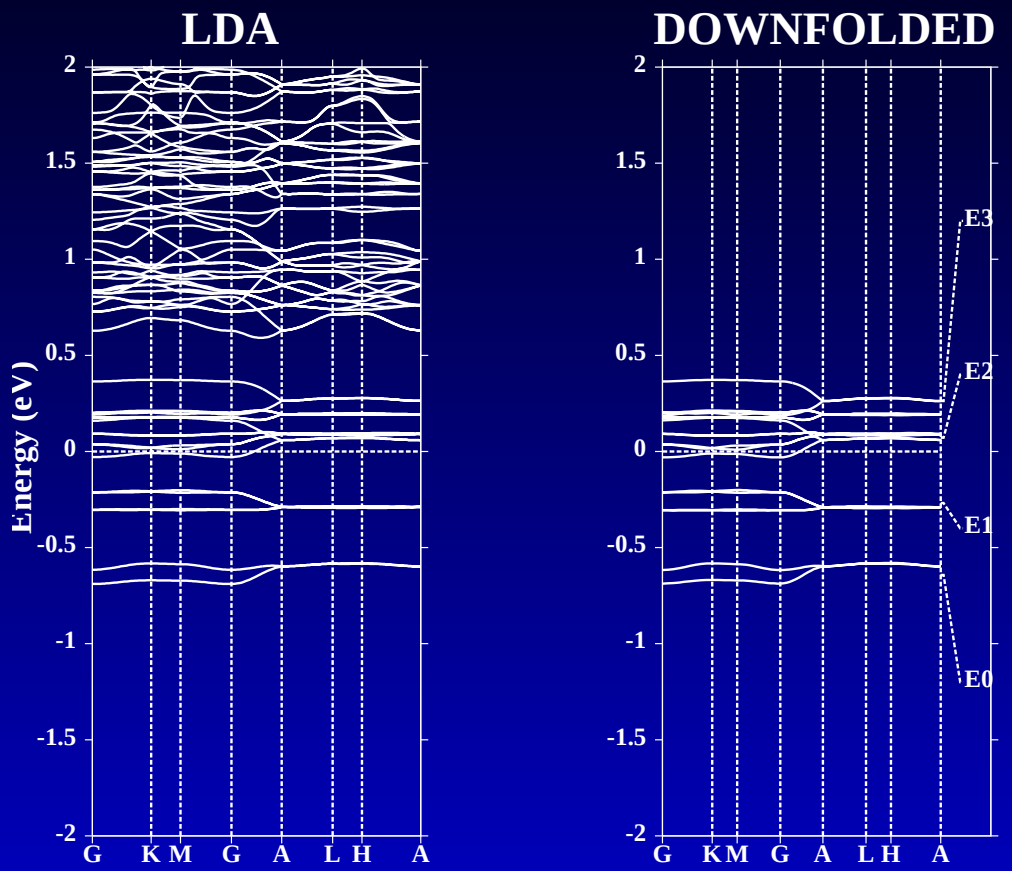
P.B.C



Even-leg: spin-singlets → **spin-gap**

Odd-leg : O.B.C → **no spin-gap**, : P.B.C → spin + chirality → **spin-gap**

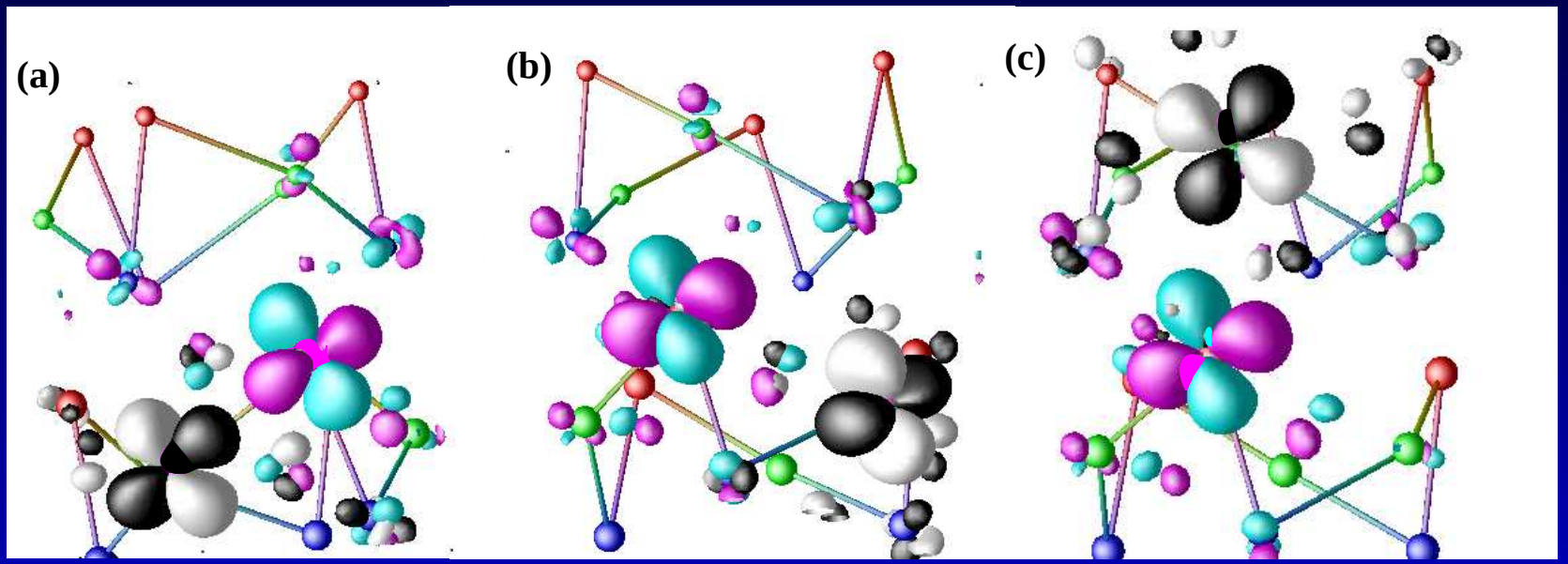
Na2V3O7: Electronic Structure



- V- d_{xy} character at EF.
- For modeling only the low-energy part matters.

$Na_2V_3O_7$ - Effective Model

● V1 ● V2 ● V3



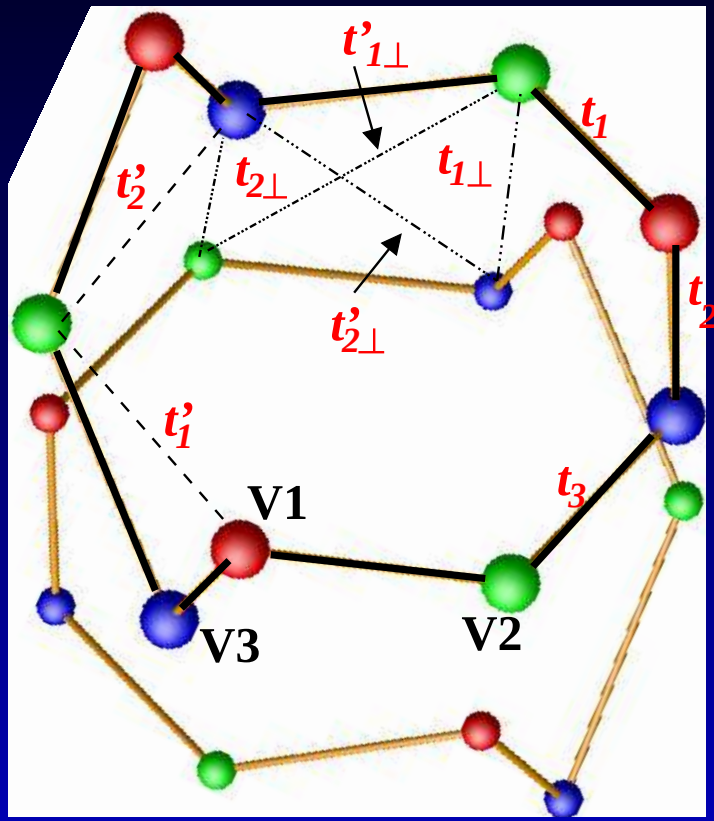
edge−sharing intra−ring V1−V2 (t_1 = −0.18 eV)

corner−sharing intra−ring V1−V2 (t_1' = −0.13 eV)

corner−sharing inter−ring V1−V2 ($t_\perp$ = −0.03 eV)

The edge-shared coupling is as strong as corner-shared

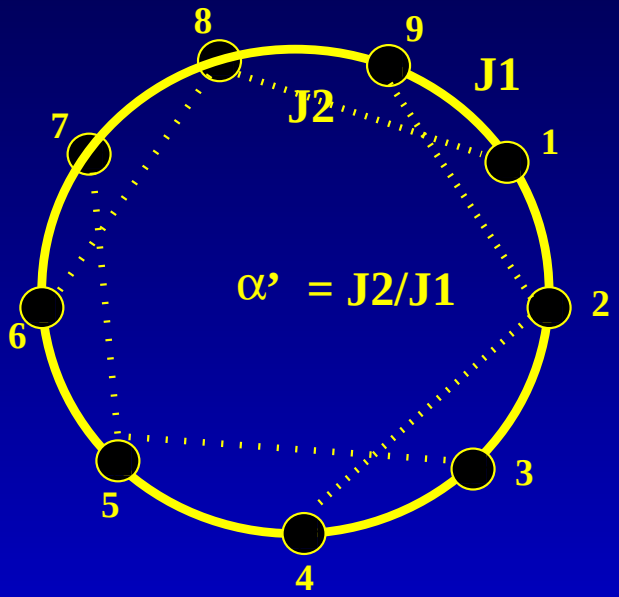
$Na_2V_3O_7$ - Effective Model



Intra−ring (eV)					Inter−ring (eV)			
t_1	t_2	t_3	t'_1	t'_2	$t_{1\perp}$	$t_{2\perp}$	$t'_{1\perp}$	$t'_{2\perp}$
−.18	−.15	−.14	−.13	−.14	−.03	−.02	−.02	−.03

$Na_2V_3O_7$ - Effective Model

description: tubes consisting of weakly coupled nine-site rings with partial frustration



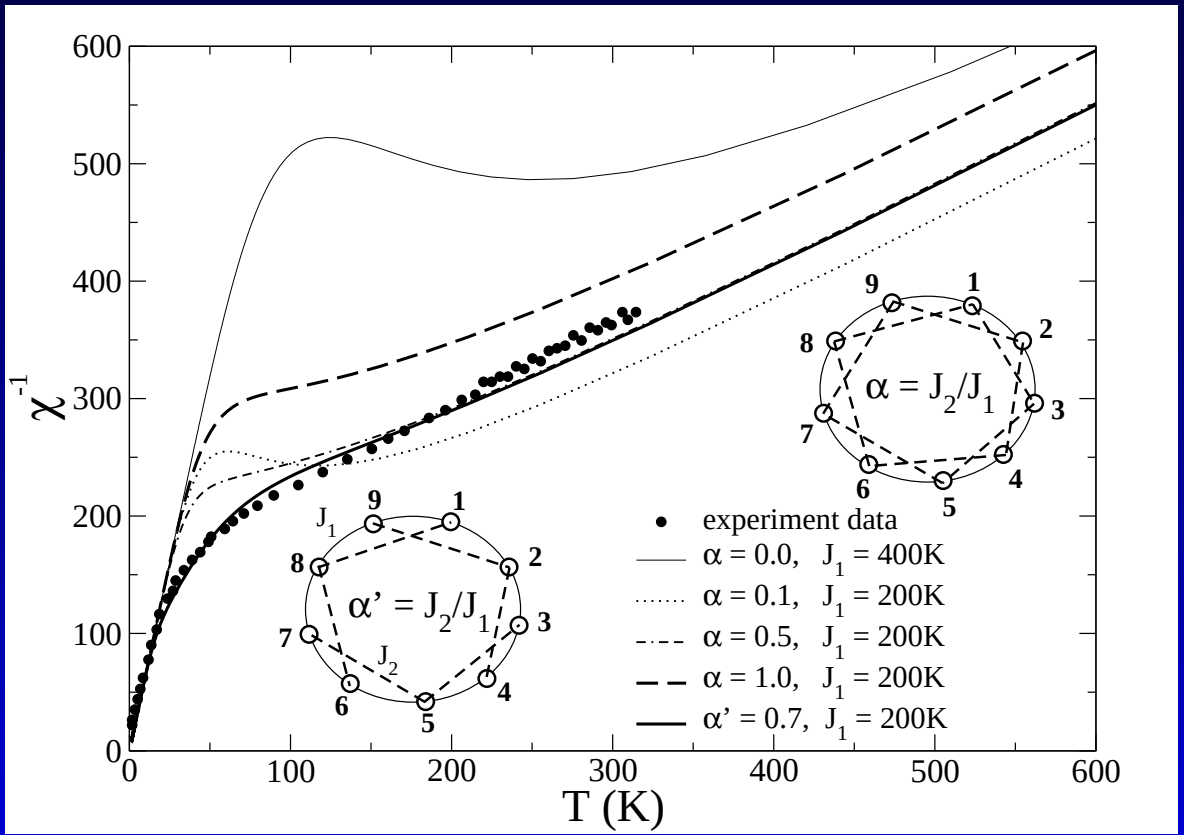
Effective spin Model :

- **neglect inter−ring coupling**
- **t1 ~ t2 ~ t3**
- **t'1 ~ t'2**

$$H = J_1 \sum_{i=1}^{9} (S_i . S_{i+1} + \alpha_i^{'} S_i . S_{i+2})$$

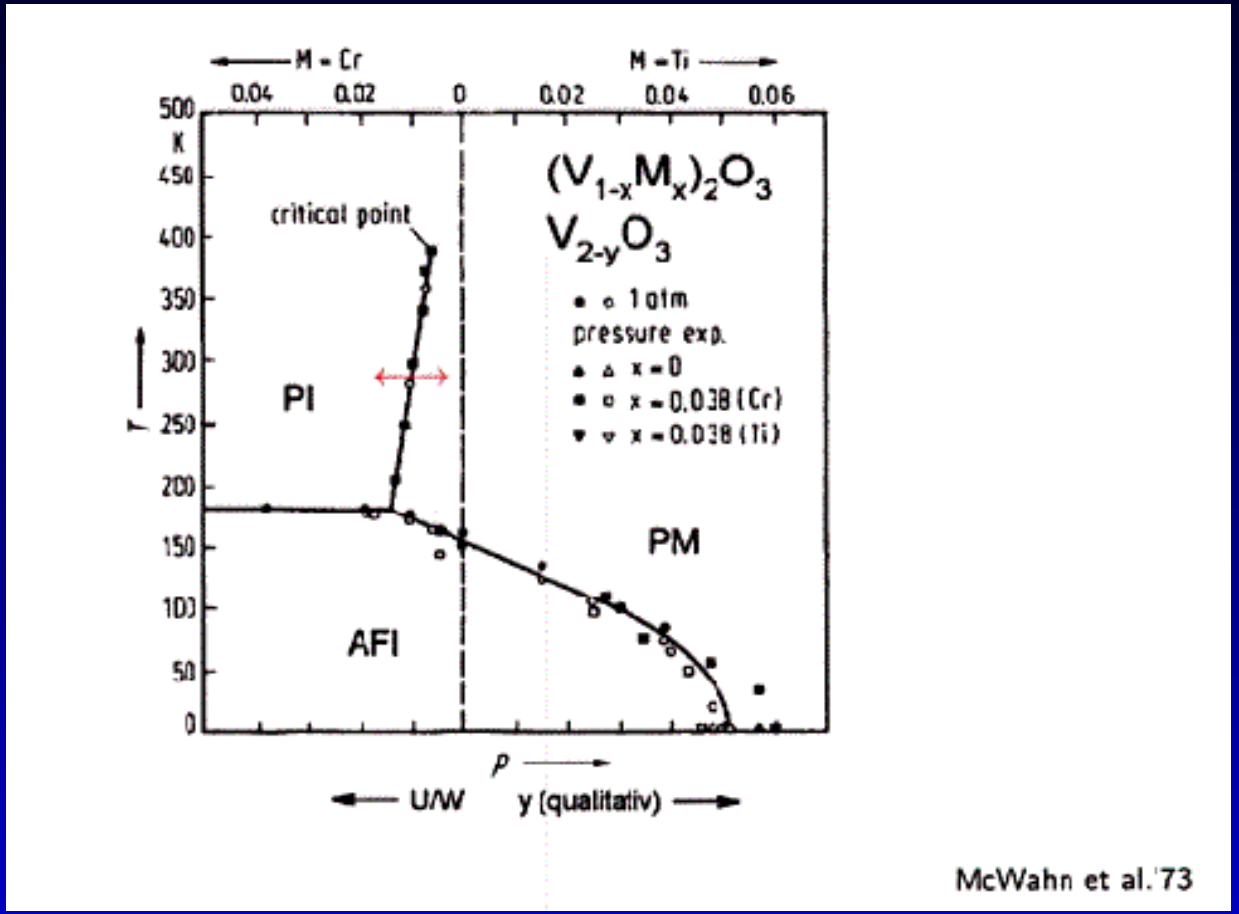
$Na2V_3O_7$ - Magn. Susceptibility

Exact diagonalization of the derived spin-Hamiltonian



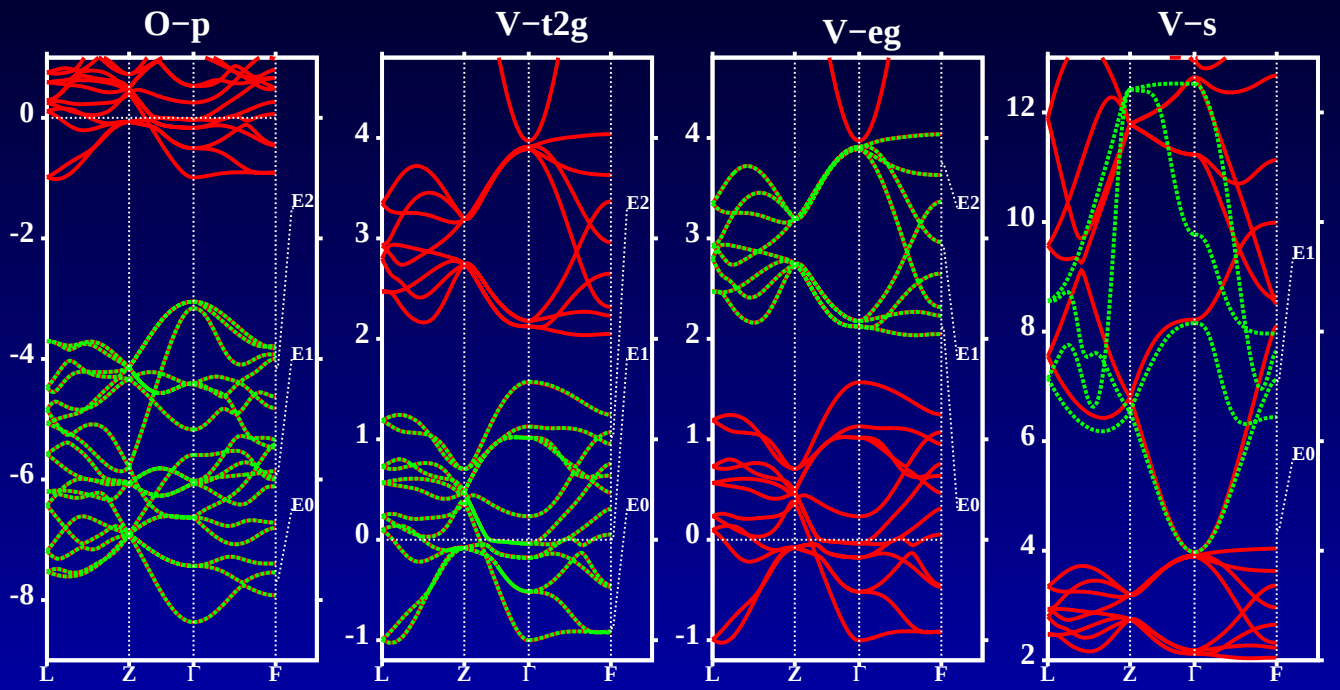
PRL 95, 107201, PRB 68, 024411, PRB 67, 245110, PRB 66, 054426, ..

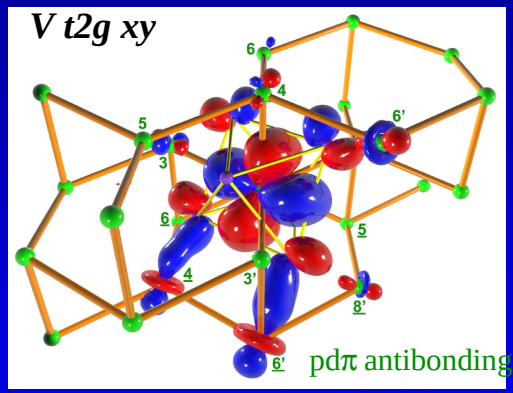
Phase diagram of V_2O_3

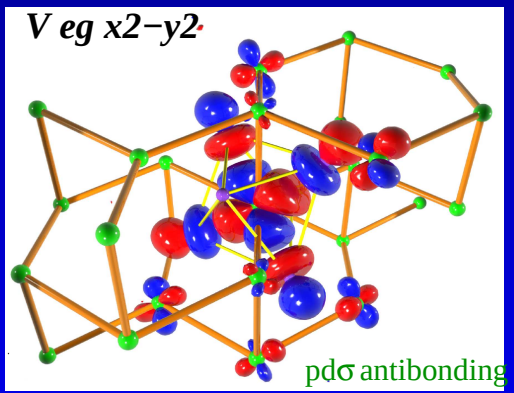


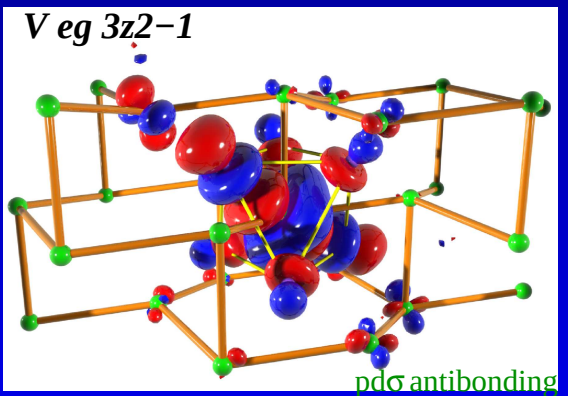
* undergoes 1st−order M−I transition − can be induced by temp., pressure, alloying
* PM−PI : same crystal (corundum) & magn. structure
* only known example among transition−metal oxides to show aPM−PI transition

NMTO-downfolding



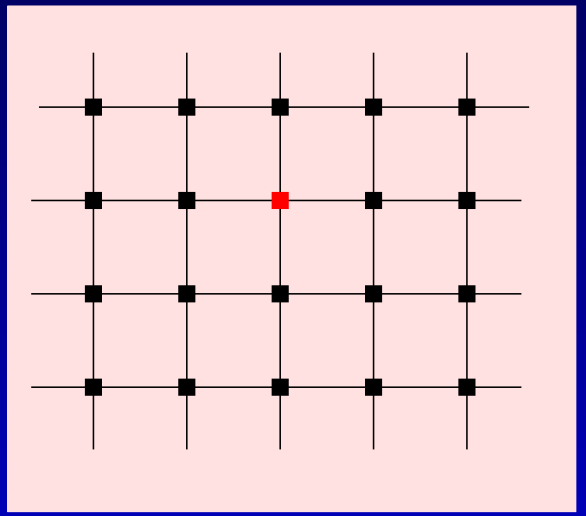






DMFT: General Idea (RMP, 96)

Replace a LATTICE MODEL of itinerant electrons by a SINGLE-SITE (impurity orbital) hybridized with a SELF-CONSISTENT BATH



Single out one site
= impurity site

Embed it in an
Effective medium

which is built out of
the other sites in a
self−consistent manner,
so as to restore translation invariance

- Freezes the space fluctuation, but keeps the dynamics.
- Needs to solve a quantum impurity problem.

V_2O_3: LDA(NMTO)+DMFT

Input Hamiltonian - low-energy, multi-band Hamiltonian defined in a localized t_{2g} basis:

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

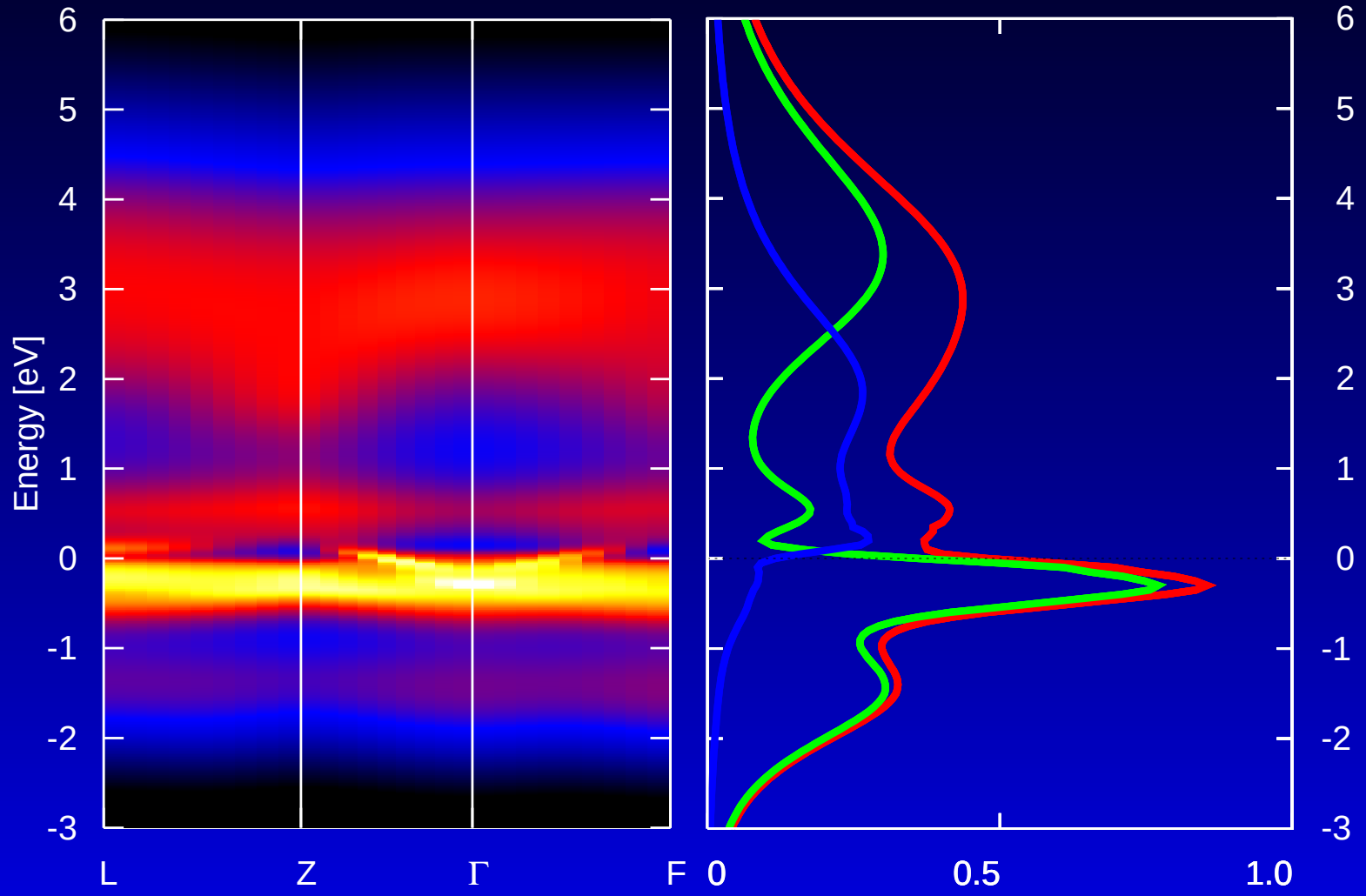
The many-body Hamiltonian depends on the choice of the basis func.– **NMTO's are the ideal candidates!**

$\Rightarrow$ Many-body Hamiltonian solve by DMFT.

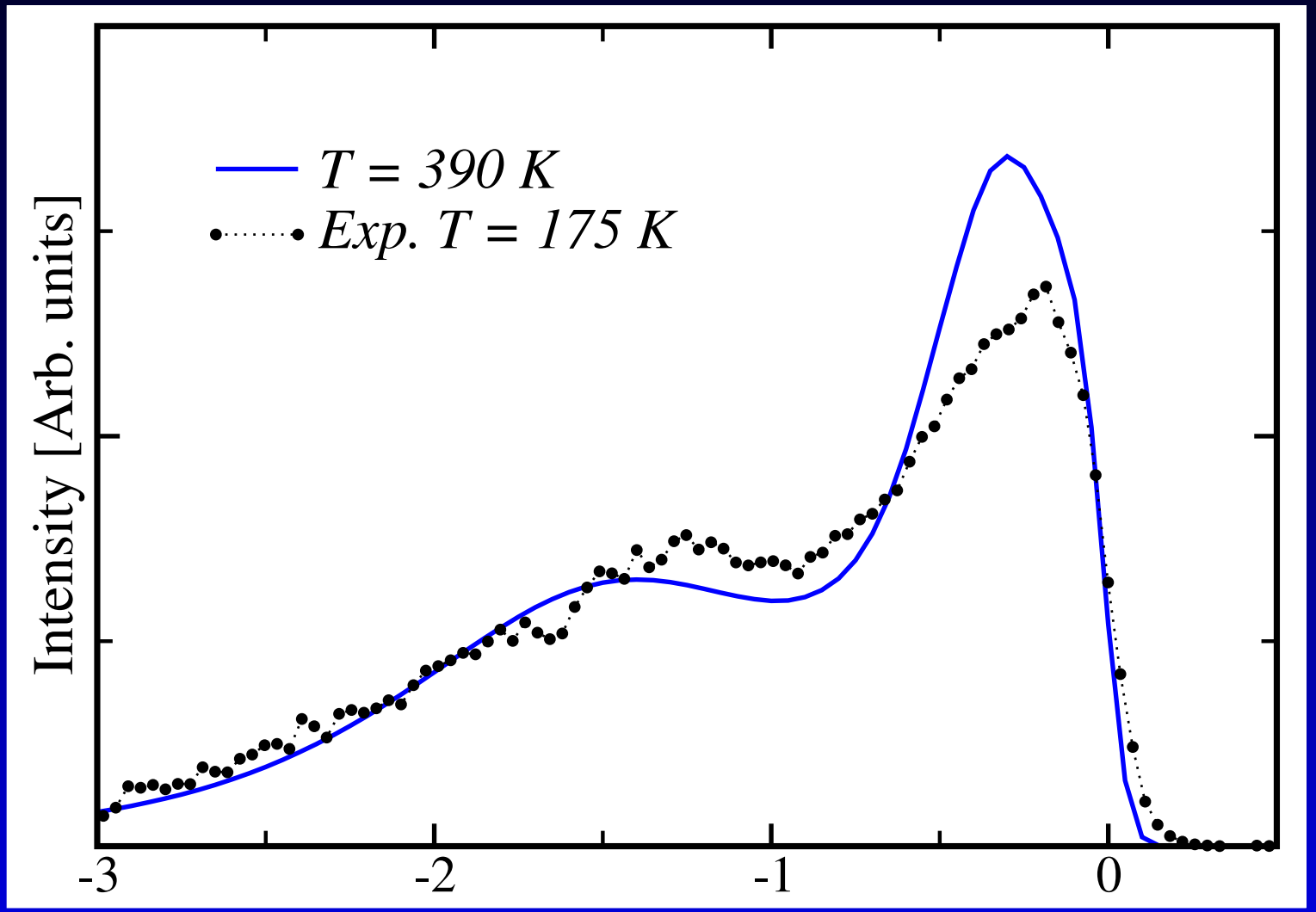
$\Rightarrow$ Multi-orbital quantum impurity problem solve by QMC.

$\Rightarrow$ Takes into account full structure of the self-energy.

DMFT results



PM spectra - comp. with PES



Expt:

Mo *et.al.*

Conclusion

♣ NMTO method can be employed very efficiently to unravel chemical bonding and physical properties of novel materials.

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