LDA+U: a simple Hubbard correction for correlated ground states

Matteo Cococcioni

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Outline

- Brief introduction to some of DFT most notable failures
- The Hubbard model
- DFT+U: formulation
- Breaking the symmetry
- Computing U from linear response
- LDA+U for metals: FLL and AMF flavors
- Band and Mott insulators: the LDA+U+V extension
- Magnetism and particle/hole localization
- Energy derivatives from the LDA+U ground state
- Summary

Density Functional Theory

W. Kohn,
1998 Nobel Laureate
in Chemistry

Main advantage: using $\rho(\mathbf{r})$ instead of $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N)$

electronic charge density (3 space variable)

N-electron wave function (3N space variables)

- Hoenberg - Kohn: $V_{ext}(\mathbf{r}) \leftrightarrow \rho_{GS}(\mathbf{r})$ $E[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$
- Minimization of the *total energy* functional ($\int \rho(\mathbf{r})d\mathbf{r} = N$) ➡ ground state

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- Mapping onto a non interacting system with the same density

$$E[\rho(\mathbf{r})] = T_0[\rho(\mathbf{r})] - e^2 \sum_I \int \frac{Z_I \rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} d\mathbf{r} + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho(\mathbf{r})]$$

$$\rho(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$ (from the mapping on to an independent electron system)

P. Hoenberg and W. Kohn, *Phys. Rev.* 136, B864 (1964)

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- While exact in principle, actual implementations of DFT require approximations for E_{xc}

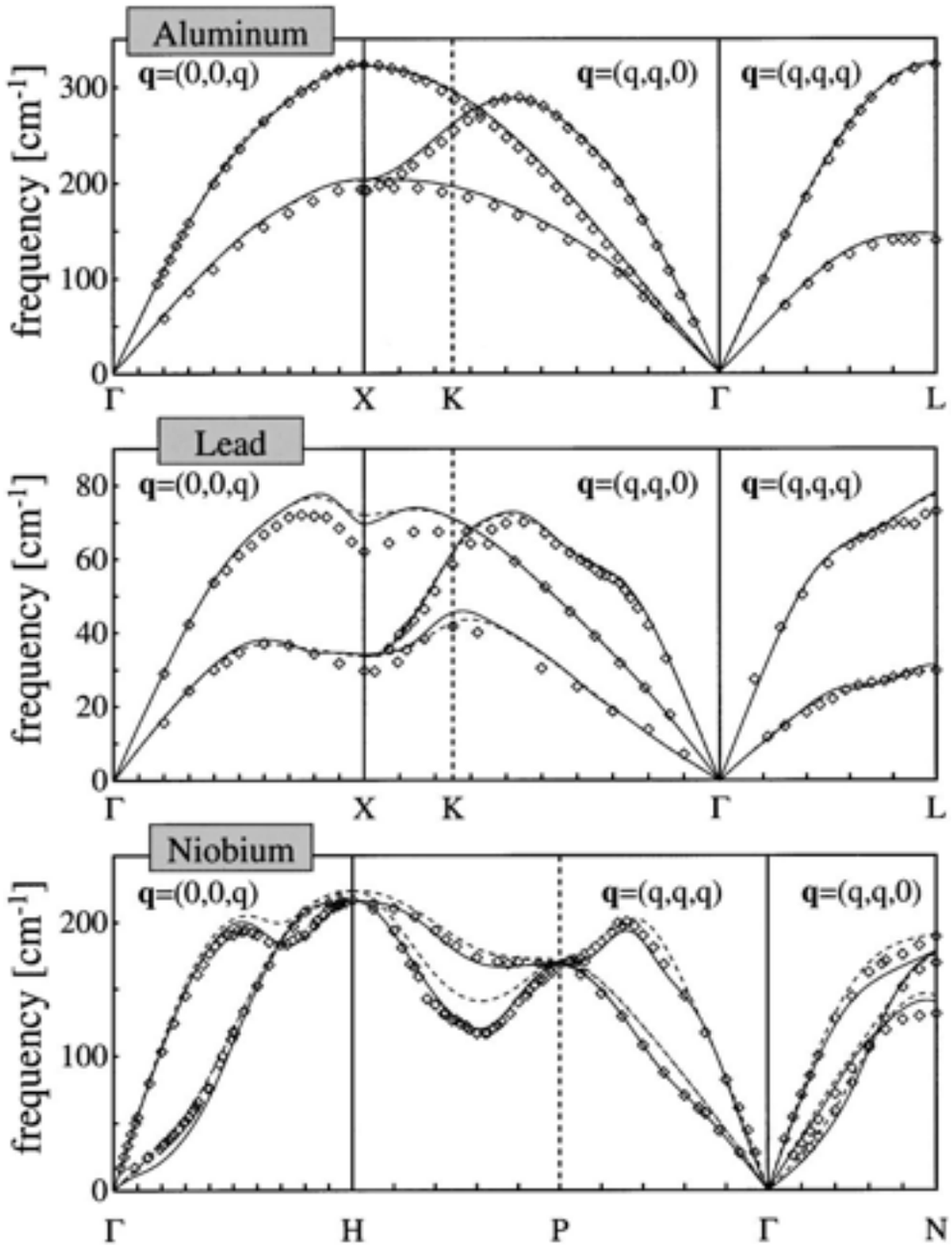
LDA

$$E_{xc}[\rho] = \int \epsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}$$

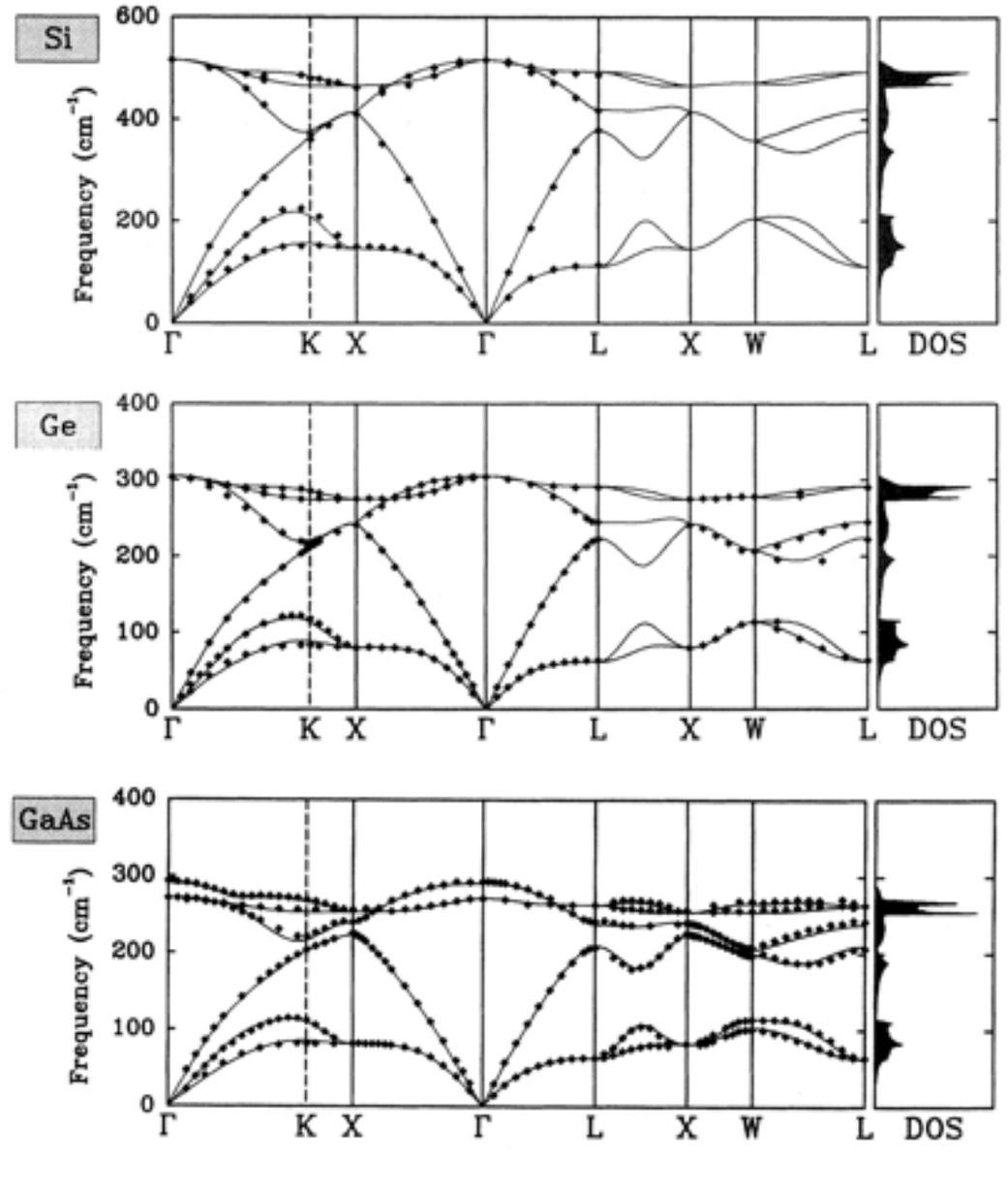
GGA

$$E_{xc}[\rho] = \int \epsilon_{xc}(\rho(\mathbf{r}); |\nabla\rho(\mathbf{r})|)\rho(\mathbf{r})d\mathbf{r}$$

How well does DFT work?

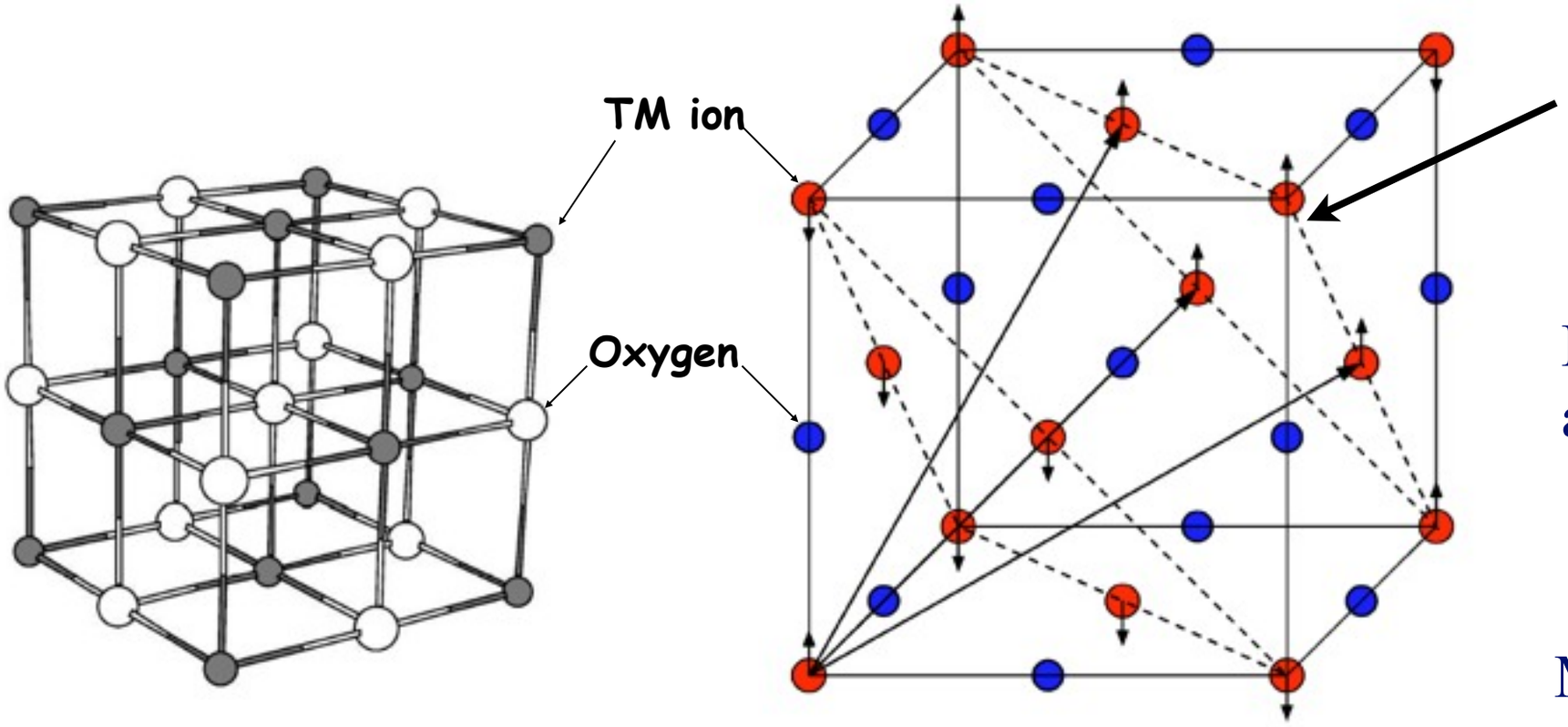


S. Baroni *et al.*, *Rev. Mod. Phys.* 73, 515 (2001)



P. Giannozzi *et al.*, *Phys. Rev. B* 43, 7231 (1991)

Problematic cases: TMOs



AFII ground state

Rhombohedral symmetry and (possible) distortions

INSULATORS

Mott localization of valence electrons on *d* states

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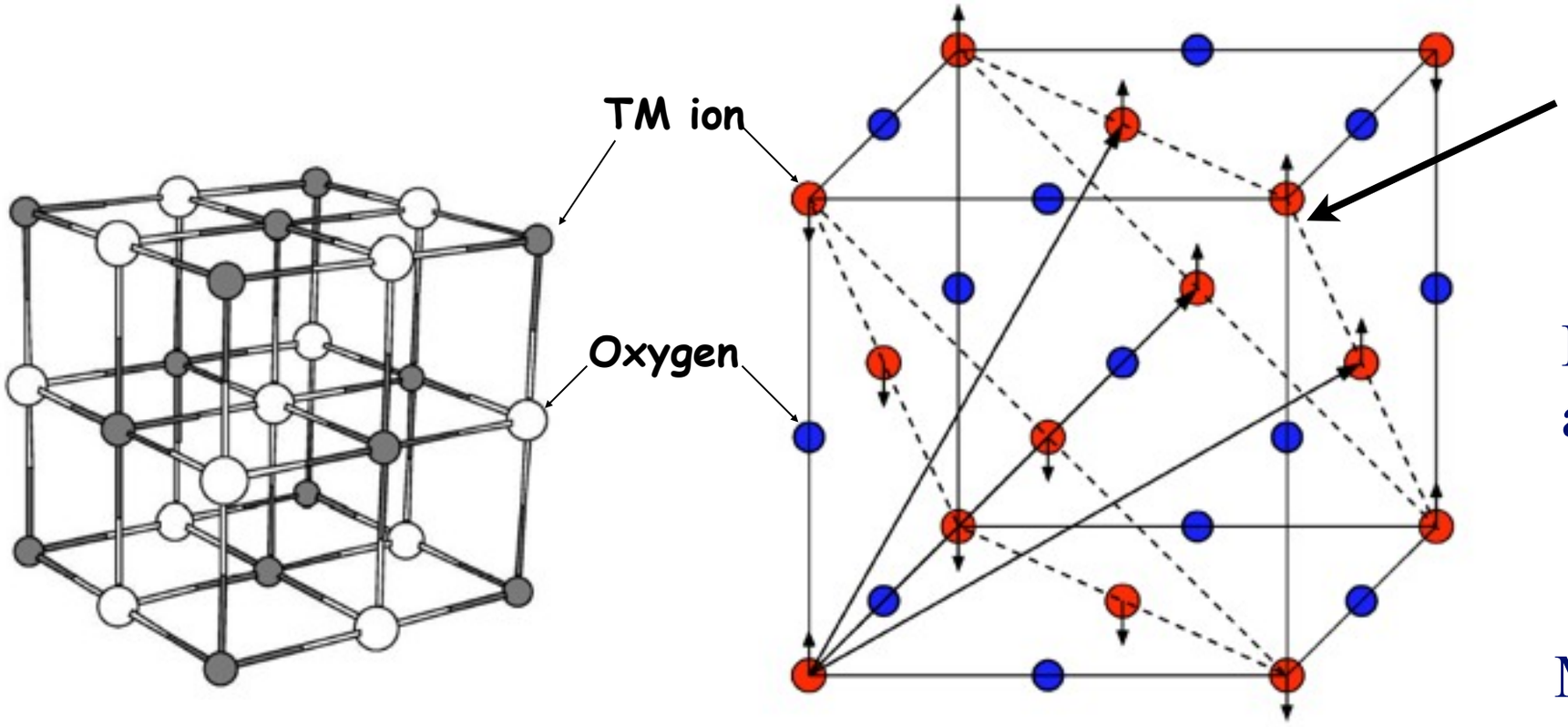

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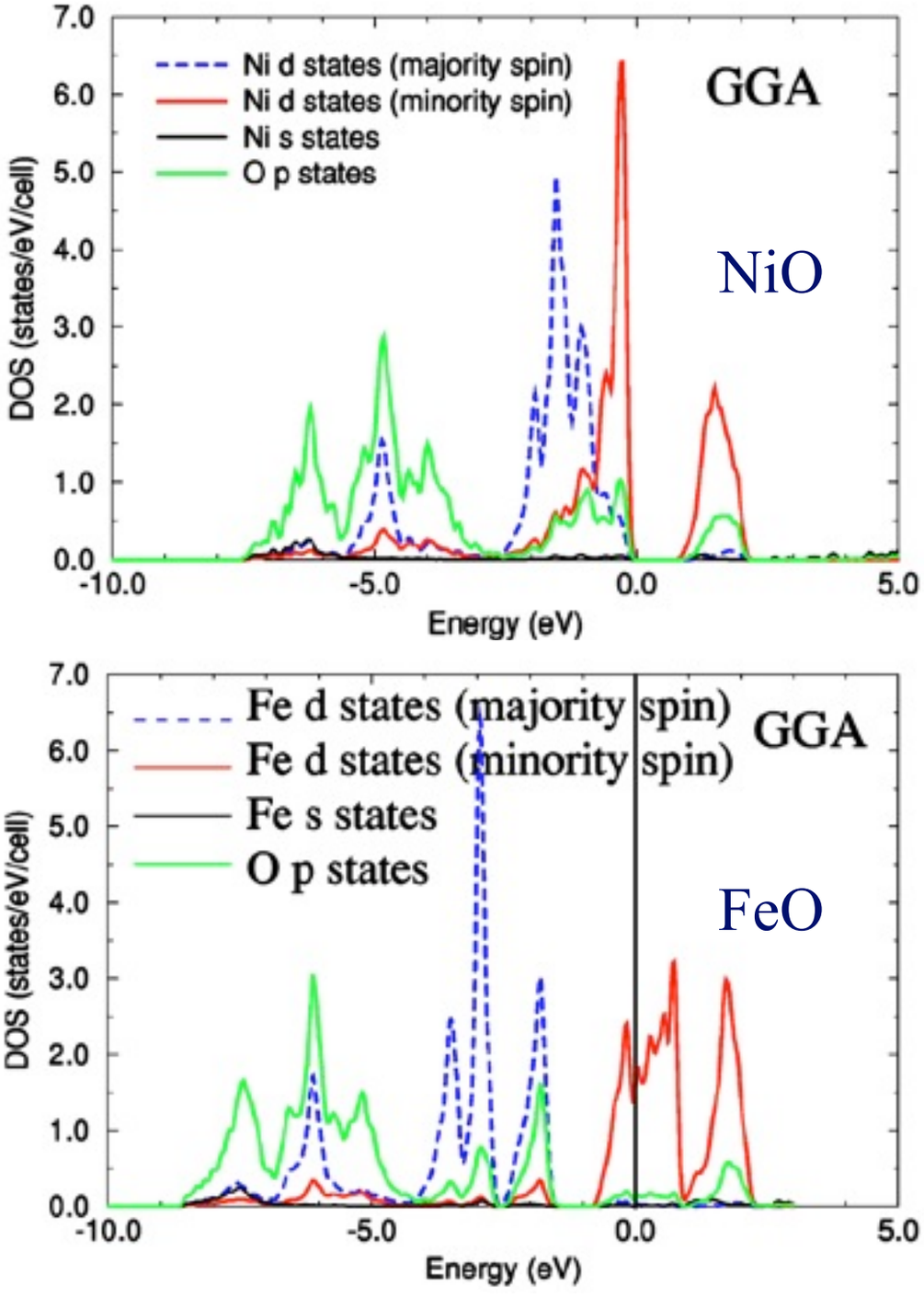
Approximate DFT (e.g., LDA or GGA):

- Rhombohedral distortion overestimated
- Poor estimate of structural properties
- **FM ground state (FeO)**
- Too small or no gap at all
- Magnetization underestimated
- Wrong ordering of states

Problematic cases: NiO and FeO



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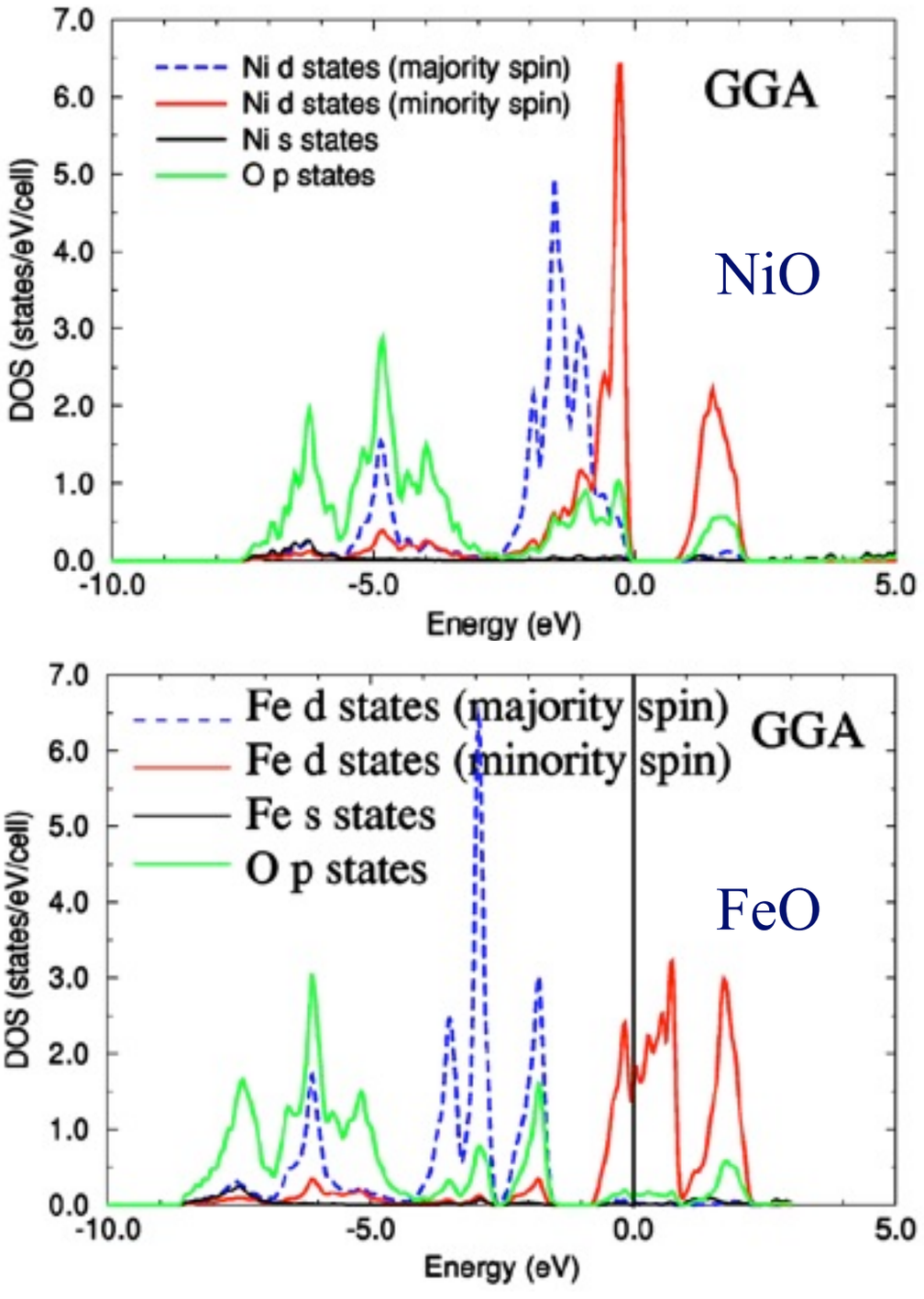
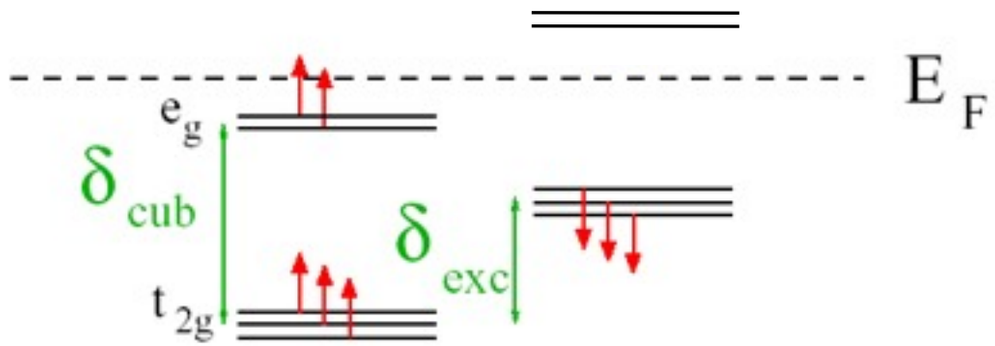
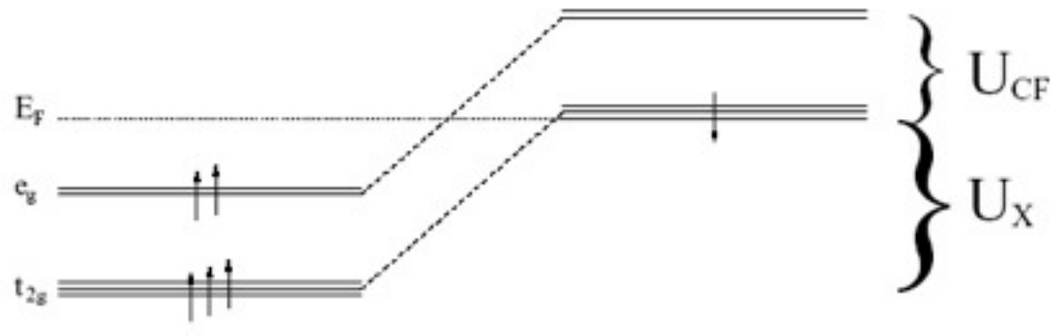


Ni^{2+}



The gap is underestimated
O *p* states not at the to of valence band

Fe^{2+}



No gap at all: metallic ground state

Notable failures of DFT: molecular dissociation

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Let's consider the dissociation of H_2

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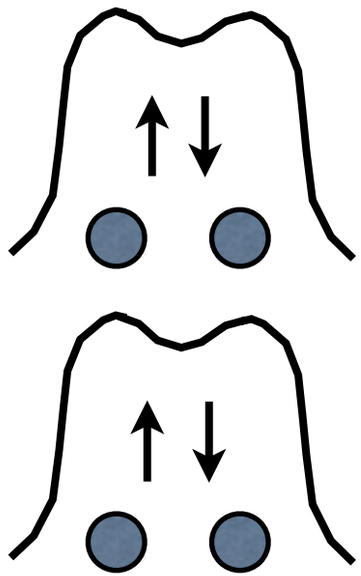
Exact:



DFT:

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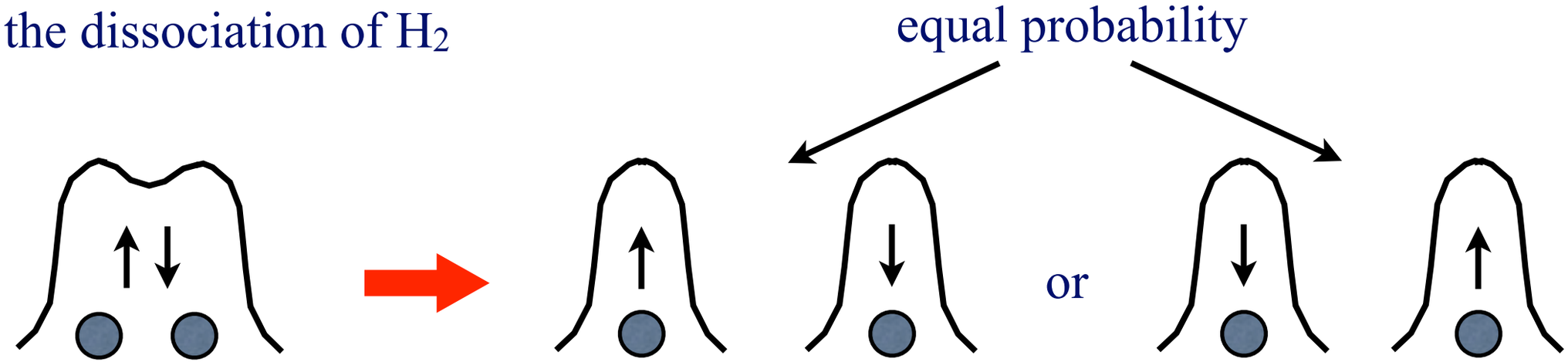

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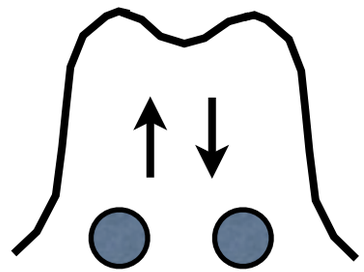

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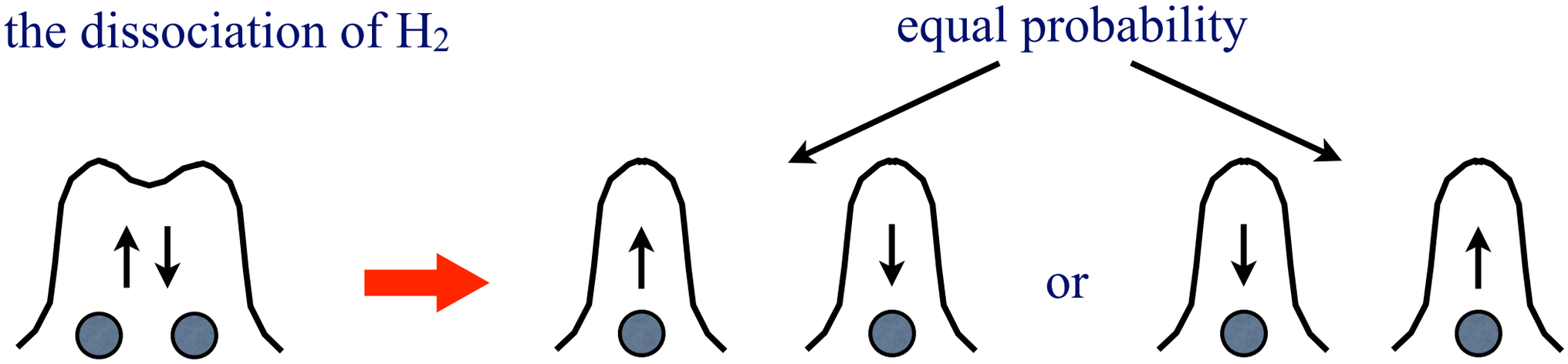

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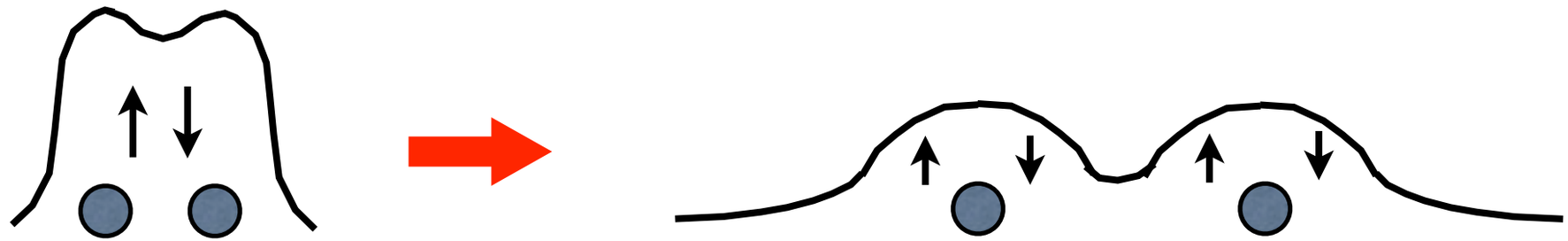

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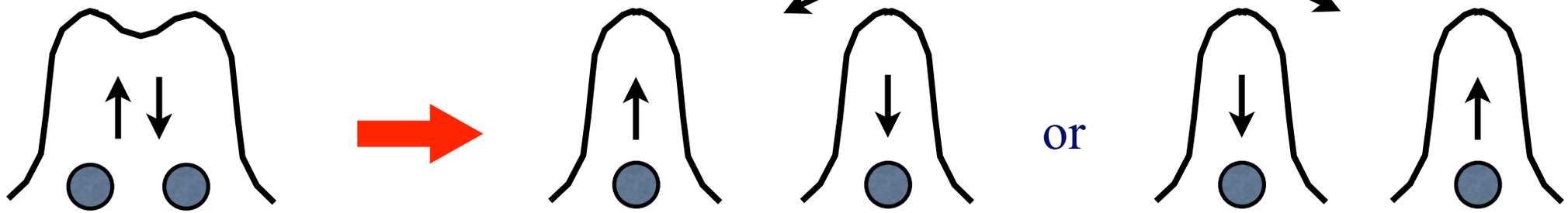

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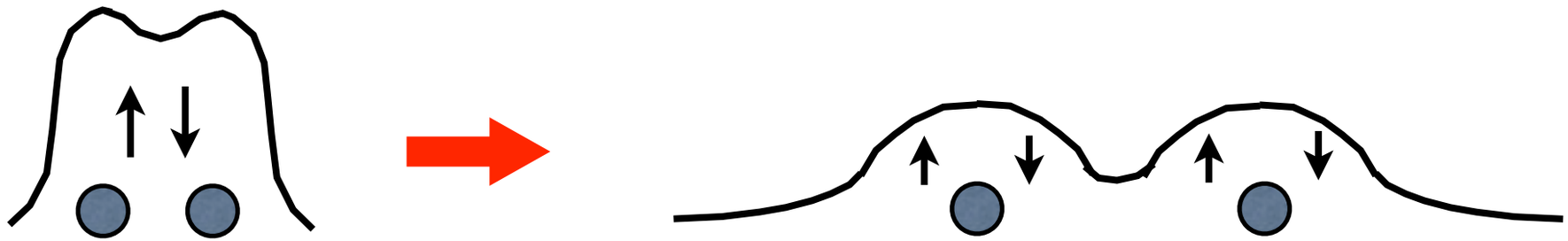

Many possible ways to interpret these results:

- electronic self-interaction
- misrepresentation of exchange interactions
- single determinant wave function
- absence of potential discontinuity
- over-delocalization of electrons
- over-stabilization of metallic solutions
- inability to capture statistical ensembles

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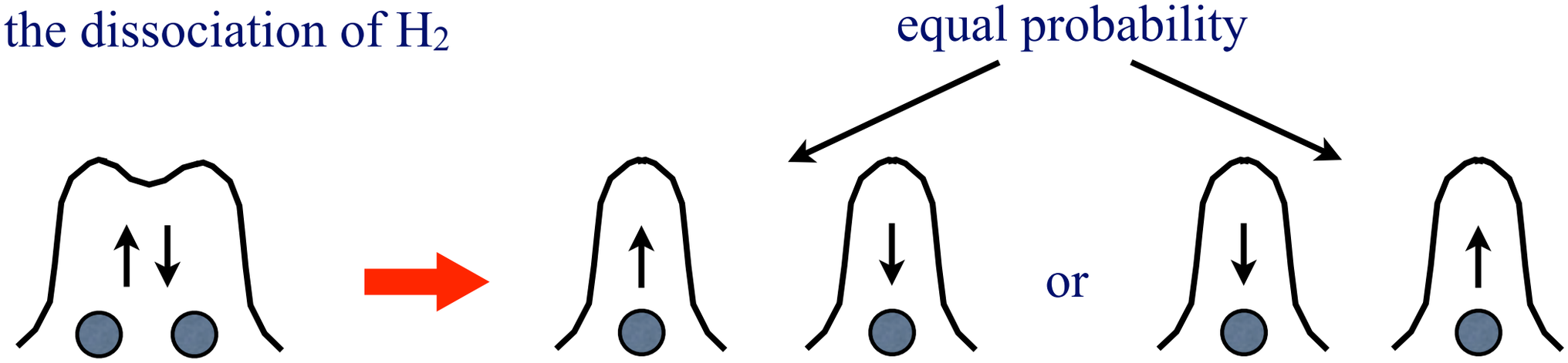

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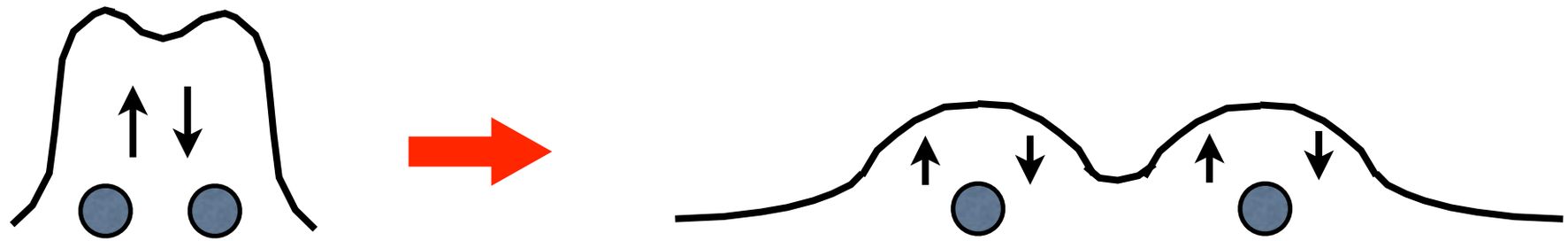

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Misrepresentation of electronic localization → consequences for magnetism, mixed valence states, structural properties, etc

The Hubbard Model

$$\hat{H}_{Hub} = t \sum_{\langle i,j \rangle,\sigma} \left(\hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma} + h.c. \right) + U \sum_{i} \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow}$$

N. F. Mott
(1905-1996)
1977 Nobel Laureate

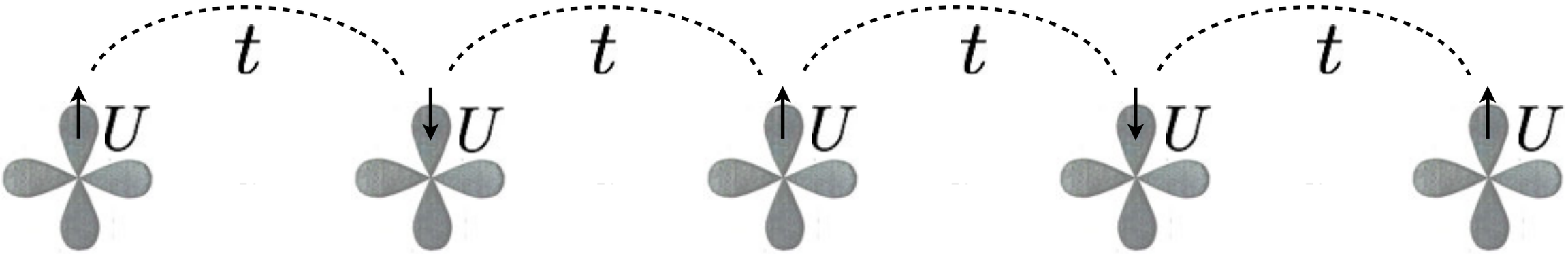
J. Hubbard, *Proc. Roy. Soc. Lond.* (1963-67)

I. G. Austin and N. F. Mott, *Science* 168, 71 (1970)

Energy is expanded around the strongly-localized limit (on atomic orbitals):

t is the "hopping" amplitude; kinetic term: **well represented in DFT**

U is the effective repulsion between electrons *localized* on the same site;
not well represented in DFT



LDA+U

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A very simple idea:

let's describe localized *d* or *f* electrons using the Hubbard model. We need to "embed" the Hubbard Hamiltonian in the DFT energy functional

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We add the Hubbard functional, subtract its MF value....

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + E_{Hub}[\{n_i\}] - E_{dc}[\{n_i\}]$$

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Original formulation:

$$E_{Hub} = \frac{U}{2}\sum_{i\neq j} n_i n_j \qquad E_{dc} = \frac{U}{2}N(N-1)$$

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The Hubbard correction acts selectively on localized states:

$$E_U = E_{Hub} - E_{dc} = E_U[\{n_i\}] \qquad n_i = \sum_{kv} f_{kv}\langle\phi_i|\psi_{kv}\rangle\langle\psi_{kv}|\phi_i\rangle$$

DFT+U: rotationally invariant formulation

The expression of the corrective "+U" functional should be independent from the specific choice of localized states

$$E_{Hub}[\{n^I_{mm'}\}] = \frac{1}{2}\sum_{\{m\},\sigma,I}\{\langle m,m''|V_{ee}|m',m'''\rangle n^{I\sigma}_{mm'}n^{I-\sigma}_{m''m'''}$$

$$+(\langle m,m''|V_{ee}|m',m'''\rangle - \langle m,m''|V_{ee}|m''',m'\rangle)n^{I\sigma}_{mm'}n^{I\sigma}_{m''m'''}\}$$

$$E_{dc}[\{n^I_{mm'}\}] = \sum_I\{\frac{U^I}{2}n^I(n^I-1) - \frac{J^I}{2}[n^{I\uparrow}(n^{I\uparrow}-1)+n^{I\downarrow}(n^{I\downarrow}-1)]\}$$

A. Liechtenstein *et al.* PRB 52, R 5467 (1995)

where:

$$n^{I\sigma}_{mm'} = \sum_i f_i\langle\psi^\sigma_i|\phi^I_{m'}\rangle\langle\phi^I_m|\psi^\sigma_i\rangle \qquad n^{I\sigma} = \sum_m n^{I\sigma}_{mm} \qquad n^I = \sum_\sigma n^{I\sigma}$$

ψ^σ_i are Kohn-Sham states ϕ^I_m are *localized* atomic orbitals (*d* or *f*)

A simpler formulation

Effective interactions:

$$\langle m, m'' | V_{ee} | m', m''' \rangle = \sum_k a_k(m, m', m'', m''') F^k$$

$$F^k = \int d\mathbf{r} \int d\mathbf{r}' \phi^*_{lm}(\mathbf{r}) \phi_{lm'}(\mathbf{r}) \frac{r_<^k}{r_>^{k+1}} \phi^*_{lm''}(\mathbf{r}') \phi_{lm'''}(\mathbf{r}') \qquad a_k(m, m', m'', m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y^*_{kq} | lm''' \rangle$$

Let's neglect interaction anisotropy:

$$U = F^0 \neq 0 \qquad\qquad J = \frac{F^2 + F^4}{14} = 0$$

After some algebra....

Dudarev *et al.*, PRB 57, 1505 (1998)

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + \sum_{I,\sigma} \frac{U^I}{2} Tr\left[\mathbf{n}^{I\sigma}\left(\mathbf{1} - \mathbf{n}^{I\sigma}\right)\right]$$

How does it work?

Because of the rotational invariance we can use a diagonal representation:

$$E_U = E_{Hub} - E_{dc} = \sum_I \frac{U^I}{2} \sum_{m,\sigma} \left[\lambda_m^{I\sigma}(1-\lambda_m^{I\sigma})\right]$$

where:

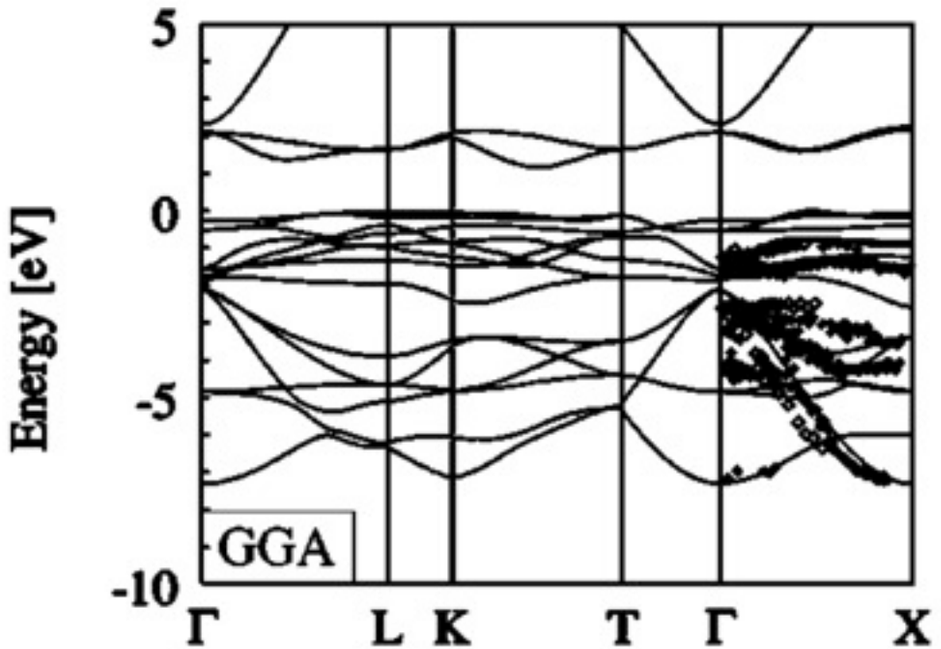
$$\mathbf{n}^{I\sigma}\mathbf{v}_m = \lambda_m^{I\sigma}\mathbf{v}_m \qquad \lambda_m^{I\sigma} = \sum_{k,v} f_{kv}\langle\psi_{kv}^\sigma|\phi_m^I\rangle\langle\phi_m^I|\psi_{kv}^\sigma\rangle$$

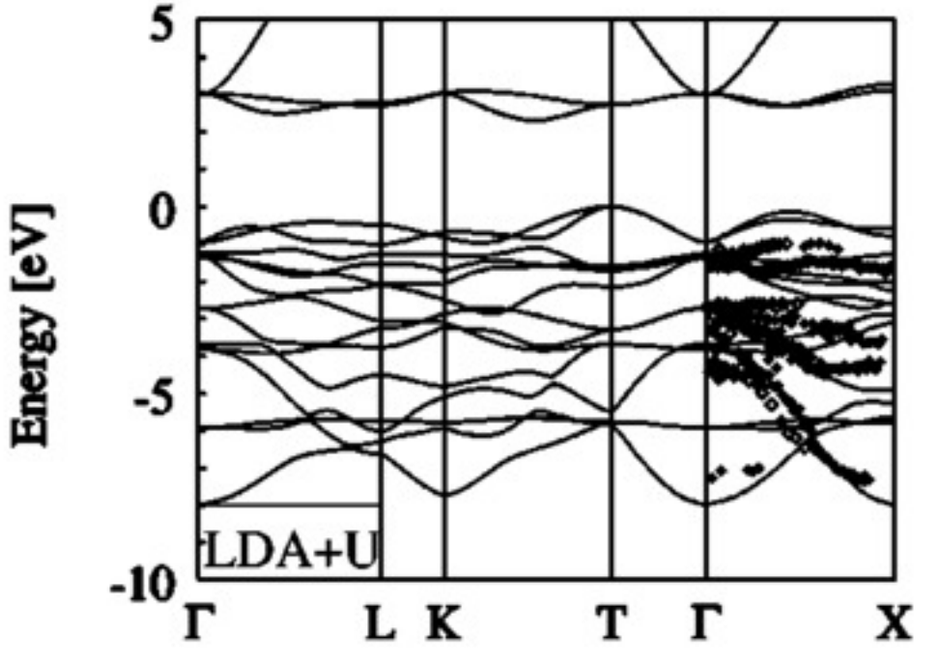
Potential:

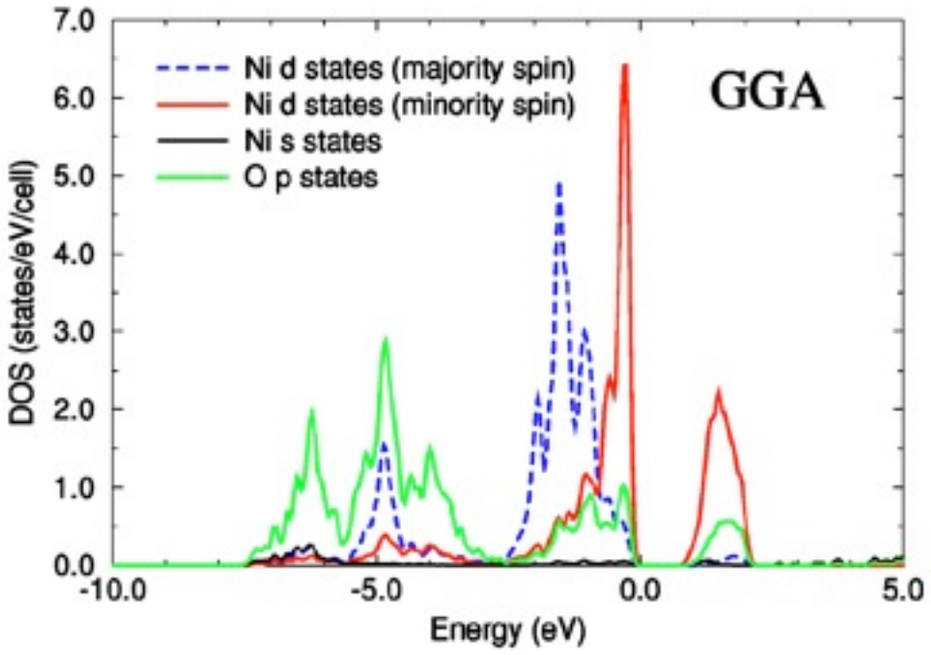
$$V_U|\psi_{kv}^\sigma\rangle = \frac{\delta E_U}{\delta(\psi_{kv}^\sigma)^*} = \sum_I \frac{U^I}{2} \sum_{m,\sigma} \left(1-2\lambda_m^{I\sigma}\right)|\phi_m^I\rangle\langle\phi_m^I|\psi_{kv}^\sigma\rangle$$

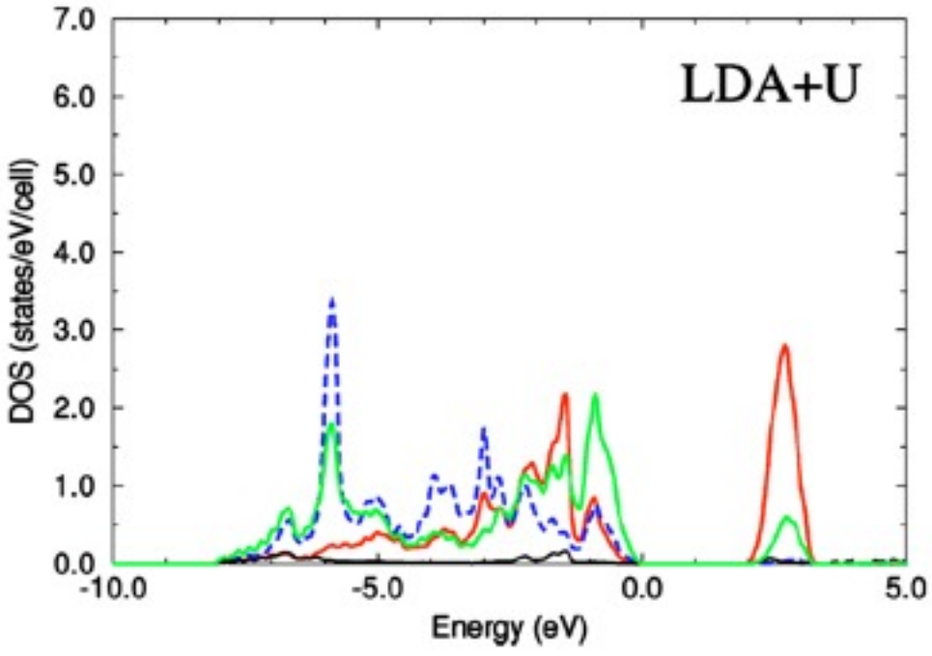
$$\left.\begin{aligned} \lambda_m^{I\sigma} > \frac{1}{2} \Rightarrow V_U < 0 \\ \lambda_m^{I\sigma} < \frac{1}{2} \Rightarrow V_U > 0 \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} &\text{Partial occupations of atomic states are discouraged} \\ &\text{Potential discontinuity re-established} \\ &\text{A gap opens: } E_g \approx U \end{aligned}\right.$$

LDA+U NiO









M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

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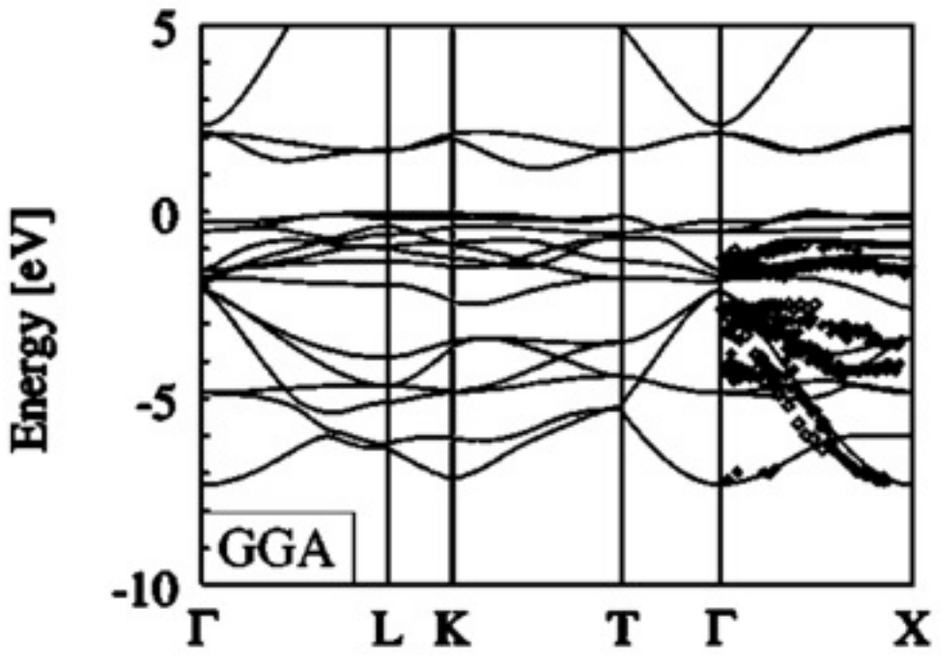
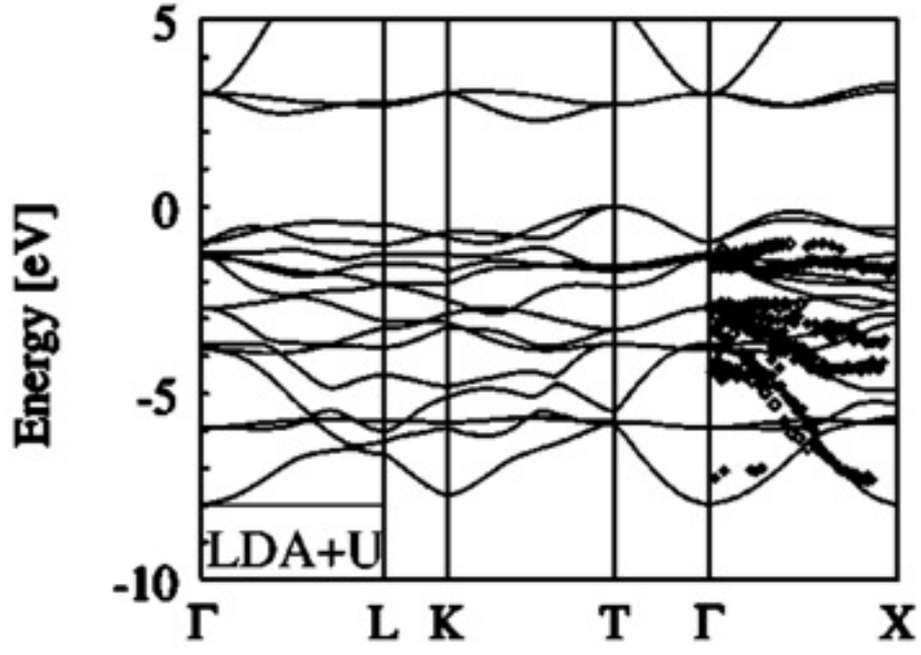
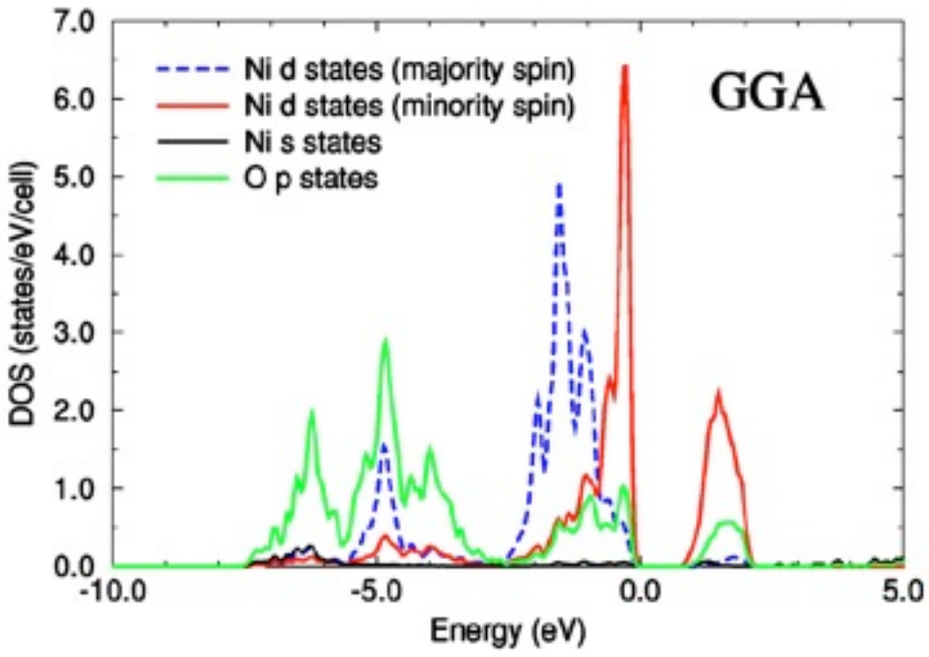
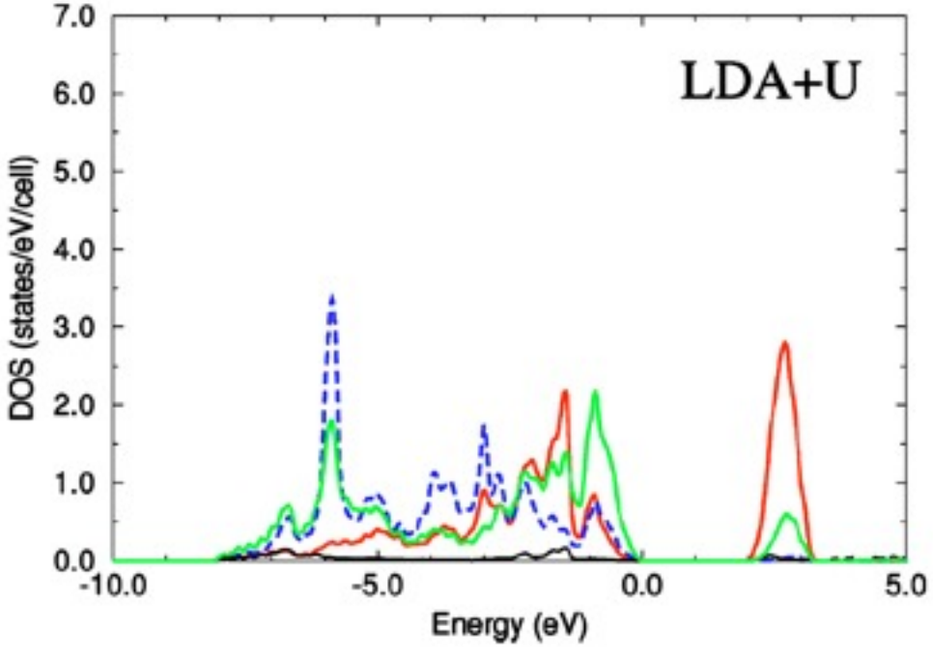




✓Gap improves

✓O *p* states on top of the valence band





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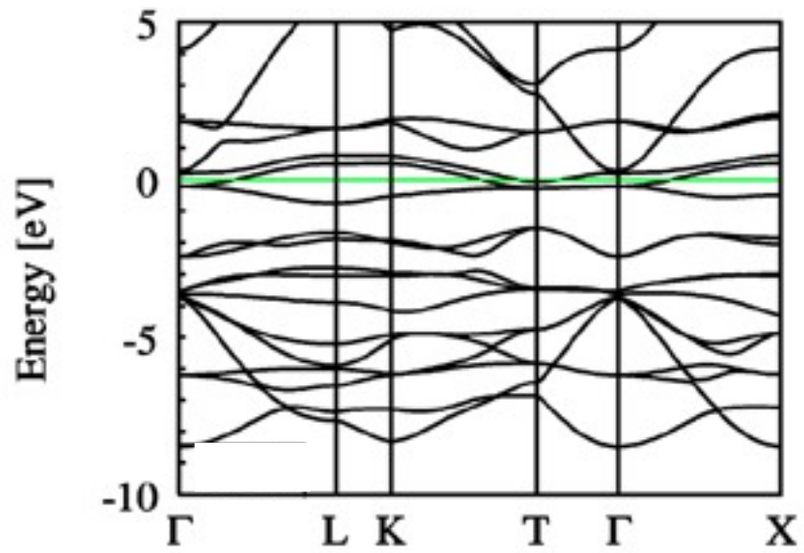
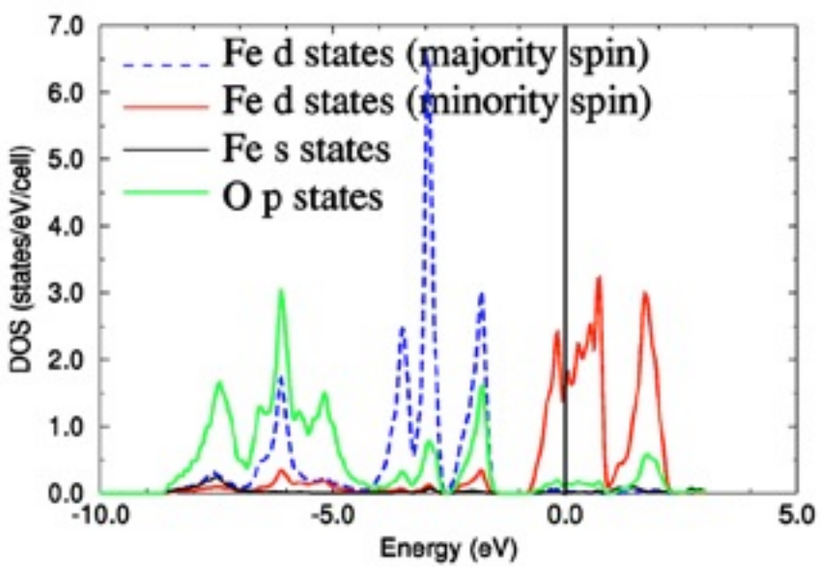
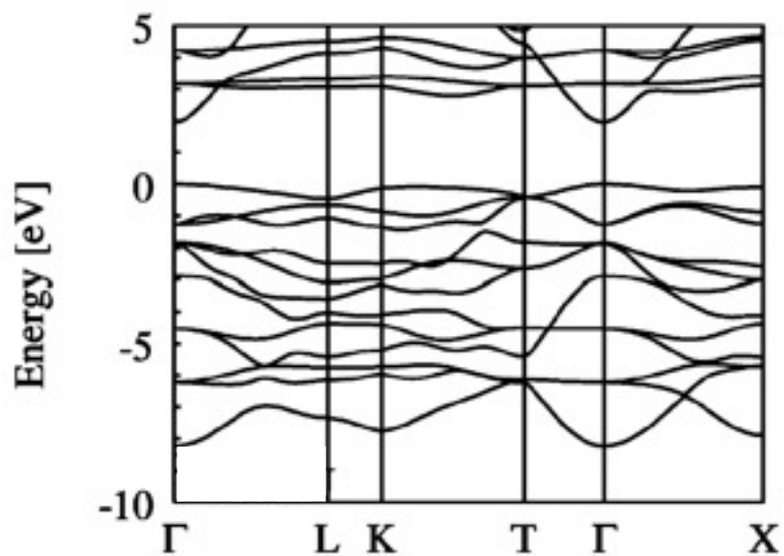
FeO: DFT and DFT+U

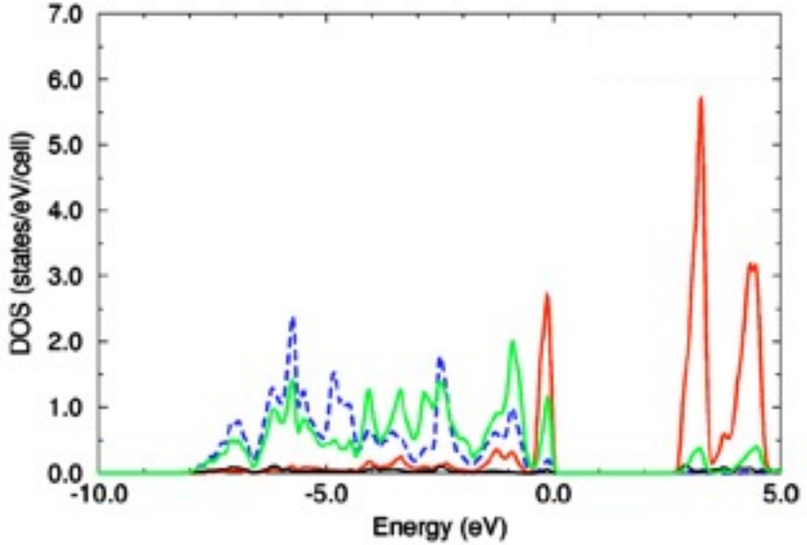
DFT





DFT+U

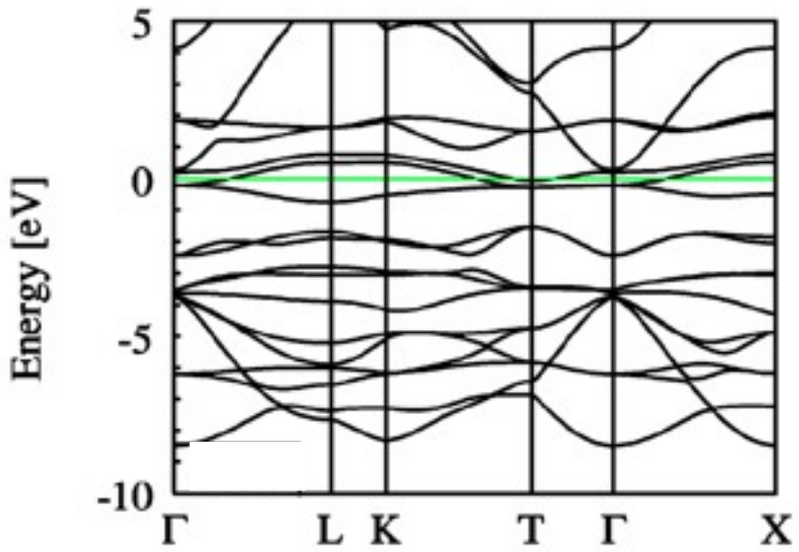




M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

FeO: DFT and DFT+U

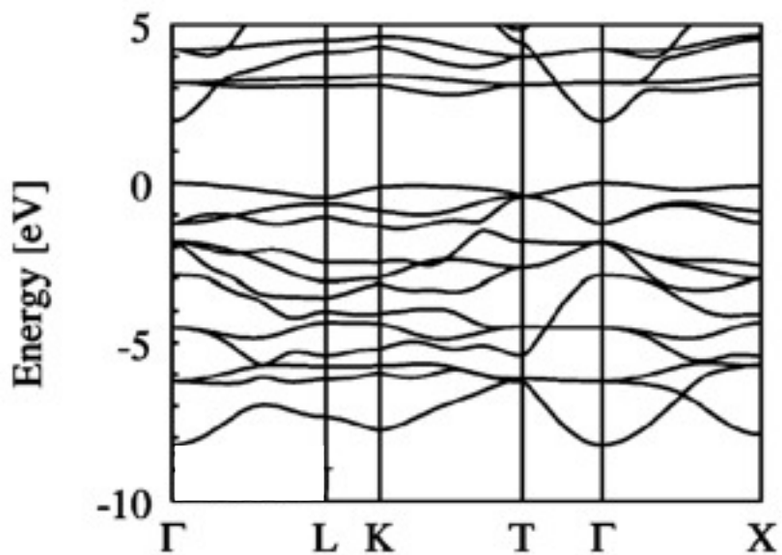
DFT

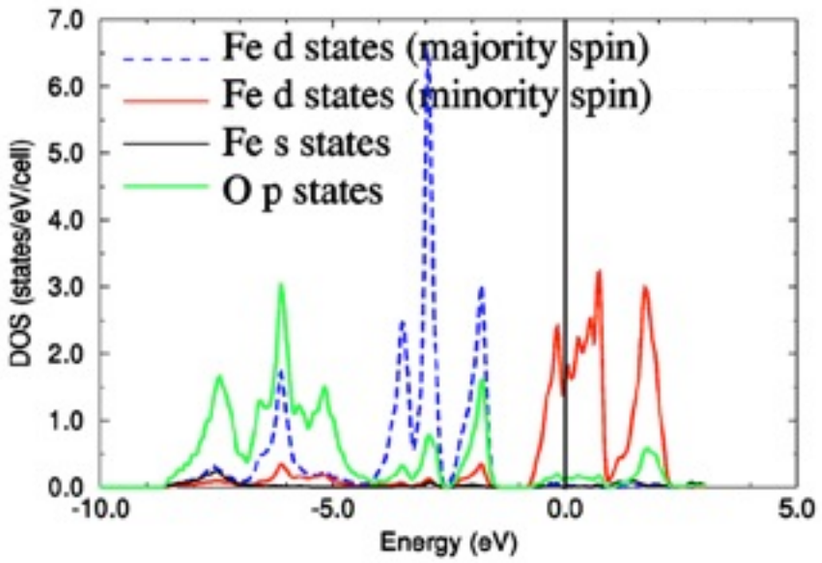


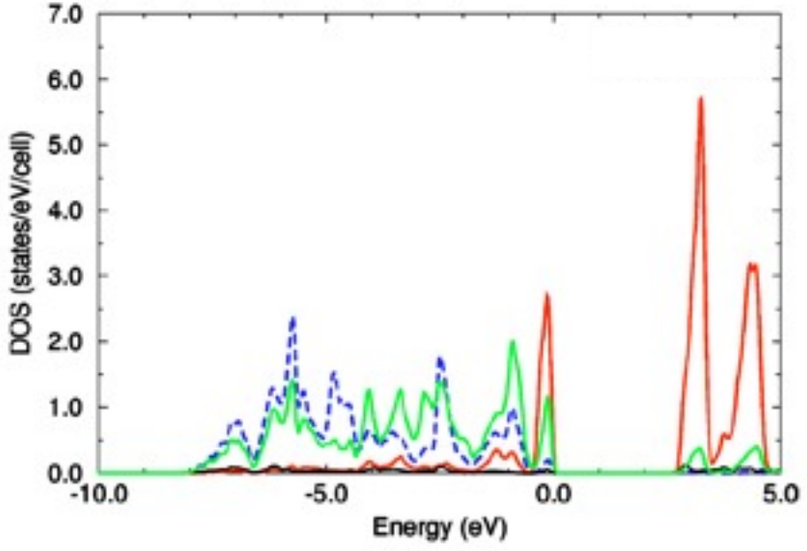
✓Insulating character
(Gap of right size)

✓AFM ground state
(AFII)

DFT+U





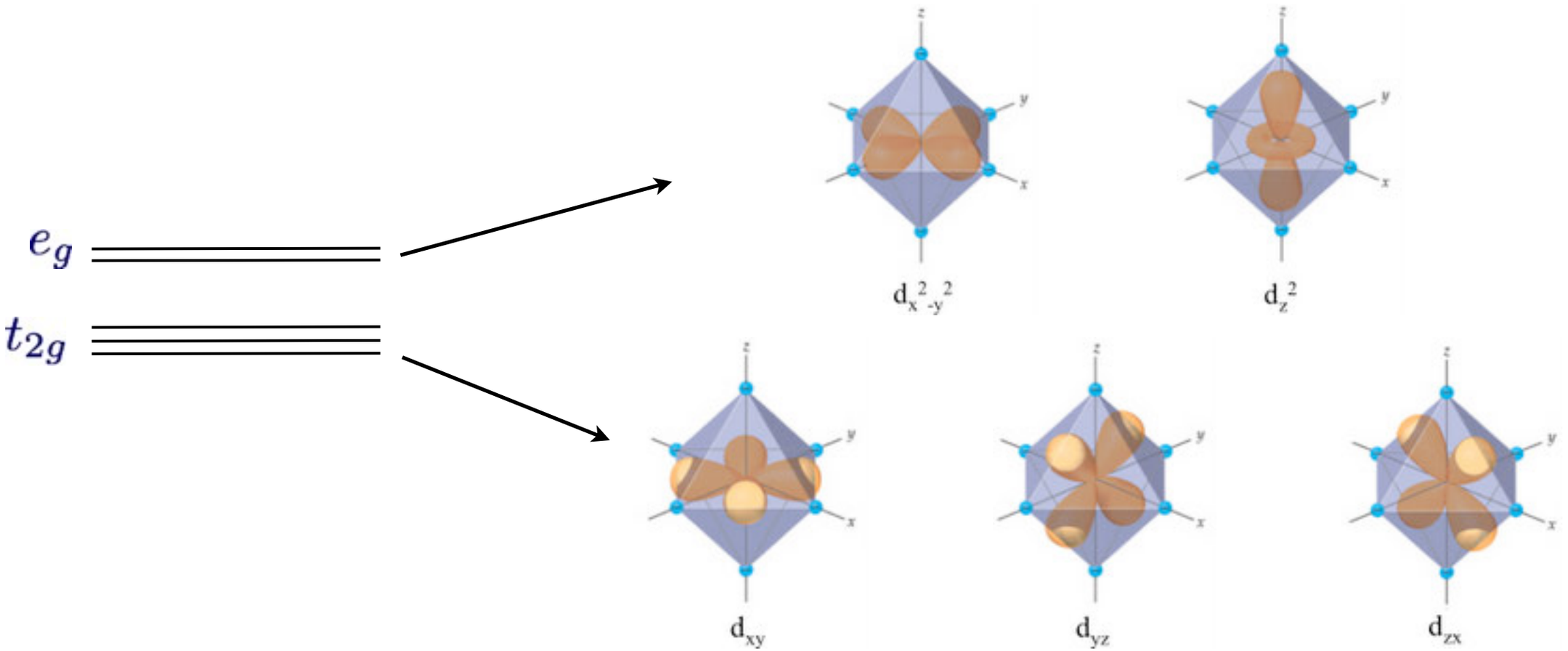


M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

Symmetry and degeneracy of *d* states

In an isolated atom all the *d* states are all degenerate

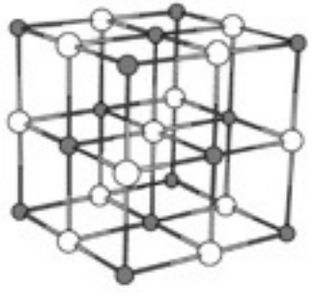
In a cubic crystal (highest possible symmetry) they split in two group



FeO: breaking the symmetry

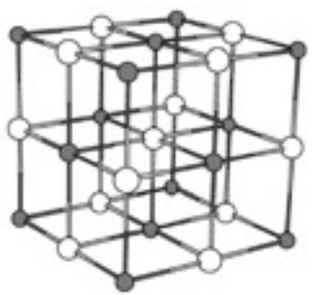
FeO: breaking the symmetry

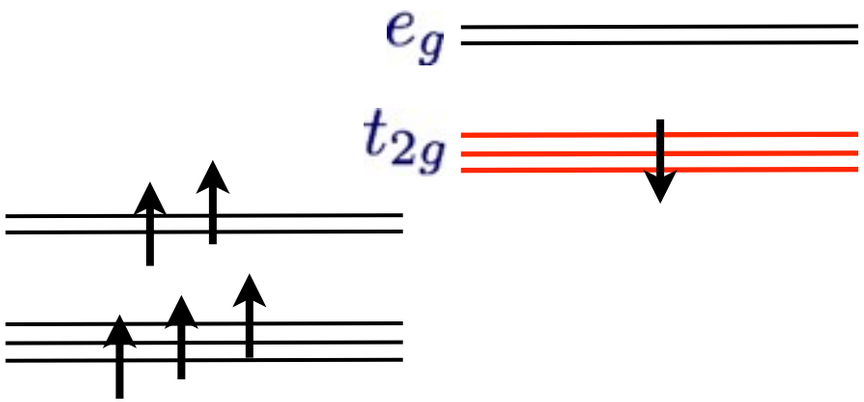
Cubic



FeO: breaking the symmetry

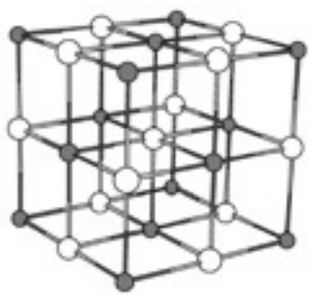
Cubic

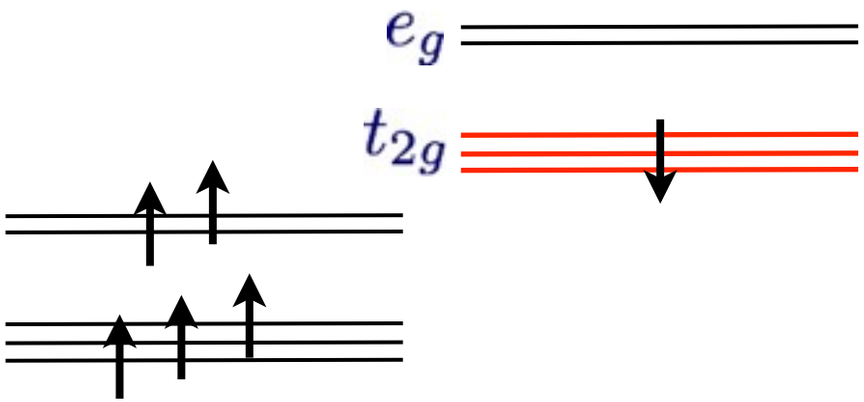


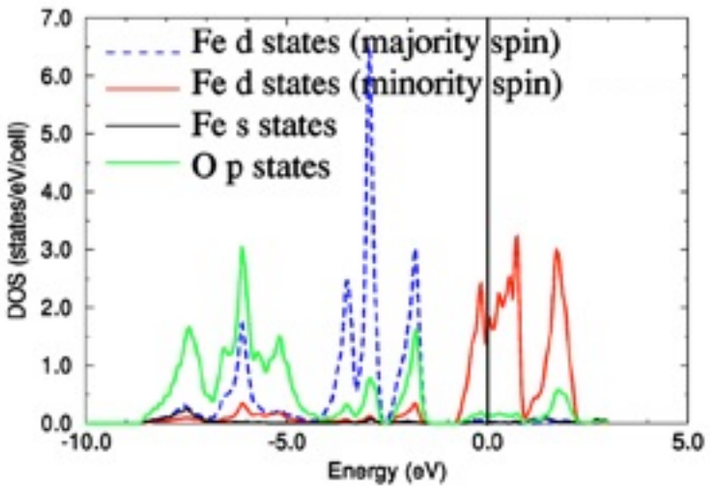


FeO: breaking the symmetry

Cubic

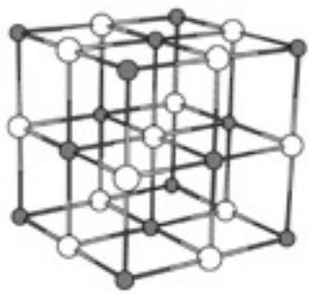


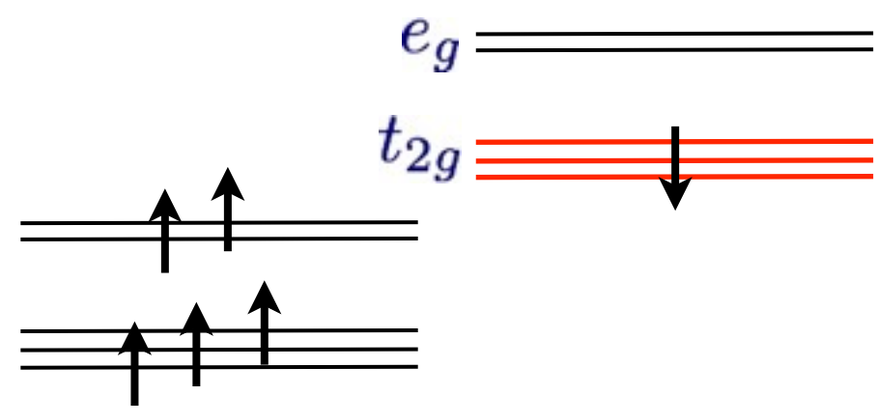




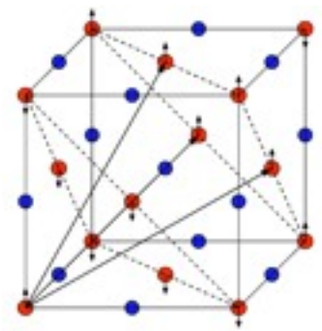
FeO: breaking the symmetry

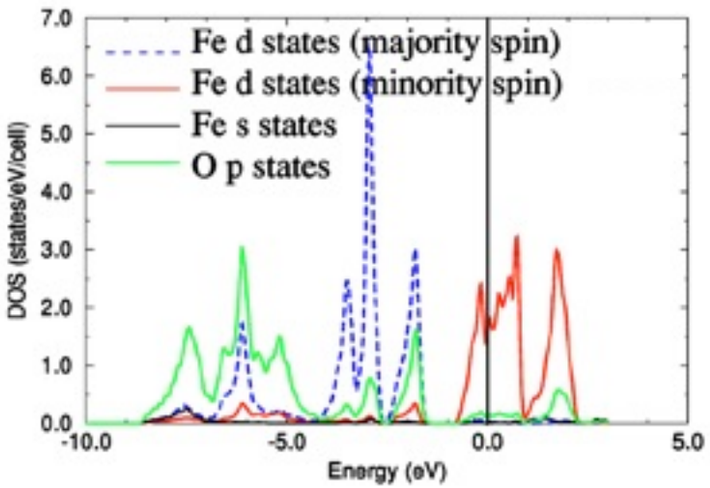
Cubic





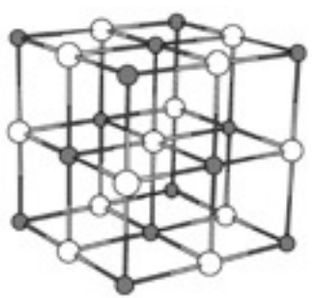
Rhombohedral





FeO: breaking the symmetry

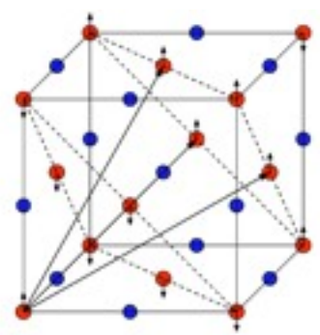
Cubic



e_g

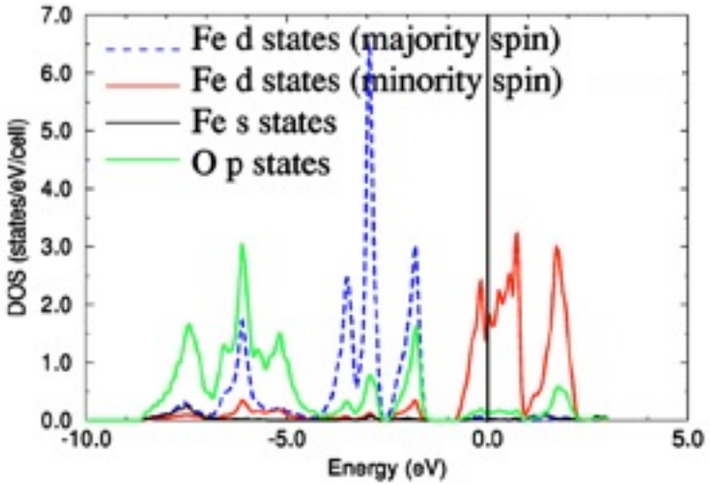
t_{2g}

Rhombohedral



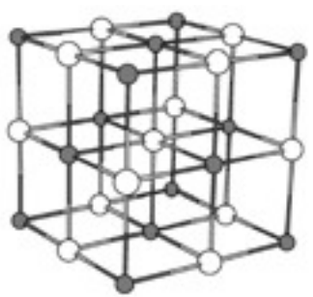
e_g

a_{1g}



FeO: breaking the symmetry

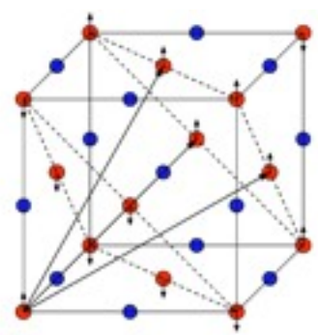
Cubic



e_g

t_{2g}

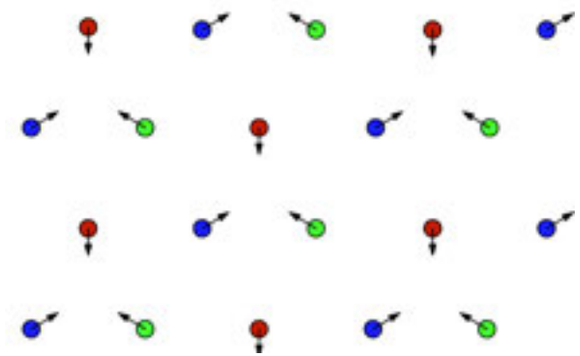
Rhombohedral

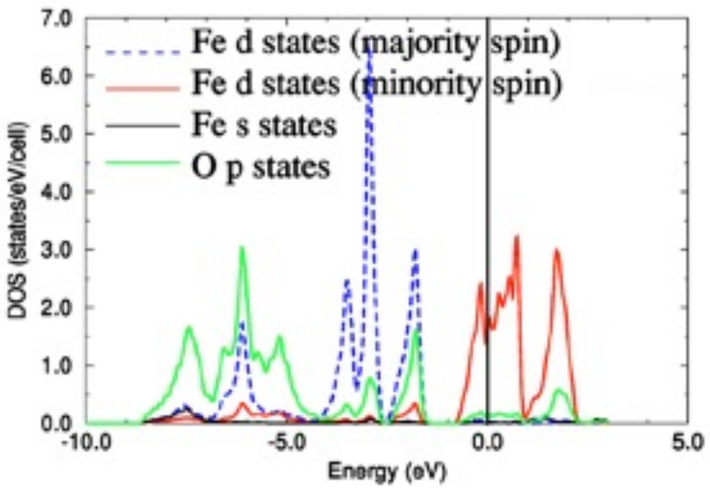


e_g

a_{1g}

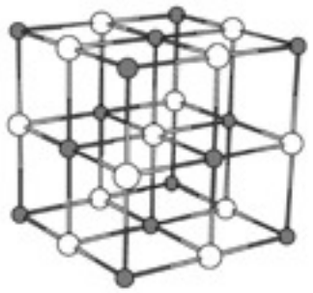
Tripartition of (111) planes

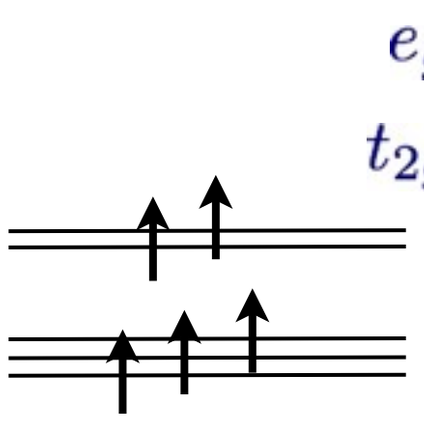




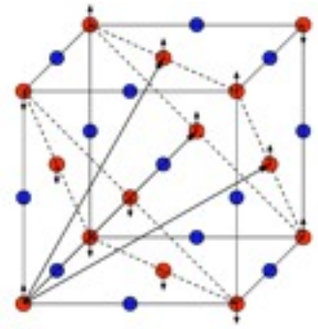
FeO: breaking the symmetry

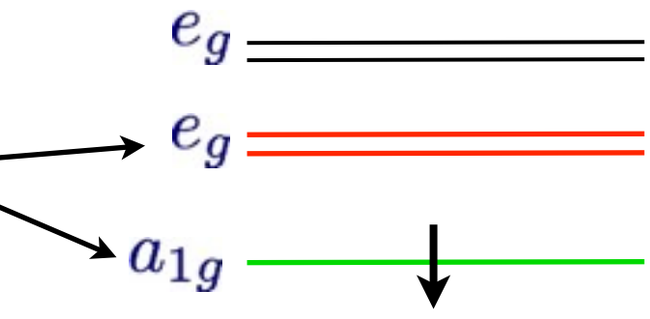
Cubic



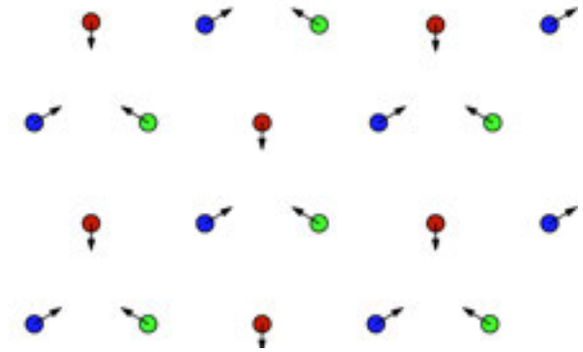


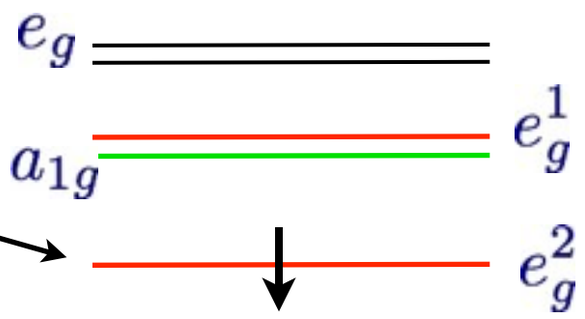
Rhombohedral

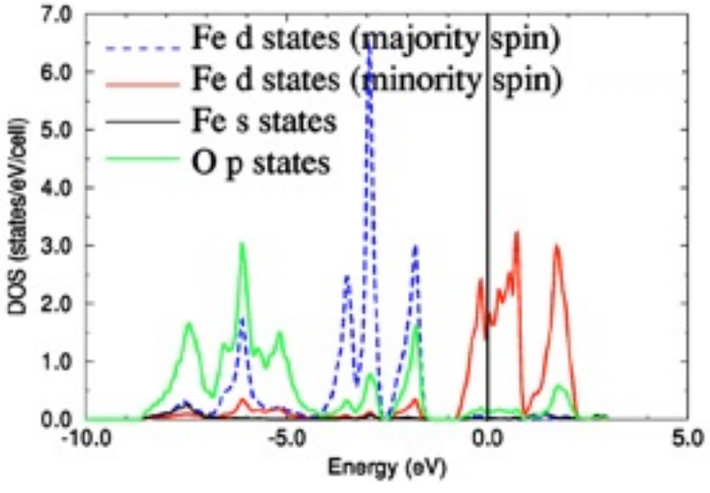




Tripartition of (111) planes

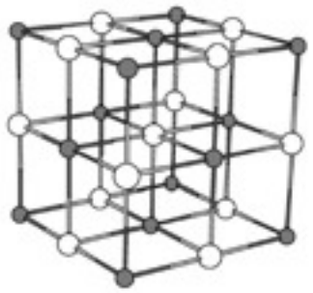


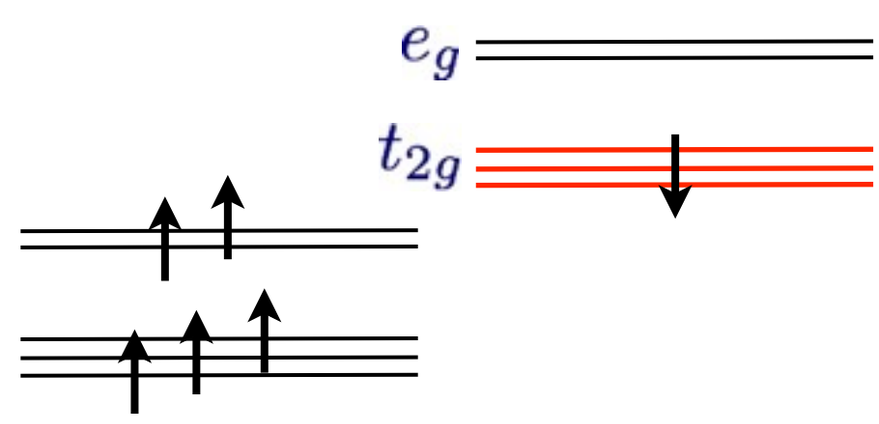


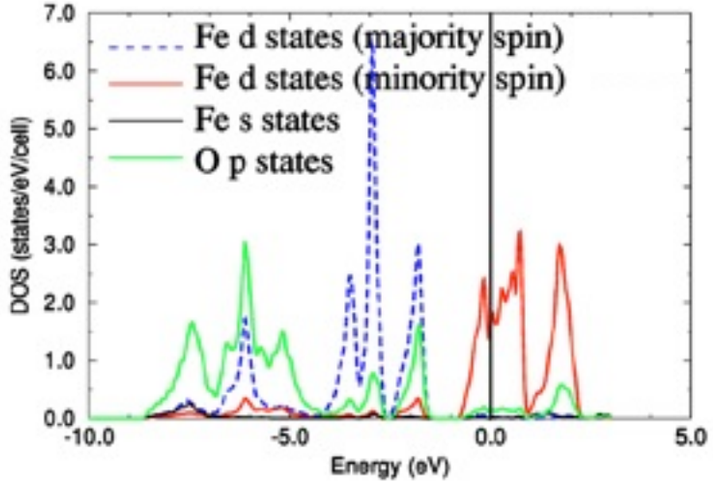


FeO: breaking the symmetry

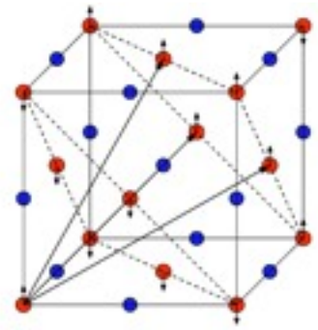
Cubic

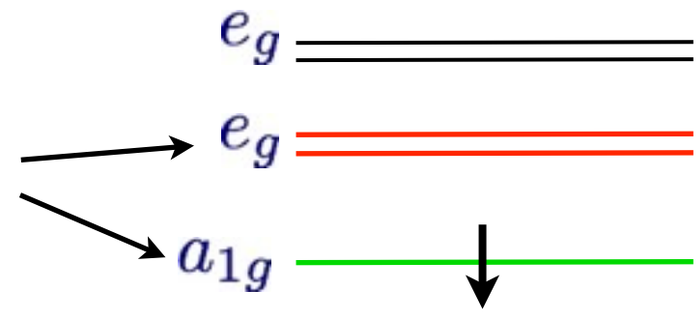


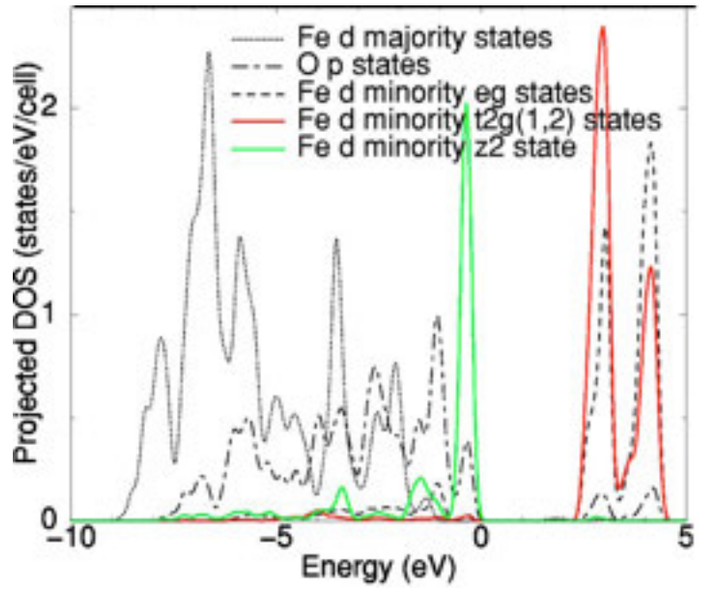




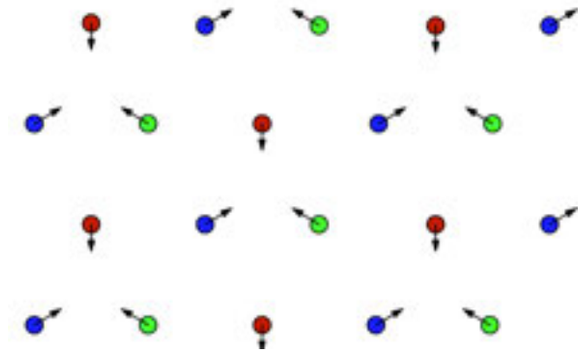
Rhombohedral

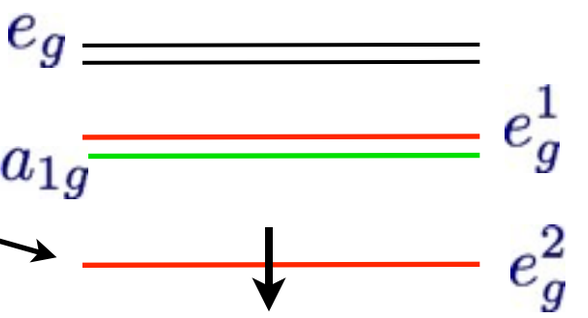


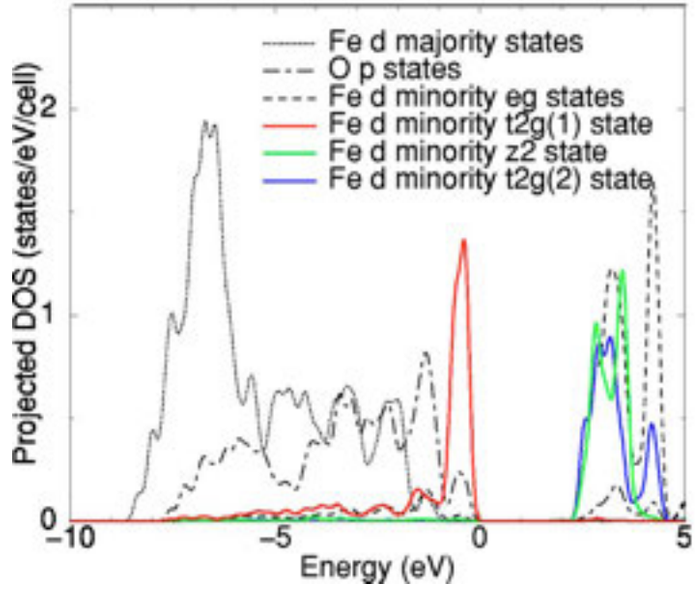




Tripartition of (111) planes

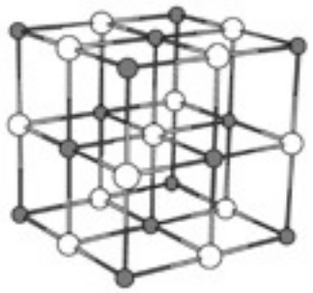


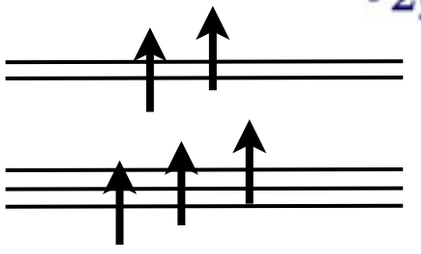




FeO: breaking the symmetry

Cubic

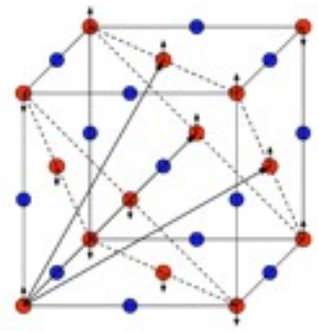




e_g

t_{2g}

Rhombohedral

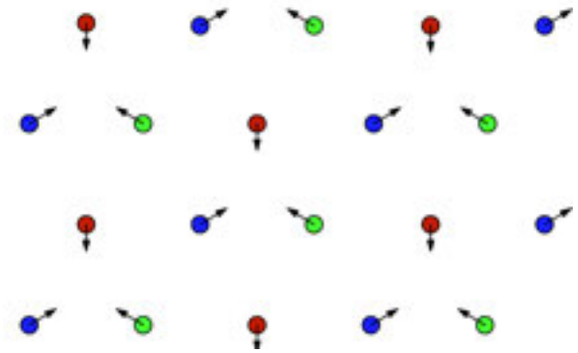


e_g

e_g

a_{1g}

Tripartition of (111) planes

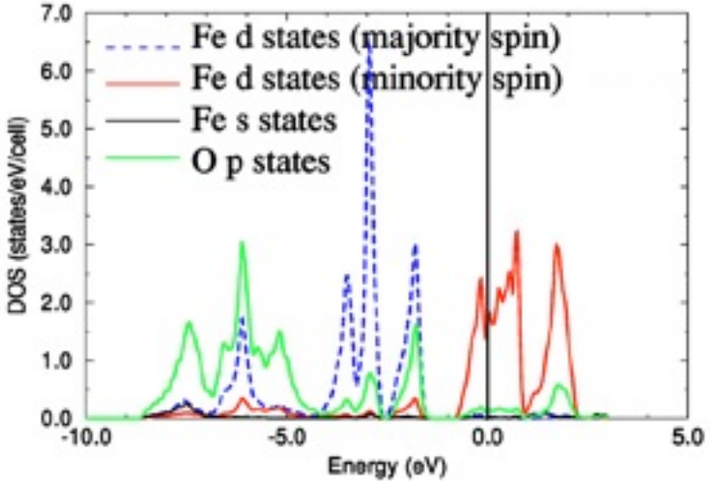


e_g

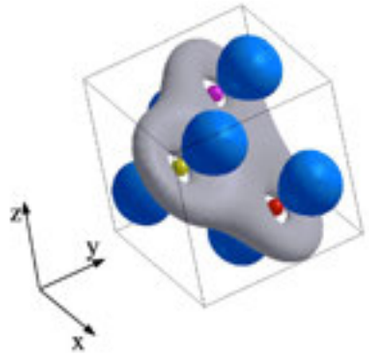
a_{1g}

e_g^1

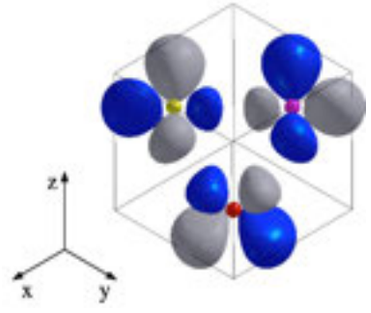
e_g^2



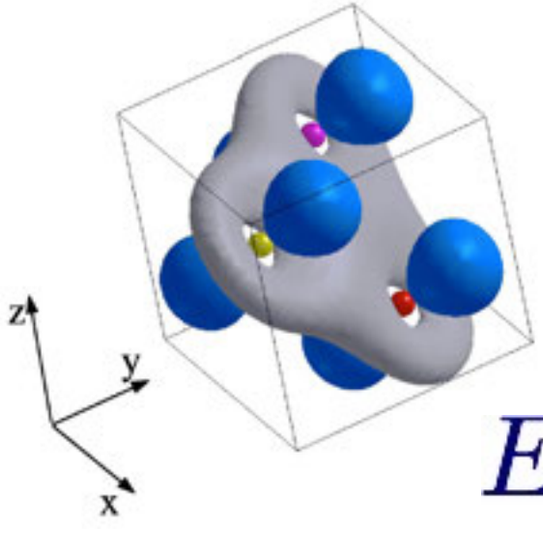
a_{1g}



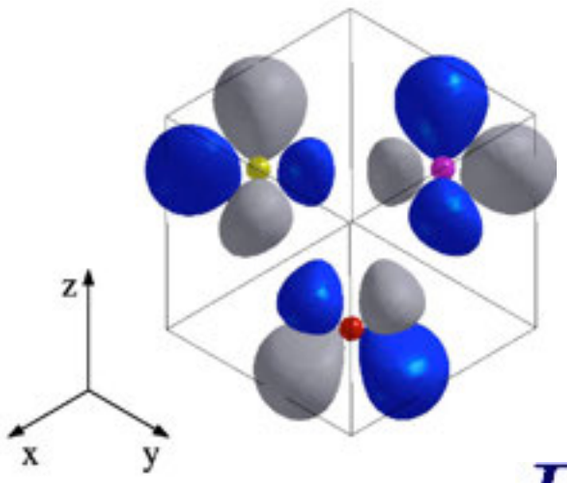
e_g^2



FeO: which insulating state?



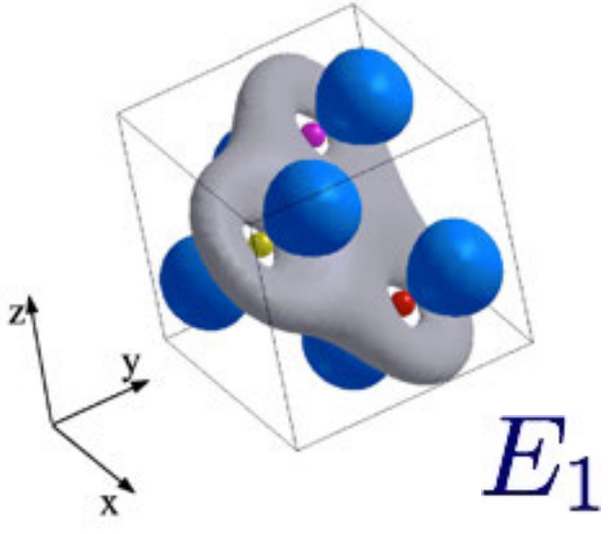
E_1



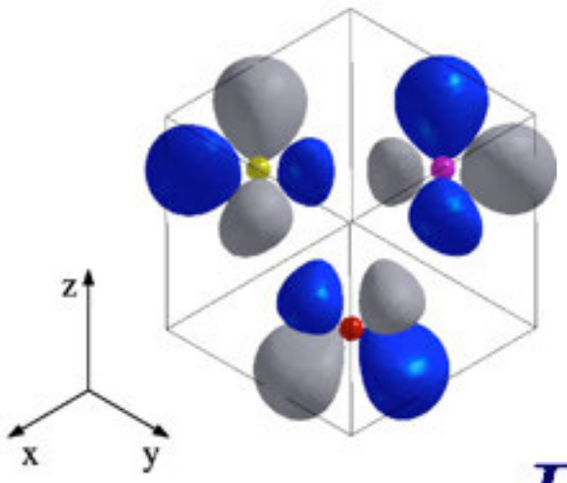
E_2

FeO: which insulating state?

Total energy: $E_1 > E_2$

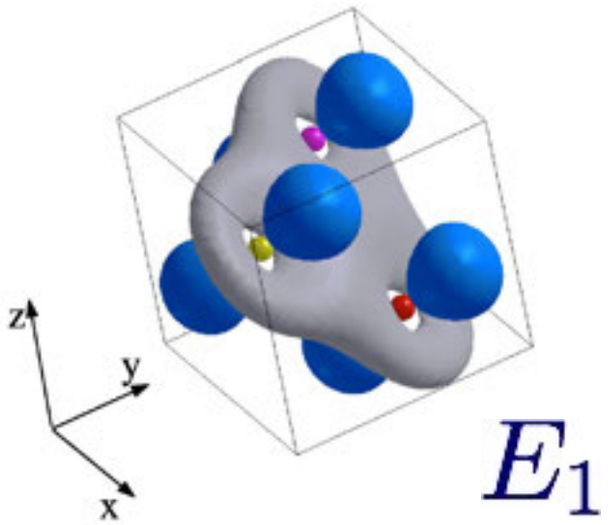


E_1

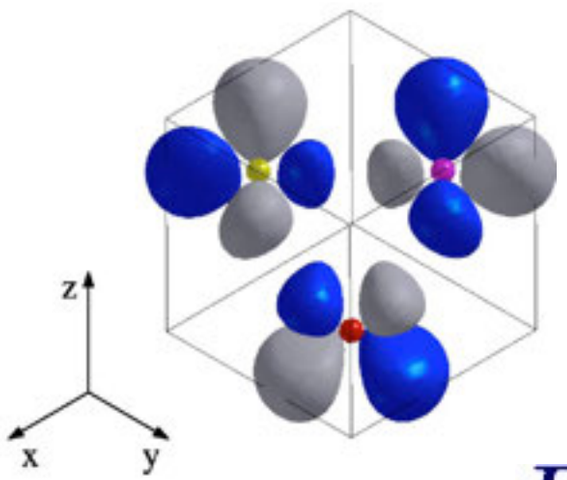


E_2

FeO: which insulating state?



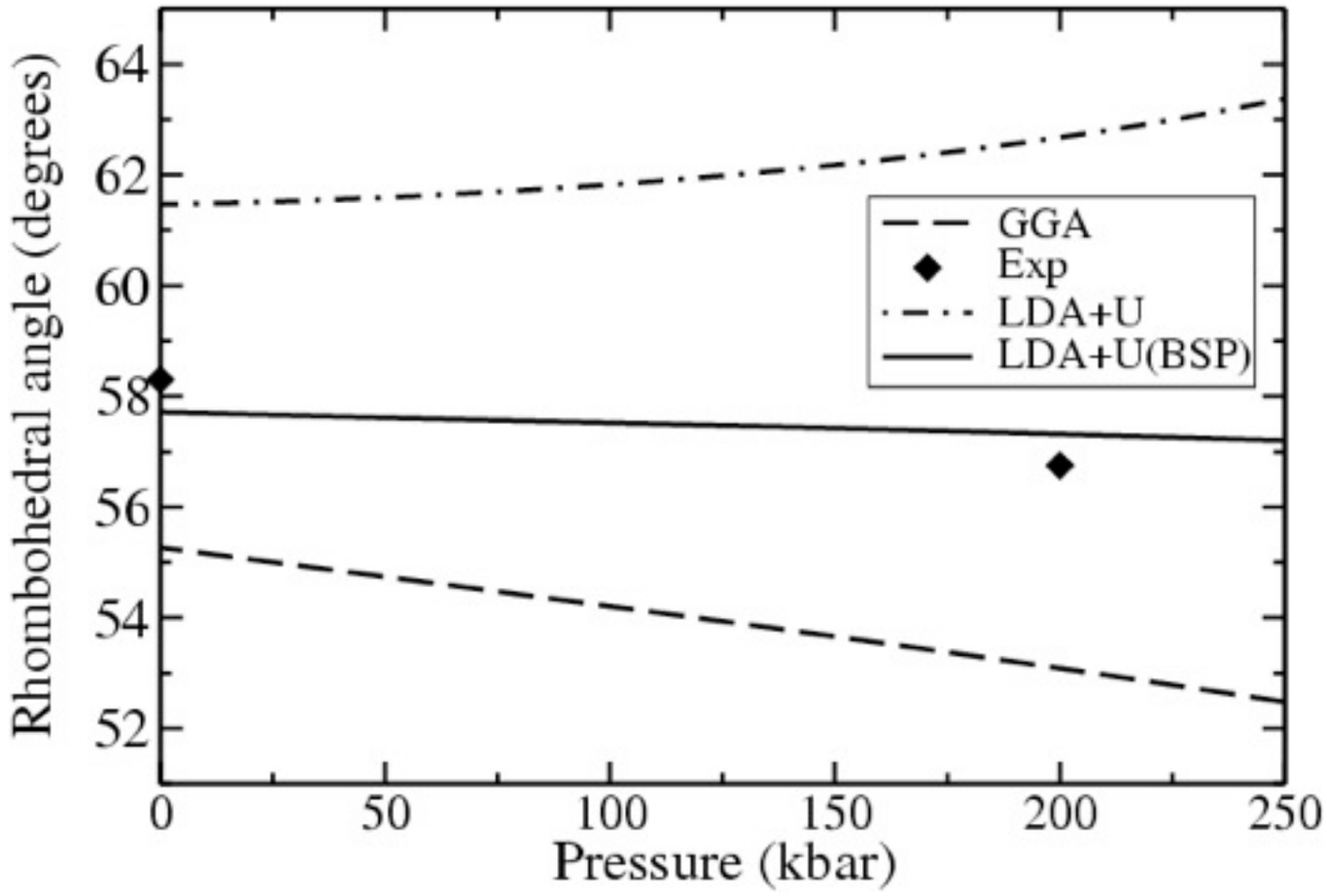
E_1



E_2

Total energy: $E_1 > E_2$

Structural distortion under pressure



M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

What about U?

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + \sum_{I,\sigma} \frac{U^I}{2} Tr\left[\mathbf{n}^{I\sigma}\left(\mathbf{1}-\mathbf{n}^{I\sigma}\right)\right]$$

Many possible ways to interpret the "+U" correction:

- Additive correction shaped on the Hubbard model
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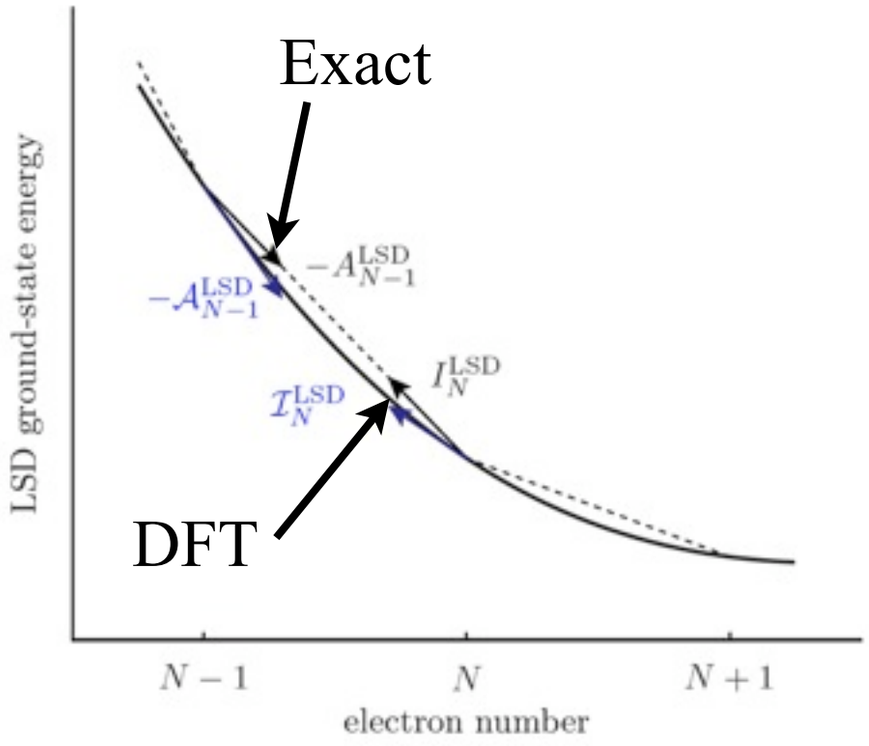

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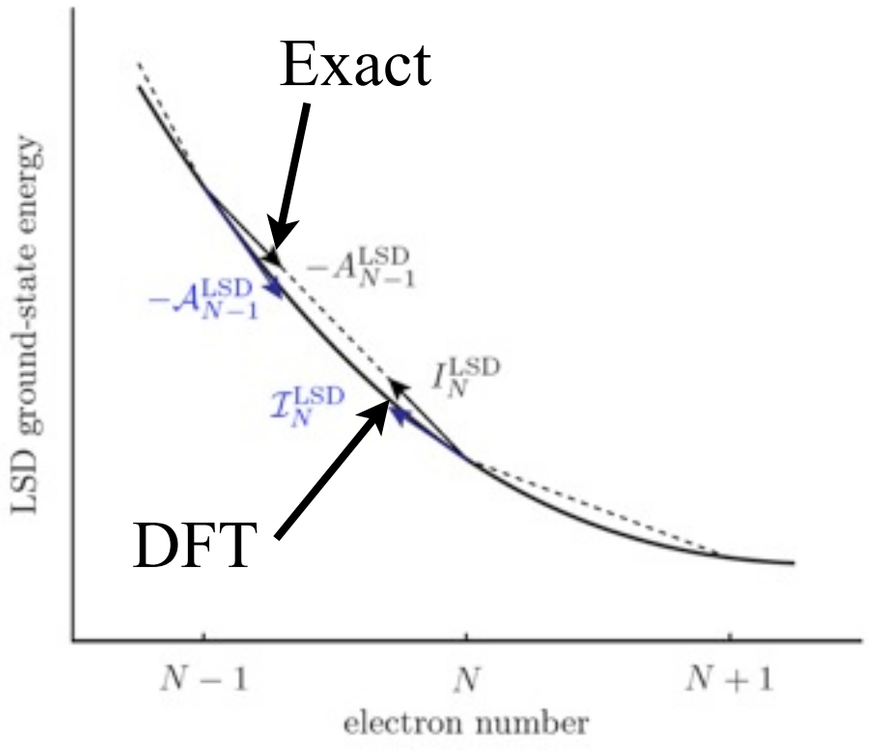


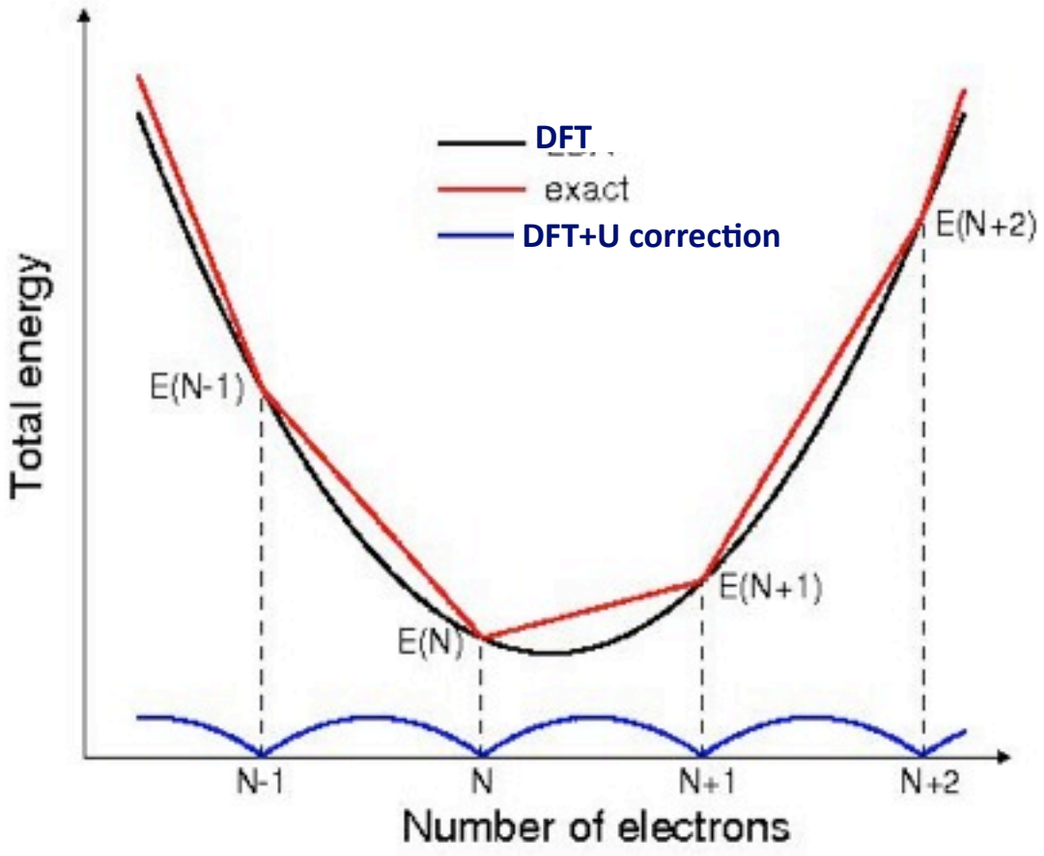
Open system in contact with a charge reservoir:

- Energy should be linear between integer N
- Potential should be discontinuous at integer N
- Discontinuity of 1st derivative: fundamental gap

$$\Delta\left(\frac{dE}{dN}\right) = I - A$$

The DFT + Hubbard U approach

$$E_{exact} \neq E_{DFT}$$



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U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, and coworkers PRB (1995)

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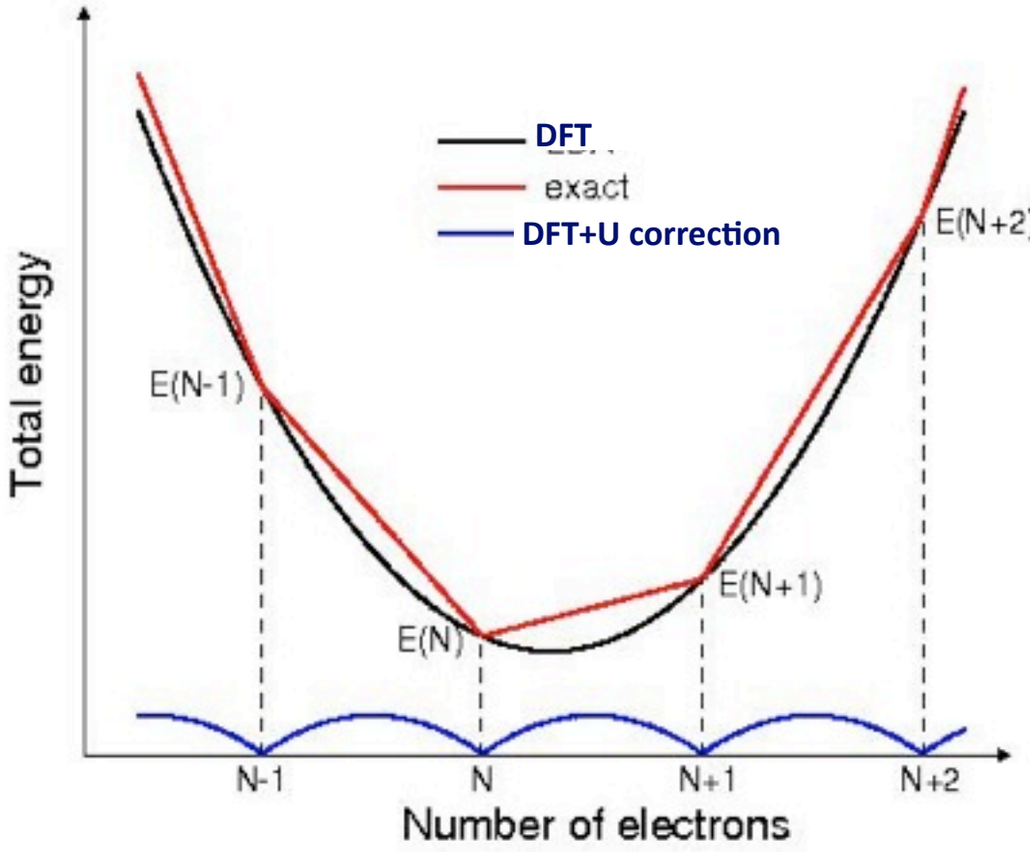

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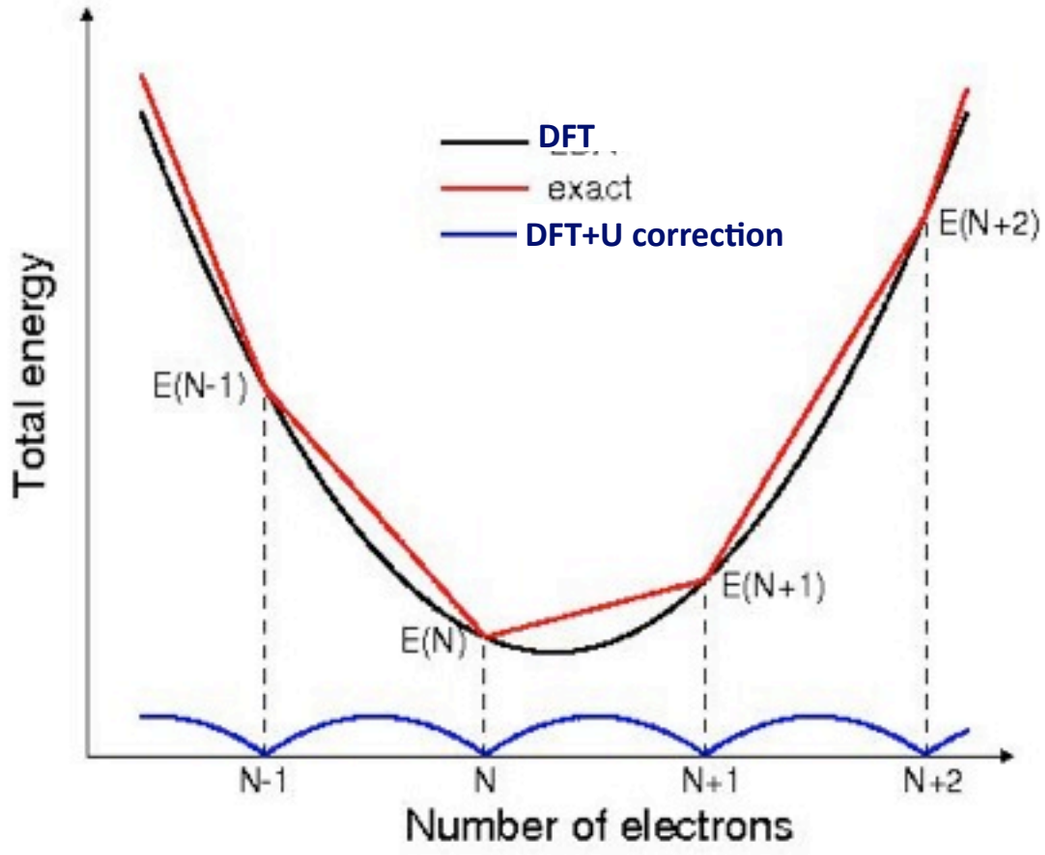

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LRT U: M. Cococcioni PhD (2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)

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Second derivatives

- Second derivatives can not be directly obtained from DFT calculations
- Legendre transforms can help us:

Let's apply a shift to the potential acting on localized states:

$$E[\{\alpha^I\}] = \min_{\rho} \left\{ E[\rho(\mathbf{r})] + \sum_I \alpha^I n^I \right\}$$

A functional of the atomic occupations can be defined as:

$$E[\{n^I\}] = E[\{\alpha^I\}] - \sum_I \alpha^I n^I_{min}$$

First and second derivatives can be easily obtained:

$$\frac{dE[\{n^I\}]}{dn^I} = -\alpha^I(\{n^J\}) \qquad \frac{d^2E[\{n^J\}]}{d(n^I)^2} = -\frac{d\alpha^I(\{n^J\})}{dn^I}$$

M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

Linear response

Apply a perturbation to the potential acting on the localized states of each Hubbard atom and compute the response of the occupations

$$V_{tot}|\psi^{\sigma}_{kv}\rangle = V_{KS}|\psi^{\sigma}_{kv}\rangle + \alpha^I \sum_m |\phi^I_m\rangle\langle\phi^I_m|\psi^{\sigma}_{kv}\rangle \;\Rightarrow\; \Delta n^I$$

Response matrices:

$$\chi^{IJ} = \frac{dn^I}{d\alpha^J} \qquad \chi_0^{IJ} = \frac{dn_0^I}{d\alpha^J}$$

Effective interactions:

$$U^I = \left(\chi_0^{-1} - \chi^{-1}\right)_{II}$$

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Using linear-response theory and the definitions given in the previous slides, one obtains:

$$U_{ijkl} = \int\int \phi_i(\mathbf{r})^* \phi_j(\mathbf{r}) \left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right] \phi_k(\mathbf{r}')^* \phi_l(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'$$

The U^I actually computed is a "renormalized" atomically-averaged quantity.
The renormalization is due to other (non-localized) states.

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- Easy implementation in different computational schemes.

- Captures the variation of *U* with species, spin, crystal structure, volume and symmetry

Examples of LDA+U calculations

$$E_{DFT+U} = E_{DFT} + \sum_I \frac{U^I}{2} \sum_{mm'\sigma} \left[n^{I\sigma}_{mm'} (\delta_{mm'} - n^{I\sigma}_{m'm}) \right]$$

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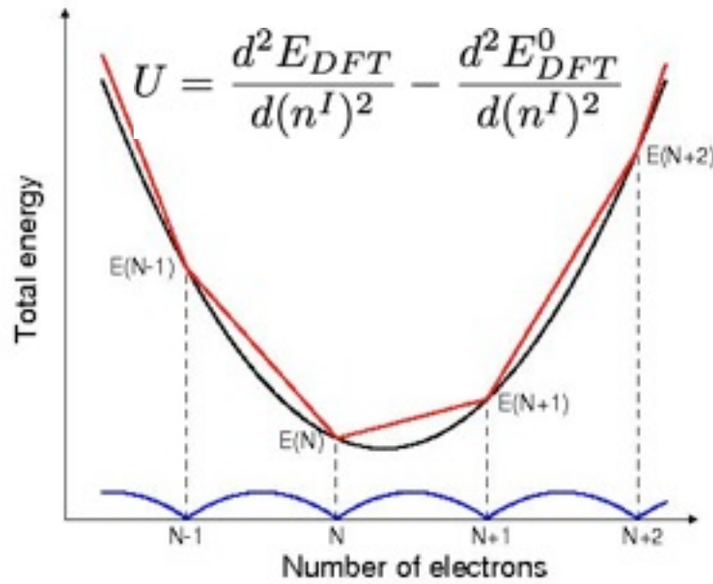

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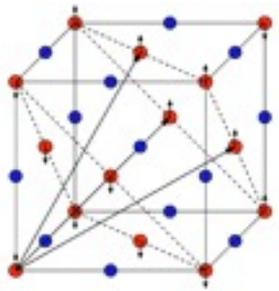
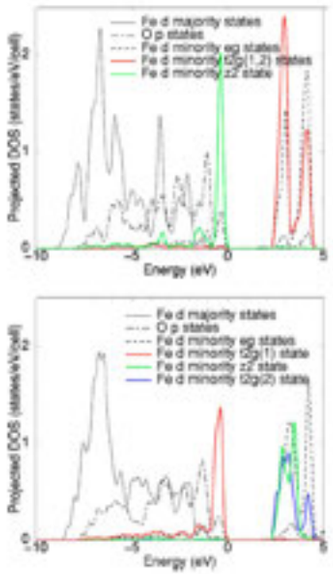
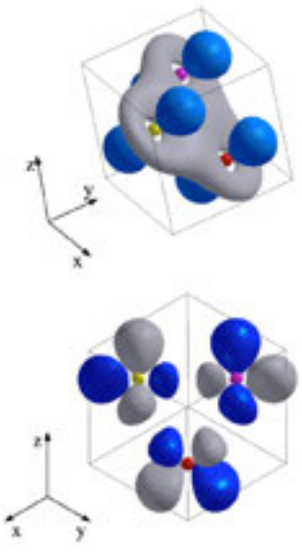


M. Cococcioni and S. de Gironcoli, PRB (2005)

Transition-metal oxides: structural and electronic properties





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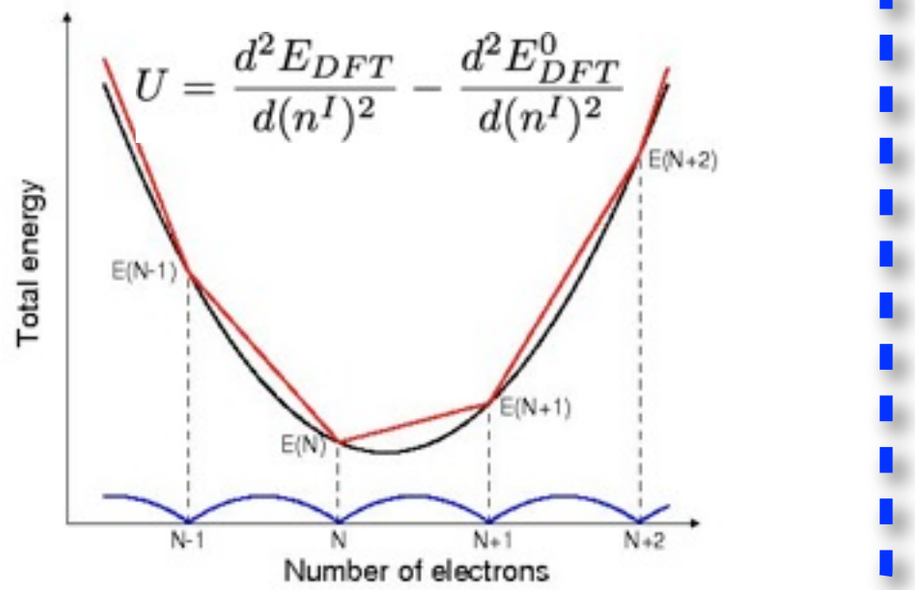

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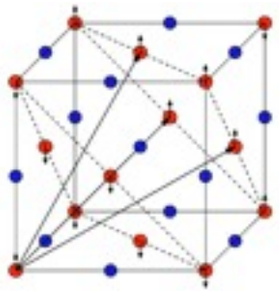

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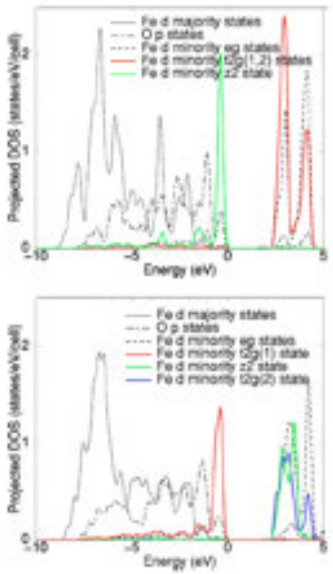

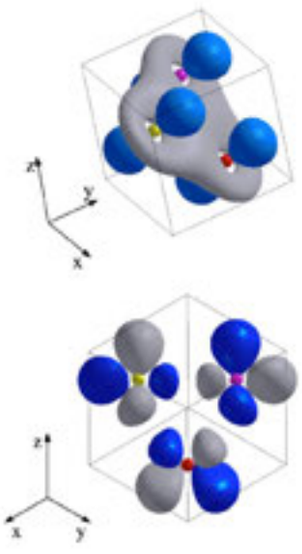

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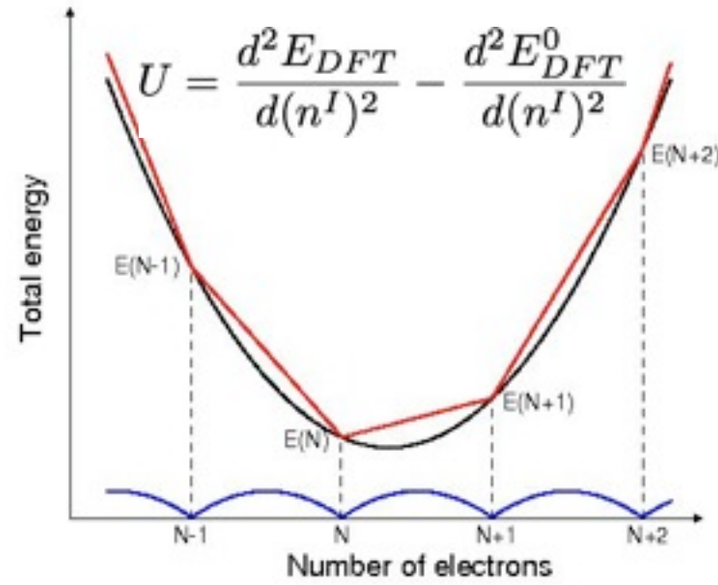

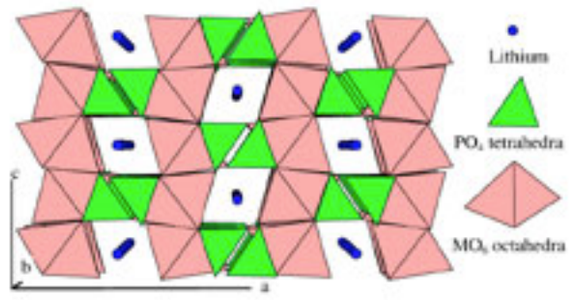

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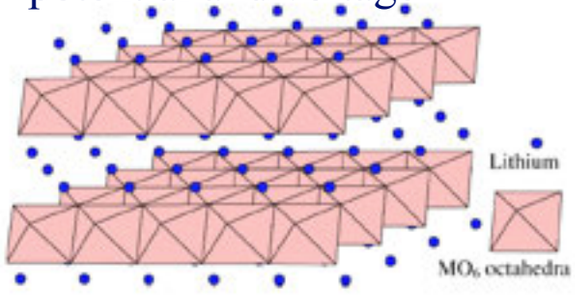

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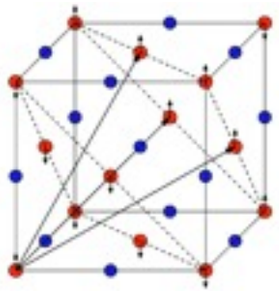

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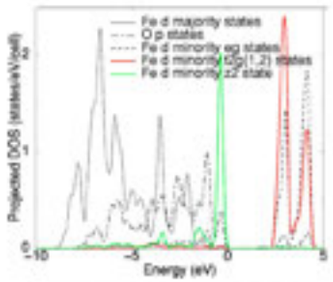

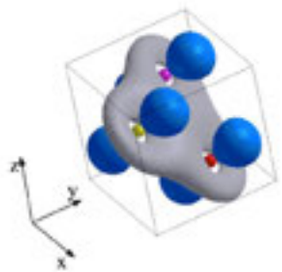

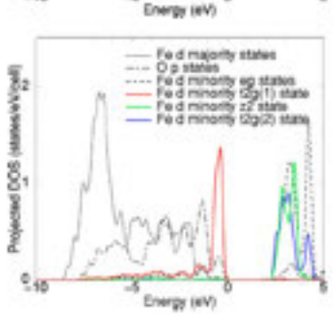

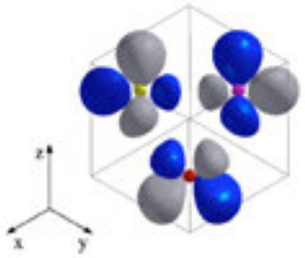

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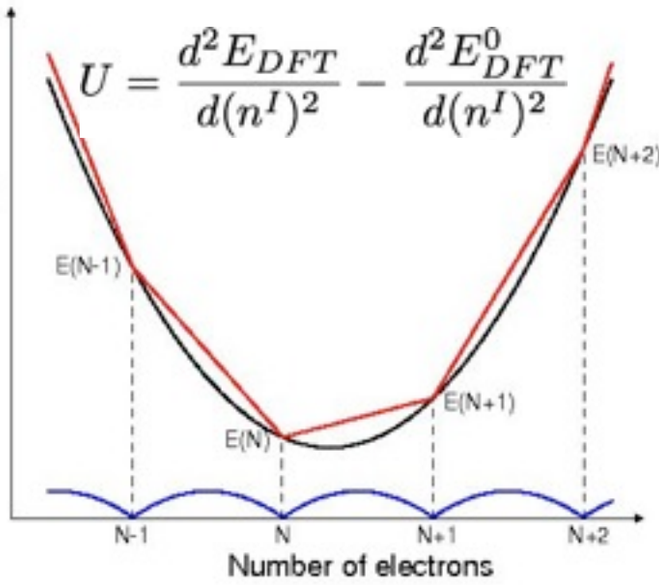

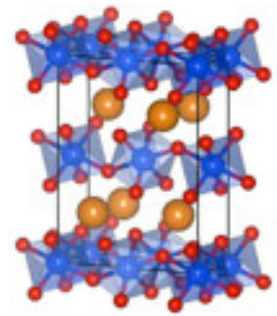

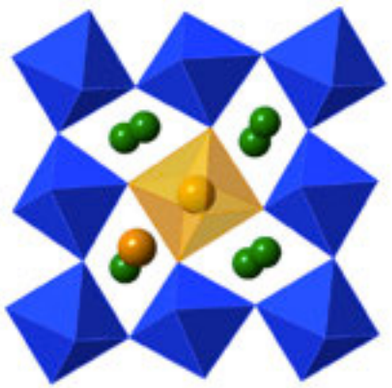

Fe minerals: structural and magnetic transitions

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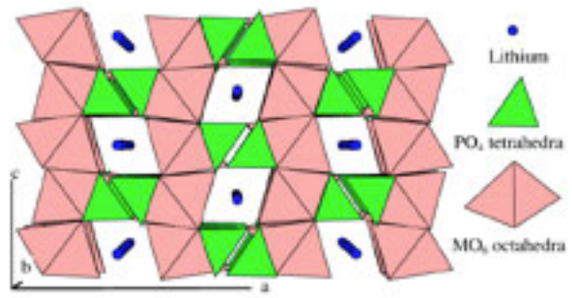

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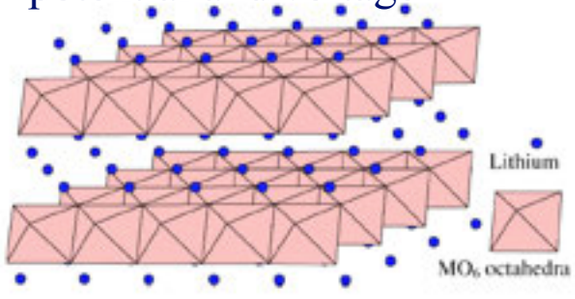

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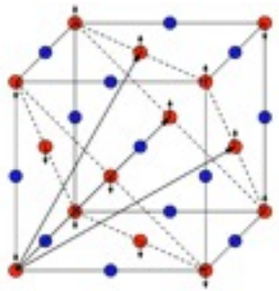

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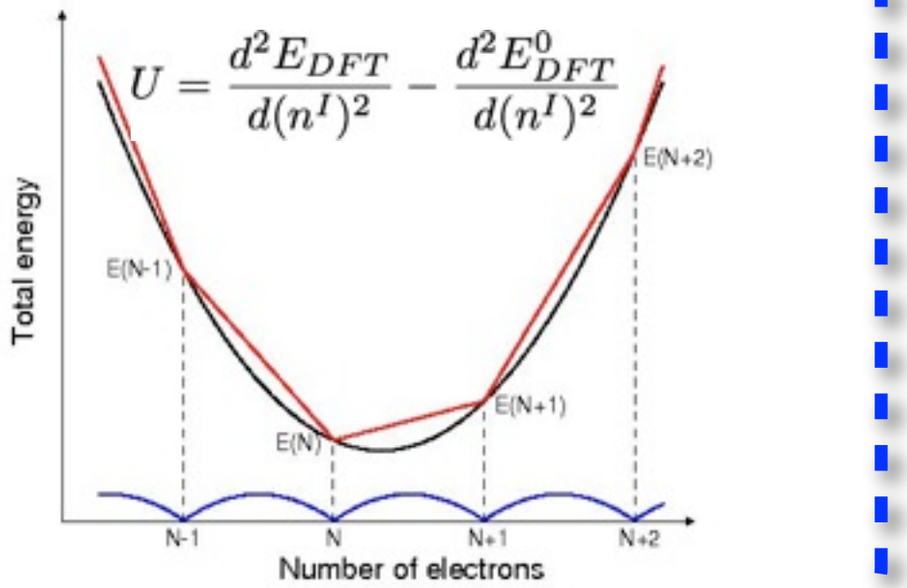

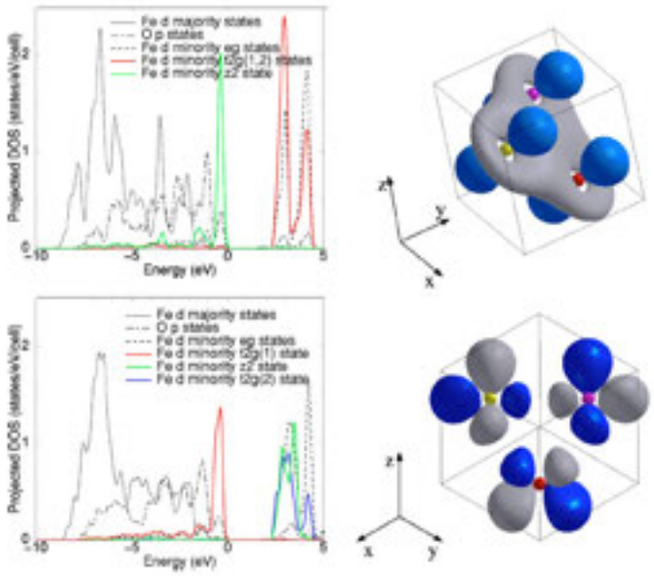

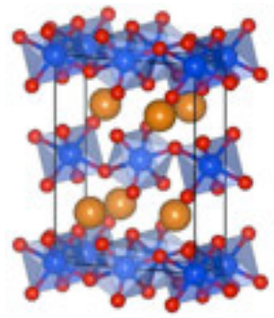

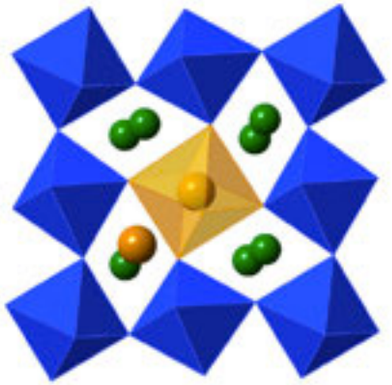

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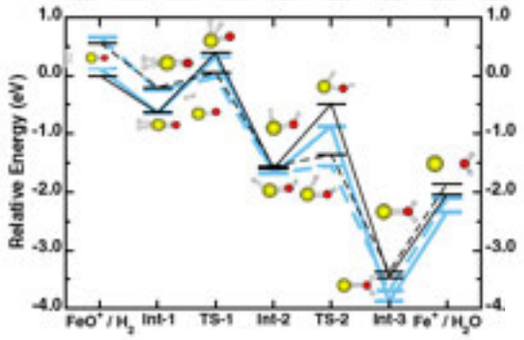
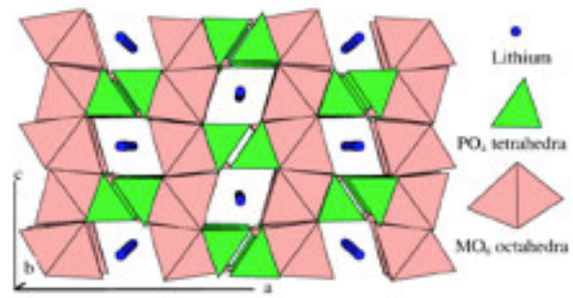
H. Hsu *et al.* Phys Earth Plan. Int. (2011)
H. Hsu *et al.* PRB (2009)

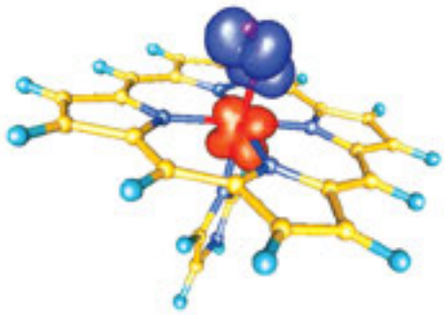


Transition-metal chemistry (gas phase)

H. Kulik *et al.*, PRL (2006)



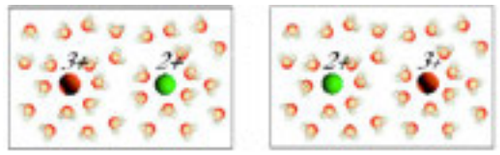
Li-ion battery materials: redox potential and voltage



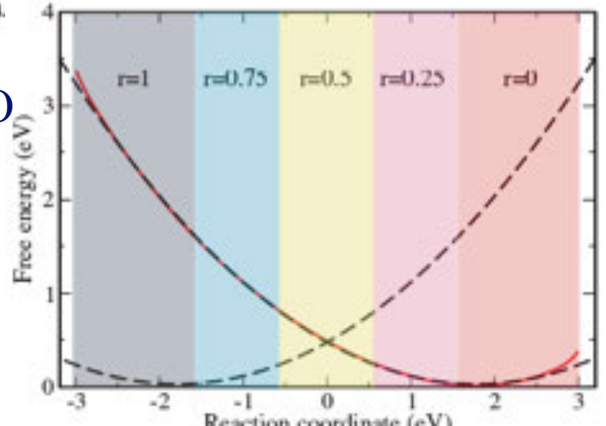
Spin-state energetics in Heme

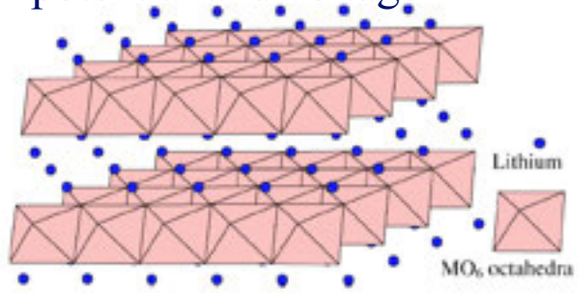
D. Scherlis *et al.*, JPCB (2007)

Electron-transfer reactions in H_2O



P. H.-L. Sit *et a.*, PRL (2006)
P. H.-L. Sit *et a.*, JEC (2007)





F. Zhou *et al.*, PRB (2004),
F. Zhou *et al.*, Elec. Comm. (2004)

LDA+U_{scf}: computing U from a LDA+U ground state

LDA and LDA+U ground states can be qualitatively different.

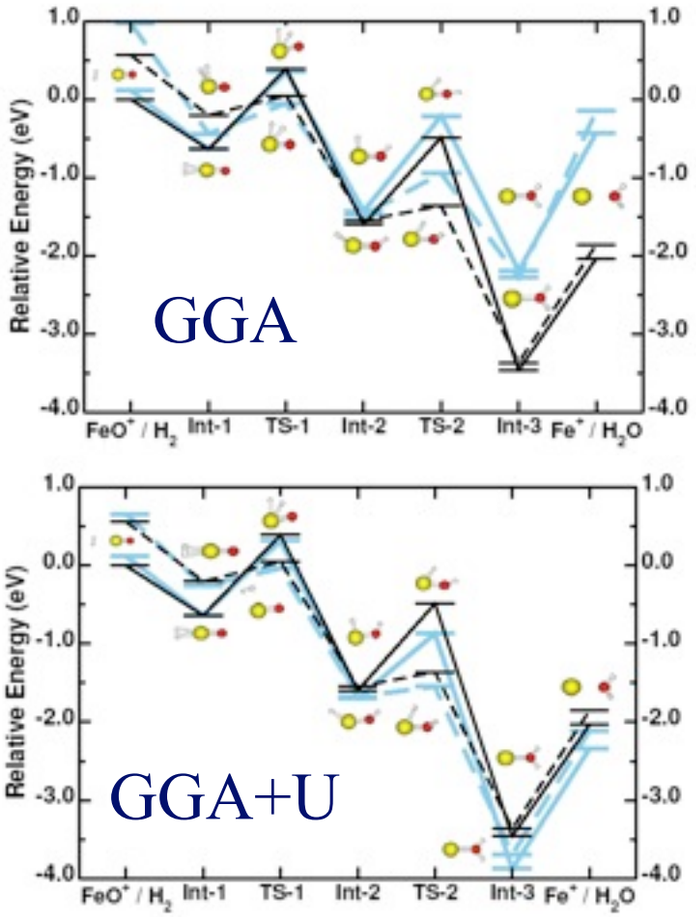
U cab be calculated as the curvature of the DFT part of the energy corresponding to a LDA+U ground state

$$E[\{\alpha_I\}] = \min_{\rho} \left\{ E_{DFT}[\rho(\mathbf{r})] + E_U[\{n^I\}] + \sum_I \alpha^I n^I \right\}$$

In the perturbed run we keep the Hubbard potential "frozen" (we construct it with the same n^I of the unperturbed scf calculation

U is recomputed until consistent with the one used in the expression of E_U

LDA+U_{scf} results



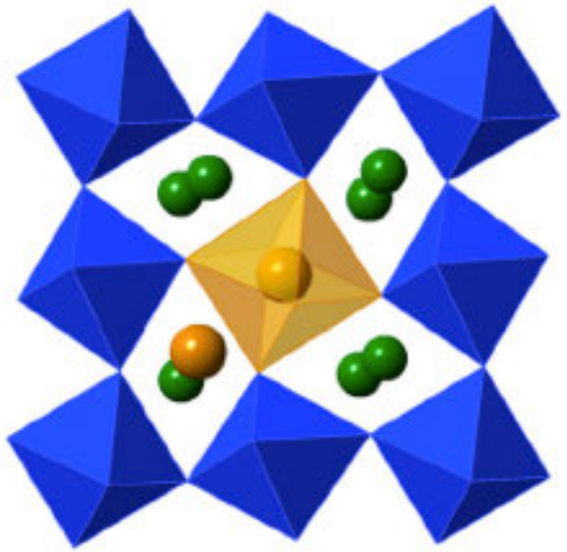
Reaction in the gas phase:

$FeO^+ + H_2 \rightarrow Fe^+ + H_2O$

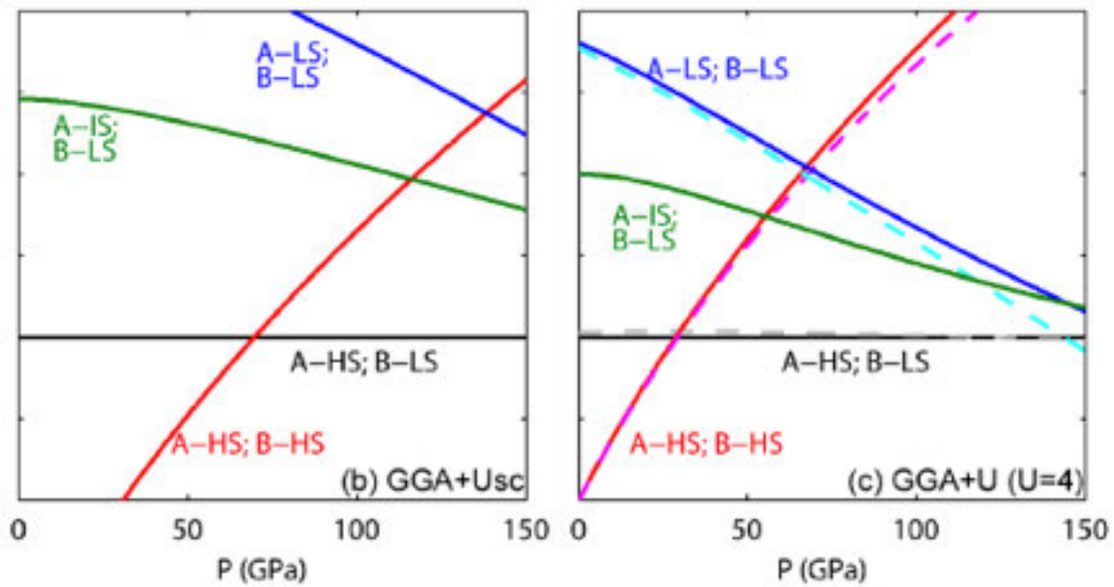
	Forward Reaction			Back Reaction		
ΔE_a	GGA	GGA+U	CCSD(T)	GGA	GGA+U	CCSD(T)
TS-1[4]	0.39	0.22	0.25	1.43	1.64	1.60
TS-1[6]	0.99	0.96	1.03	1.60	2.02	1.99
TS-2[4]	0.54	0.13	0.19	1.34	2.15	2.01
TS-2[6]	1.22	0.82	1.11	2.01	3.01	2.98
		(1.16)				

H. J. Kulik *et al.* PRL 97, 103001 (2006)

$(Mg,Fe)(Si,Fe)O_3$ perovskite



$(Mg_{0.875}Fe_{0.125})(Si_{0.875}Fe_{0.125})O_3$



H. Hsu *et al.* PRL 106, 118501 (2011)

LDA+U for metals: FLL vs AMF limits

Fully Localized Limit (FLL)

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + \sum_{I,\sigma} \frac{U^I}{2} Tr\left[\mathbf{n}^{I\sigma}\left(\mathbf{1}-\mathbf{n}^{I\sigma}\right)\right]$$

Favors integer occupations

V. I. Anisimov *et al.*, PRB 48, 16929 (1993)

A. Liechtenstein *et al.* PRB 52, R 5467 (1995)

V. I. Anisimov *et al.*, J. Phys. Condens. Matter 9, 767 (1997)

S. L. Dudarev *et al.*, PRB 57, 1505 (1998)

Around Mean-Field (AMF)

$$E_{DFT+U} = E_{DFT} + \sum_{I} \frac{U^I}{2} Tr(\mathbf{n}^I - \langle n^I \rangle)^2$$

Energy costs of fluctuations around even distribution of electrons

V. I. Anisimov *et al.* PRB 44, 943 (1991)

V. I. Anisimov *et al.*, J. Phys. Condens. Matter 19, 106206 (2007)

M. T. Czyzyk *et al.* PRB 49, 14211 (1994)

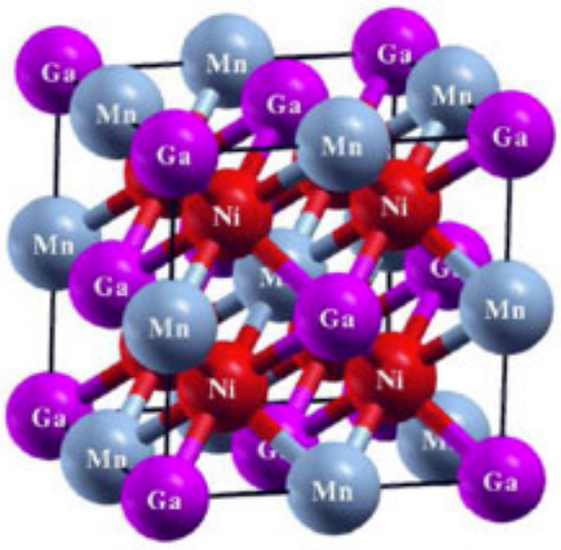
A. G. Petukhov *et al.*, PRB 67, 153106 (2003)

End of the first part

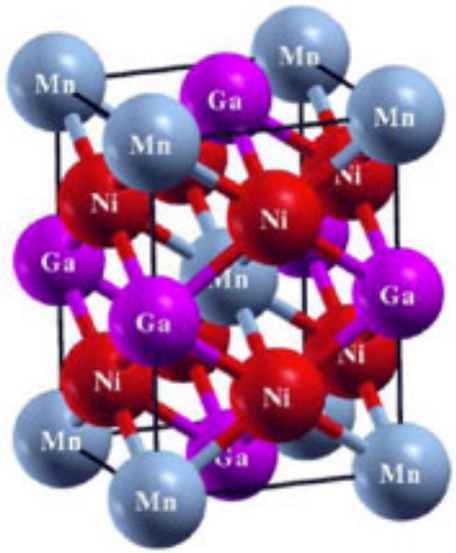
Questions?

Magnetic Shape Memory Alloys (Heusler): magnetism and phase transformation

Ni_2MnGa



Austenite



Martensite
(non modulated)

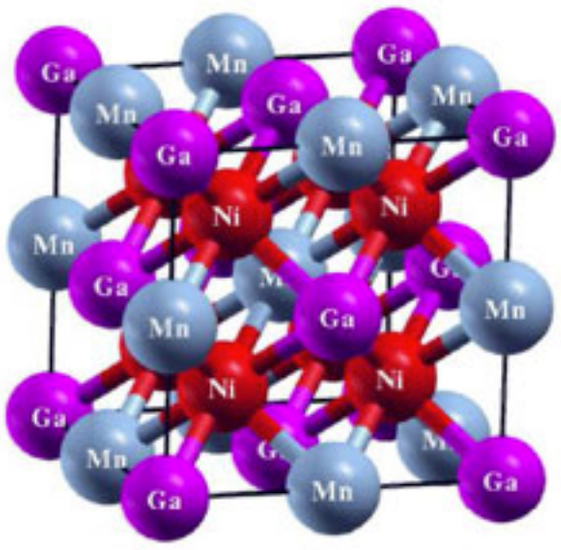
Martensitic transitions

High T: austenite cubic (FCC)

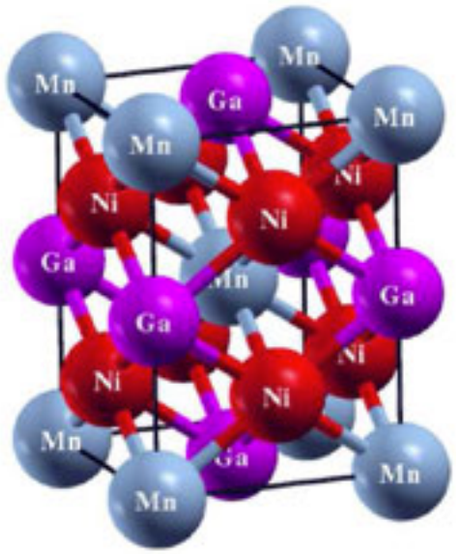
Low T: martensite (modulated tetragonal)

Magnetic Shape Memory Alloys (Heusler): magnetism and phase transformation

Ni_2MnGa



Austenite



Martensite
(non modulated)

Martensitic transitions

High T: austenite cubic (FCC)

Low T: martensite (modulated tetragonal)

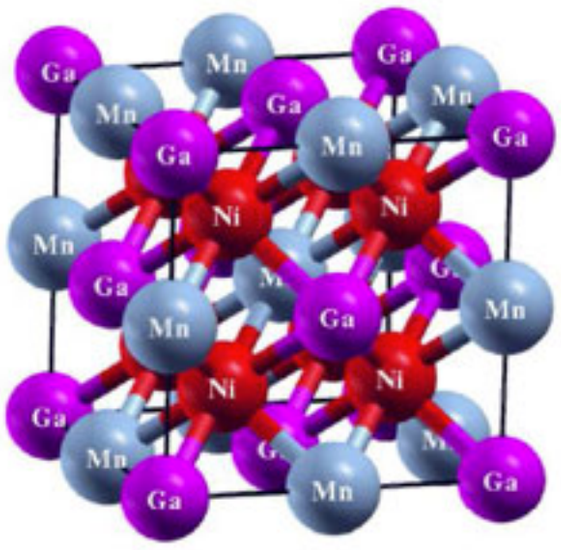
Experiments

Alloy	Content (at %) Ni	Mn	*e/a*	Phase
1	50.7	28.4	7.685	5M
2	50.7	28.3	7.681	5M
3	50.7	27.8	7.661	5M
4	50.6	28.5	7.682	5M
5	50.0	29.8	7.692	5M
6	50.0	28.9	7.656	5M
7	49.9	29.9	7.690	5M
8	49.7	29.1	7.643	5M
9	49.6	29.2	7.640	5M
10	49.2	30.6	7.668	5M
11	49.1	30.7	7.665	5M
12	49.0	30.3	7.642	5M
13	48.5	30.3	7.607	5M
14	51.0	28.5	7.710	7M
15	50.5	29.4	7.711	7M
16	49.5	30.3	7.677	7M
17	48.8	31.4	7.672	7M
18	54.9	23.8	7.795	NM
19	54.0	24.7	7.768	NM
20	53.9	24.4	7.749	NM
21	53.7	26.4	7.815	NM
22	53.3	24.6	7.715	NM
23	52.9	25.0	7.703	NM
24	52.8	25.7	7.724	NM
25	52.7	26.0	7.729	NM
26	52.4	25.6	7.692	NM
27	52.3	27.4	7.757	NM
28	51.7	27.7	7.726	NM
29	51.5	26.8	7.677	NM
30	51.2	27.4	7.68	NM
31	51.0	28.7	7.721	NM
32	50.5	30.4	7.751	NM
33	47.0	33.1	7.614	NM

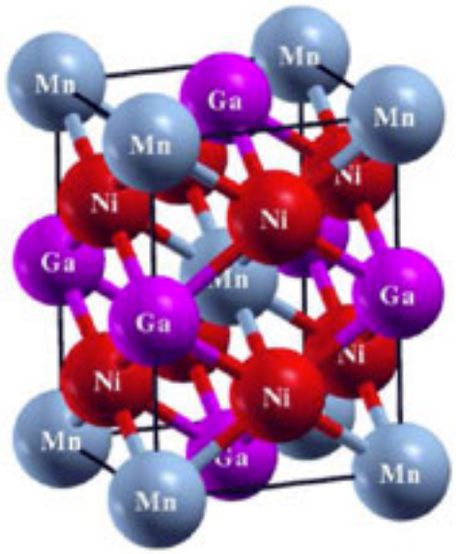
Lanska *et al.*, *J. Appl. Phys.* **95**, *8074 (2004)*

Magnetic Shape Memory Alloys (Heusler): magnetism and phase transformation

Ni_2MnGa



Austenite



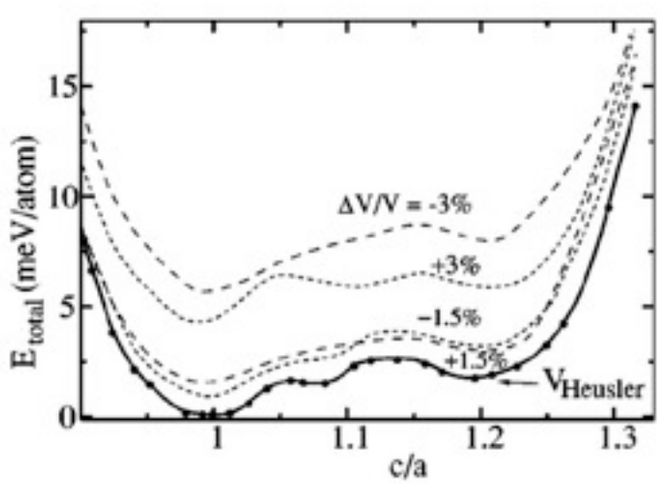
Martensite
(non modulate

Martensitic transitions

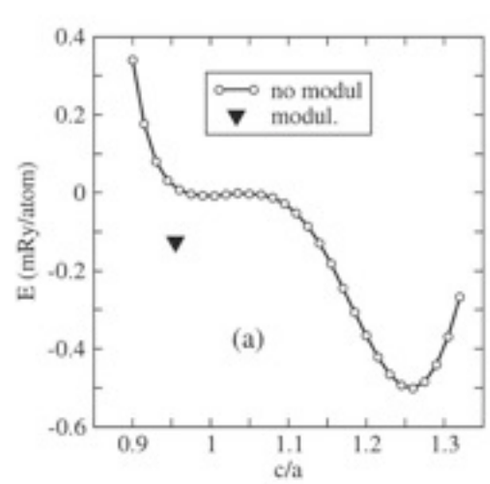
High T: austenite cubic (FCC)

Low T: martensite (modulated tetragonal)

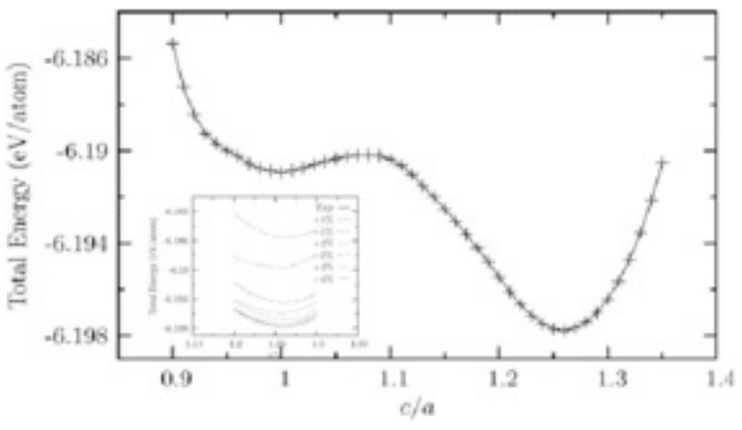
Calculations: A and non modulated M



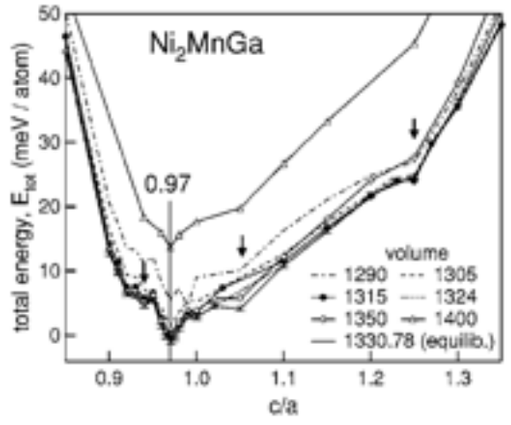
Godlevsky et. al. PRB 63, 134407 (2000)



Zayak et. al. J. Phys. Condens. Matter 15, 159 (2003)



Kart et. al. Phys. Stat. Sol. 205, 1026 (2008)

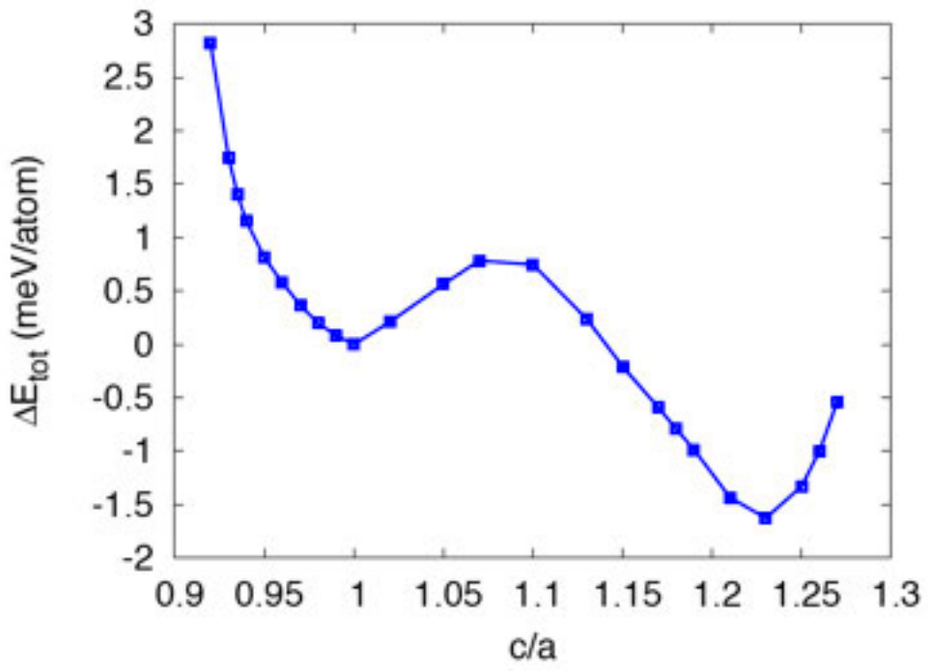


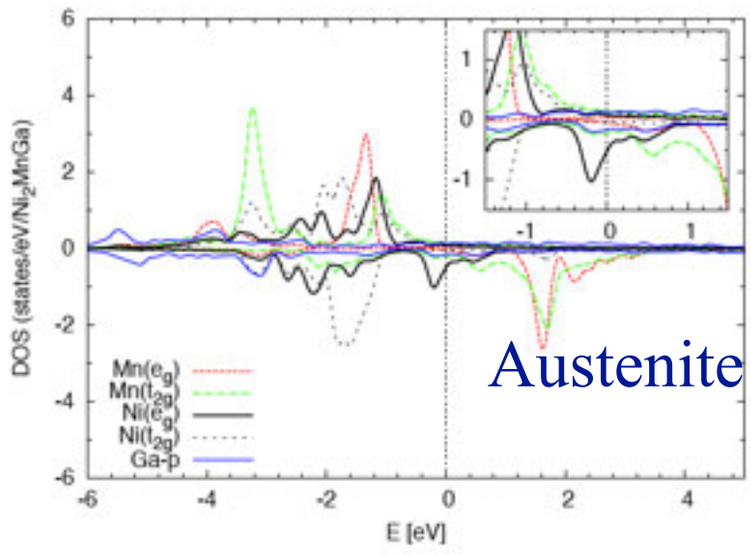
Barman *et al.*, *Phys. Rev. B* **72**, 184410 (2005)

Ni_2MnGa: localization and structural stability

Ni_2MnGa: localization and structural stability

GGA

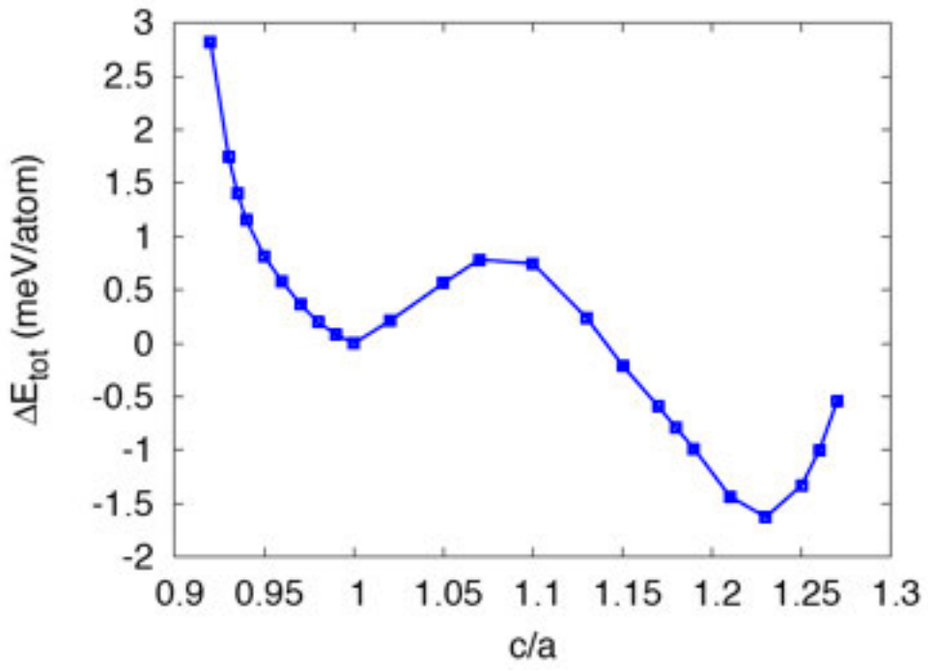




a_0 (Å)	$\mu_{\mathrm{Mn}}\,(\mu_B)$	$\mu_{\mathrm{Ni}}\,(\mu_B)$	$\mu_{\mathrm{Ga}}\,(\mu_B)$	$\mu_{\mathrm{tot}}\,(\mu_B/\mathrm{cell})$
5.83	3.67	0.34	−0.13	4.22

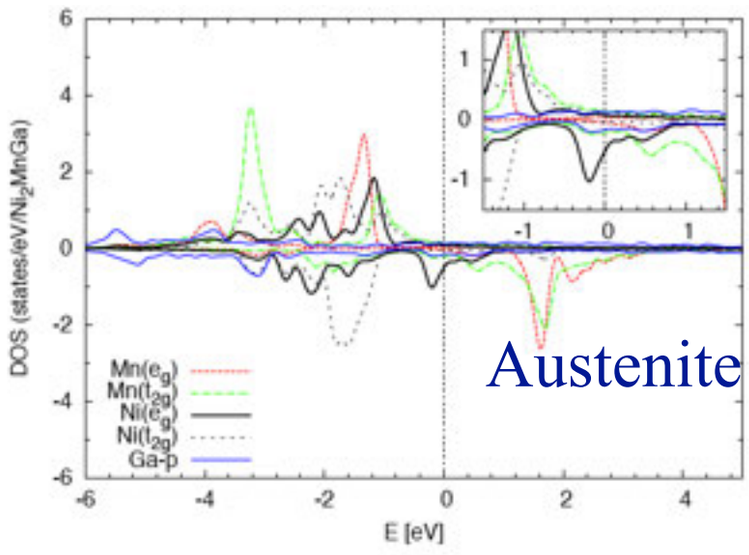
Ni_2MnGa: localization and structural stability

GGA



Mn: magnetism

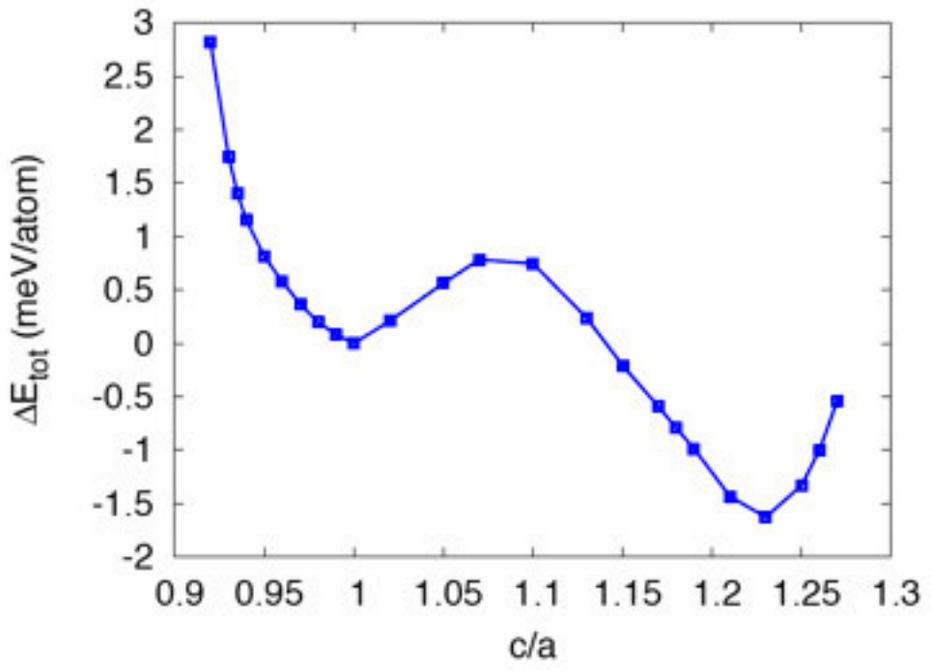
Ni: metallic character



a_0 (Å)	$\mu_{\mathrm{Mn}}\,(\mu_B)$	$\mu_{\mathrm{Ni}}\,(\mu_B)$	$\mu_{\mathrm{Ga}}\,(\mu_B)$	$\mu_{\mathrm{tot}}\,(\mu_B/\mathrm{cell})$
5.83	3.67	0.34	−0.13	4.22

Ni_2MnGa: localization and structural stability

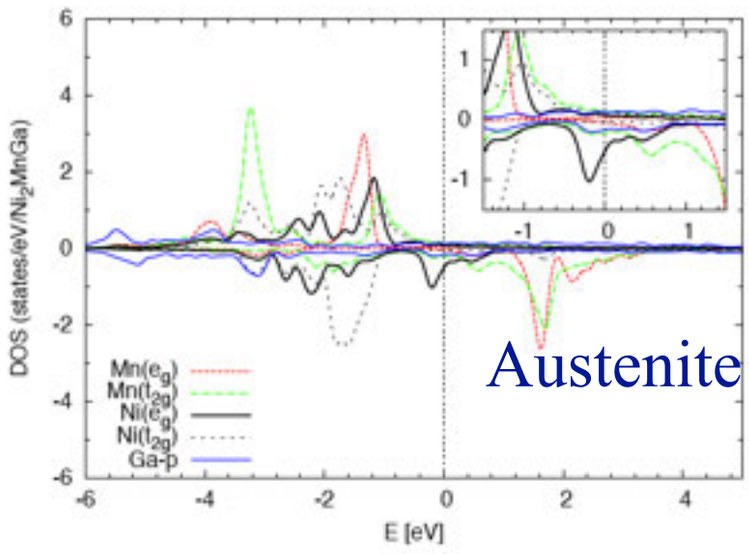
GGA



Mn: magnetism

Ni: metallic character

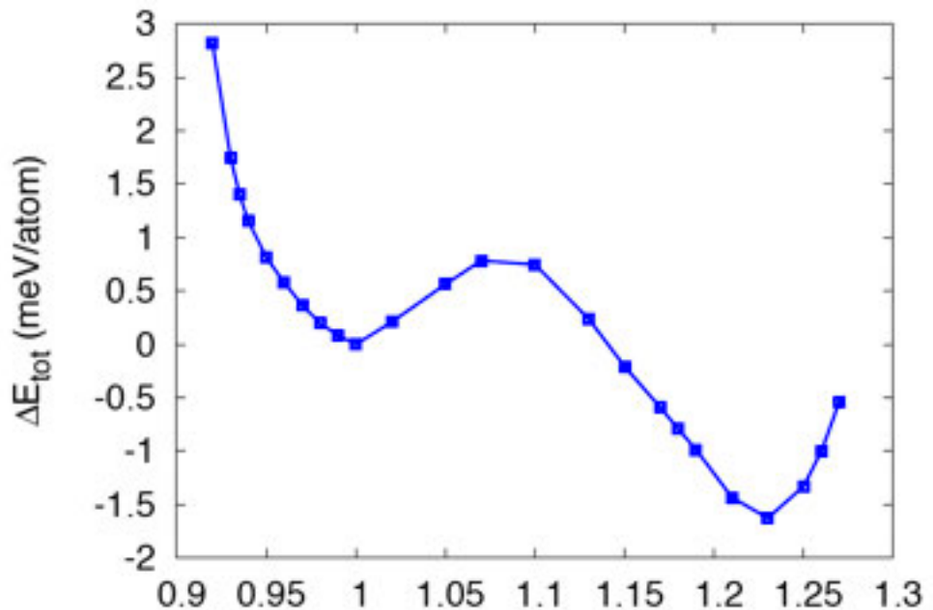
The d states of Mn are localized: +U correction needed?

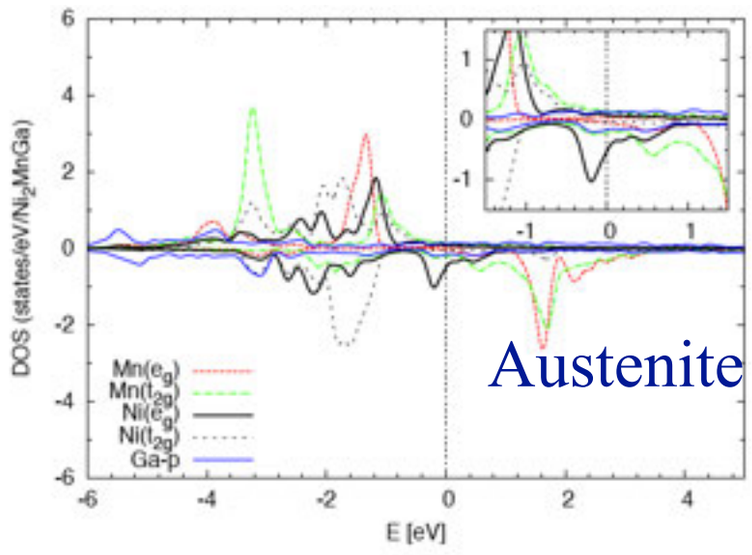


a_0 (Å)	$\mu_{\mathrm{Mn}}\,(\mu_B)$	$\mu_{\mathrm{Ni}}\,(\mu_B)$	$\mu_{\mathrm{Ga}}\,(\mu_B)$	$\mu_{\mathrm{tot}}\,(\mu_B/\mathrm{cell})$
5.83	3.67	0.34	−0.13	4.22

Ni_2MnGa: localization and structural stability

GGA





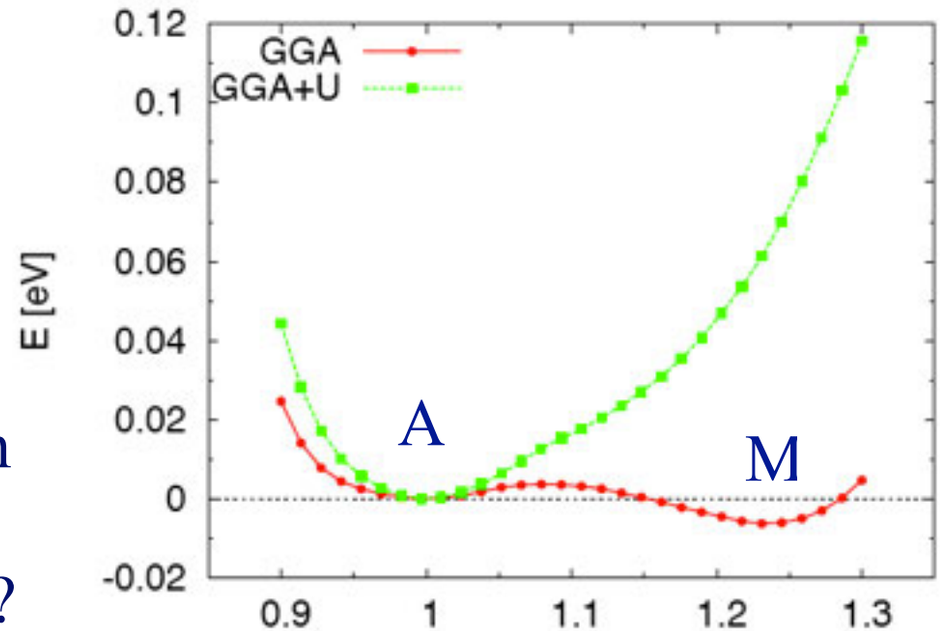
a_0 (Å)	μ_{Mn} (μ_B)	μ_{Ni} (μ_B)	μ_{Ga} (μ_B)	μ_{tot} (μ_B/cell)
5.83	3.67	0.34	−0.13	4.22

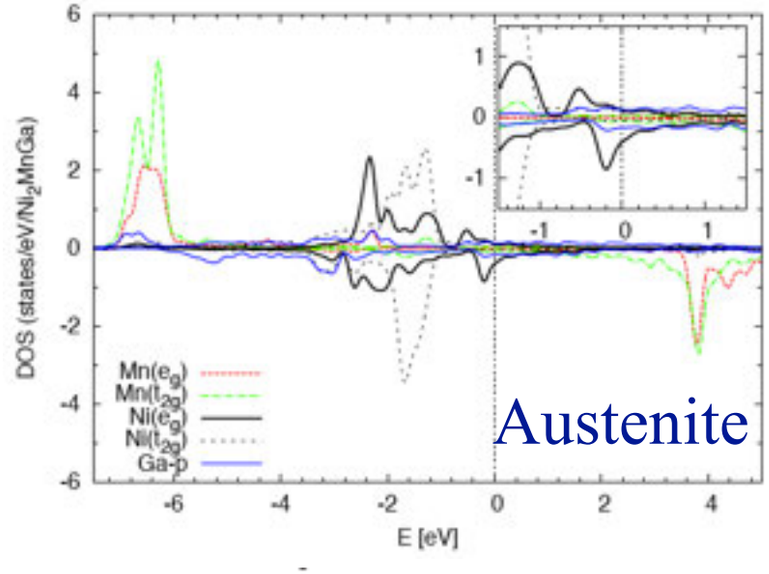
Mn: magnetism

Ni: metallic character

The d states of Mn are localized: +U correction needed?

GGA+U

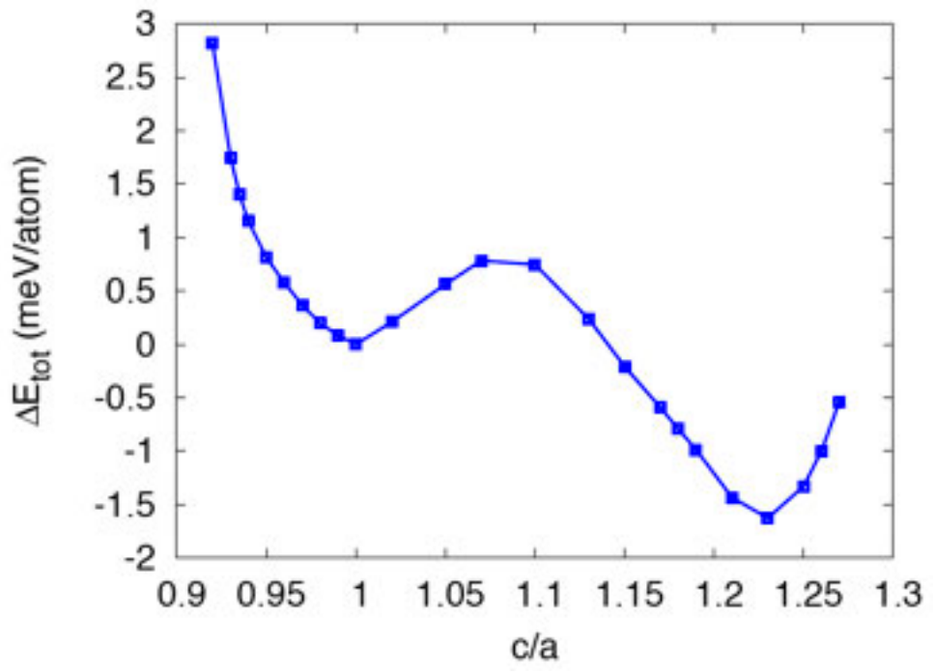


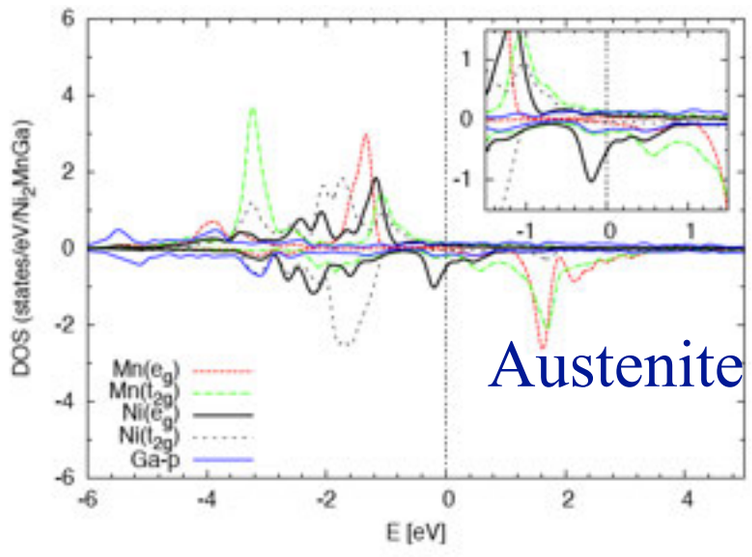


μ_{Mn} (μ_B)	μ_{Ni} (μ_B)	μ_{Ga} (μ_B)	μ_{tot} (μ_B/cell)
4.52	0.16	−0.13	4.80

Ni_2MnGa: localization and structural stability

GGA





a_0 (Å)	μ_{Mn} (μ_B)	μ_{Ni} (μ_B)	μ_{Ga} (μ_B)	μ_{tot} (μ_B/cell)
5.83	3.67	0.34	−0.13	4.22

Mn: magnetism

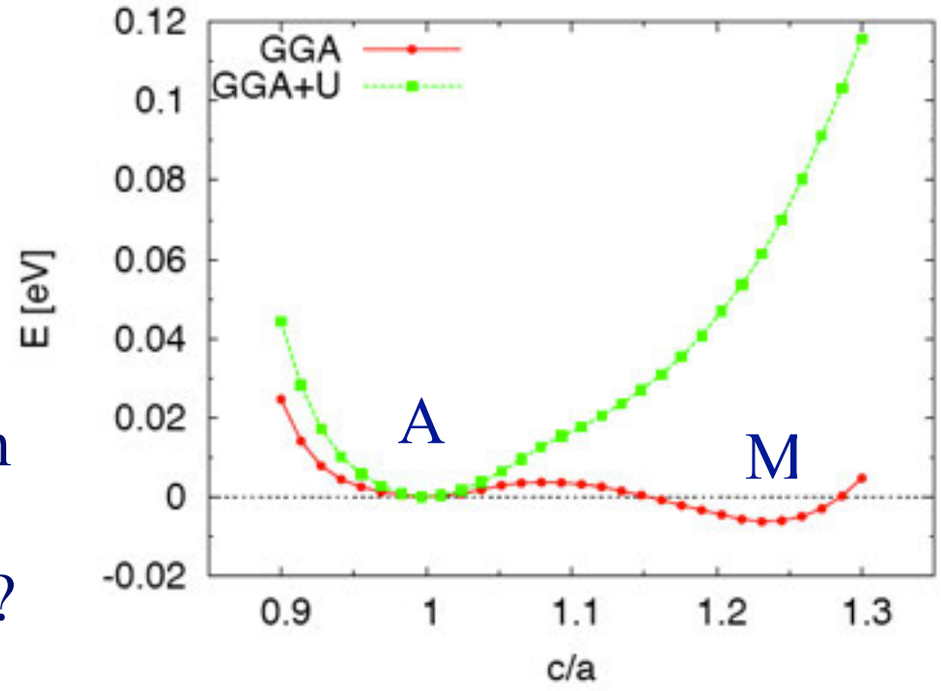
Ni: metallic character

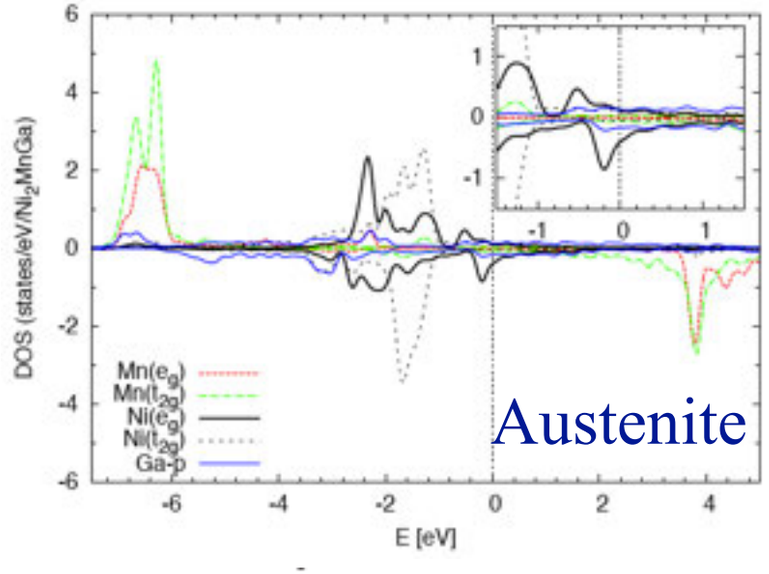
The d states of Mn are localized: +U correction needed?

A more pronounced electronic localization destabilizes the non-modulated martensite

What is the underlying mechanism?

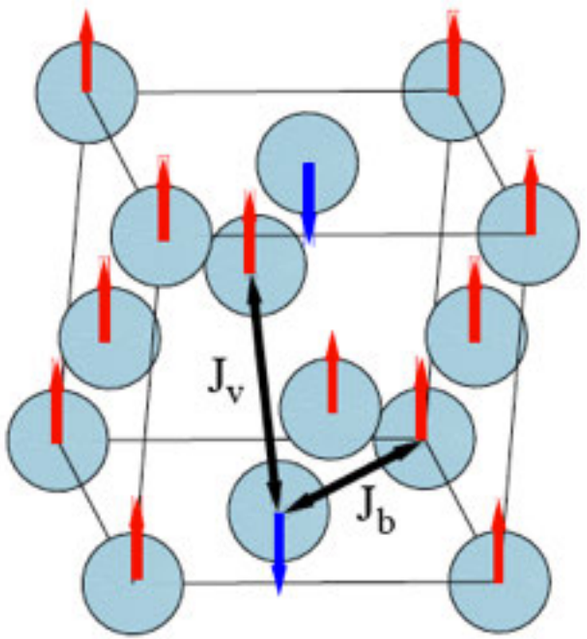
GGA+U





μ_{Mn} (μ_B)	μ_{Ni} (μ_B)	μ_{Ga} (μ_B)	μ_{tot} (μ_B/cell)
4.52	0.16	−0.13	4.80

Magnetic interaction energy

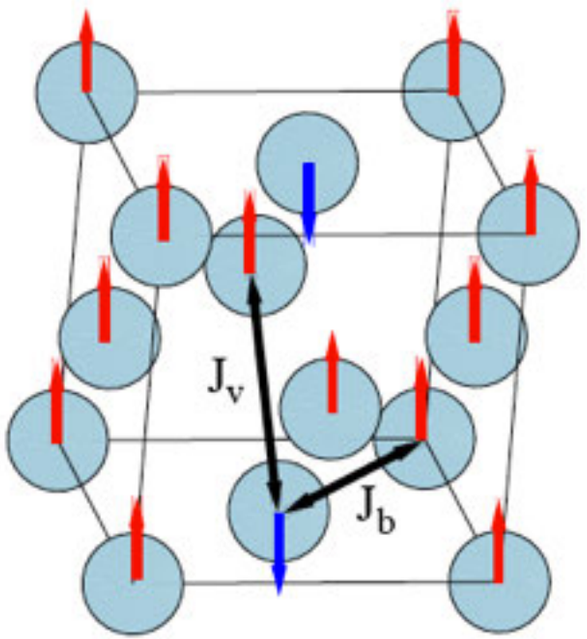


Heisenberg map for the energy

$$H_{mag} = \sum_{<i,j>} J_{i,j} S_i \cdot S_j$$

B. Himmetoglu V. M. Katukuri and M. Cococcioni, J. Phys. Condens. Matter 24, 185501 (2012)

Magnetic interaction energy



Heisenberg map for the energy

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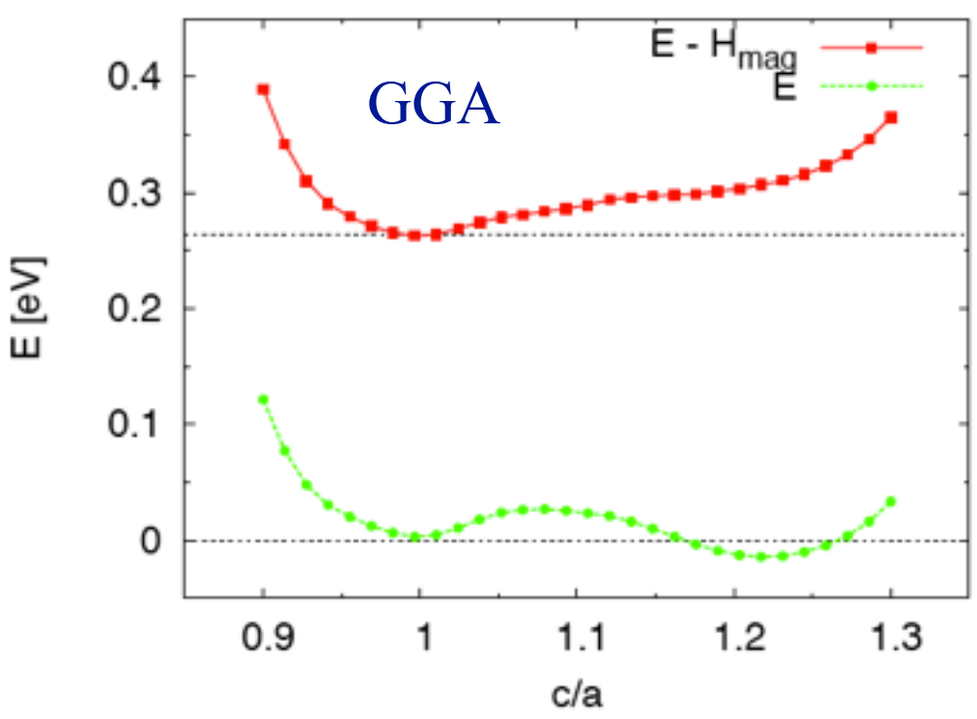

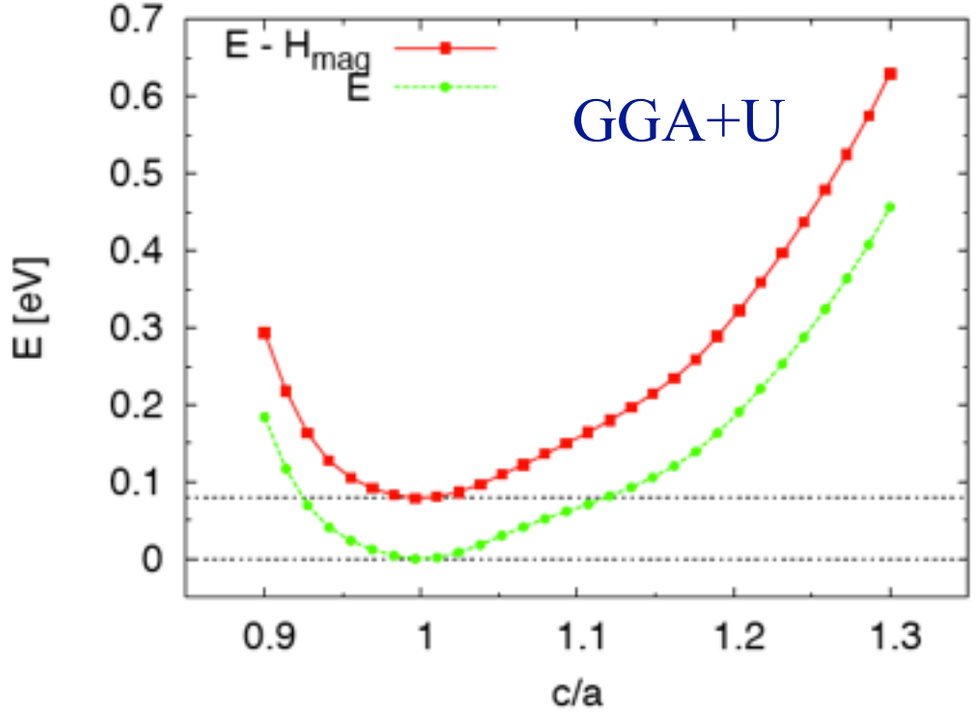

B. Himmetoglu V. M. Katukuri and M. Cococcioni, J. Phys. Condens. Matter 24, 185501 (2012)

Ni_2MnGa: modeling magnetism

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Mn atoms: Anderson magnetic impurities in Ni *d* and Ga *p* conduction electrons

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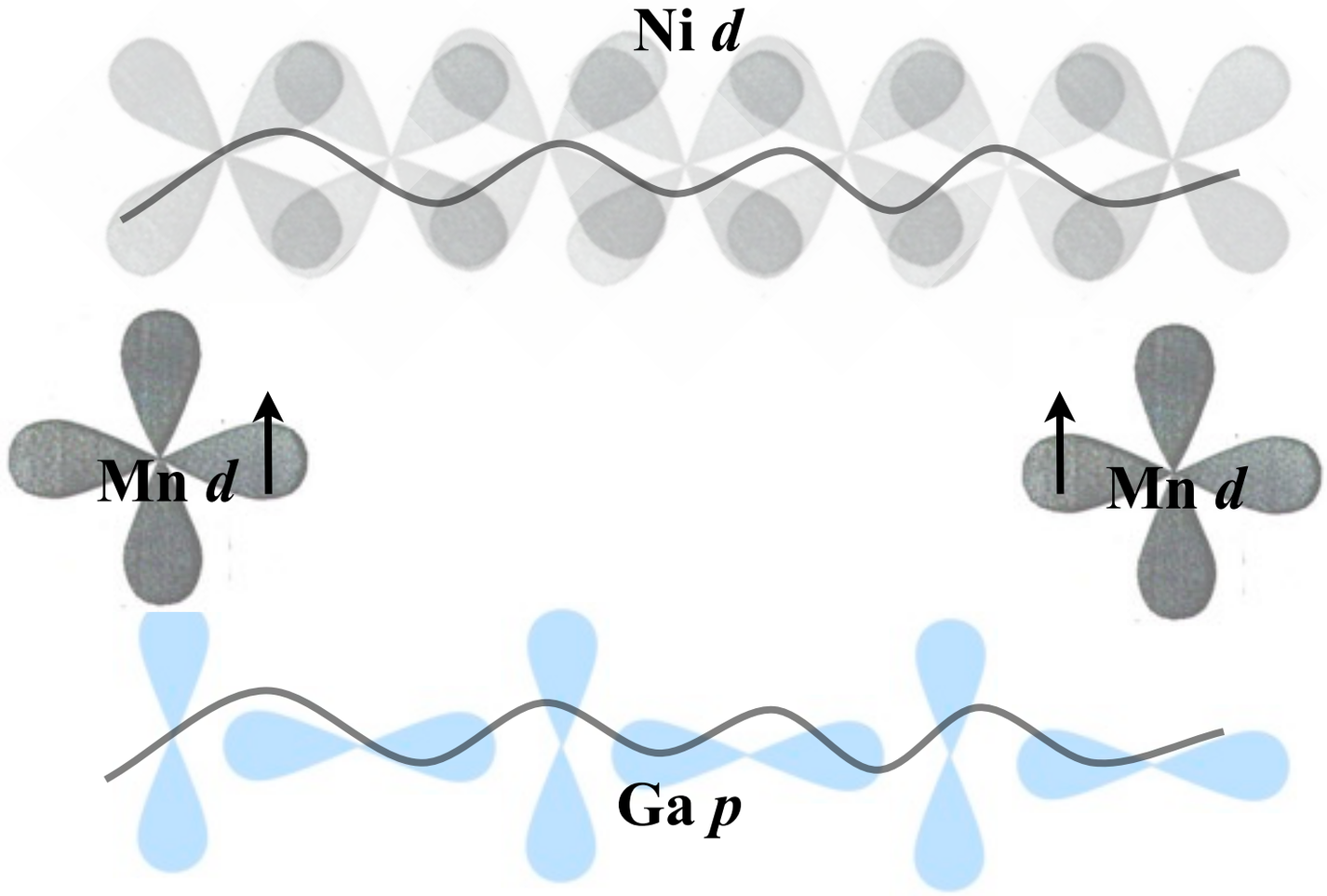

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Anderson model ➡ RKKY magnetic interactions (*J*)

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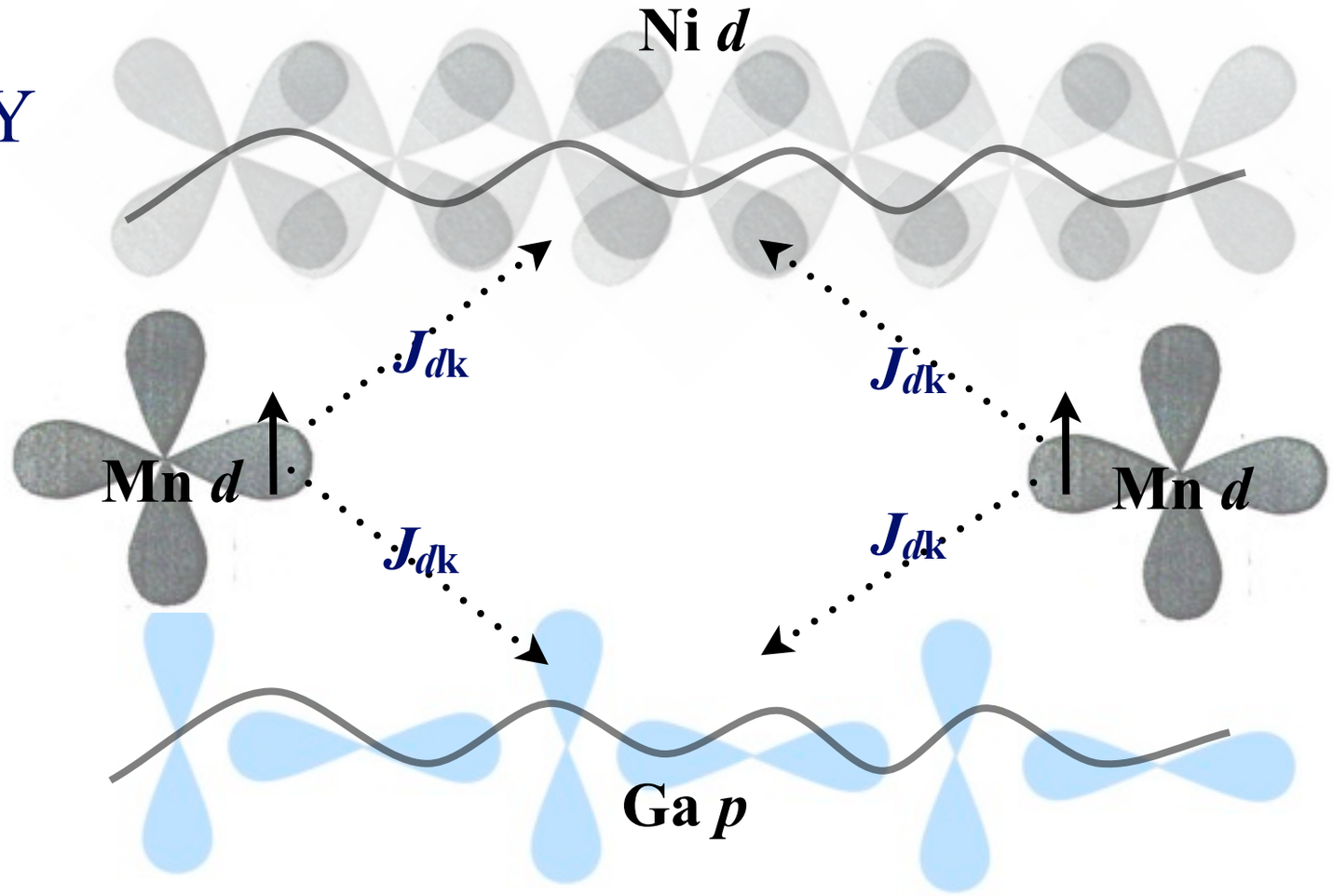

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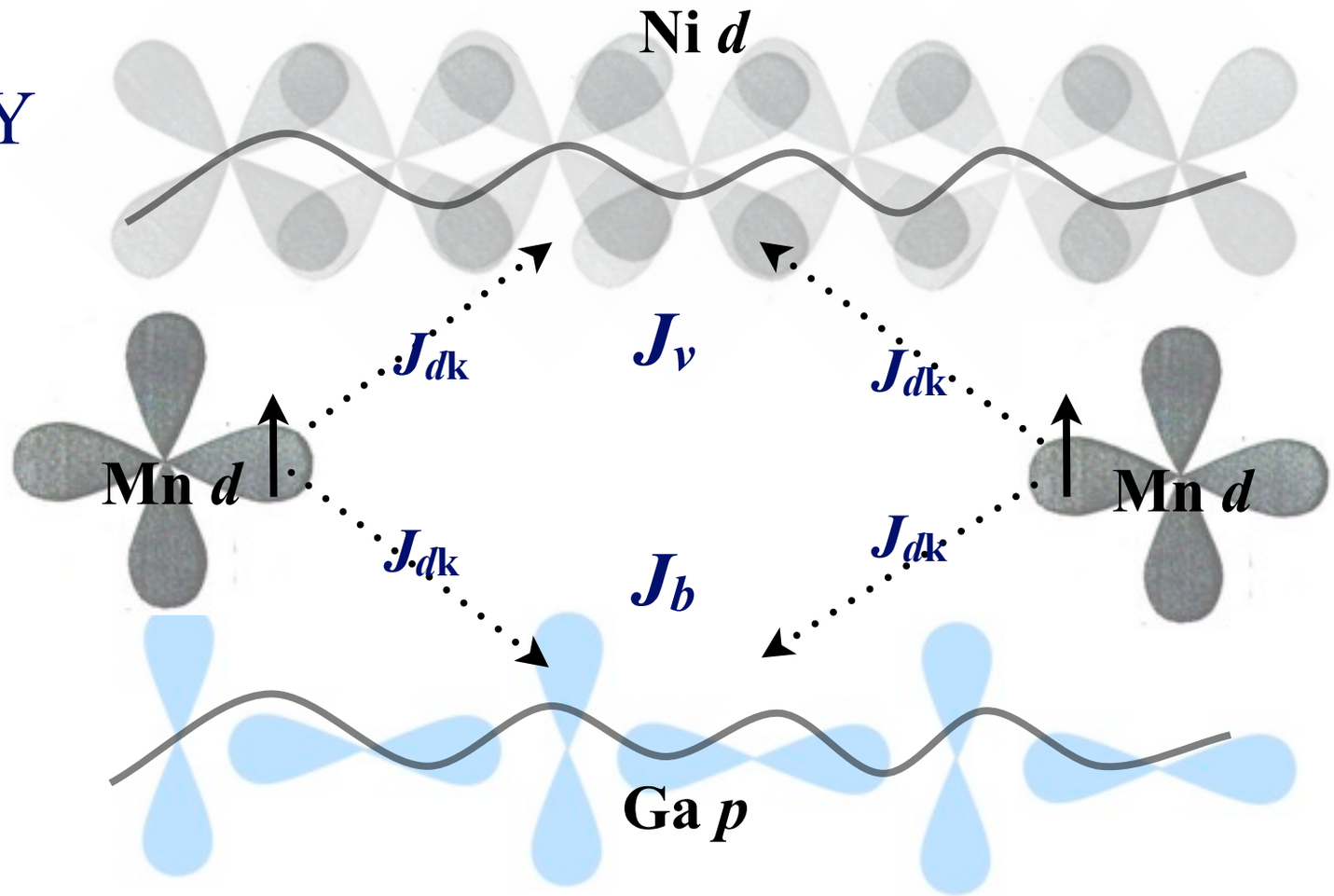
Super-exchange couplings and magnetization

$$J_{d\,d} \sim m\,k_F^4\,|J_{d\,\mathbf{k}}|^2 \quad \text{(FM)}$$

$$\mu_{\mathbf{k}} \simeq \frac{1}{2}\,|V_{d\,\mathbf{k}}|^2\,\frac{d\rho}{d\epsilon}\ln\left[\frac{E^2+\Delta^2}{(E+U)^2+\Delta^2}\right]$$



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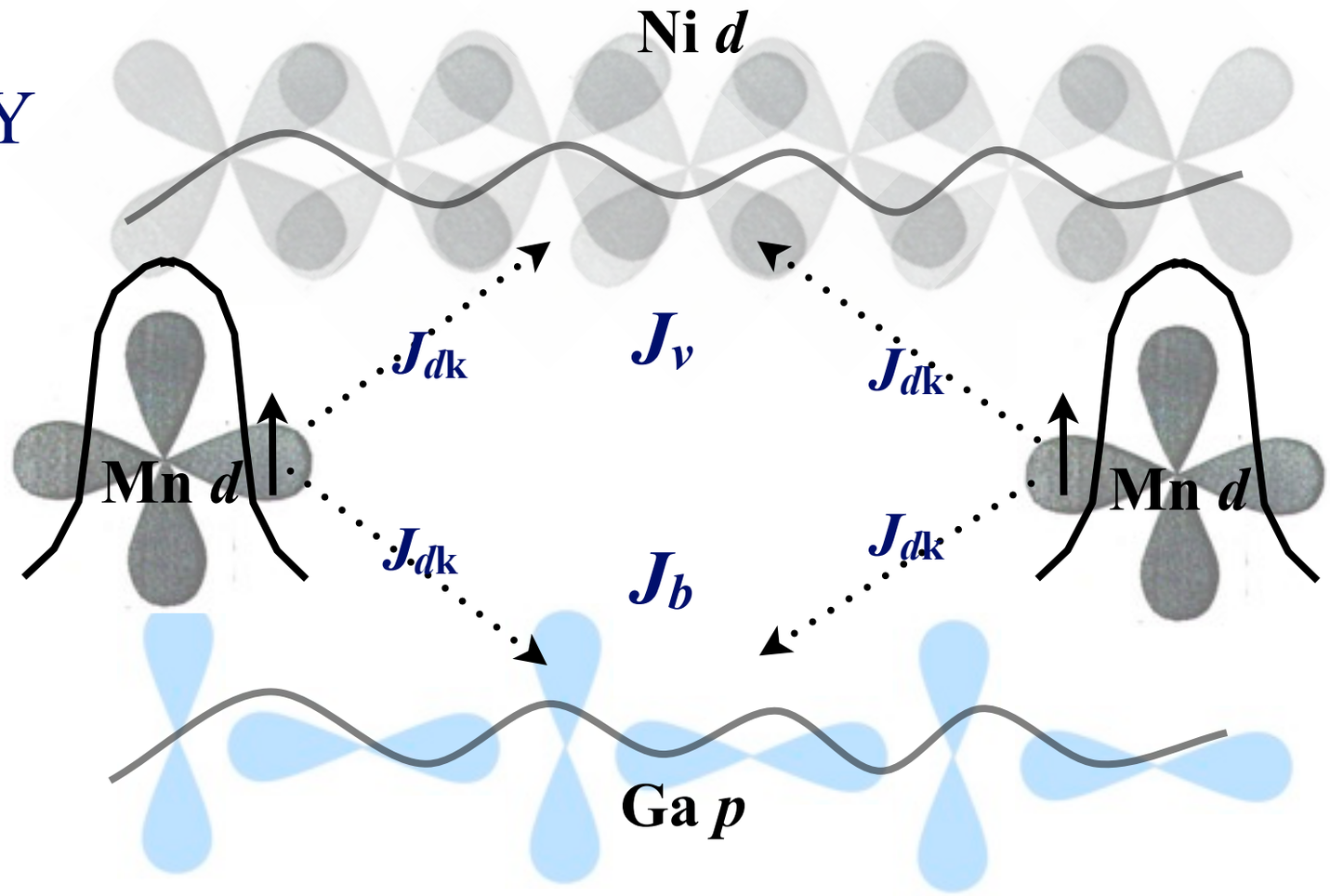

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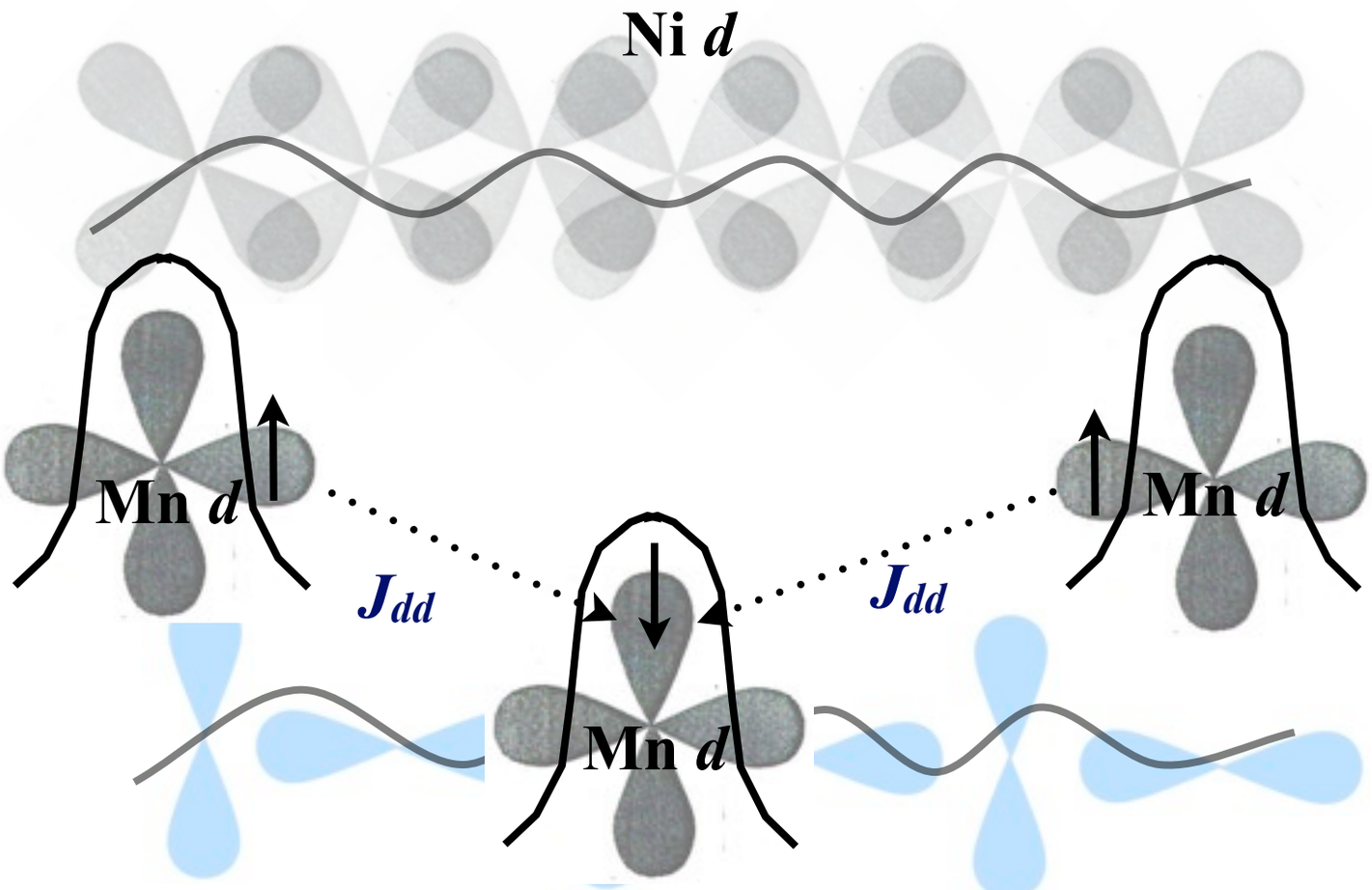
Electronic localization essential for magnetism: “+U” functional needed to capture this behavior

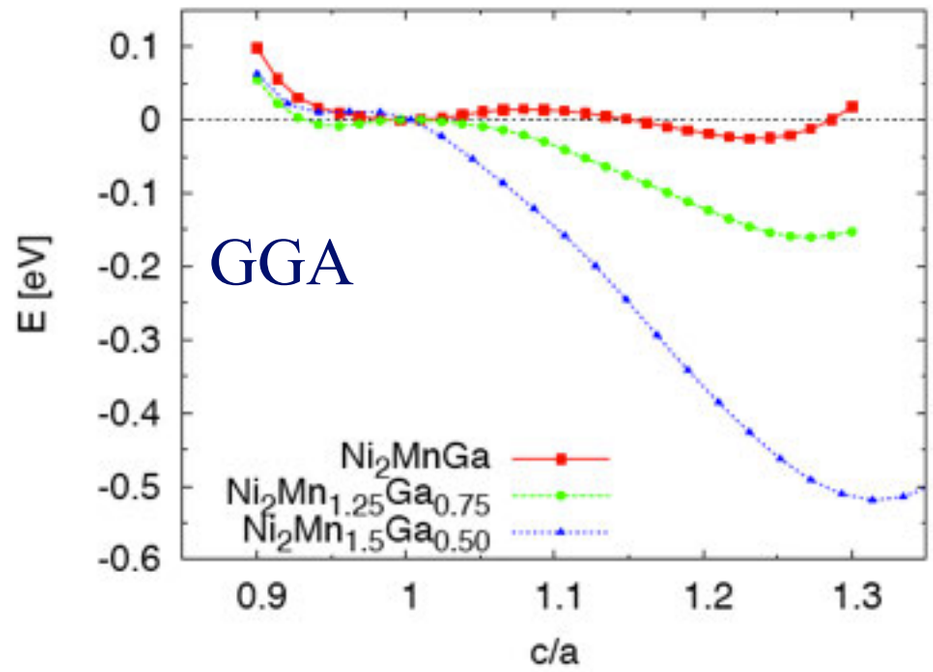
Ni_2MnGa: predicting the effect of doping

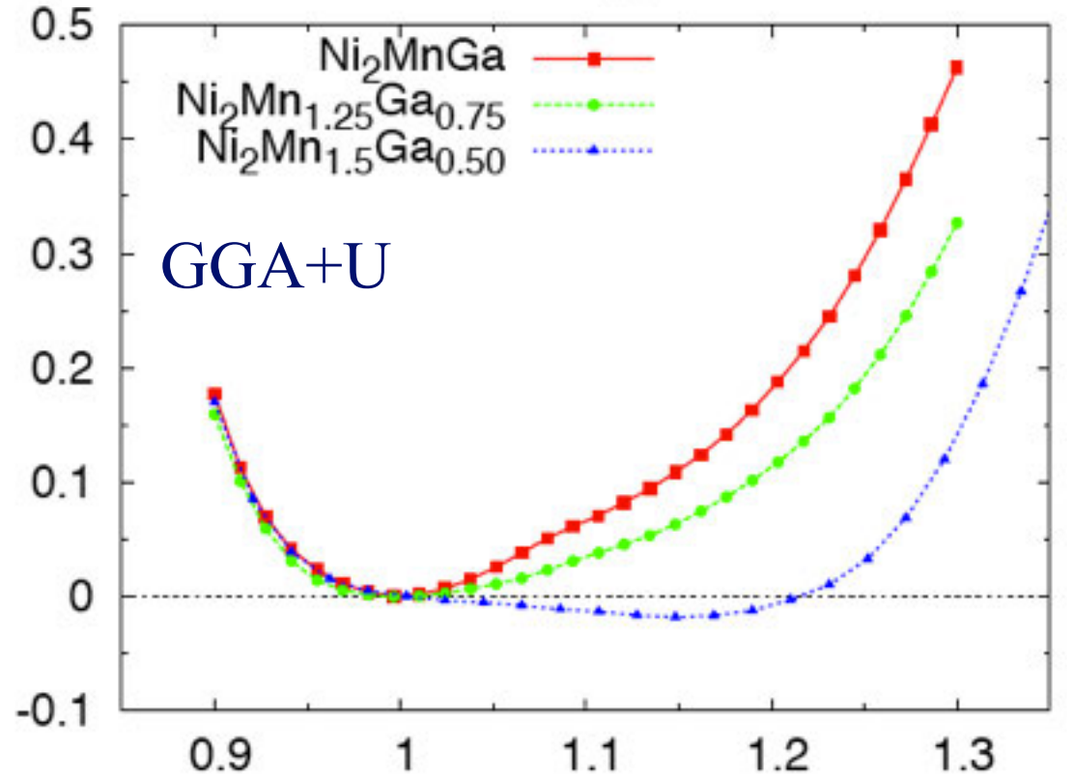


Mn substitutional impurity

Effect of doping: excess Mn stabilizes the (NM) tetragonal phase

B. Himmetoglu V. M. Katukuri and M. Cococcioni,
J. Phys. Condens. Matter 24, 185501 (2012)
arXiv:1203.1553v1 [cond-mat.mtrl-sci]





The fundamental gap problem

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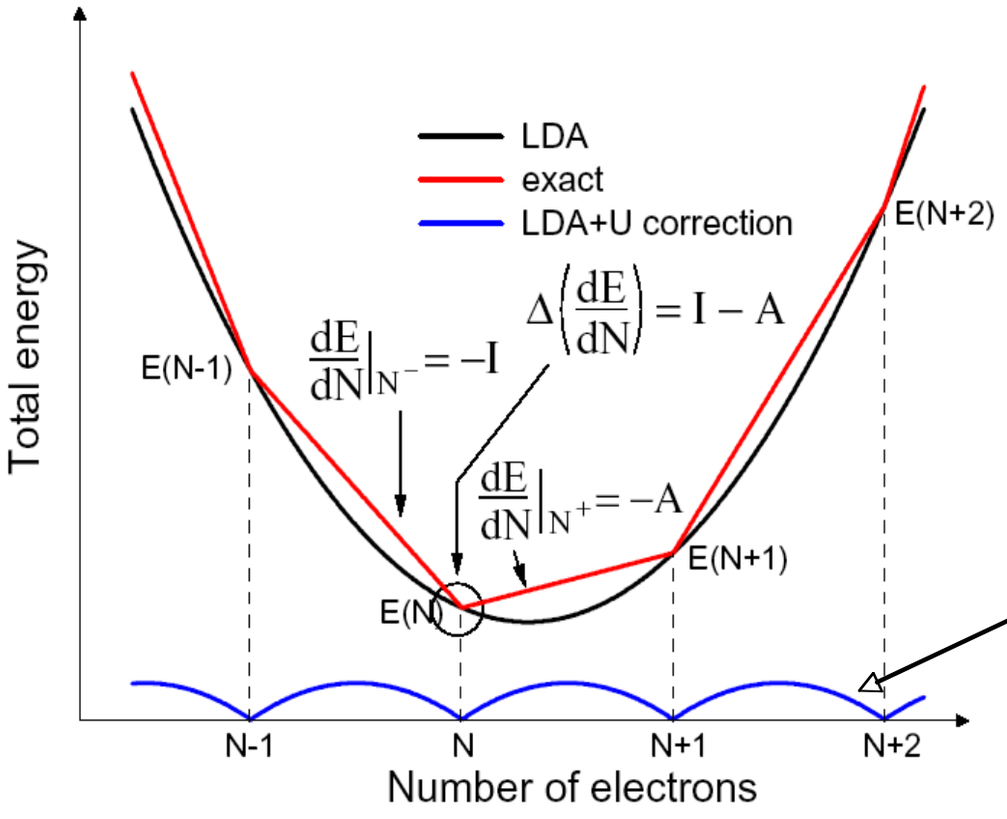
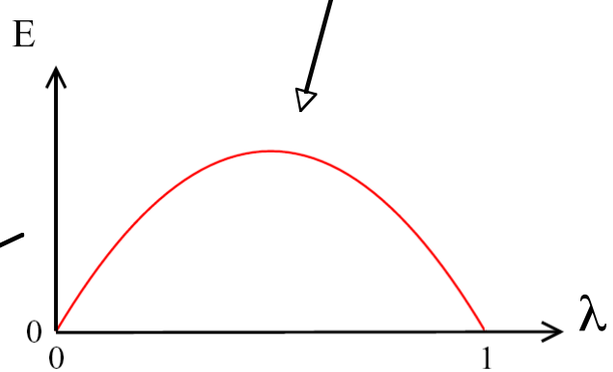


$$E_U = \frac{U}{2}\sum_{I,\sigma}\sum_{m}\left[\lambda_m^{I\sigma}\left(1-\lambda_m^{I\sigma}\right)\right]$$



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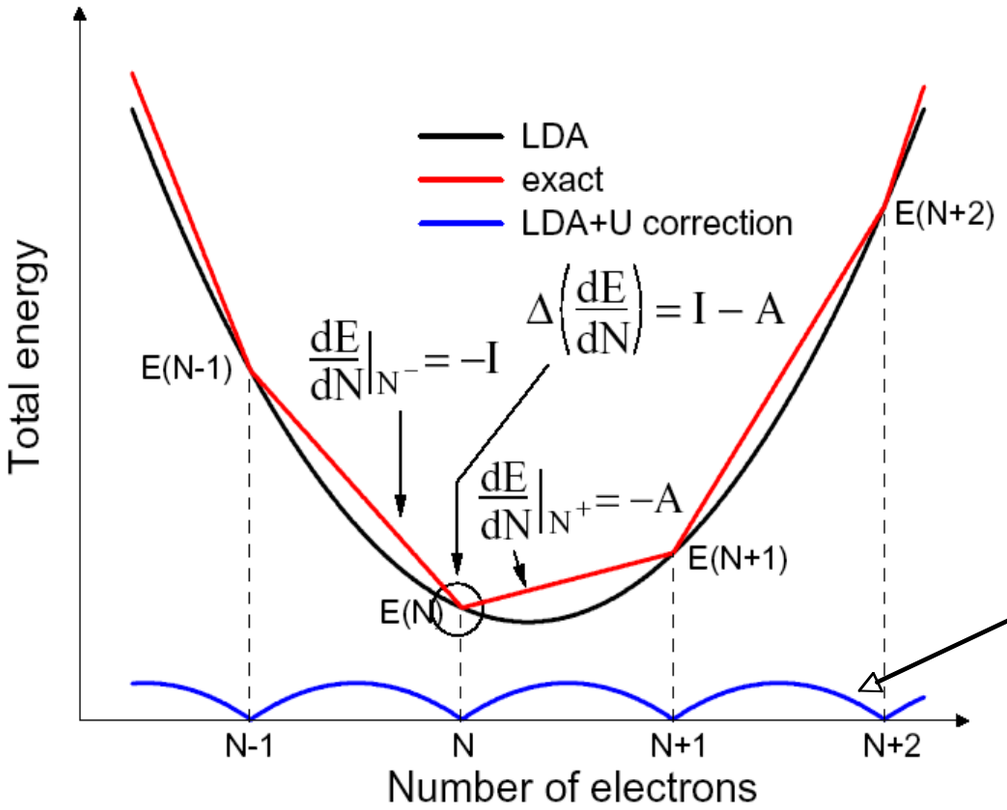

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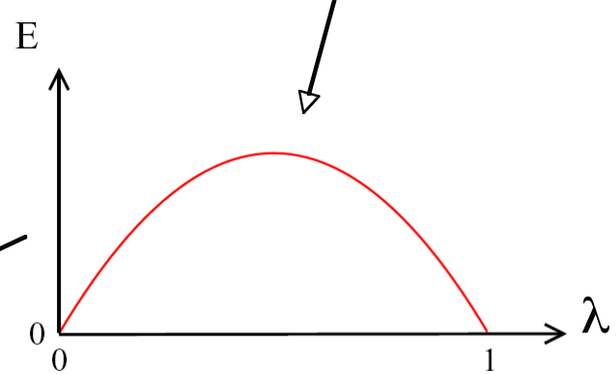

If computed as the second derivative of the energy, *U* re-establishes energy discontinuities: the **fundamental band gap:**

$$\Delta = \Delta_{KS} + \Delta_{xc}$$

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + \sum_{I,\sigma}\frac{U^I}{2}Tr\left[\mathbf{n}^{I\sigma}\left(\mathbf{1}-\mathbf{n}^{I\sigma}\right)\right]$$

DFT+U for covalent semiconductors

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Can the “+U” functional improve the band gap of band semiconductors?

DFT+U for covalent semiconductors

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	Si			GaAs		
	a (A)	B (GPa)	E_g (eV)	a (A)	B (GPa)	E_g (eV)
GGA	5.48	83.0	0.64	5.77	58.4	0.19
GGA+U	5.36	93.9	0.39	5.74	52.6	0.00
Exp	5.43	98.0	1.12	5.65	75.3	1.42

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Unfortunately not: **inter-site hybridization suppressed by *U***

The DFT+U+V functional

DFT+U energy functional

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U is the *on-site* interaction, *V* is the *inter-site* one; they are **in competition**

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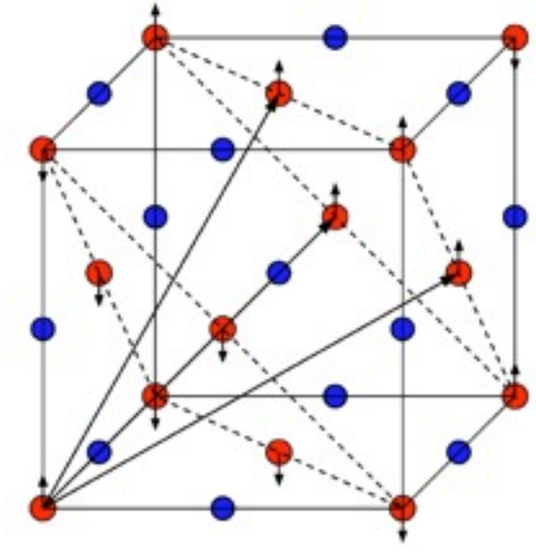
V. L. Campo Jr and M. Cococcioni, J. Phys.: Condens Matter 22 055602 (2010)

NiO

Typical TMO:

- Rock-salt structure
- AFII: rhombohedral symmetry
- Mott or Charge transfer insulator



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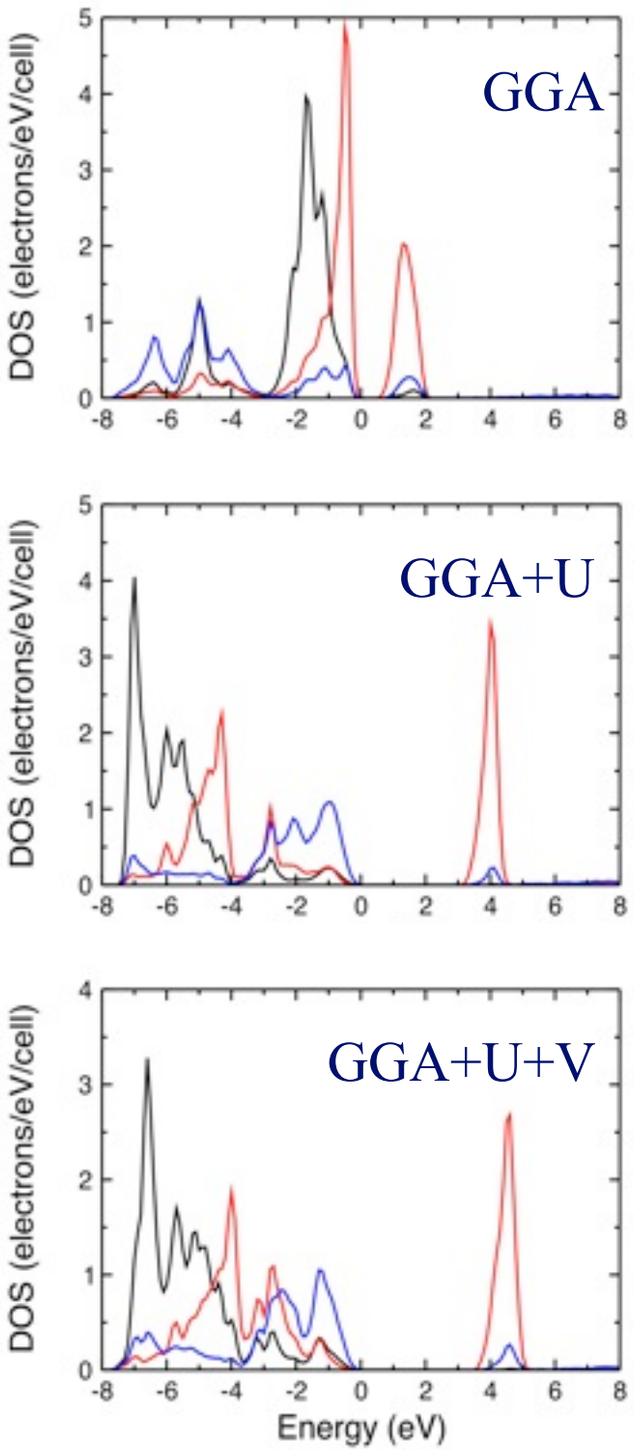

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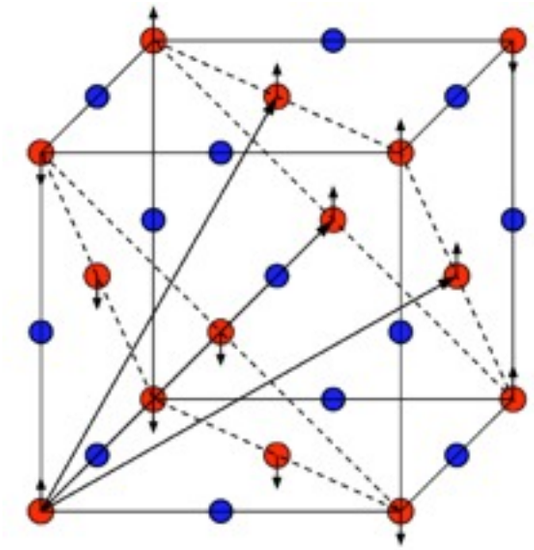

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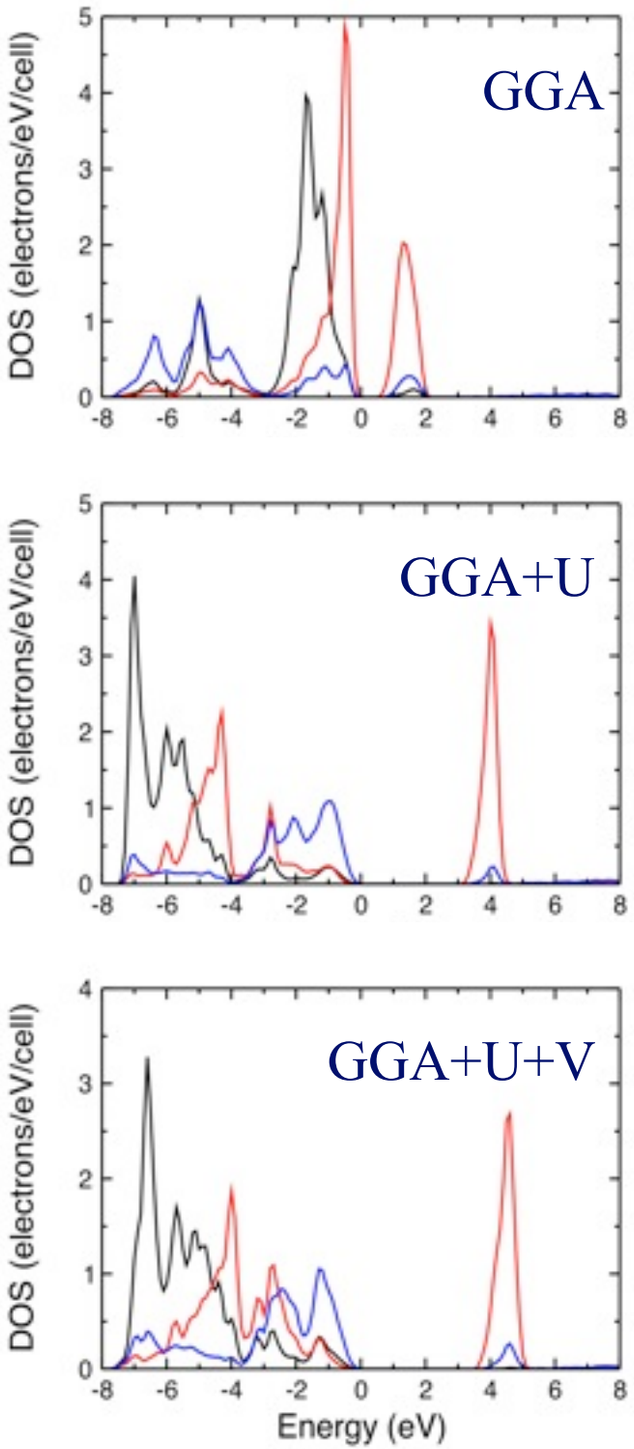

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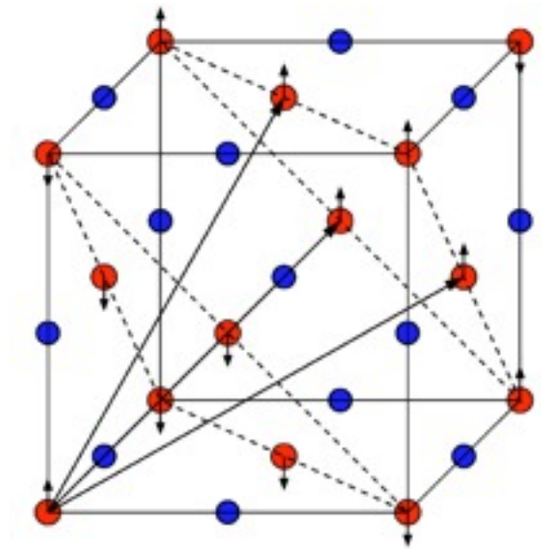
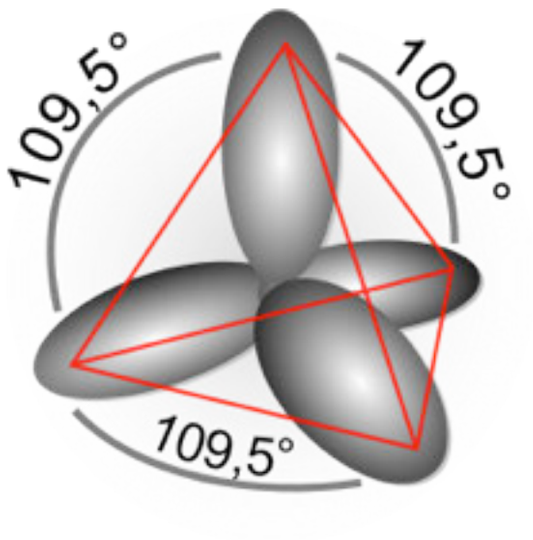


	NiO		
	a (bohr)	B (GPa)	E_g (eV)
GGA	7.93	188	0.6
GGA+U	8.07	181	3.2
GGA+U+V	8.031	189	3.6
GGA+U+V_{sc}	7.99	197	3.2
Exp	7.89	166-208	3.1-4.3

Band semiconductors: sp^3 hybridization



U and *V* computed and used on
p and *s* states

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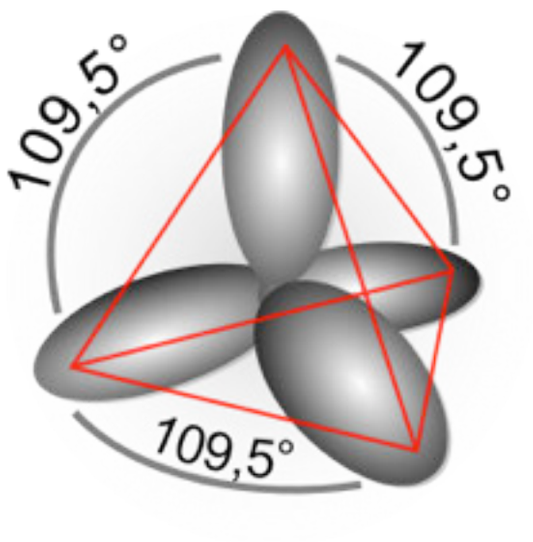

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	U_{ss}	U_{sb}	U_{bs}	U_{bb}	V_{ss}	V_{sb}	V_{bs}	V_{bb}
Si-Si	2.82	3.18	3.18	3.65	1.34	1.36	1.36	1.40
Ga-Ga	3.14	3.56	3.56	4.17				
As-As	4.24	4.38	4.38	4.63				
Ga-As					1.72	1.68	1.76	1.75

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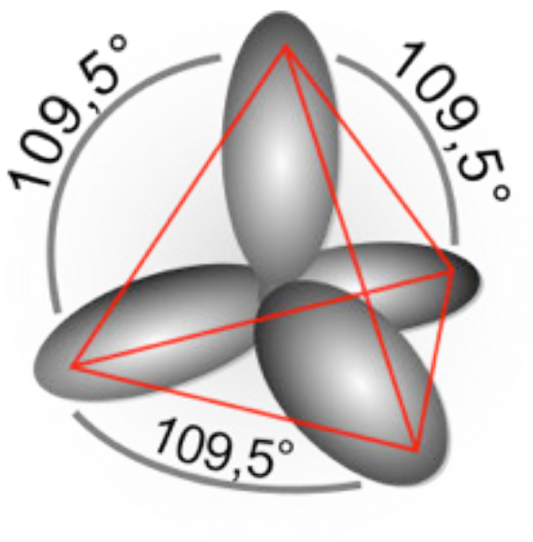

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DFT+U+V band structure of Si and GaAs

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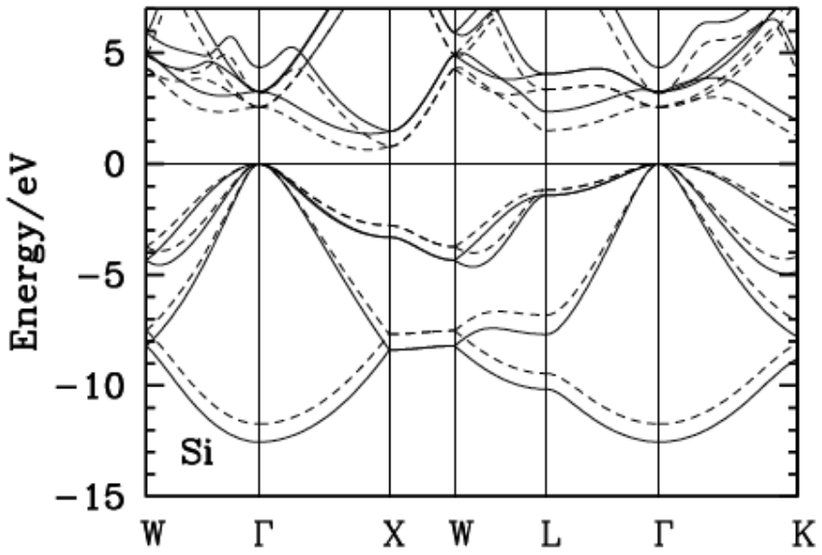

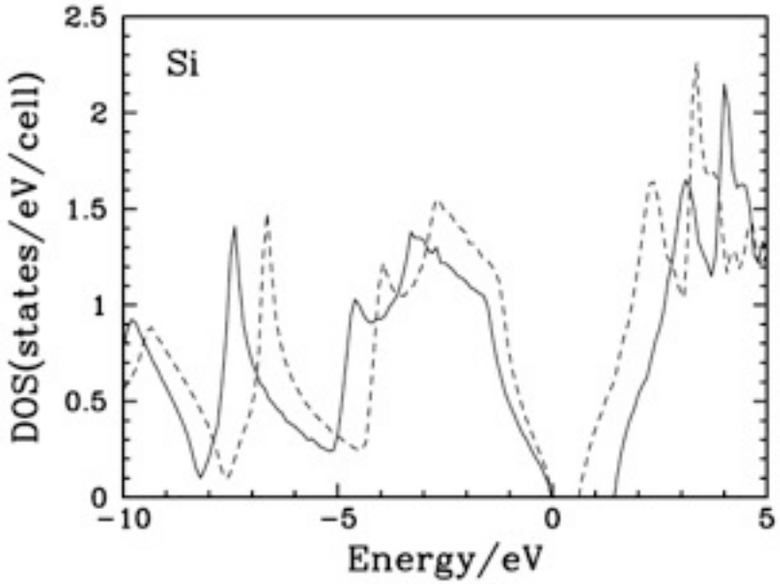

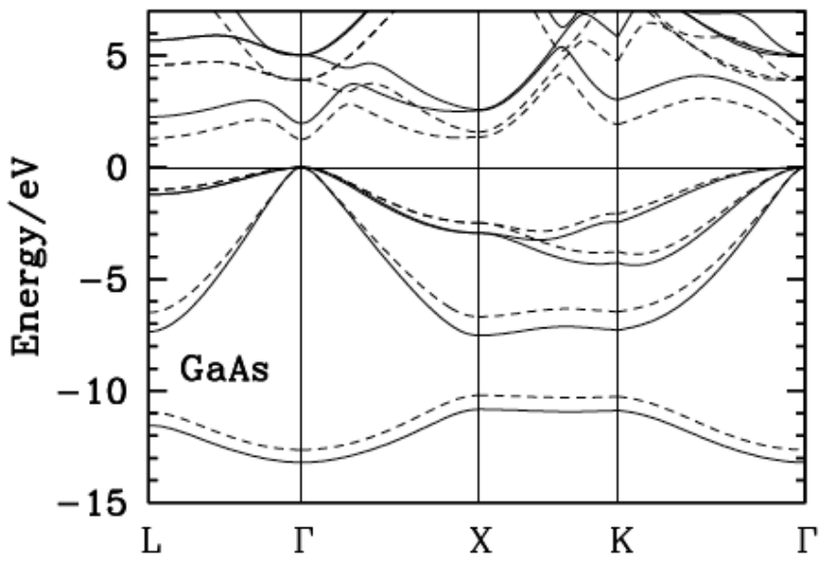

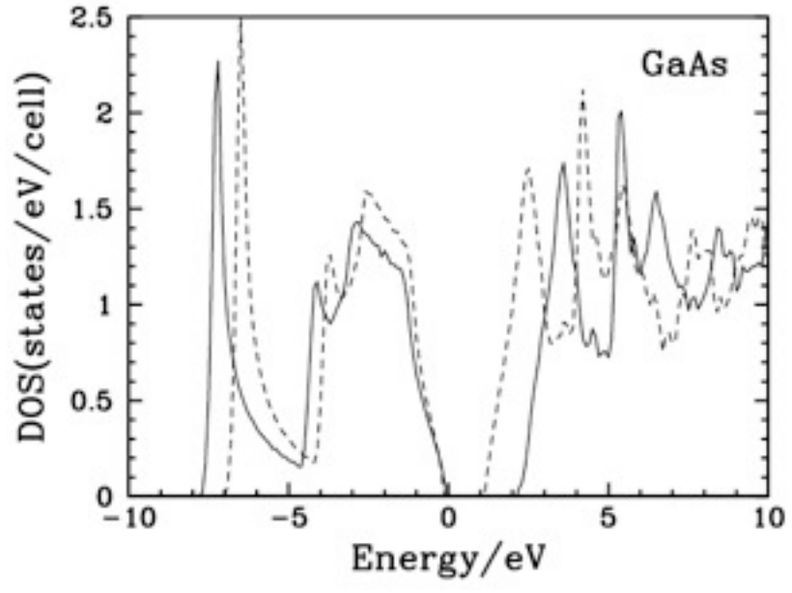

V. L. Campo Jr and M. Cococcioni, J. Phys.: Condens Matter 22 055602 (2010)

Structural properties of Si and GaAs

	Si			GaAs		
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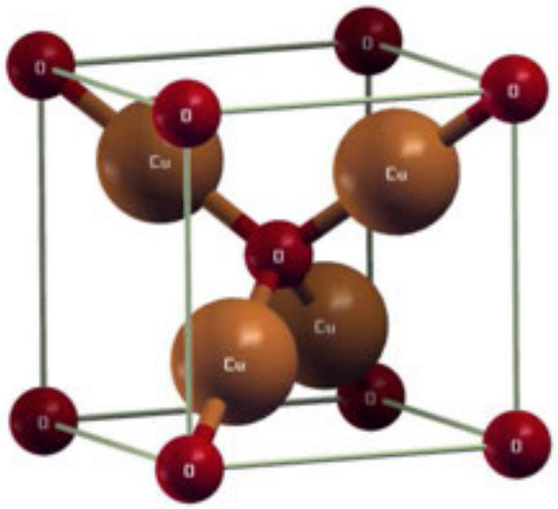
*** from http://www.ioffe.ru/SVA/NSM/Semicond/**

V. Leiria Campo Jr and M. Cococcioni, *J. Phys.: Condens Matter* 22 055602 (2010)

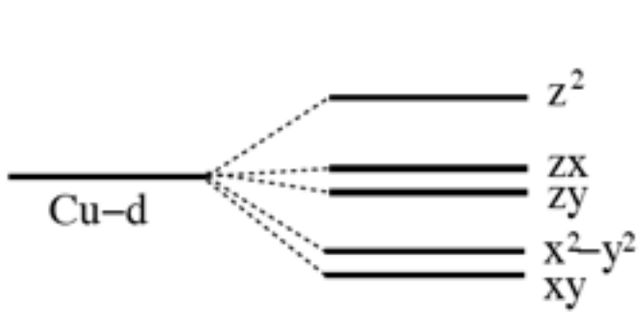
Cu_2O: a case for on-site V

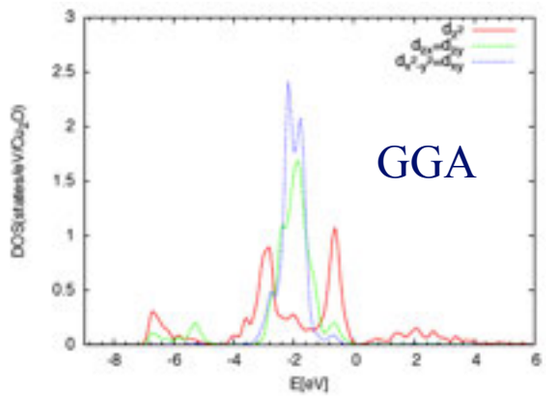


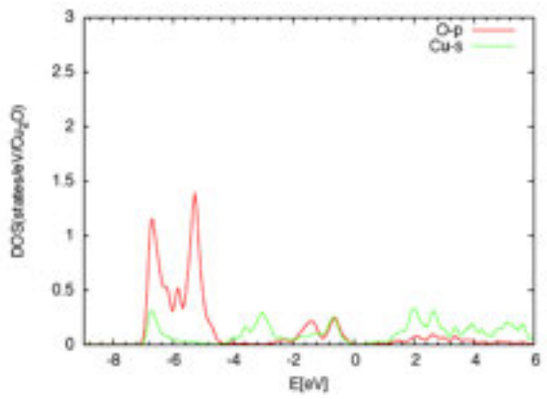
Expectation:
- *d* states full
- bonding between Cu *s* and O *p*

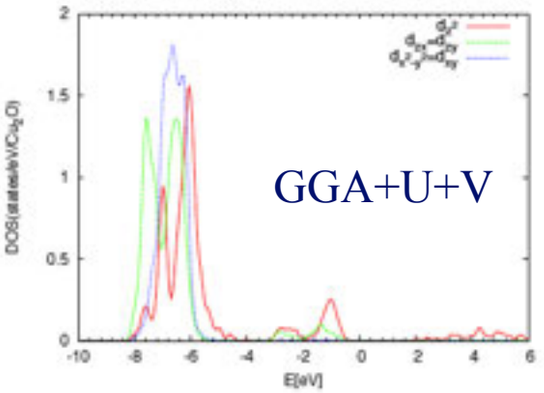
GGA+U over-stabilizes *d* states of Cu

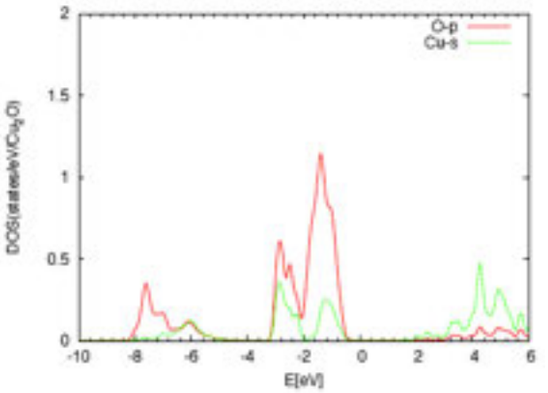
On-site V between *d* and *s* needed correct the composition of the occupied manifold











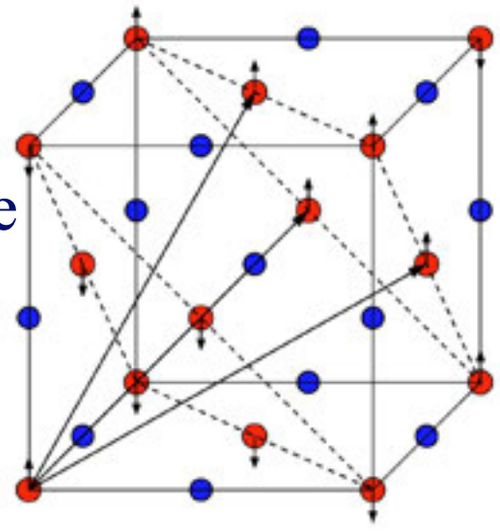
	a_0	k_0	E_g
GGA	4.37 Å	93.6 GPa	0.5 eV
GGA+U	4.58 Å	59.5 GPa	1.5 eV
GGA+U+V	4.48 Å	80.3 GPa	2.0 eV
Exp	4.27 Å	112 GPa	2.17 eV

CuO: a “strange” transition-metal oxide

Other TMOs:

cubic structure
rhombohedral
symmetry

AFII



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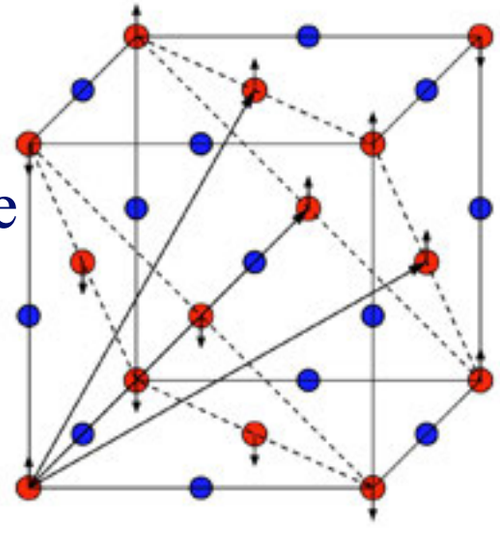

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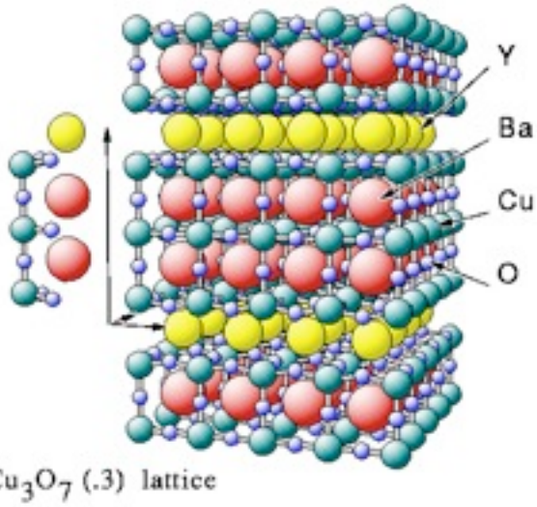
- proxy material of HTSC
- role of electron-phonon
- structural distortion: Jahn-Teller?



$YBa_2Cu_3O_7$ (.3) lattice

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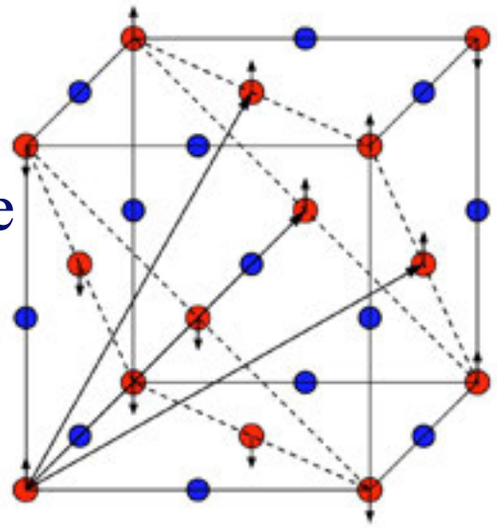

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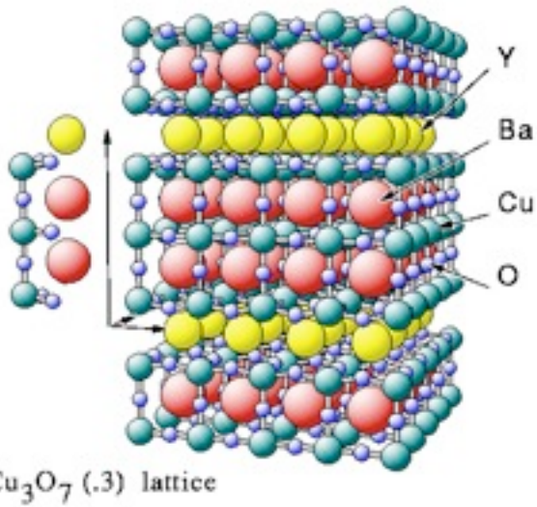

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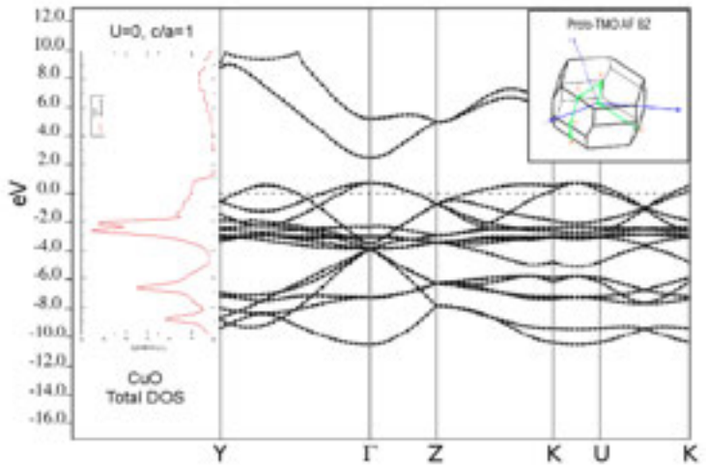
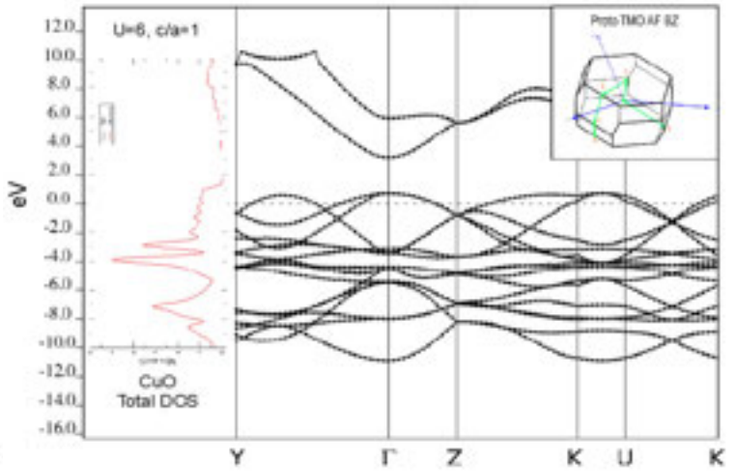
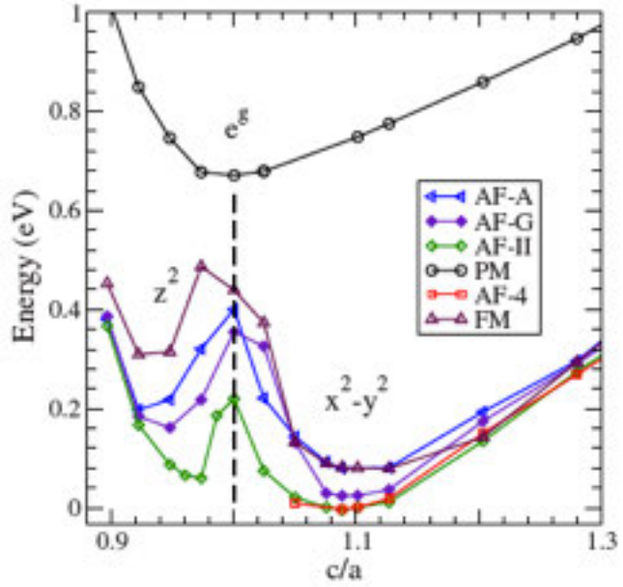




P. Grant, *J. Phys. Conf. Ser.*, 129, 012042 (2008)

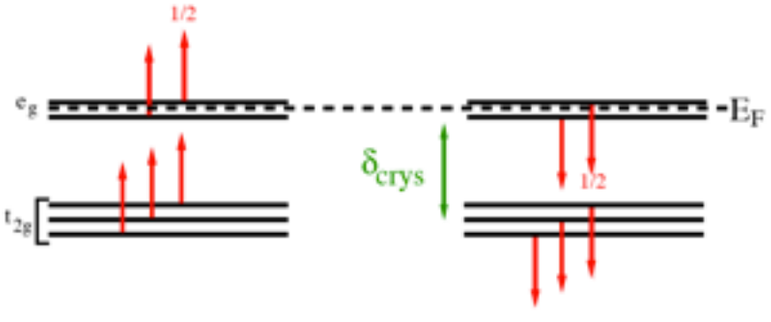


G. Peralta et al., *PRB* 80, 140408 (2009)

Is the cubic ($c/a = 1$) phase really metallic?

CuO: electronic structure

Cu: 9 *d* electrons



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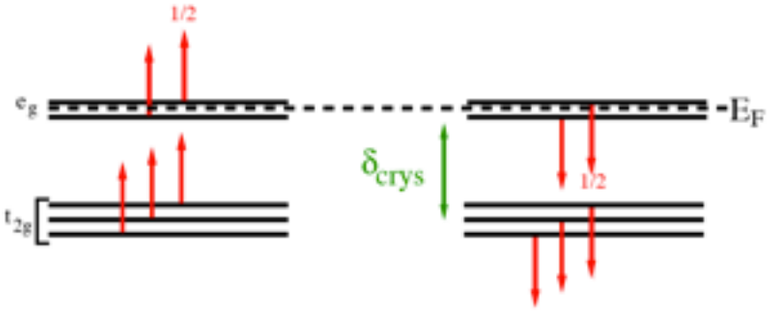

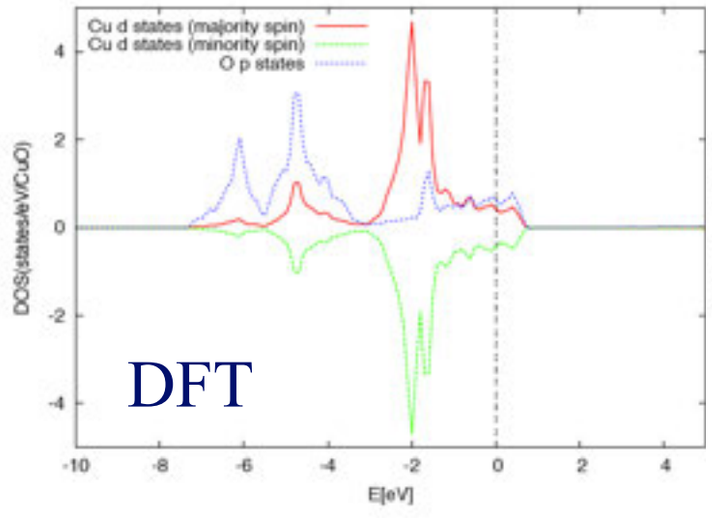

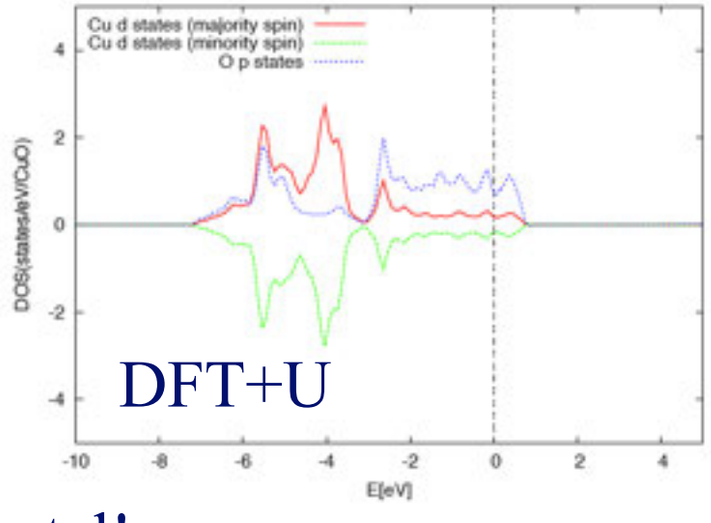

metal!

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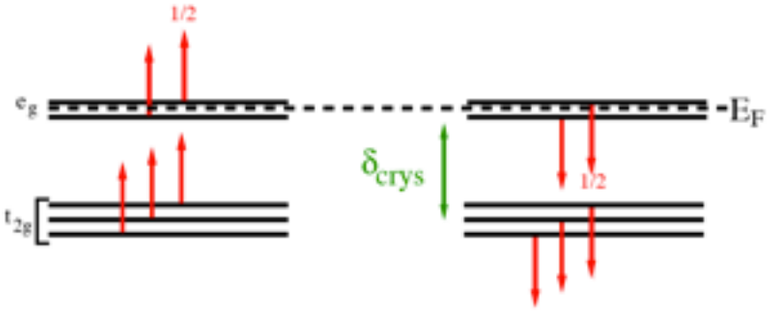

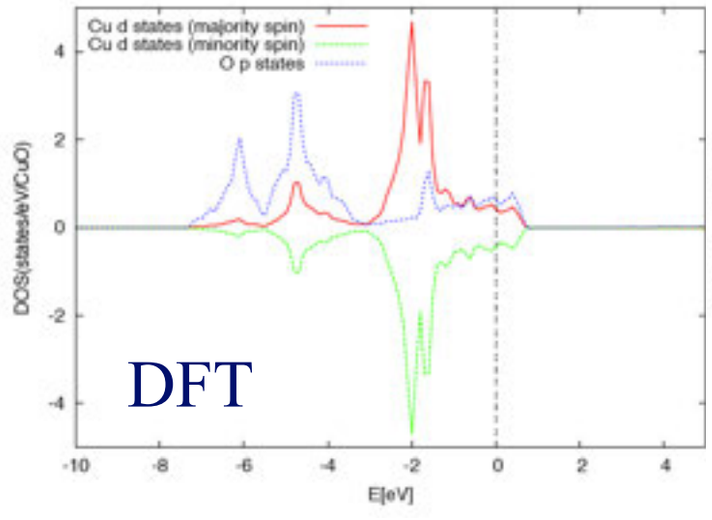

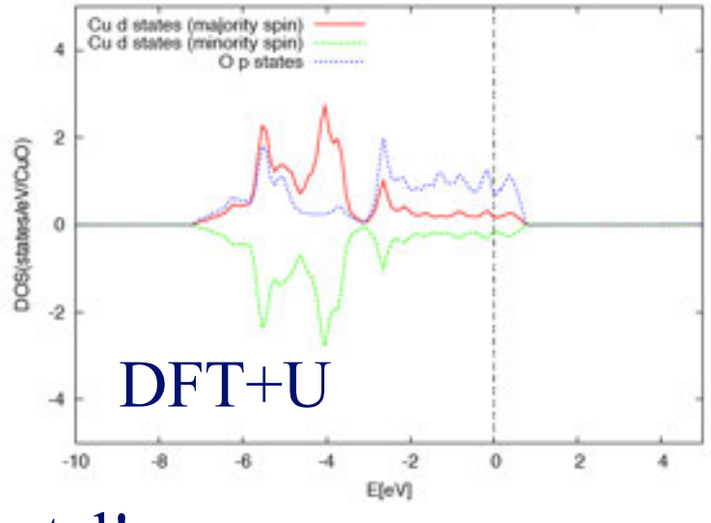

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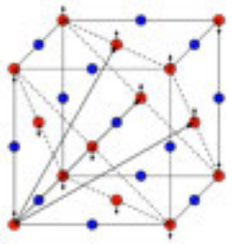
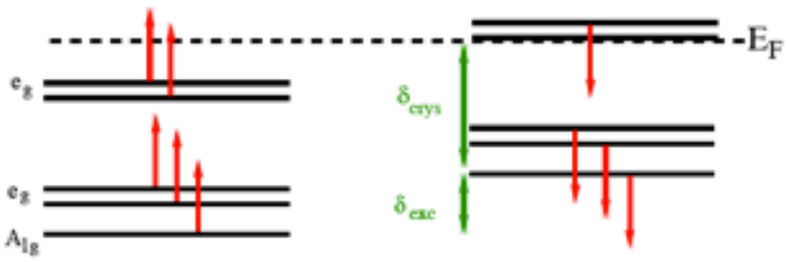


Rhombohedral rock-salt (AFII)



AFII: rhombohedral cell (stabilized by U_p)

CuO: electronic structure

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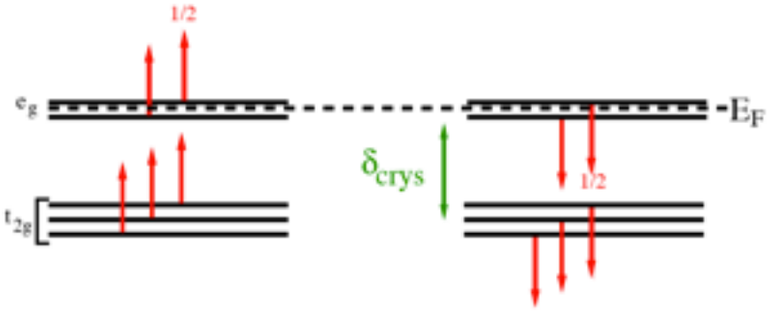

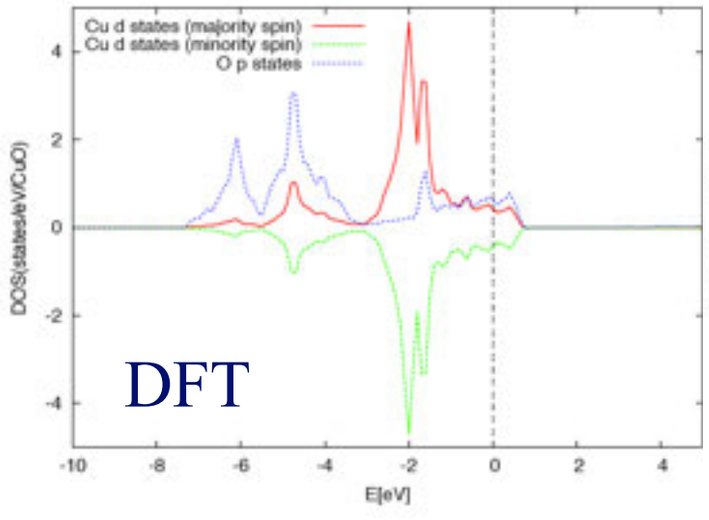

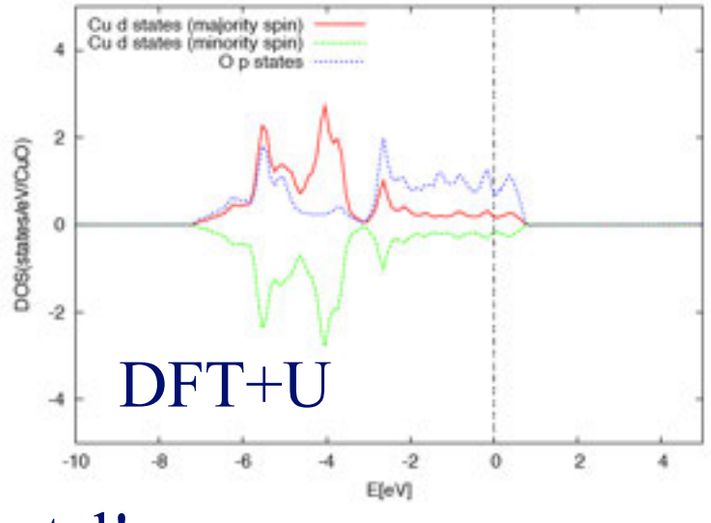

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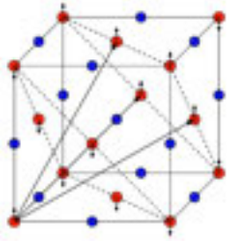

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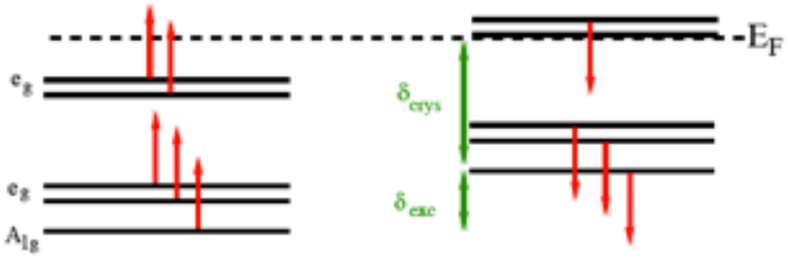

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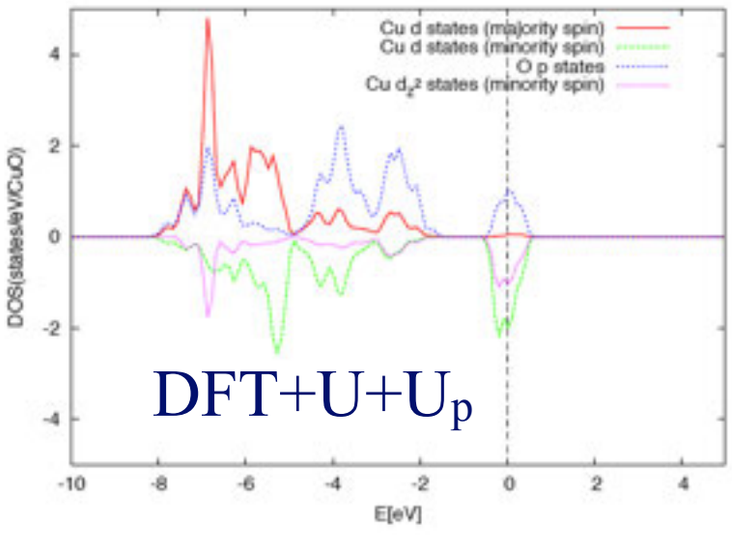
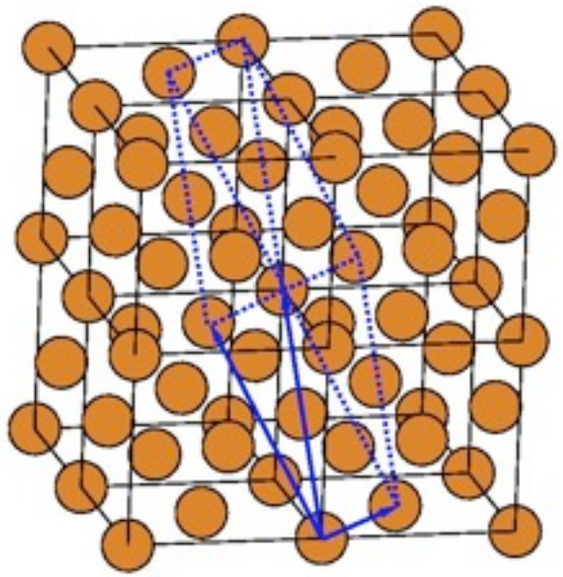


Occupations:
Cu *d* states: 9.36 e-
O *p* states: 5.27 e-

still a metal!

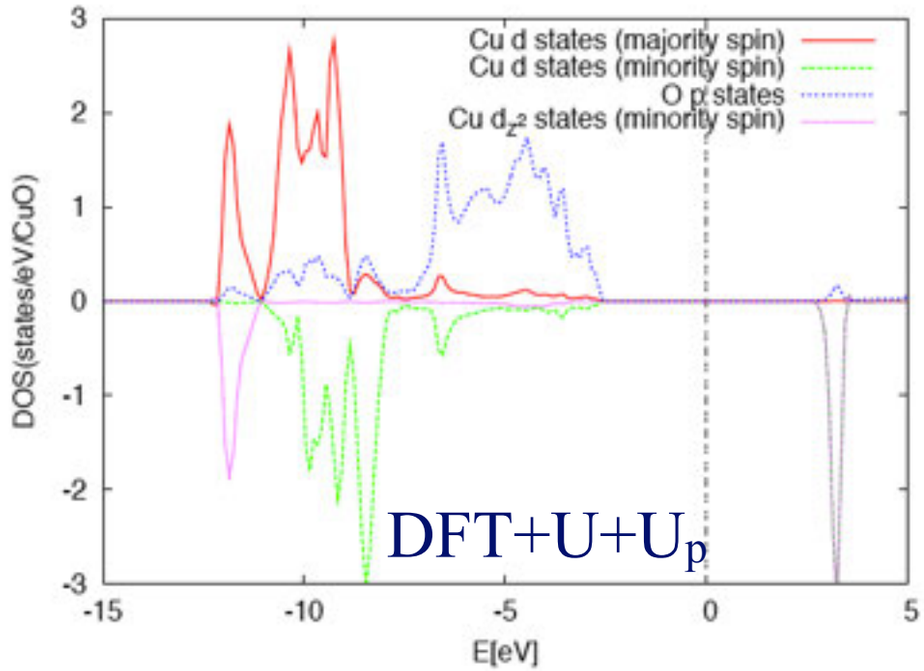
B. Himmetoglu R. M. Wentzcovitch and M. Cococcioni, *Phys Rev B* (2011)

CuO: broken symmetry



triclinic cell: the equivalence of e_g states is broken

CuO is insulator (cubic phase)



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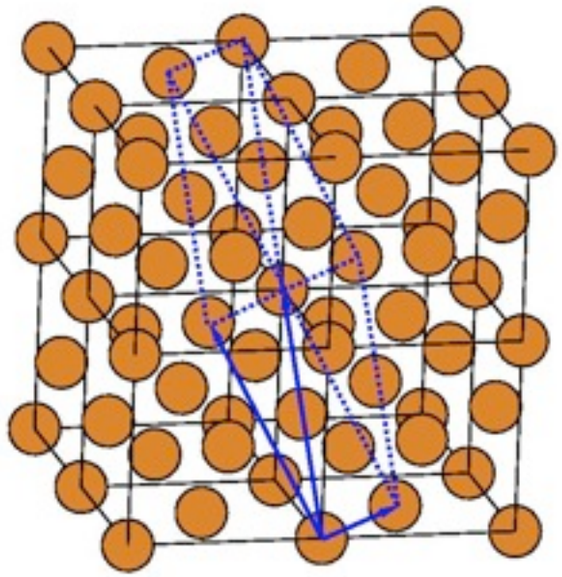

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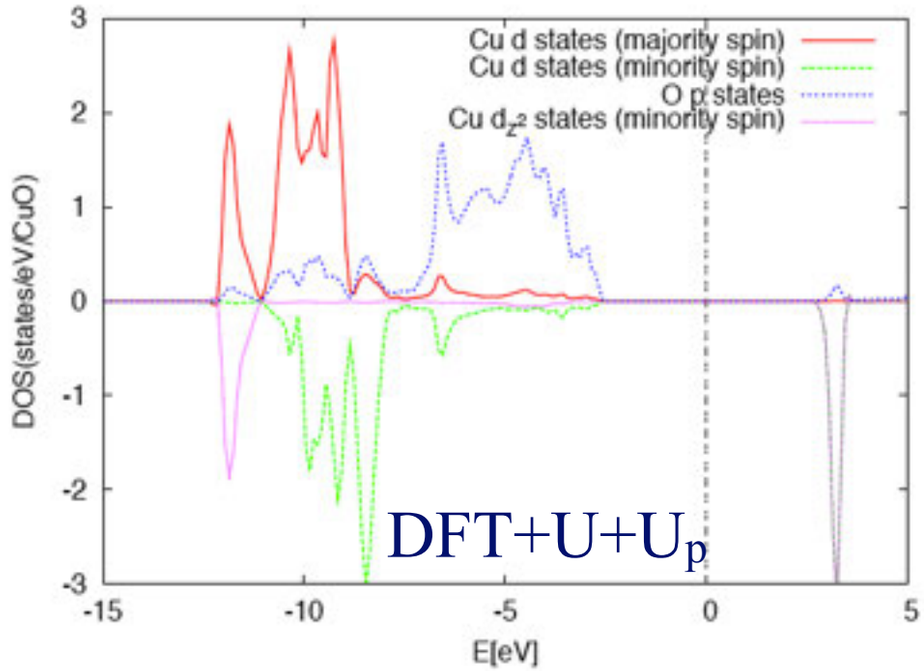

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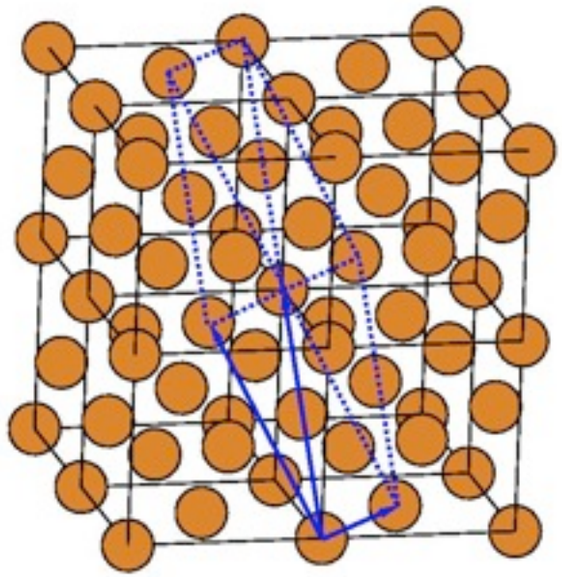

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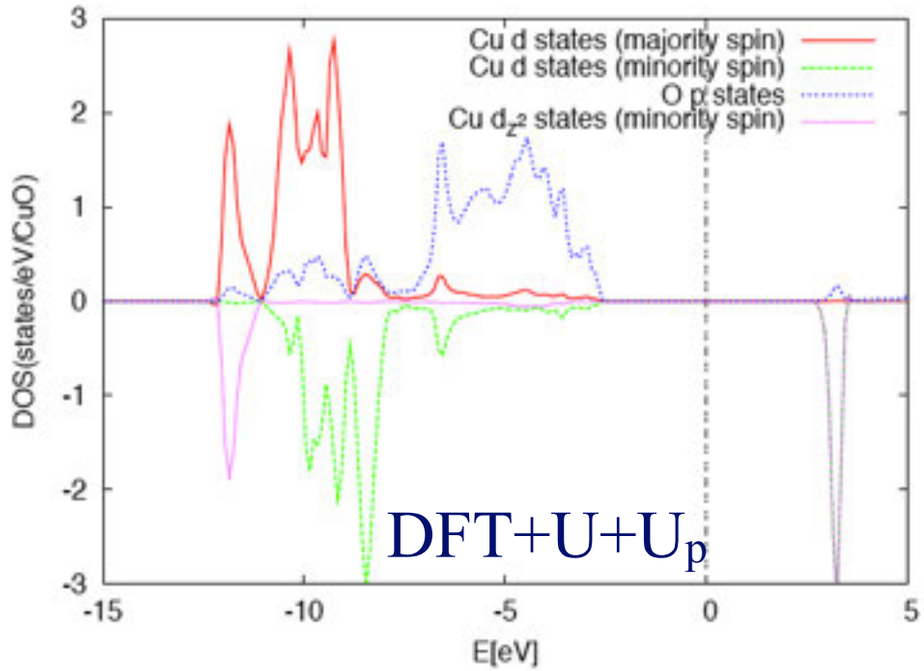

$U_p = 0$ ==> non magnetic state ==> cubic symmetry ==> metallic state

A competition exists between two tendencies: **filling up the *d* shell**, and **magnetism**

A better description of magnetic interactions on *d* states is necessary

DFT+U+J

DFT+U energy functional

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + \sum_{I,\sigma} \frac{U^I}{2} Tr\left[\mathbf{n}^{I\sigma}\left(\mathbf{1}-\mathbf{n}^{I\sigma}\right)\right]$$

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Explicit magnetic interactions: DFT+U+J energy functional

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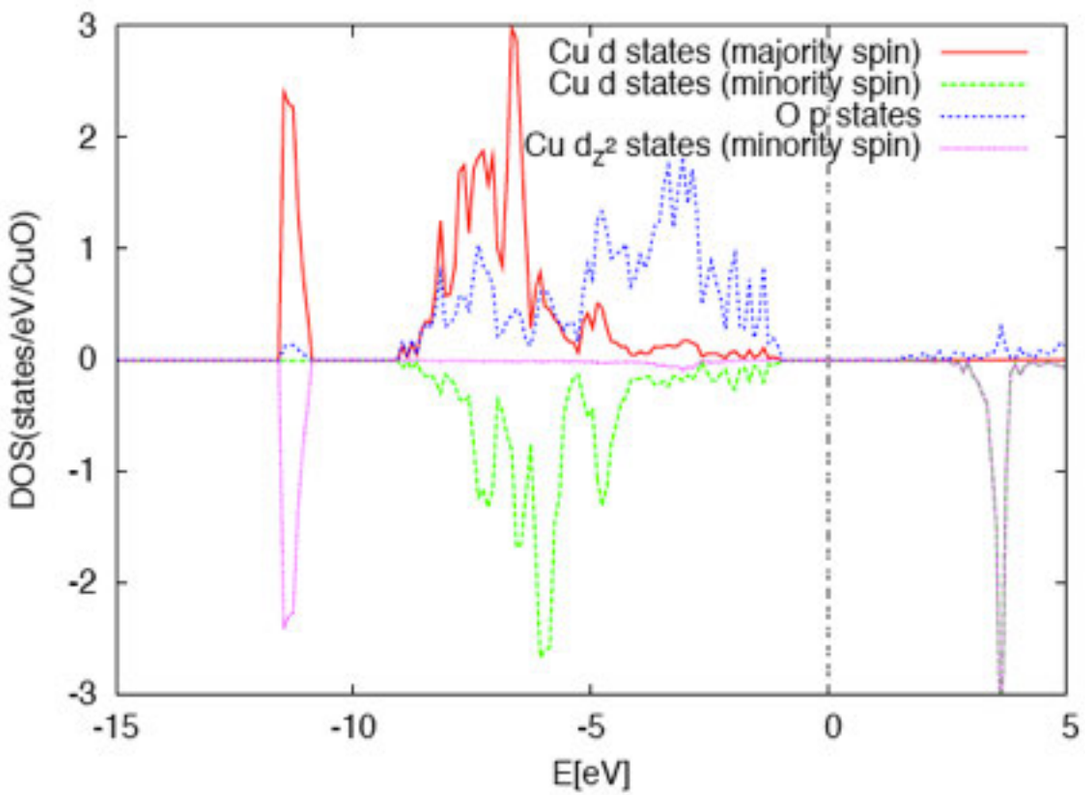
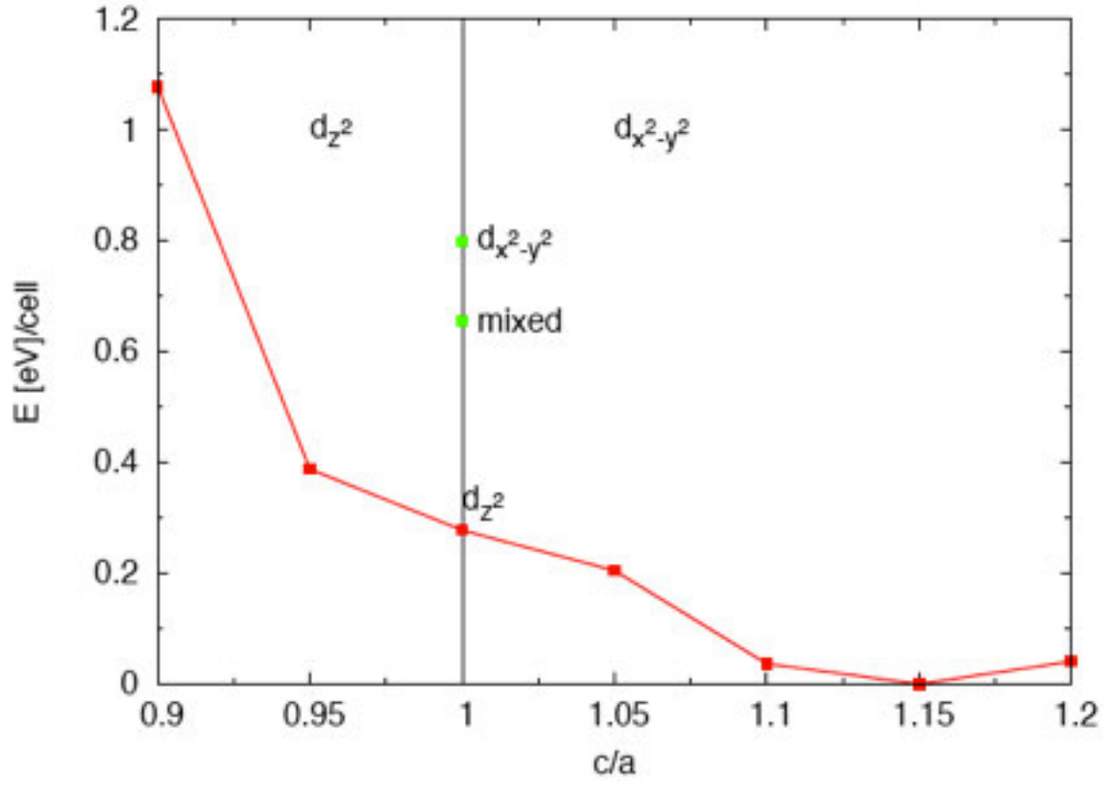
B. Himmetoglu R. M. Wentzcovitch and M. Cococcioni, *Phys Rev B* (2011)

CuO: DFT+U+J ground state





B. Himmetoglu R. M. Wentzcovitch and M. Cococcioni, *Phys Rev B* (2011)

Computing energy derivatives (forces and stresses)

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$$\mathbf{F}_I = -\int \rho_{\mathbf{R}}(\mathbf{r}) \frac{dV_{\mathbf{R}}(\mathbf{r})}{d\mathbf{R}_I} d\mathbf{r} - \frac{dE_N(\mathbf{R})}{d\mathbf{R}_I}$$

$$F^U_{I\alpha} = -\frac{\partial E_U}{\partial \tau_{\alpha i}} = -\sum_{J,m,m',\sigma} \frac{dE_U}{dn^{J\sigma}_{m,m'}} \frac{\partial n^{I\sigma}_{m,m'}}{\partial \tau_{I\alpha}} = -\frac{U}{2} \sum_{J,m,m',\sigma} (\delta_{mm'} - 2n^{J\sigma}_{m'm}) \frac{\partial n^{J\sigma}_{m,m'}}{\partial \tau_{I\alpha}}$$

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Stresses:

$$\sigma_{\alpha\beta} = -\frac{1}{\Omega} \frac{dE_{tot}}{d\epsilon_{\alpha\beta}}$$

$$\sigma^U_{\alpha\beta} = -\frac{1}{\Omega} \frac{\partial E_U}{\partial \epsilon_{\alpha\beta}} = -\frac{1}{\Omega} \sum_{I,m,m',\sigma} \frac{dE_U}{dn^{I\sigma}_{m,m'}} \frac{\partial n^{I\sigma}_{m,m'}}{\partial \epsilon_{\alpha\beta}} = -\frac{1}{\Omega} \frac{U}{2} \sum_{I,m,m',\sigma} (\delta_{mm'} - 2n^{I\sigma}_{m'm}) \frac{\partial n^{I\sigma}_{m,m'}}{\partial \epsilon_{\alpha\beta}}$$

Second derivatives: phonons

Matrix of force constants:

$$D_{I\alpha J\beta} = -\frac{d^2 E(\mathbf{R})}{d\mathbf{R}^I_\alpha d\mathbf{R}^J_\beta} = \frac{dF_{I\alpha}}{d\mathbf{R}^J_\beta} = \frac{dF_{J\beta}}{d\mathbf{R}^I_\alpha}$$

Contribution from the Hubbard potential:

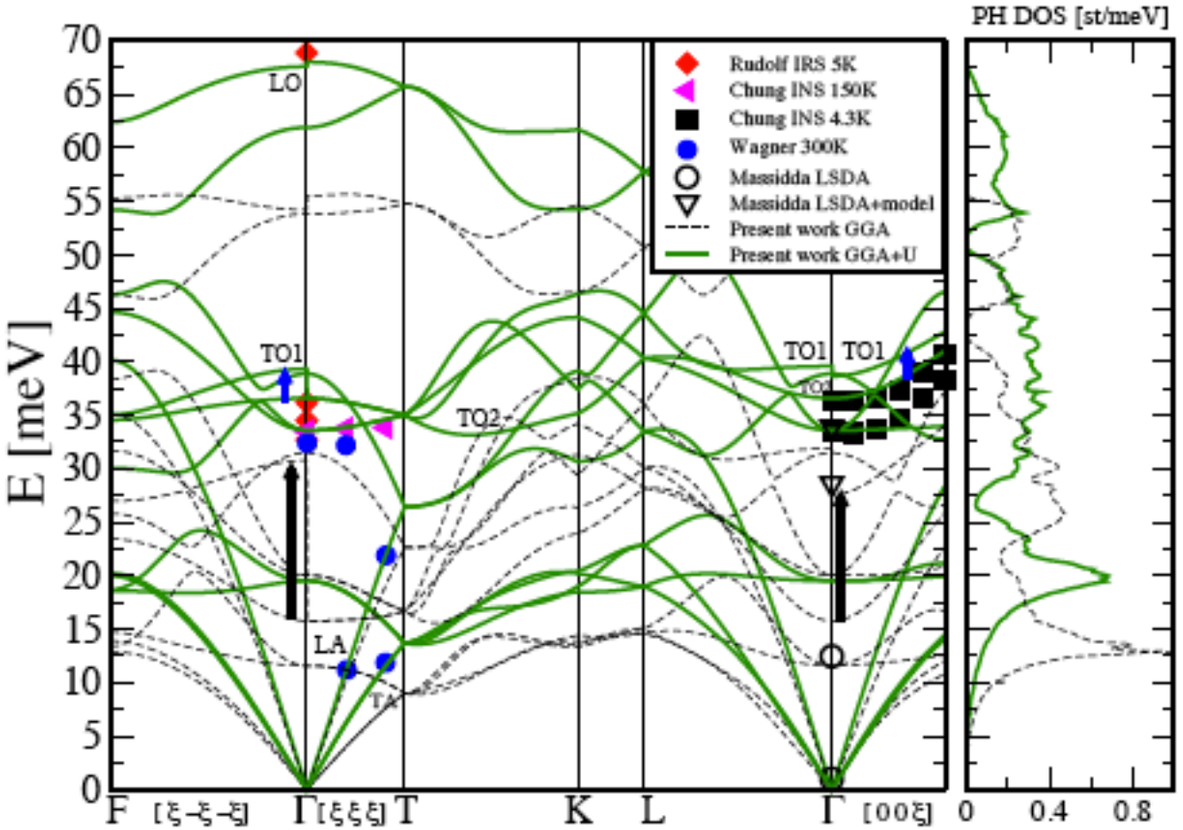
$$\Delta^\mu(\partial^\lambda E_{\mathrm{Hub}}) = \sum_{I\sigma mm'} U^I \left[\frac{\delta_m m'}{2} - n^{I\sigma}_{mm'}\right] \Delta^\mu\left(\partial^\lambda n^{I\sigma}_{mm'}\right) - \sum_{I\sigma mm'} U^I \Delta^\mu n^{I\sigma}_{mm'} \partial^\lambda n^{I\sigma}_{mm'}$$

Variation of the occupations:

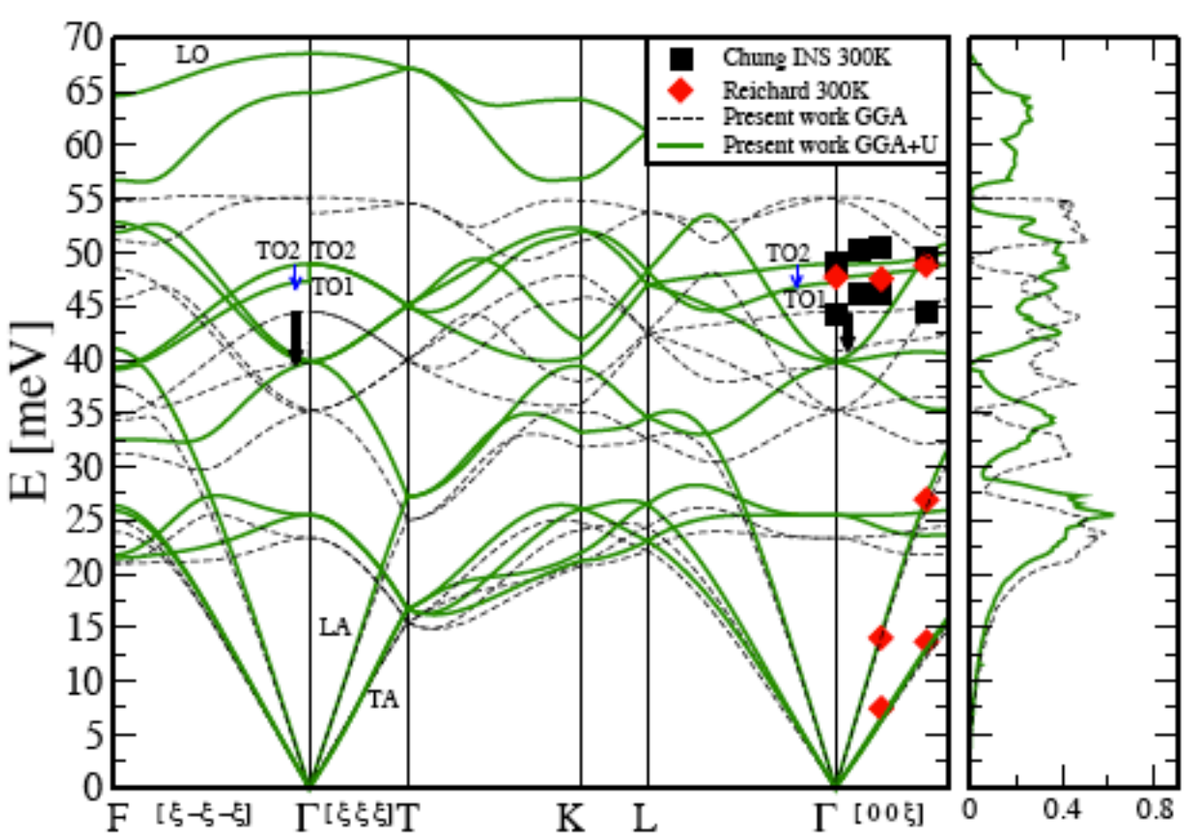
$$\Delta n^{I\sigma}_{m_1 m_2} = \sum_i^{occ} \{\langle\psi^\sigma_i|\Delta\phi^I_{m_1}\rangle\langle\phi^I_{m_2}|\psi^\sigma_i\rangle + \langle\psi^\sigma_i|\phi^I_{m_1}\rangle\langle\Delta\phi^I_{m_2}|\psi^\sigma_i\rangle\}$$
$$+ \sum_i^{occ} \{\langle\Delta\psi^\sigma_i|\phi^I_{m_1}\rangle\langle\phi^I_{m_2}|\psi^\sigma_i\rangle + \langle\psi^\sigma_i|\phi^I_{m_1}\rangle\langle\phi^I_{m_2}|\Delta\psi^\sigma_i\rangle\}$$

A. Floris, S. de Gironcoli, E. K. U. Gross, and M. Cococcioni, PRB 84, 161102 (2011)

Vibrational properties of TM oxides from DFPT+U



MnO



NiO

A. Floris, S. de Gironcoli, E. K. U. Gross, and M. Cococcioni, PRB 84, 161102 (2011)

Summary

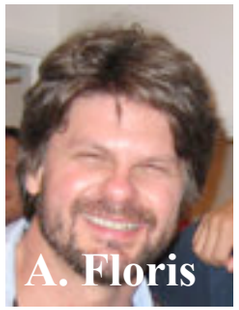
- DFT+U: a simple correction for ground state properties
- Ab-initio LDA+U: linear response calculation of U
- Broken-symmetry solution for degenerate ground states
- LDA+U for metals: FLL vs AMF flavors
- Localized states in metals: the case of Ni_2MnGa
- Band and Mott insulators: Si, GaAs, NiO and Cu_2O from the extended LDA+U+V
- Hole localization in CuO from the LDA+U+J correction
- Phonon spectra of NiO and MnO from their LDA+U ground state

Acknowledgements

Collaborators


I. Dabo


B. Himmetoglu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The End

Questions?