Corrections to xc functionals for correlated systems: DFT+U

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Outline

- Success stories and notable failures of DFT: metals, semiconductors and Mott insulators

- Introduction to Mott physics and to the Hubbard model

- DFT+U: formulation and implementation

- Calculation of U from linear response theory

- Examples and advanced +U functionals

ABC of Density Functional Theory

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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)

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Unfortunately, the exact $E_{xc}[\rho] = \langle \Psi[\rho] | \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi[\rho] \rangle - \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r} d\mathbf{r}' + T[\rho] - T_0[\rho]$

is not known and approximations are needed

Approximate DFT functionals

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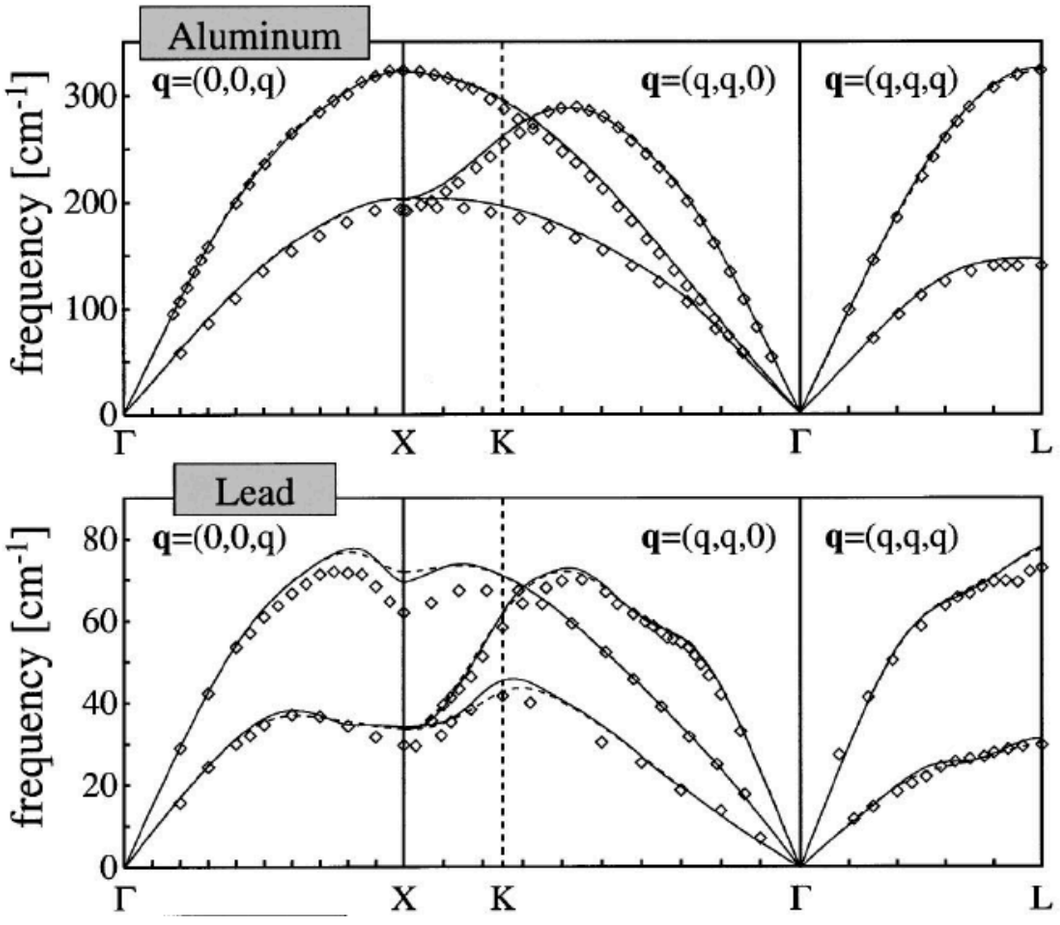

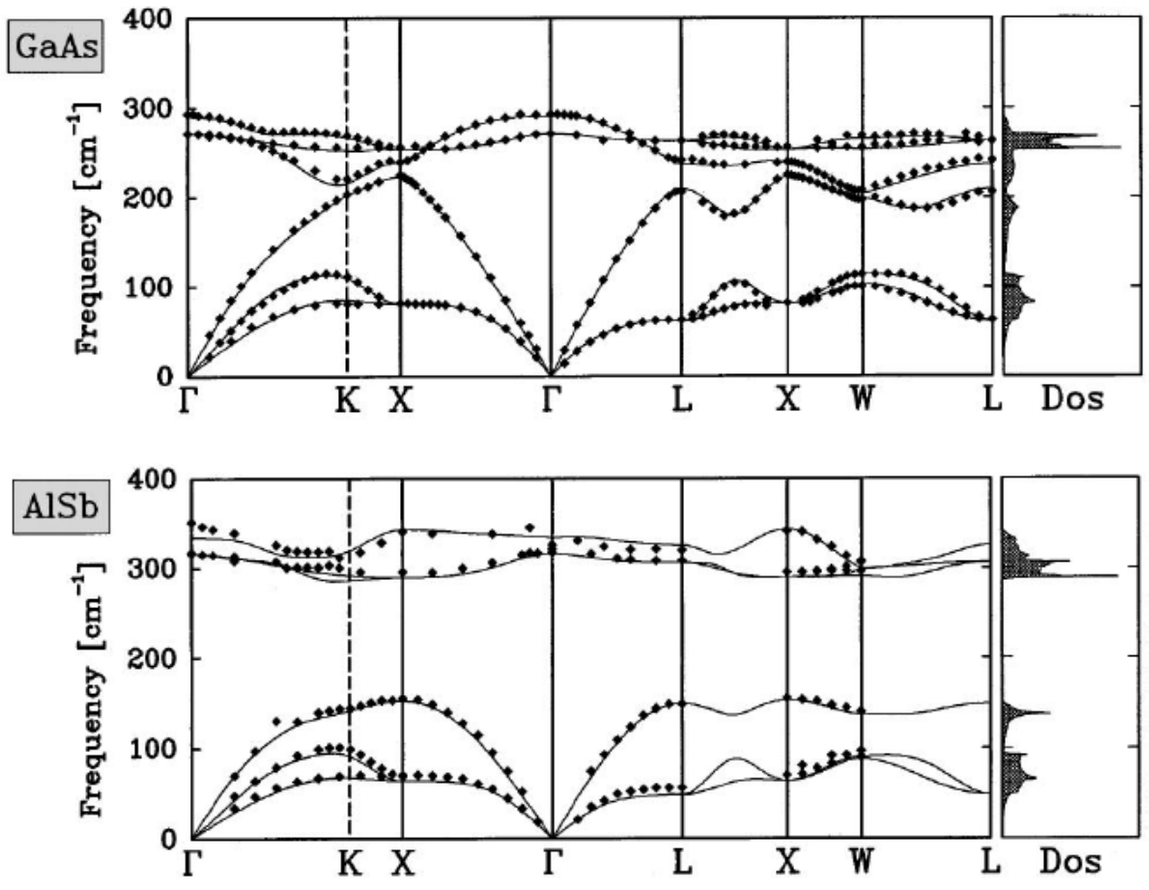

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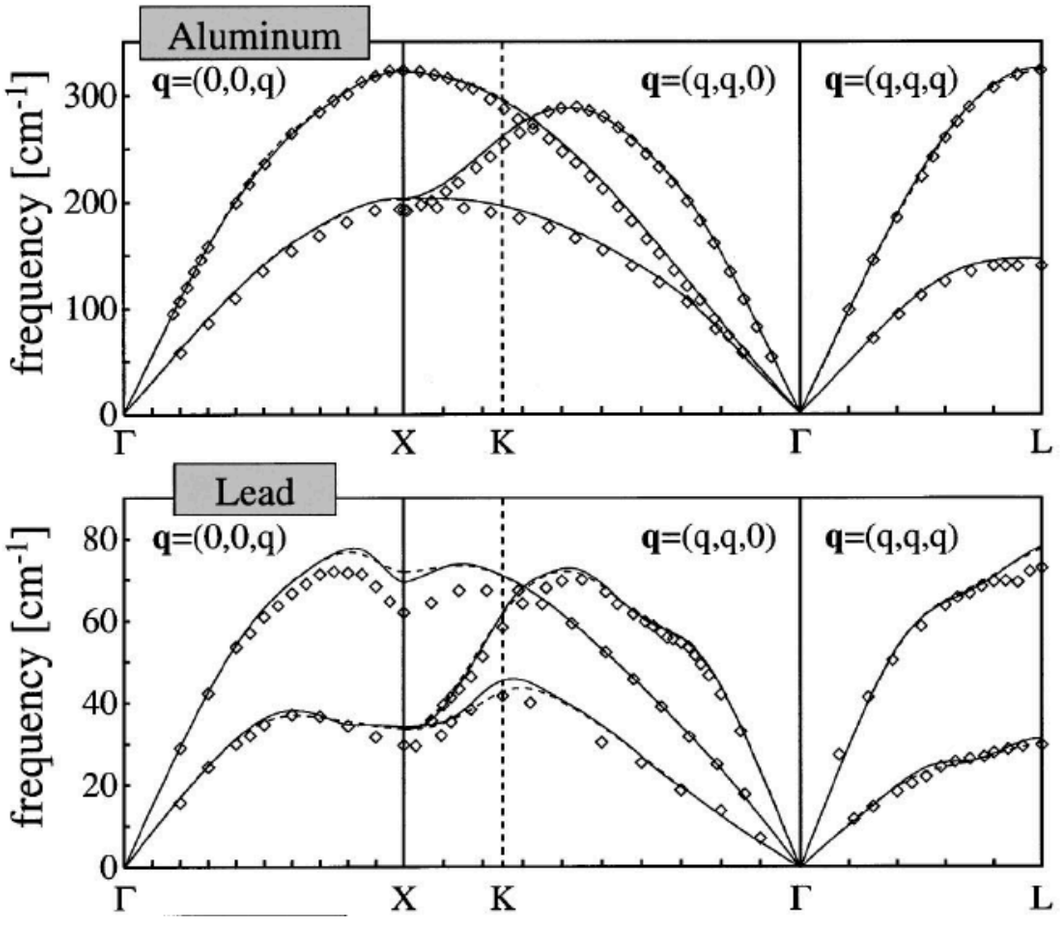
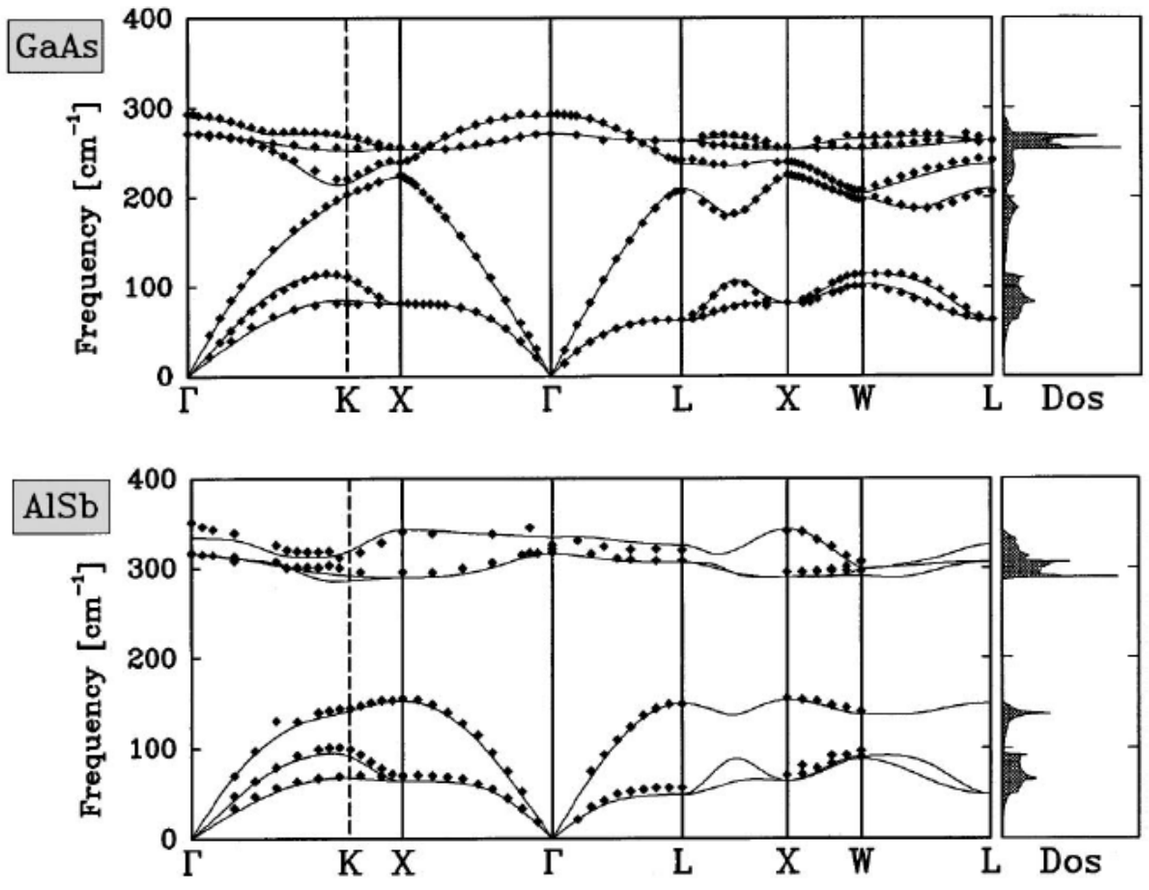
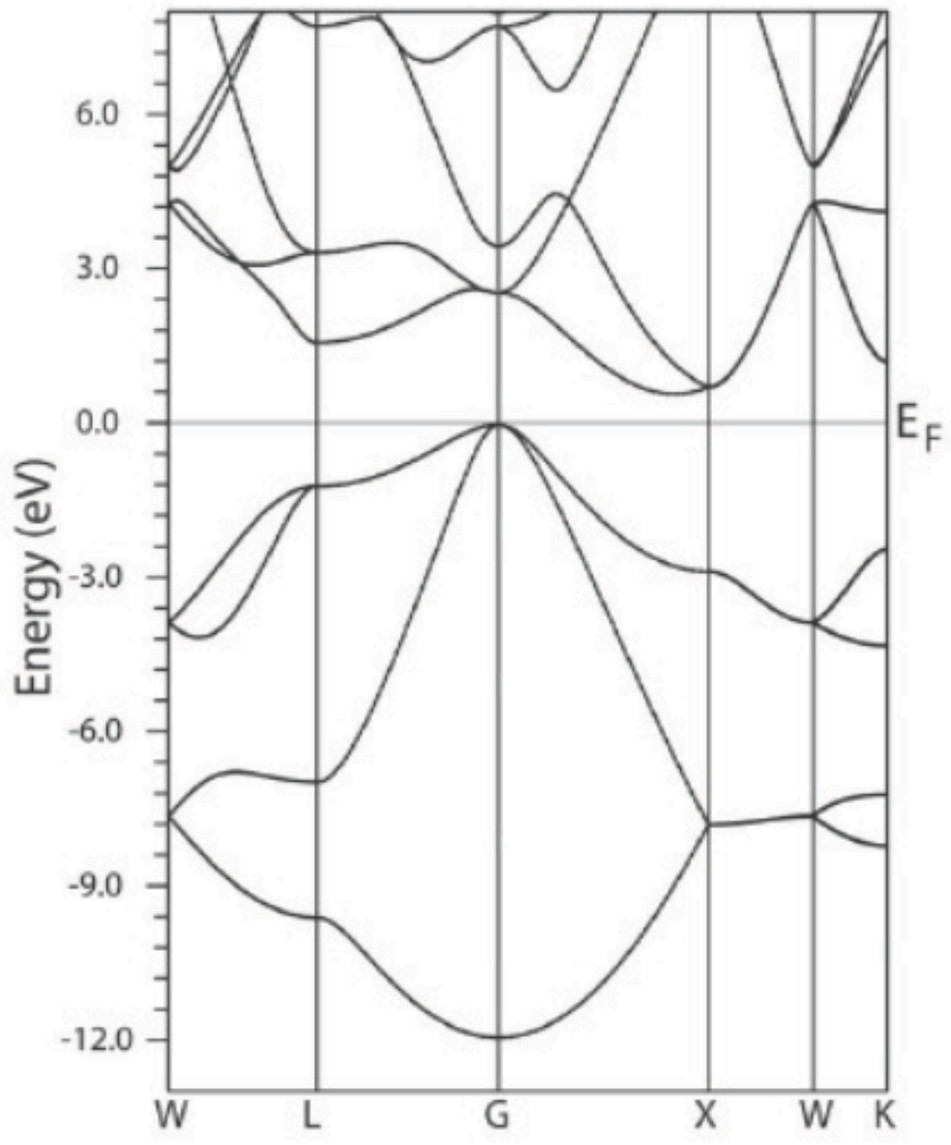




Most widely used approximations (Local Density Approximation - LDA, and Generalized Gradient Approximation - GGA) are based on the homogeneous electron gas limit

The band gap “problem”

Si band structure



http://lamp.tu-graz.ac.at/~hadley/ss2/fermigas/dft/si/Si.php

The band gap from (approximate) DFT is ~0.6 eV, smaller than the experimental gap, ~1.1 eV

However, remember: DFT is a ground state theory! (we are not supposed to use it to compute the gap)

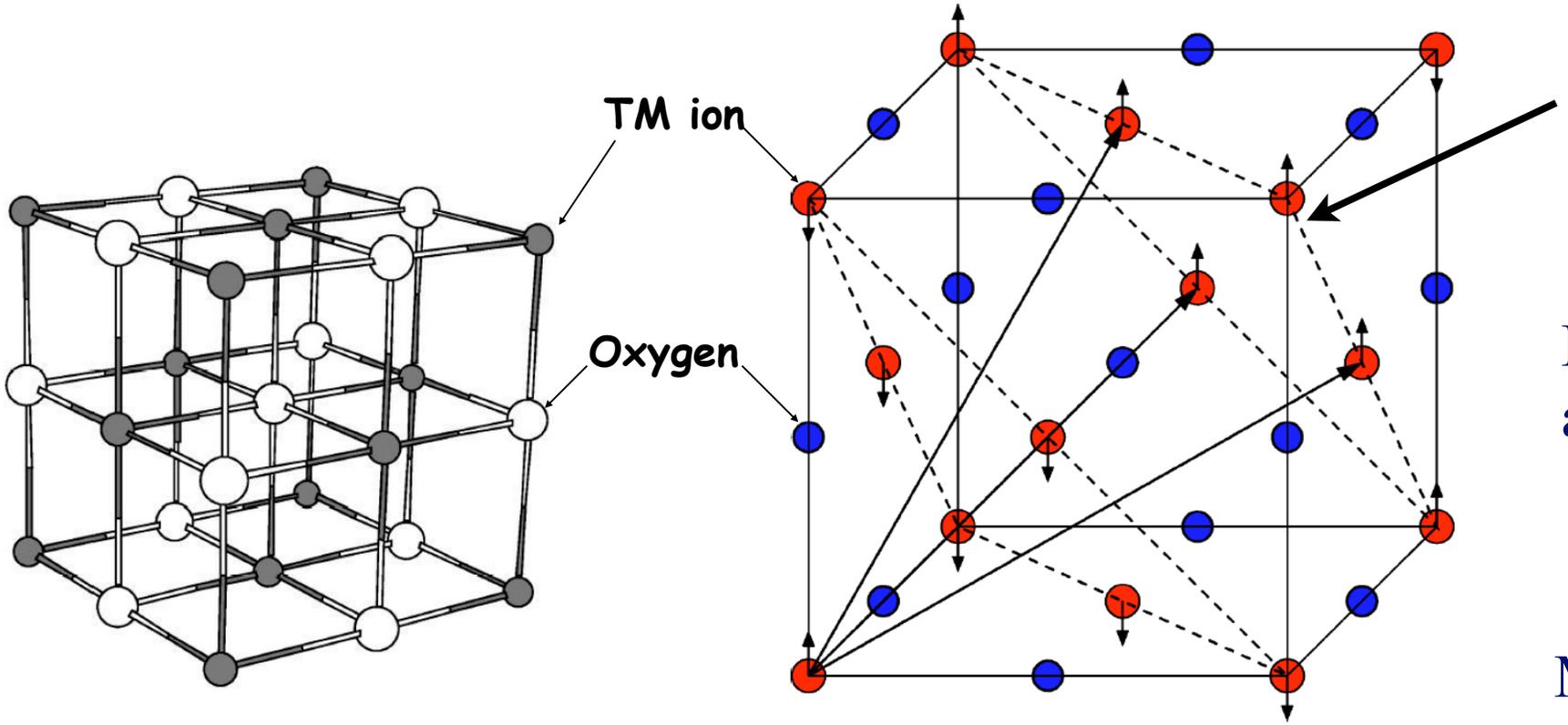
Fundamental gap:

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

with approximate xc functionals:

- the first term is approximate
- the second term is absent
- other inaccuracies may arise as well (e.g., on the structure)

Problematic cases: Transition-Metal Oxides



AFII ground state

Rhombohedral symmetry and (possible) distortions

INSULATORS

Mott localization of valence electrons on *d* states

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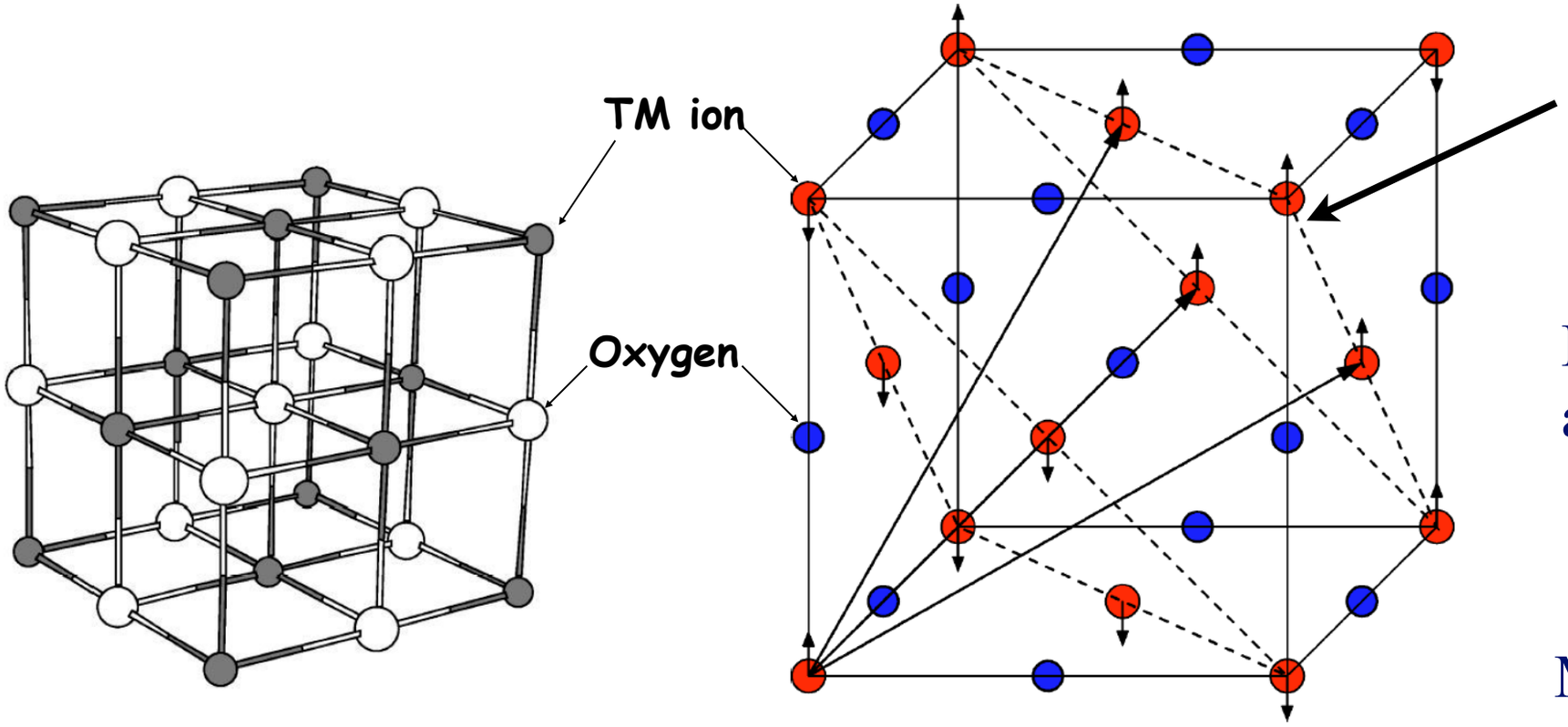

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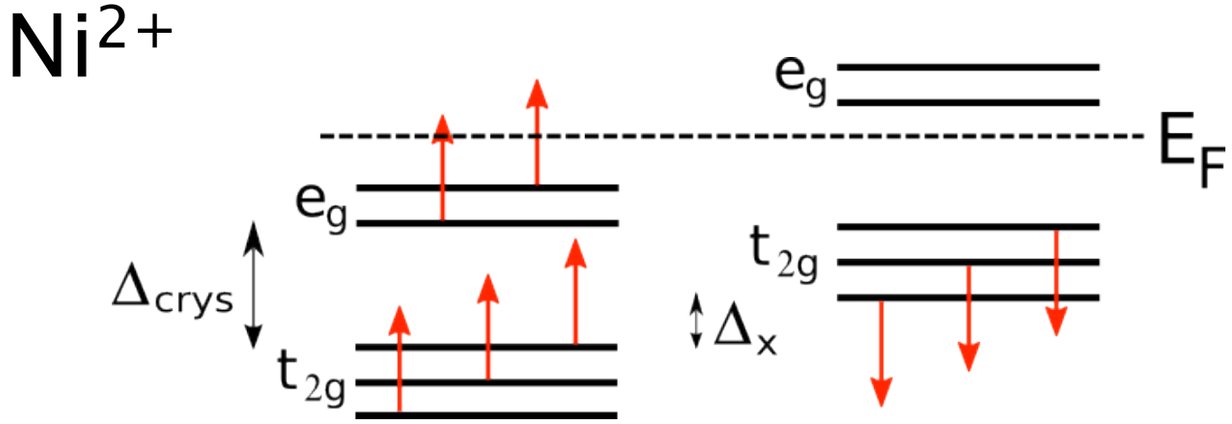
Approximate DFT (e.g., LDA or GGA):

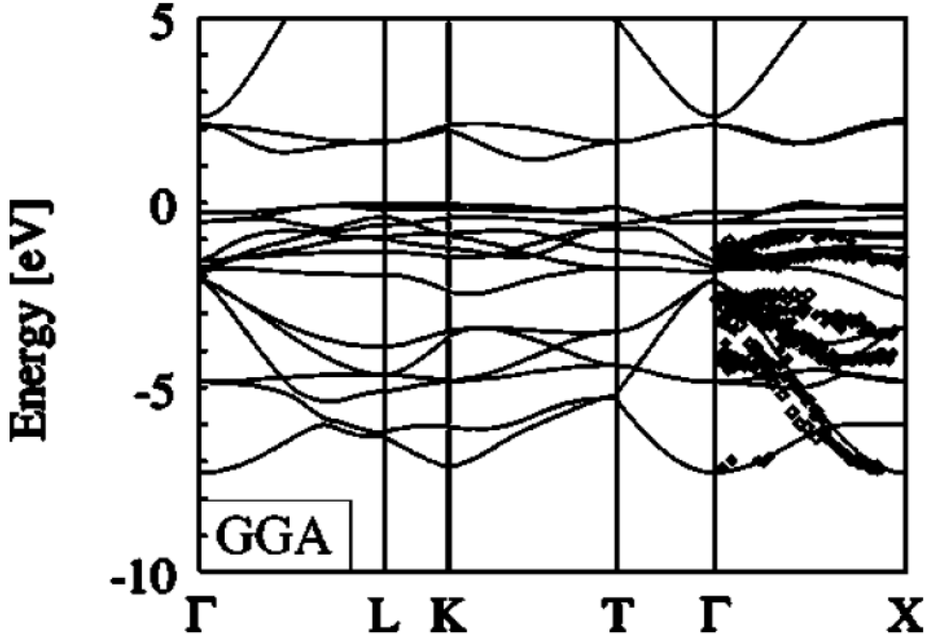
- Rhombohedral distortion overestimated
- Poor estimate of structural properties
- **FM ground state (FeO)**
- Too small or no gap at all
- Magnetization underestimated
- Wrong ordering of states

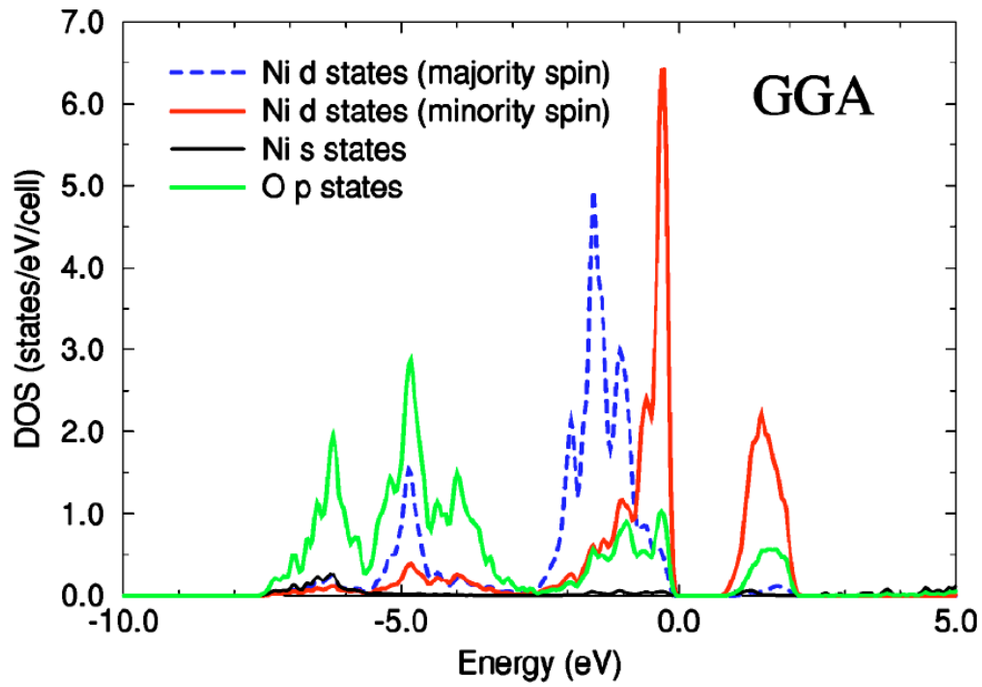
Example: GGA results for NiO



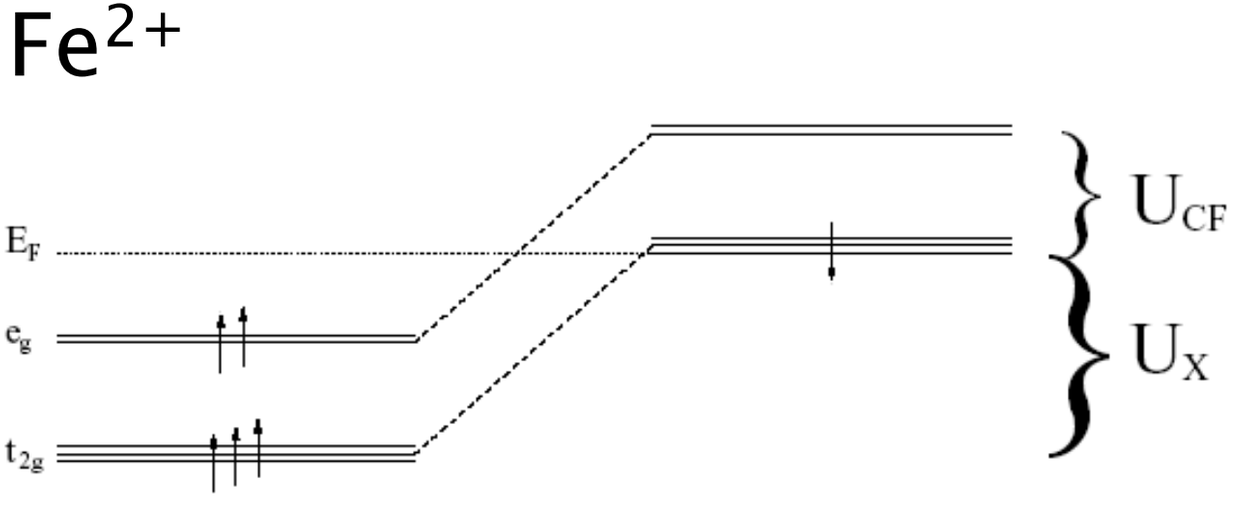
- Anti-ferromagnetic: OK
- Crystal structure cubic: OK
- Crystal field produces the band gap.

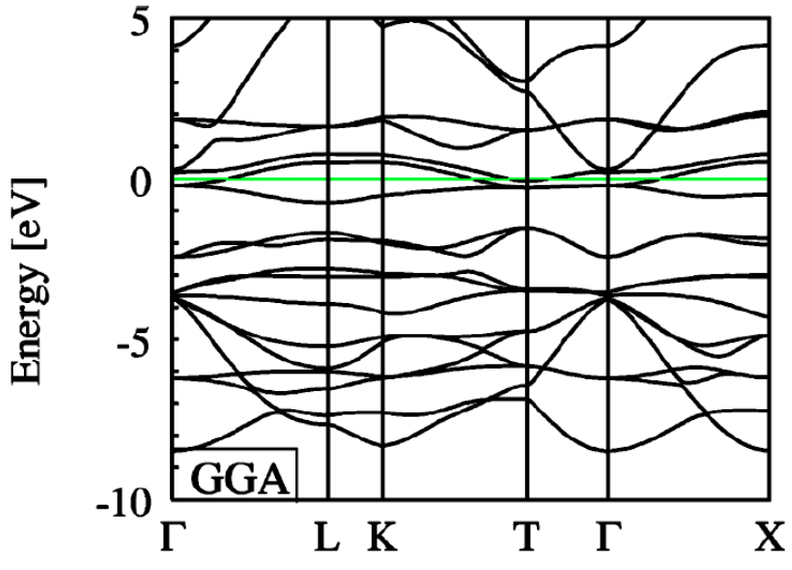
- **Band gap is too small**
- **O-p states should be at the top of the valence band.**





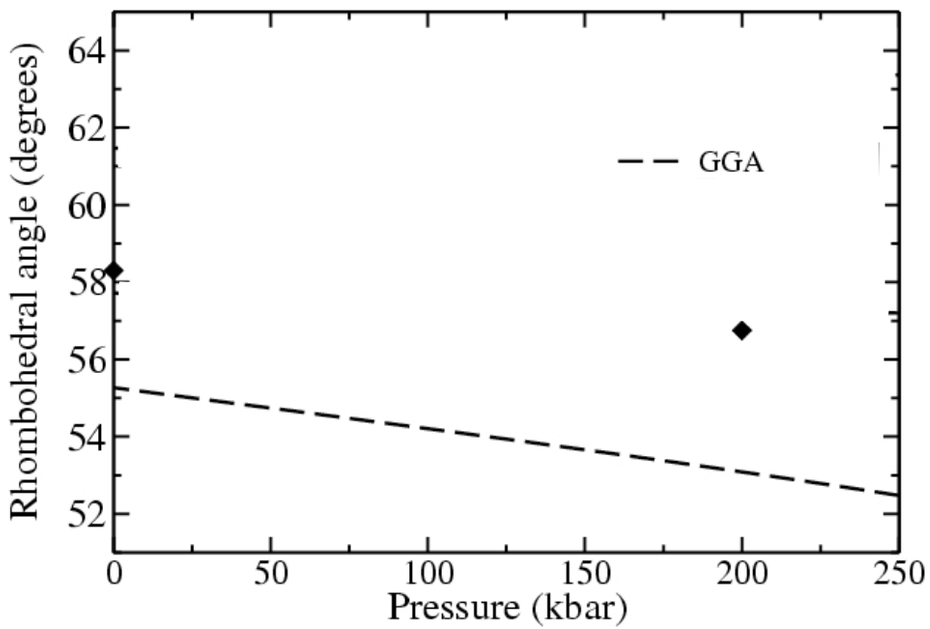
Example: GGA results for FeO





- Antiferromagnetic order: NO → **FM**
- Crystal structure cubic: OK
- Rhombohedral distortion: overestimated
- Ground state is metallic

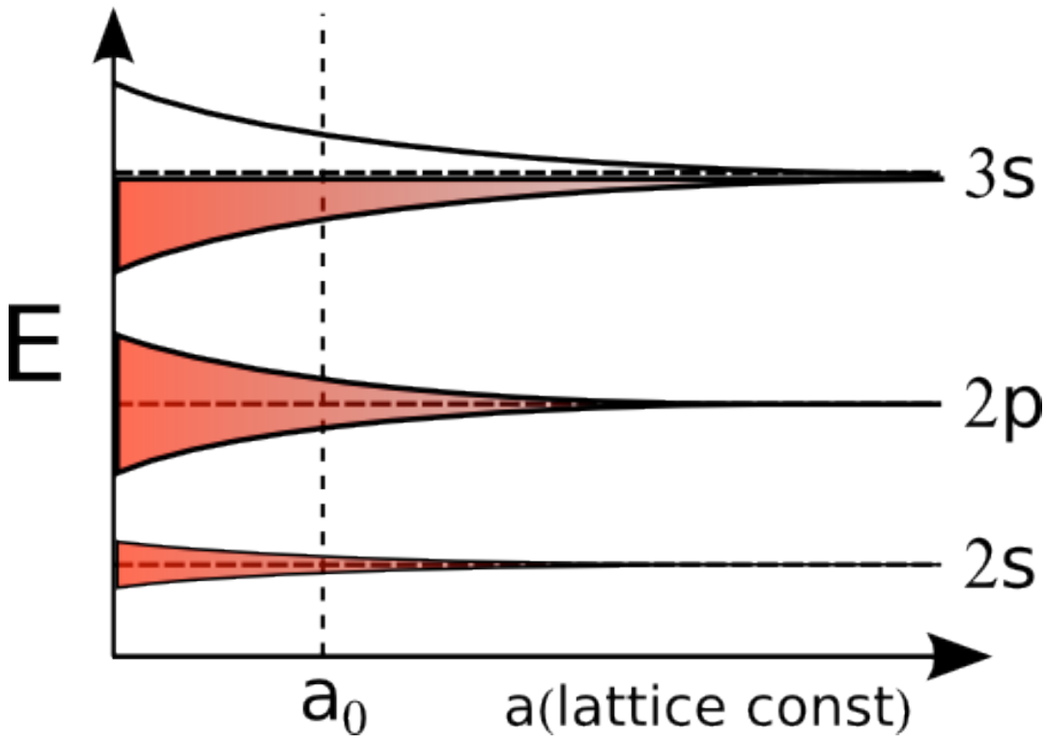
Structural distortion under pressure



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

Band theory

Consider solid Na($2s^2 2p^6 3s^1$):

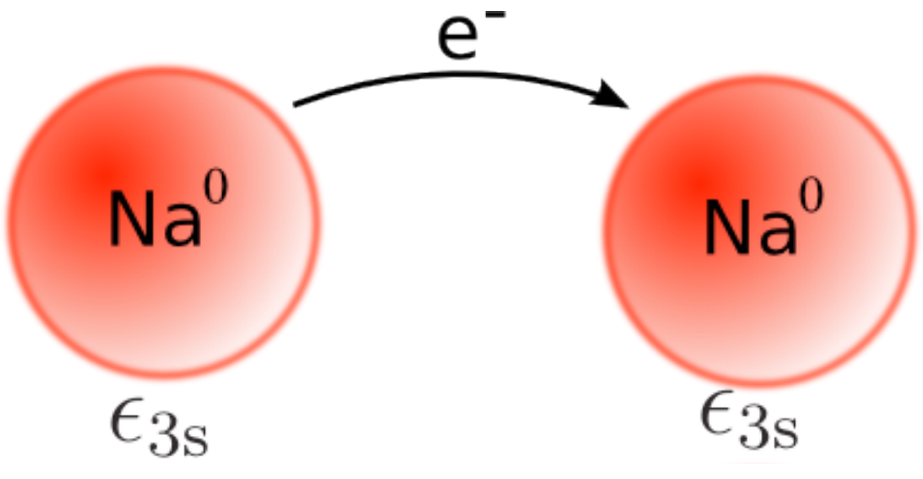


At the equilibrium lattice constant a_0:
Independent electrons: band theory
Half filled band → metal

Consider very large a:
- Half-filled 3s orbital becomes narrower, but it is still half-filled.
- **Band theory still predicts a metal!**

Isolated Na atoms still described as a metal; what is going wrong?

Single- vs many-electrons perspectives: Mott localization



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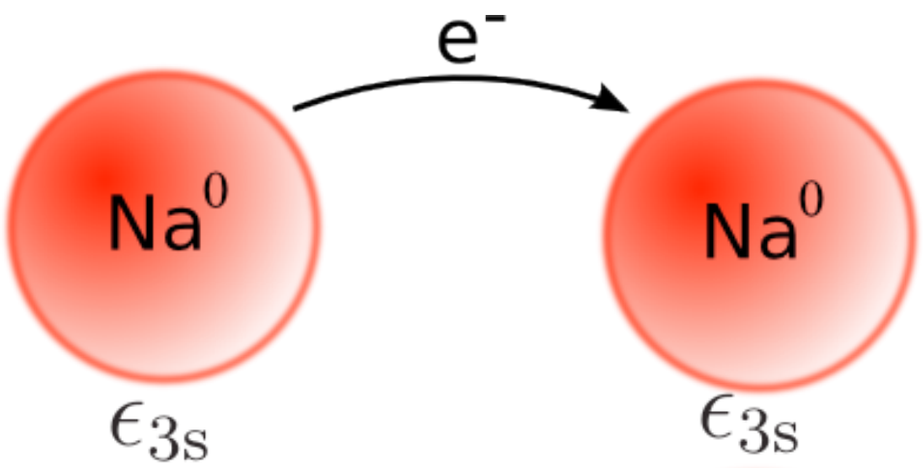
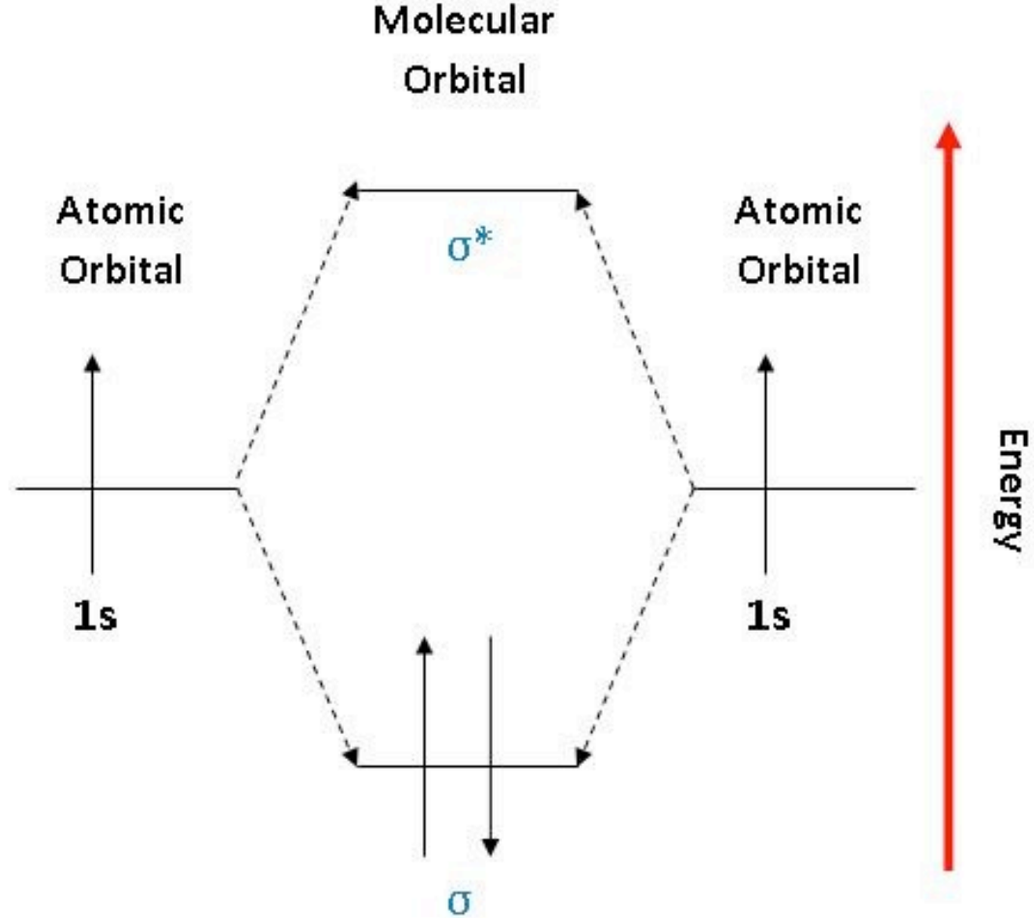


$$H = \begin{pmatrix} h_{aa} & v_{ab} \\ v_{ab} & h_{aa} \end{pmatrix}$$



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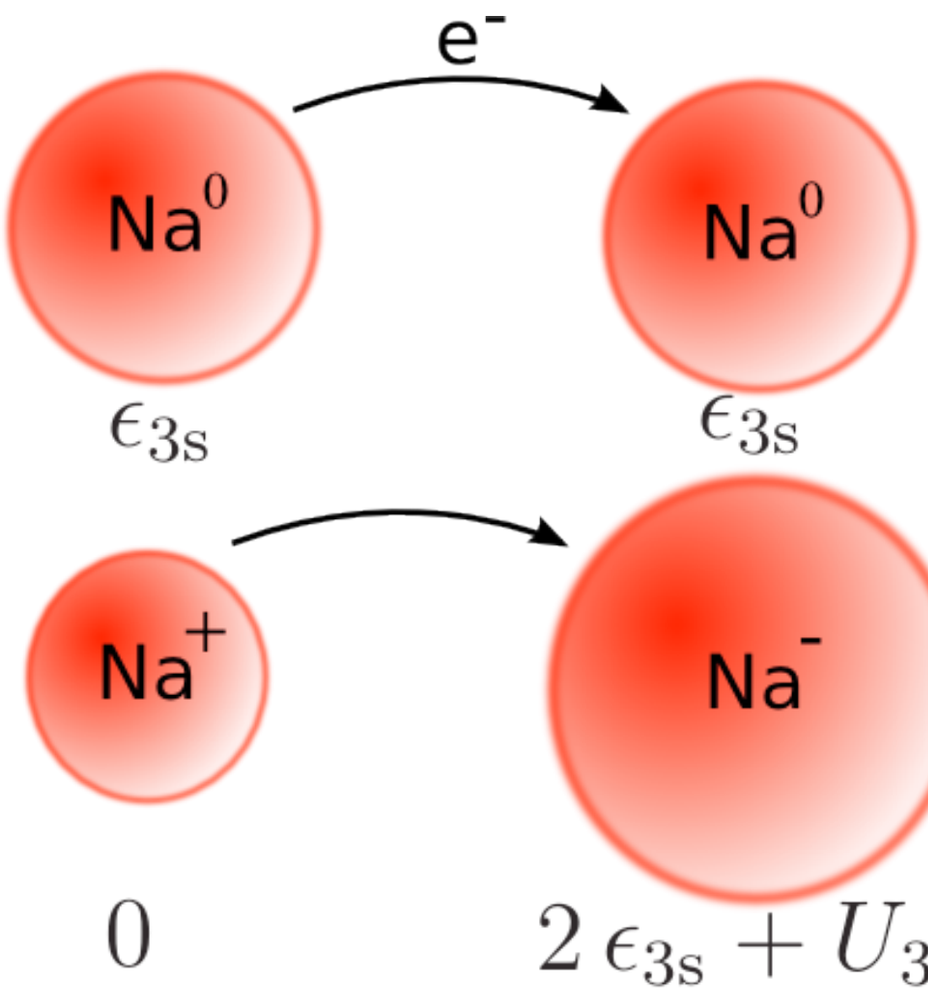
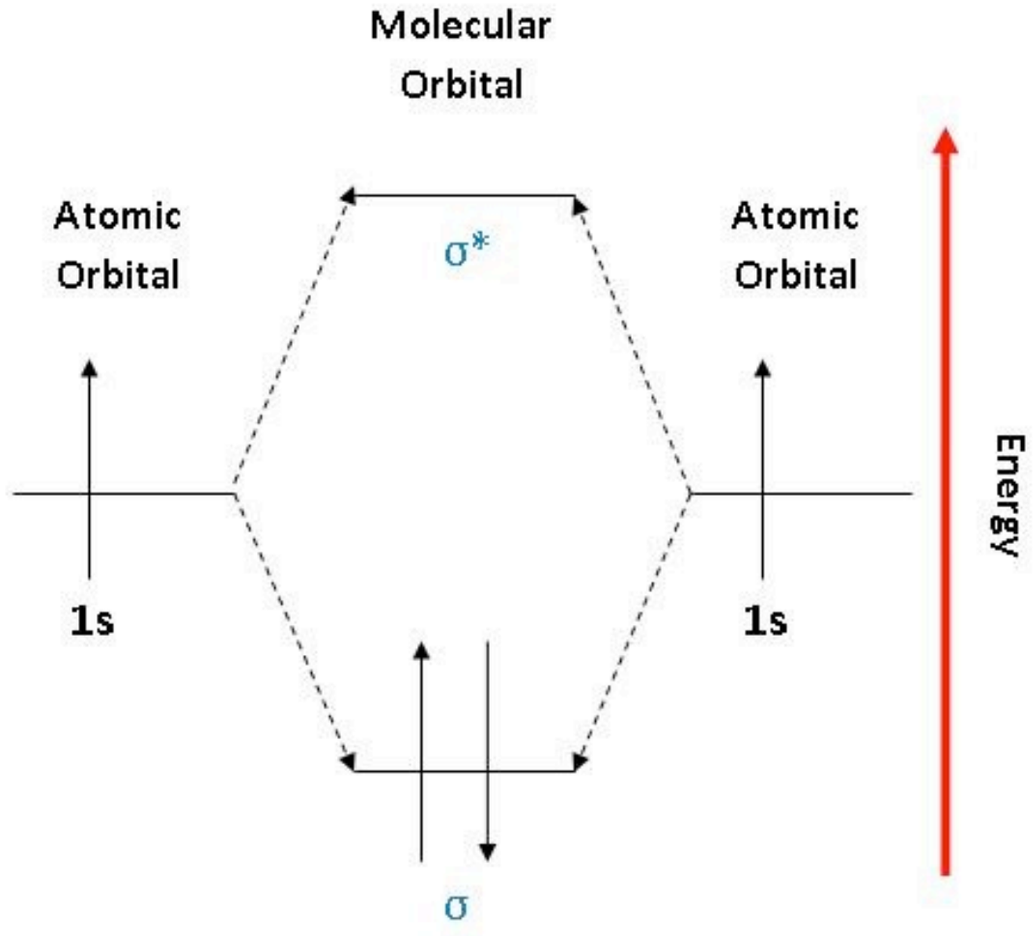
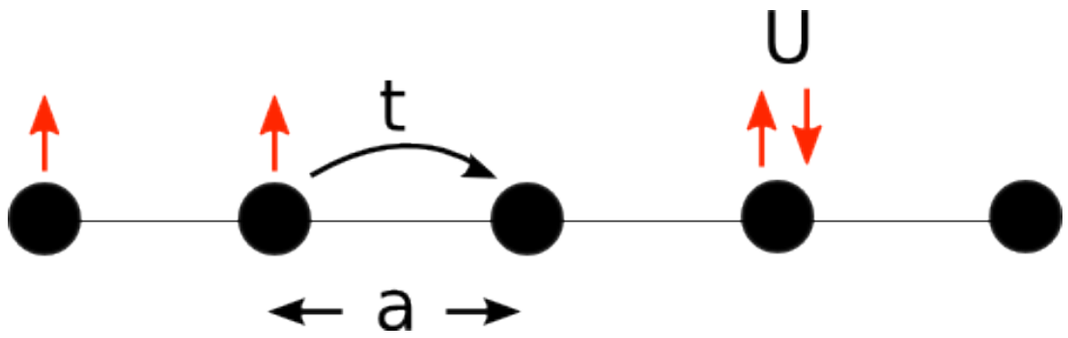


$$H = \begin{pmatrix} h_{aa} & v_{ab} \\ v_{ab} & h_{aa} \end{pmatrix}$$

$$U_{3s} = \int d^3r \int d^3r' \, |\phi_{3s}(\mathbf{r})|^2 \, \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \, |\phi_{3s}(\mathbf{r}')|^2$$



Introduction to the Hubbard model



t → hopping matrix element
U → on-site Coulomb repulsion

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

$\mathcal{H}_{\text{band}}$ $\mathcal{H}_{\text{Coulomb}}$

J.Hubbard, Proc. Roy. Soc. Lond. (1963–1967)

$\hat{n}_{i\sigma} = \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma}$ $\hat{c}^{\dagger}_{i\sigma}$, $\hat{c}_{i\sigma}$ creation/annihilation operators

Band term is easy to solve; introduce → $\hat{c}_{j\sigma} = \frac{1}{\sqrt{N}} \sum_{k} e^{i \frac{2\pi k}{N} j} \hat{b}_{k\sigma}$

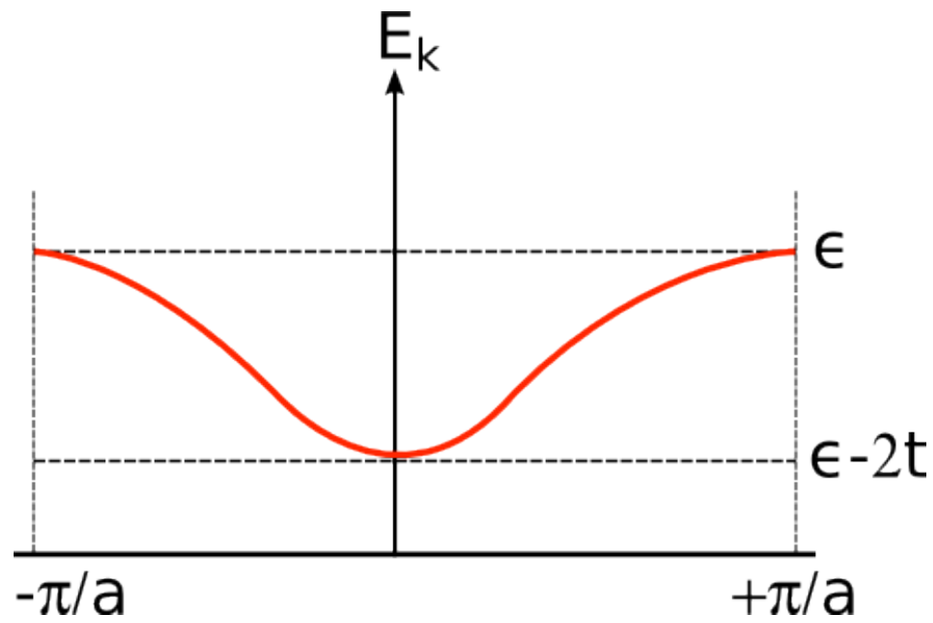
N: number of atoms

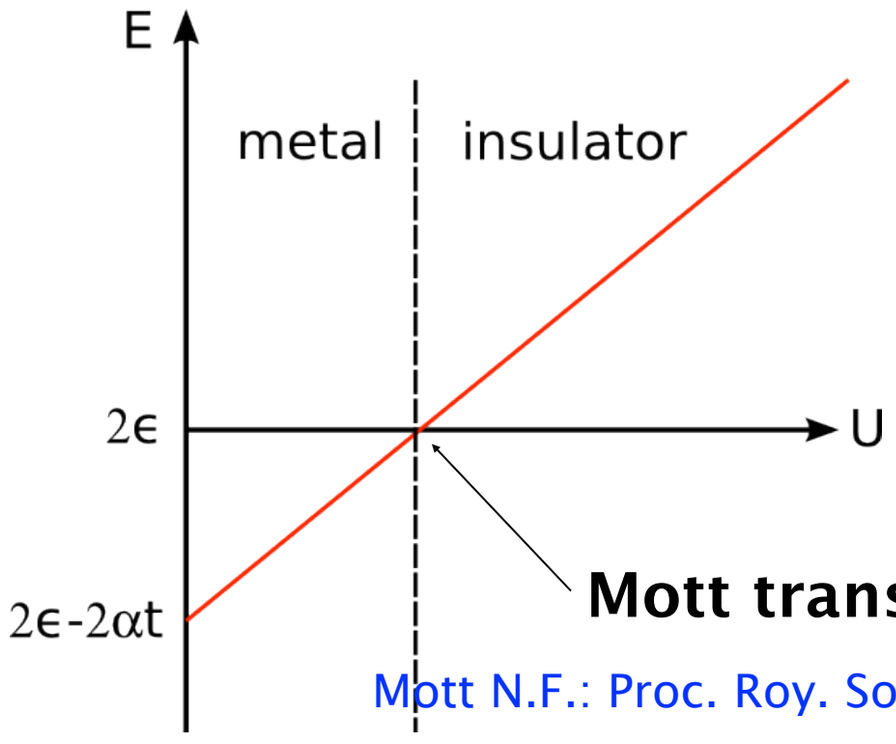
More on the Hubbard model

$$\mathcal{H}_{\text{band}} = \sum_{k,\sigma} \left[\epsilon - 2\,t\,\cos\left(\frac{2\pi k}{N}\right) \right] \hat{b}^{\dagger}_{k\sigma}\,\hat{b}_{k\sigma}$$

$$\langle \mathcal{H}_{\text{band}} \rangle \simeq 2N(\epsilon - \alpha\, t)$$

$$\langle \mathcal{H}_{\text{Coulomb}} \rangle \simeq N\,U$$





Mott transition

Mott N.F.: Proc. Roy. Soc. A62, 416 (1949)

$$E = \langle \mathcal{H}_{\text{band}} \rangle + \langle \mathcal{H}_{\text{Coulomb}} \rangle$$

$$E = N(2\epsilon + U - \alpha\, t)$$

band-shape dependent constant

- Metallic when t >> U
- Insulating when t << U

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A “simple” case: the dissociation of H_2

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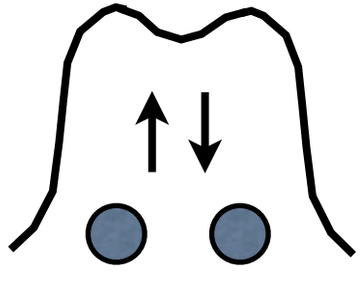
Exact:



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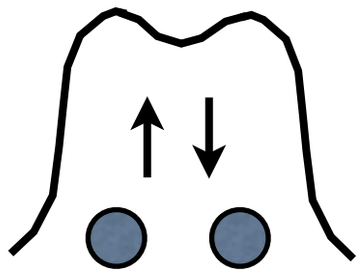

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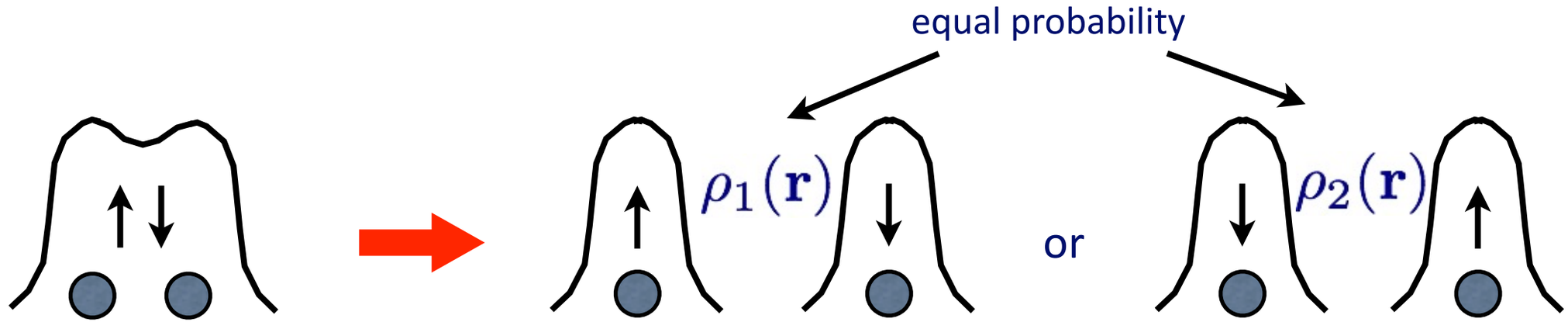

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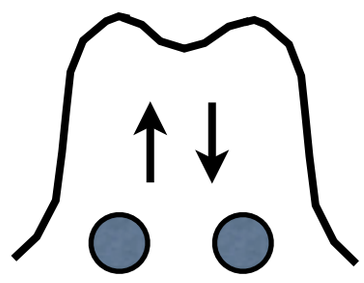

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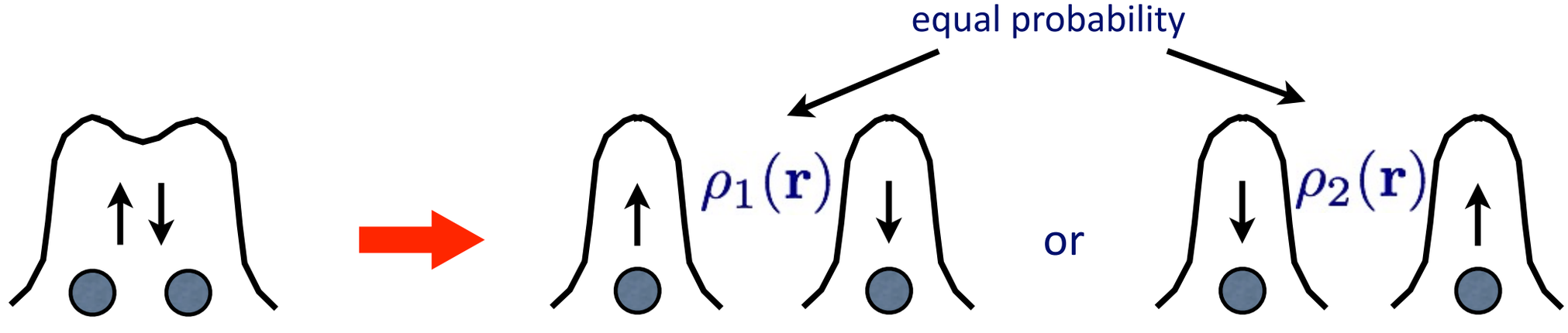

DFT:

$$\rho(\mathbf{r}) = \tfrac{1}{2}\rho_1(\mathbf{r}) + \tfrac{1}{2}\rho_2(\mathbf{r})$$

How good is DFT?

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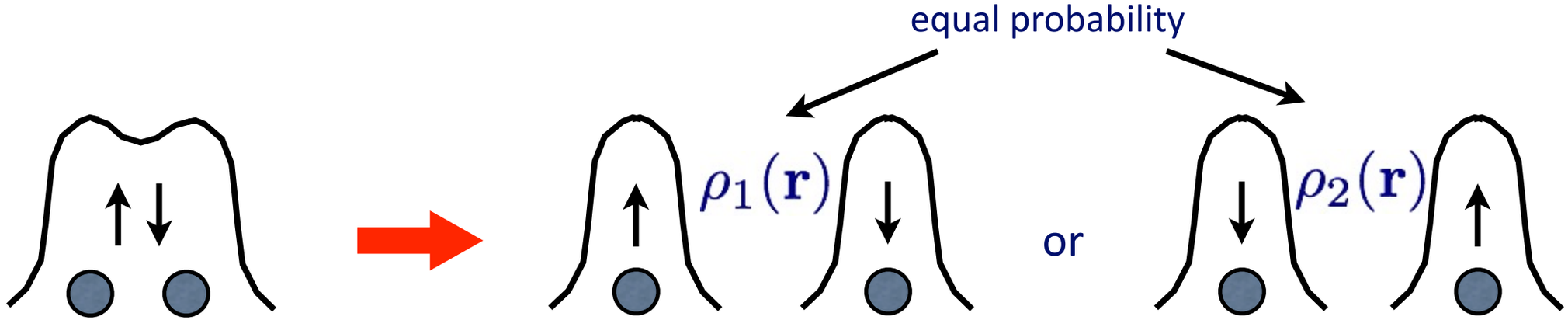

$$E = \tfrac{1}{2}E_1 + \tfrac{1}{2}E_2$$

DFT:

$$\rho(\mathbf{r}) = \tfrac{1}{2}\rho_1(\mathbf{r}) + \tfrac{1}{2}\rho_2(\mathbf{r}) \qquad E[\rho(\mathbf{r})] \neq \tfrac{1}{2}\mathbf{E}[\rho_1(\mathbf{r})] + \tfrac{1}{2}\mathbf{E}[\rho_2(\mathbf{r})]$$

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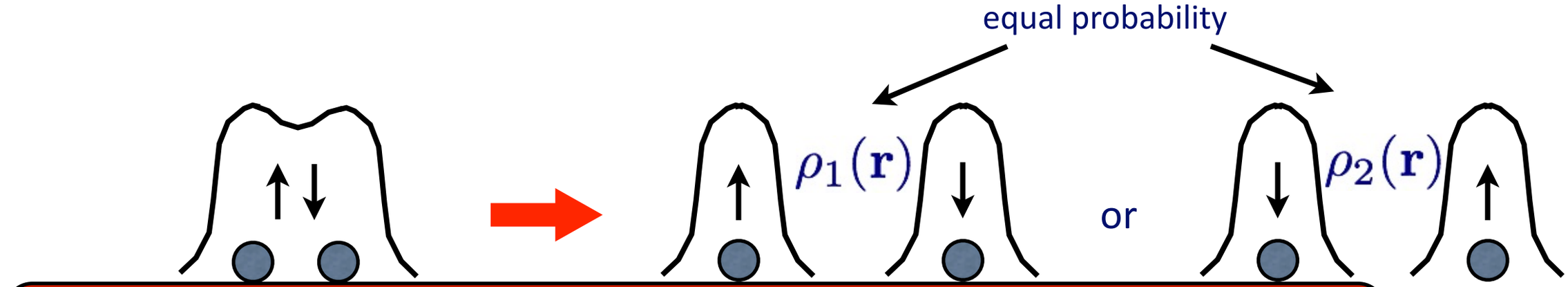
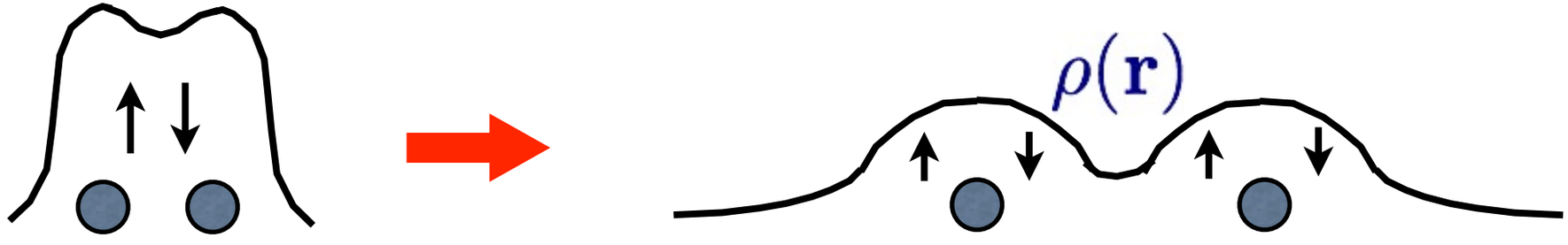


The curvature of the energy is exaggerated

DFT:



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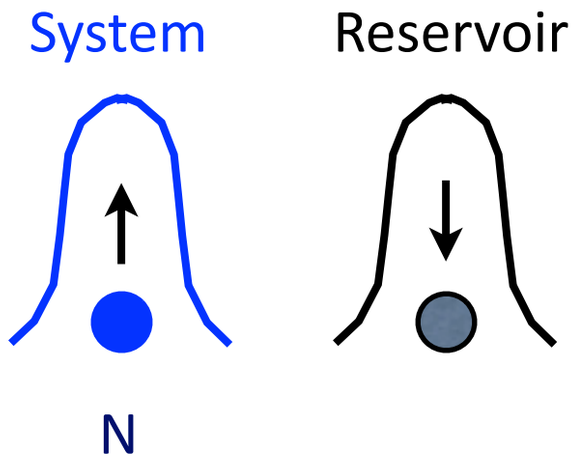
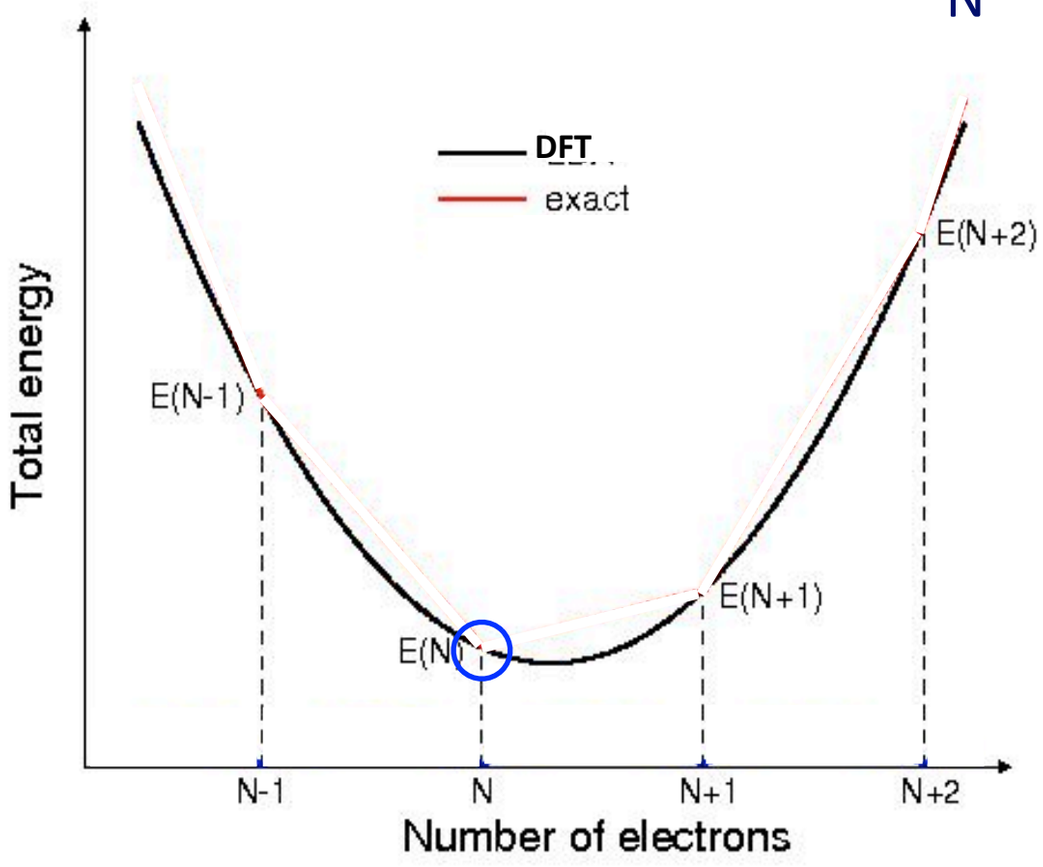
Energy linearity





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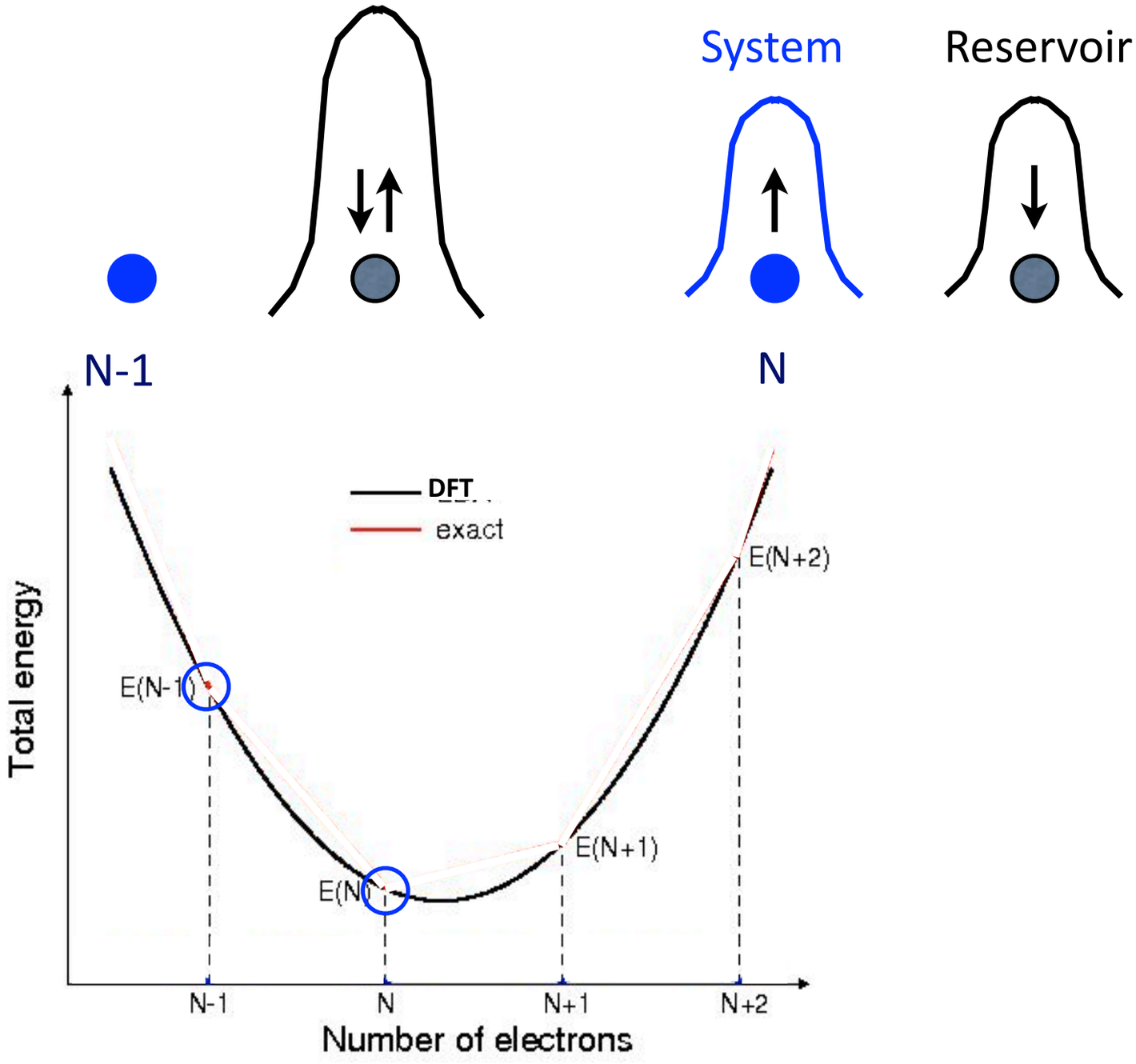

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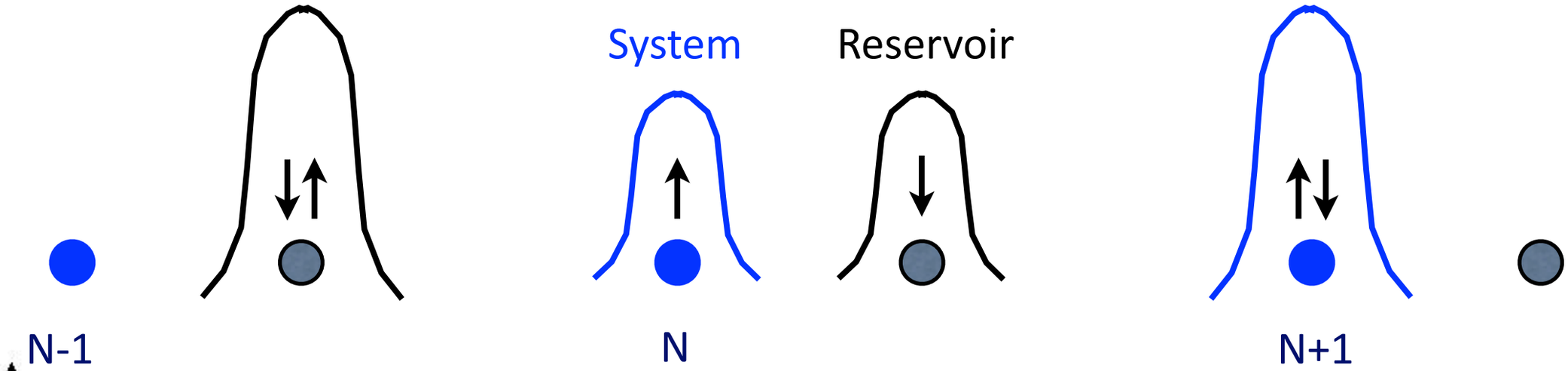
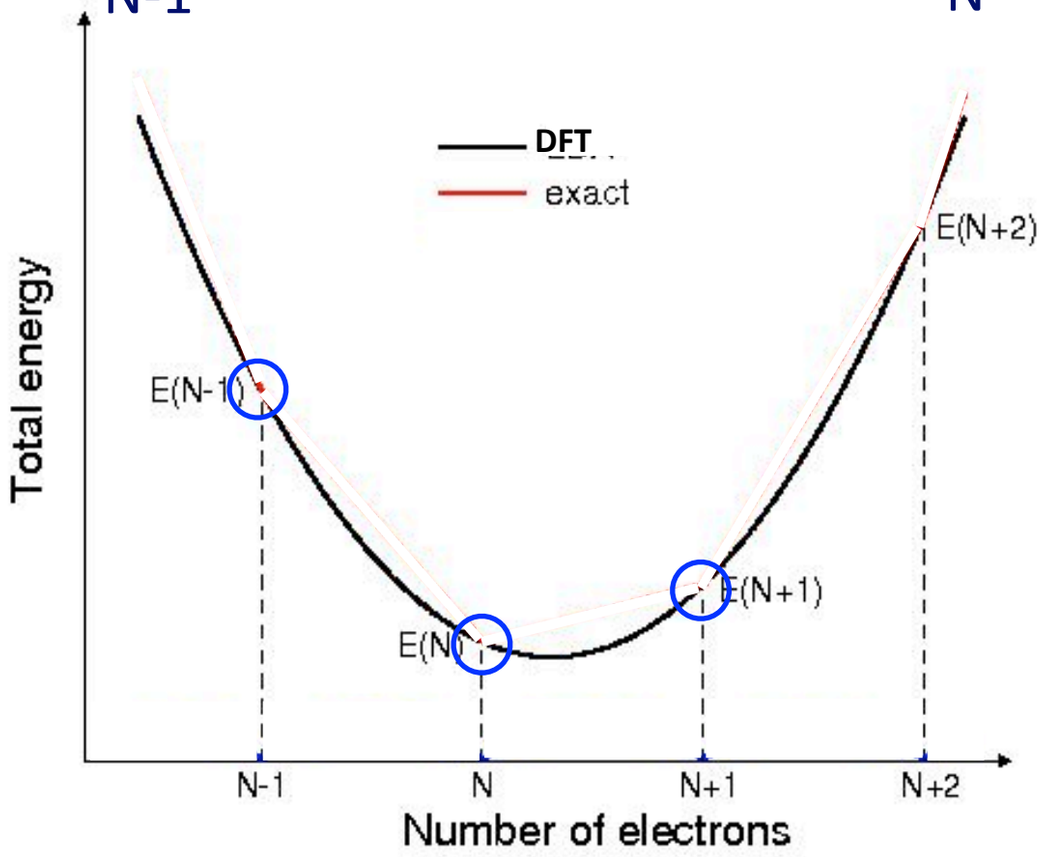
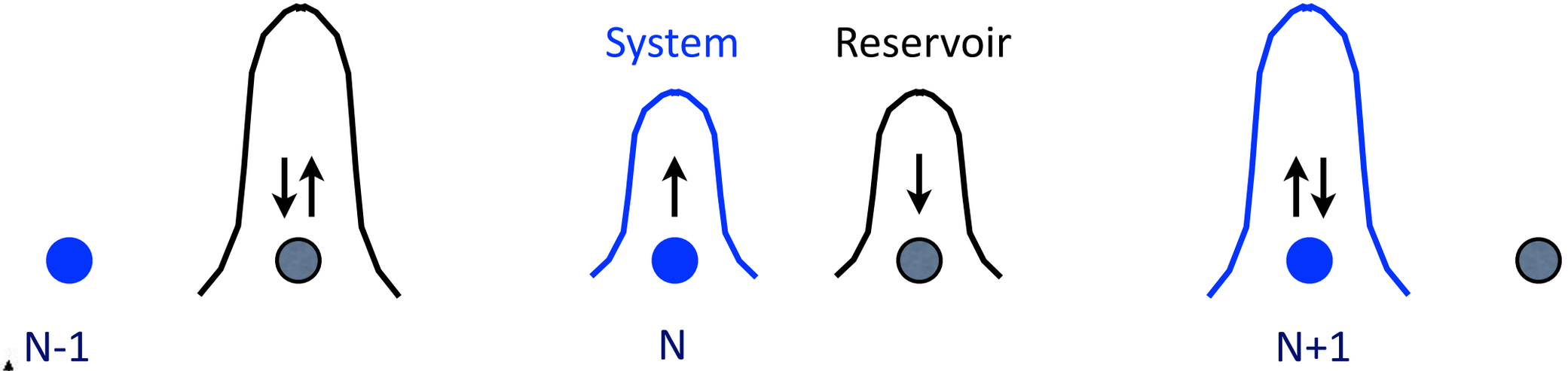
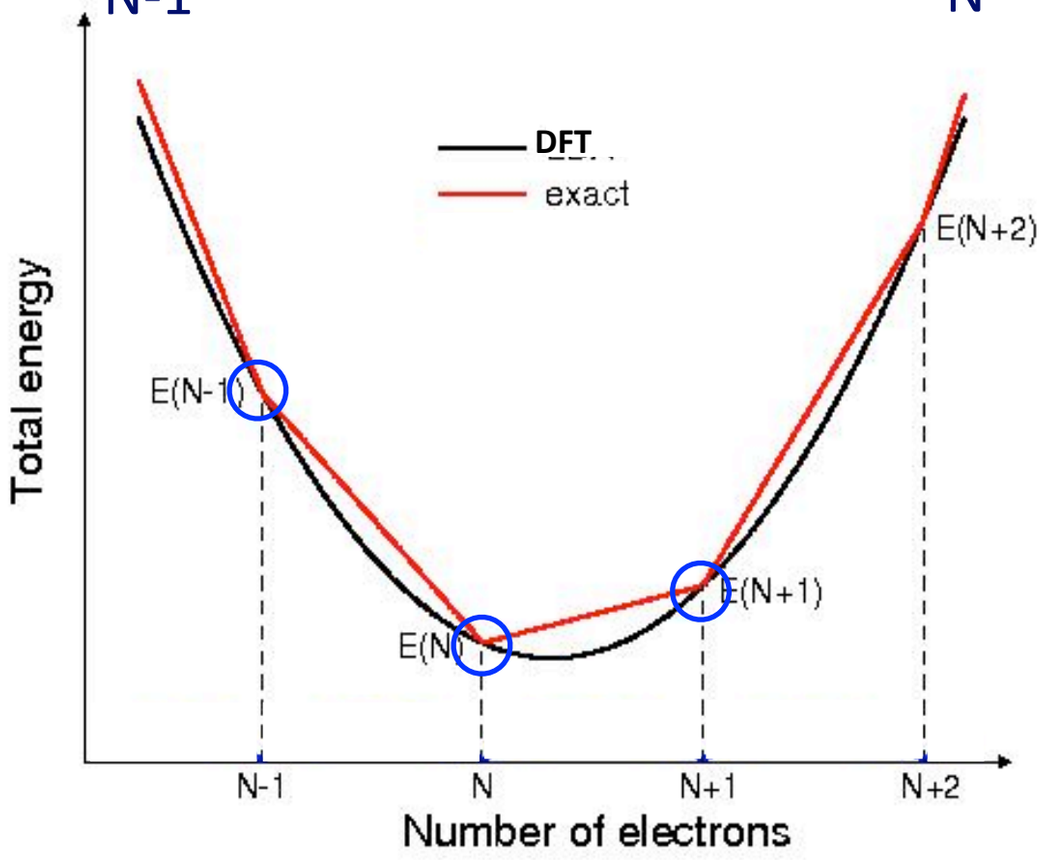




Energy linearity

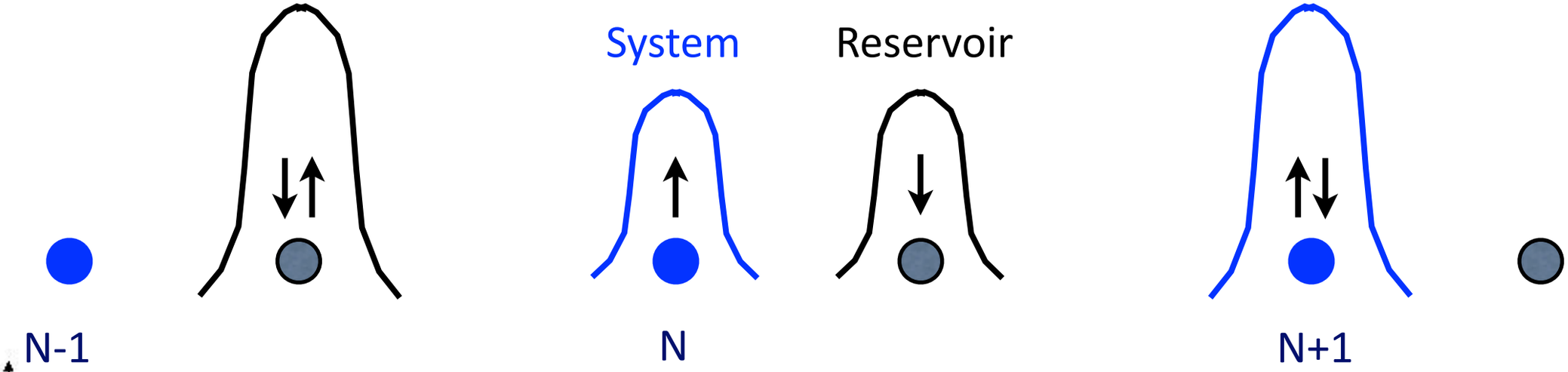


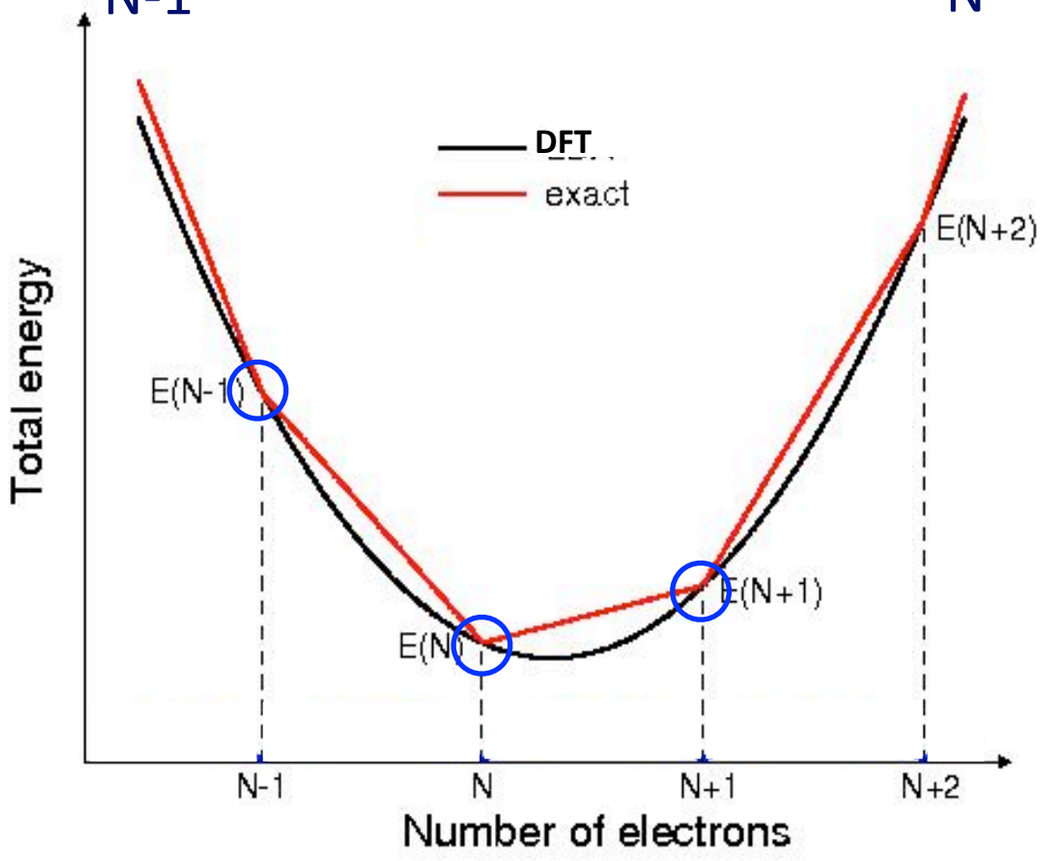


The exact energy is piece-wise linear (statistical ensemble)

J. Perdew et al., PRL 23, 1691 (1982)

Energy linearity





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The chemical potential μ should be discontinuous

$$\Delta\mu = I - A$$

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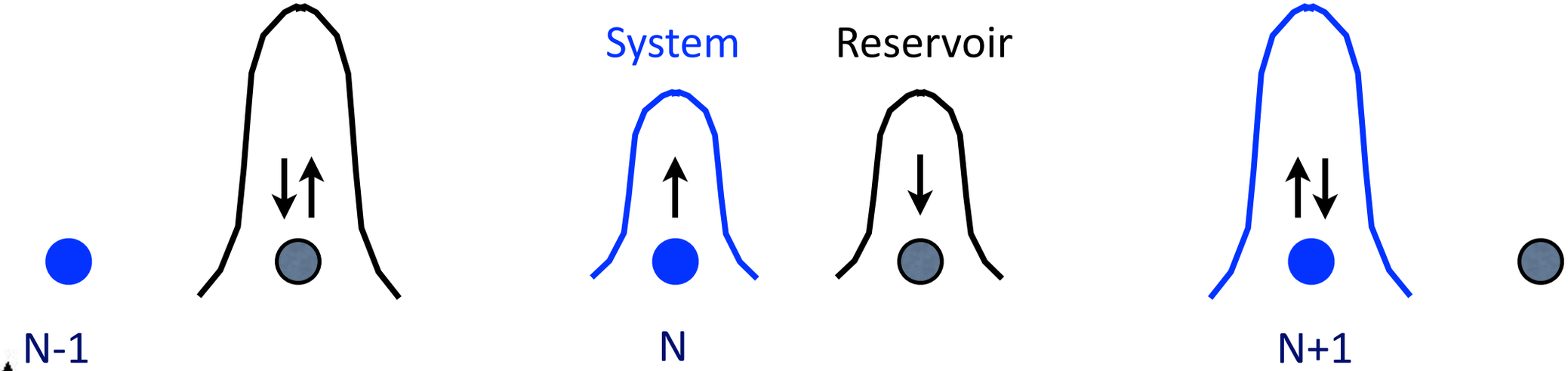

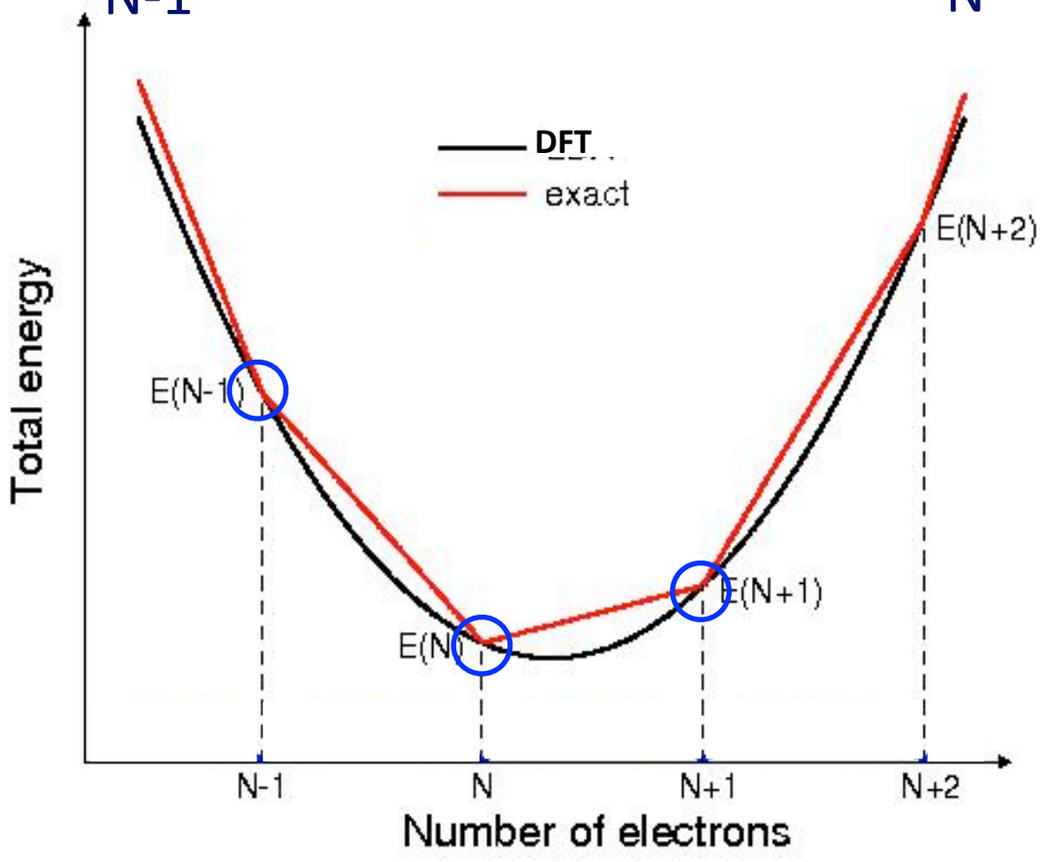

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Why does DFT fail in capturing localization? Approximations are based on the homogeneous e- gas!

DFT+U

DFT+U

A very simple idea: let's describe localized *d* or *f* electrons as located on isolated (atomic) states in a "crystal bath". Let's use the Hubbard model to describe their behavior.
We need to "embed" the Hubbard Hamiltonian in the DFT energy functional

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

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

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We add the Hubbard functional, subtract its MF value (to avoid double-counting)

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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

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

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

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

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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

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Effective interactions:

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

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

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

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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?

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

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

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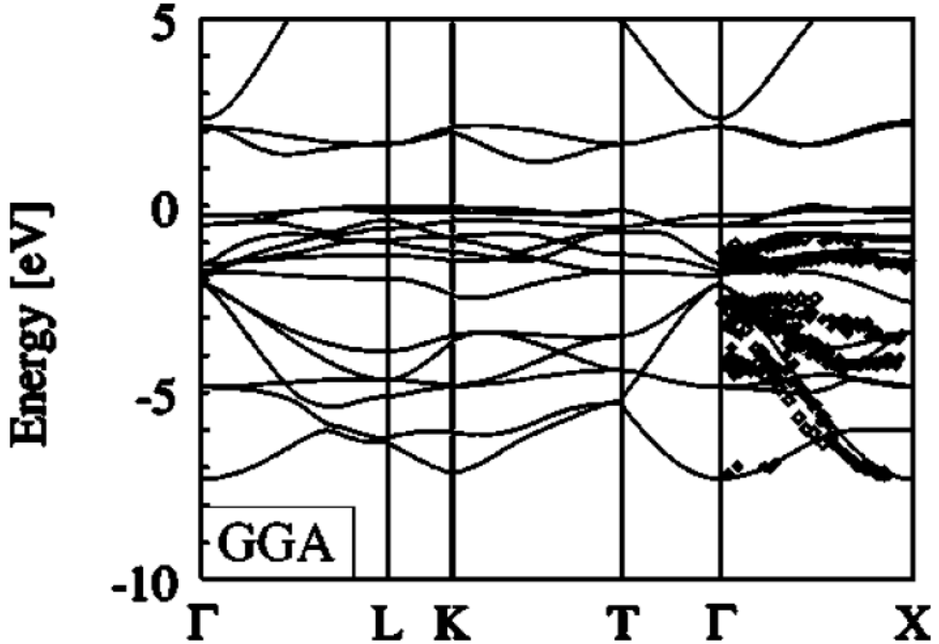
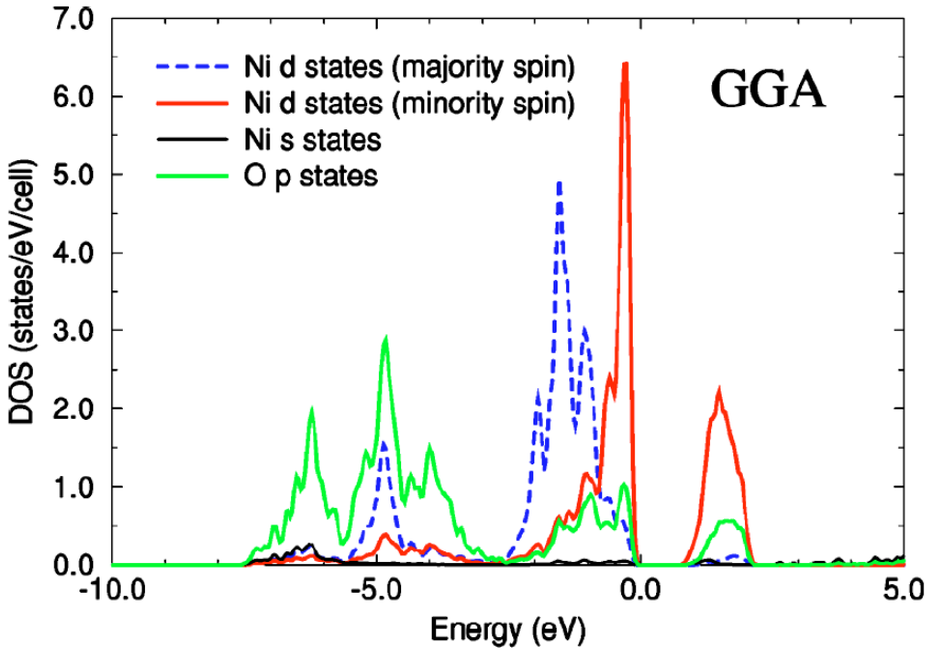
$$\left.\begin{array}{l} \lambda_m^{I\sigma} > \frac{1}{2} \Rightarrow V_U < 0 \\ \lambda_m^{I\sigma} < \frac{1}{2} \Rightarrow V_U > 0 \end{array}\right\} \Rightarrow$$

- Partial occupations of atomic states are discouraged
- Potential discontinuity re-established (and inserted in the spectrum)
- A gap opens: $E_g \approx U$

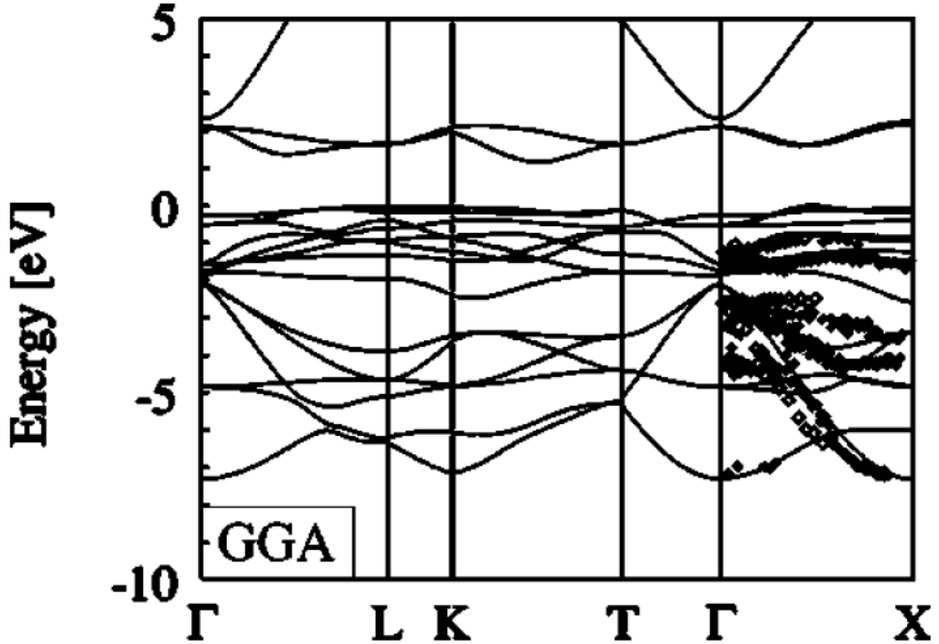
LDA+U NiO

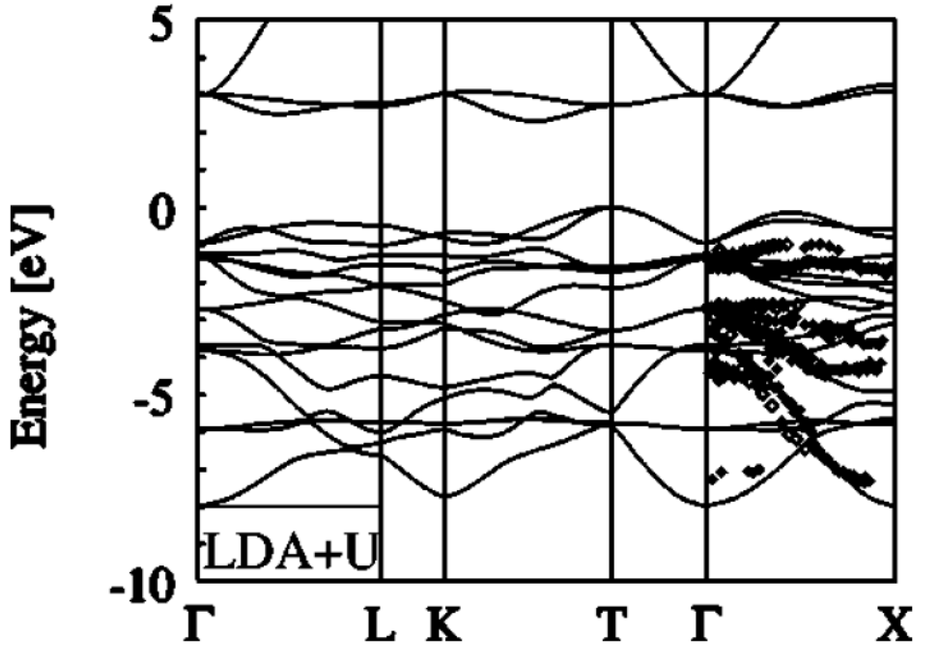


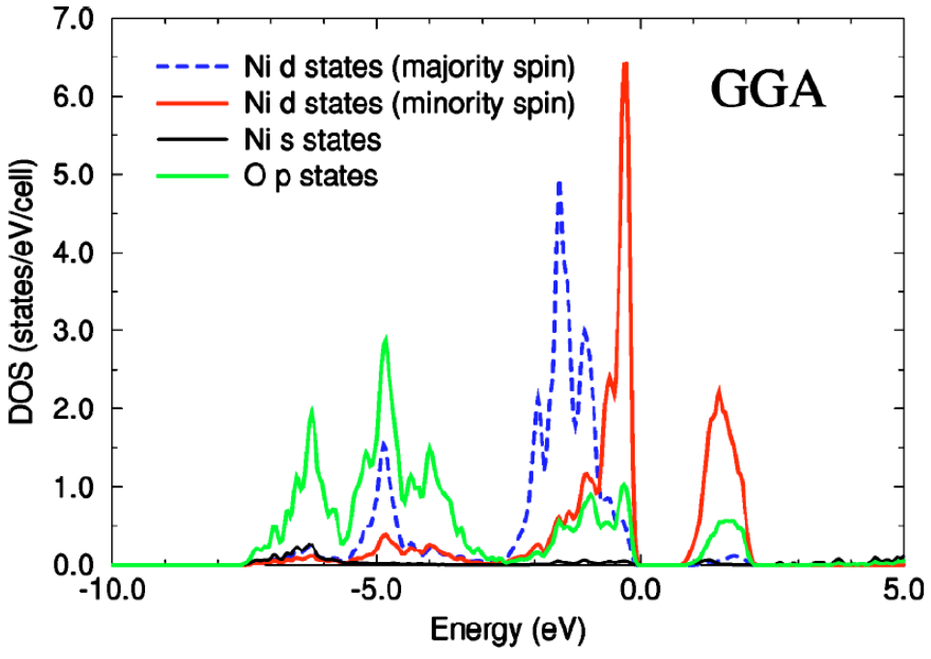


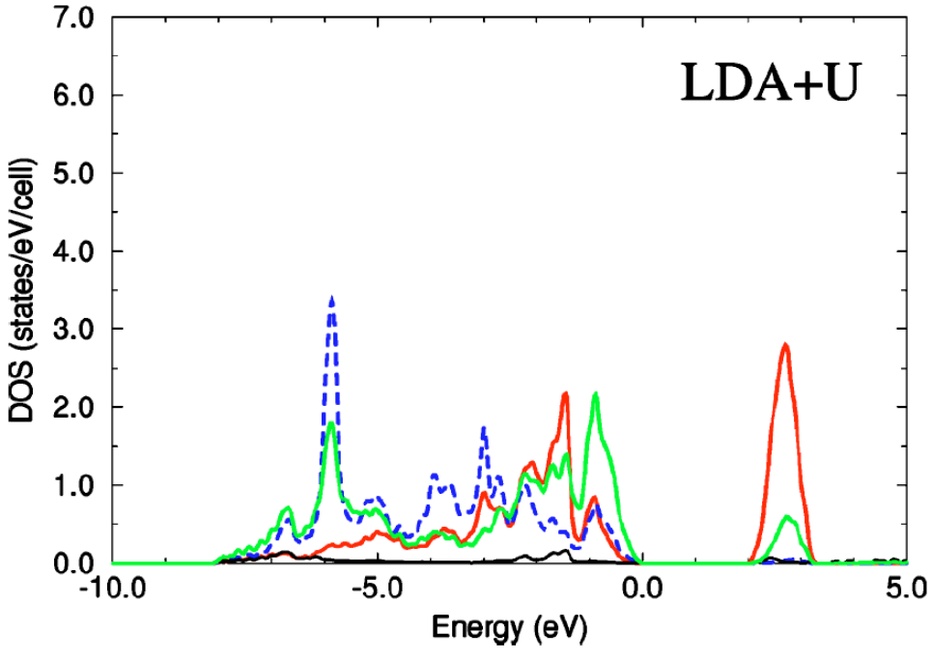
M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

LDA+U NiO









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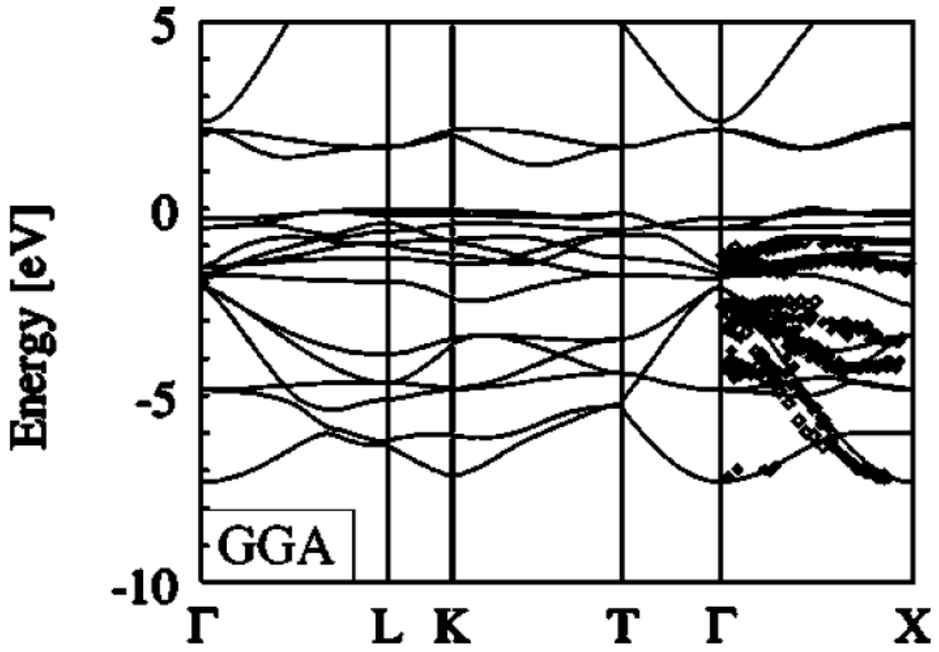
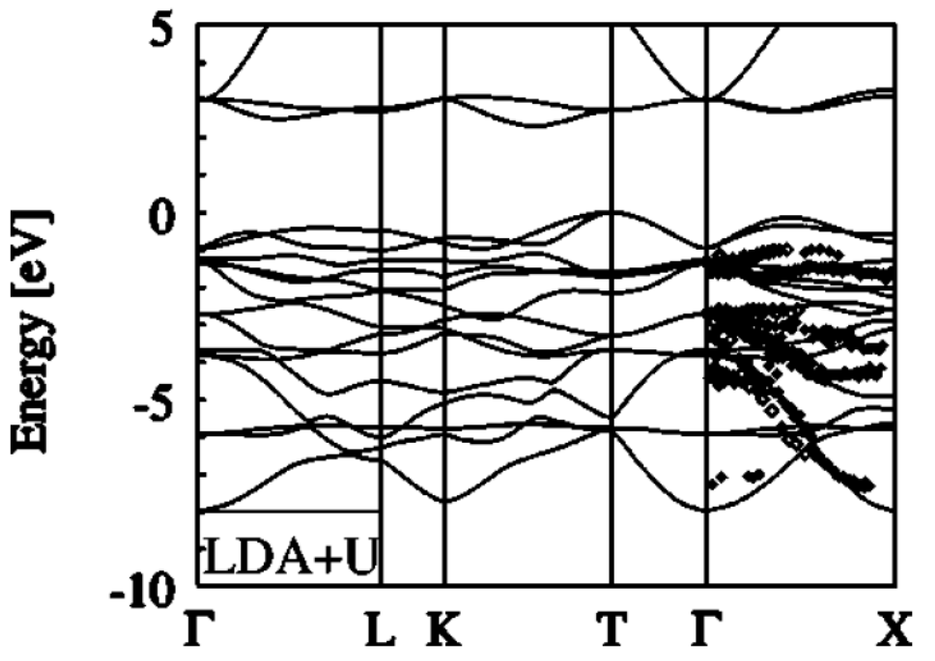
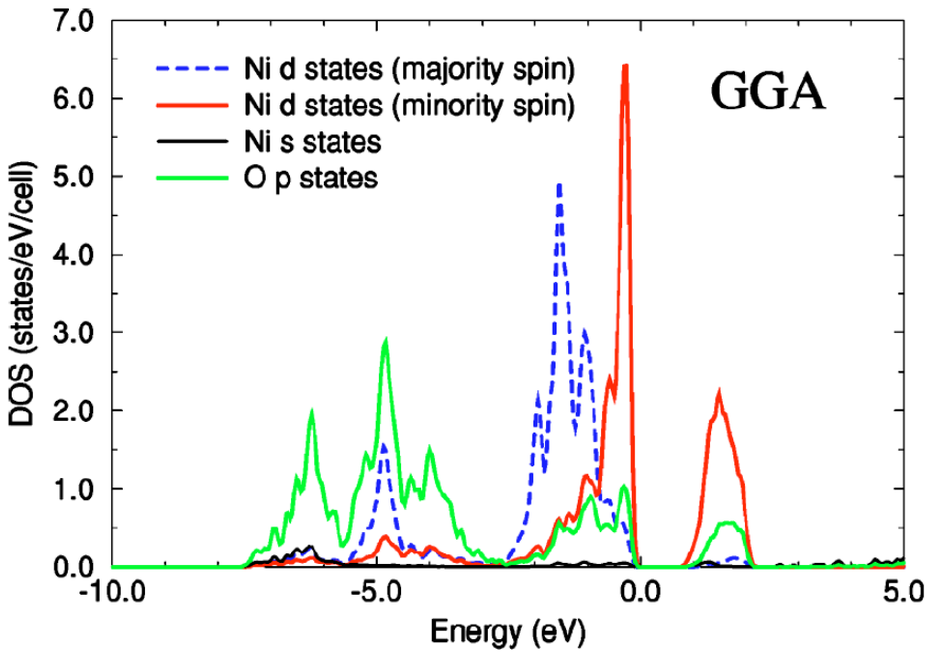
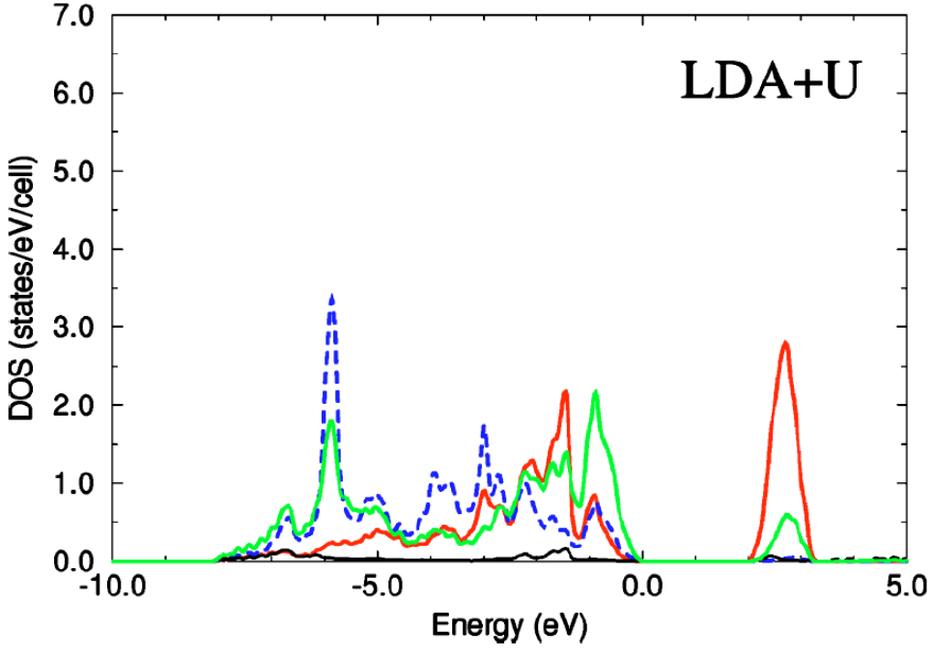


✓Gap improves

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







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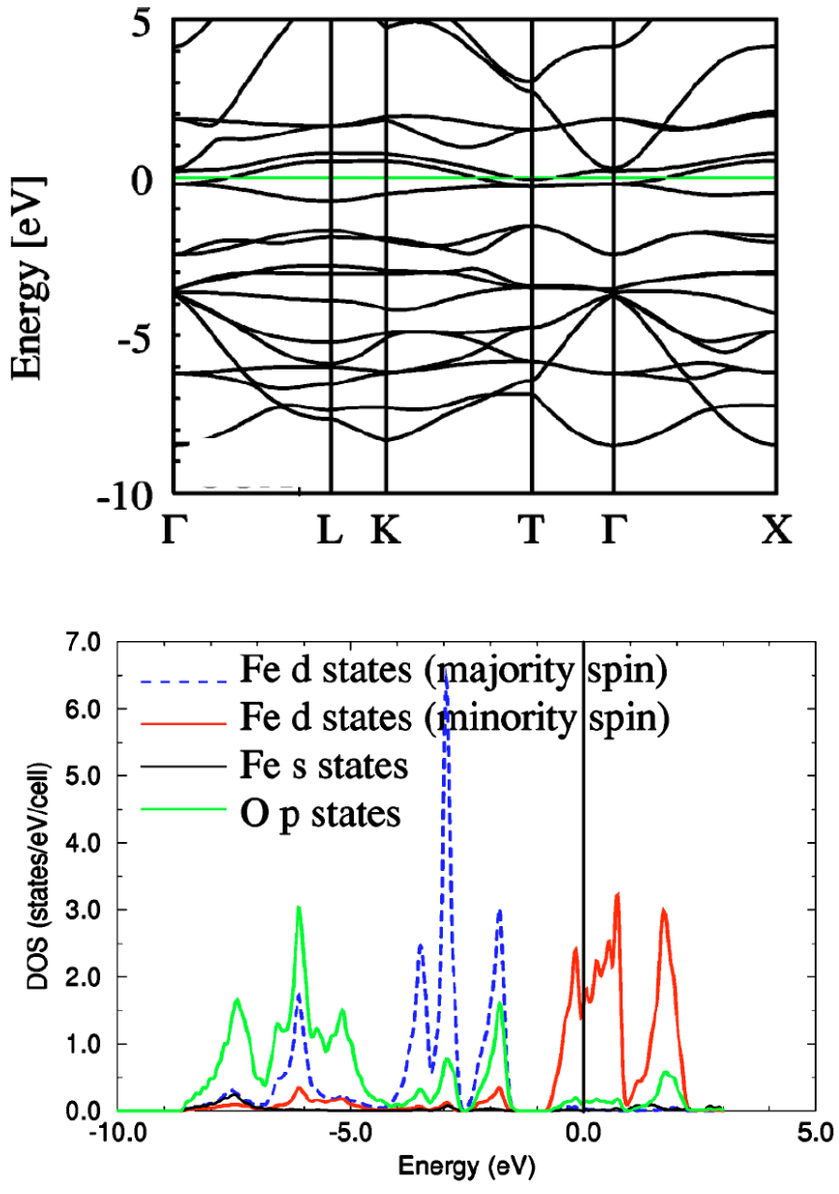
FeO: DFT and DFT+U

DFT

DFT+U



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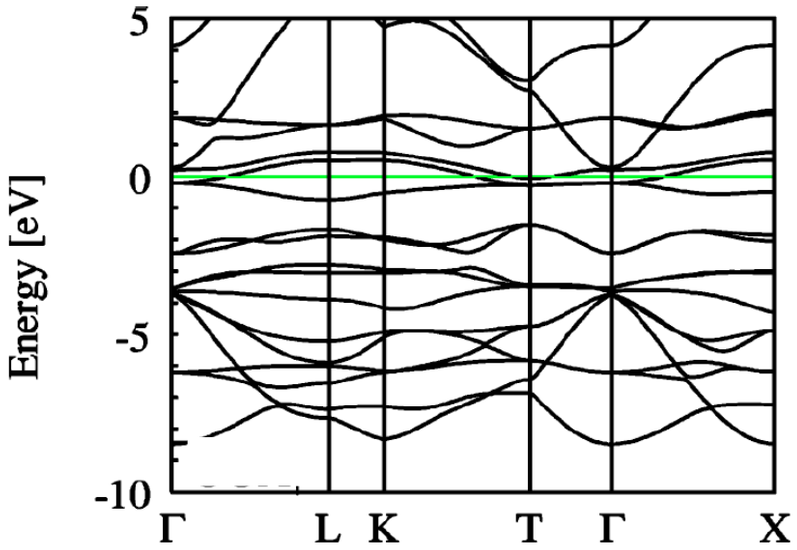
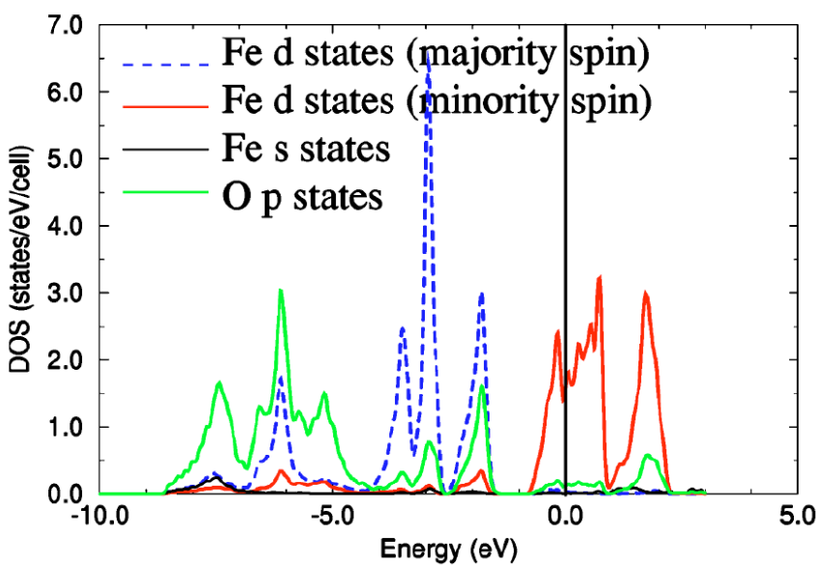
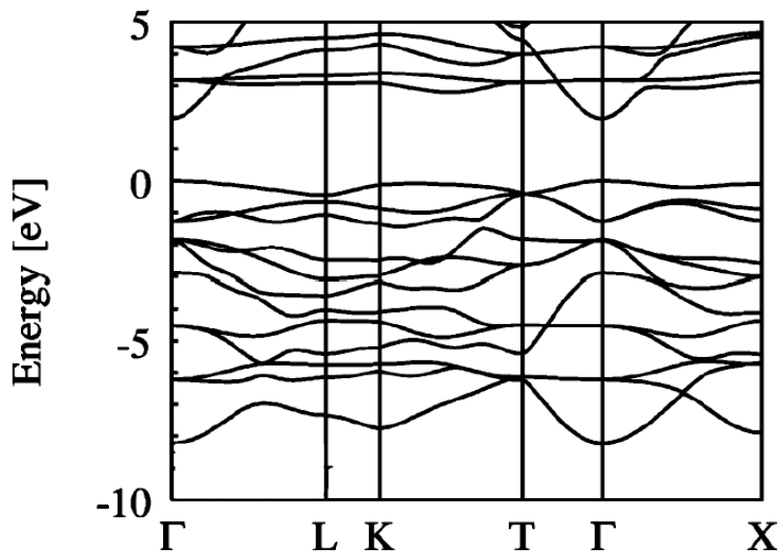
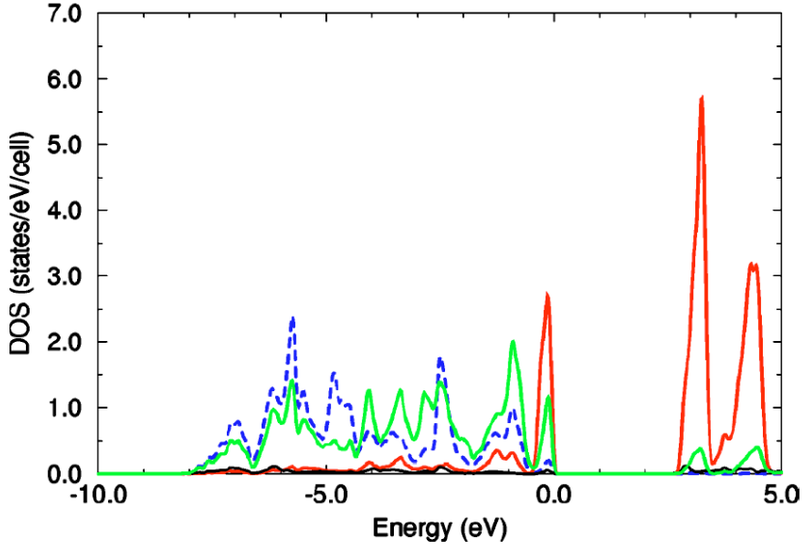




DFT+U





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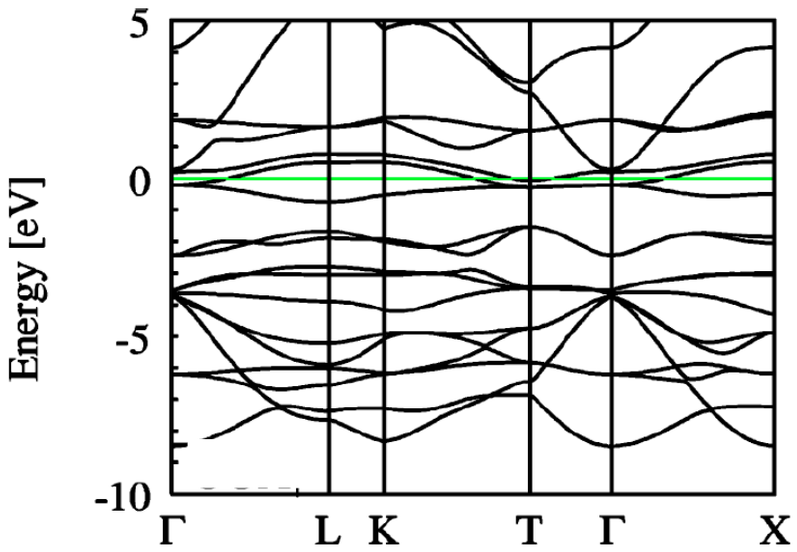
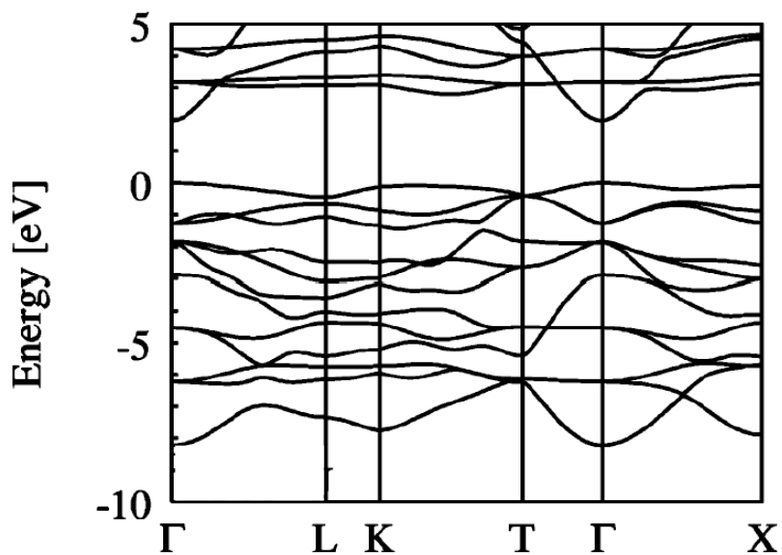
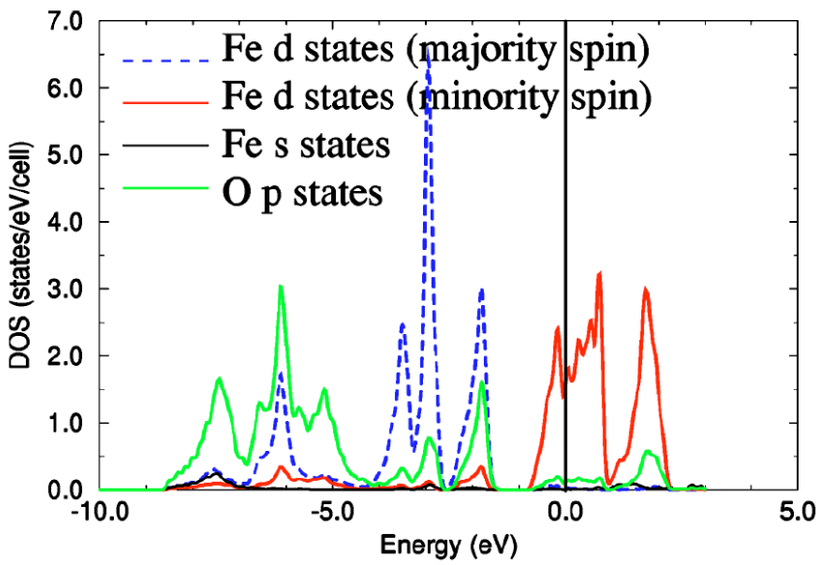


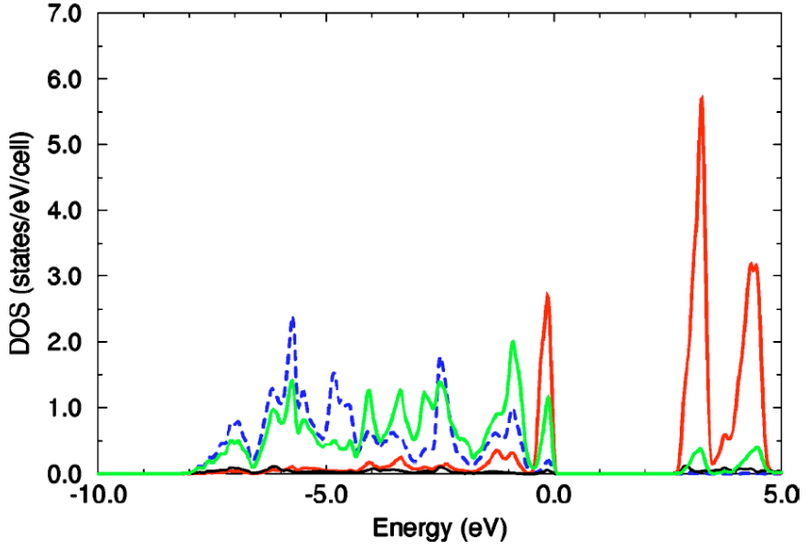
✓Insulating character
(Gap of right size)

DFT+U



✓AFM ground state
(AFII)



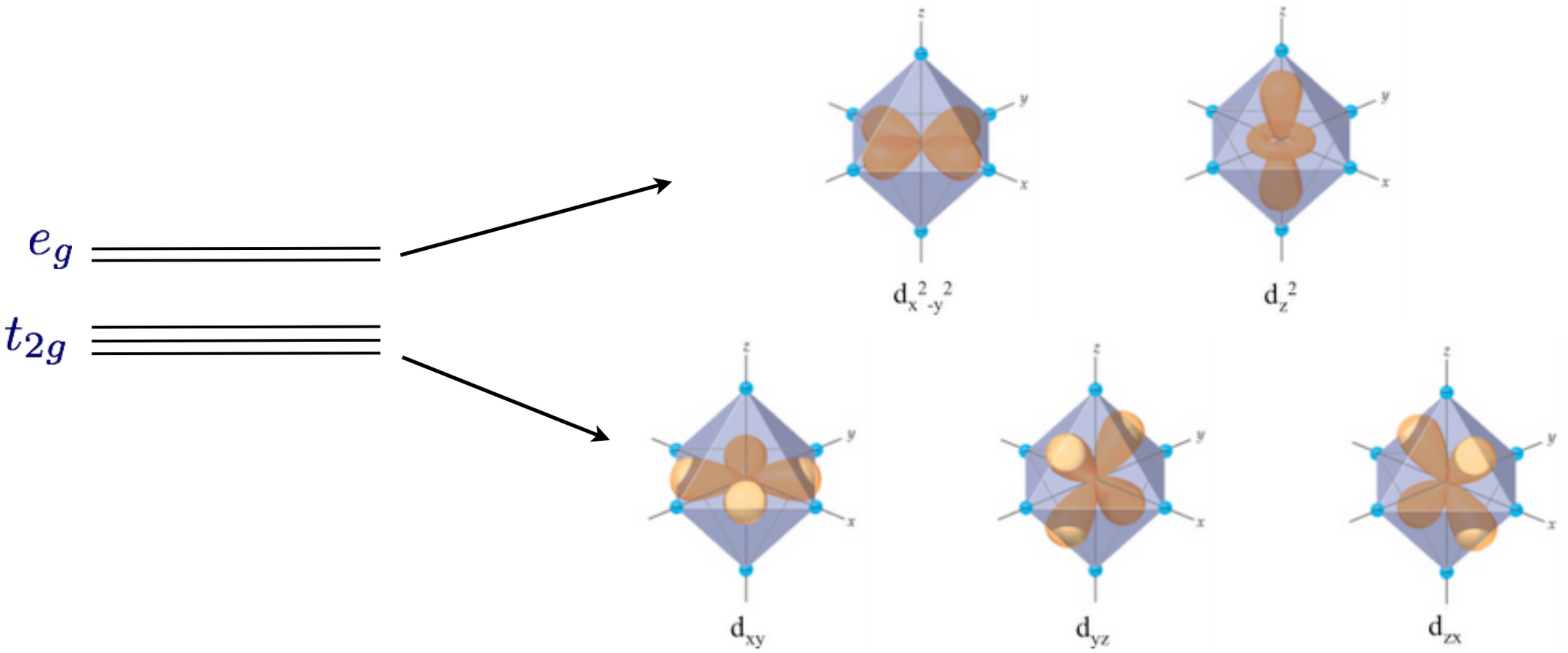


M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

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

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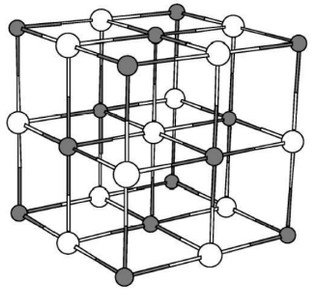
Cubic



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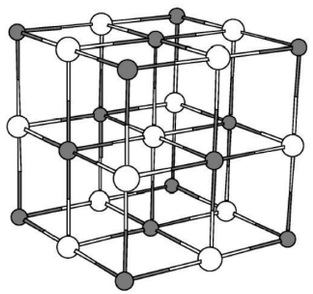

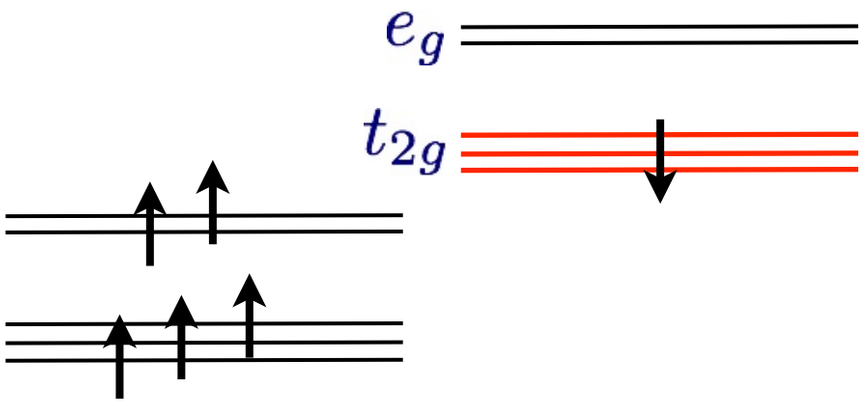

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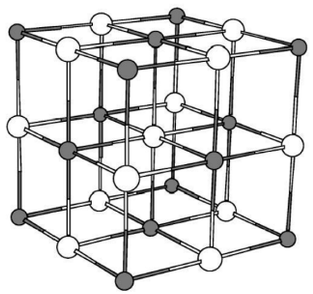
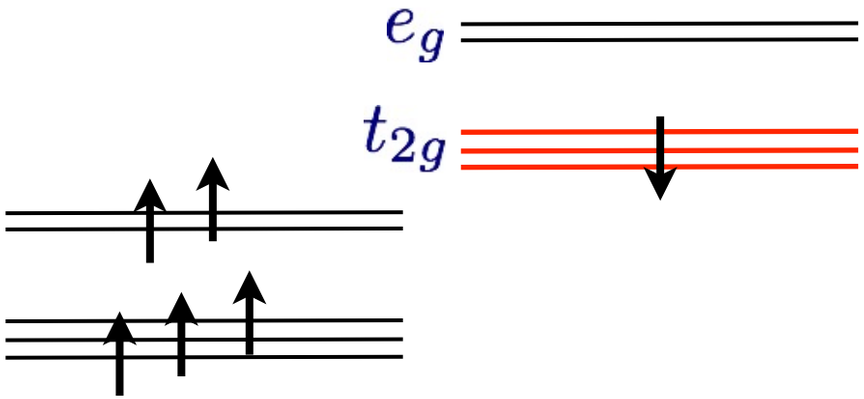
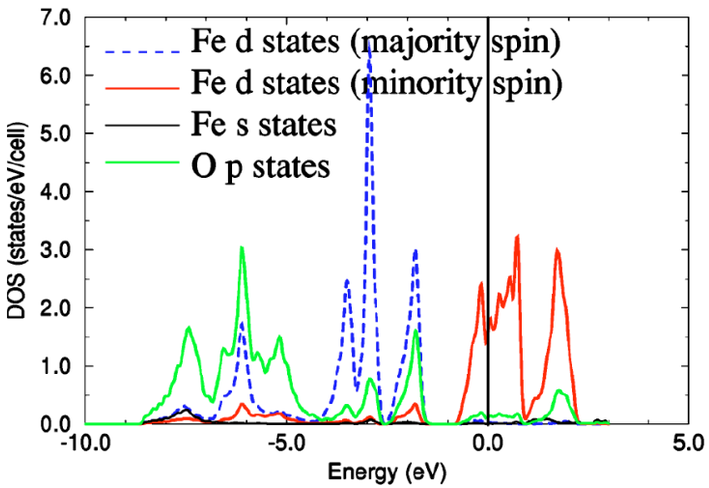
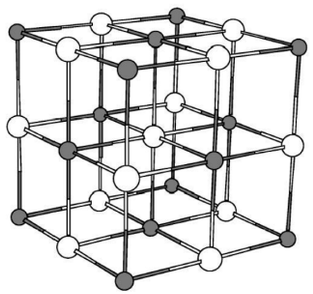


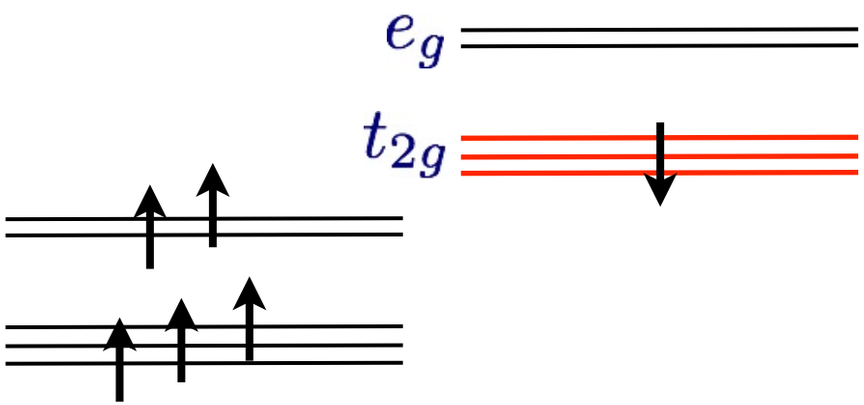




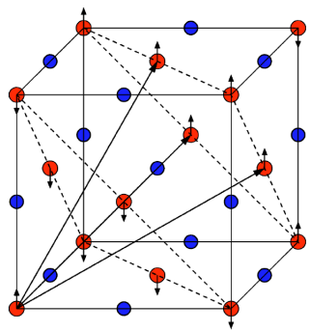
FeO: breaking the symmetry

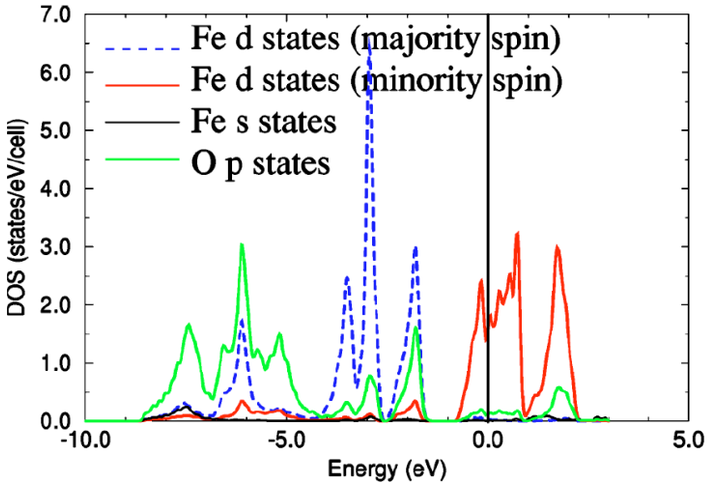
Cubic





Rhombohedral





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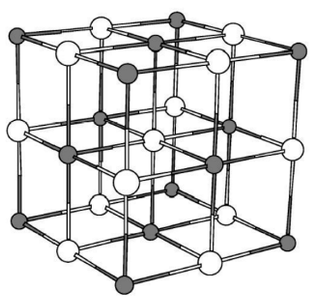

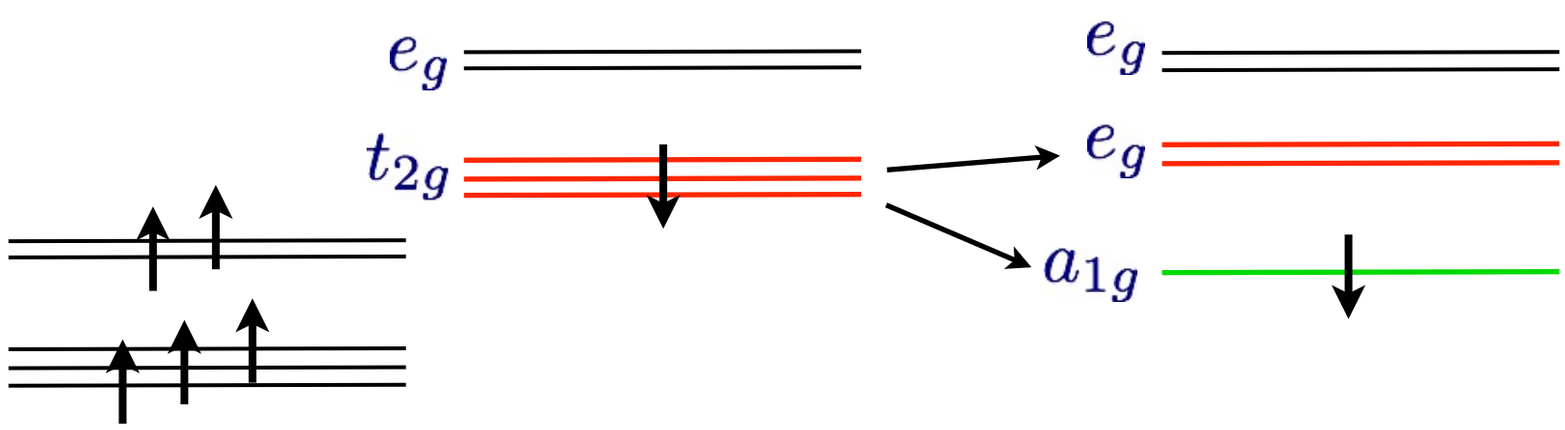

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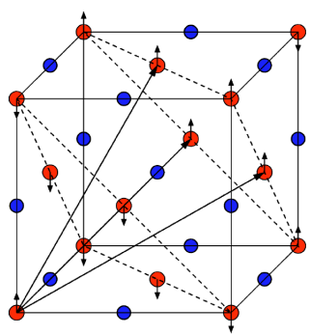

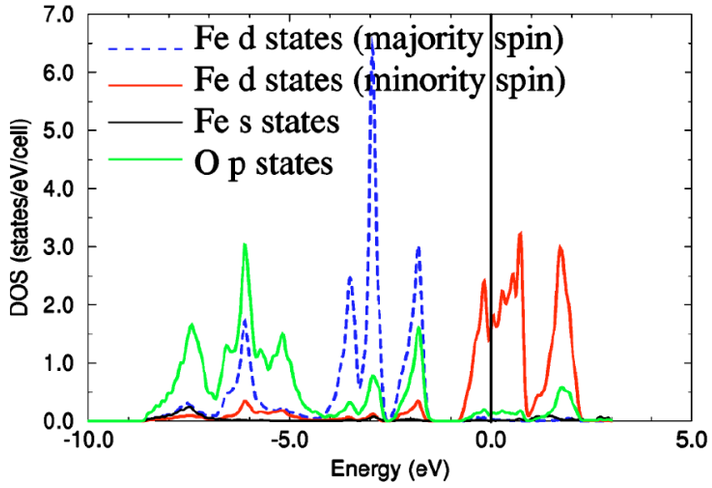

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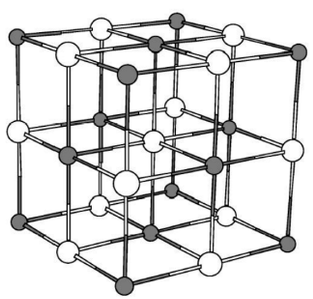
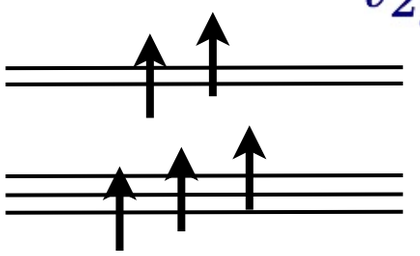


e_g

t_{2g}



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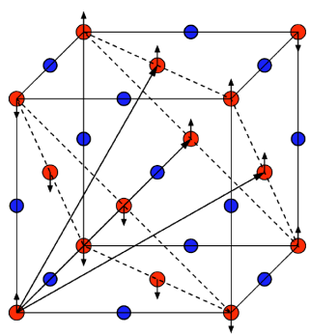
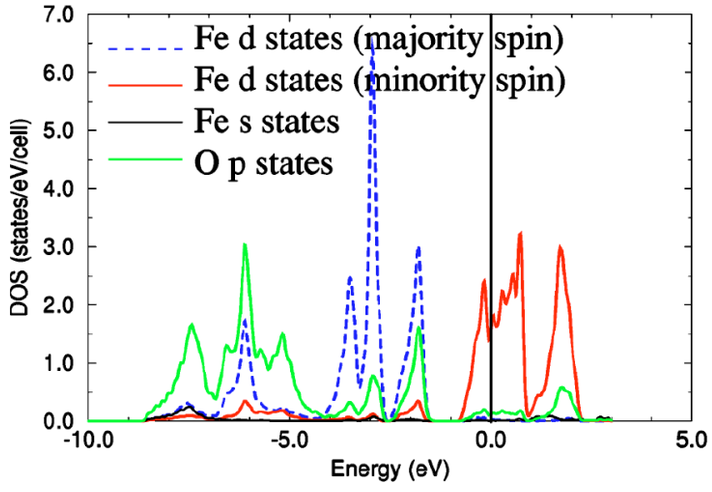
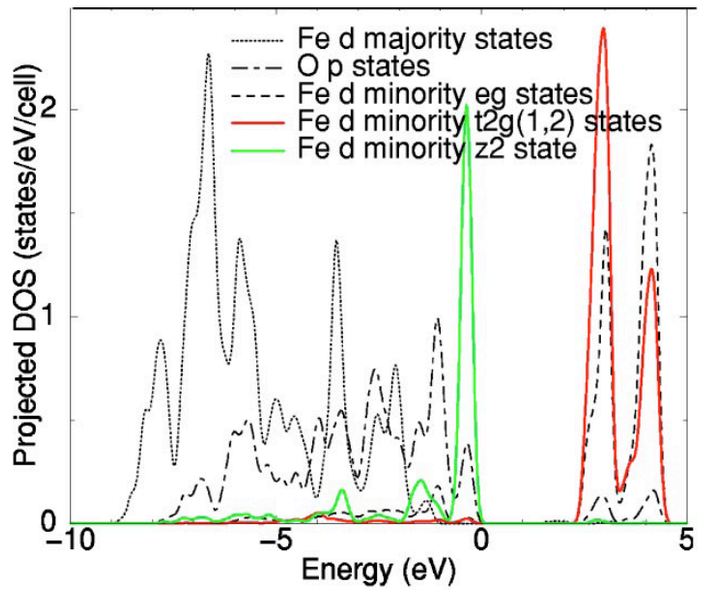


e_g

a_{1g}





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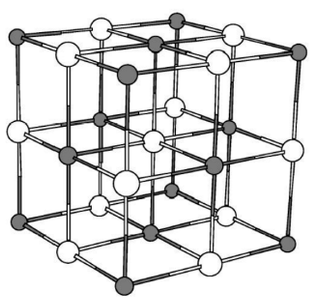

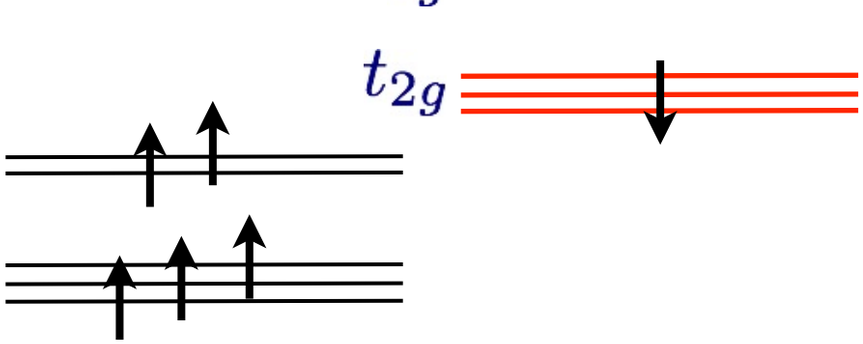

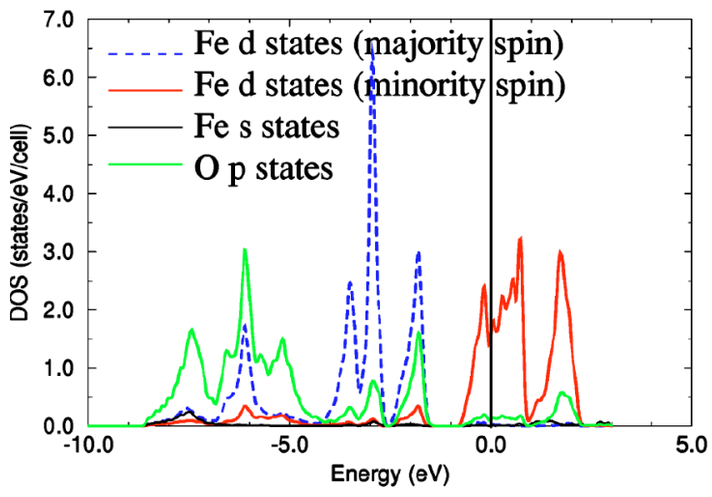

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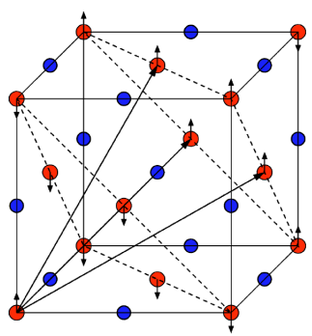
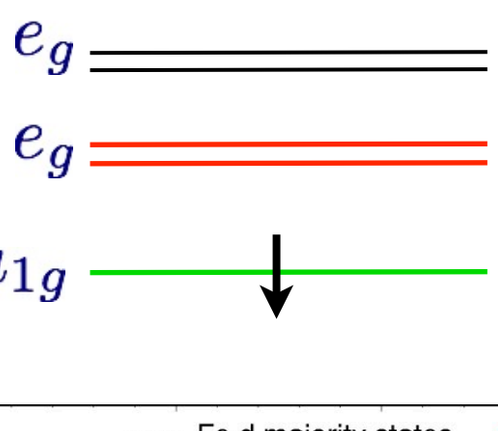
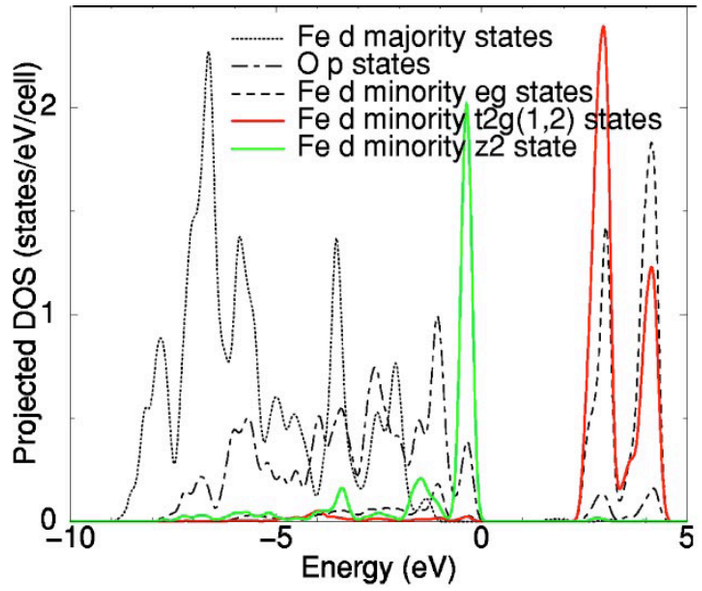
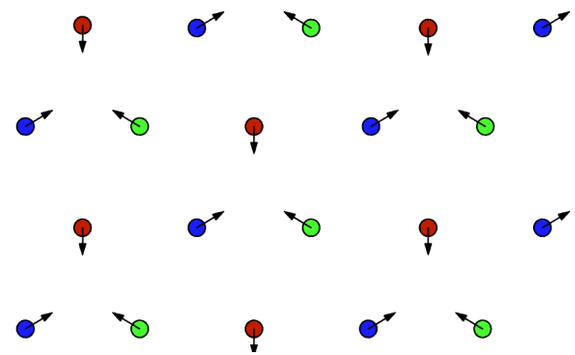






Tripartition of (111) planes



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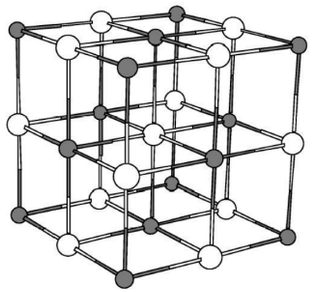
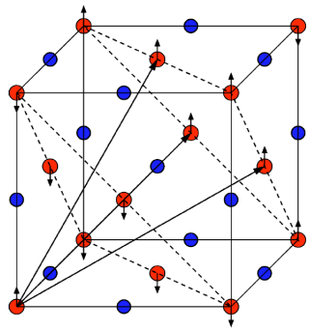


Rhombohedral



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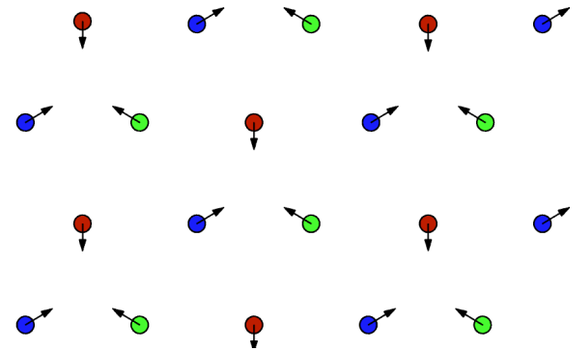
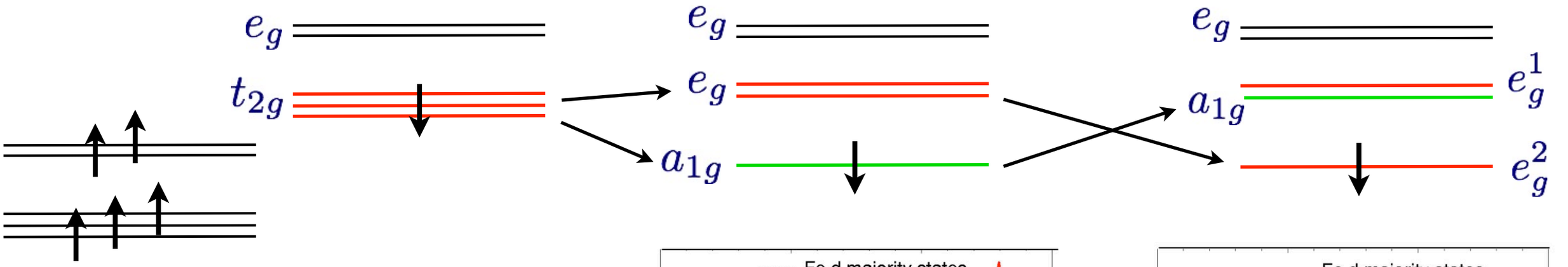
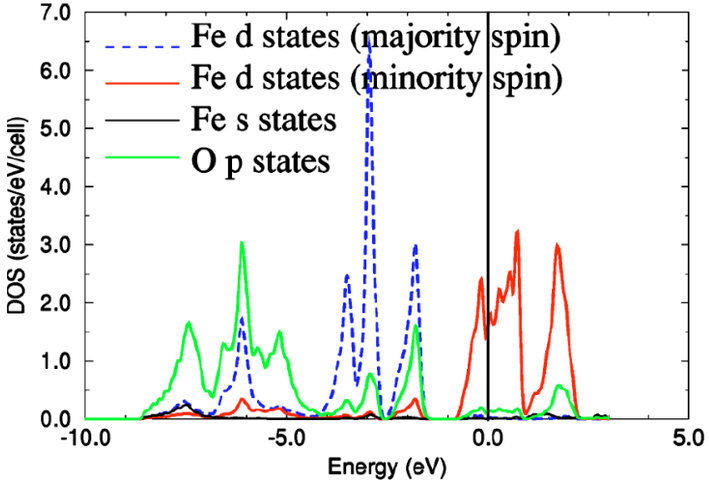
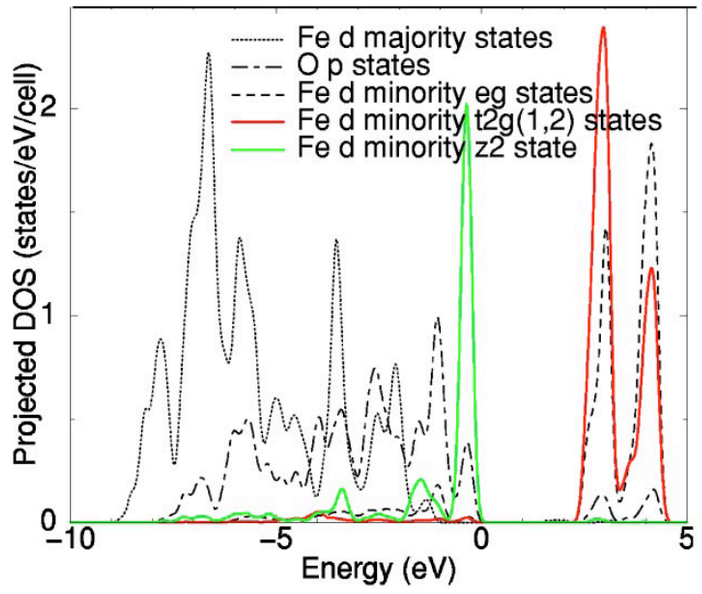
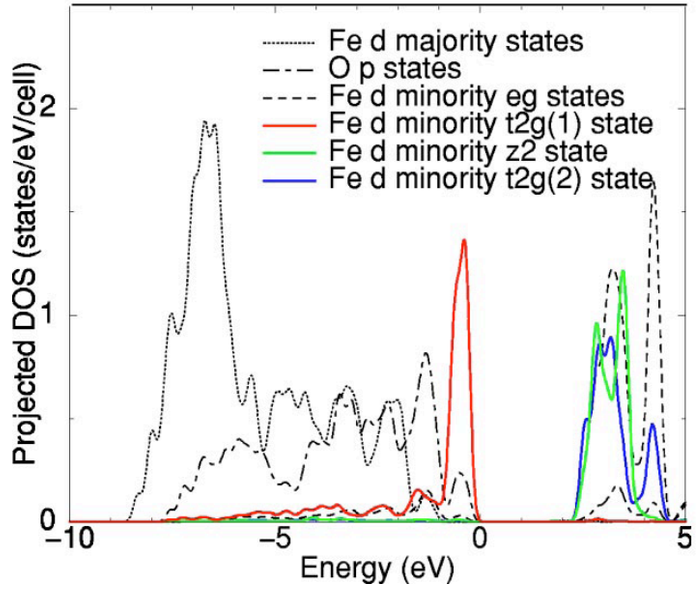




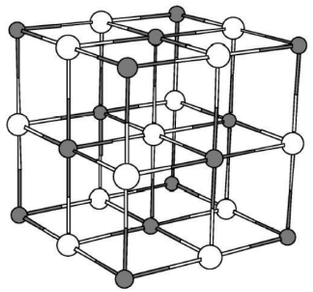




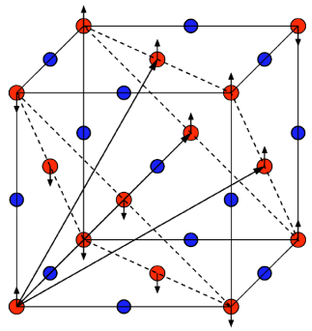


FeO: breaking the symmetry

Cubic



Rhombohedral



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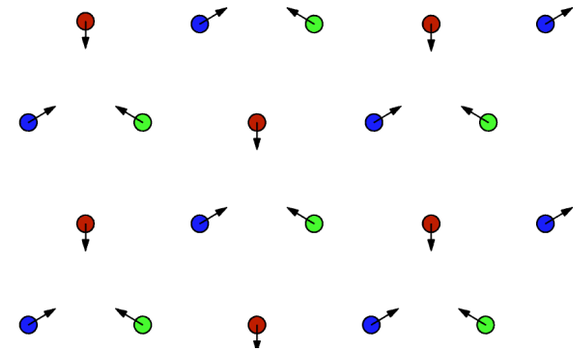
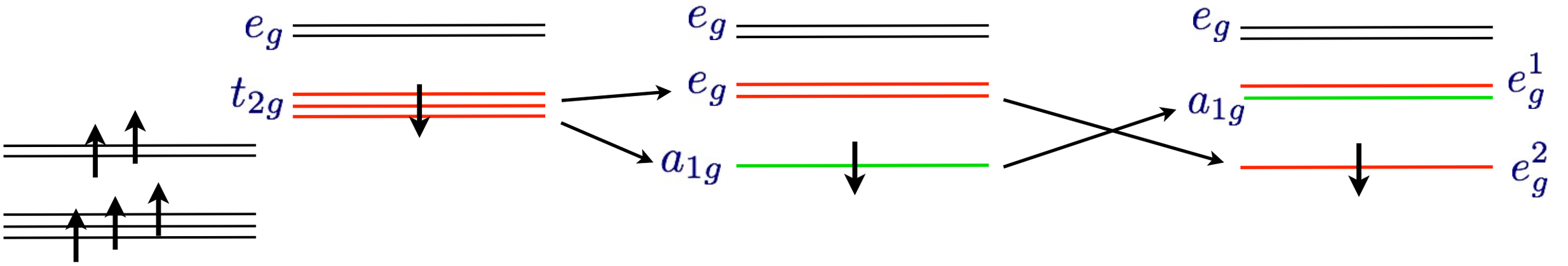
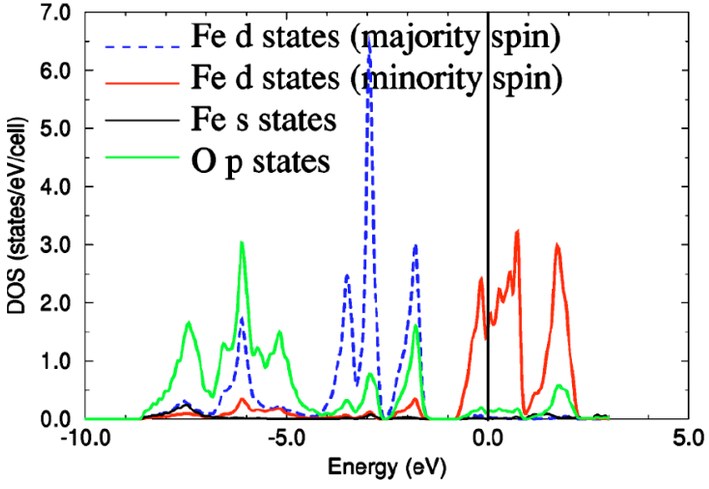
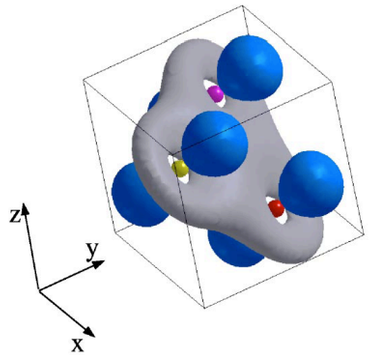


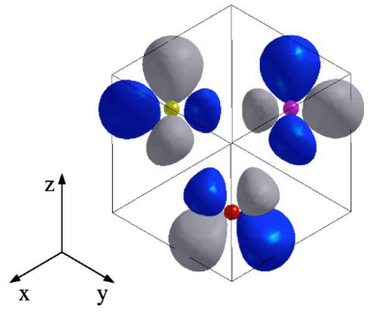




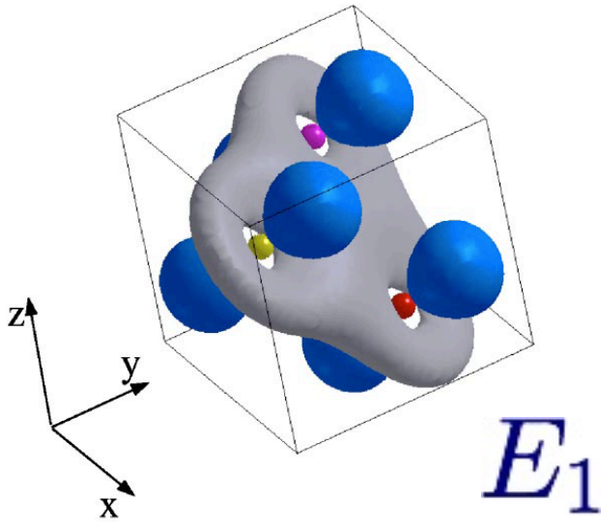
a_{1g}



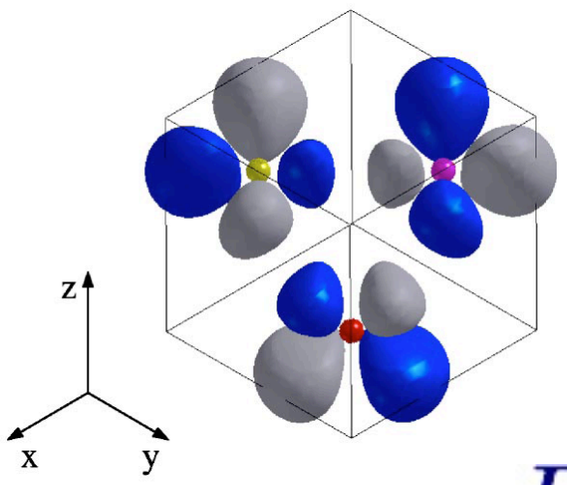
e_g^2



FeO: which insulating state?



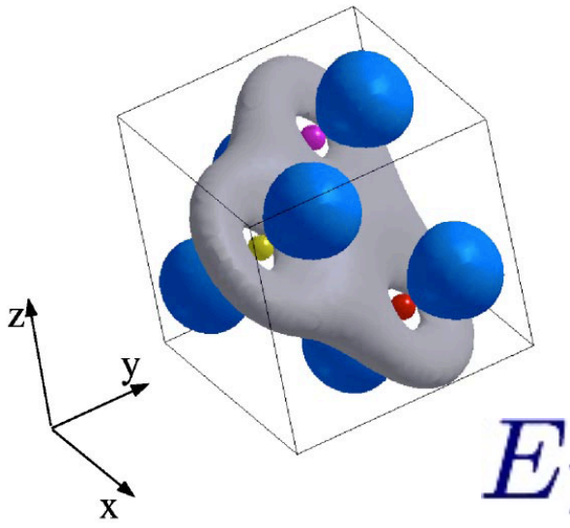
E_1



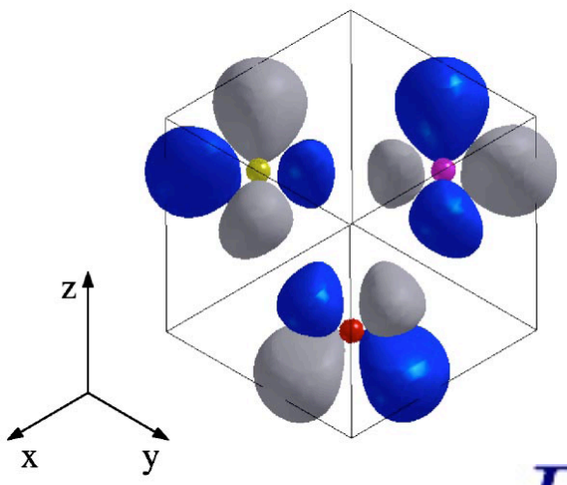
E_2

FeO: which insulating state?

Total energy: $E_1 > E_2$



E_1



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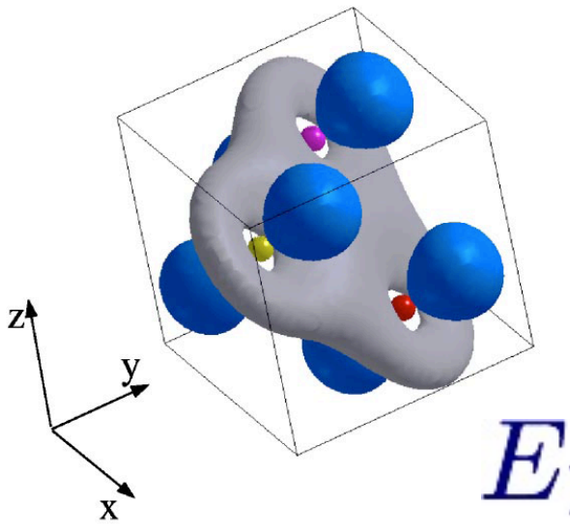

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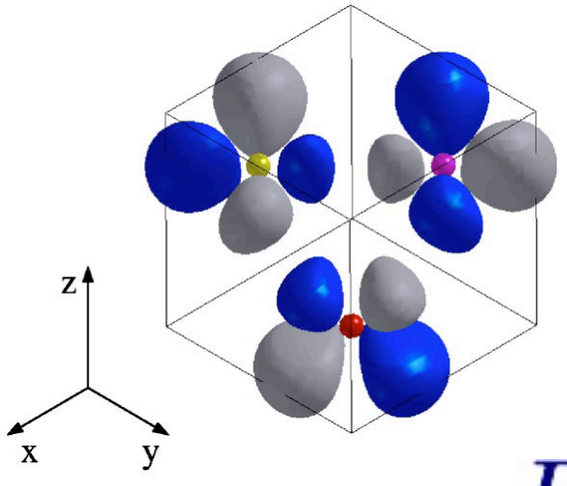

E_2

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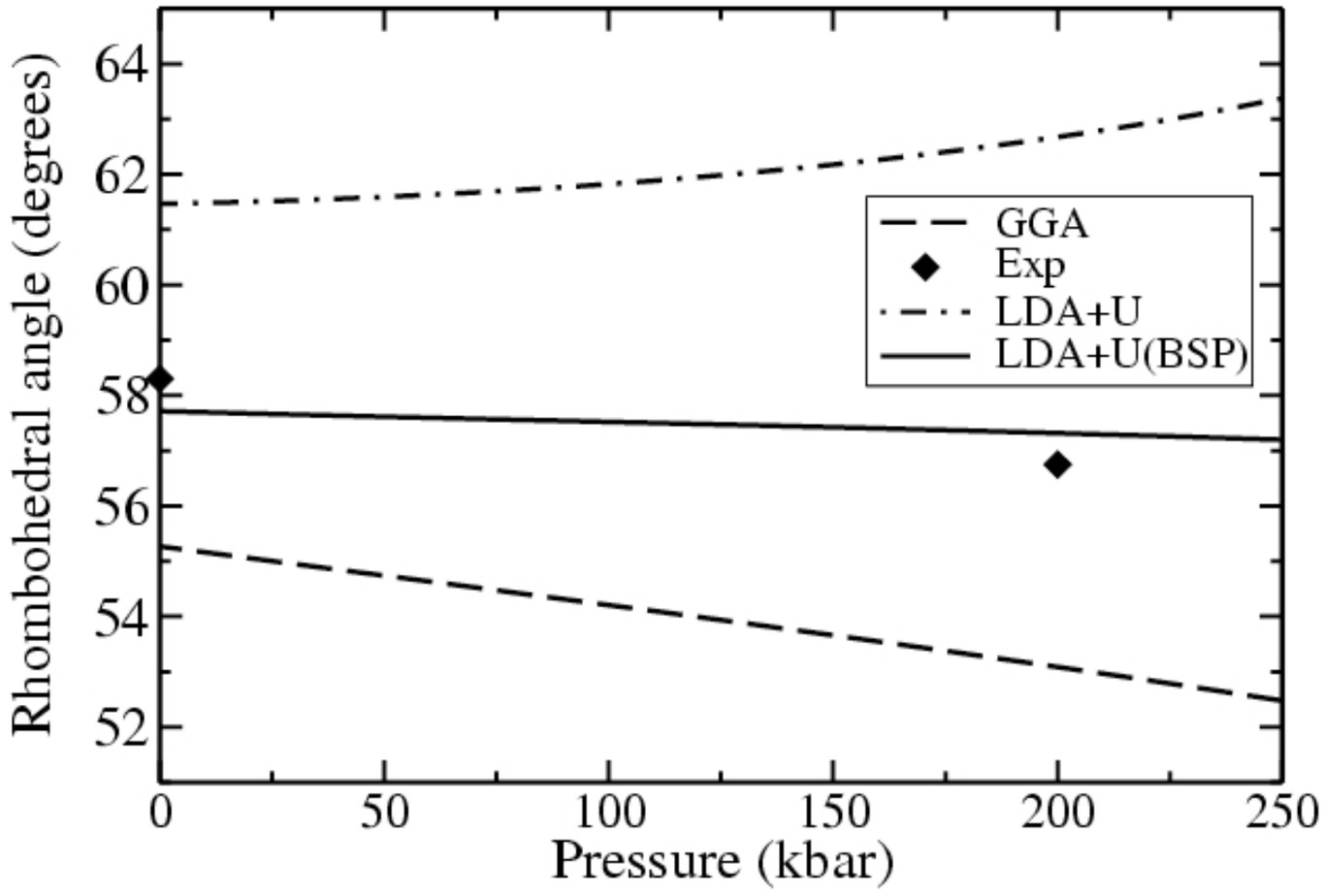
Structural distortion under pressure



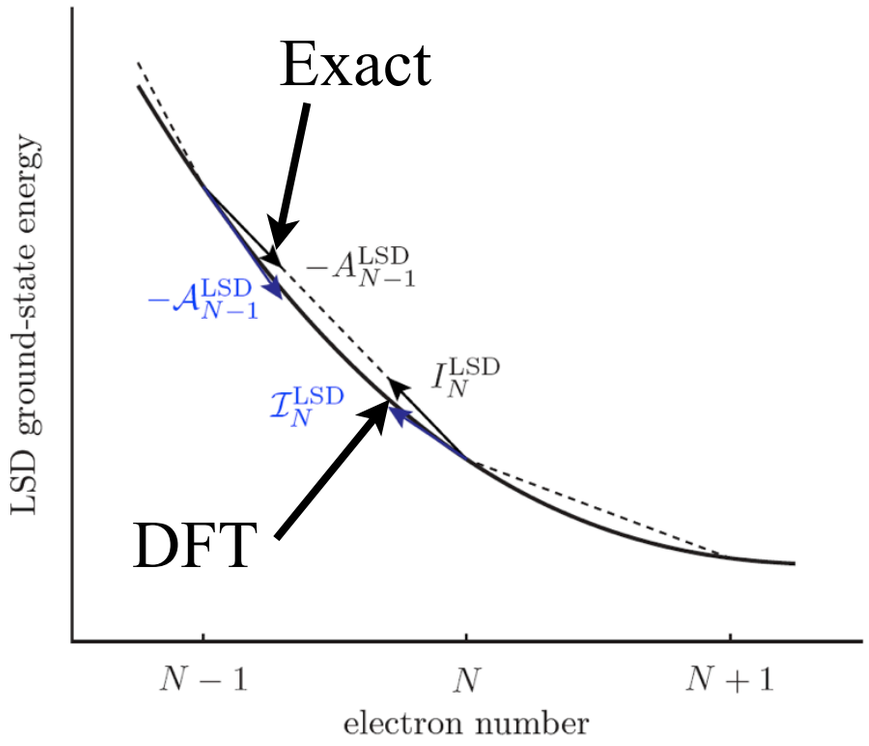
M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

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
- Linearization of the total energy wrt n



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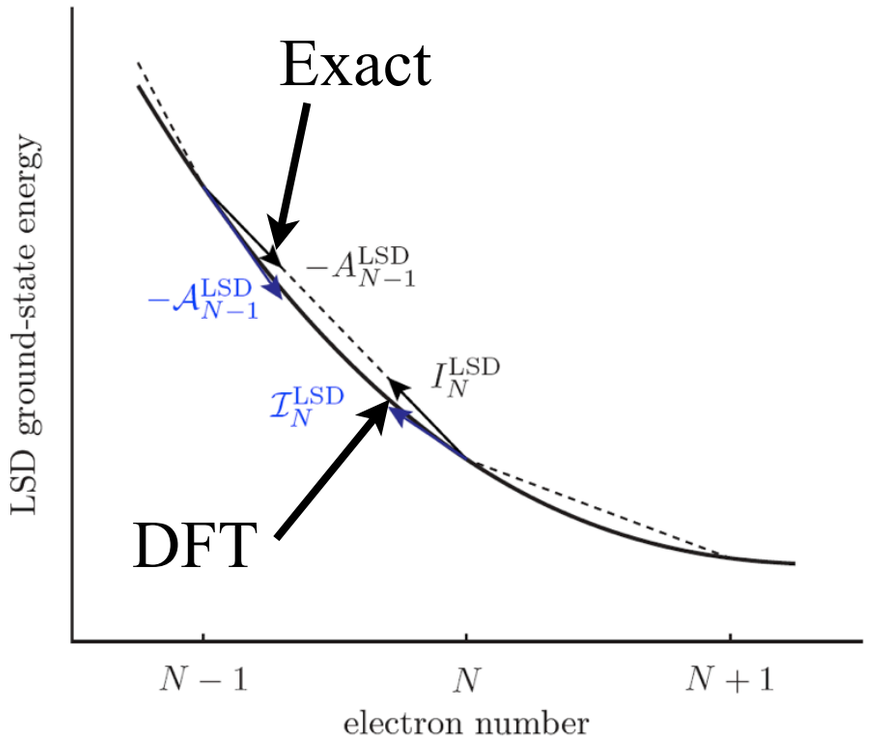


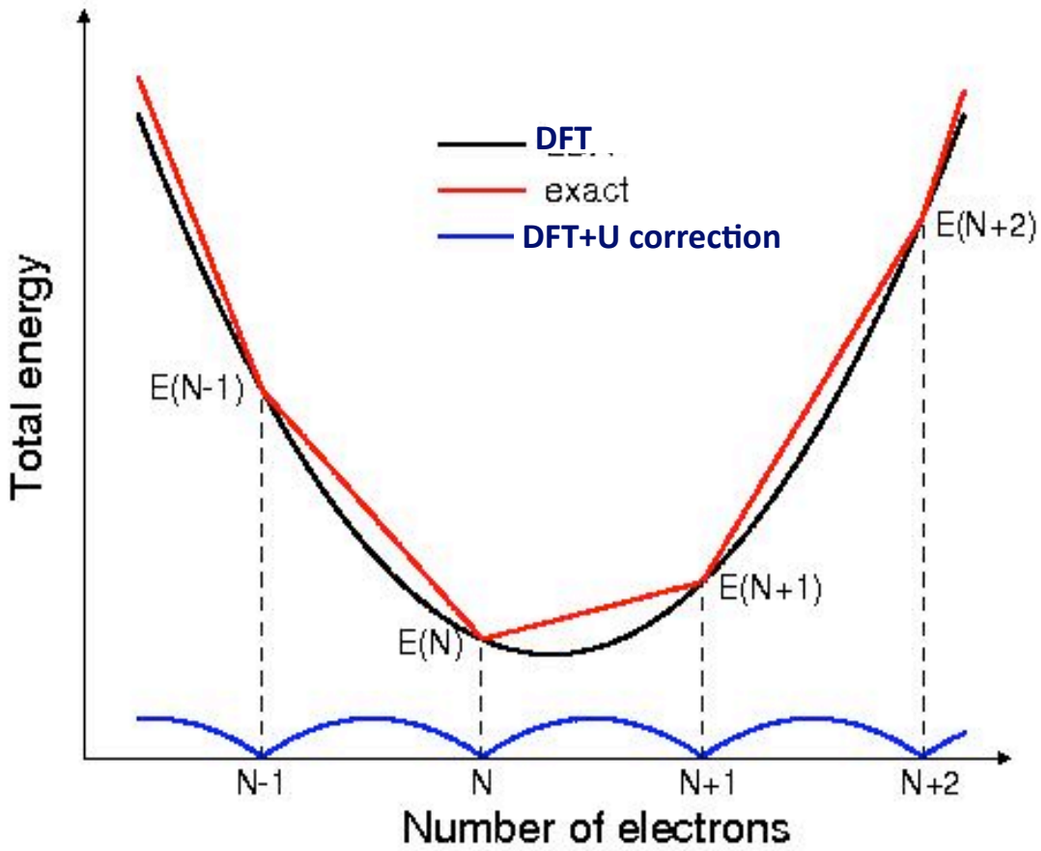
Open system in contact with a charge reservoir:

- 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 meaning of U in DFT+U

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



<u>The (approximate) DFT energy</u> has an *unphysical curvature*

<u>The exact solution</u> *is piecewise linear*

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

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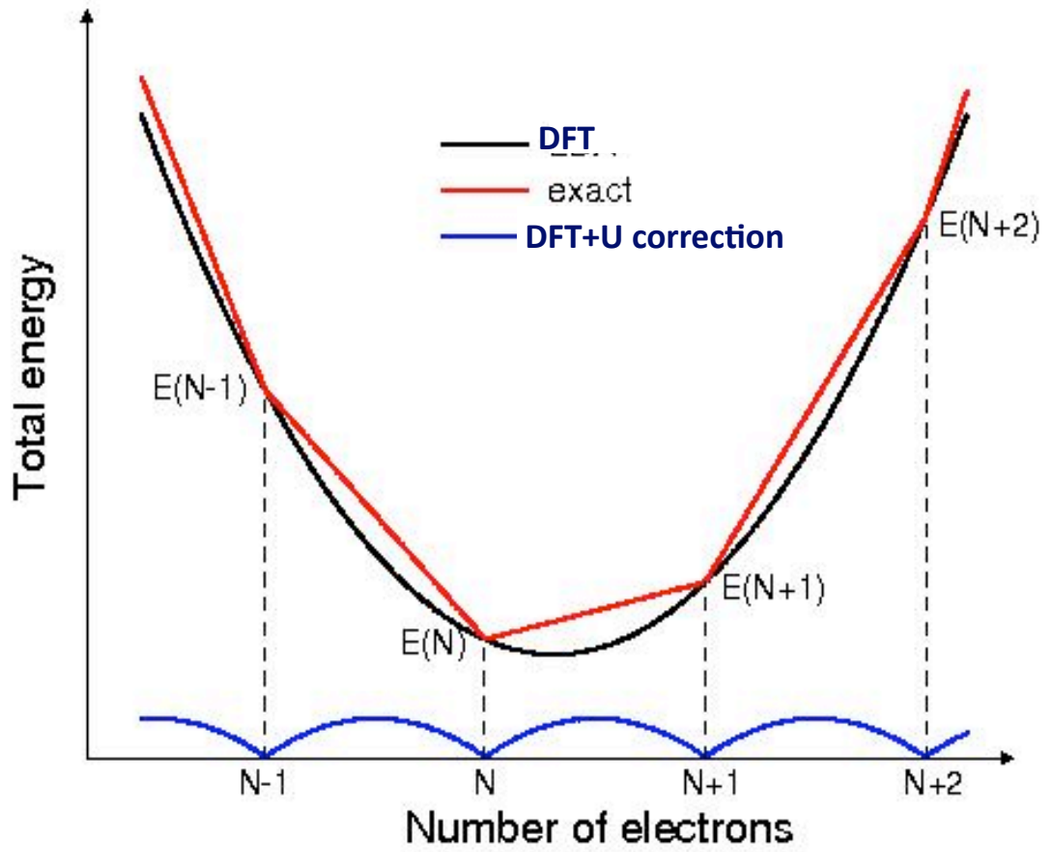

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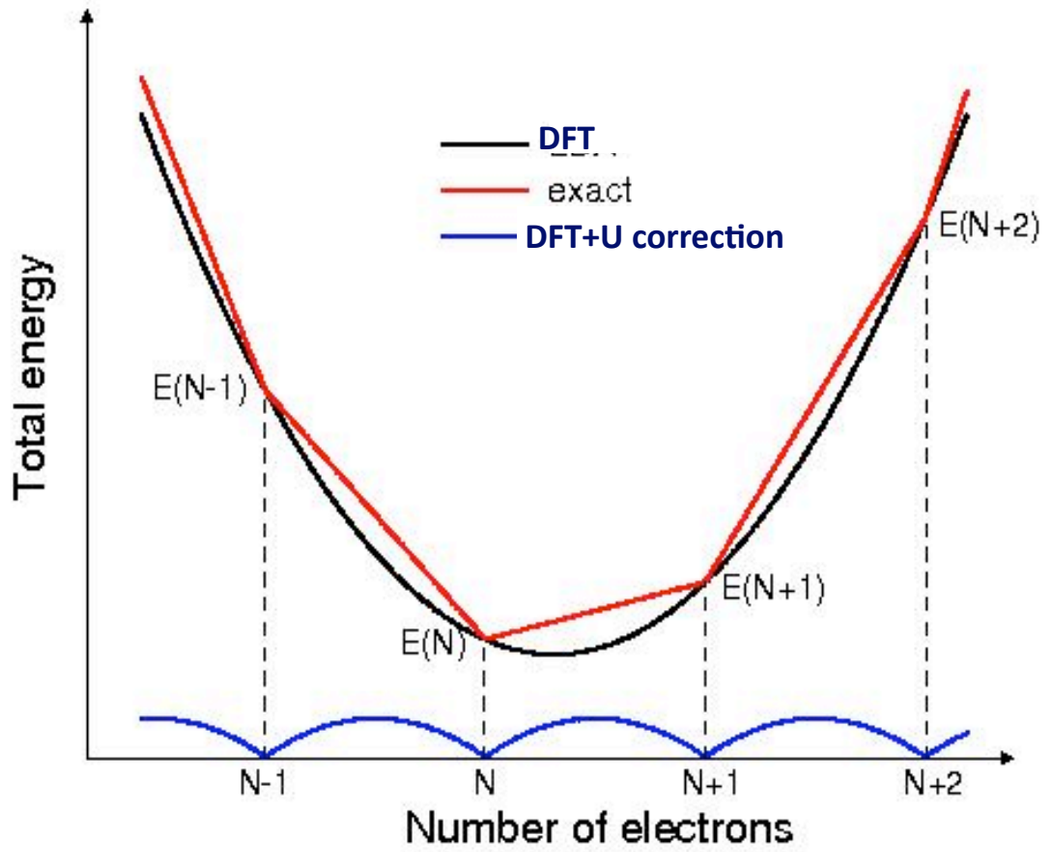

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LRT U: M. Cococcioni PhD (2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)

Computing U

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

First and second derivatives can then be easily obtained as:

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

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

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

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

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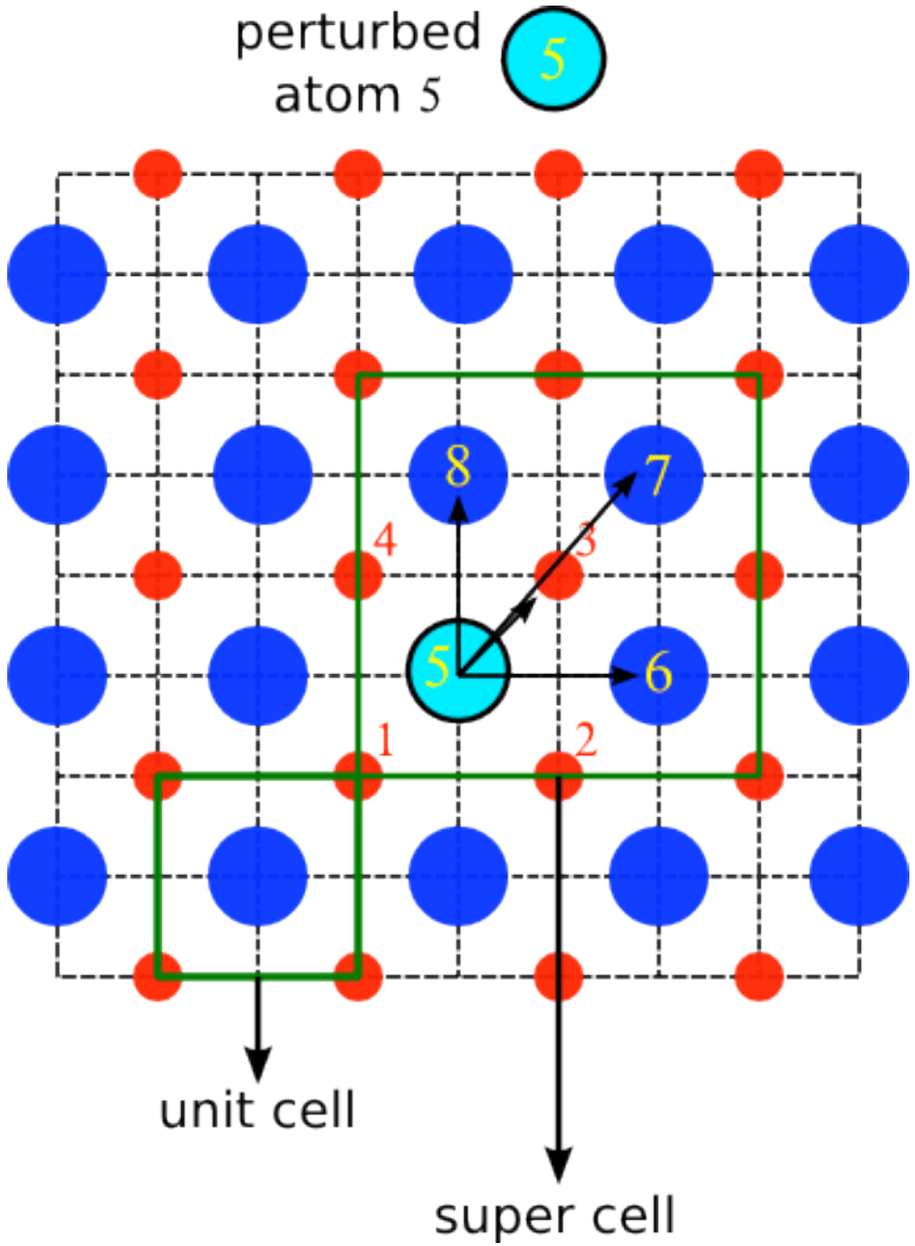
Effective interactions:

$$U^{I} = \left(\chi_{0}^{-1} - \chi^{-1}\right)_{II}$$

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

Some technical details

- The perturbation is applied in a supercell to assure it is isolated from its periodic replica
- The value of U should be converged with the size of the supercell
- The perturbation is applied on all the non-equivalent “Hubbard atoms”
- Often also non-Hubbard atoms and states are perturbed to evaluate the response of the “crystal bath” (charge reservoir)



Expression of U

B. Himmetoglu, A. Floris, S. de Gironcoli, M. Cococcioni, Int. J. Quant. Chem. 2014

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Let's use a more general perturbing potential (*i* runs over all atomic states):

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

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

B. Himmetoglu, A. Floris, S. de Gironcoli, M. Cococcioni, Int. J. Quant. Chem. 2014

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

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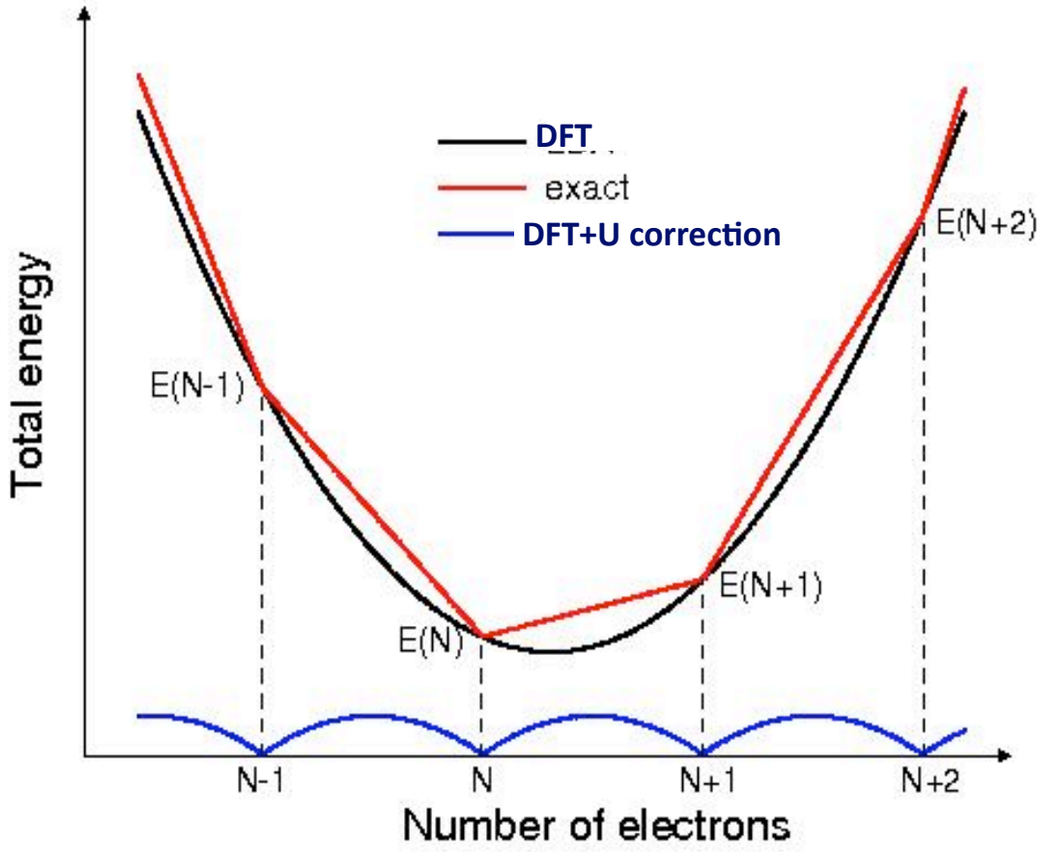

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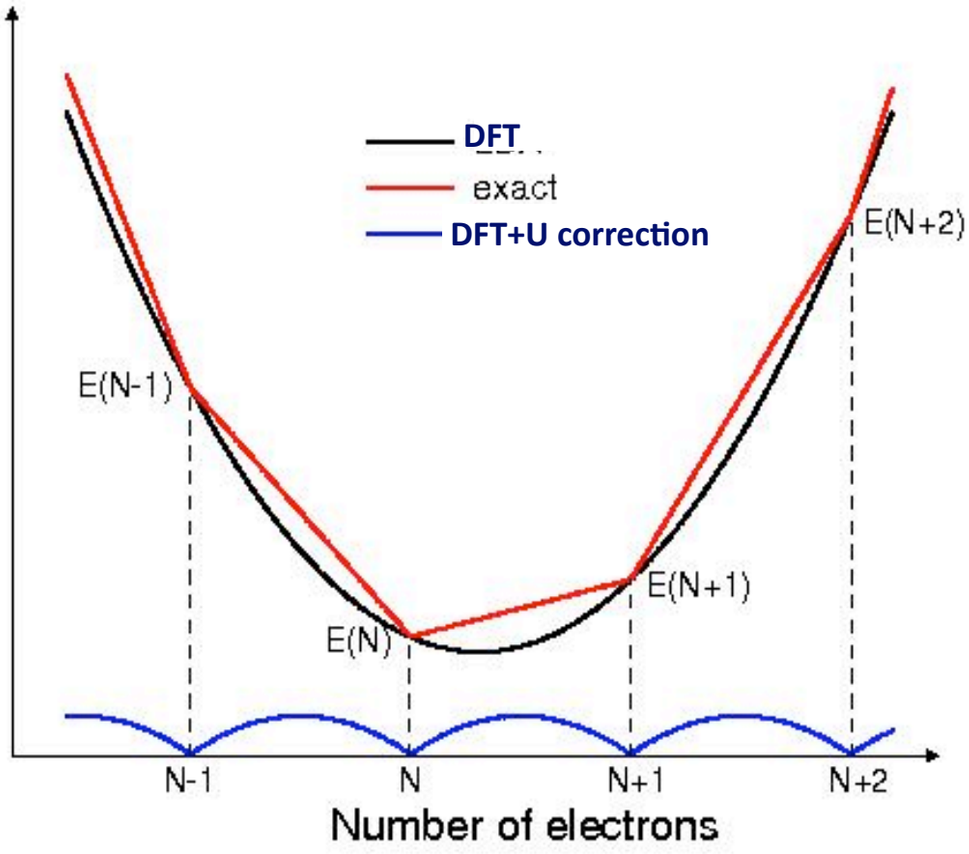

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- The "+U" correction aims at eliminating this curvature

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

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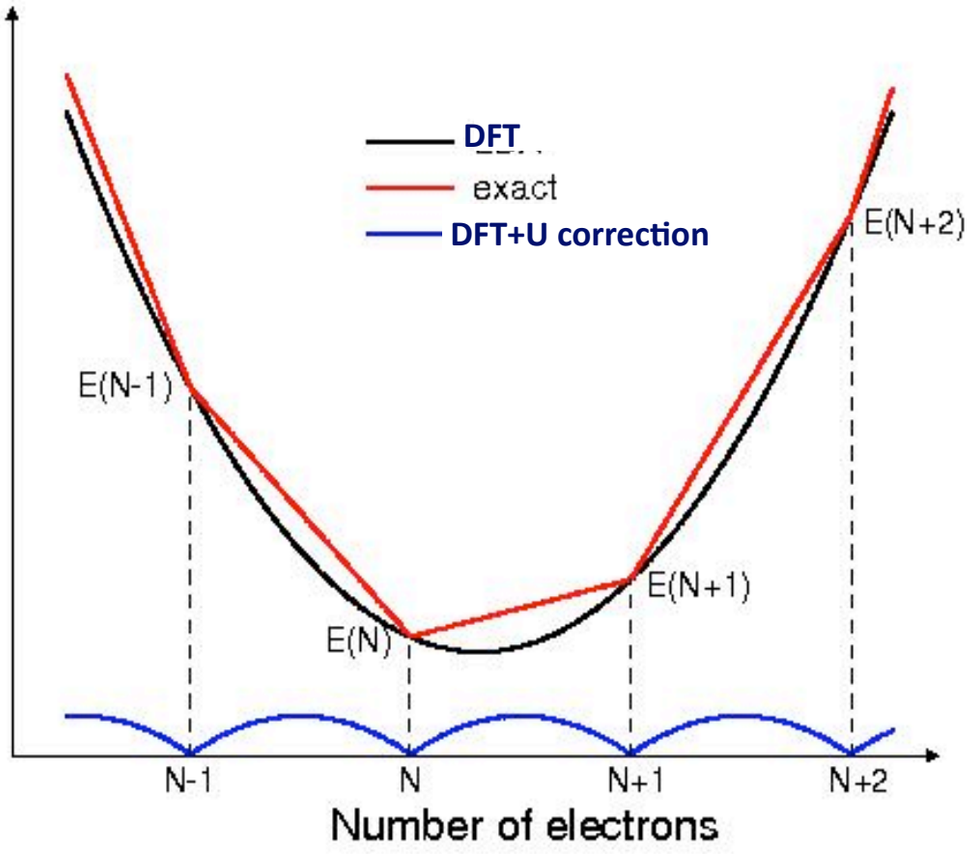

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- U can be evaluate (from linear response theory) as the effective curvature of the energy:

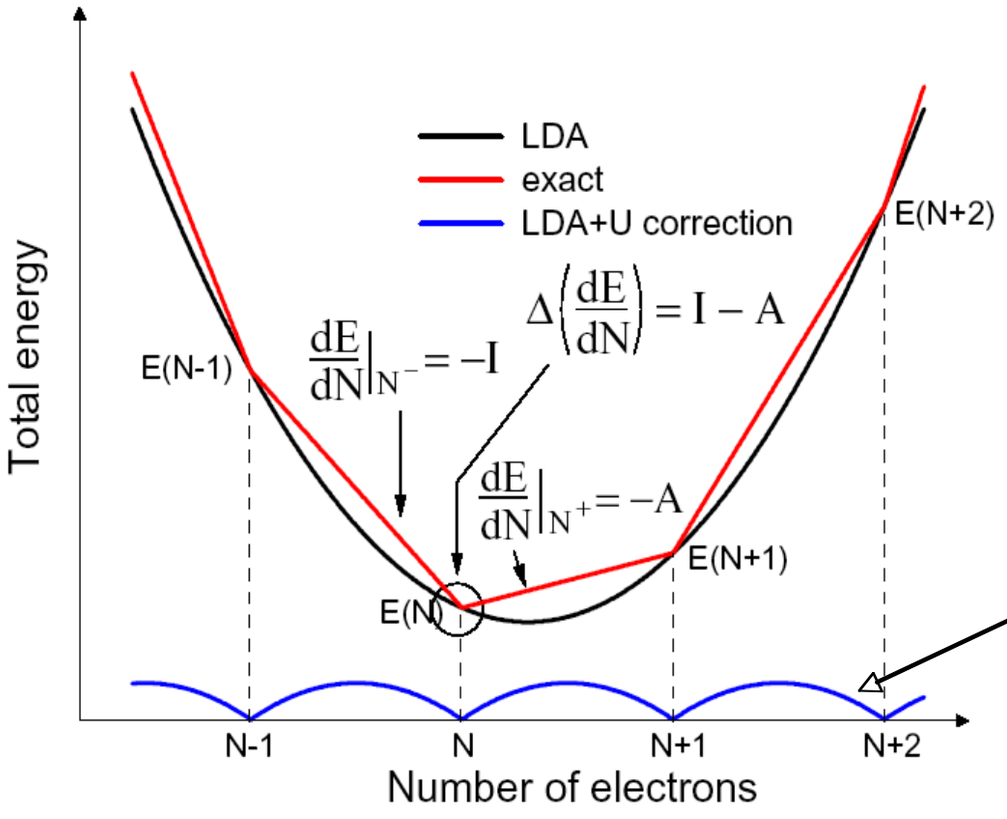
$$U^I = \left(\chi_0^{-1} - \chi^{-1}\right)_{II}$$

End of the introductive part

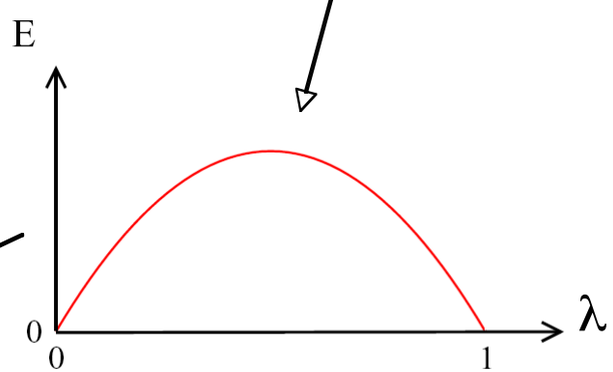
Questions?

The fundamental gap problem

The fundamental gap problem



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



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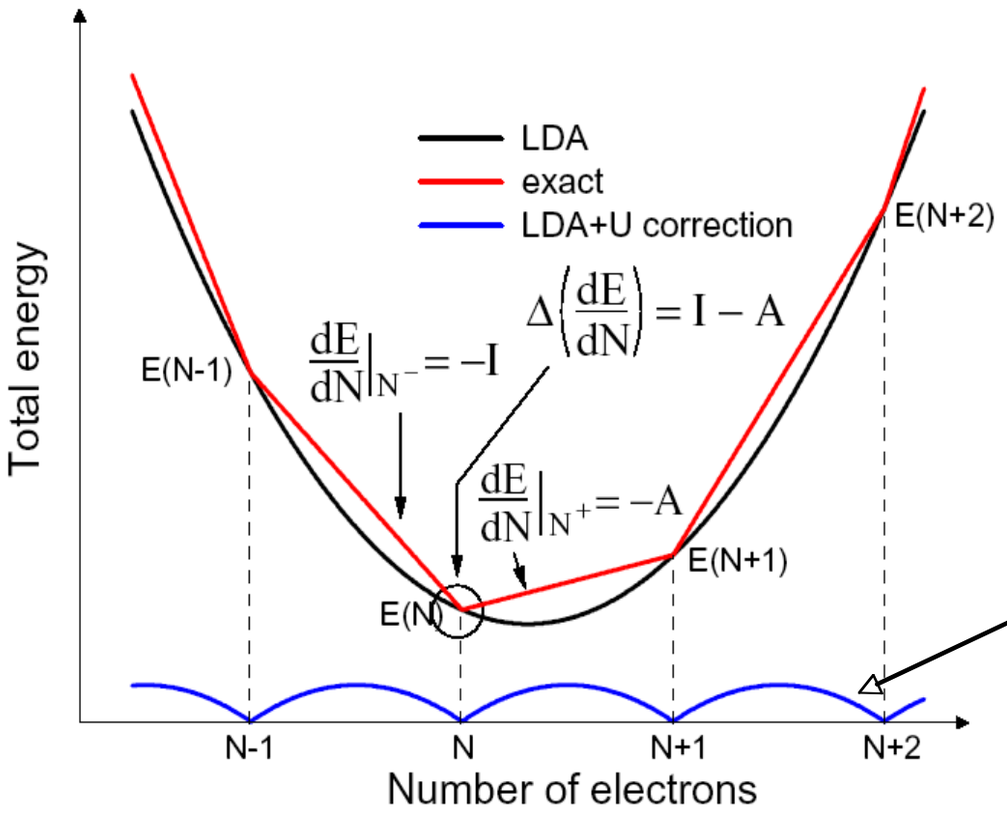

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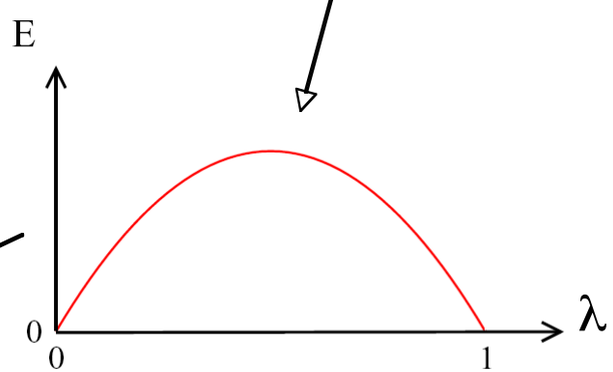

If computed as the second derivative of the energy, *U* re-establishes energy discontinuities: the **fundamental band gap:**

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

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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***

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DFT+U energy functional

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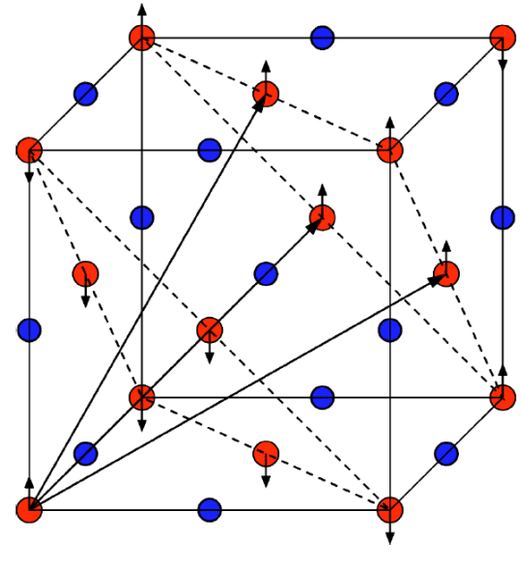
V. L. Campo Jr and M. Cococcioni, J. Phys.: Condens Matter 22 055602 (2010)

NiO

Typical TMO:

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



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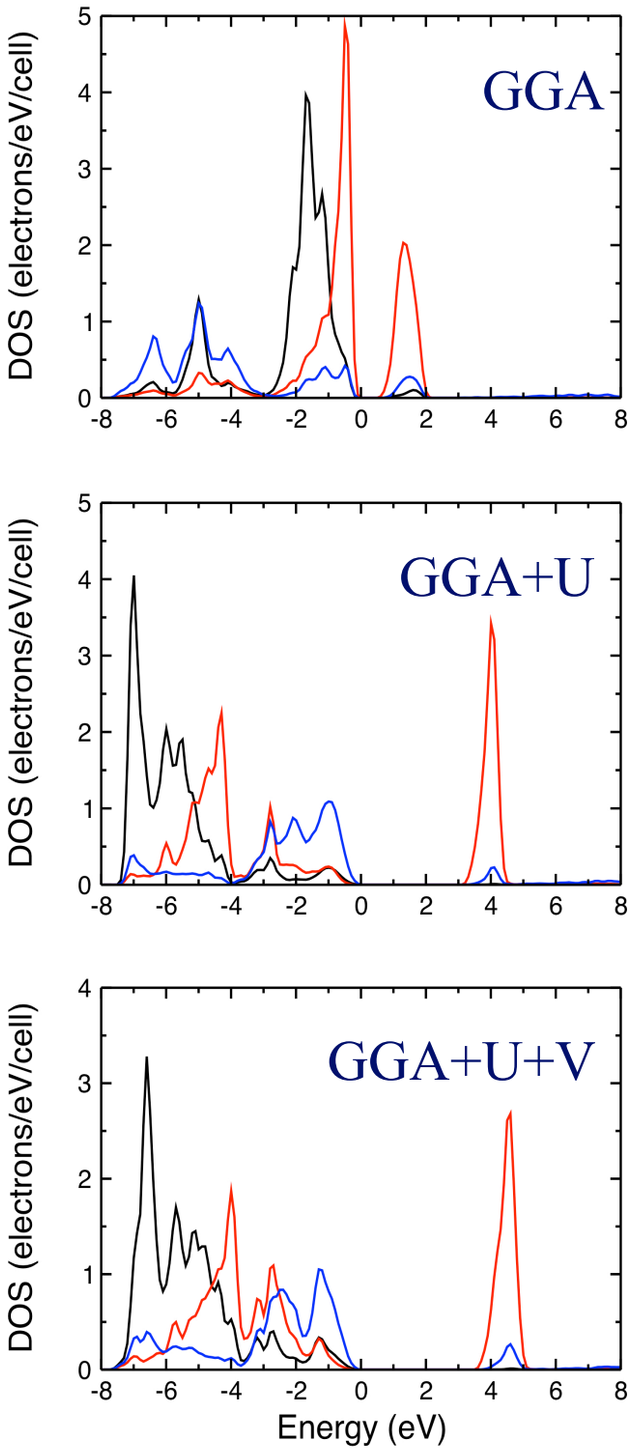

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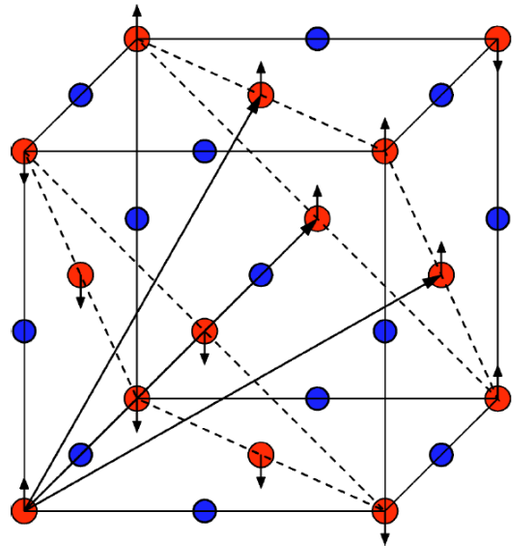

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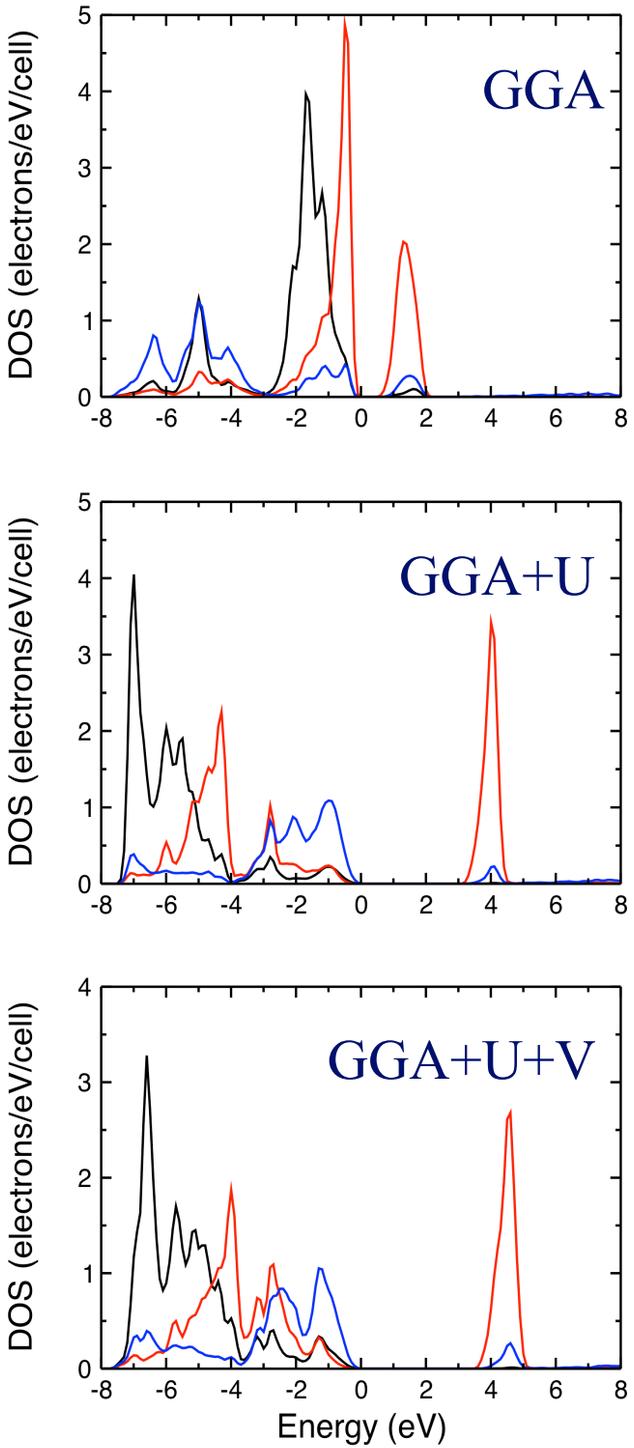

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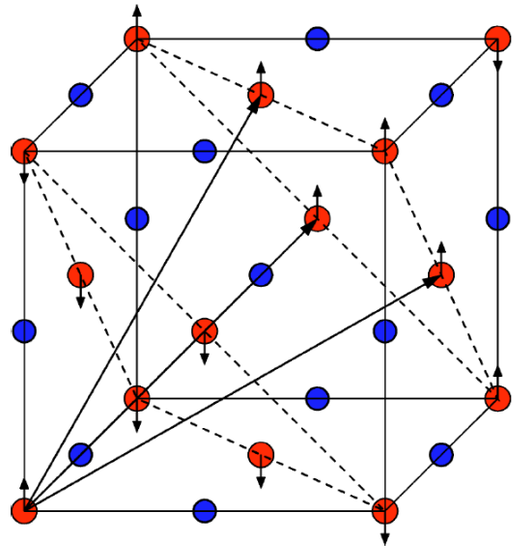

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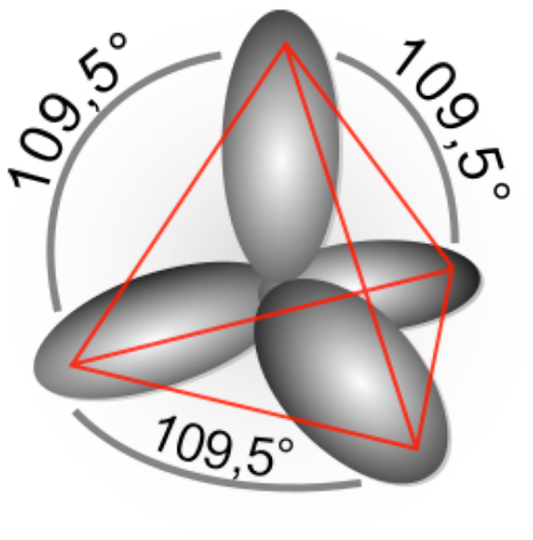
Band semiconductors: sp^3 hybridization



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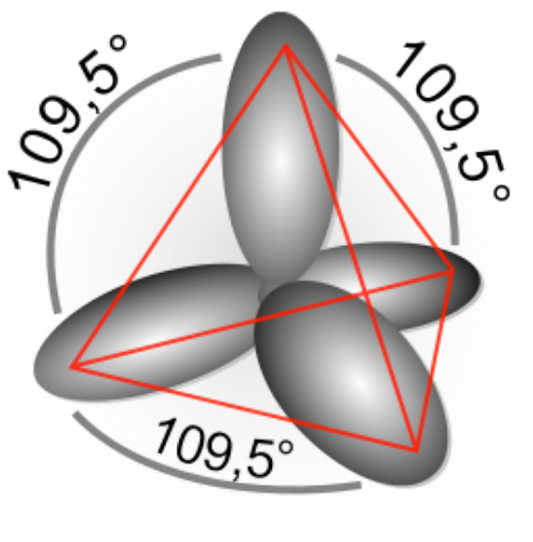

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Si-Si	2.82	3.18	3.18	3.65	1.34	1.36	1.36	1.40
Ga-Ga	3.14	3.56	3.56	4.17				
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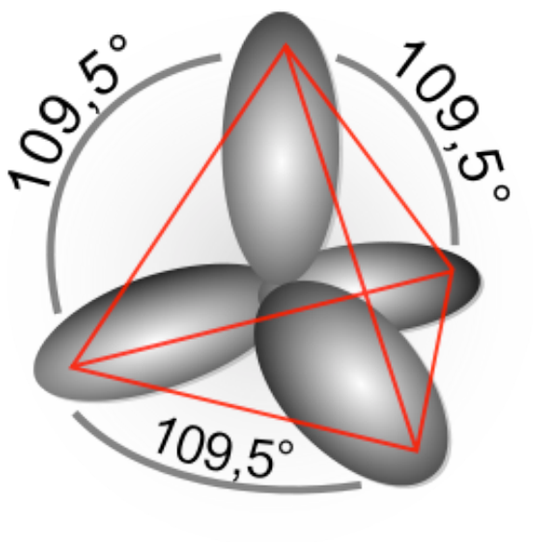

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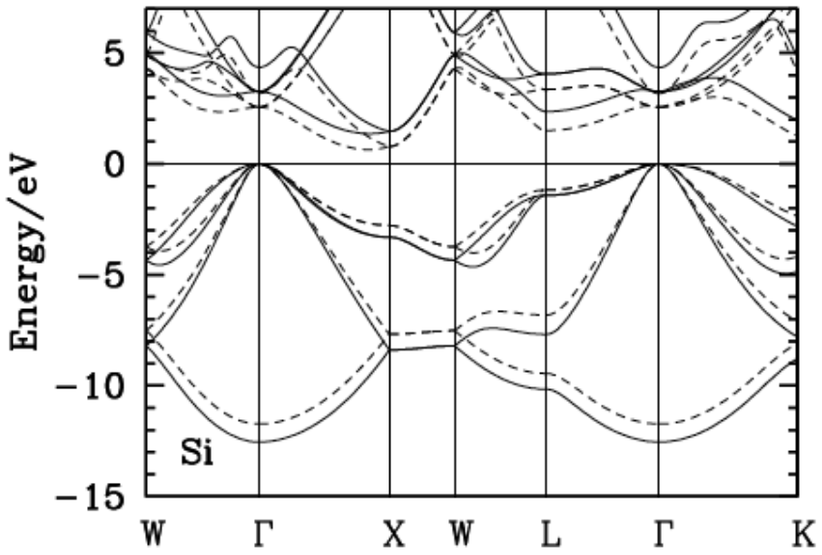
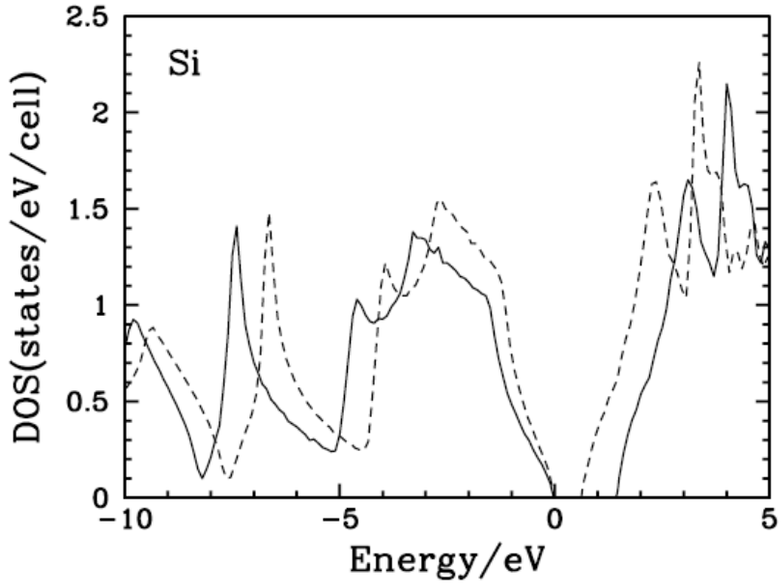
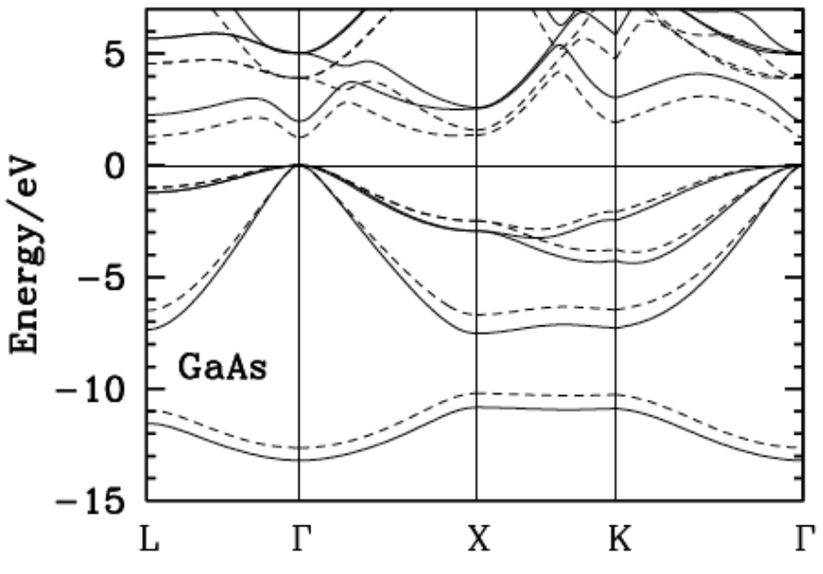
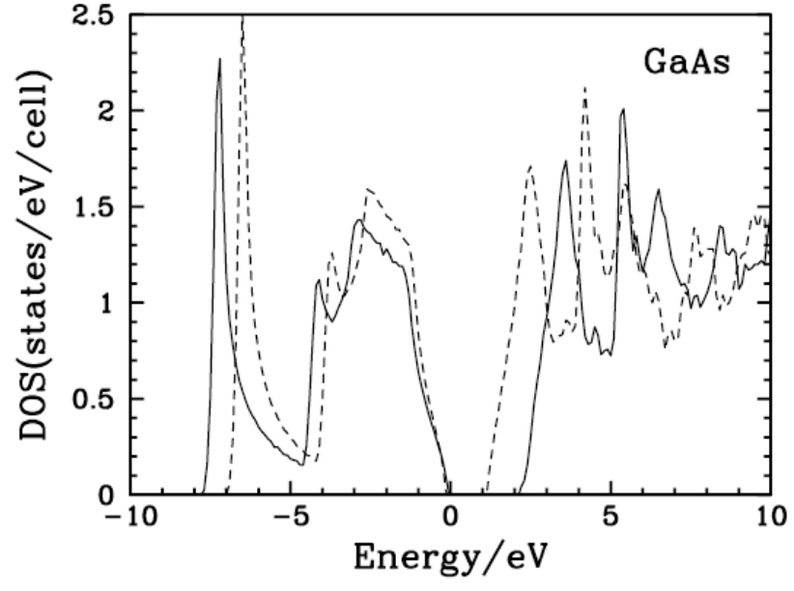








V. L. Campo Jr and M. Cococcioni, J. Phys.: Condens Matter 22 055602 (2010)

Structural properties of Si and GaAs

	Si			GaAs		
	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
GGA+U+V	5.37	102.5	1.36	5.65	67.5	0.90
Exp*	5.43	98.0	1.12	5.65	75.3	1.42

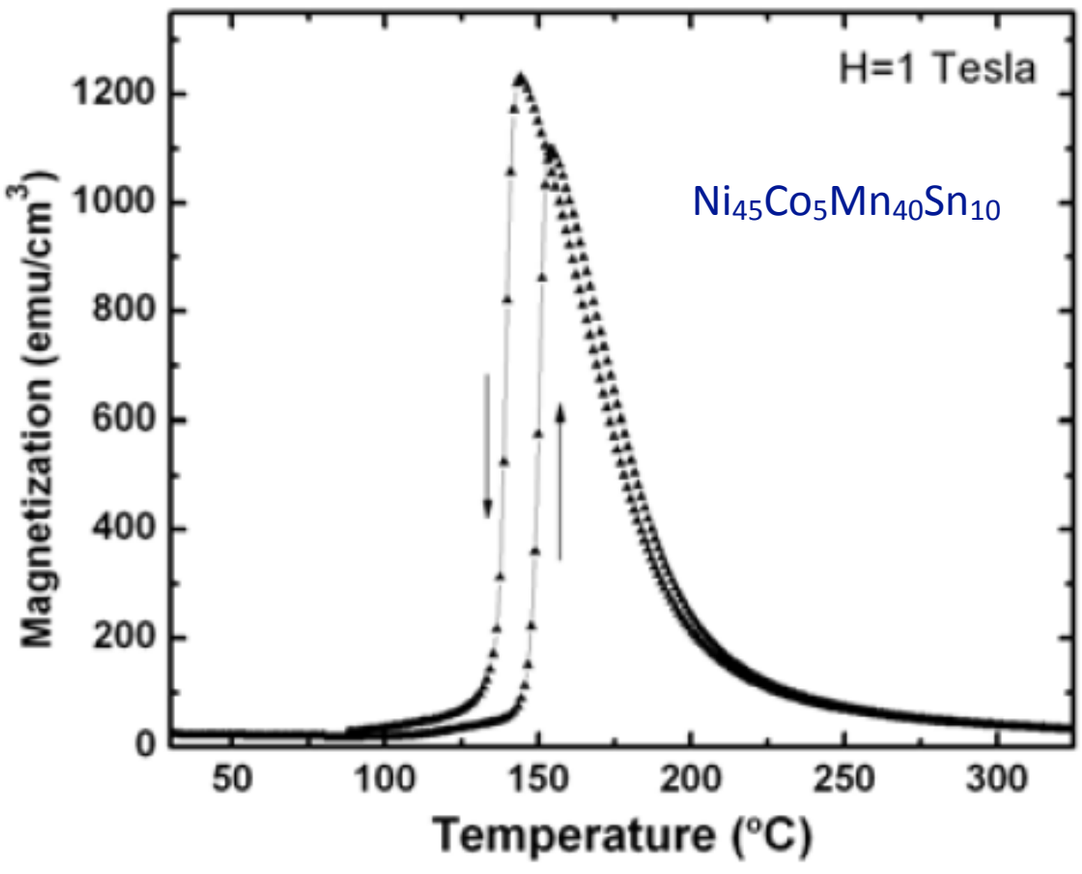
*** from http://www.ioffe.ru/SVA/NSM/Semicond/**

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

Magnetism in Ni_2MnGa

Magnetism in Ni_2MnGa

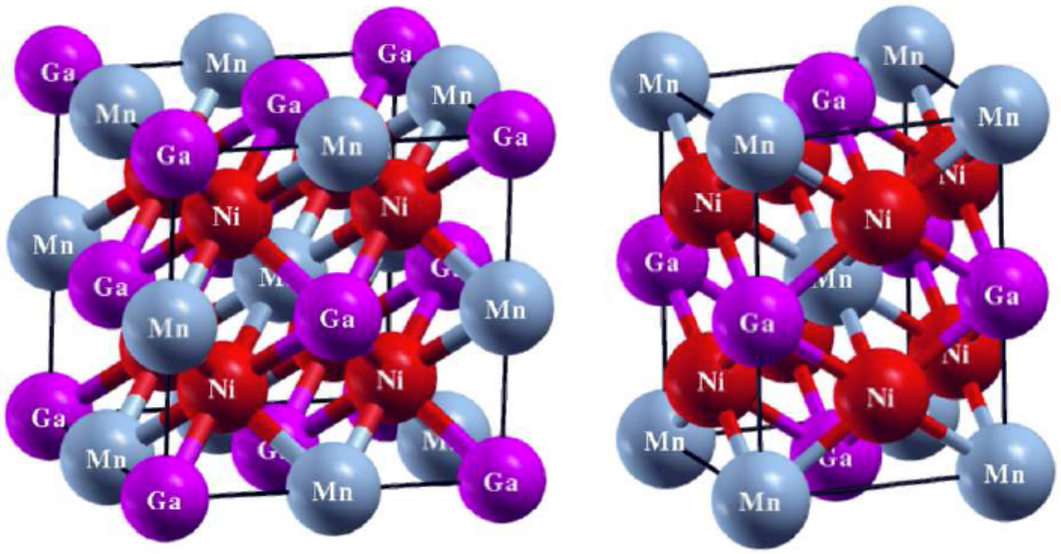
Motivation



V. Srivastava *et al.*, Adv. Energy Mater. 1, 97-104 (2011)

Magnetism in Ni_2MnGa

Ni_2MnGa



Austenite

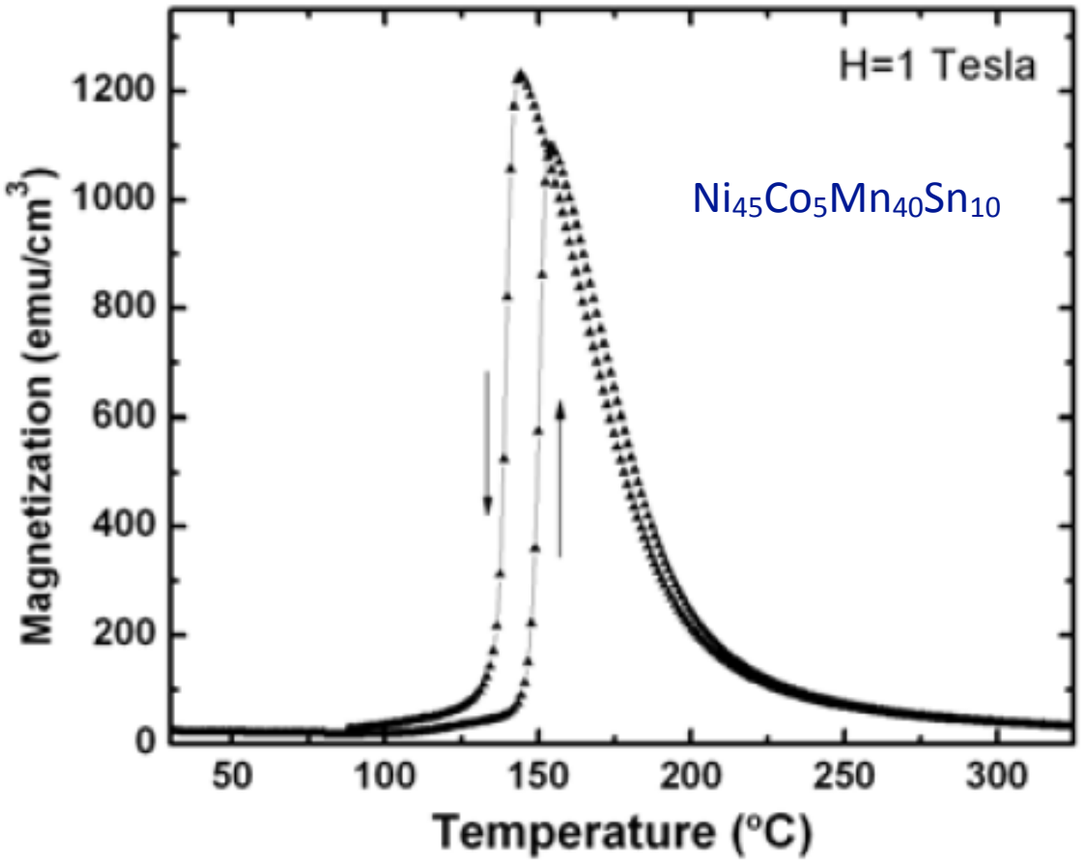
Martensite
(non modulated)

Martensitic transitions

High T: austenite cubic (FCC)

Low T: martensite (modulated tetragonal)

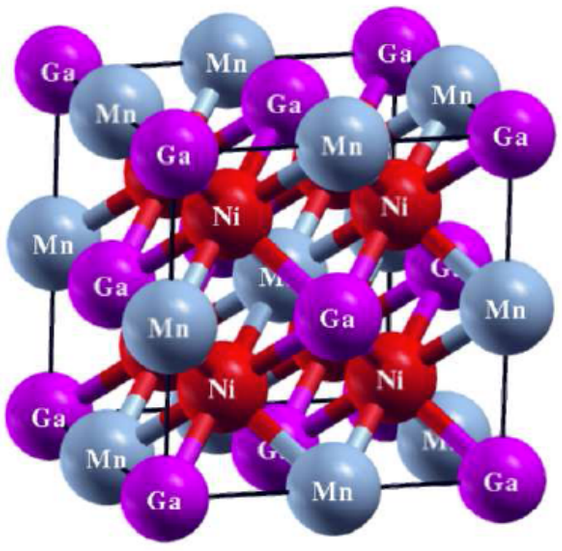
Motivation



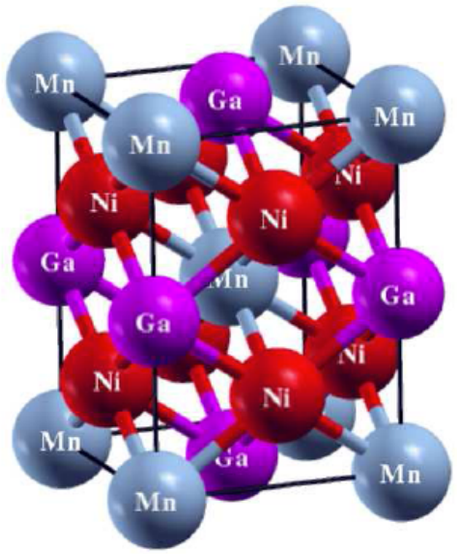
V. Srivastava *et al.*, Adv. Energy Mater. 1, 97-104 (2011)

Magnetism in Ni_2MnGa

Ni_2MnGa



Austenite



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Martensitic transitions

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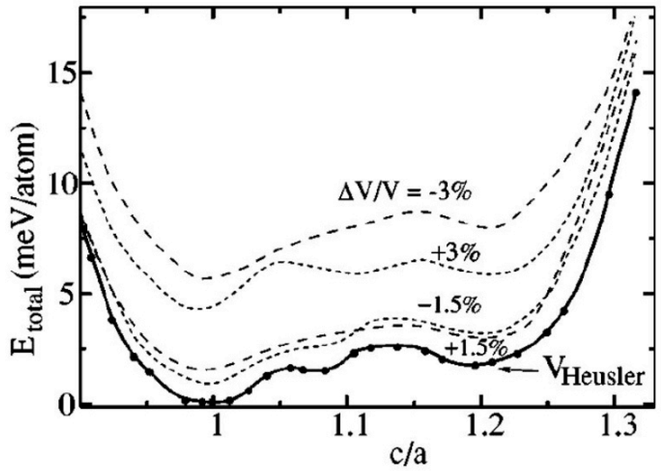
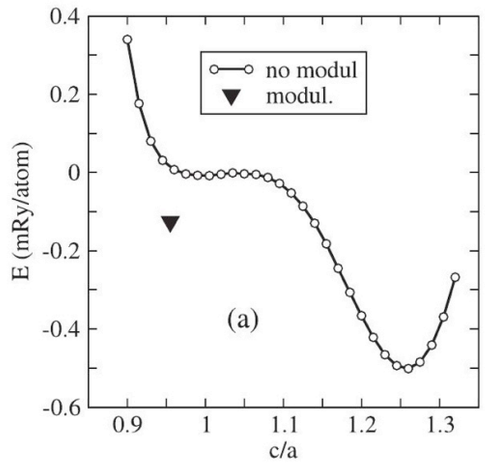
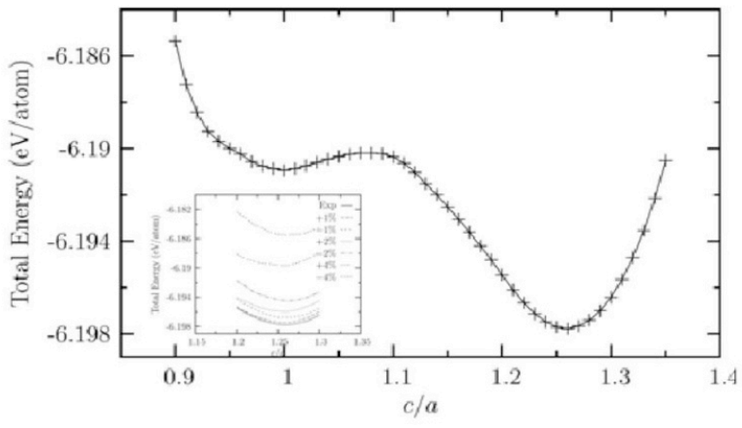
Calculations: A vs non modulated M



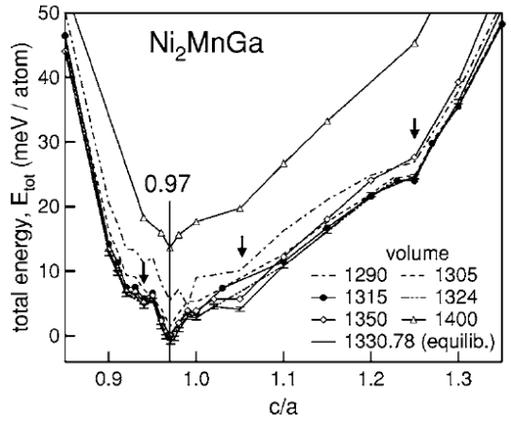
Godlevsky et. al. PRB 63, 134407 (2000)



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



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

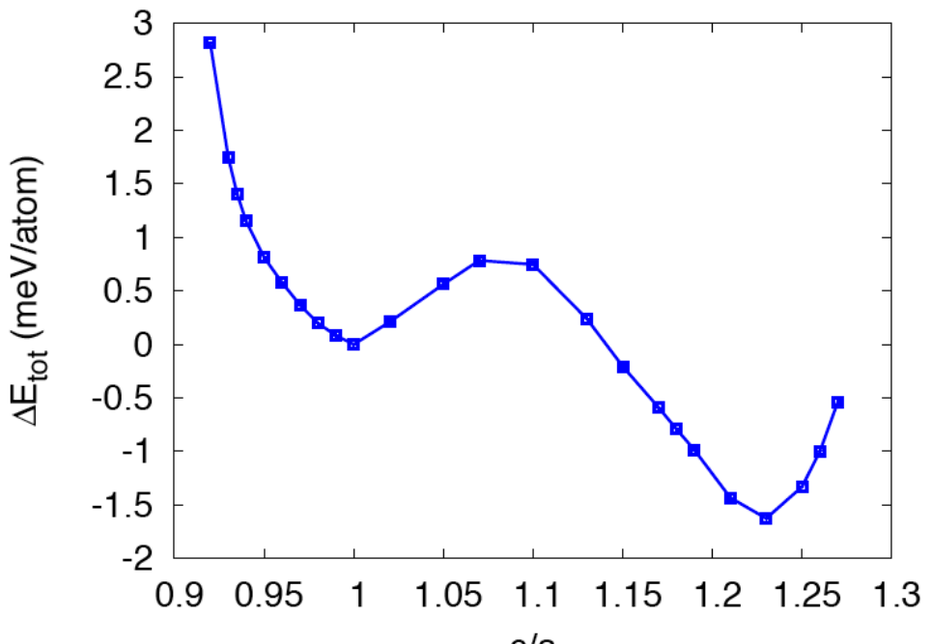


Barman *et al.*, *Phys. Rev. B* **72**, 184410 (2005)

Ni_2MnGa: localization and structural stability

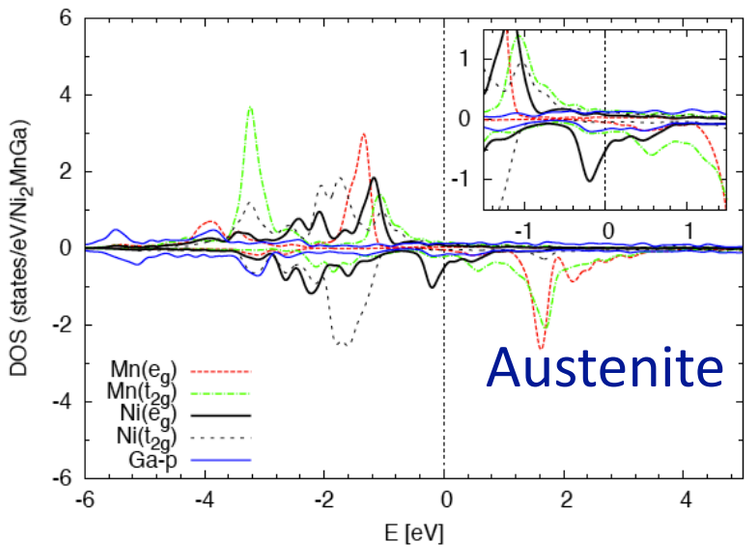
Ni_2MnGa: localization and structural stability

GGA



Mn: magnetism

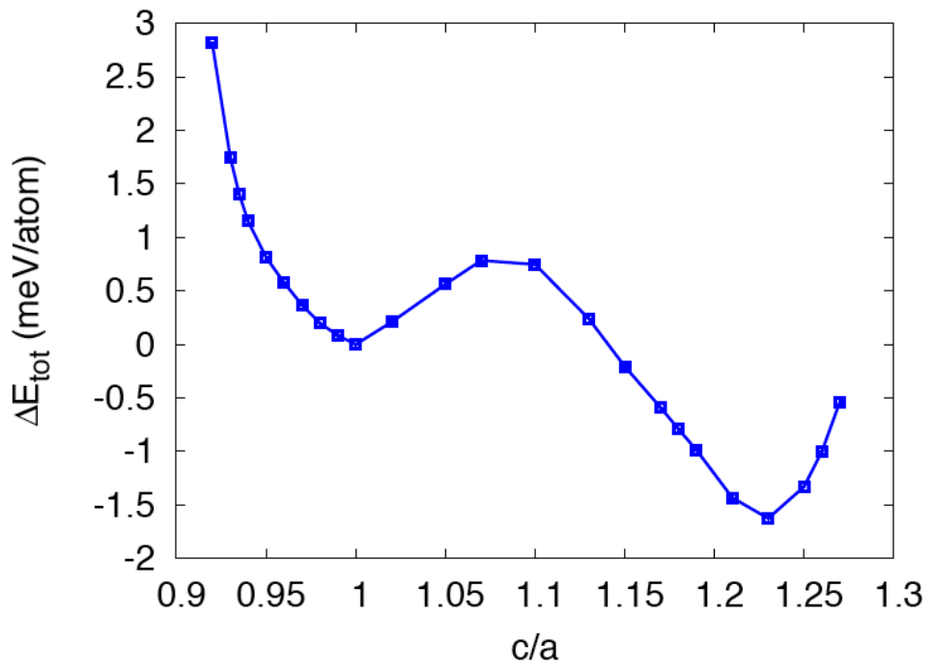
Ni: metallic character

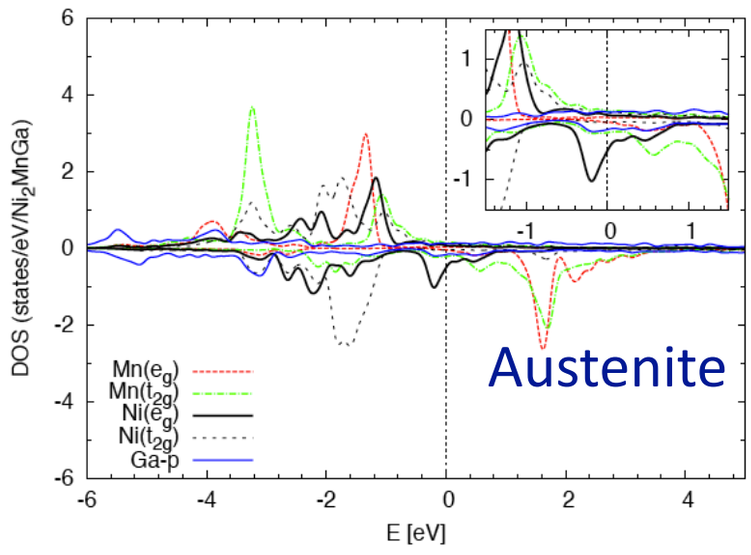


a_0 (Å)	$\mu_{\mathrm{Mn}}\,(\mu_B)$	$\mu_{\mathrm{Ni}}\,(\mu_B)$	$\mu_{\mathrm{Ga}}\,(\mu_B)$	$\mu_{\mathrm{tot}}\,(\mu_B/\mathrm{cell})$
5.83	3.67	0.34	−0.13	4.22

Ni_2MnGa: localization and structural stability

GGA





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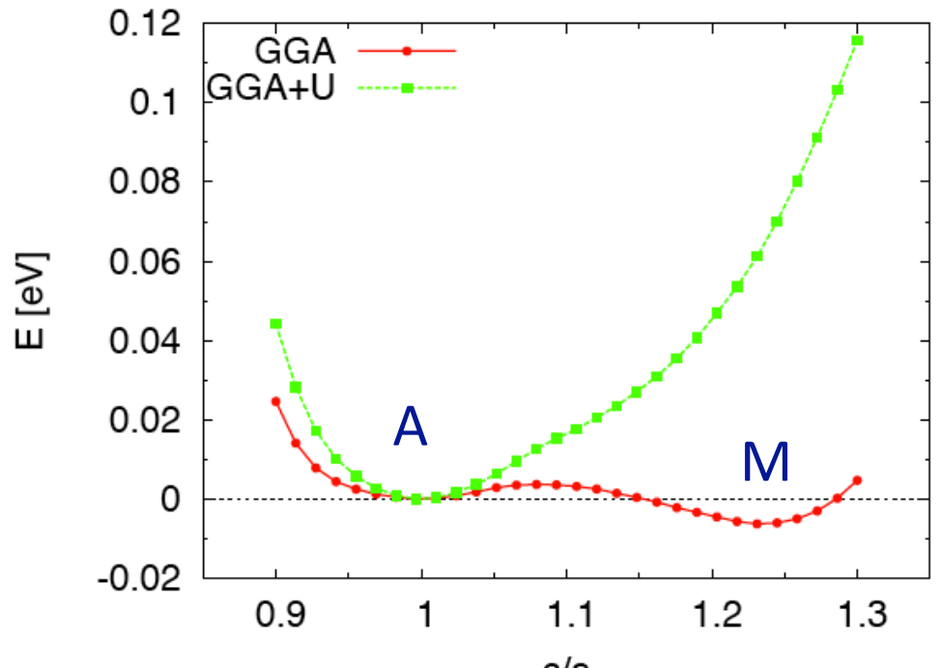
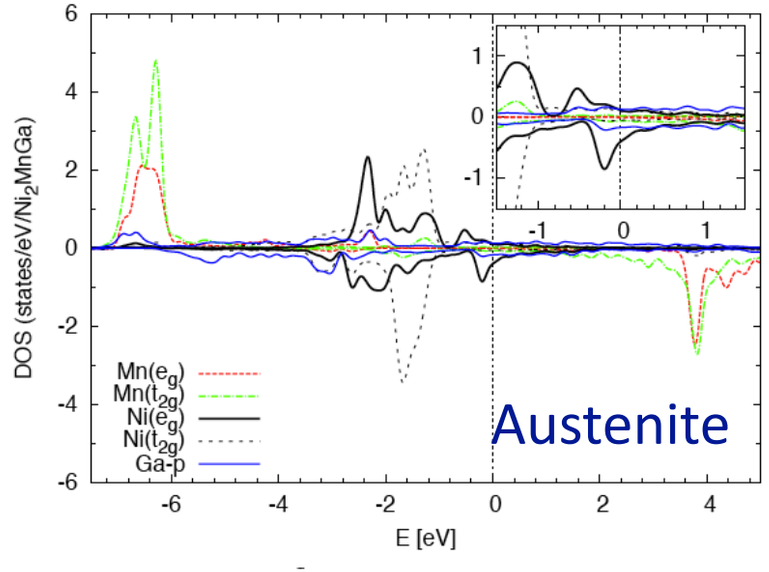
Mn: magnetism

Ni: metallic character

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

GGA+U

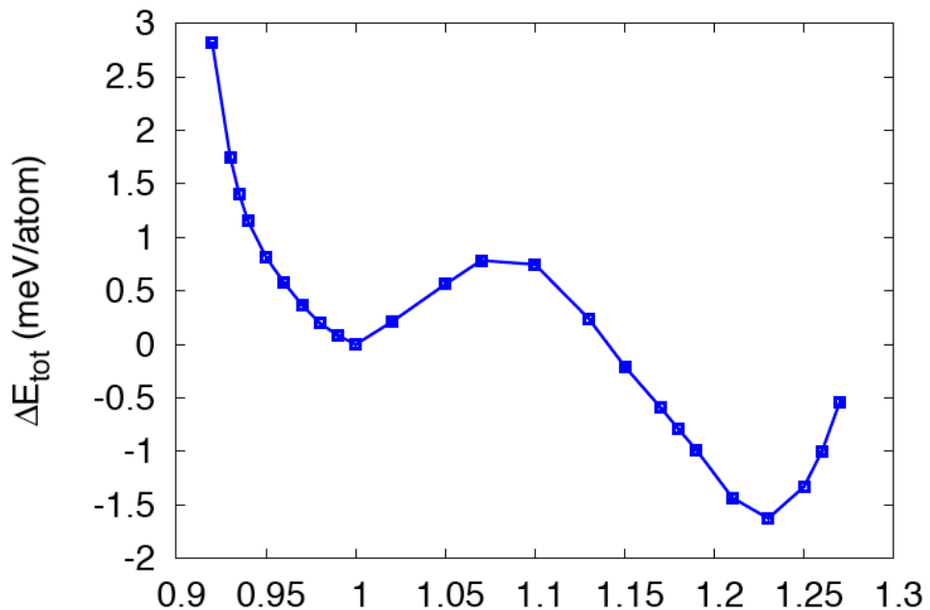




$\mu_{\mathrm{Mn}}\,(\mu_B)$	$\mu_{\mathrm{Ni}}\,(\mu_B)$	$\mu_{\mathrm{Ga}}\,(\mu_B)$	$\mu_{\mathrm{tot}}\,(\mu_B/\mathrm{cell})$
4.52	0.16	−0.13	4.80

Ni_2MnGa: localization and structural stability

GGA



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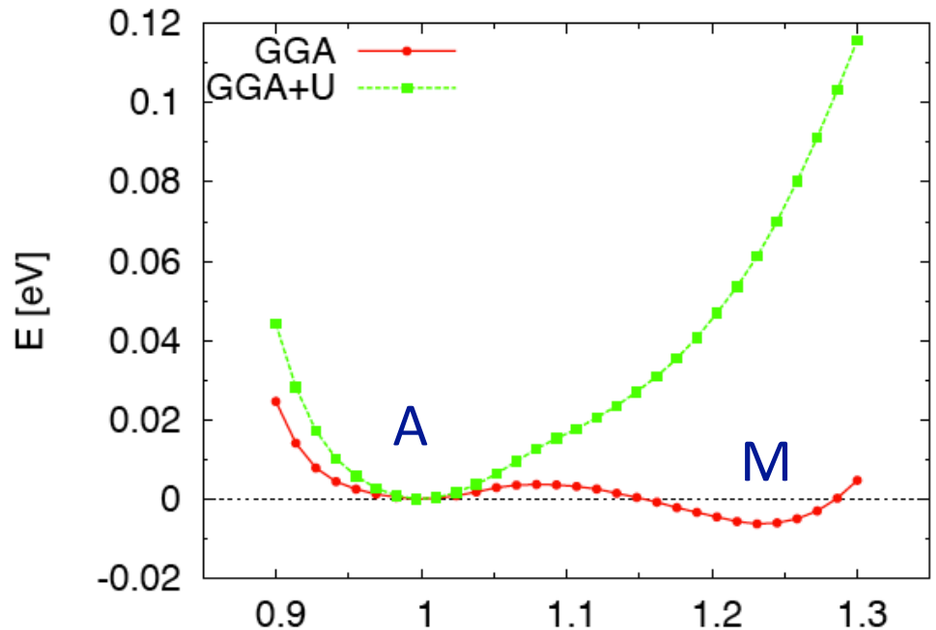
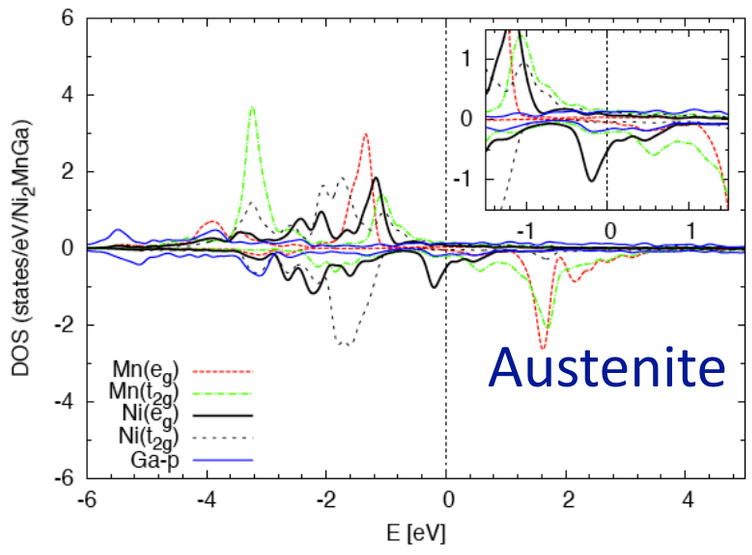


c/a



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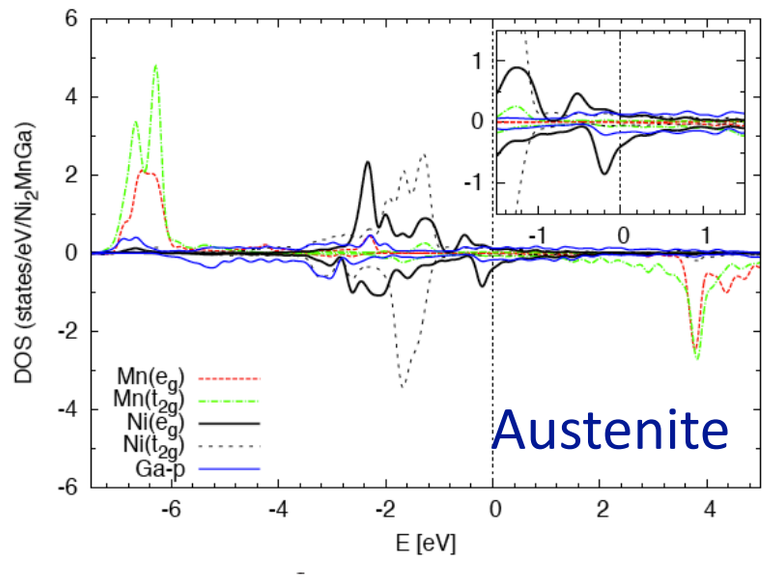
A more pronounced electronic localization destabilizes the non-modulated martensite

RKKY magnetic interactions

c/a



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Ni_2MnGa: modeling magnetism

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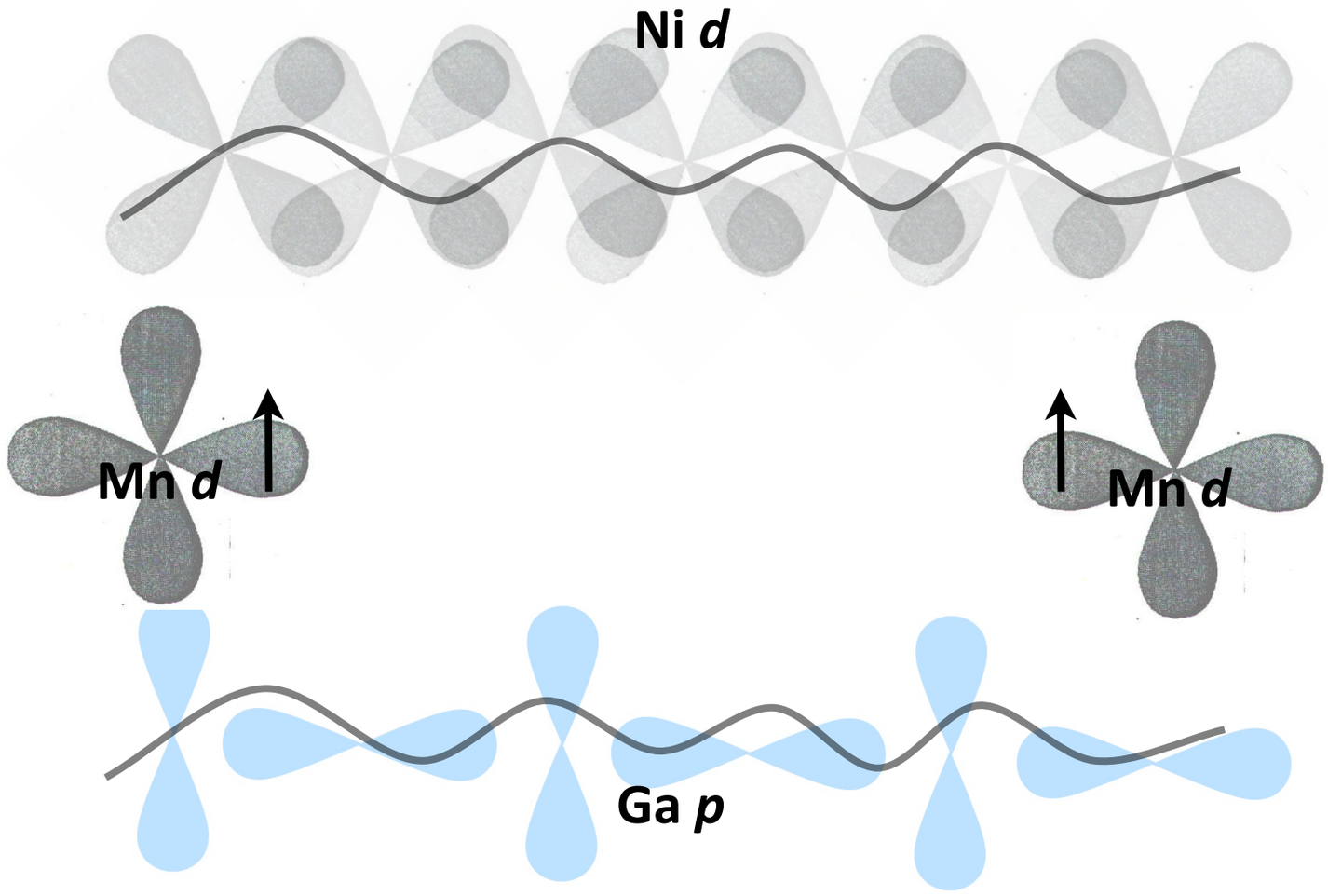
Mn atoms: Anderson magnetic impurities in Ni *d* and Ga *p* conduction electrons



Ni_2MnGa: modeling magnetism

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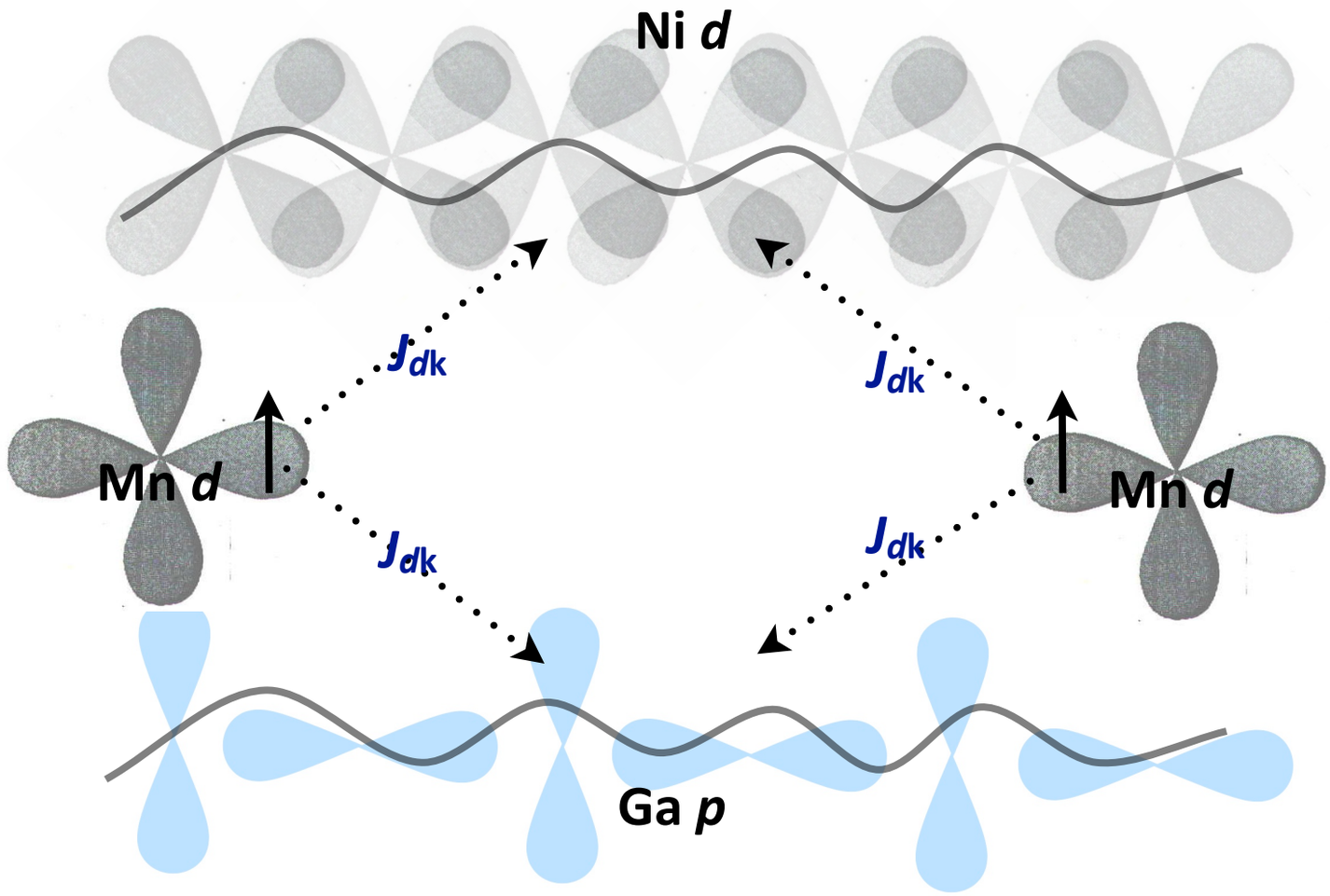
Anderson model ➡ RKKY magnetic interactions (*J*)

$$J_{d\,\mathbf{k}} \simeq \frac{2\,|V_{d\,\mathbf{k}}|^2\,U}{|E|\;(U-|E|)}$$



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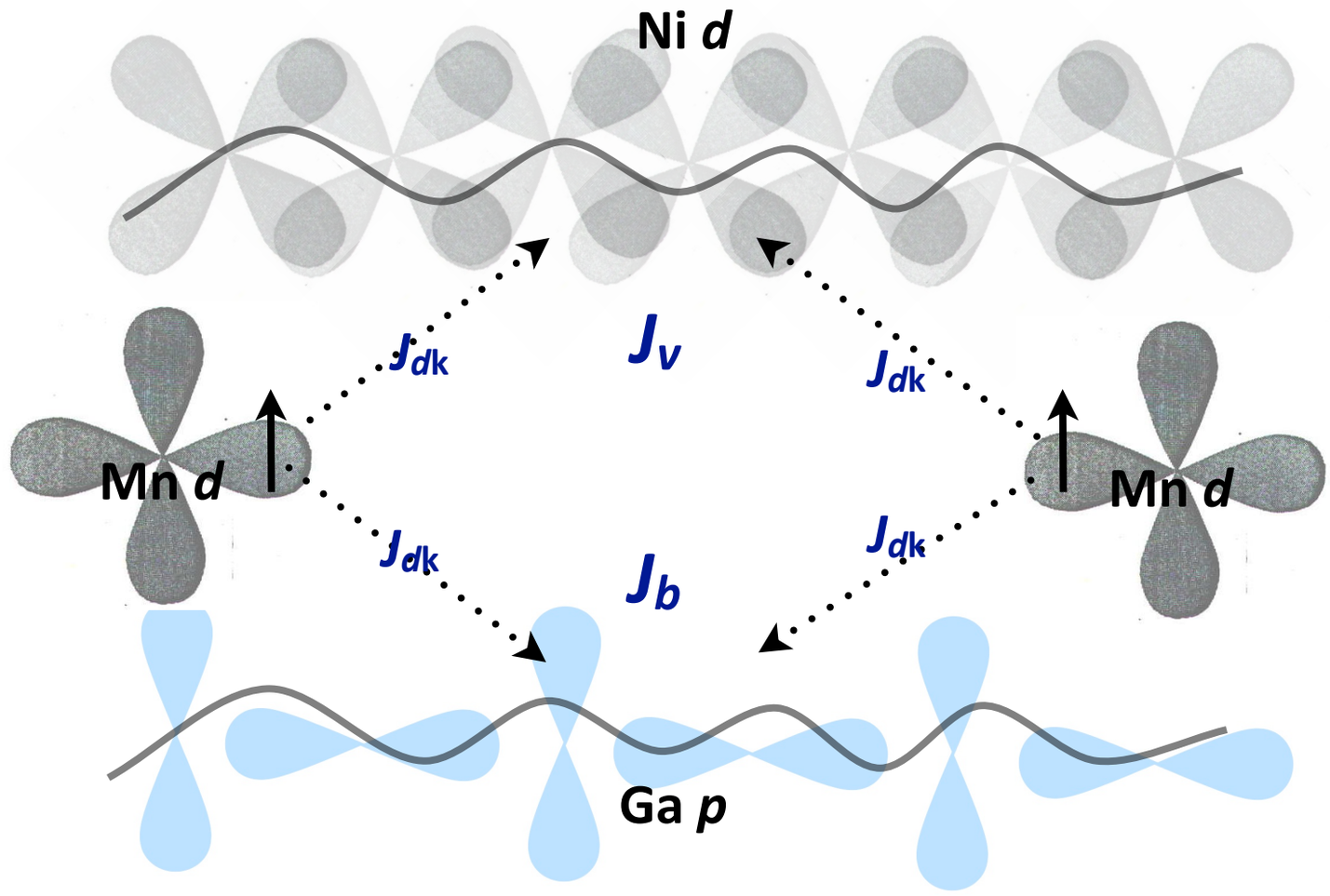
Super-exchange couplings and magnetization

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

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



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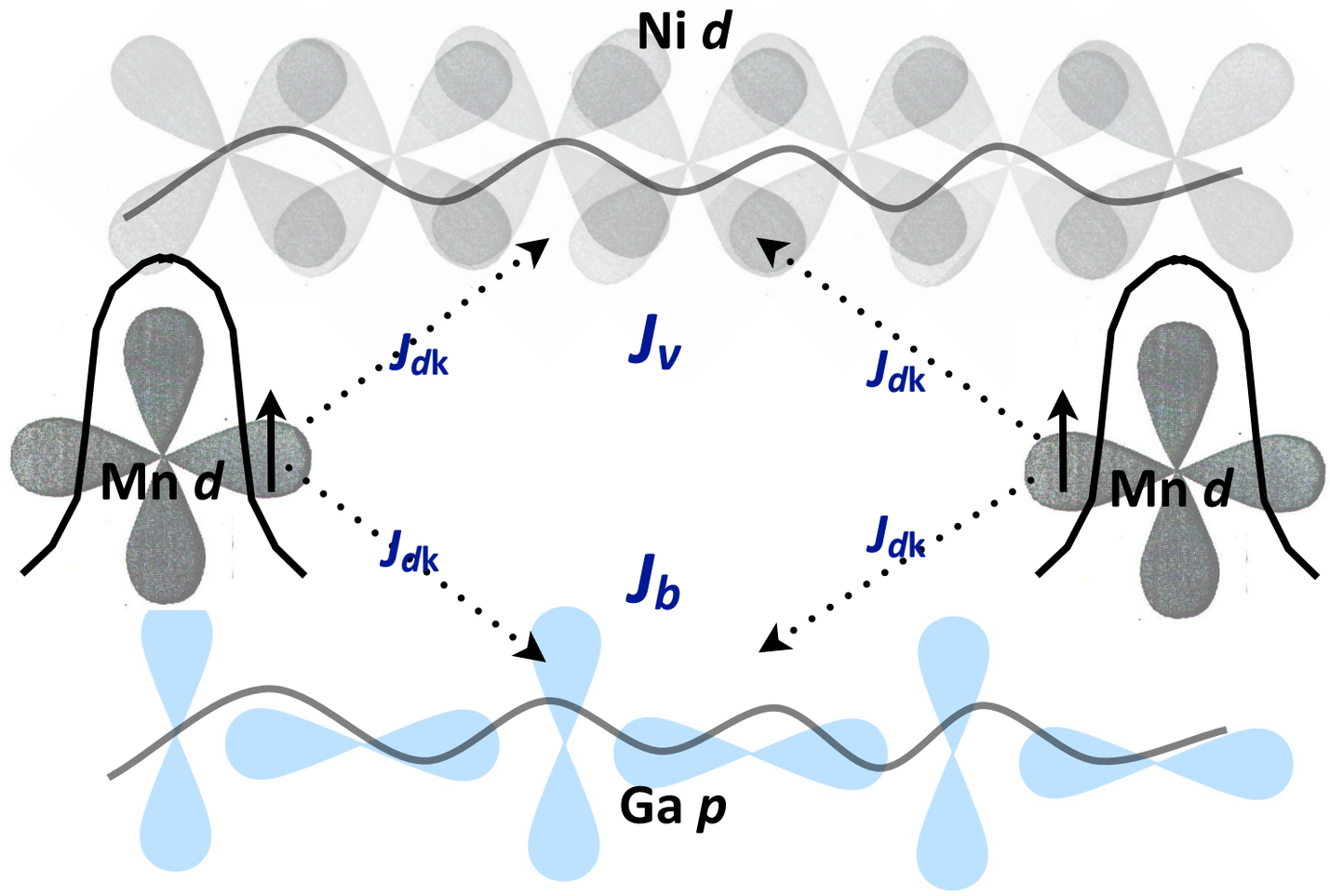

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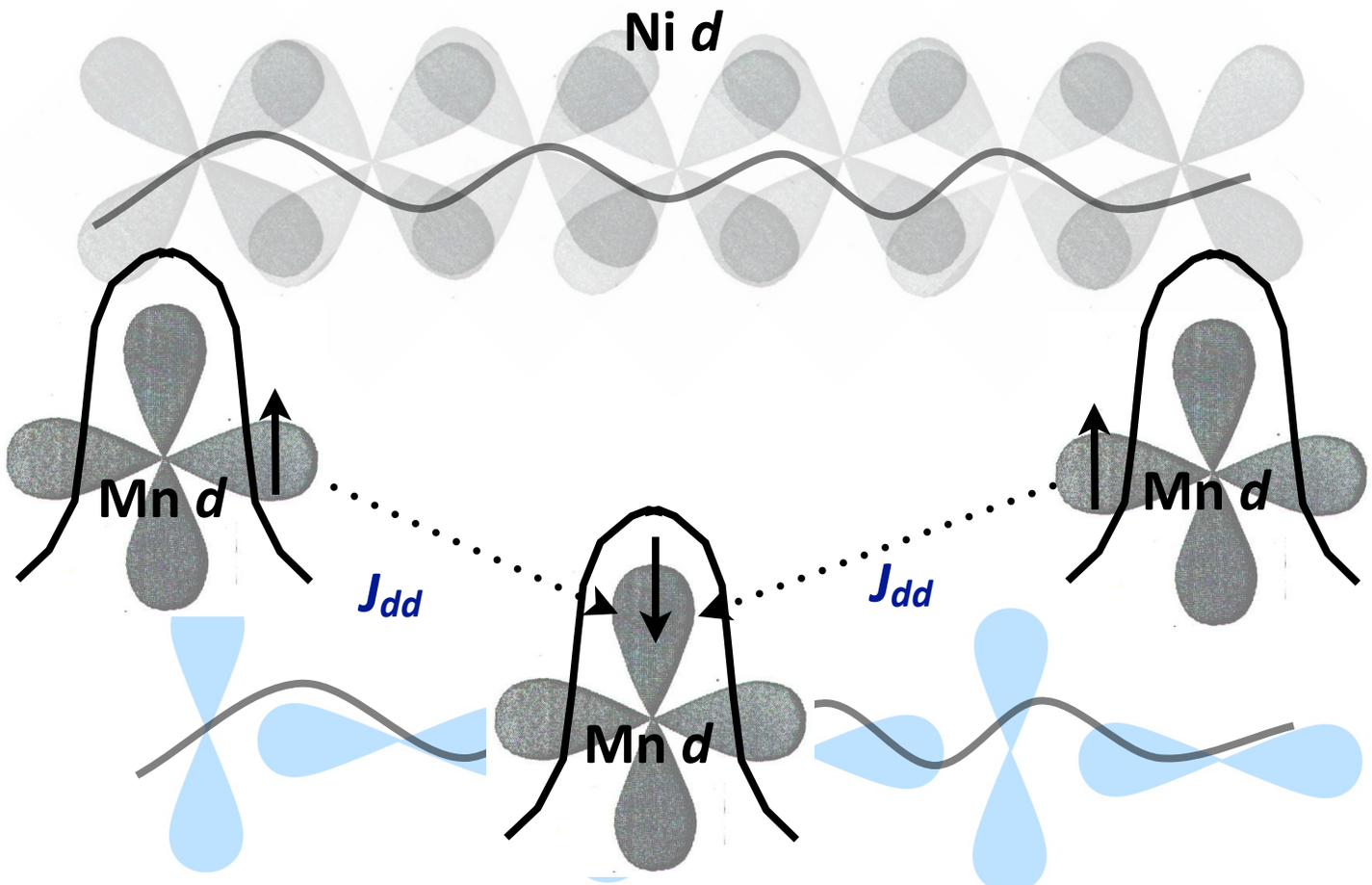
"+U" correction is essential to capture electronic localization and to correct the distance between Hubbard bands

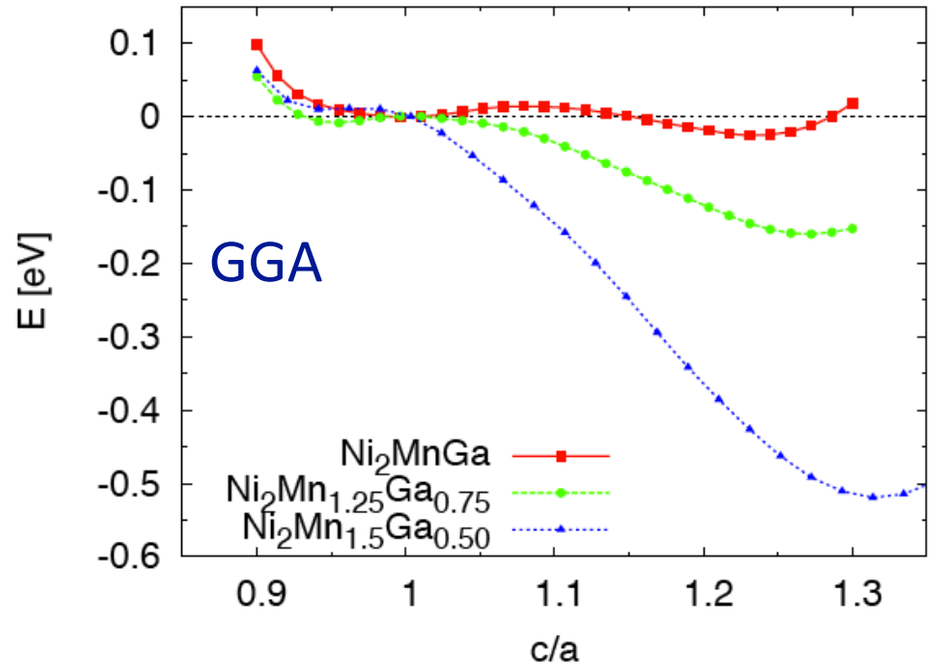
Ni_2MnGa: predicting the effect of doping

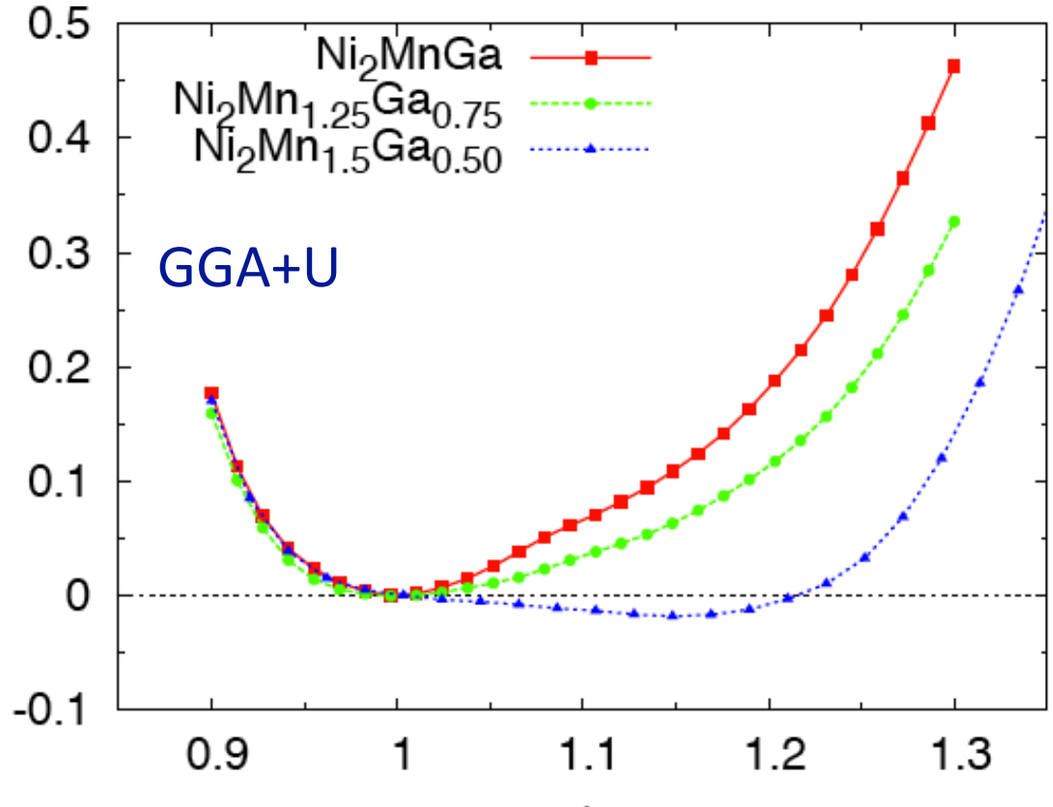


Mn substitutional impurity

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)





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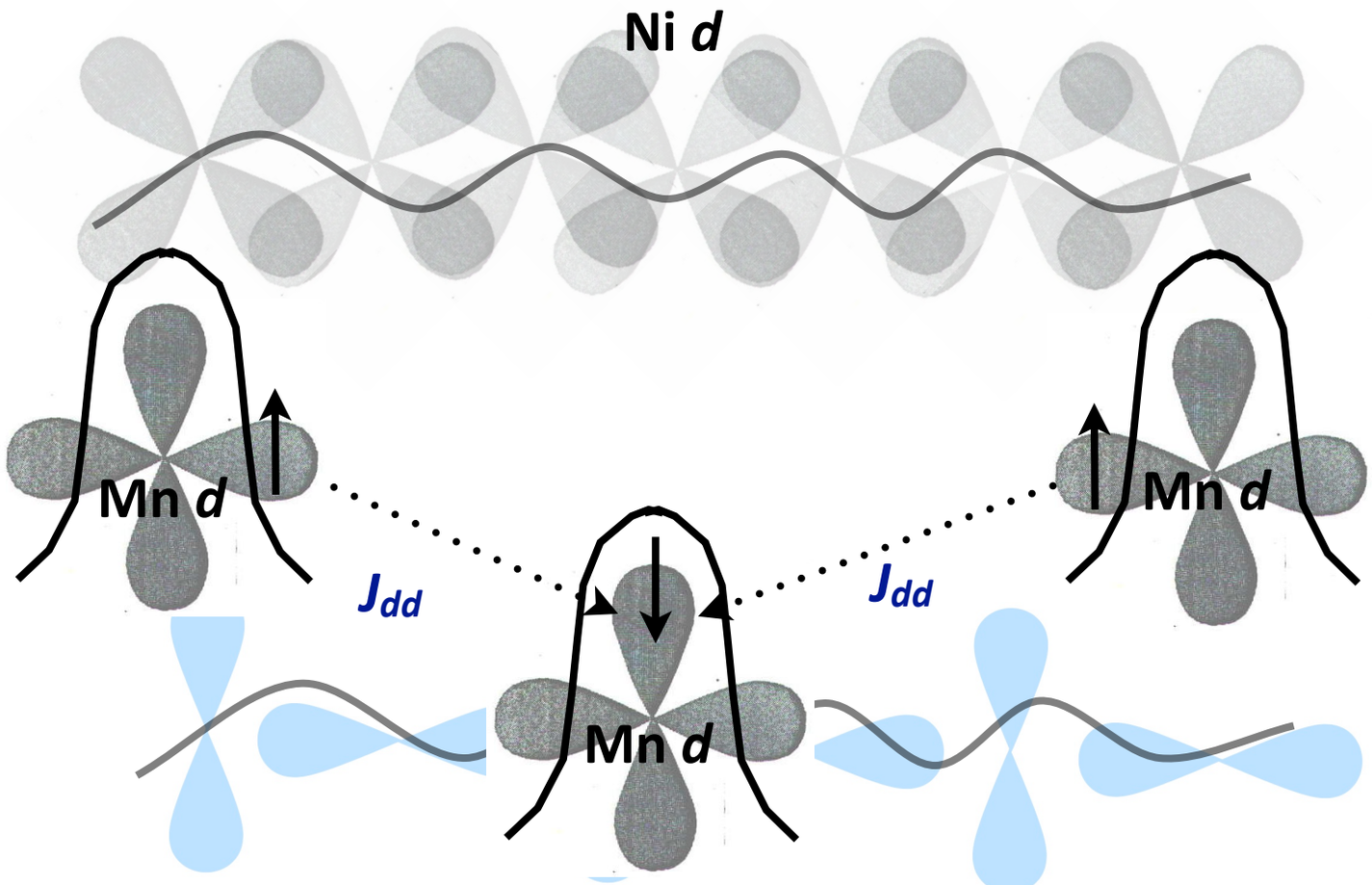

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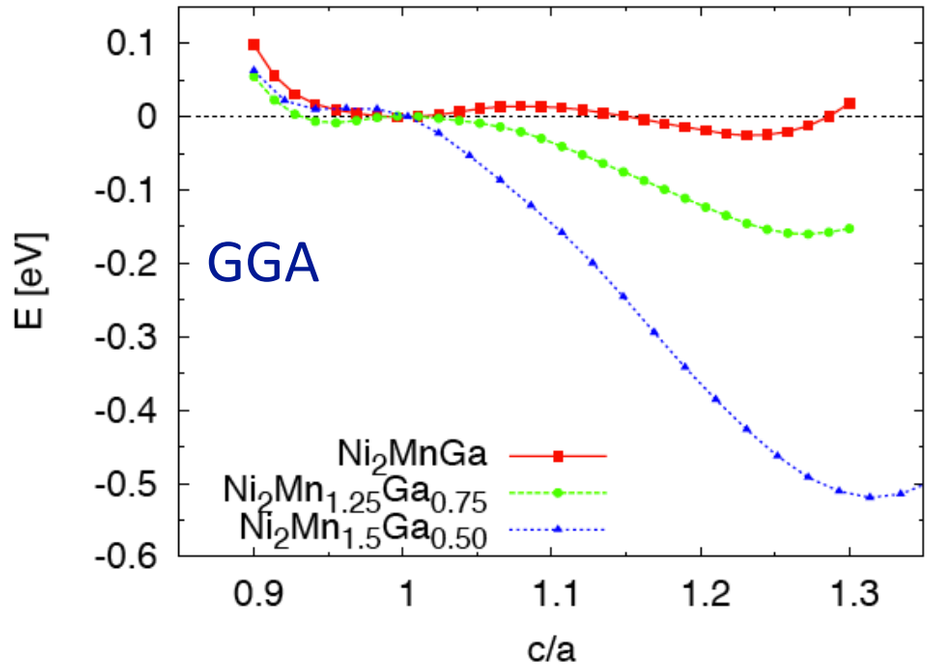
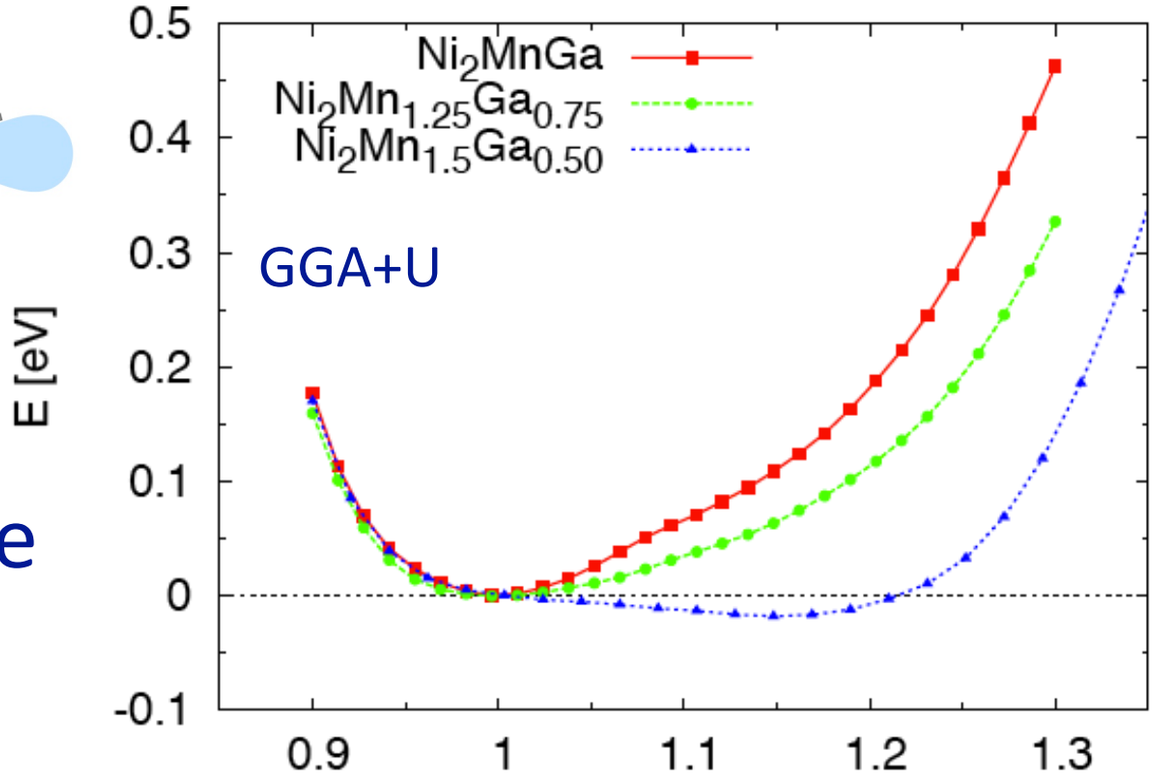


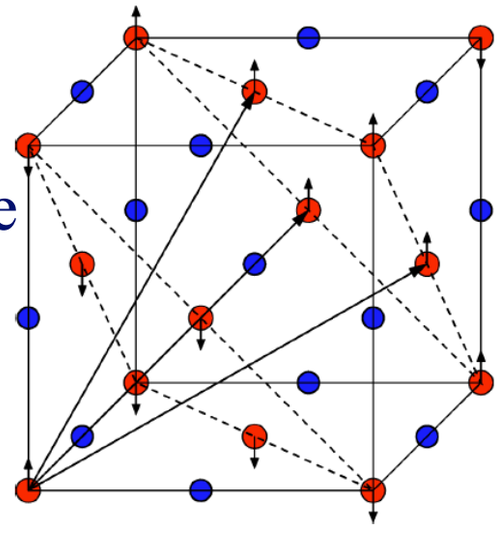


CuO: a “strange” transition-metal oxide

Other TMOs:

cubic structure
rhombohedral
symmetry

AFII



CuO:

monoclinic
(tenorite)

epitaxially
grown as
tetragonal RS

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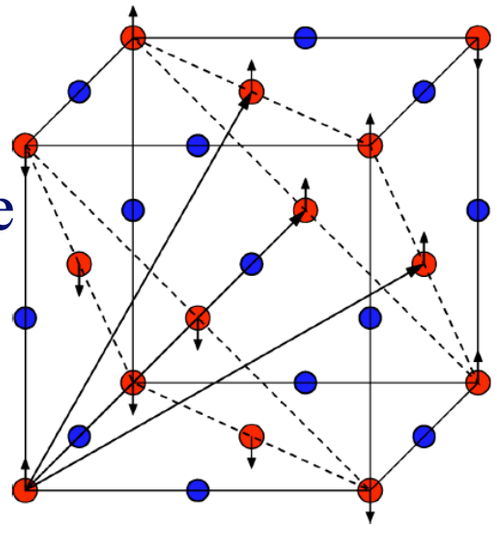

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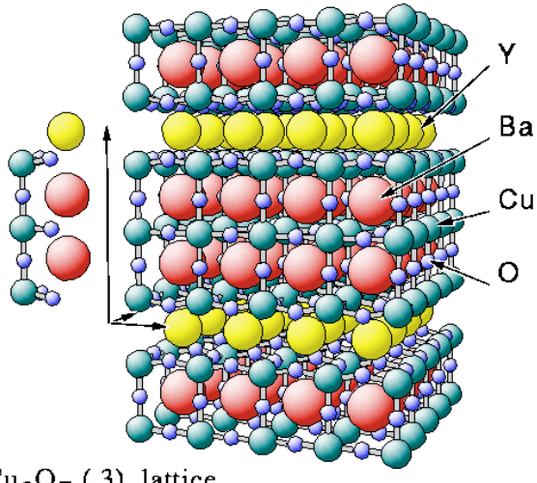
Why studying the cubic structure?

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



$YBa_2Cu_3O_7$ (.3) lattice

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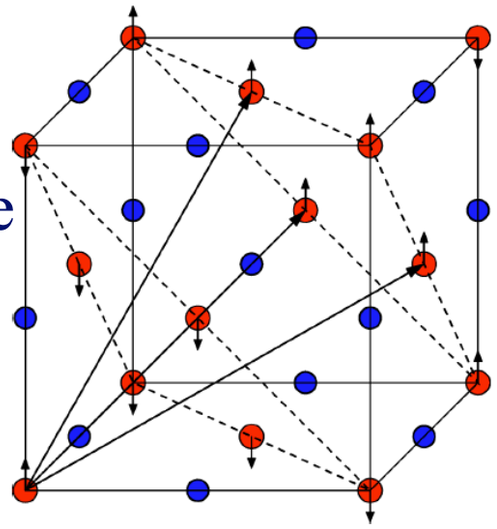

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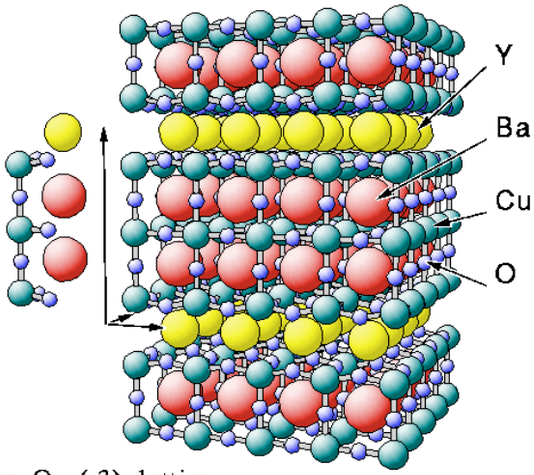

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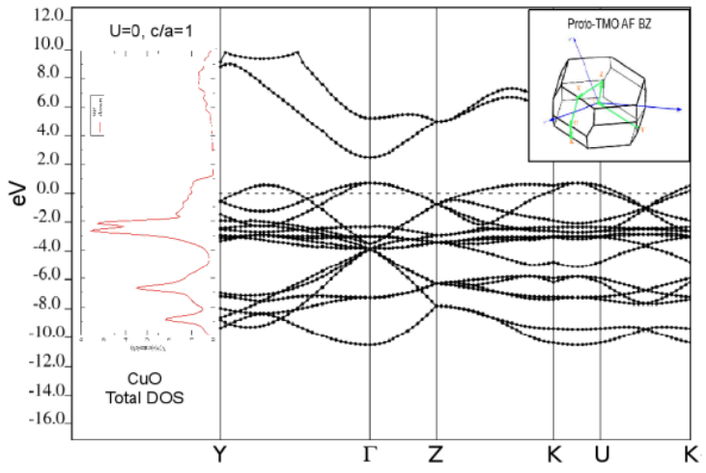
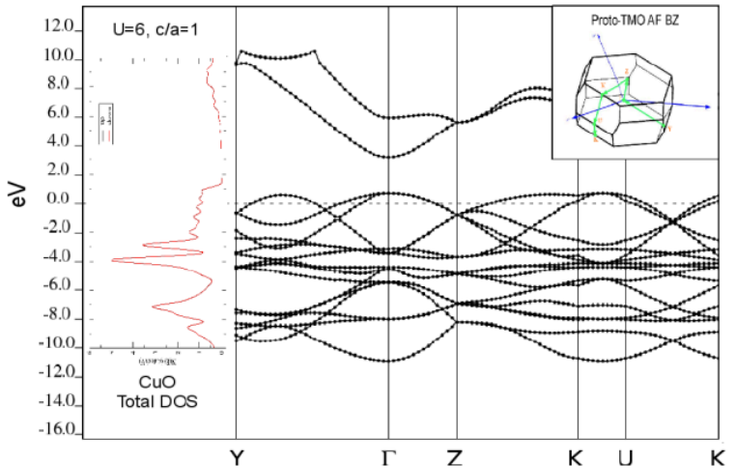
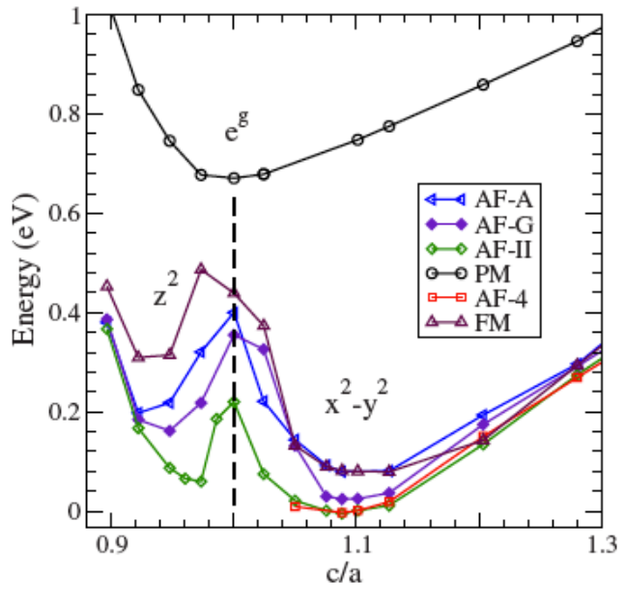




P. Grant, *J. Phys. Conf. Ser.*, 129, 012042 (2008)

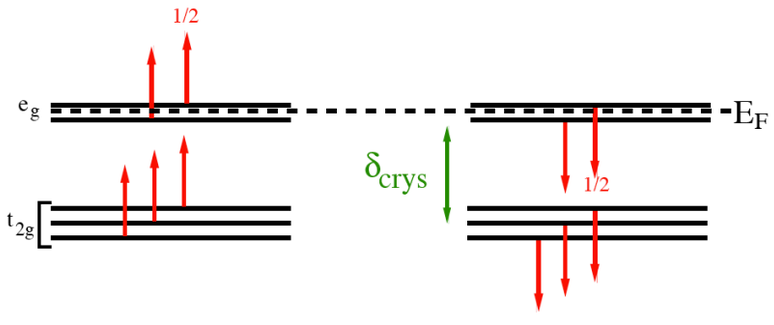


G. Peralta et al., *PRB* 80, 140408 (2009)

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

CuO: electronic structure

Cu: 9 *d* electrons



Non-magnetic, cubic phase

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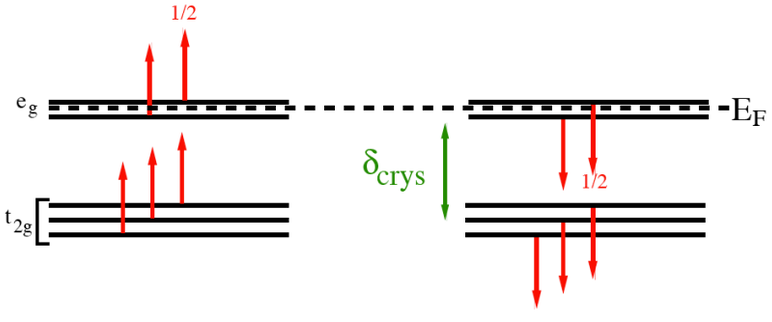
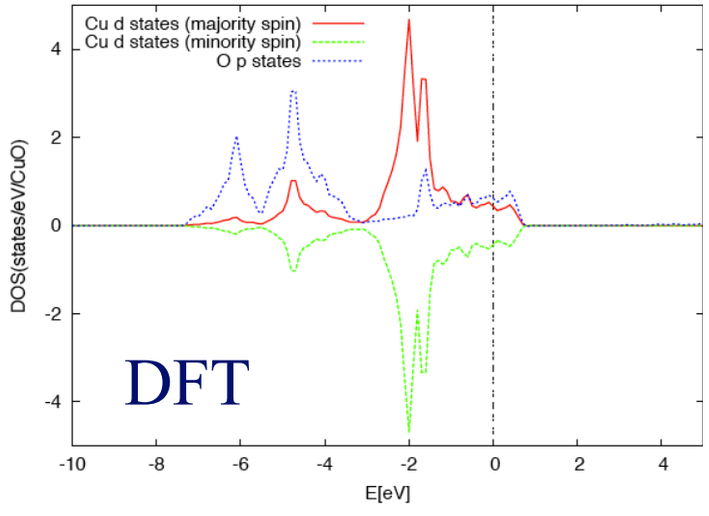
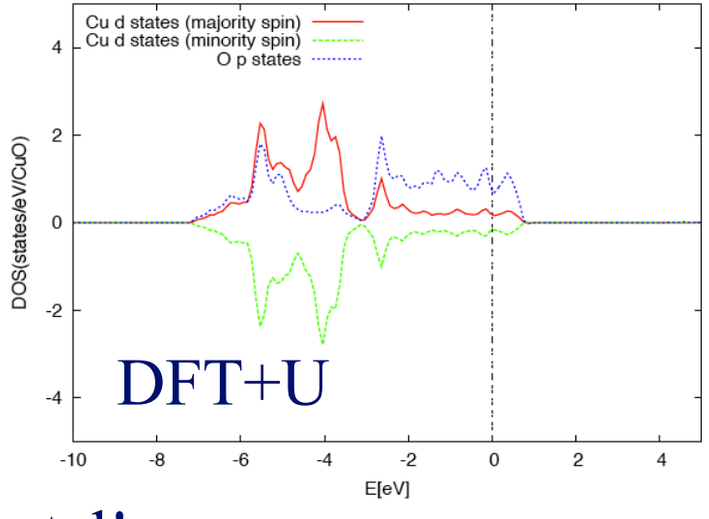






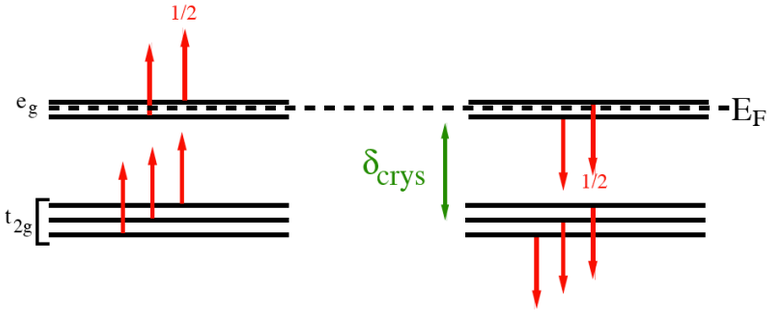
metal!

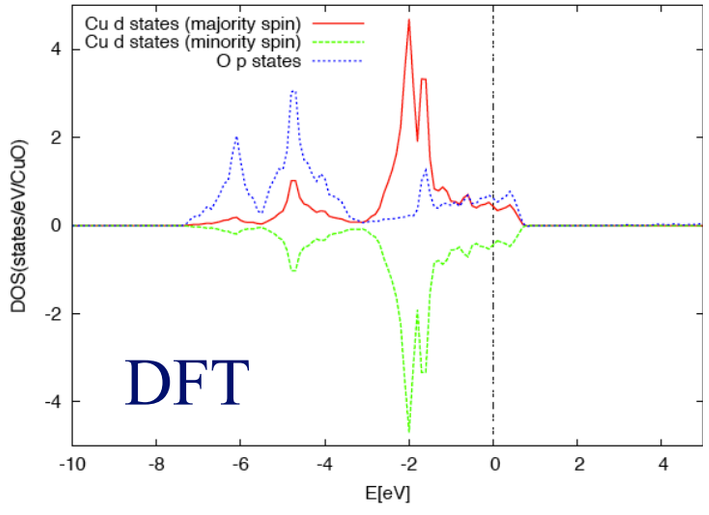
Non-magnetic, cubic phase

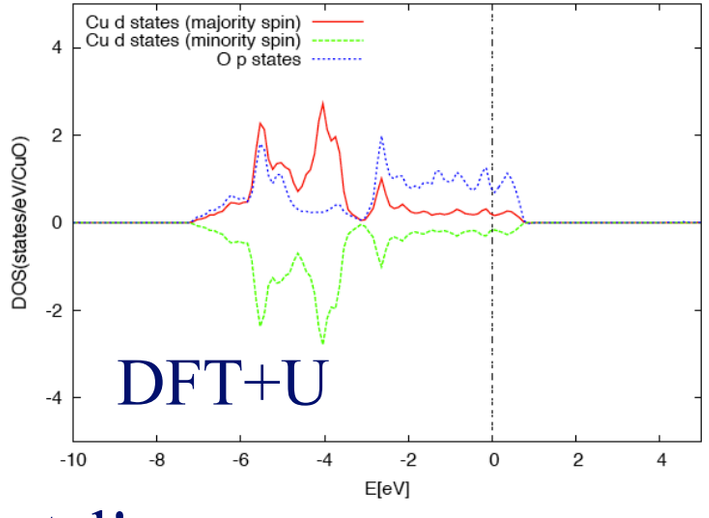
Occupations: Cu *d* states: 9.68 e-; O *p* states: 4.94 e-

CuO: electronic structure

Cu: 9 *d* electrons



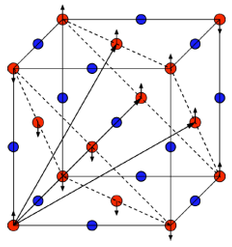




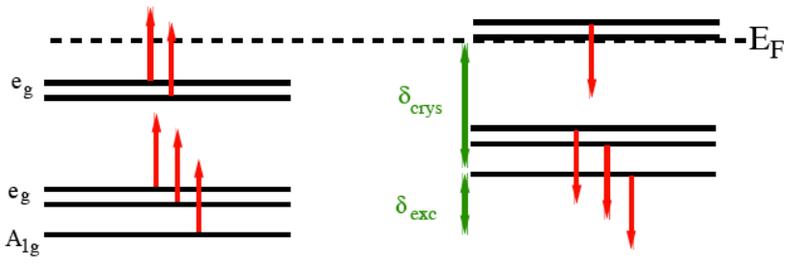
metal!

Non-magnetic, cubic phase

Occupations: Cu *d* states: 9.68 e-; O *p* states: 4.94 e-



Rhombohedral rock-salt (AFII)



AFII: rhombohedral cell (stabilized by U_p)

CuO: electronic structure

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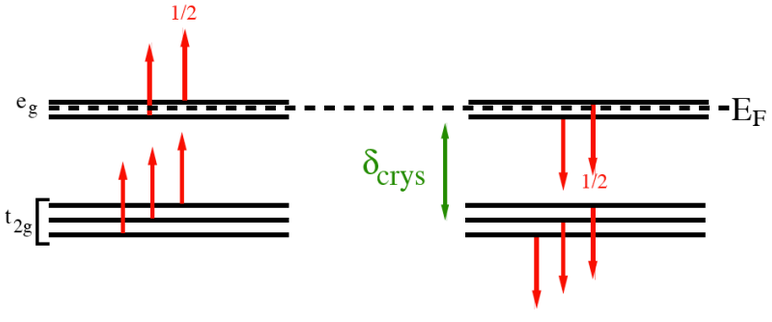

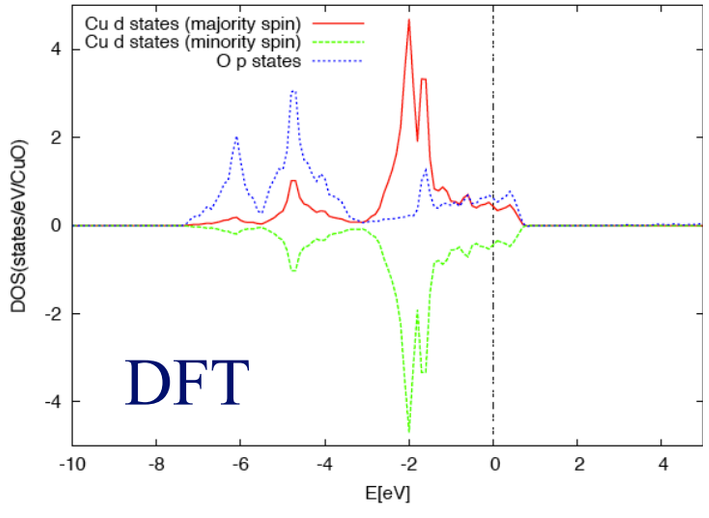

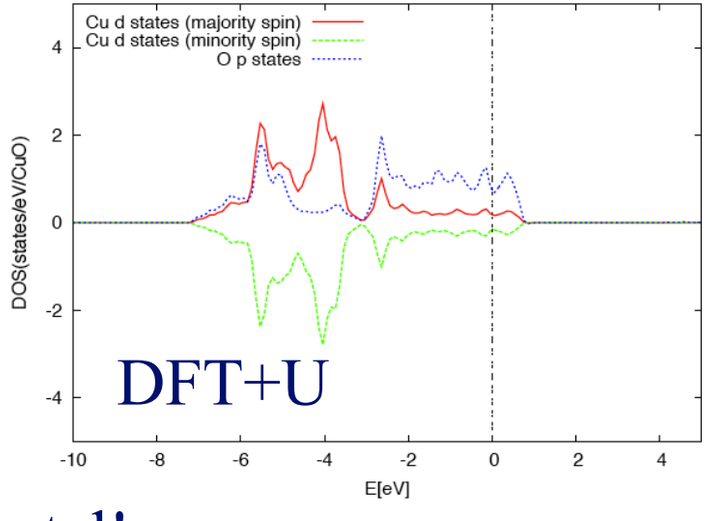

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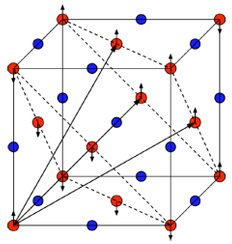

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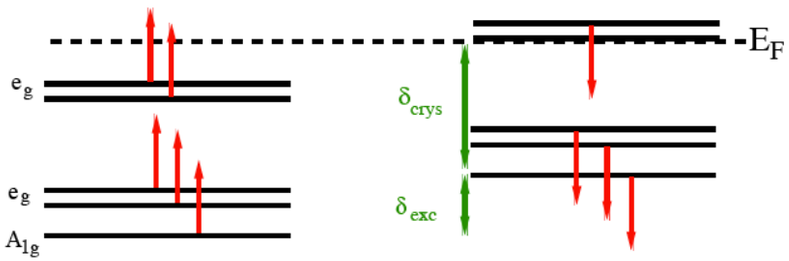
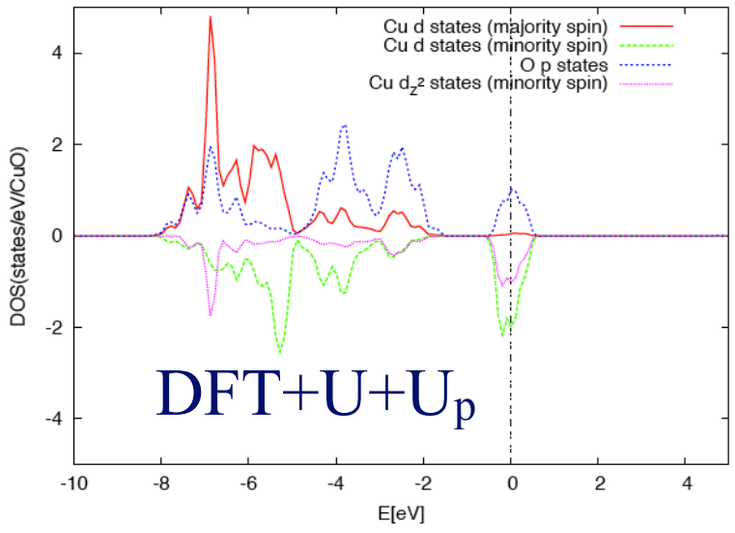


AFII: rhombohedral cell (stabilized by U_p)



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

still a metal!

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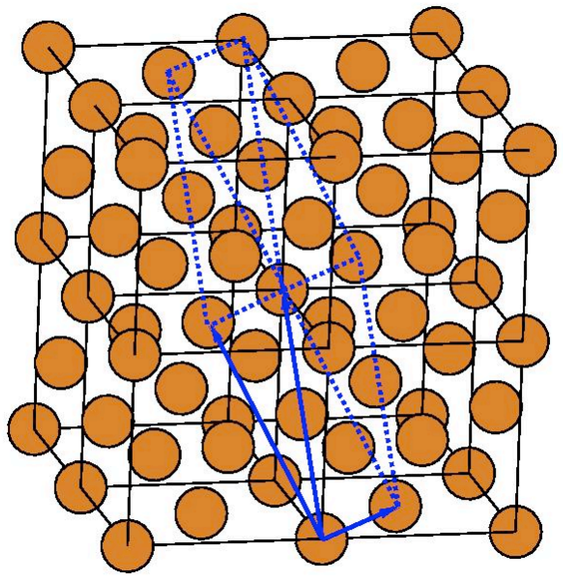
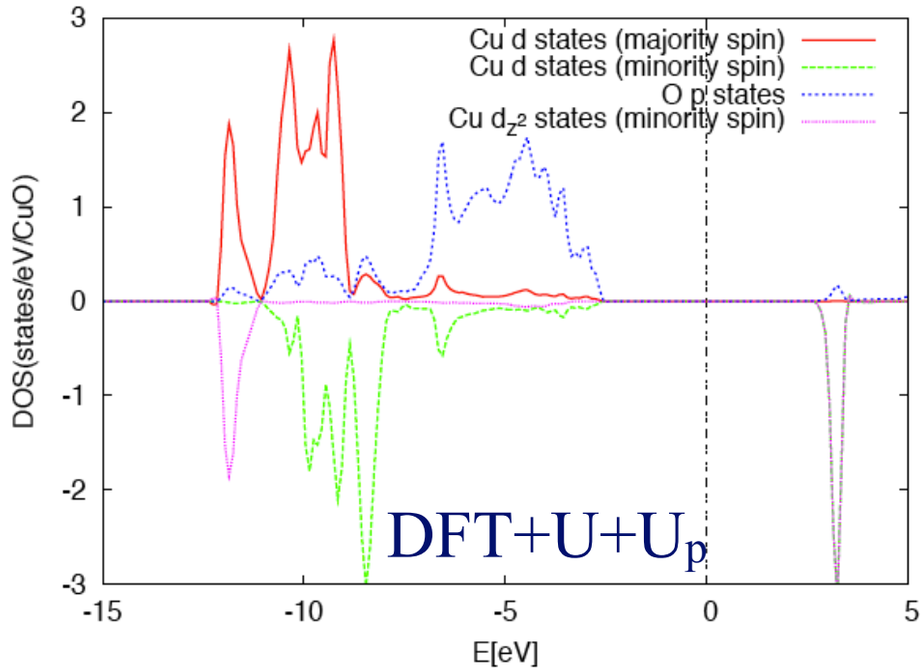
CuO: broken symmetry



triclinic cell: the equivalence of e_g states is broken

CuO is insulator (cubic phase)



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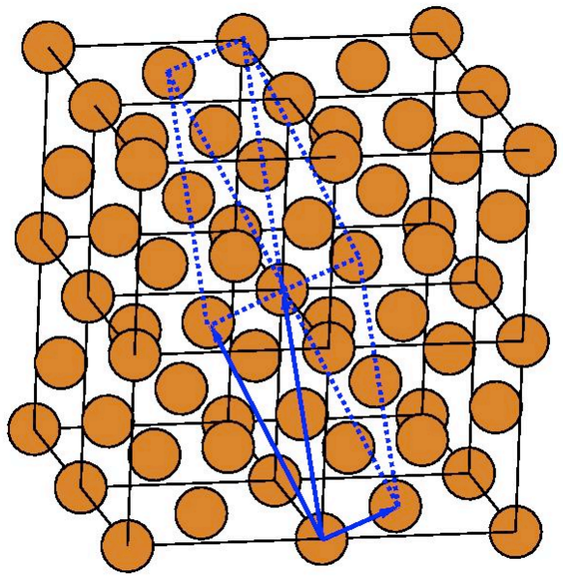

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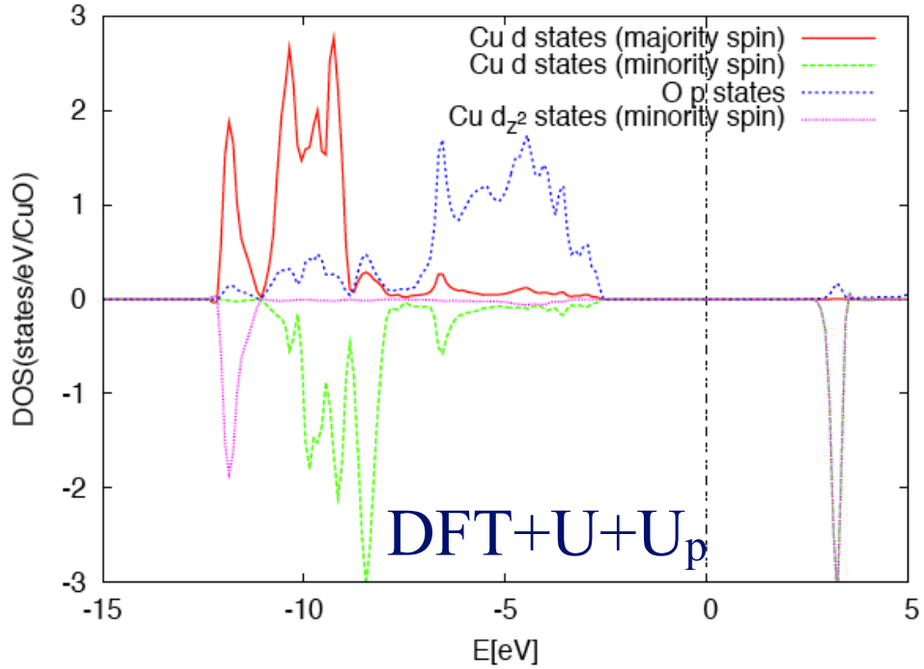

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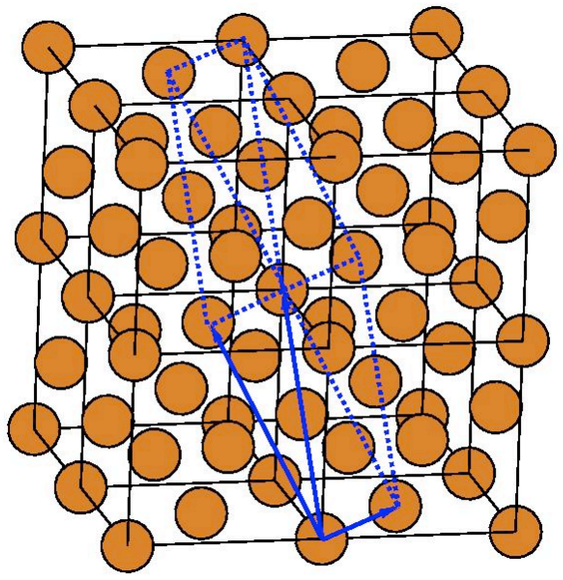

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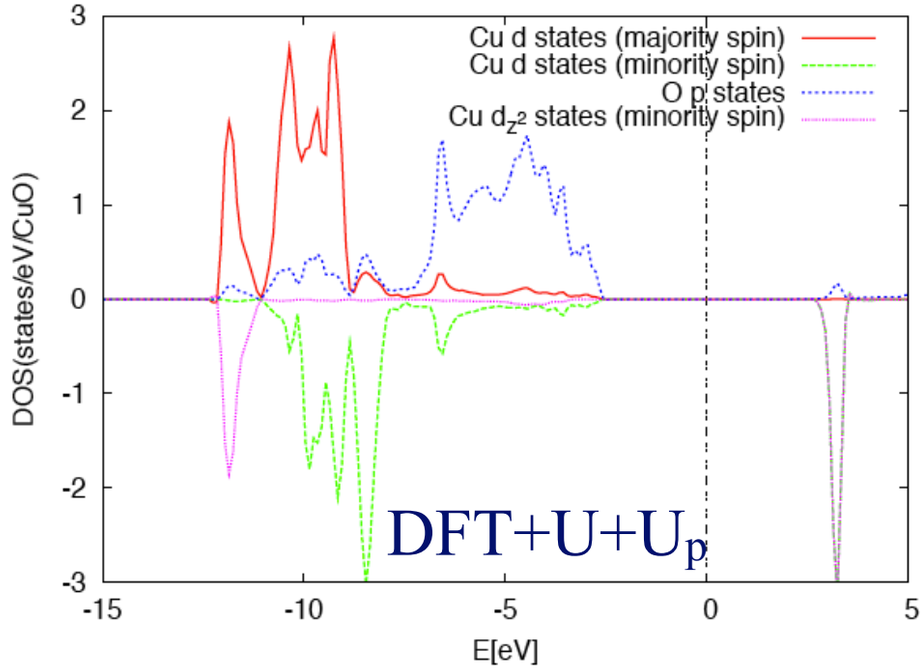

$U_p = 0$ ==> non magnetic state ==> cubic symmetry ==> metallic state

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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The "+J" term improves the description of magnetic interactions between localized electrons and leads to the localization of hole on Cu *d* states

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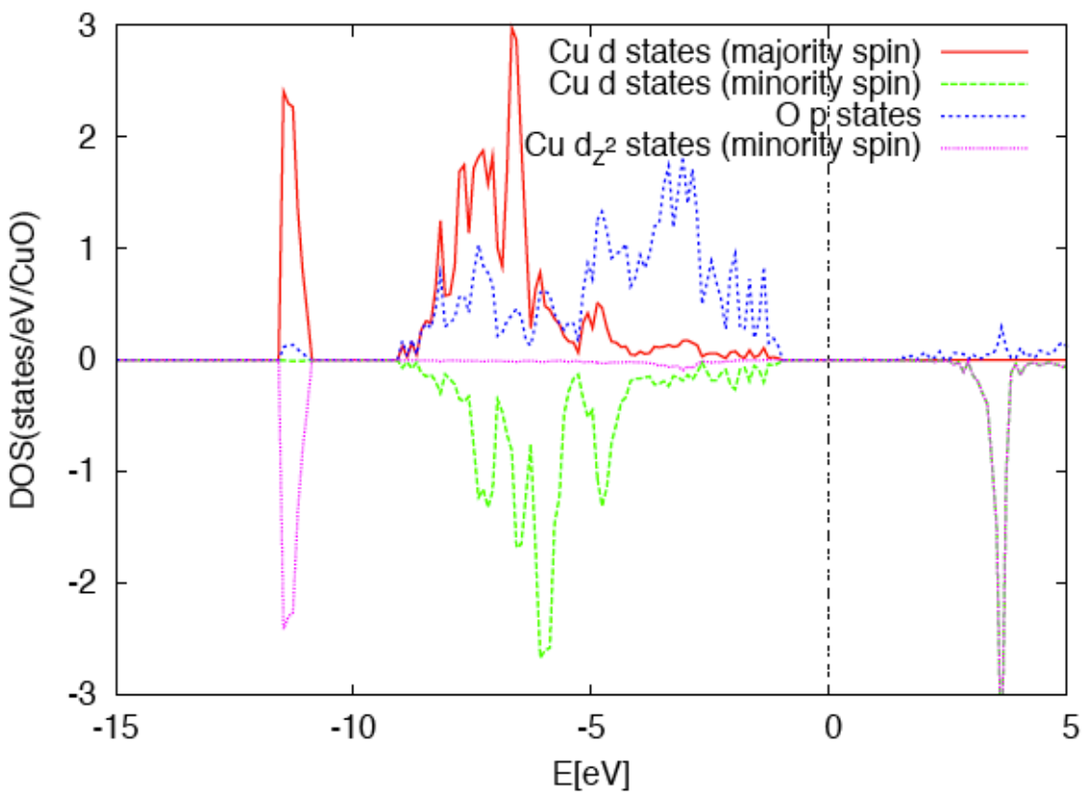
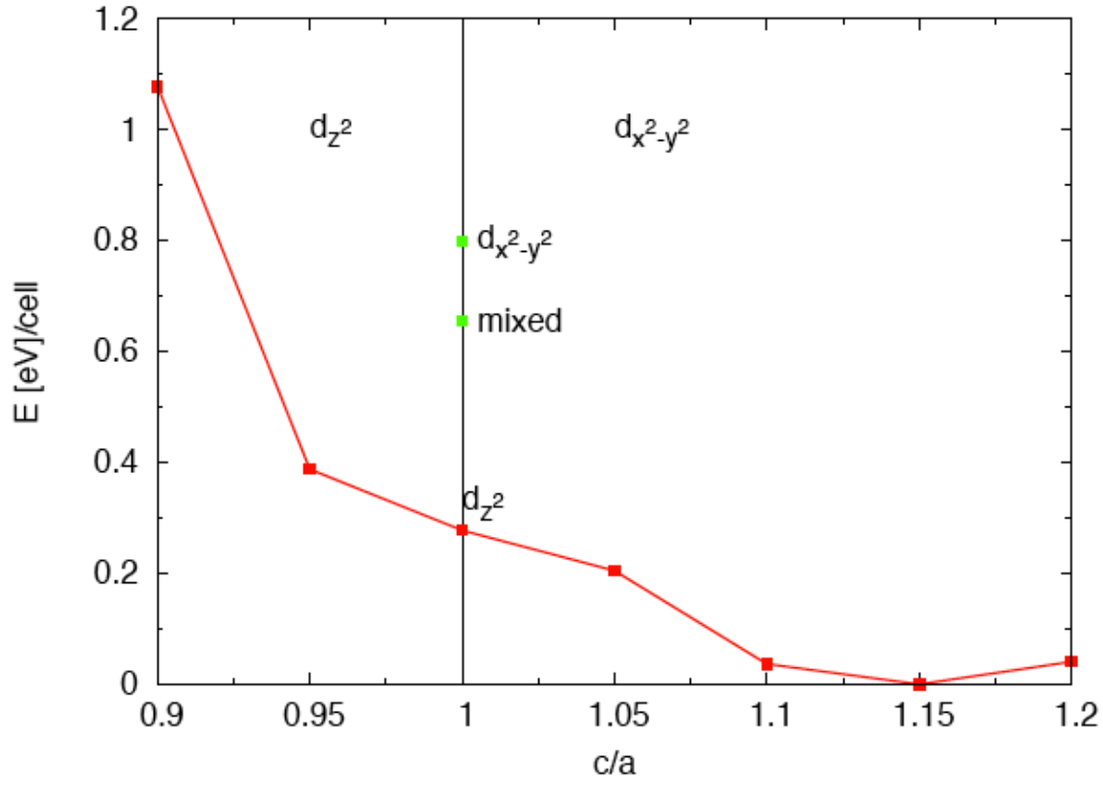
CuO: DFT+U+J ground state





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The End

More questions?