Extended LDA+U functional for covalent systems

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Who and where

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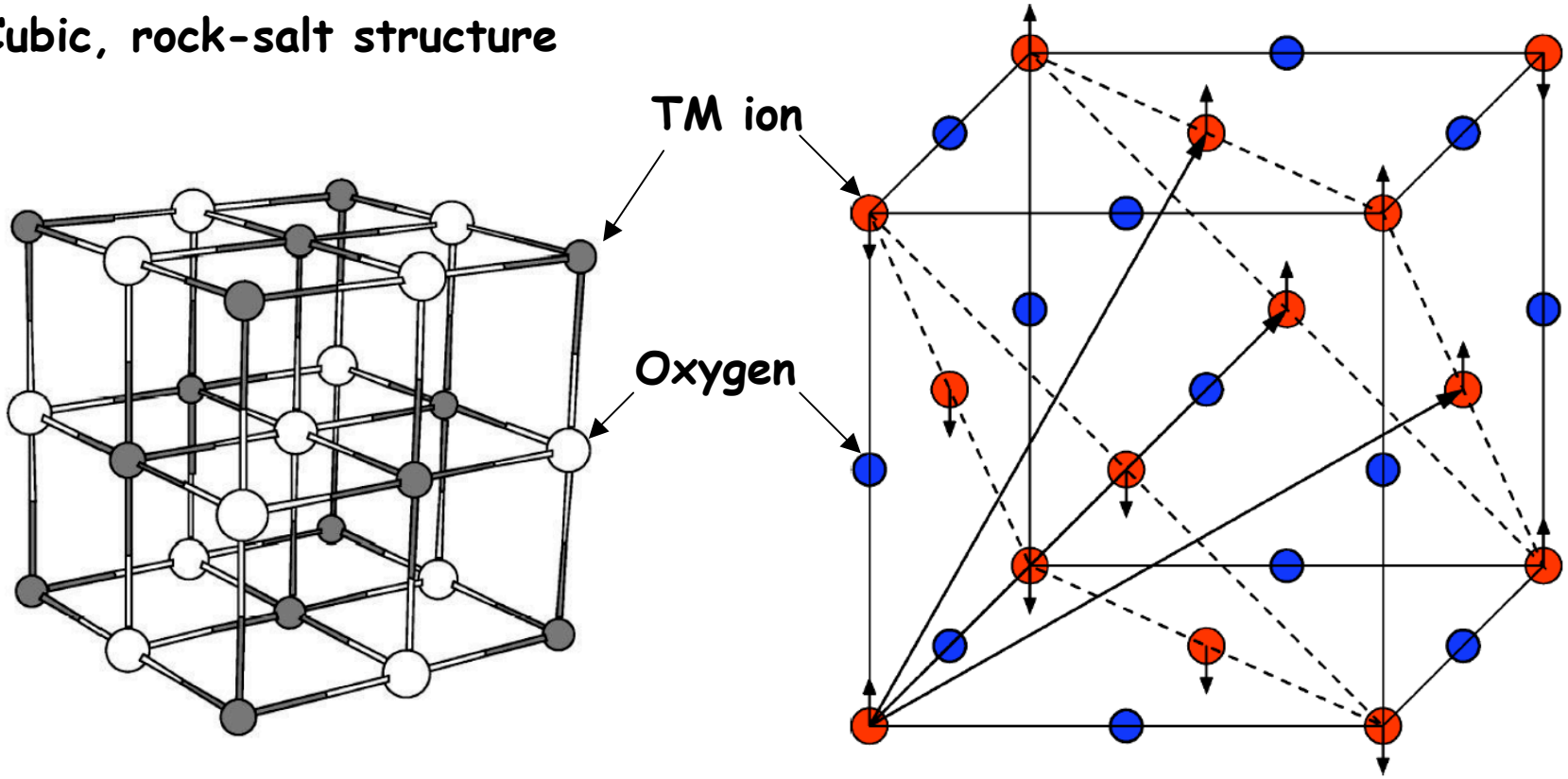
Outline

- Notable failures of LDA/GGA: transition-metal oxides
- Mott and band insulators
- LDA+U: general formulation and implementation
- The LDA+U+V extension
- Calculation of the effective interactions
- Case studies: band semiconductors and charge-transfer insulators

Failures of LDA/GGA: transition metal oxides

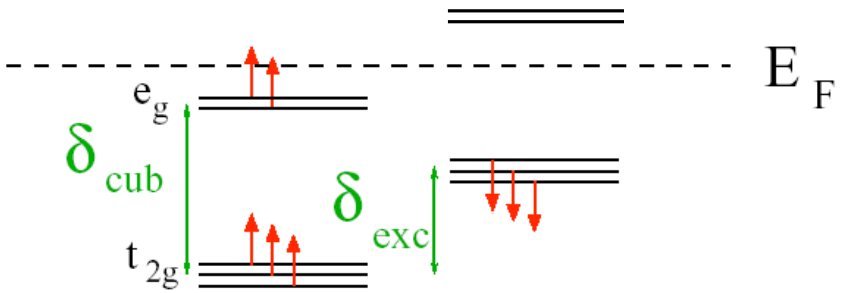
- Cubic, rock-salt structure



- Antiferromagnetic (AF) ground state ⟹ rhombohedral symmetry and possible structural distorsions (FeO)

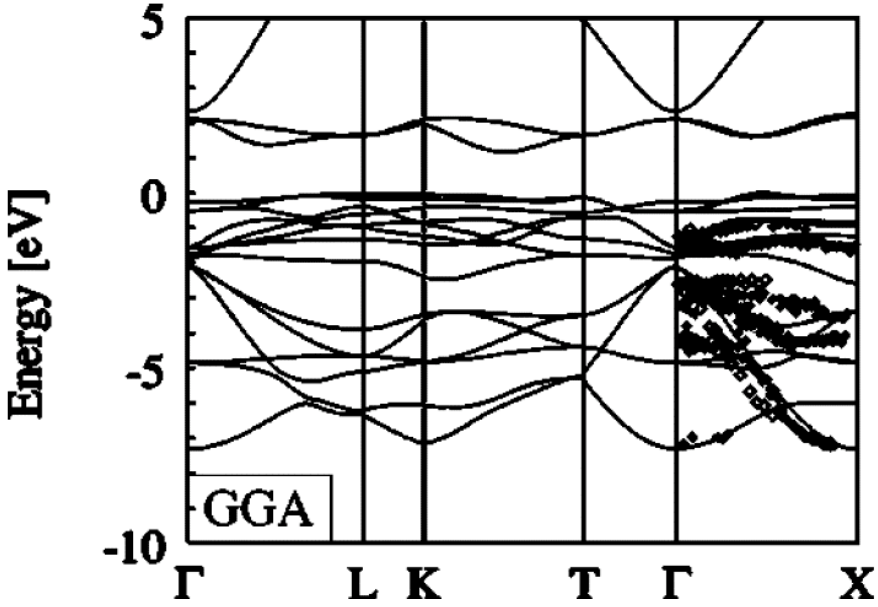
- Conduction properties (exp): insulators (Mott/charge-transfer kind)

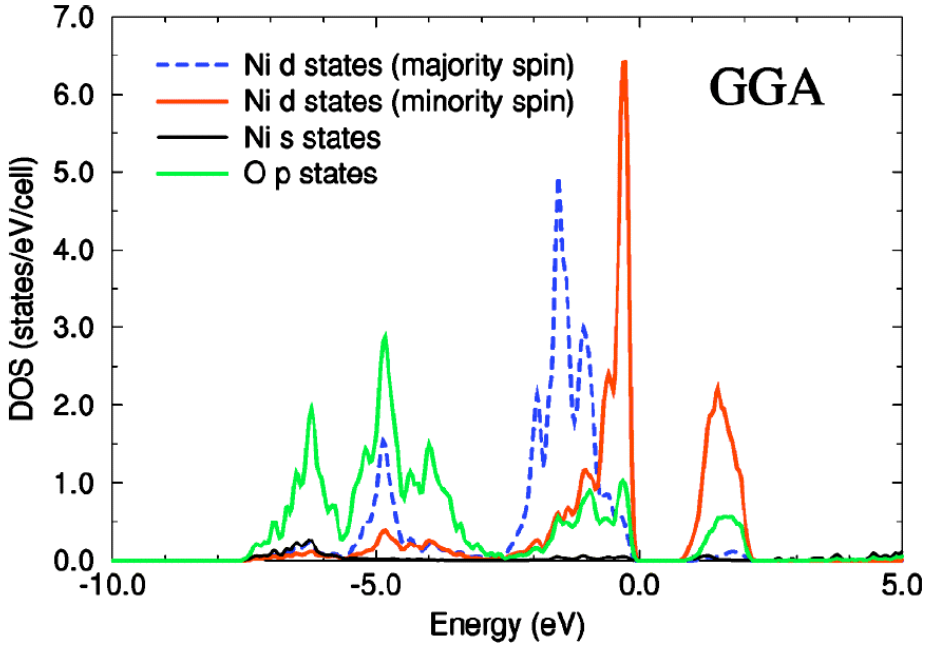
NiO: GGA results



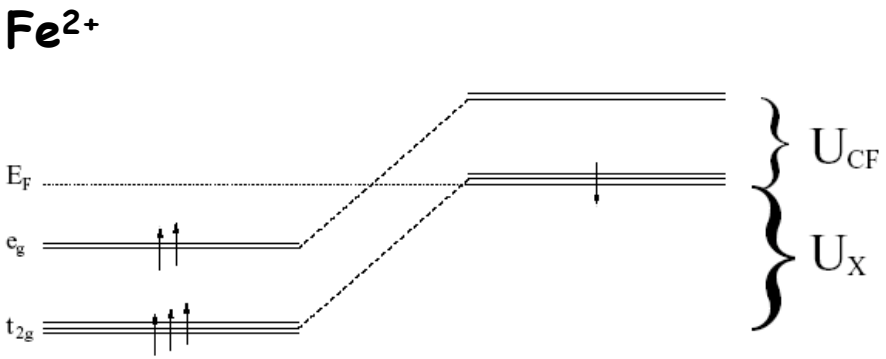
- Antiferromagnetic ground state: OK
- crystal structure (cubic): OK
- Crystal field produces a band gap, but…

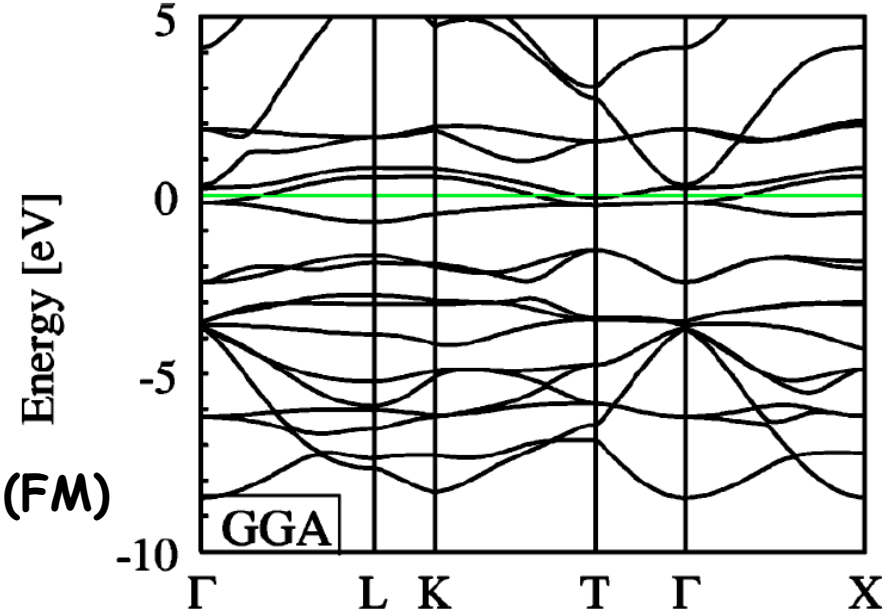
The energy gap is too small





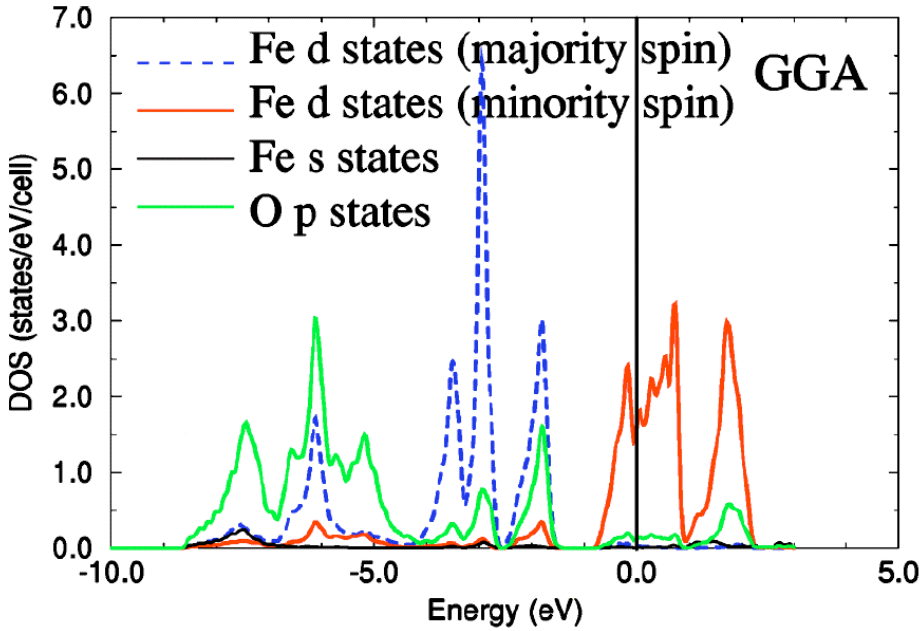
FeO: GGA results





- Antiferromagnetic ground state: NO (FM)
- crystal structure (cubic): OK
- but…

We obtain a metal !!!



Mott insulators: U vs W

Two quantities are to be considered:

- U "on-site" electron-electron repulsion
- W bandwidth (one-body term of the energy)

Two different regimes:

- W/U >> 1: the energy is minimized making the kinetic term as small as possible through delocalization (the cost of on-site repulsion U is easily overcome)
- W/U << 1: the kinetic energy of electrons is not large enough to overcome the on-site repulsion. Electrons undergo a Mott localization

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

LDA/GGA approximations to DFT always tend to over-delocalize electrons:

- U is not well accounted for
- electronic energy functionals are affected by self-interaction

The LDA+U energy functional

The LDA+U method consists in a correction to the approximate DFT (e.g., LDA or GGA) energy functional that is shaped on a Hubbard Hamiltonian including effective on-site interactions.
It was introduced and developed by V. I. Anisimov and coworkers ('90-'95).

$$E_{DFT+U}\left[\{n(r)\}\right] = E_{DFT}\left[\{n(r)\}\right] + E_{Hub}\left[\{n_m^{I\sigma}\}\right] - E_{dc}\left[\{n^{I\sigma}\}\right]$$

Fully rotationally invariant formulation (Lichtenstein et al. PRB 1995)

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

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

Occupations: $n^{I\sigma}_{mm'} = \sum_{k,v} f_{kv}\langle\psi^\sigma_{kv}|\varphi^I_{m'}\rangle\langle\varphi^I_m|\psi^\sigma_{kv}\rangle \quad n^{I\sigma} = \sum_m n^{I\sigma}_{mm} \quad n^I = \sum_\sigma n^{I\sigma}$

<u>Keep in mind</u>:

- **only occupations of "localized" orbitals included (e.g. *d* or *f* states)**
- **no inter-site terms: integer on-site occupation are favored and hybridization suppressed**

A simplified approach

First order approximation: let's neglect the exchange interaction J:

$$\langle m,m''|V_{ee}|m',m'''\rangle = \delta_{mm'}\delta_{m''m'''}U \qquad J=0$$

We get:

$$E_U\left[\left\{n^{I\sigma}_{mm'}\right\}\right] = E_{Hub}\left[\left\{n^{I\sigma}_{mm'}\right\}\right] - E_{dc}\left[\left\{n^{I\sigma}\right\}\right] =$$

$$\frac{U}{2}\sum_I\sum_{m,\sigma}\left\{n^{I\sigma}_{mm} - \sum_{m'} n^{I\sigma}_{mm'}n^{I\sigma}_{m'm}\right\} = \frac{U}{2}\sum_{I,\sigma} Tr\left[\mathbf{n}^{I\sigma}\left(\mathbf{1}-\mathbf{n}^{I\sigma}\right)\right]$$

Note: a) U is the only interaction parameter in the functional
b) the rotational invariance is preserved.

<u>This is the formula implemented in PWscf</u>. We have:

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

How does it work?

Because of rotational invariance we can use a diagonal representation:

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

where

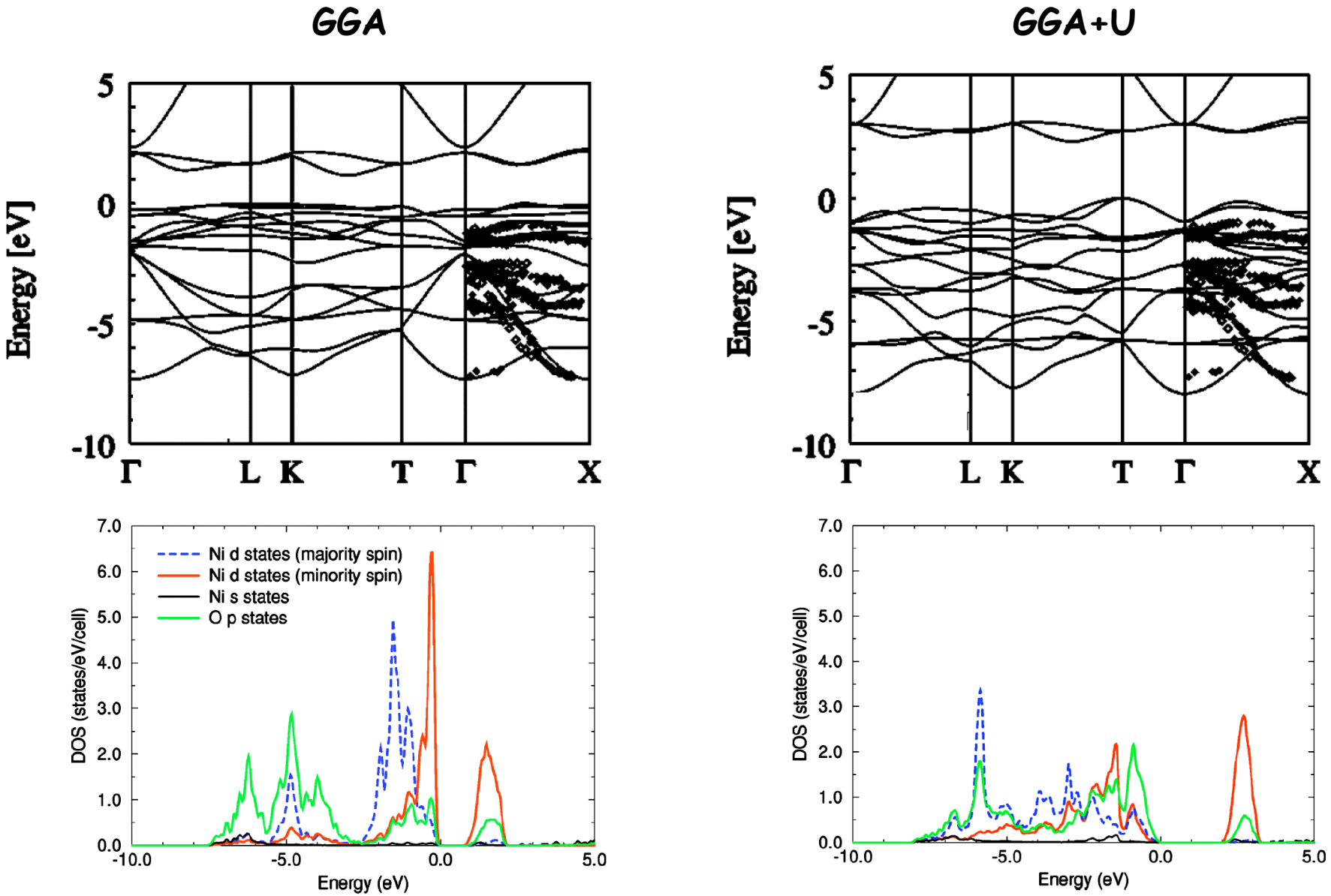
$$\mathbf{n}^{I\sigma}\mathbf{v}_m = \lambda_m^{I\sigma}\mathbf{v}_m \qquad \lambda_m^{I\sigma} = \sum_{k,v} f_{kv}\left\langle\psi_{kv}^{\sigma}\middle|\phi_m^I\right\rangle\left\langle\phi_m^I\middle|\psi_{kv}^{\sigma}\right\rangle$$

Potential:

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

$$\left.\begin{array}{l}\lambda_m^{I\sigma} > \dfrac{1}{2} \Rightarrow V_U < 0 \\ \lambda_m^{I\sigma} < \dfrac{1}{2} \Rightarrow V_U > 0\end{array}\right\} \Longrightarrow \left\{\begin{array}{l}\text{Partial occupations of atomic states are discouraged} \\ \\ \text{Gap opens: } E_g \uparrow\end{array}\right.$$

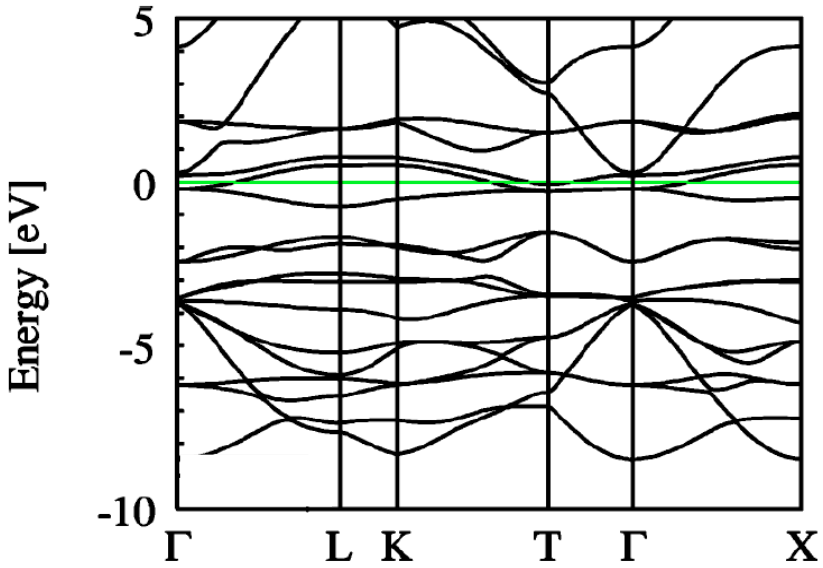
GGA+U NiO



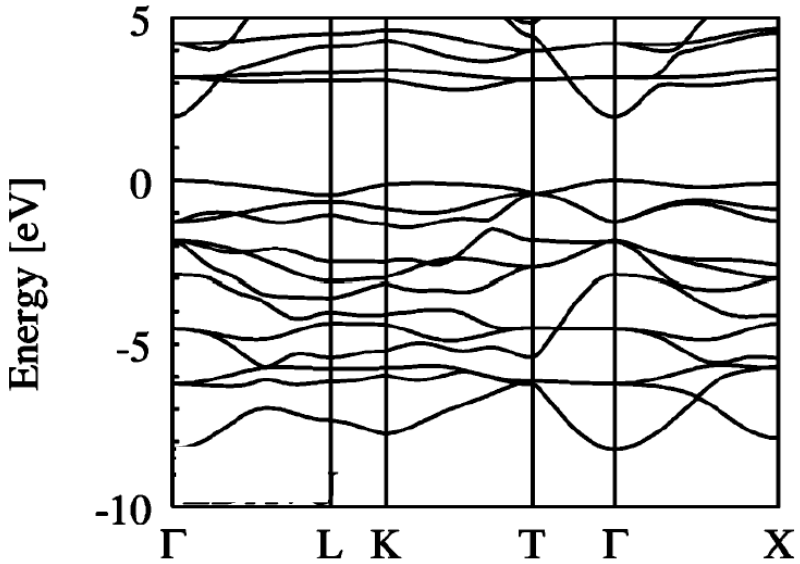
M. Cococcioni and S. de Gironcoli PRB 71, 035105 (2005)

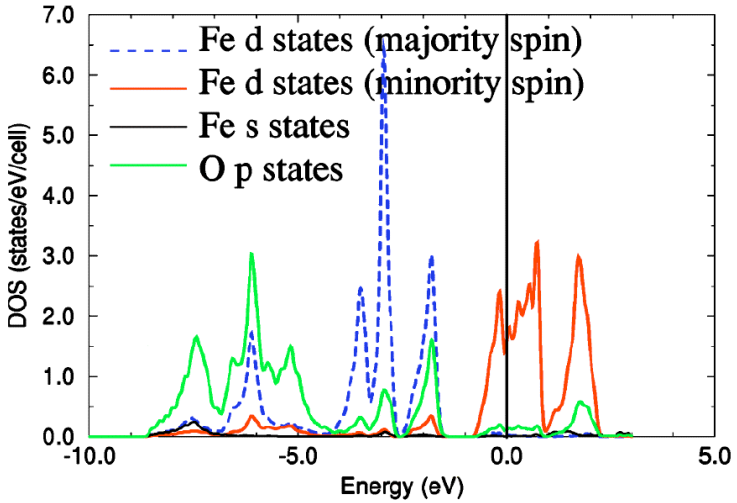
GGA+U FeO

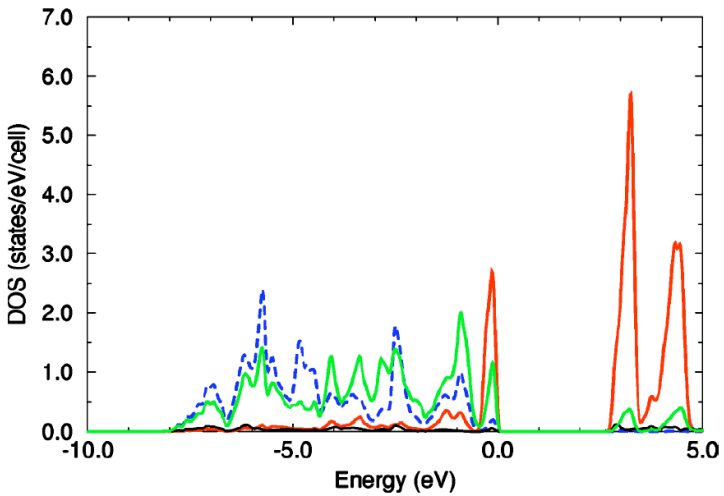
GGA



GGA+U



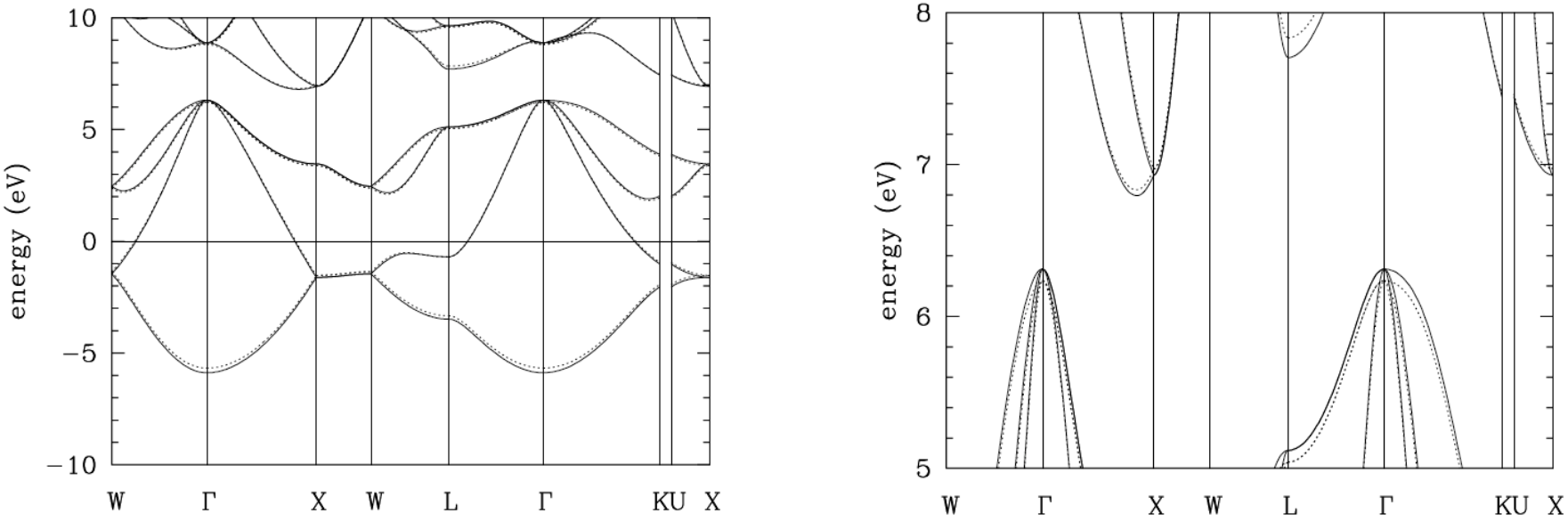




M. Cococcioni and S. de Gironcoli PRB 71, 035105 (2005)

LDA+U description of covalent systems

Si band structure



Si and GaAs: a, B, and E_g

	Si	GaAs(v)[a]
GGA	5.479, 83.0, 0.64	5.774, 58.4, 0.19
+U	5.363, 93.9, 0.39	5.736, 52.6, 0.00
Exp.[c]	5.431, 98.0, 1.12	5.653, 75.3, 1.42

The LDA+U+V functional

Standard DFT+U corrective energy functional:

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

Extended DFT+U+V energy functional:

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

U is the <u>on-site</u> effective interaction, V is the <u>inter-site</u> one.

Occupations are defined in a similar way:

$$n_{mm'}^{IJ\sigma} = \sum_{k,v} f_{kv} \left\langle \psi_{kv}^{\sigma} \middle| \phi_{m'}^{J} \right\rangle \left\langle \phi_{m}^{I} \middle| \psi_{kv}^{\sigma} \right\rangle$$

How does it work?

Energy functional:

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

Potential:

$$V_{U+V}\left|\psi_{kv}^{\sigma}\right\rangle = \frac{\delta E_{U+V}}{\delta \psi_{kv}^{\sigma\,*}} = \sum_{I,\sigma} \frac{U^I}{2} \sum_{m} \left(1-2n_{m'm}^{I\sigma}\right)\left|\phi_{m'}^{I}\right\rangle\left\langle\phi_{m}^{I}\left|\psi_{kv}^{\sigma}\right.\right\rangle$$

$$-\sum_{I,J,\sigma} \frac{V^{IJ}}{2} \sum_{m,m'} n_{m'm}^{JI\sigma}\left|\phi_{m'}^{J}\right\rangle\left\langle\phi_{m}^{I}\left|\psi_{kv}^{\sigma}\right.\right\rangle$$

U encourages on-site occupations;
V favors hybridization (e.g., molecular orbitals)

What are we including/neglecting?

In the inter-site term only some <u>two-site/two orbital</u> terms are included

Coupling between charges on different sites

$$\langle \phi_i^I \phi_j^J \,|V_{ee}|\, \phi_i^I \phi_j^J \rangle \left(n_{ii}^{II\sigma} n_{jj}^{JJ\sigma'} - \delta_{\sigma\sigma'} n_{ij}^{IJ\sigma} n_{ji}^{JI\sigma'} \right)$$

Included

Coupling between cross charge exchanges

$$\langle \phi_i^I \phi_j^J \,|V_{ee}|\, \phi_j^J \phi_i^I \rangle \left(n_{ij}^{IJ\sigma} n_{ji}^{JI\sigma'} - \delta_{\sigma\sigma'} n_{ii}^{II\sigma} n_{jj}^{JJ\sigma'} \right)$$

Neglected

Coupling between "parallel" charge exchanges

$$\langle \phi_i^I \phi_{i'}^I \,|V_{ee}|\, \phi_j^J \phi_{j'}^J \rangle \left(n_{ij}^{IJ\sigma} n_{i'j'}^{IJ\sigma'} - \delta_{\sigma\sigma'} n_{ij'}^{IJ\sigma} n_{i'j}^{IJ\sigma'} \right)$$

Neglected

Coupling between intra-site charge exchanges

$$\langle \phi_i^I \phi_j^J \,|V_{ee}|\, \phi_{i'}^I \phi_{j'}^J \rangle \left(n_{ii'}^{II\sigma} n_{jj'}^{JJ\sigma'} - \delta_{\sigma\sigma'} n_{ij'}^{IJ\sigma} n_{ji'}^{JI\sigma'} \right)$$

Neglected

Coupling between charge and hopping

$$\langle \phi_i^I \phi_{i'}^I \,|V_{ee}|\, \phi_i^I \phi_j^J \rangle \left(n_{ii}^{II\sigma} n_{i'j}^{IJ\sigma'} - \delta_{\sigma\sigma'} n_{ij}^{IJ\sigma} n_{i'i}^{II\sigma'} \right)$$

Neglected

Effective interactions

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

How can we determine U and V? Let's focus on U first:

$$\langle mm'' | V_{ee} | m'm''' \rangle = \int d\mathbf{r} \int d\mathbf{r}' \frac{\varphi^*_m(\mathbf{r})\varphi^*_{m''}(\mathbf{r}')\varphi_{m'}(\mathbf{r})\varphi_{m'''}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \sum_k a_k(m,m',m'',m''')F^k$$

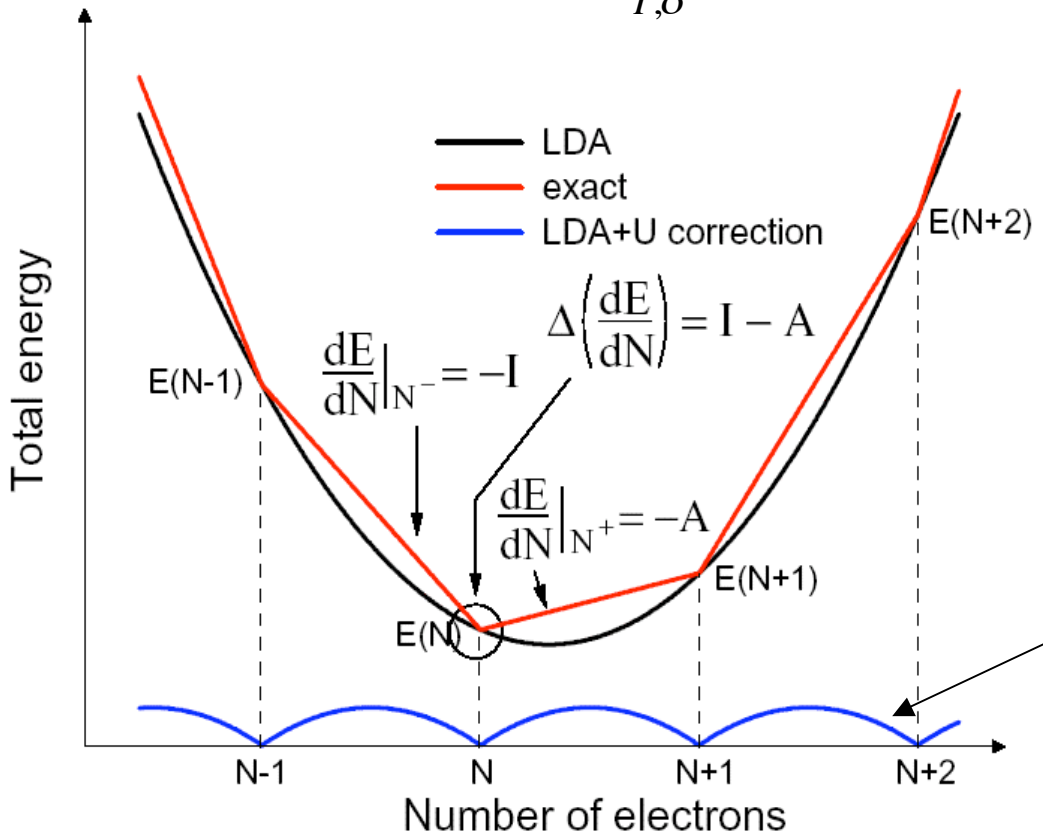
MFA: $$U = \frac{1}{(2l+1)^2} \sum_{m,m'} \langle m,m' | V_{ee} | m,m' \rangle = F^0$$

We want screened (effective) interactions; F^k are unscreened

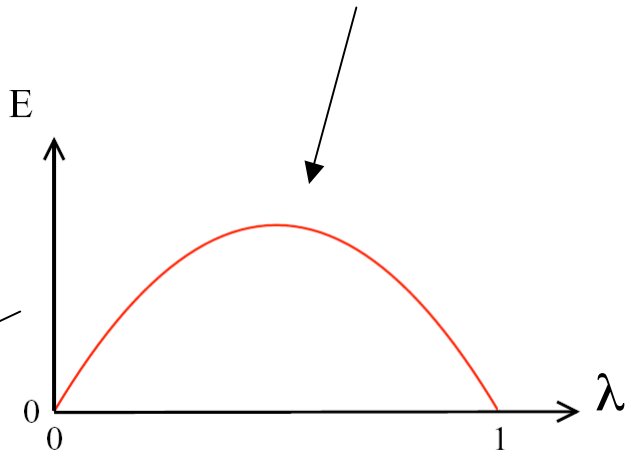
We compute U from the linear response of the system in the DFT ground state we aim to correct

What does U represent?

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



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



$$\frac{dE}{dn_i} = \epsilon_i \Rightarrow U = \frac{d^2E}{dn_i^2}$$

Evaluation of U (and V)

- U is the unphysical curvature of the DFT total energy
- We want effective interactions: we evaluate U from the DFT ground state
- A free-electron contribution (due to re-hybridization) is to be subtracted in crystals (see also Pickett, Erwin and Ethridge, PRB56, 1201):

$$U = \frac{d^2 E^{GGA}}{d(n^I)^2} - \frac{d^2 E_0^{GGA}}{d(n^I)^2}$$

From self-consistent ground state (screened response)

From fixed-potential diagonalization (Kohn-Sham response)

Band gap in semiconductors/insulators: $\Delta = \Delta_{KS} + \Delta_{xc}$

Linear response

Using potential shifts α_I as perturbation parameters we can easily evaluate response matrices:

$$E\left[\{\alpha_I\}\right] = \min_{n(\mathrm{r})}\left\{ E\left[n(\mathrm{r})\right] + \sum_I \alpha_I n^I \right\} \qquad \chi^0_{IJ} = \frac{dn^I_0}{d\alpha_J} \qquad \chi_{IJ} = \frac{dn^I}{d\alpha_J}$$

χ^0 is the bare response of the system, χ the fully interacting (screened) one

- Run a self-consistent (unperturbed) calculation.
- Starting from saved potential and wavefunction add the perturbation
- The response χ^0 is evaluated at the first iteration (at fixed potential)
- The response χ is evaluated at self consistency

The effective interaction is finally obtained as:

$$U = -\frac{d\alpha_I}{dn^I} + \frac{d\alpha_I}{dn^I_0} = \left(\chi_0^{-1} - \chi^{-1}\right)_{II} \; V^{IJ} = \left(\chi_0^{-1} - \chi^{-1}\right)_{IJ}$$

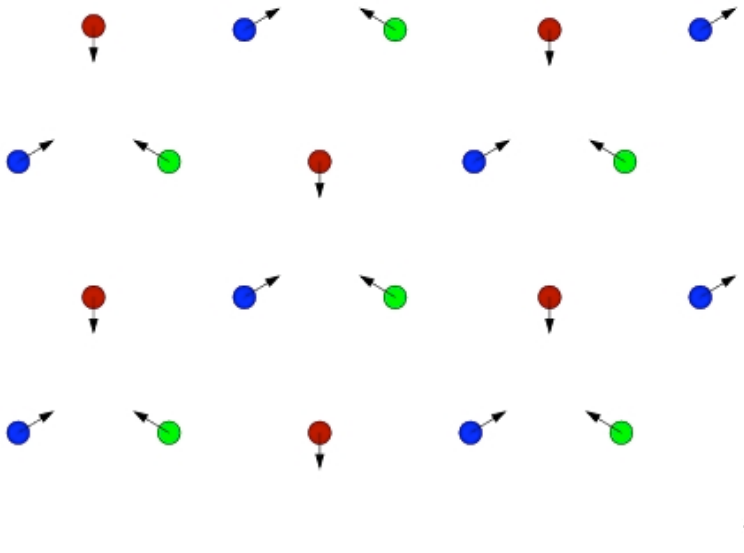
M. Cococcioni and S. de Gironcoli PRB 71, 035105 (2005)

Advantages of the method

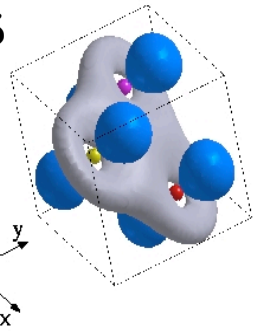
- ✓ Fully ab-initio estimate of the effective interaction (no guess or semiempirical evaluation is needed)
- ✓ Consistency of the effective interaction with the definition of the energy functional and of the on-site occupations;
  - other localized basis sets can be equivalently used: gaussians, Wannier functions etc
- ✓ Consistency with the approximation used for E_{xc}
- ✓ Dependence on structure, spin state, chemical environment
- ✓ Easy implementation in different computational schemes

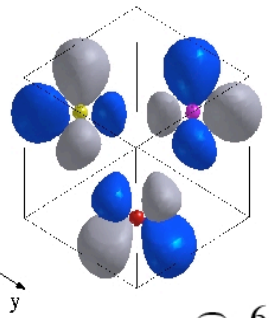
GGA+U FeO: the Broken Symmetry Phase

(111) Plane of Fe



"old" GS



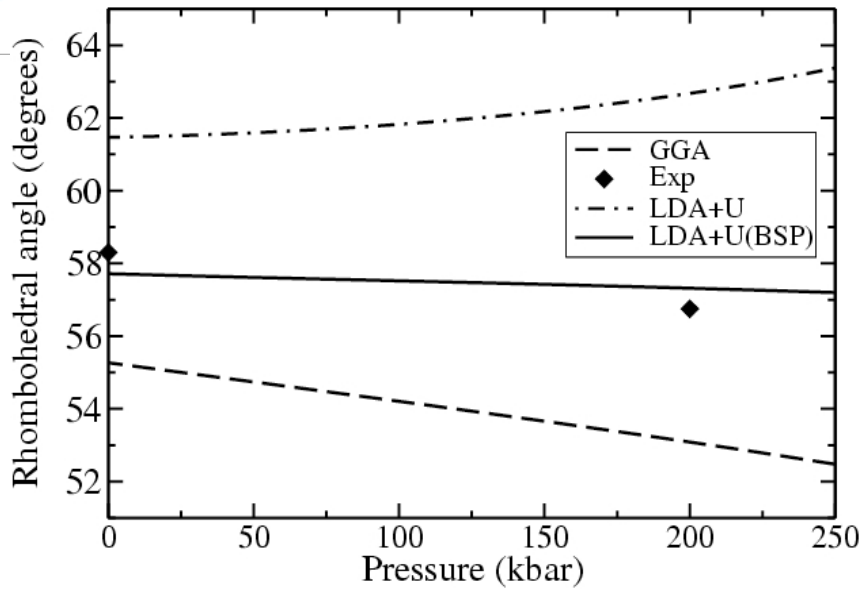


"new" GS

New frustrated electronic GS: correlation-stabilized orbital ordering

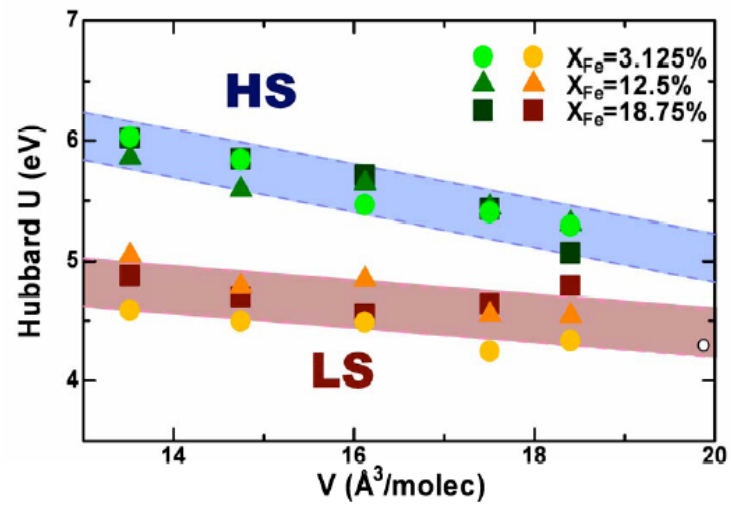
In the new electronic ground state the observed tetrahedral distorsion under pressure is reproduced.

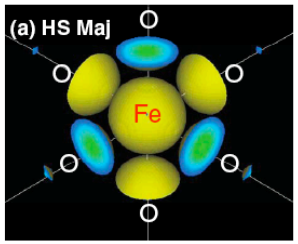
M. Cococcioni and S. de Gironcoli PRB 71, 035105 (2005)

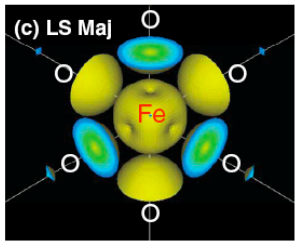


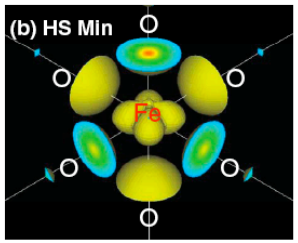
Spin Transition in Magnesiowustite

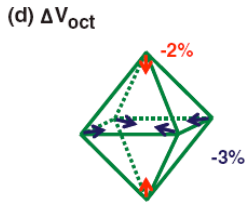
T. Tsuchiya, R. M. Wentzcovitch, C. R. S. da Silva, and S. de Gironcoli,
PRL 96, 198501 (2006)

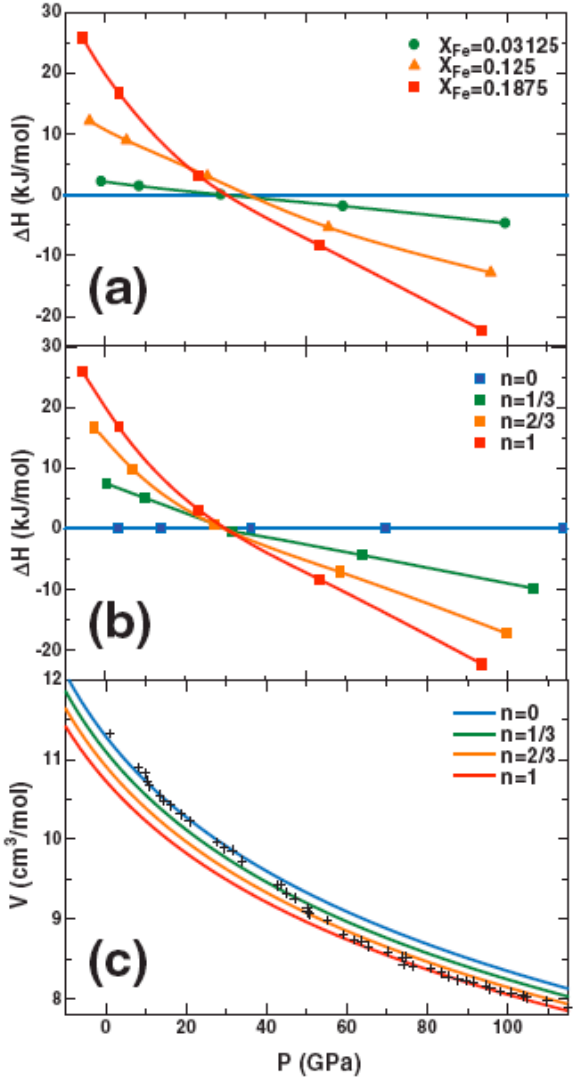




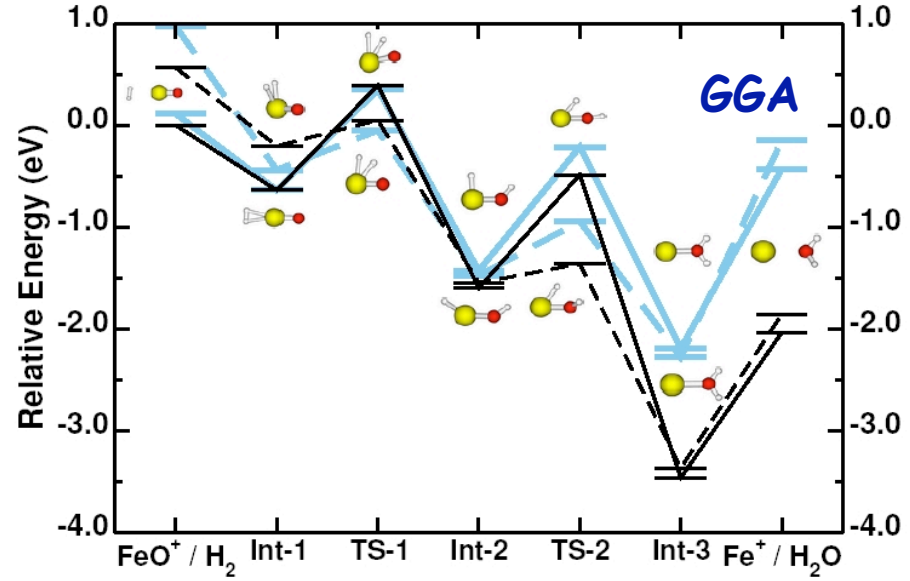


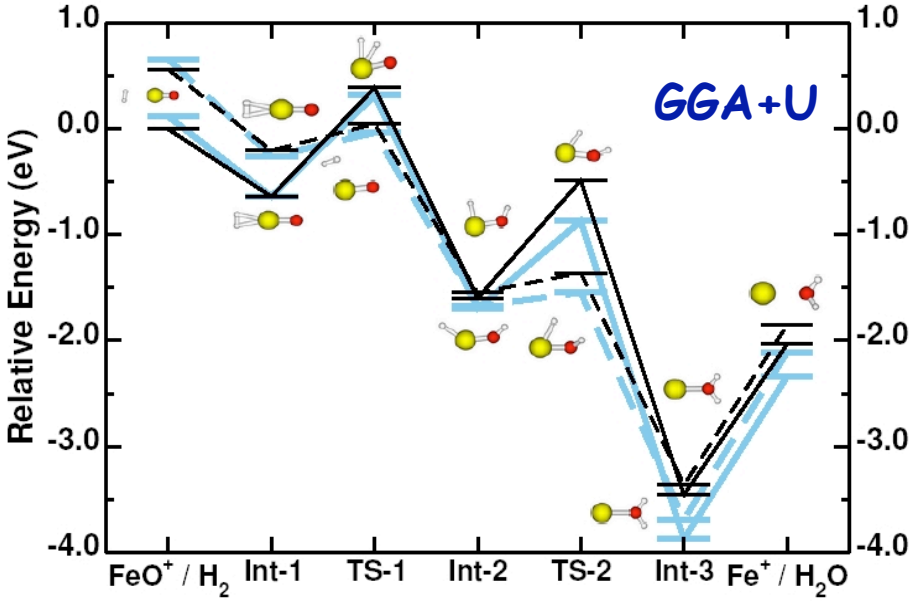






H_2 addition-elimination to FeO^+



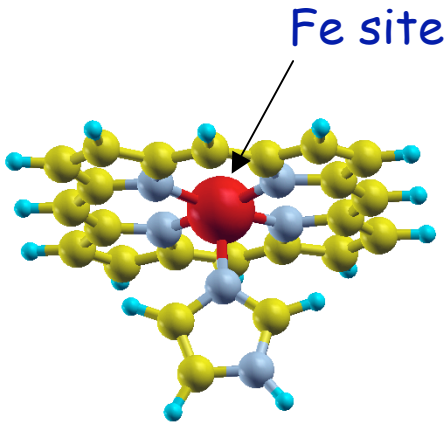


$\Delta E_{6\rightarrow 4}$	GGA	GGA+U	CCSD(T)
FeO^+	0.84	0.54	0.57
Int 1	0.20	0.38	0.43
Int 2	-0.05	0.03	0.05
Int 3	-0.09	0.19	0.09
Fe^+	0.25	0.22	0.18

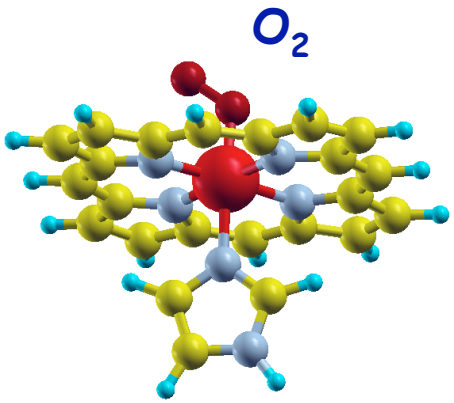
	Forward Reaction			Back Reaction		
ΔE_a	GGA	GGA+U	CCSD(T)	GGA	GGA+U	CCSD(T)
TS-1^4	0.39	0.22	0.25	1.43	1.64	1.60
TS-1^6	0.99	0.96	1.03	1.60	2.02	1.99
TS-2^4	0.54	0.13	0.19	1.34	2.15	2.01
TS-2^6	1.22	0.82	1.11	2.01	3.01	2.98
		(1.16)				

H. J. Kulik, M. Cococcioni, D. Scherlis and N. Marzari, PRL 97, 103001 (2006)

Spin states in the Heme group



Penta-coordinated iron



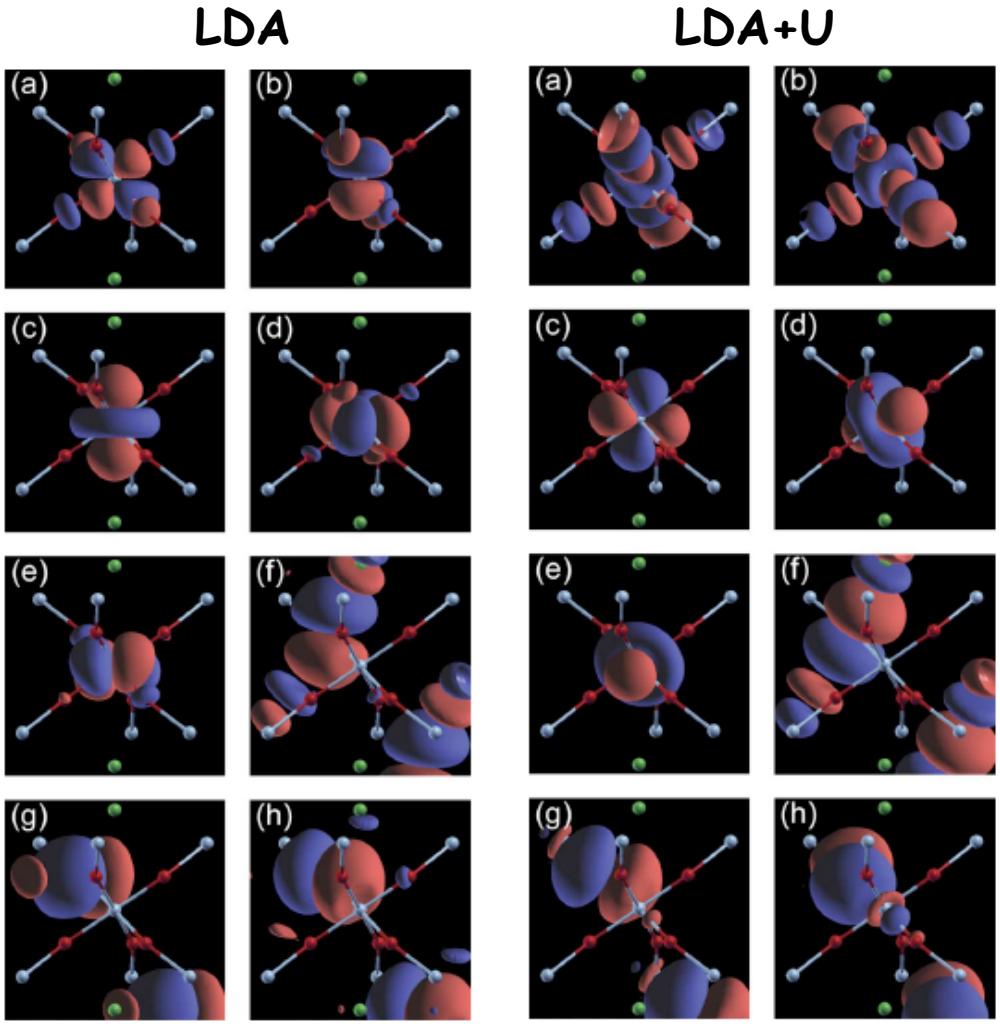
Esa-coordinated iron (O_2, CO, etc)

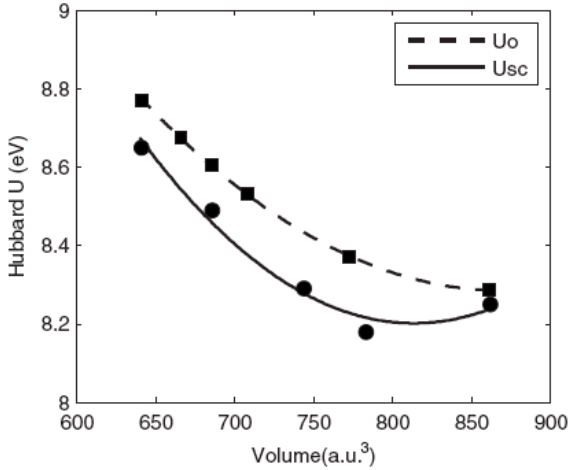
Magnetic ground state

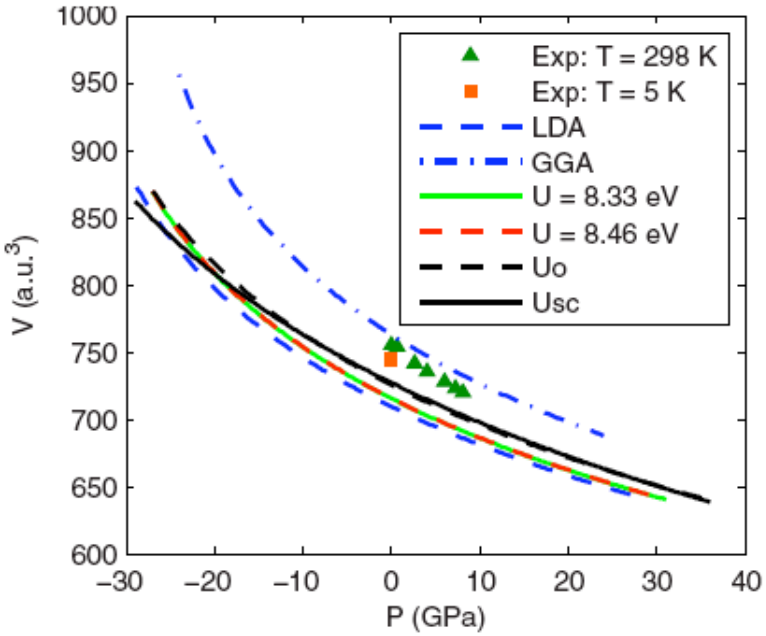
Exp	quintuplet (S=2)	singlet (S=0)
GGA	triplet	singlet
B3LYP	triplet	singlet
HF	quintuplet	quintuplet
GGA+U	quintuplet	singlet

D. Scherlis, H. L. Sit, M. Cococcioni and N. Marzari, Journ. of Phys. Chem. B 111, 7384 (2007)

Structural properties of $LaCoO_3$

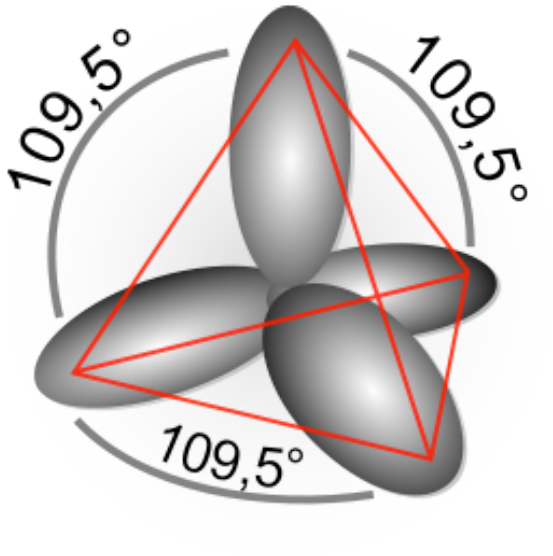






H. Hsu et al, PRB 79, 125124 (2009)

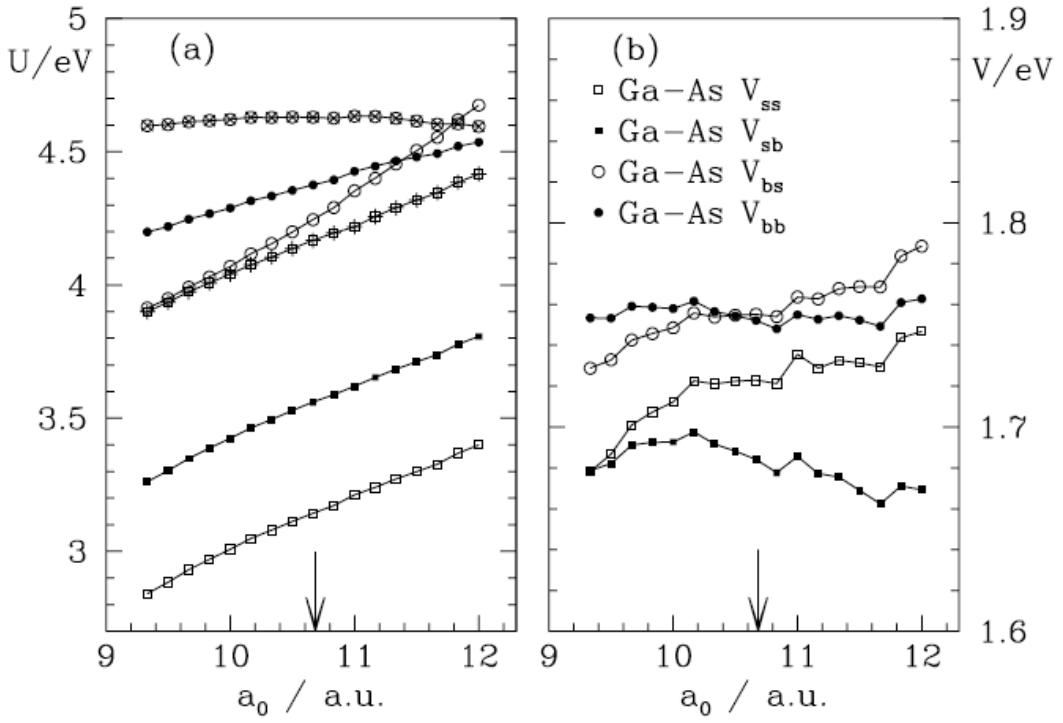
Bulk semiconductors: sp^3 hybridization



U and V computed for (and used on) p and s states.

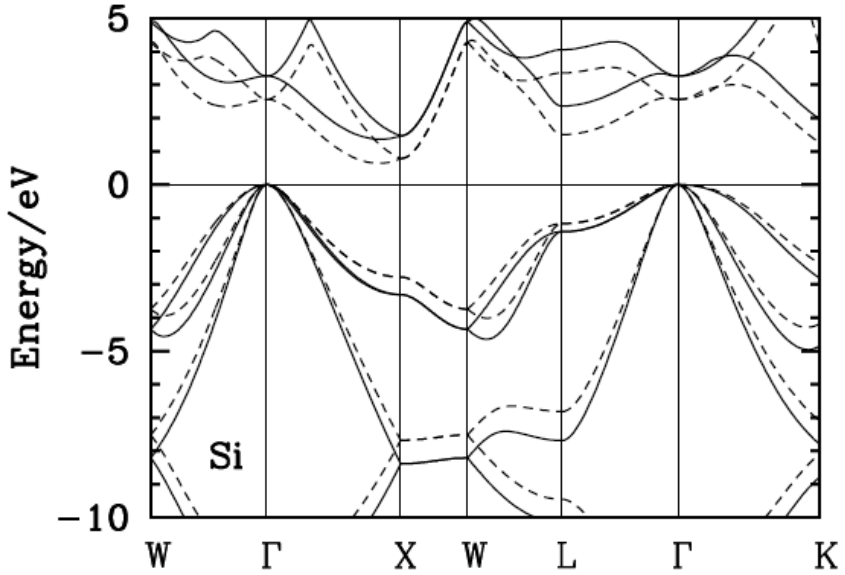
	U_{ss}	U_{sb}	U_{bs}	U_{bb}	V_{ss}	V_{sb}	V_{bs}	V_{bb}
Si-Si	2.82	3.18	3.18	3.65	1.34	1.36	1.36	1.40
Ga-Ga	3.14	3.56	3.56	4.17				
As-As	4.24	4.38	4.38	4.63				
Ga-As					1.72	1.68	1.76	1.75

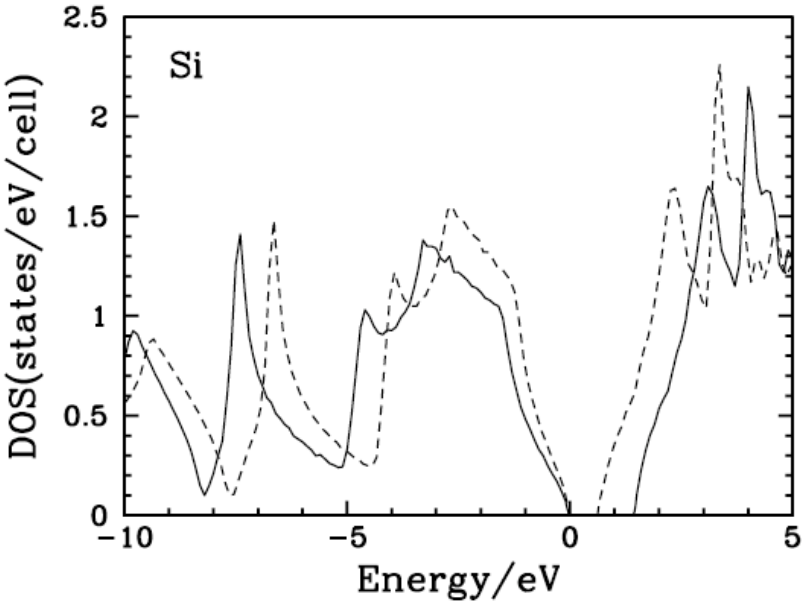
Structural properties of Si and GaAs

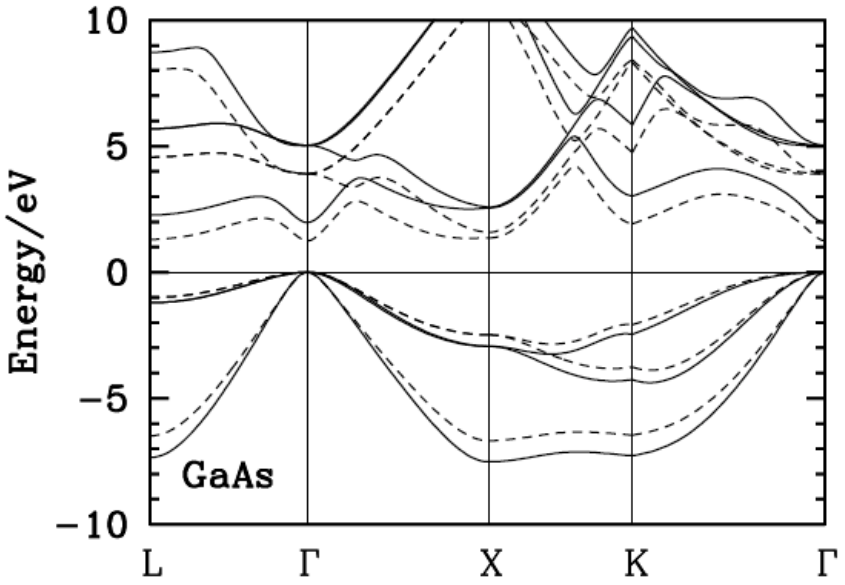


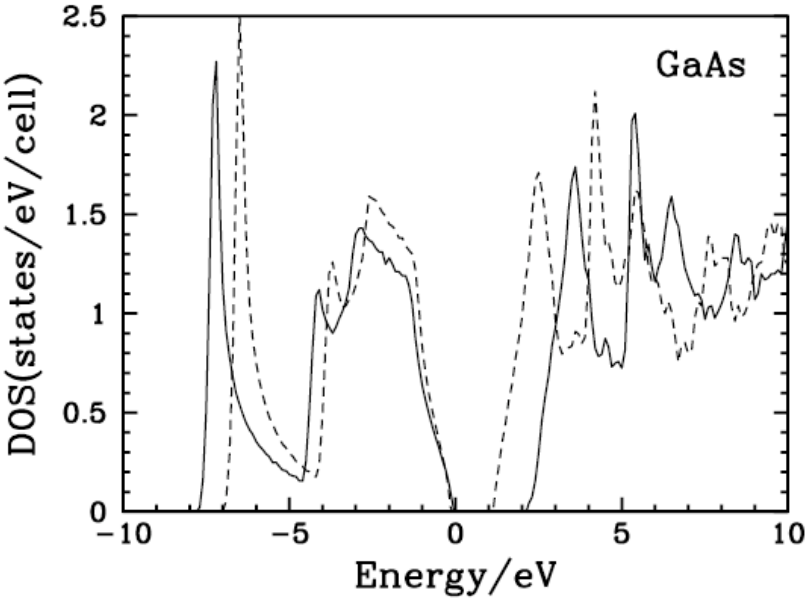
	Si	GaAs(v)[a]
GGA	5.479, 83.0, 0.64	5.774, 58.4, 0.19
+U	5.363, 93.9, 0.39	5.736, 52.6, 0.00
+U+V	5.370, 102.5, 1.36	5.654, 67.7, 0.90
Exp.[c]	5.431, 98.0, 1.12	5.653, 75.3, 1.42

Results: band structure of Si and GaAs

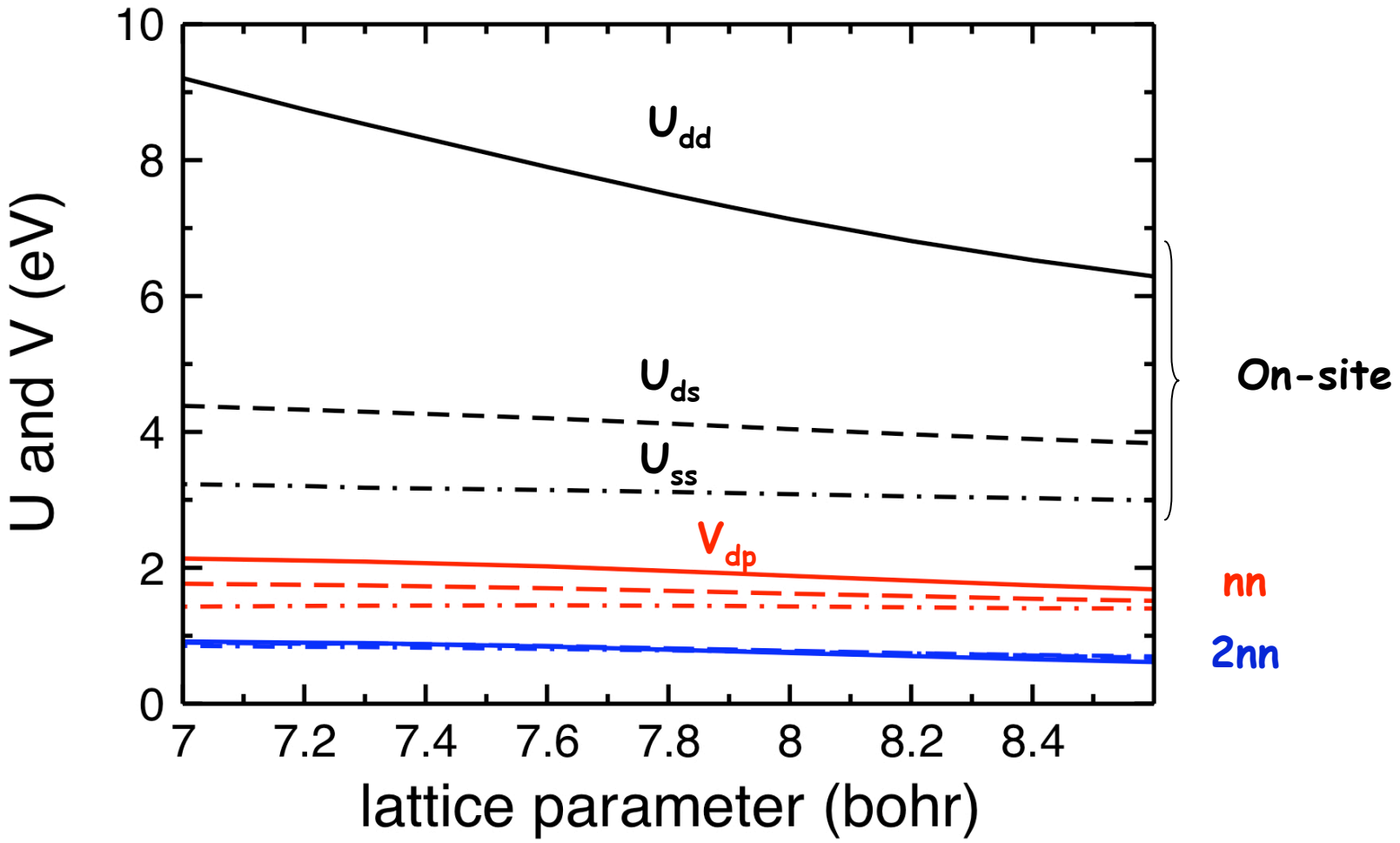




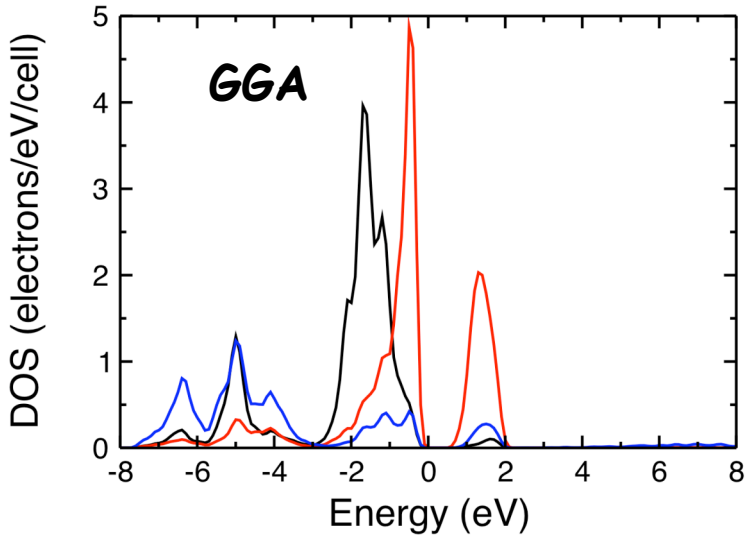


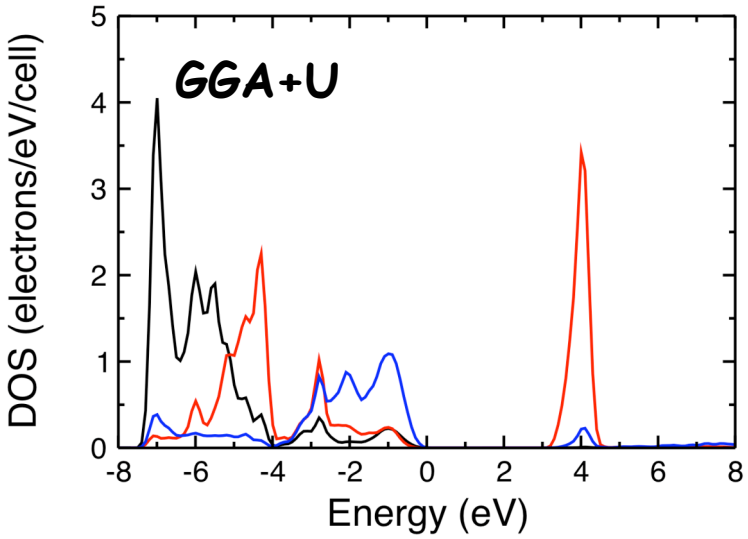


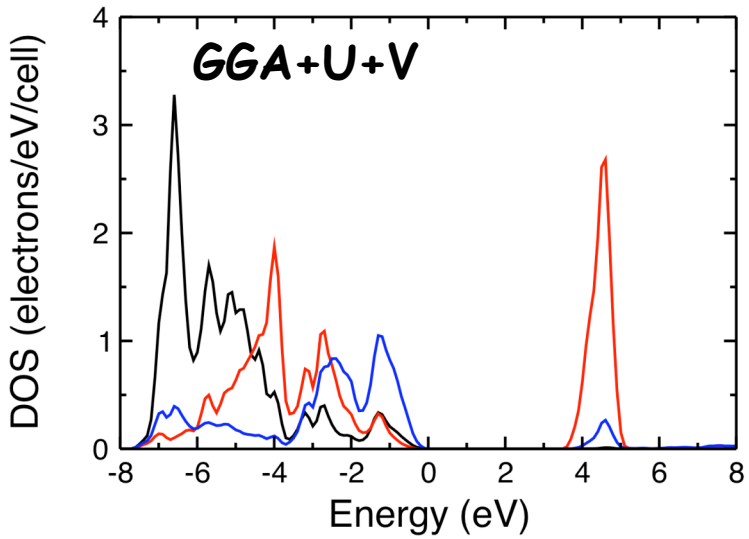
Dependence of U and V on the structure: NiO



NiO







	a	B	E_g
GGA	7.93	188	0.6
GGA+U	8.069	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

Conclusions

- Extended LDA+U+V energy functional with on-site and inter-site interactions
- Two Hubbard-corrected manifolds per atom
- Linear-response calculation of U and V
- Good results for NiO, Si and GaAs: band and Mott insulators treated within the same framework
- Potential applications: high-T_c superconductors, magnetic impurities in semiconductors, metallorganic complexes, bond breaking/forming steps, etc…

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  www.quantum-esresso.org

- Minnesota Supercomputing Institute

Essential bibliography

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