Notable failures of approximate DFT and possible remedies: DFT+U

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Theory and Simulation of Materials
EPFL, Lausanne

Advanced Workshop on High-Performance & High-Throughput Materials Simulations using Quantum ESPRESSO
17/1/2017

Outline

- Rapid refresh of DFT: theory, approximations, success stories
- Notable failures from lack of electronic correlations
- DFT+U: what it is, how it works, success stories
- The meaning of U and its calculation from linear-response
- Some extensions: calculation of U from DFPT and DFT+U+V
- Overview of examples for the afternoon hands-on section

Density functional theory (DFT)

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Variational energy functional:

$$E\left[\rho(\mathbf{r})\right] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F\left[\rho(\mathbf{r})\right]$$

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

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$$E_{xc}[\rho] = \min_{\Psi \to \rho} \langle \Psi[\rho] | - \sum_i \frac{\nabla_i^2}{2m} + \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi[\rho] \rangle - \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r} d\mathbf{r}' - T_0[\rho]$$

Unfortunately, the exact **E_{xc} is not known**.

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Most common approximations (e.g., LDA and GGA) are based on the **homogeneous electron gas**

LDA:

$$E_{xc}^{LDA} = \int \epsilon_{xc}^{heg} \left(\rho(\mathbf{r}) \right) \rho(\mathbf{r}) d\mathbf{r}$$

GGA:

$$E_{xc}^{GGA} = \int \epsilon_{xc}^{GGA} \left(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})| \right) \rho(\mathbf{r}) d\mathbf{r}$$

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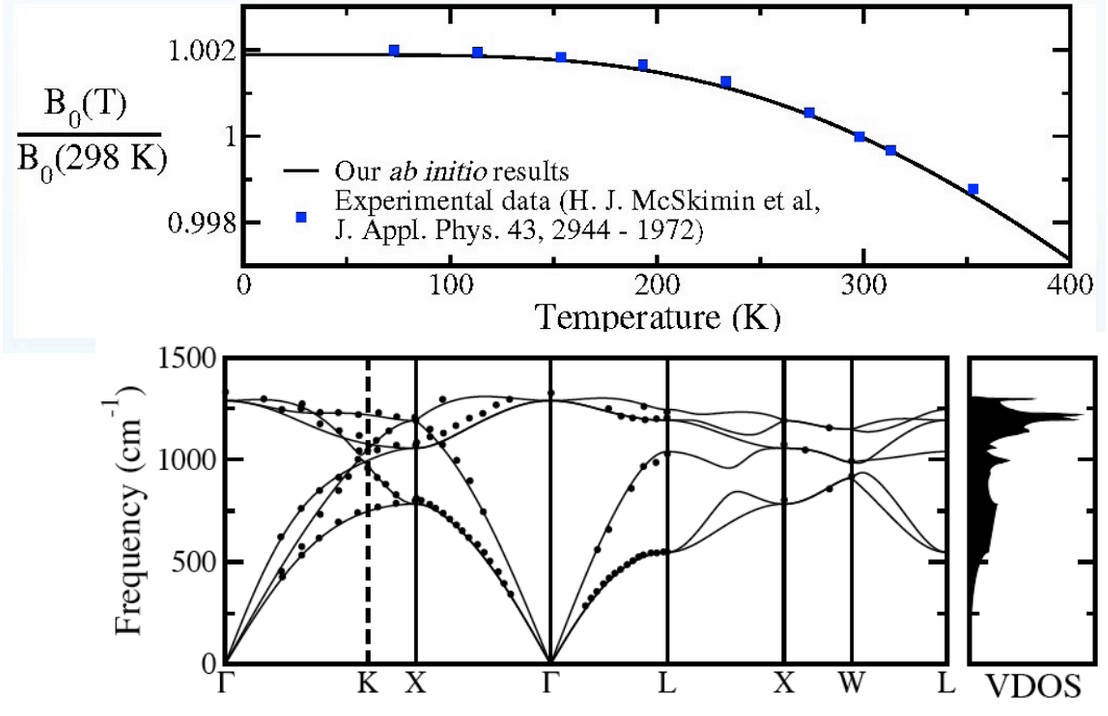
structural and vibrational properties of diamond

	GGA	Exp. (300 K)
a_0 (a.u.)	6.743 (0 k) 6.769 (300 K)	6.740
B (GPa)	432 (0 K) 422 (300 K)	442



N. Mounet, et al., PRB 71, 205214 (2005)

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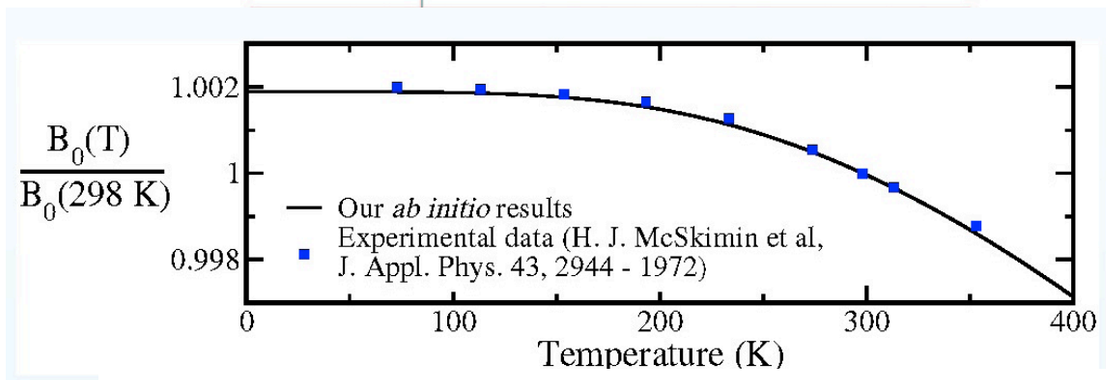

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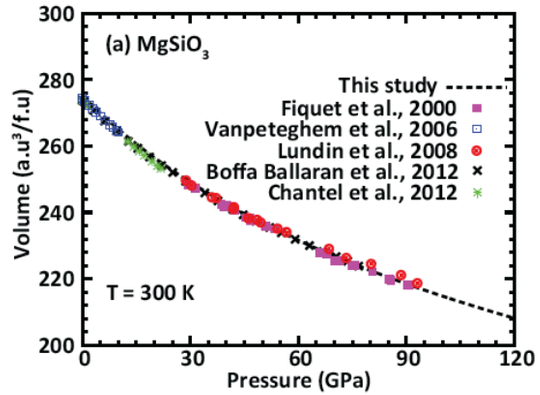
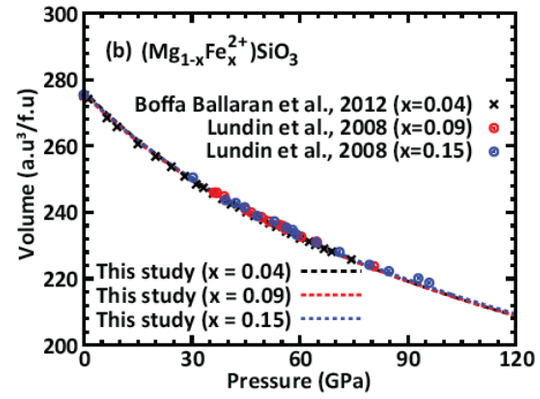
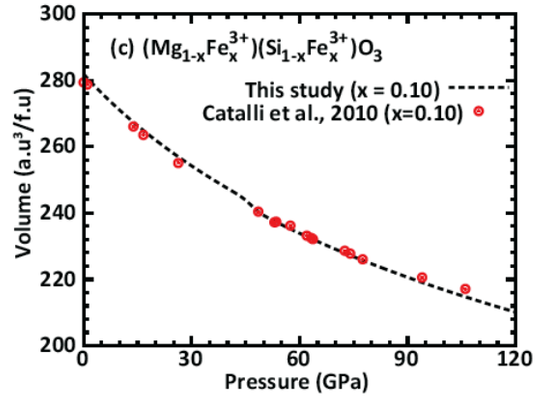
structural deformation of bridgmanite under P

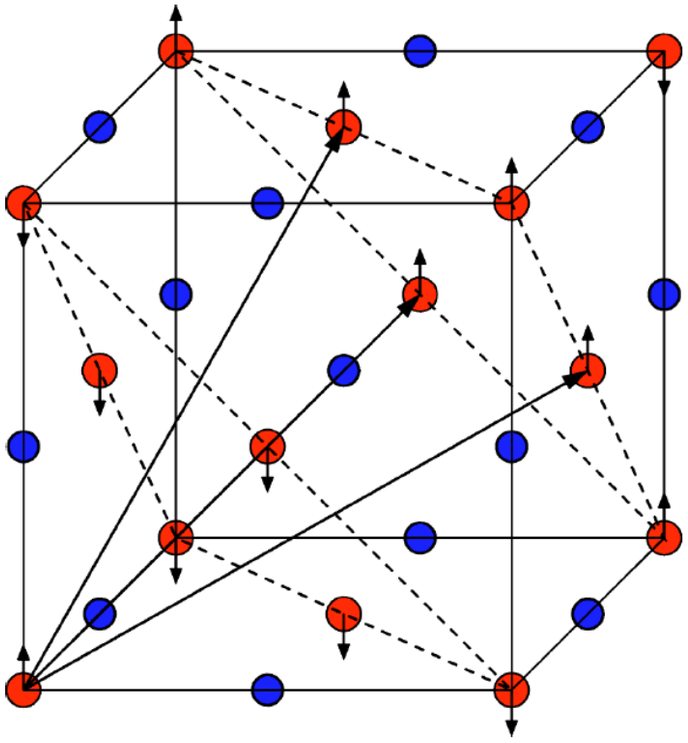






Shukla et al., arXiv:1603.08947 (2016)

Problematic materials: TM oxides



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- **FM ground state (FeO)**
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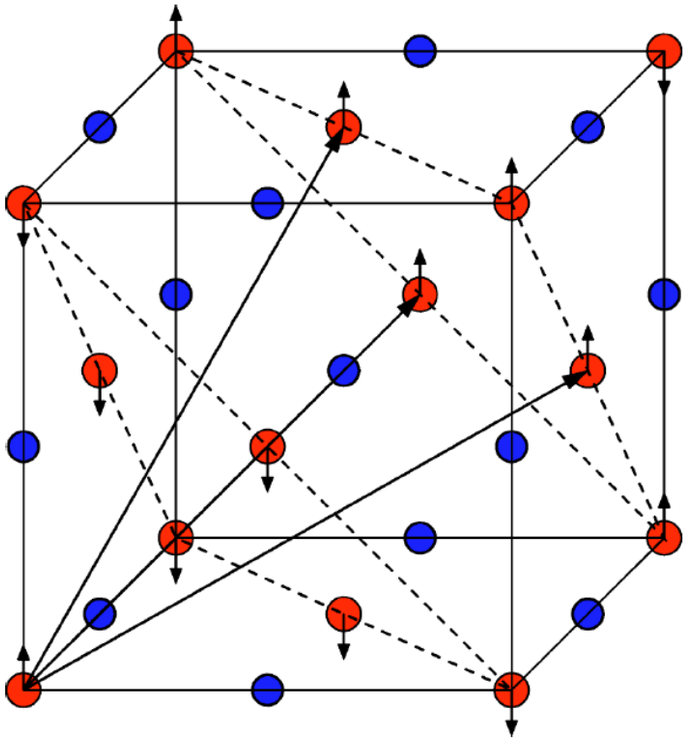

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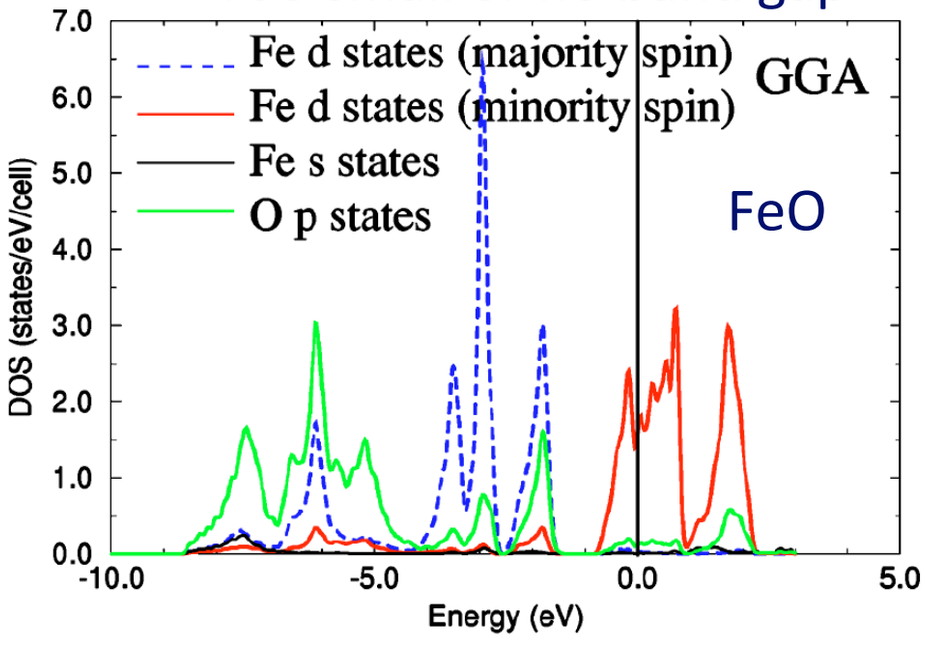

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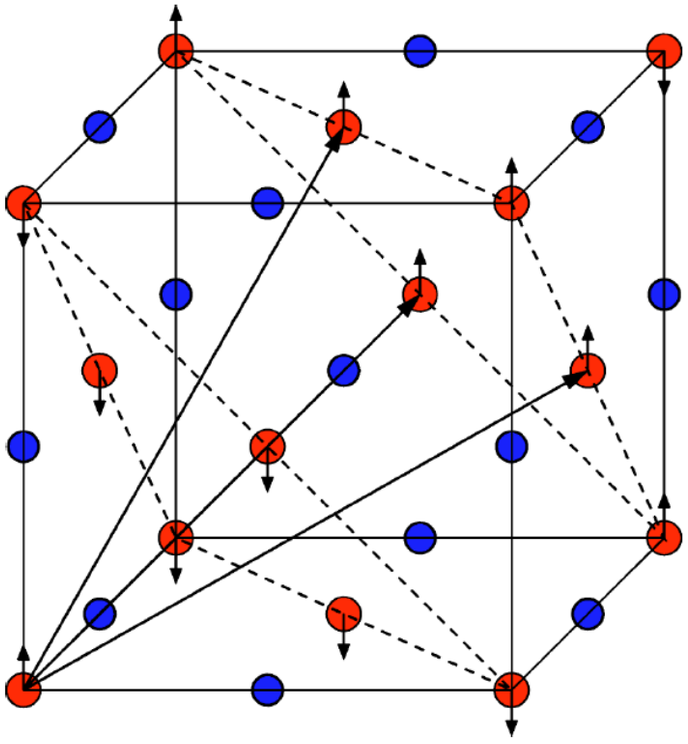

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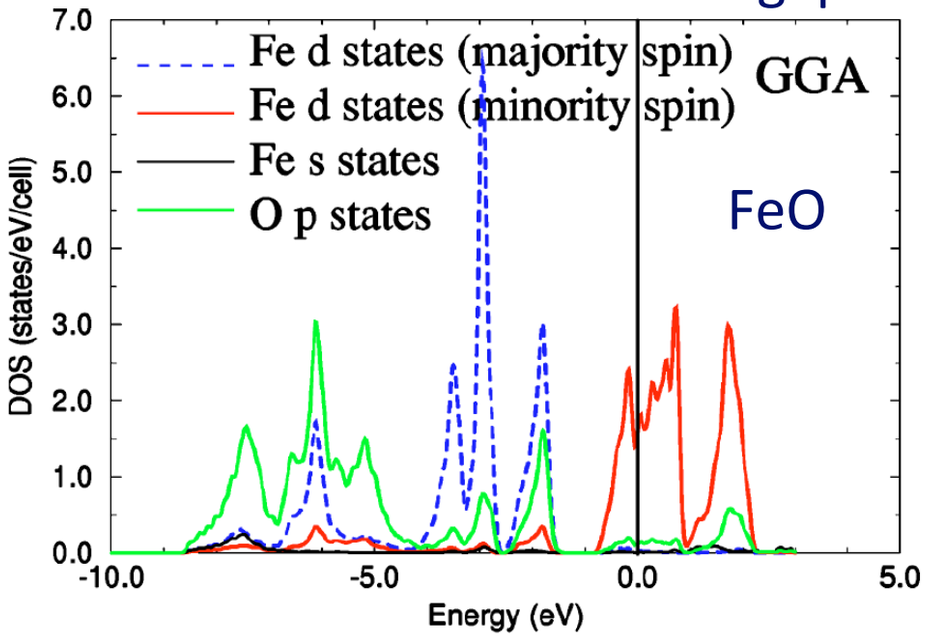
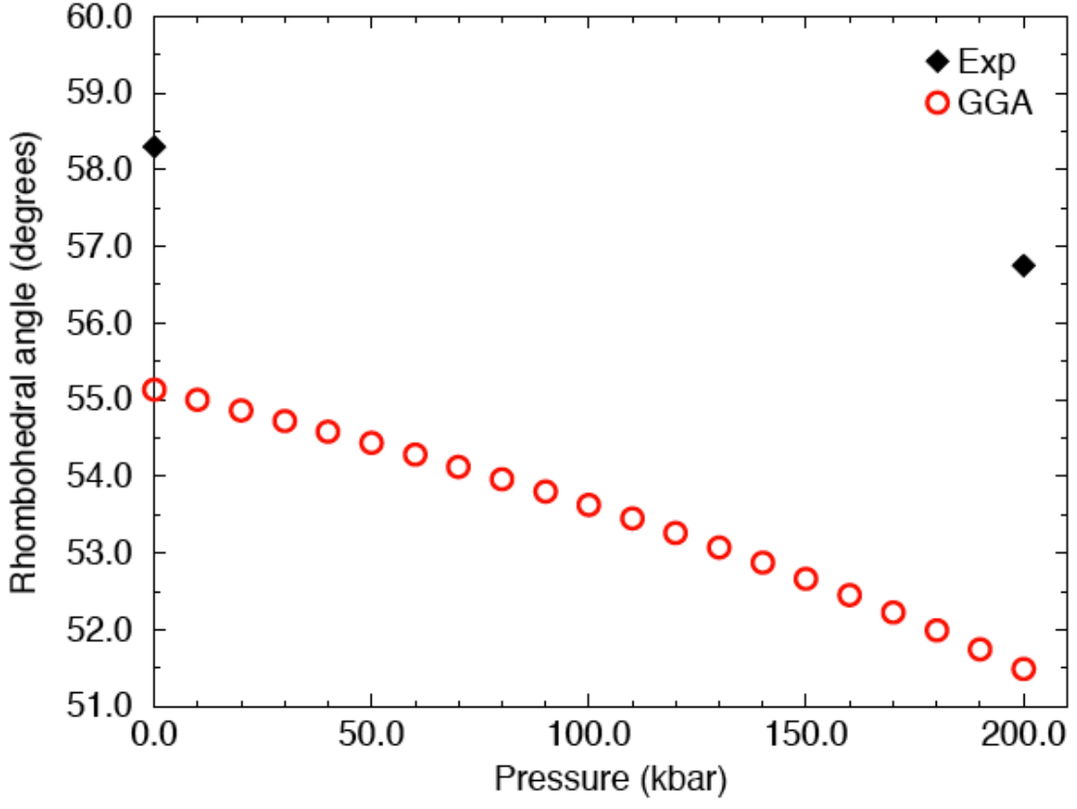
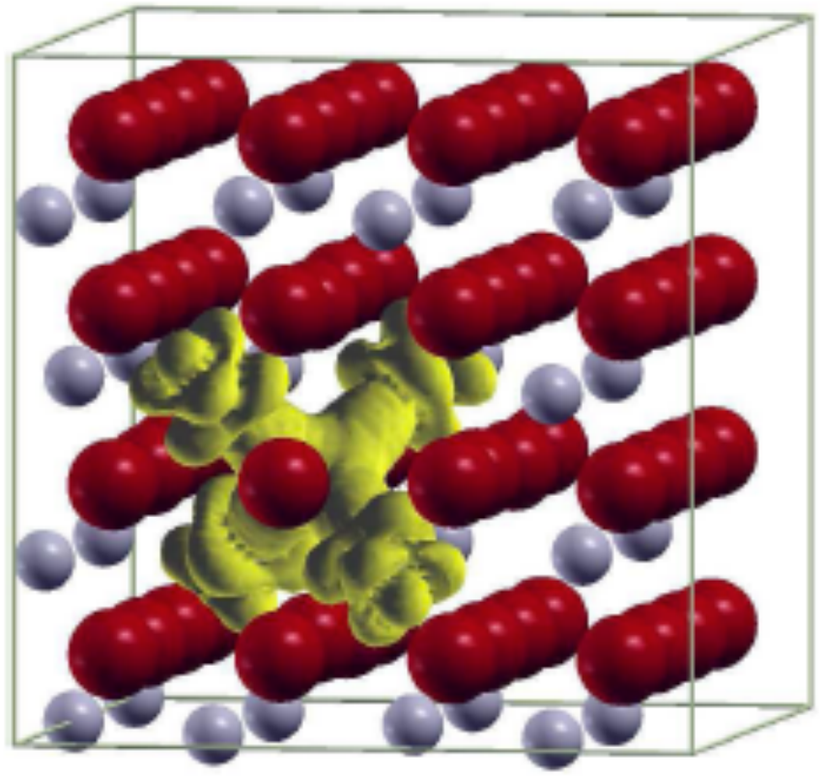


Rhombohedral distortion overestimated



Localization on defects

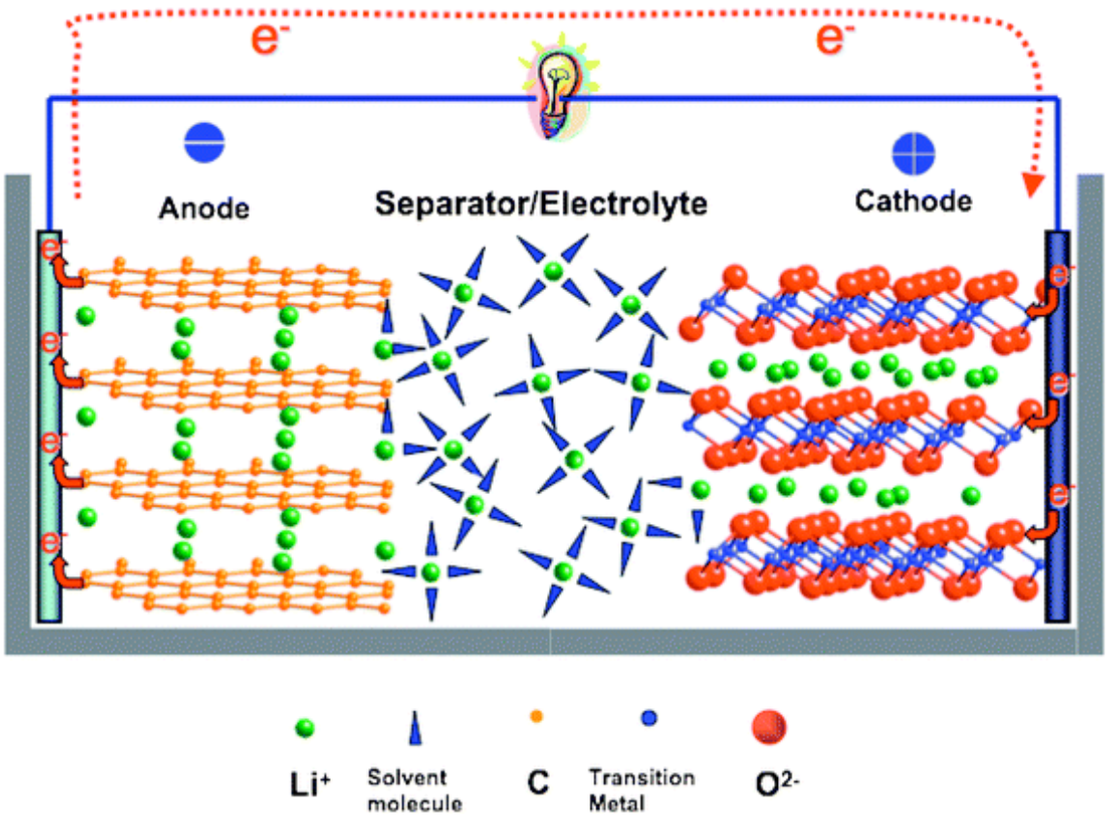
CeO_2 oxygen vacancy



S. Fabris *et al.*, *PRB* 71, 041102 (2005)

The two extra electrons left behind by the O vacancy are delocalized over 4 Ce atoms

Electronic localization and energy: mixed valence materials



Cathodes - Li_xMPO_4 olivines

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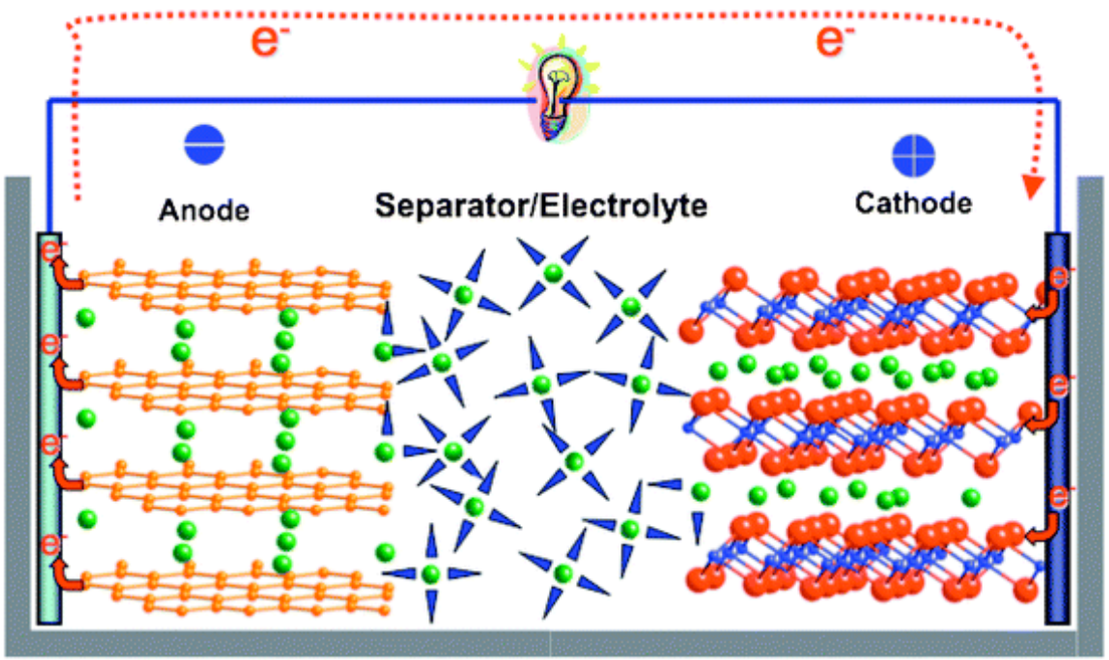

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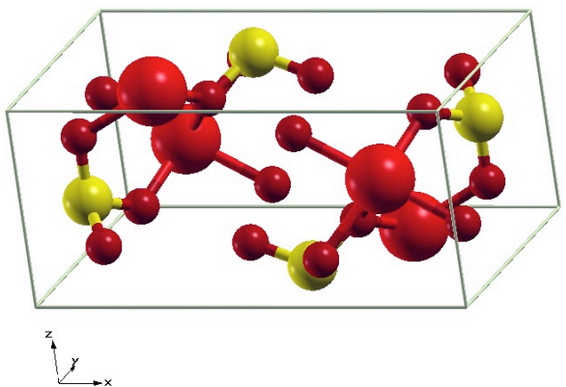
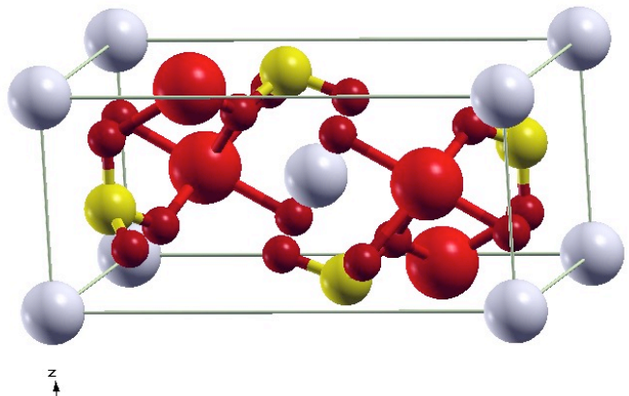
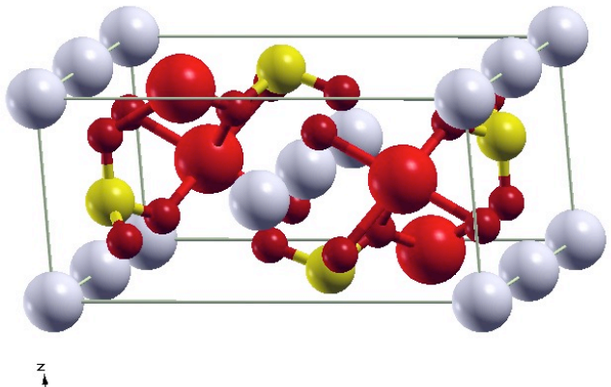
Discharge of the battery

MPO_4





$LiMPO_4$



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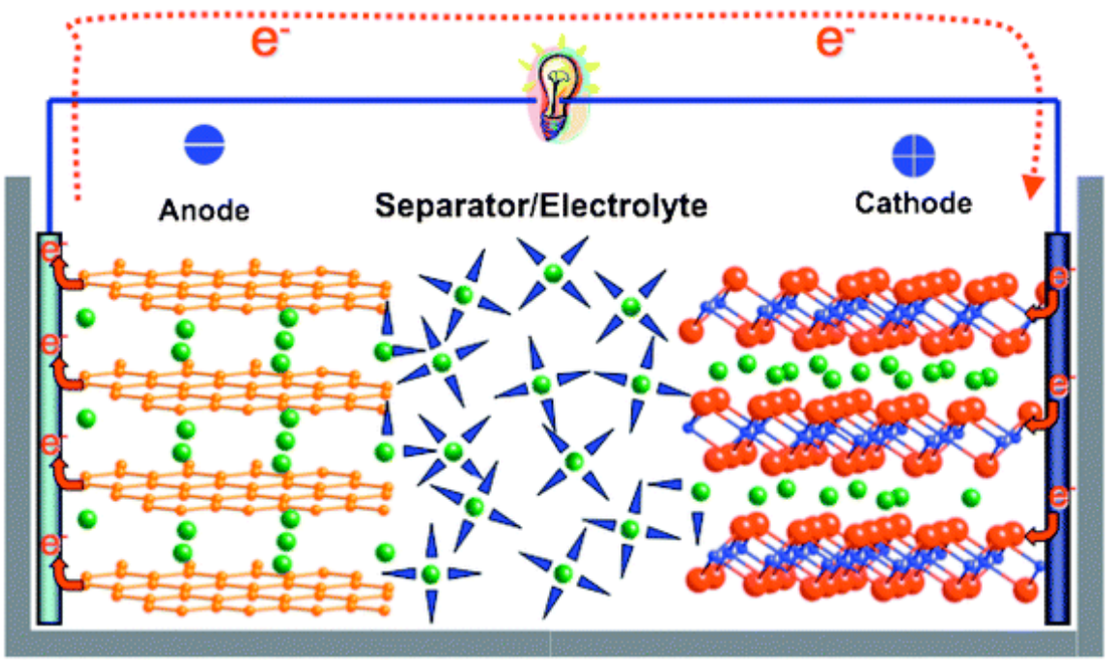

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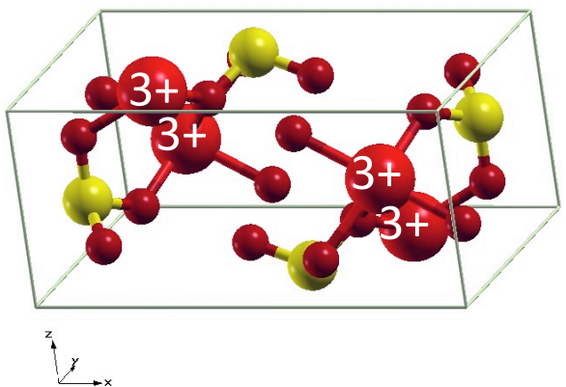

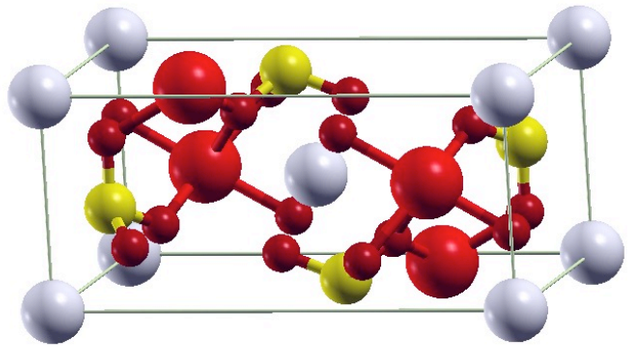

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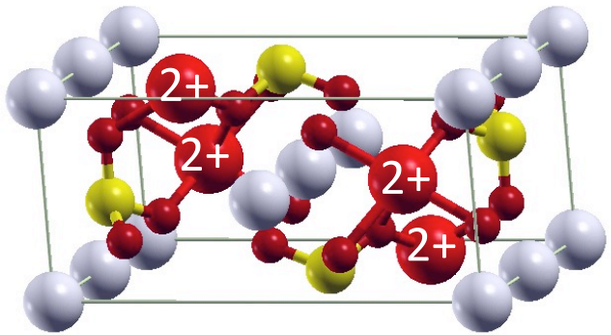

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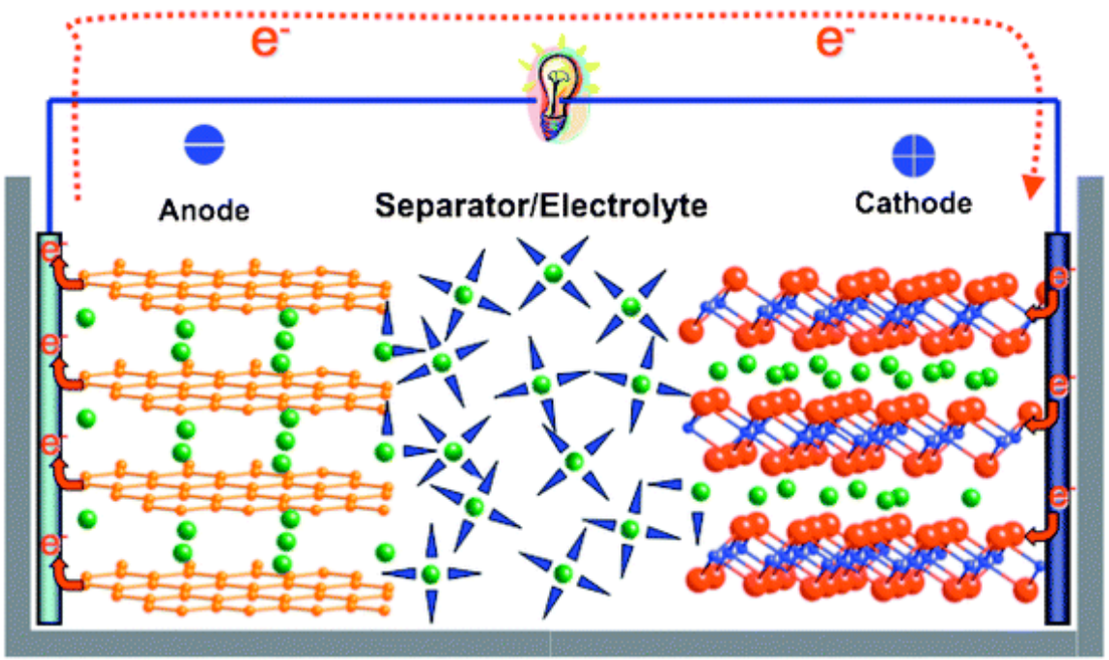

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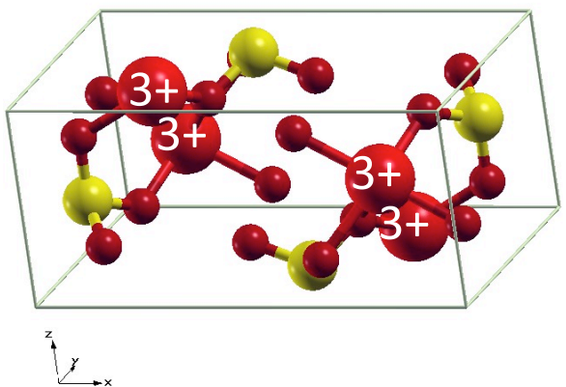

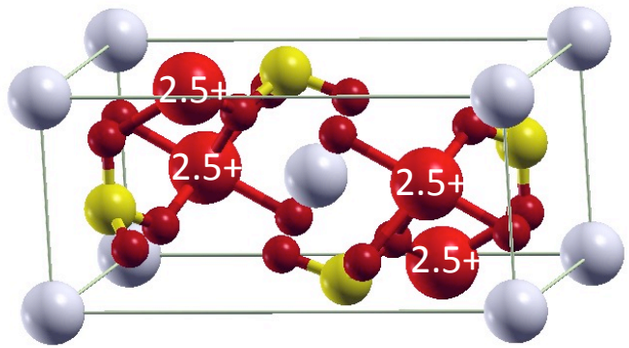

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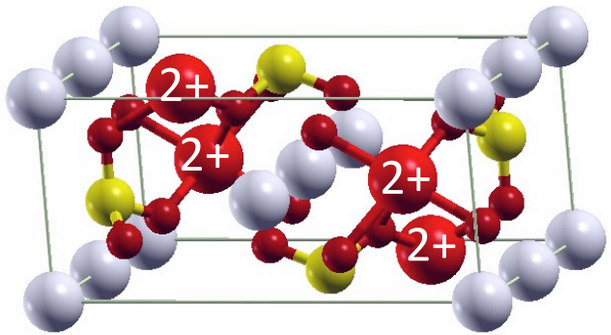

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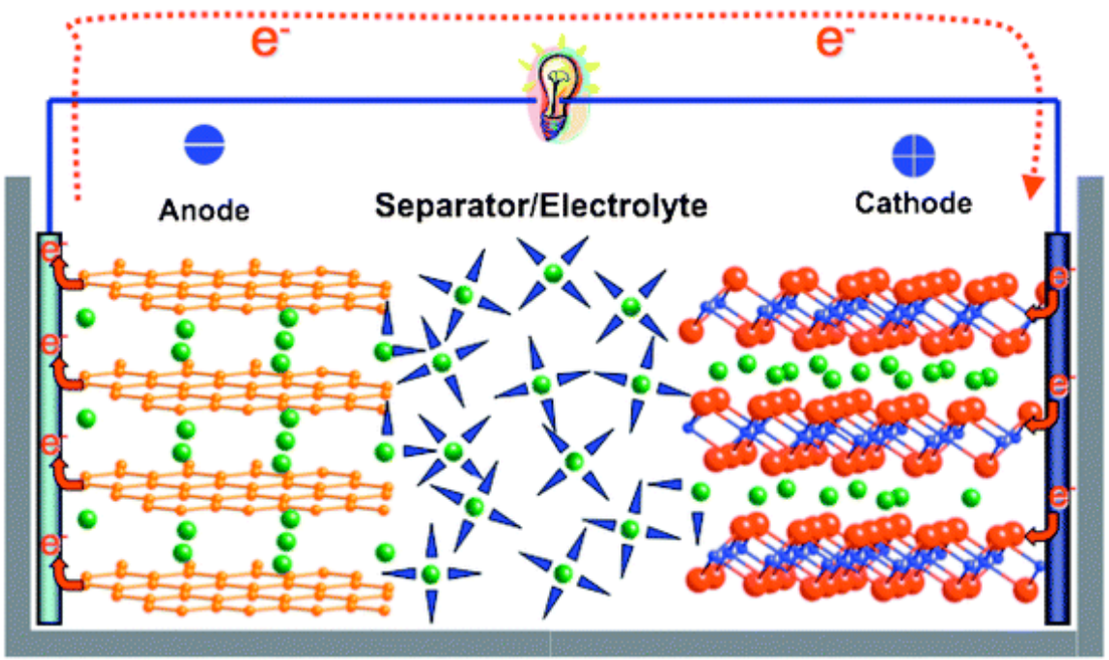

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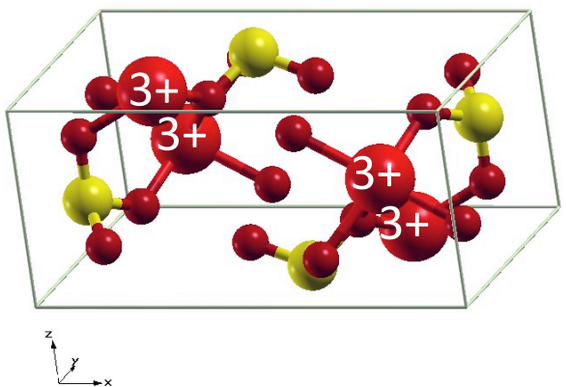
M in 2.5+ oxidation state: **metallic ground state**

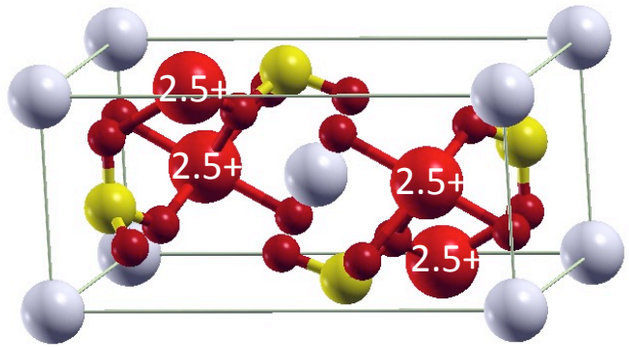
electronic delocalization compromises:

- formation energies and average voltages
- equilibrium structures, magnetization, etc

Discharge of the battery

MPO_4





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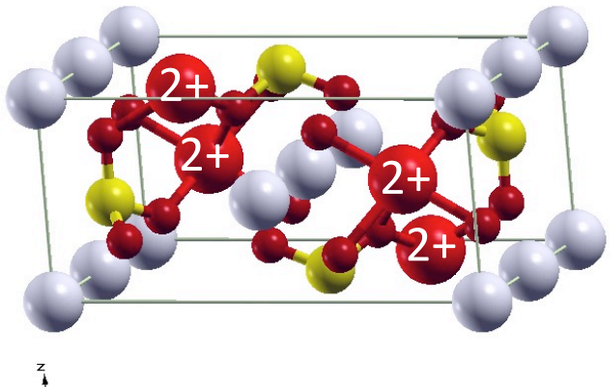

Electronic localization and energy

$$\mathrm{F.\ E.} = \mathrm{E(Li_xFePO_4)} - \mathrm{xE(LiFePO_4)} - (1-\mathrm{x})\mathrm{E(FePO_4)}$$

$$\langle V \rangle = -\frac{\mathrm{E(Li_{x_2}FePO_4)} - \mathrm{E(Li_{x_1}FePO_4)} - (\mathrm{x_2}-\mathrm{x_1})\mathrm{E(Li_{bulk}})}{F}$$

Li_xFePO_4	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 3.5
GGA	-126	2.73

Li_xMnPO_4	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 4.1
GGA	63	2.82

Other problematic materials

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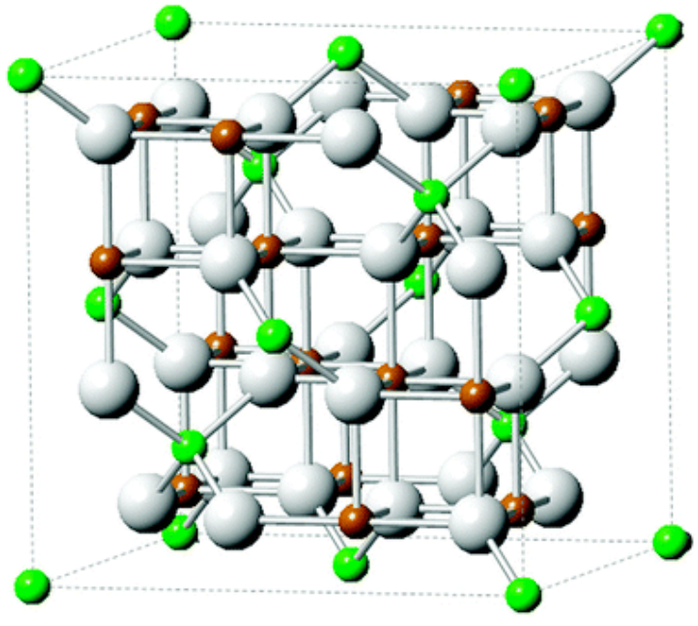

mixed-valence oxides:Fe_3O_4/Co_3O_4

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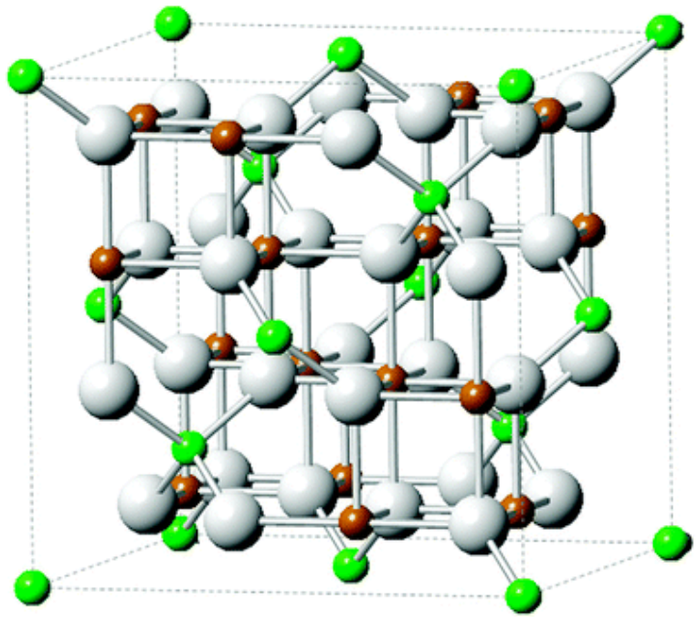

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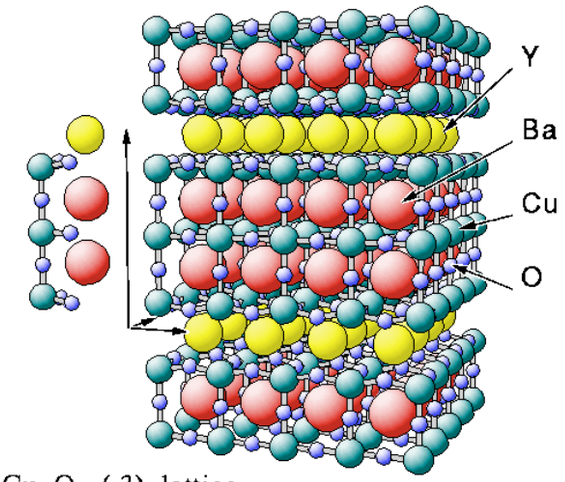
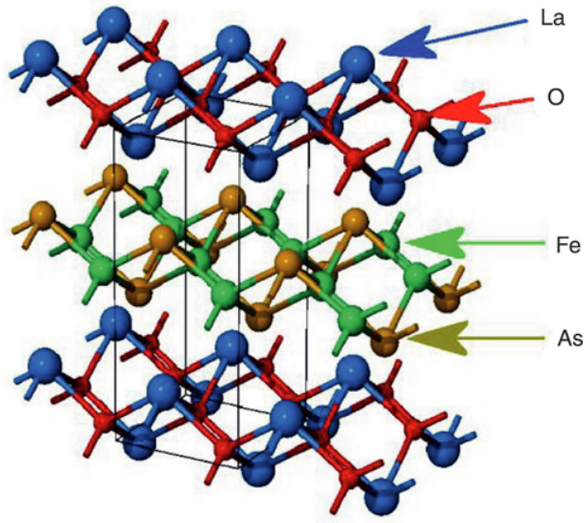


$YBa_2Cu_3O_7$ (.3) lattice



LaFeAsO

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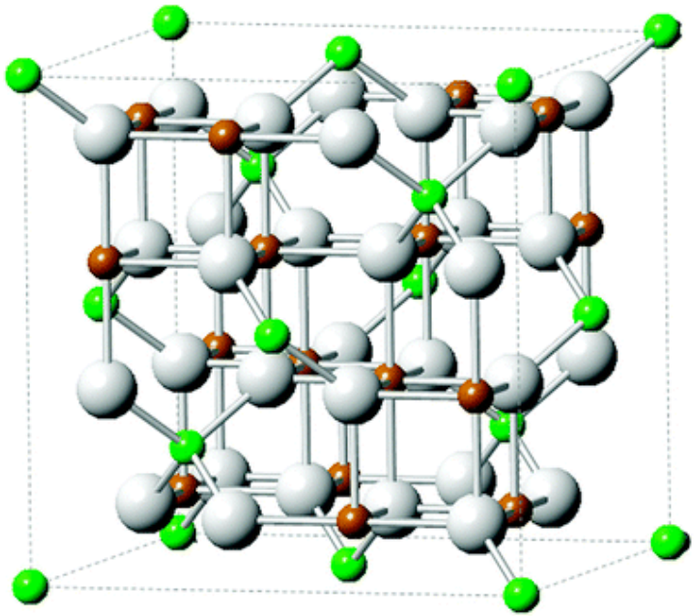

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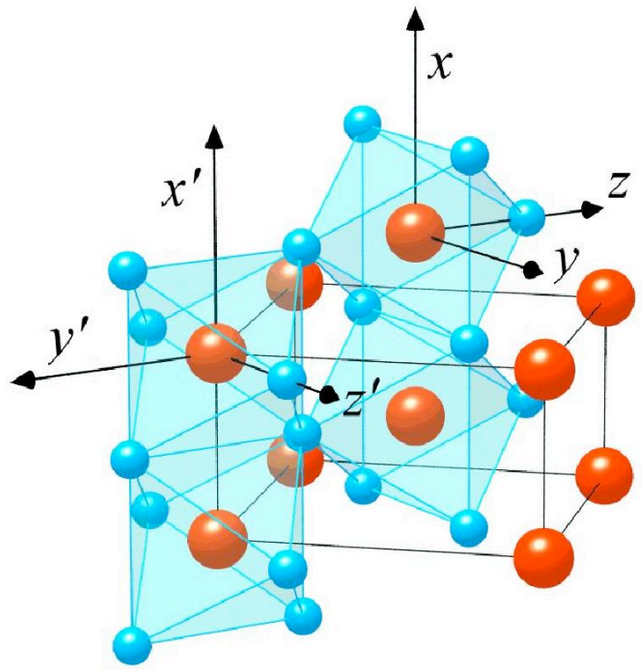

metal to insulator transitions: VO_2

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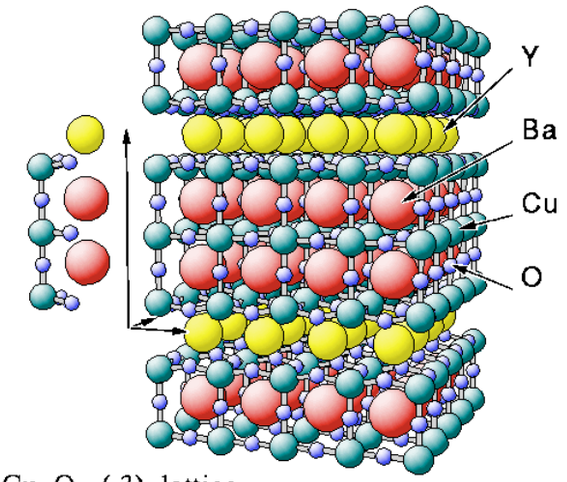

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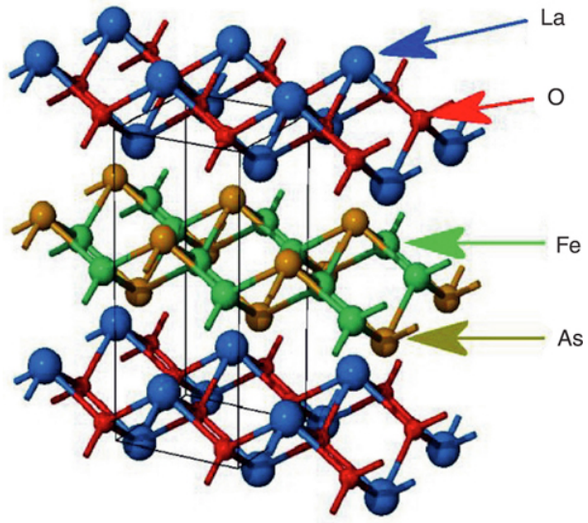

LaFeAsO

Molecular dissociation: H_2 and H_2^+

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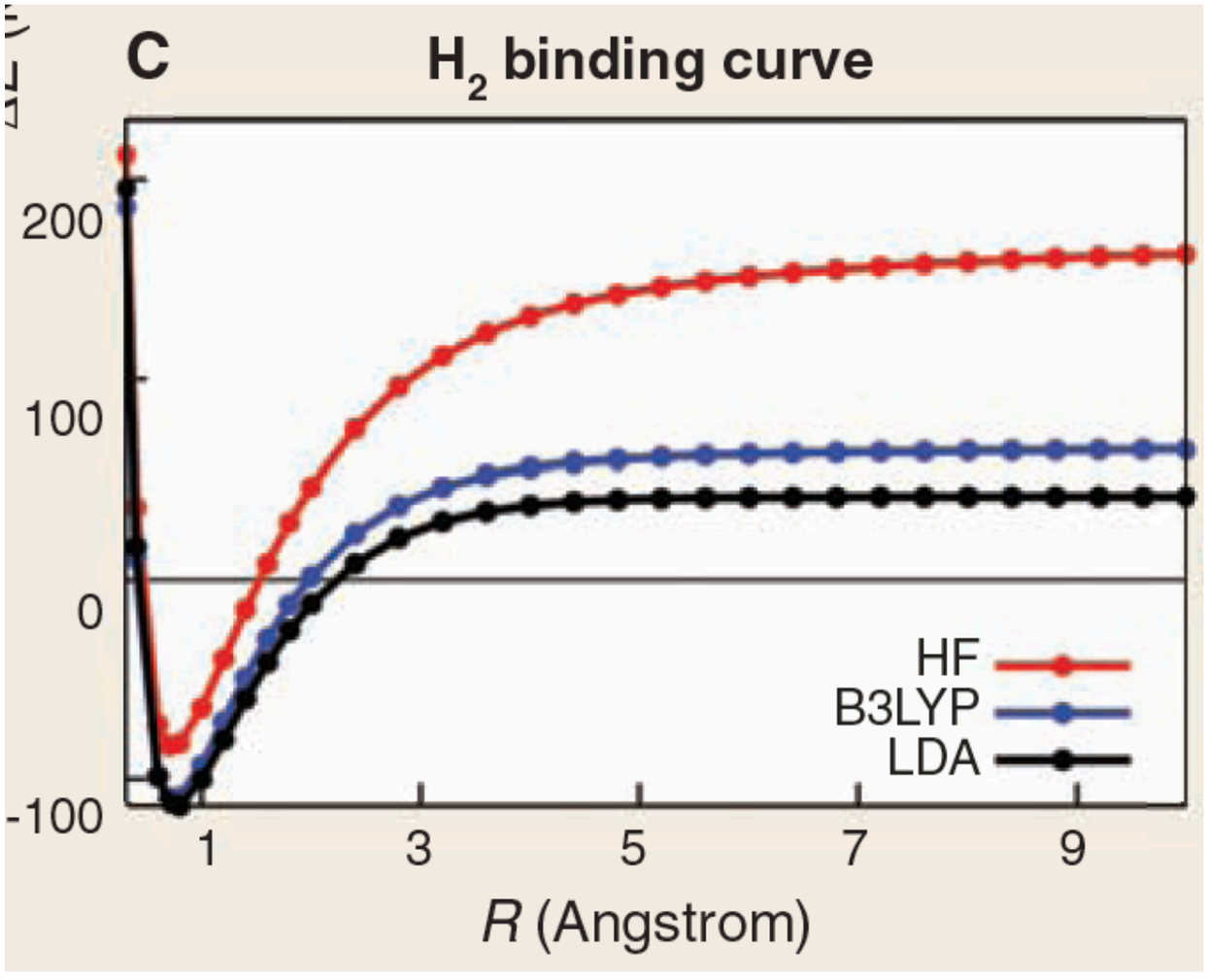

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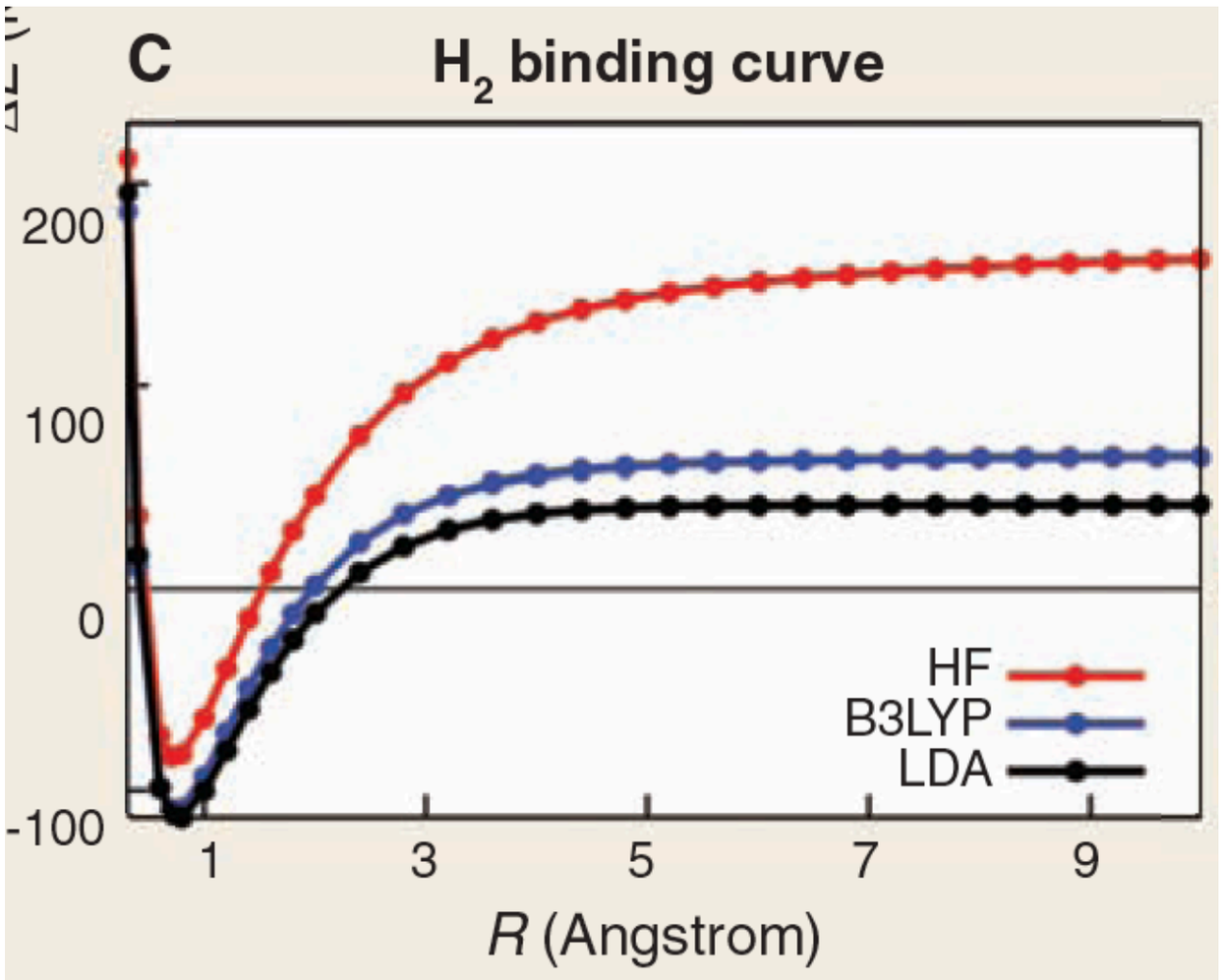
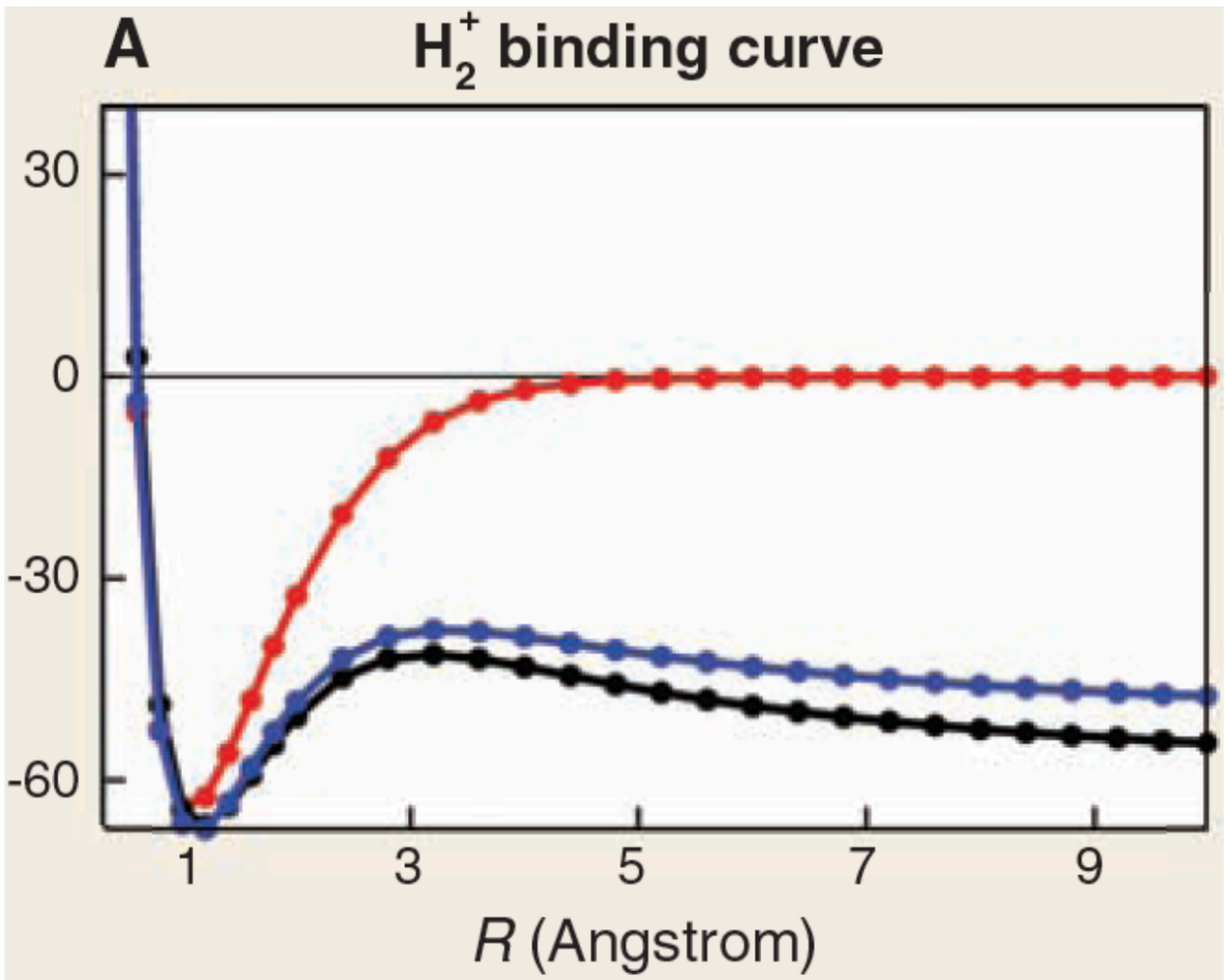
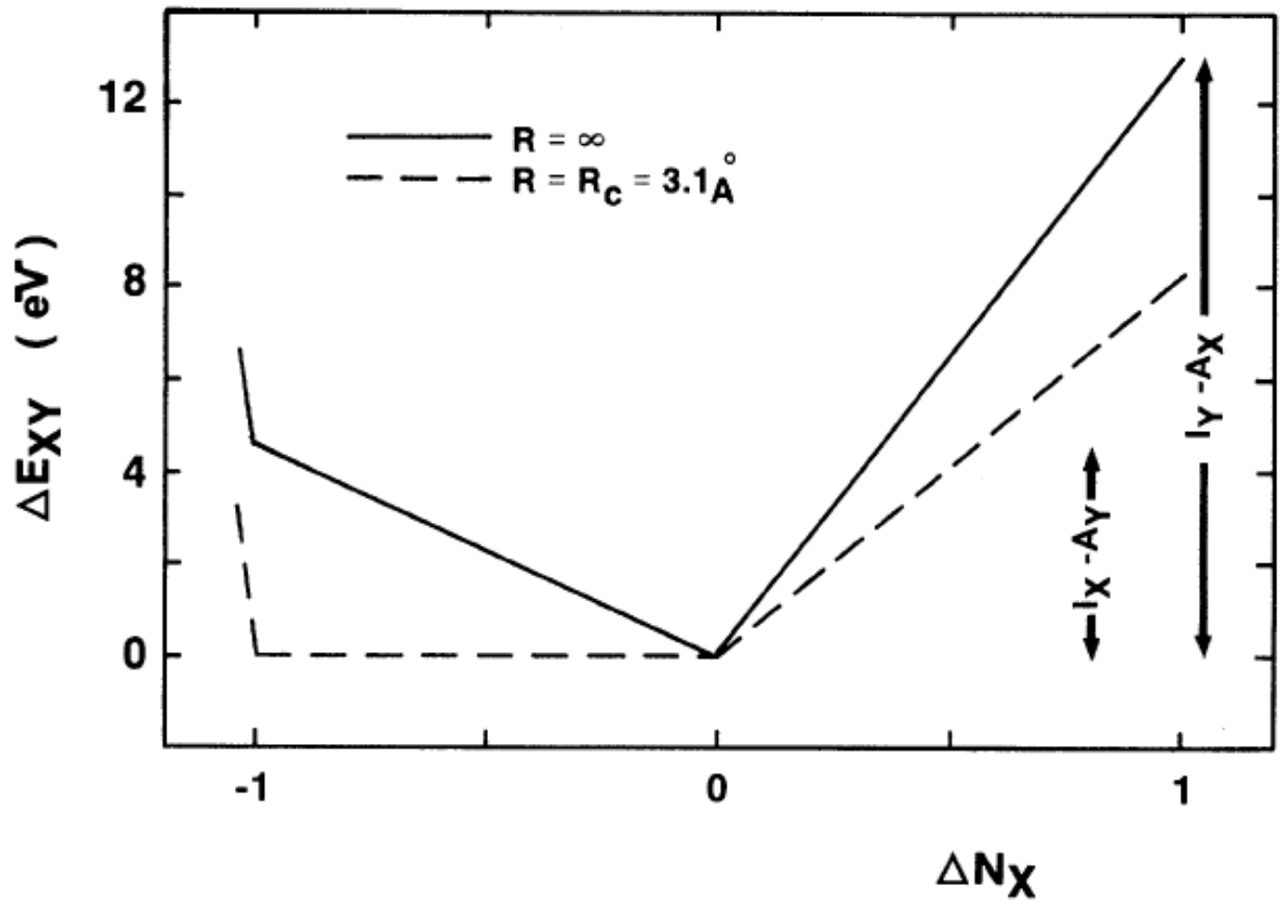




A.J. Cohen, P. Mori-Sanchez, W. Yang, Science (2008)

Linearity of the energy

Dissociation of an hetero-nuclear diatomic molecule XY



J. Perdew *et al.*, PRL 49, 1691 (1982)

The total energy is piece-wise linear (between integer values of N)

Molecular dissociation from DFT

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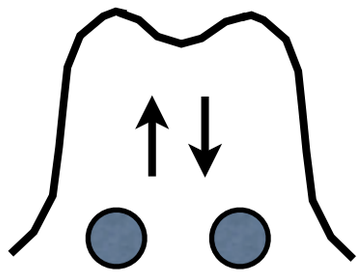
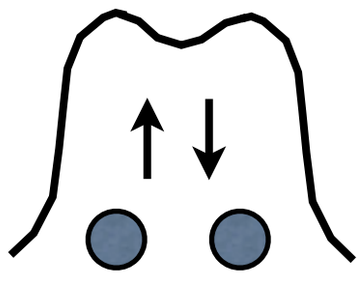
Notable failures: molecular dissociations (e.g. H_2):

Exact:



DFT:



Molecular dissociation from DFT

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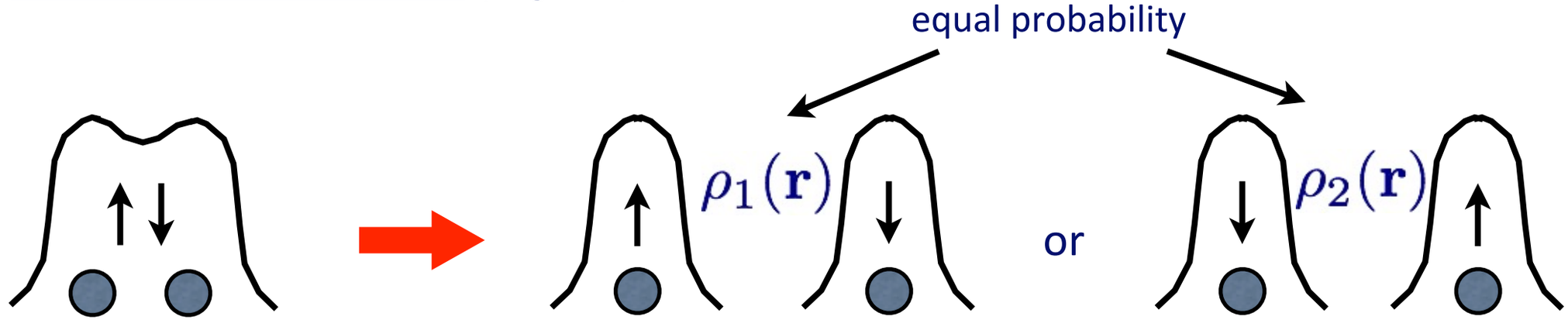

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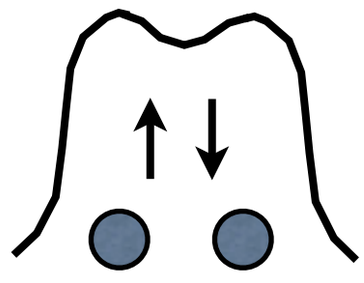

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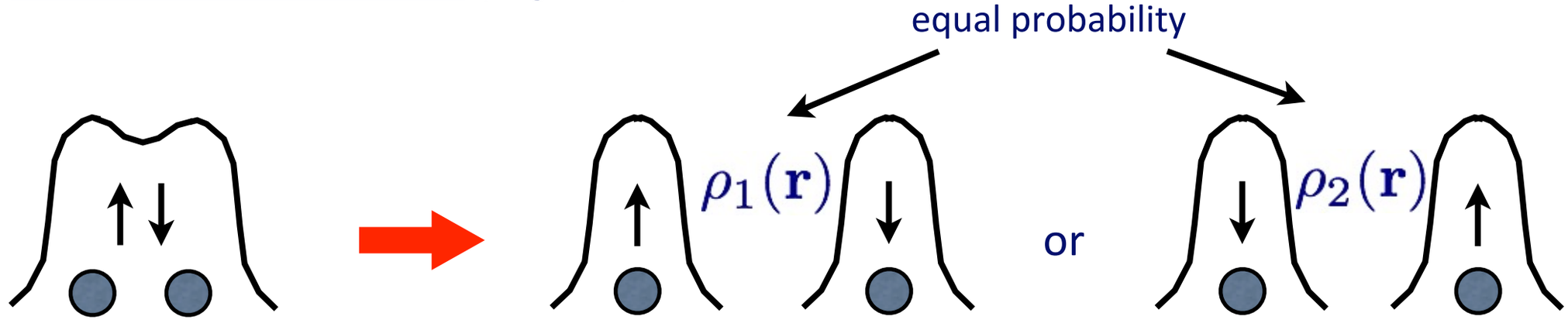

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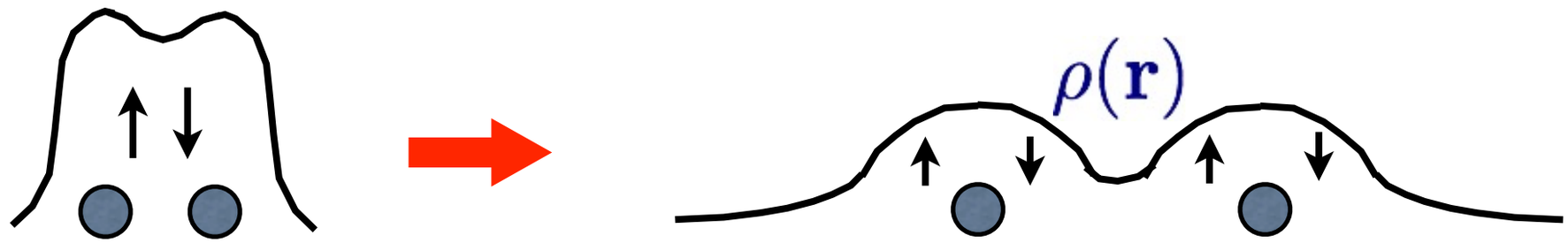

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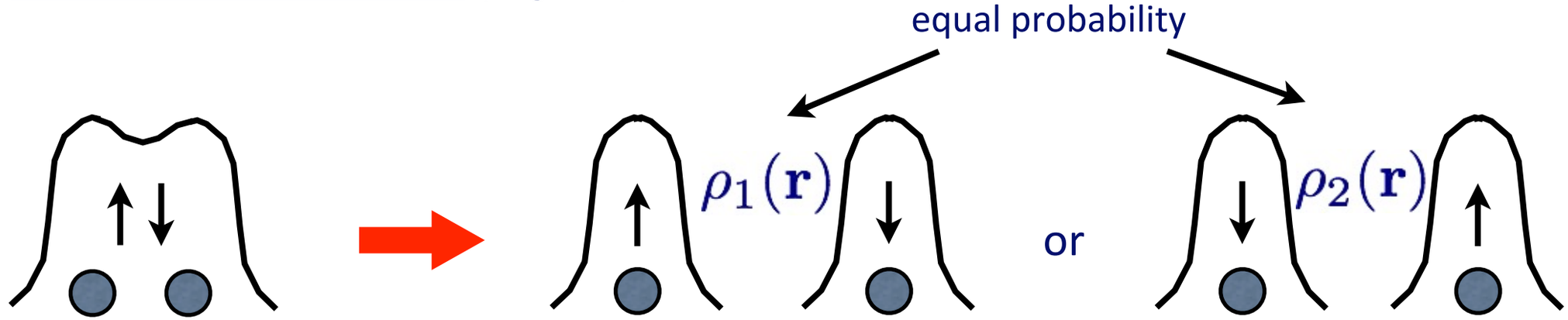

$$E = \tfrac{1}{2}E_1 + \tfrac{1}{2}E_2$$

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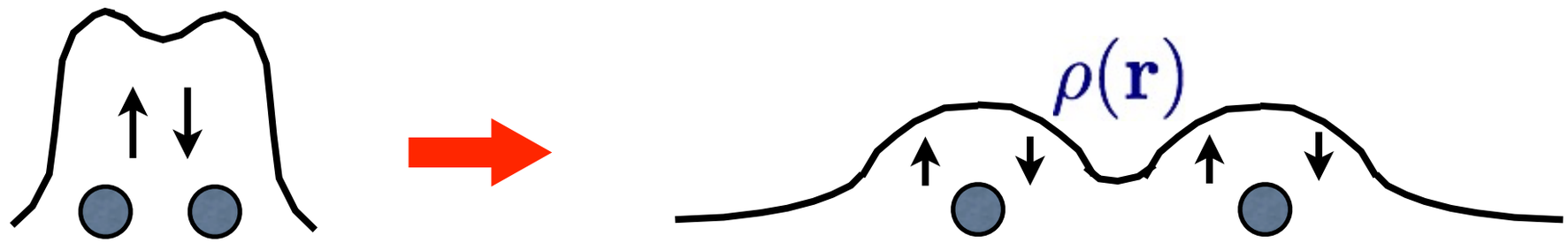

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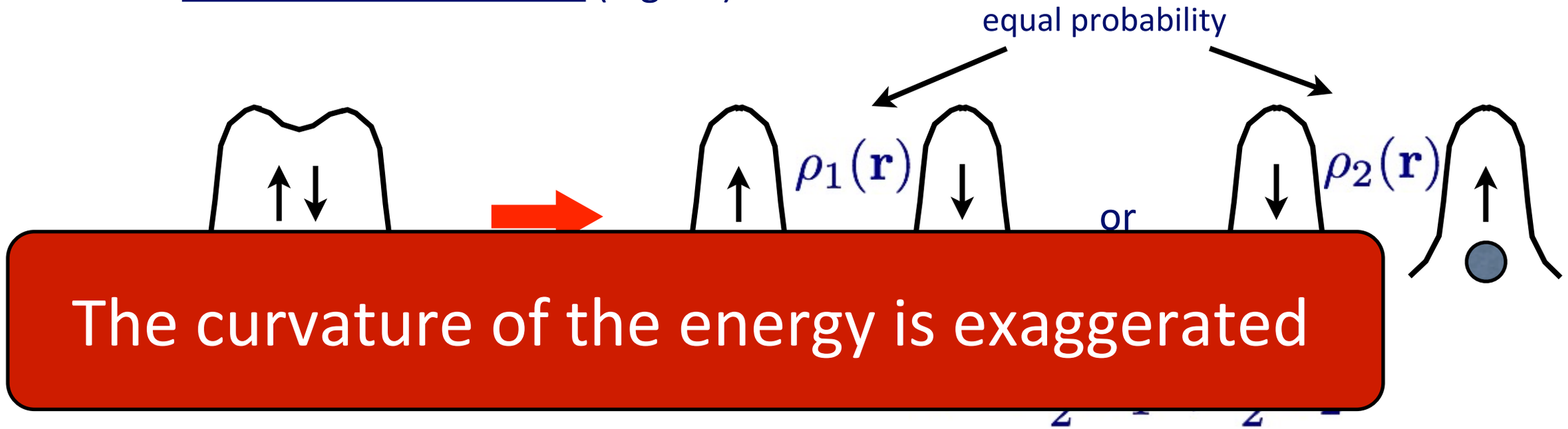

The curvature of the energy is exaggerated

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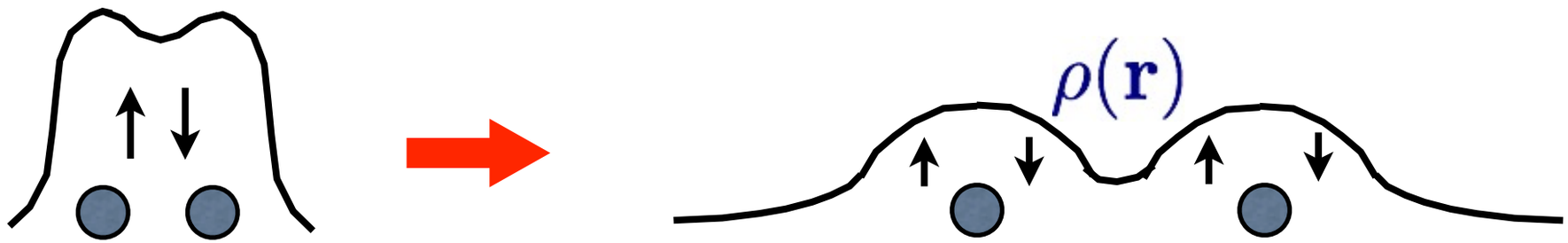

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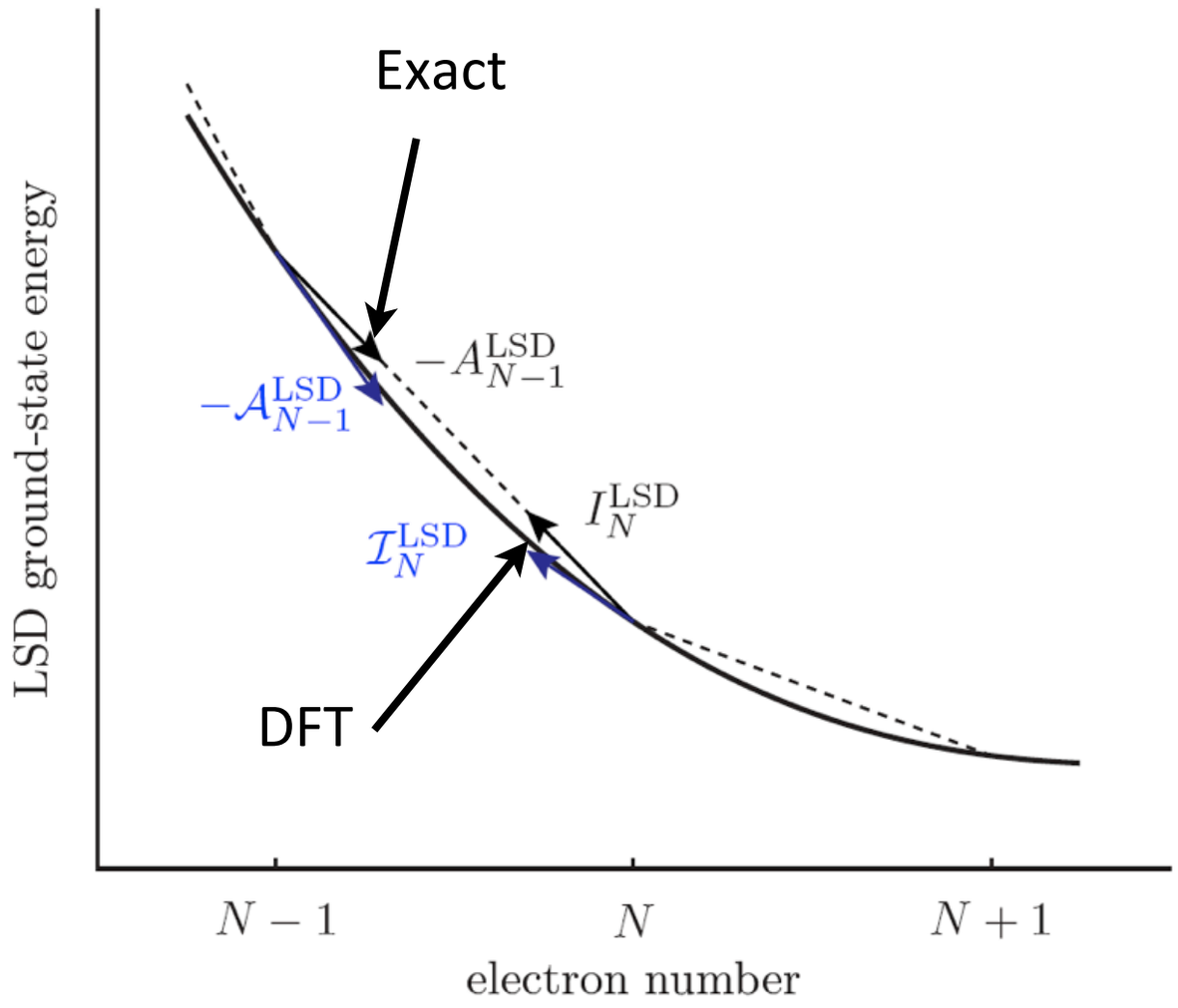
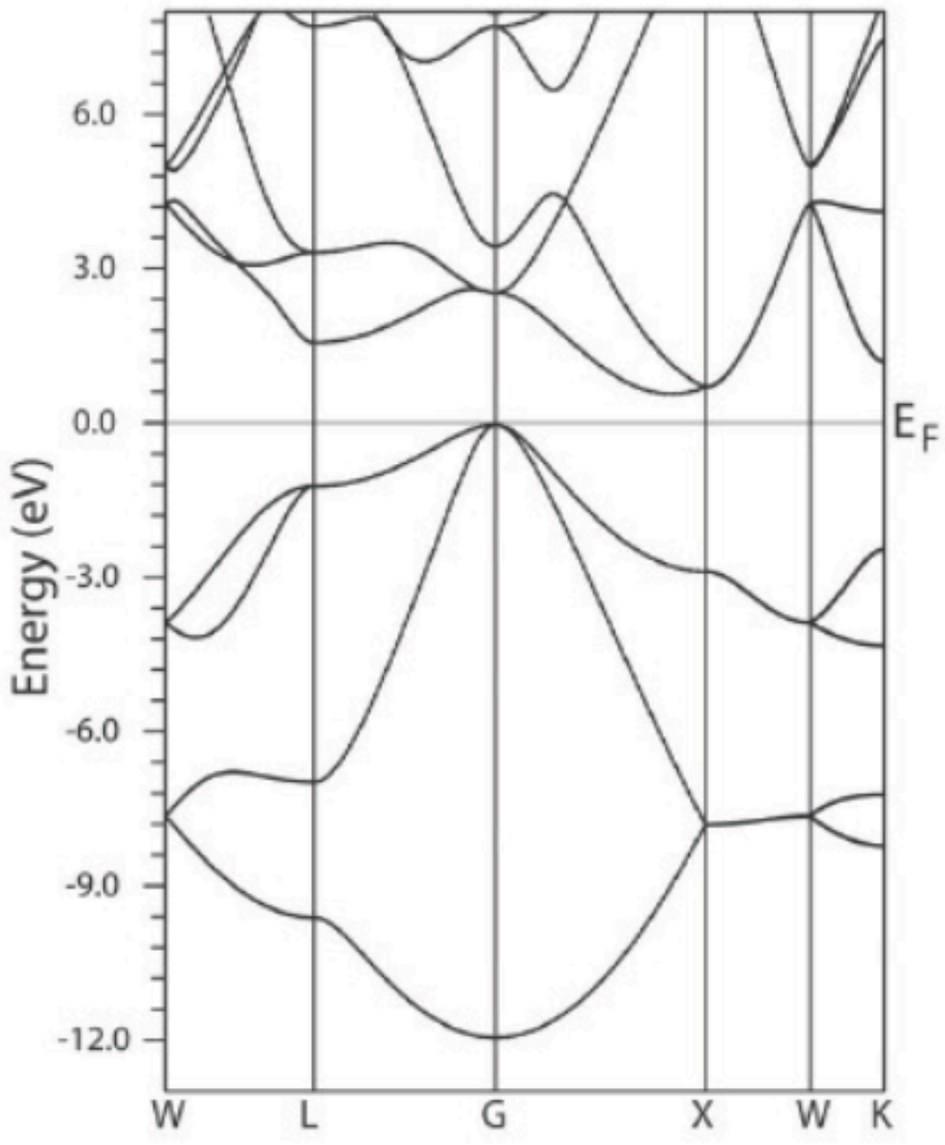
Exact vs DFT total energy



The (single-particle) band gap “problem”

Si band structure



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

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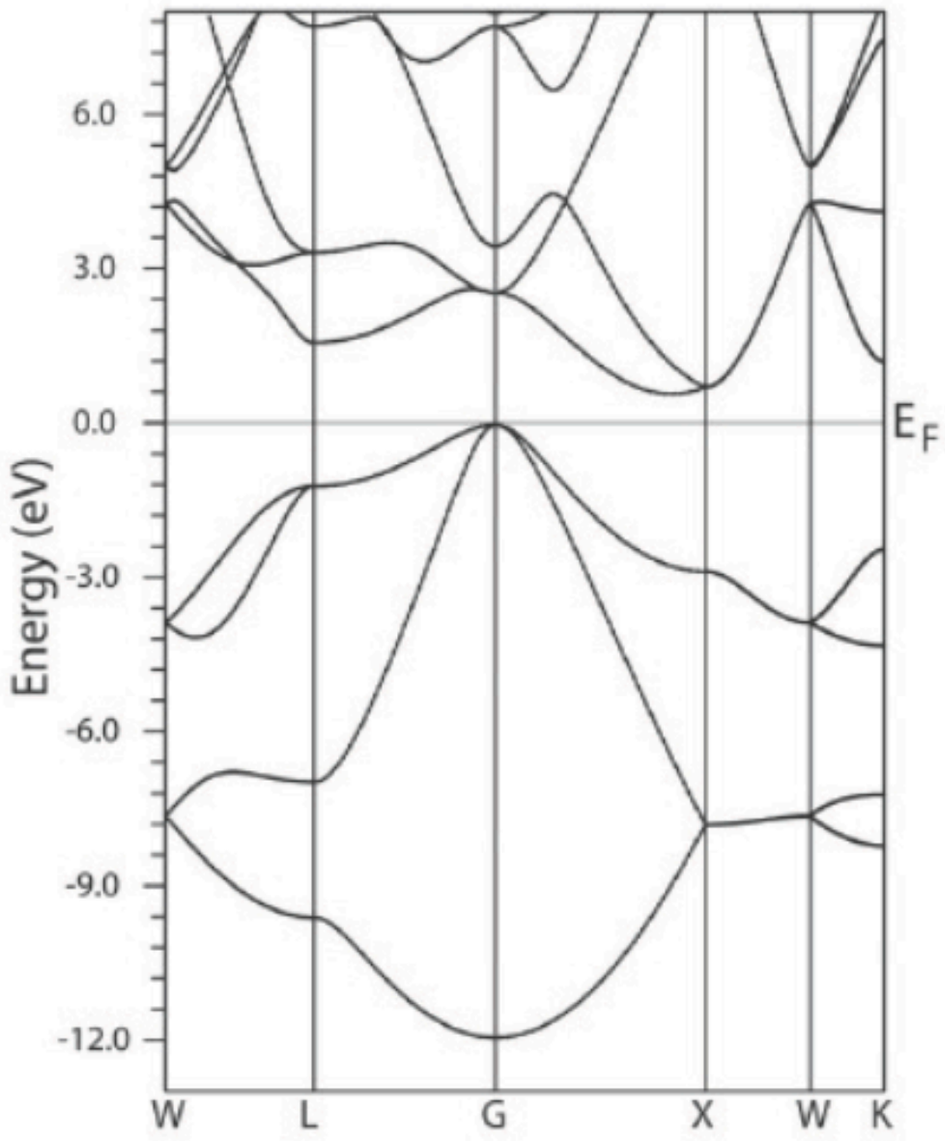

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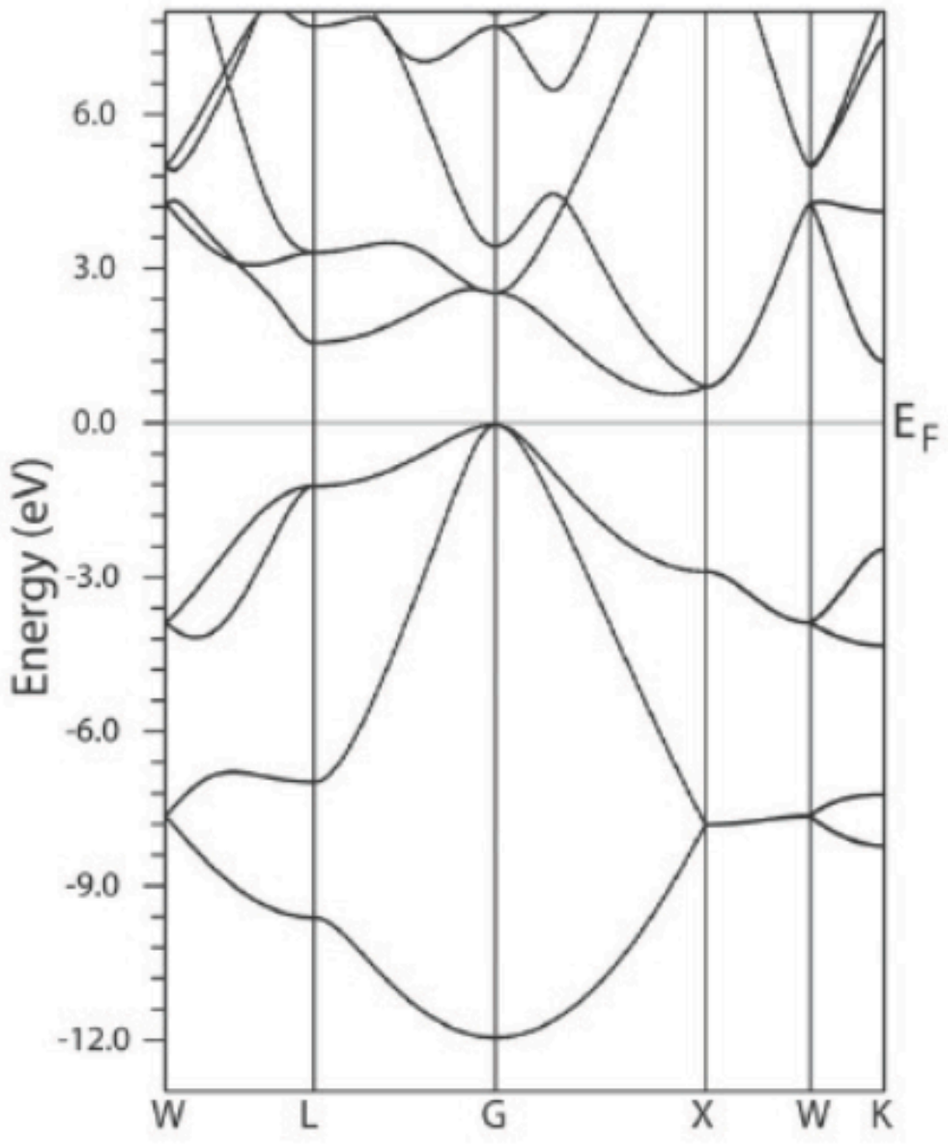

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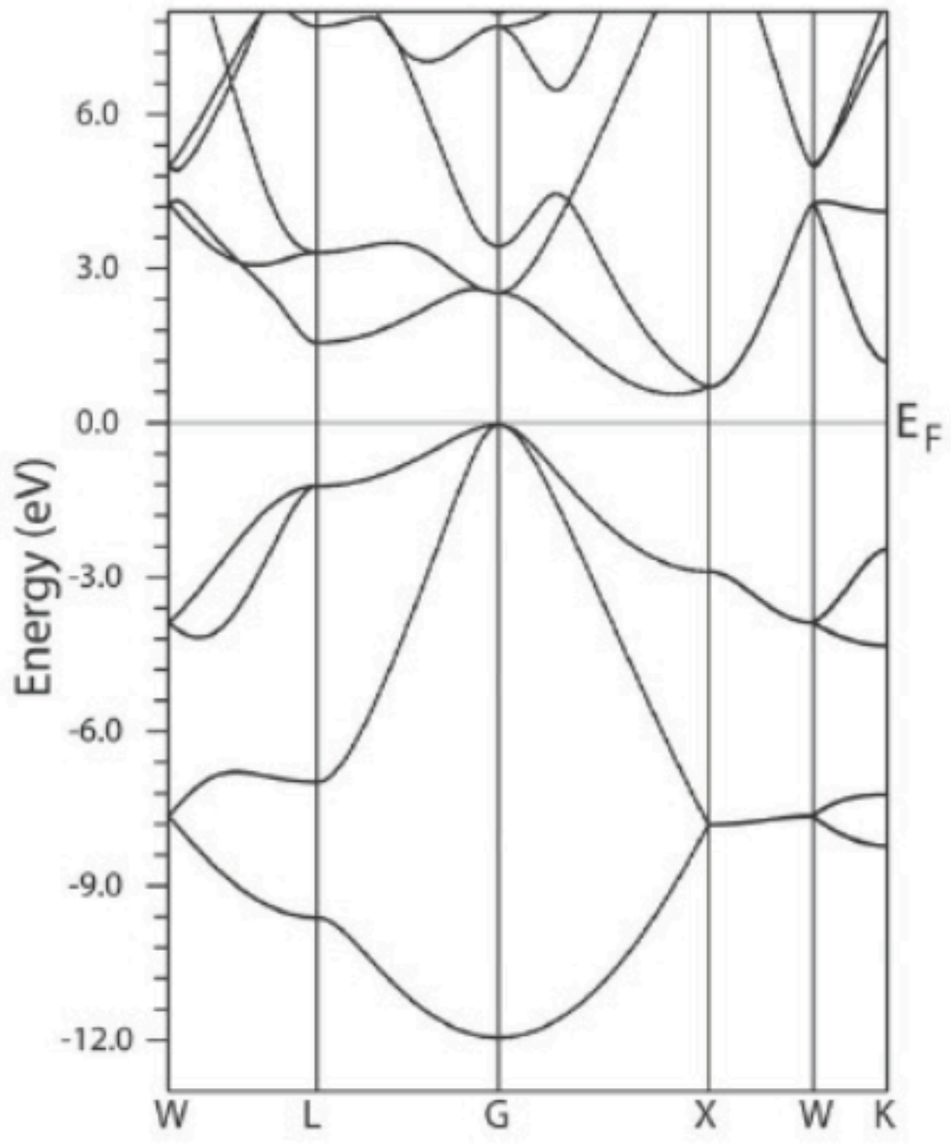

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Fundamental gap:

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

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)

DFT+U

DFT+U: general idea

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A very simple idea: let's describe localized *d* or *f* electrons with a Hubbard Hamiltonian embedded in the "crystal bath"

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The Hubbard correction acts selectively on localized (*d* or *f*) 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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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:

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

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

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After some algebra....

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

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

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

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Potential:

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

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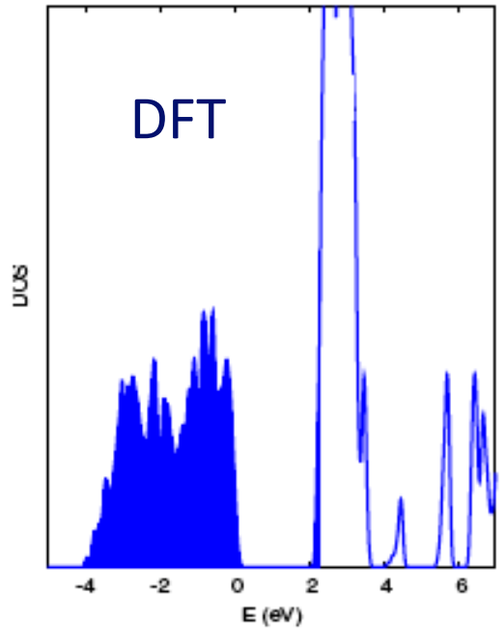
$$\left.\begin{aligned} \lambda_m^{I\sigma} > \frac{1}{2} \Rightarrow V_U < 0 \\ \lambda_m^{I\sigma} < \frac{1}{2} \Rightarrow V_U > 0 \end{aligned}\right\} \Rightarrow$$

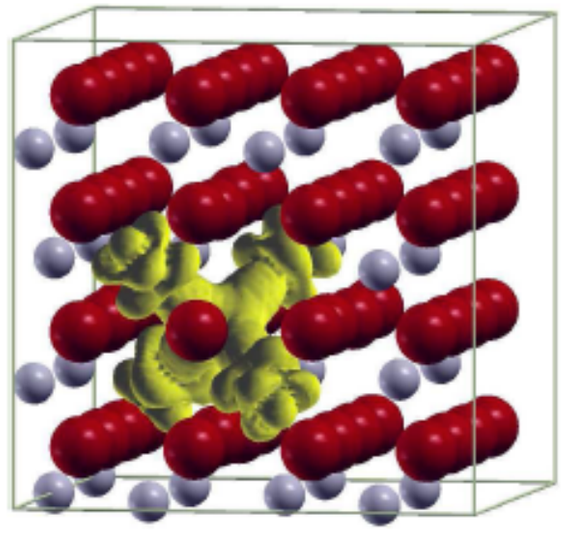
- Partial occupations of atomic states are discouraged
- Potential discontinuity re-established (and inserted in the spectrum)
- A gap opens: $E_g \approx U$

Charge localization in CeO_2

Charge localization in CeO_2

CeO_2 oxygen vacancy





DFT: delocalization of extra charge (2 e-) on 4 Ce atoms around the O vacancy

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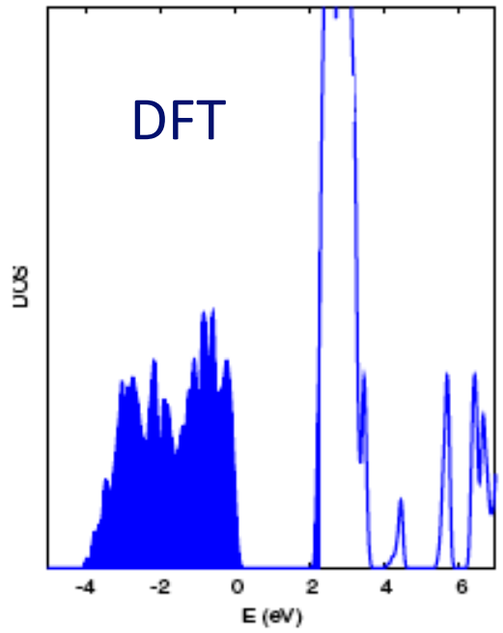
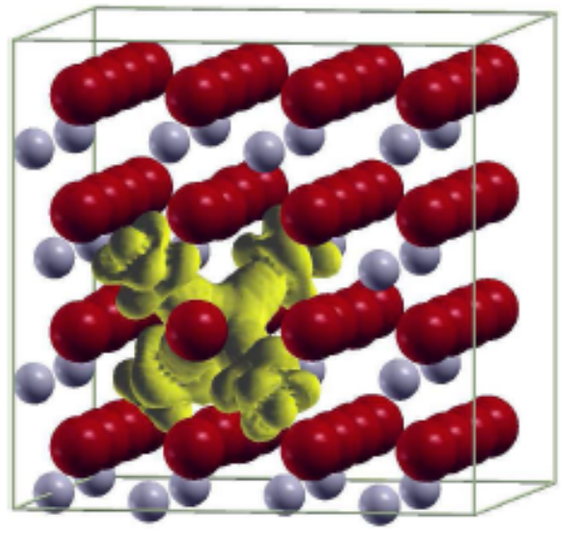
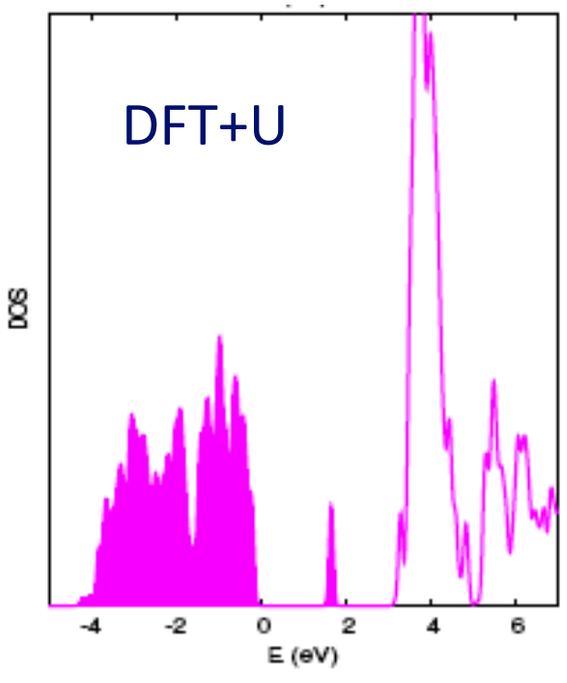
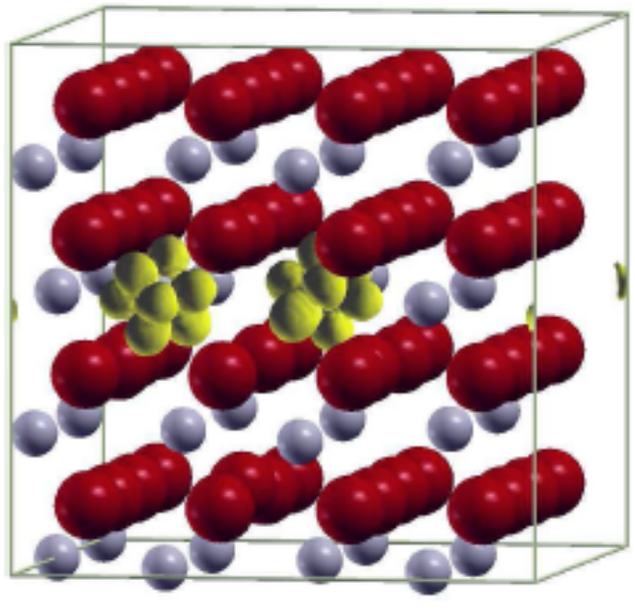




DFT: delocalization of extra charge (2 e-) on 4 Ce atoms around the O vacancy

Localization of the extra charge on two Ce atoms around the O vacancy

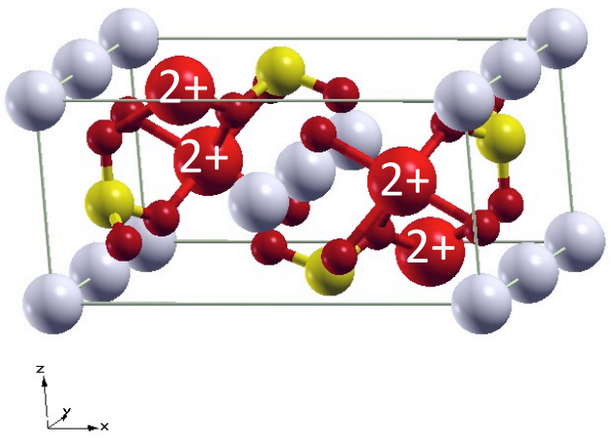




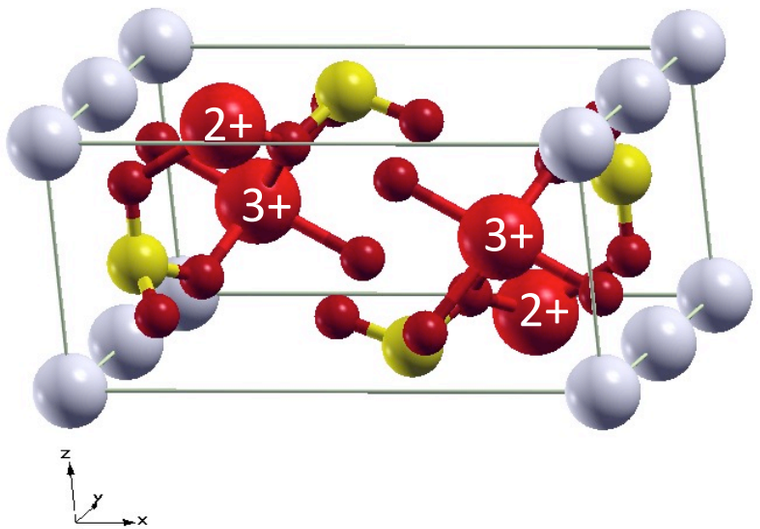
S. Fabris *et al.*, *PRB* 71, 041102 (2005)

Li_xFePO_4: charge ordering and energetics

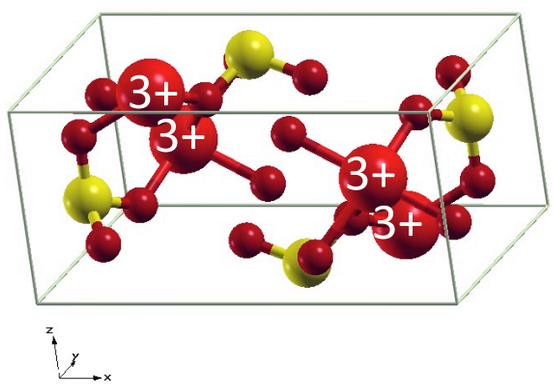
$LiMPO_4$



$Li_{0.5}MPO_4$



MPO_4



	$LiFePO_4$		$Li_{0.5}FePO_4$		$FePO_4$	
Method	2+	3+	2+	3+	2+	3+
DFT	6.22		6.11	6.08		5.93
DFT+U	6.19		6.19	5.68		5.65

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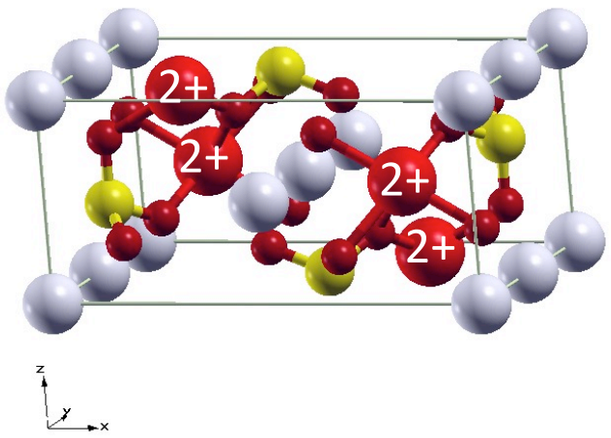

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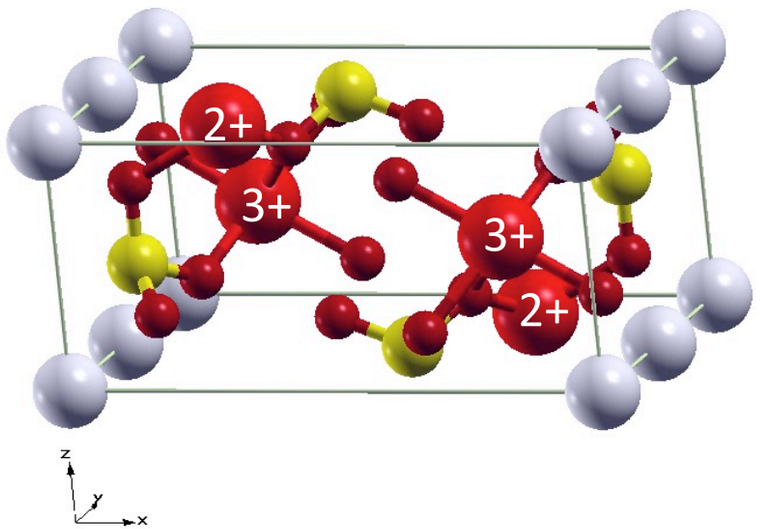

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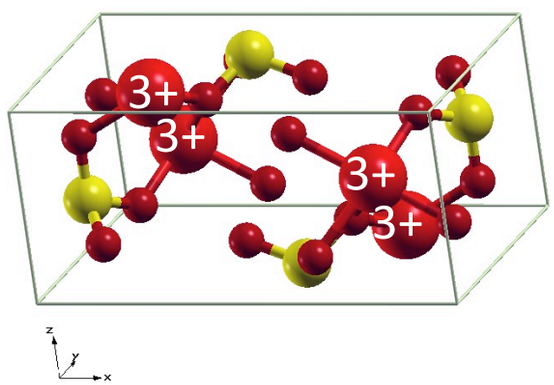

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DFT	6.22		6.11	6.08		5.93
DFT+U	6.19		6.19	5.68		5.65

Li_xFePO_4: formation energy and voltage

$$\text{F. E.} = \mathrm{E}(\mathrm{Li_xFePO_4}) - \mathrm{x}\mathrm{E}(\mathrm{LiFePO_4}) - (1-\mathrm{x})\mathrm{E}(\mathrm{FePO_4})$$

$$\langle V \rangle = -\frac{\mathrm{E}(\mathrm{Li_{x_2}FePO_4}) - \mathrm{E}(\mathrm{Li_{x_1}FePO_4}) - (\mathrm{x_2}-\mathrm{x_1})\mathrm{E}(\mathrm{Li_{bulk}})}{F}$$

Li_xFePO_4: formation energy and voltage

$$\text{F. E.} = \mathrm{E}(\mathrm{Li_xFePO_4}) - \mathrm{x}\mathrm{E}(\mathrm{LiFePO_4}) - (1-\mathrm{x})\mathrm{E}(\mathrm{FePO_4})$$

$$\langle V \rangle = -\frac{\mathrm{E}(\mathrm{Li_{x_2}FePO_4}) - \mathrm{E}(\mathrm{Li_{x_1}FePO_4}) - (\mathrm{x_2}-\mathrm{x_1})\mathrm{E}(\mathrm{Li_{bulk}})}{F}$$

Method	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 3.5
DFT	-126	2.73
DFT+U	159	4.06

Electronic localization in chemical reactions

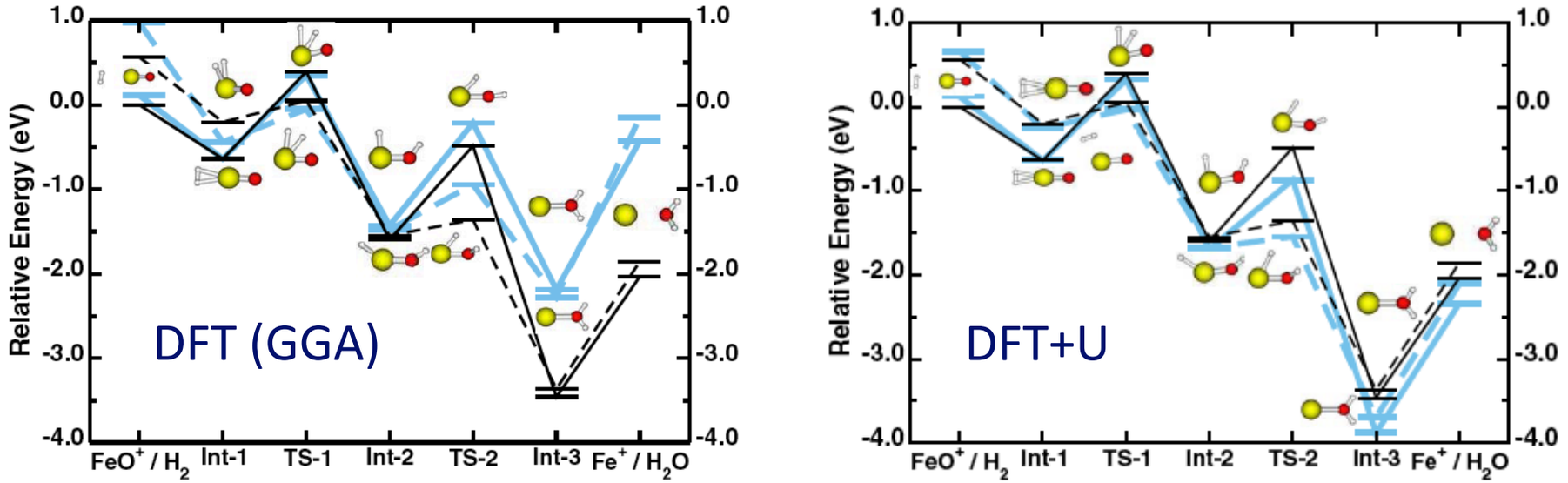

TABLE III. Equilibrium bond lengths, R_e (Å), harmonic frequencies, ω_e (cm^{-1}), and anharmonicities, $\omega_e x_e$ (cm^{-1}) for the $^6\Sigma^+$ and $^4\Phi$ states of FeO^+.

	$^6FeO^+$			$^4FeO^+$		
Method	R_e	ω_e	$\omega_e x_e$	R_e	ω_e	$\omega_e x_e$
GGA	1.62	901	328	1.56	1038	332
GGA + U	1.66	749	432	1.75	612	172
CCSD(T)	1.66	724	434	1.70	633	188

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

Vibrational properties of TM oxides: DFPT+U

DFPT+U: $(H^{scf}_{DFT+U} - \epsilon_n)|\Delta\psi_n\rangle = -(\Delta V^{scf}_{DFT+U} - \Delta\epsilon_n)|\psi_n\rangle$

Hubbard term to $D_{I\alpha J\beta}$:

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

Vibrational properties of TM oxides: DFPT+U

DFPT+U: $(H^{scf}_{DFT+U} - \epsilon_n)|\Delta\psi_n\rangle = -(\Delta V^{scf}_{DFT+U} - \Delta\epsilon_n)|\psi_n\rangle$

Hubbard term to $D_{I\alpha J\beta}$:

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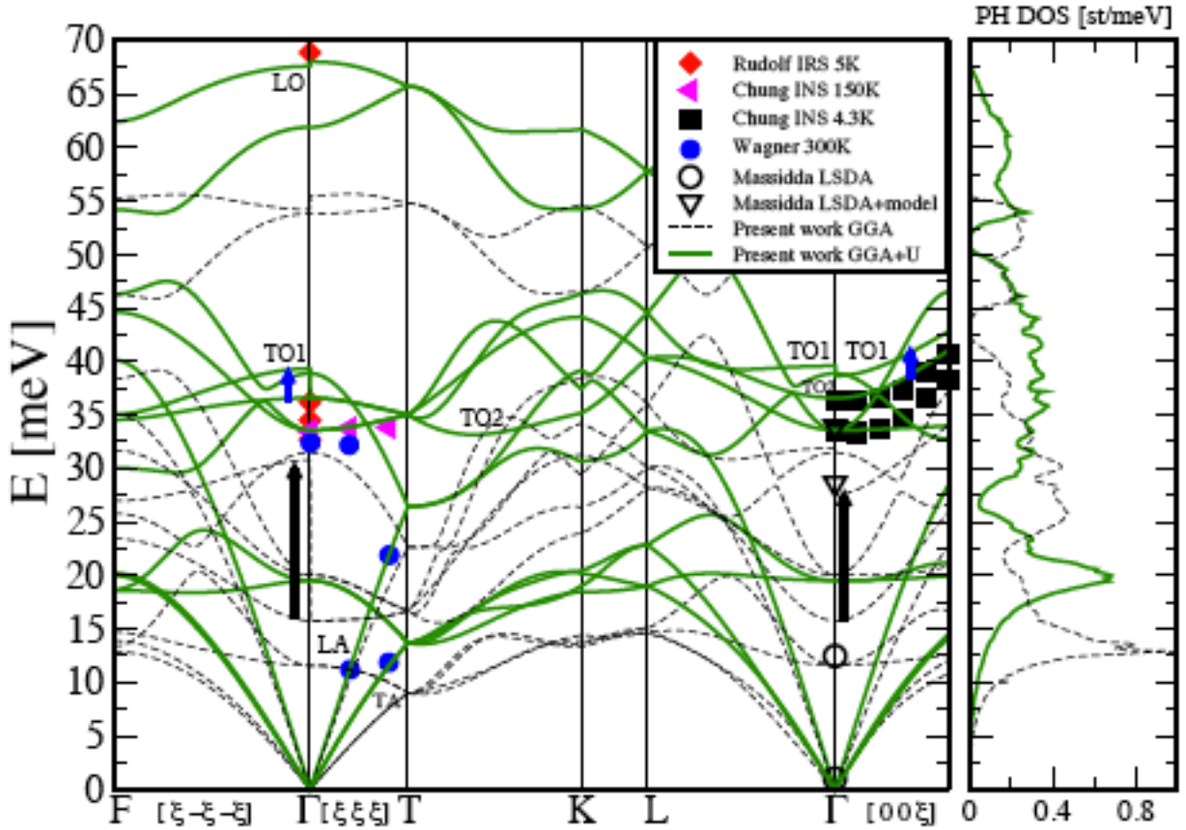
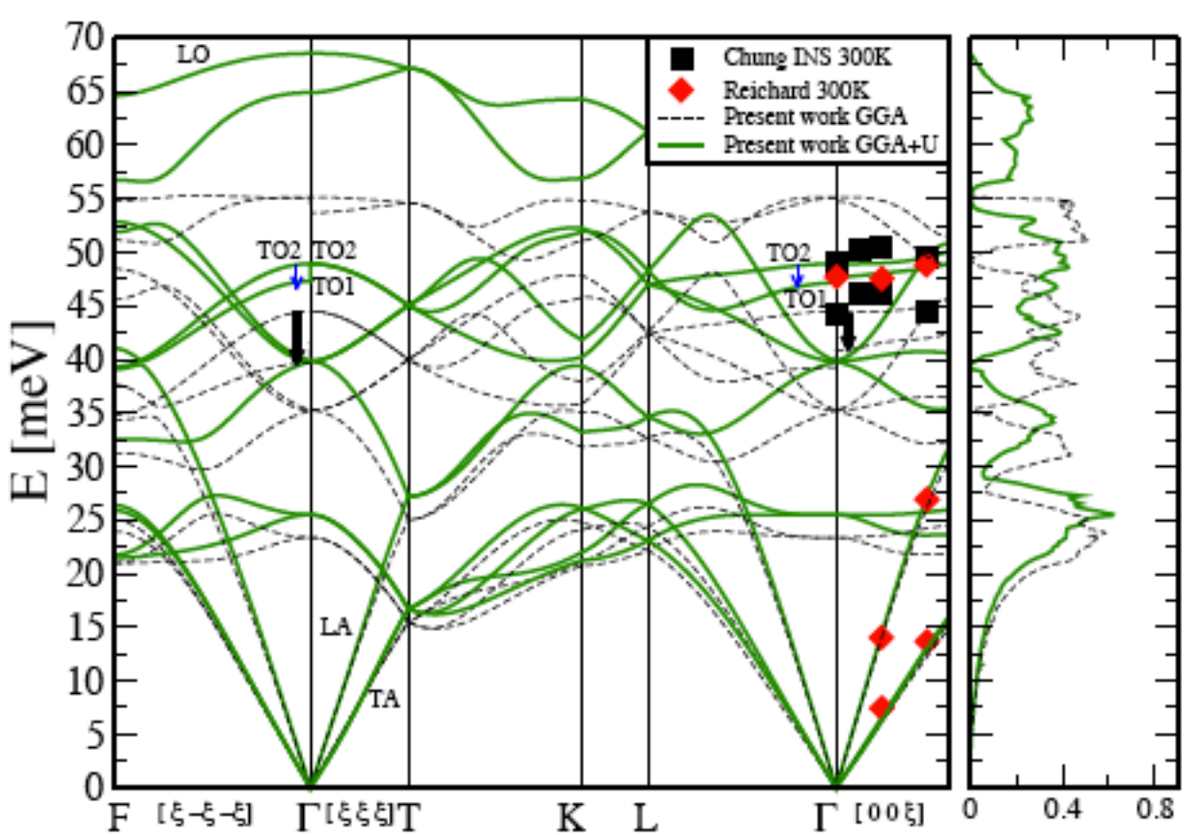


MnO

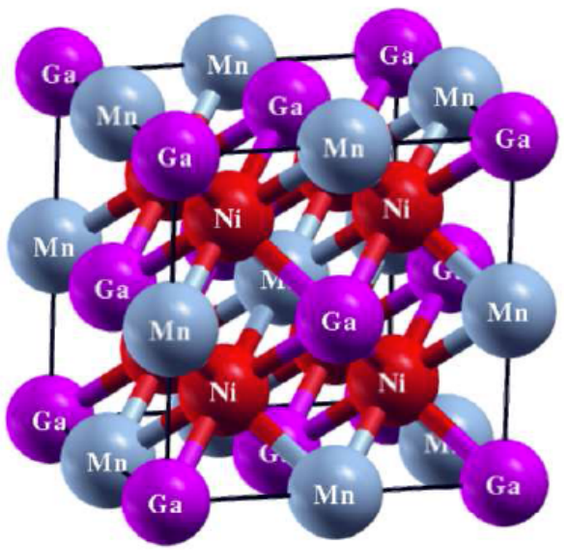


NiO

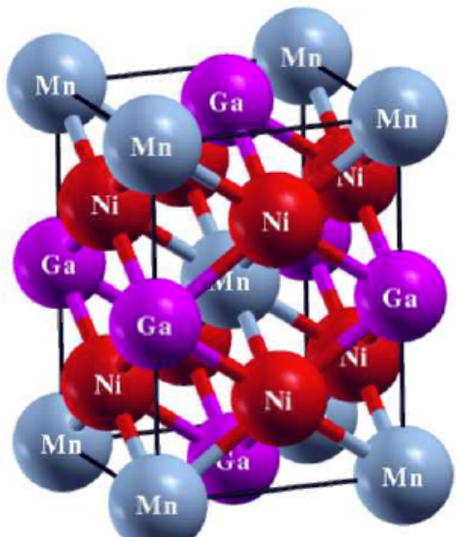
A. Floris, S. de Gironcoli, E. K. U. Gross, and M. Cococcioni, *Phys. Rev. B* 84, 161102 (2011)

Electronic localization and magnetism

Ni_2MnGa



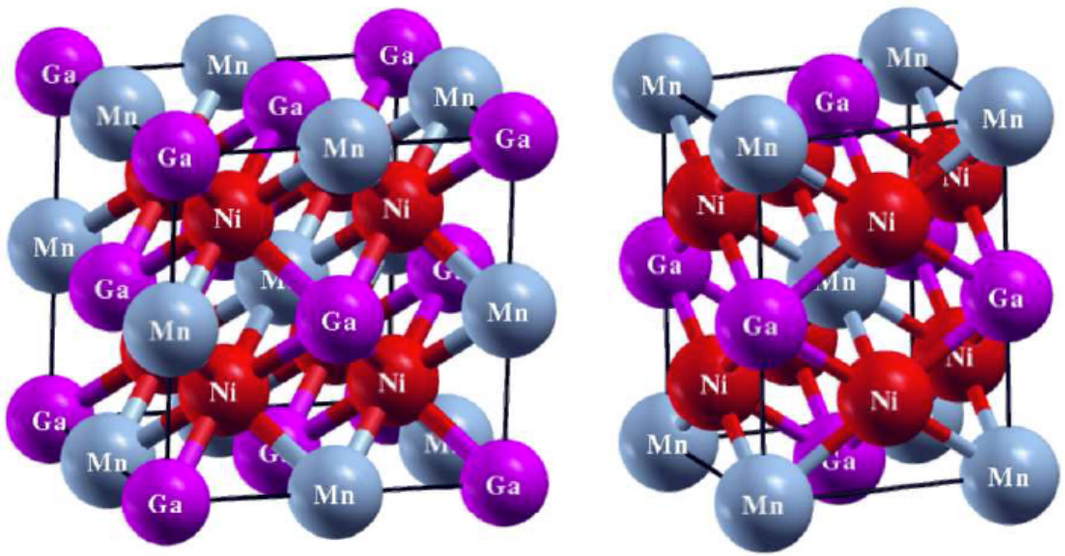
Austenite



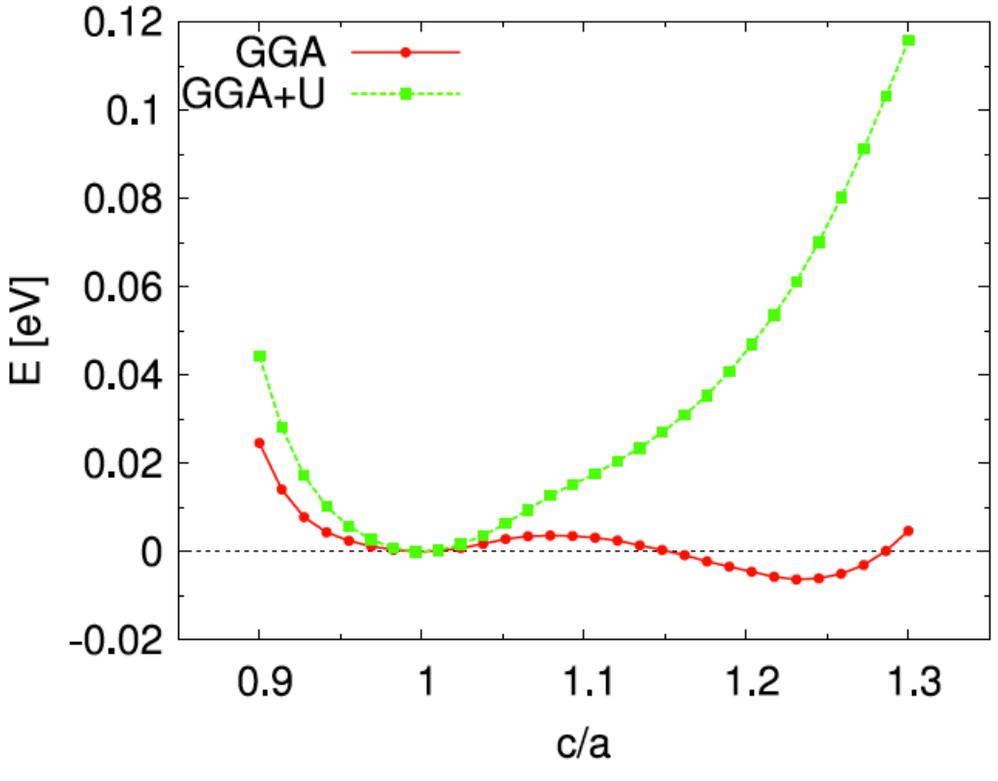
Martensite

Electronic localization and magnetism

Ni_2MnGa

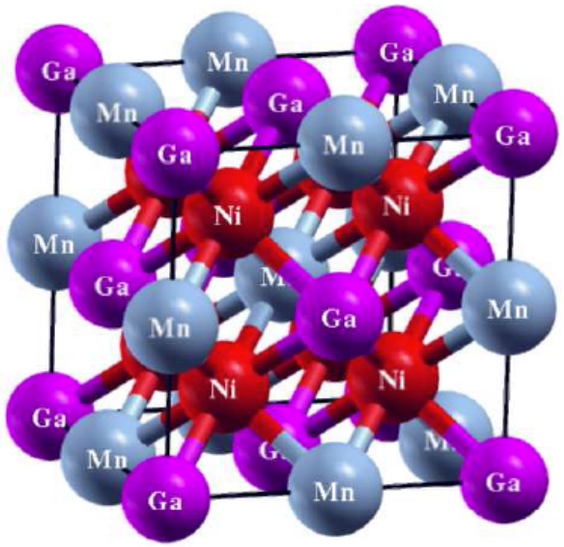


Austenite Martensite



Electronic localization and magnetism

Ni_2MnGa



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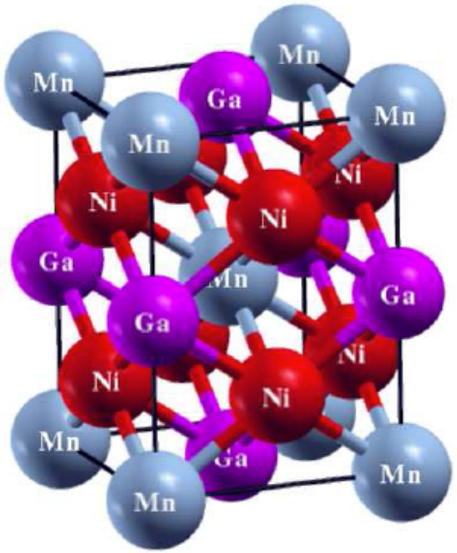
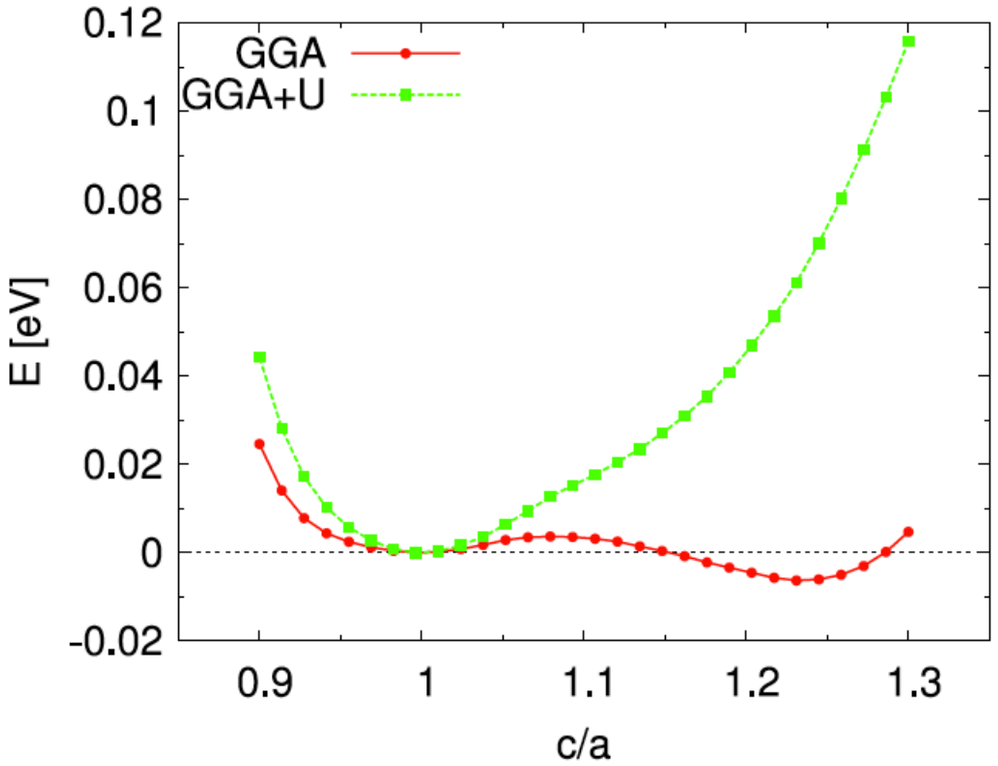
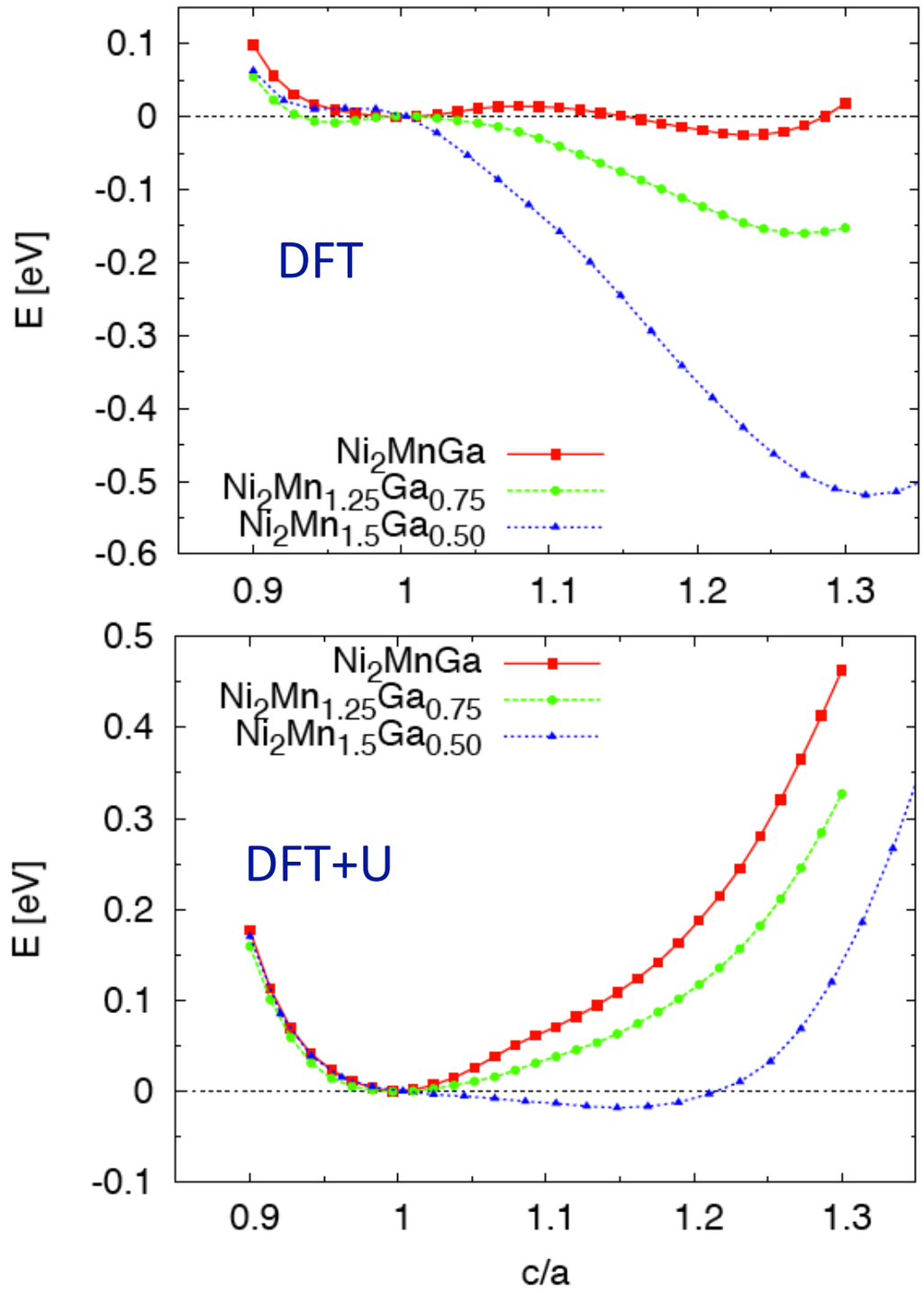


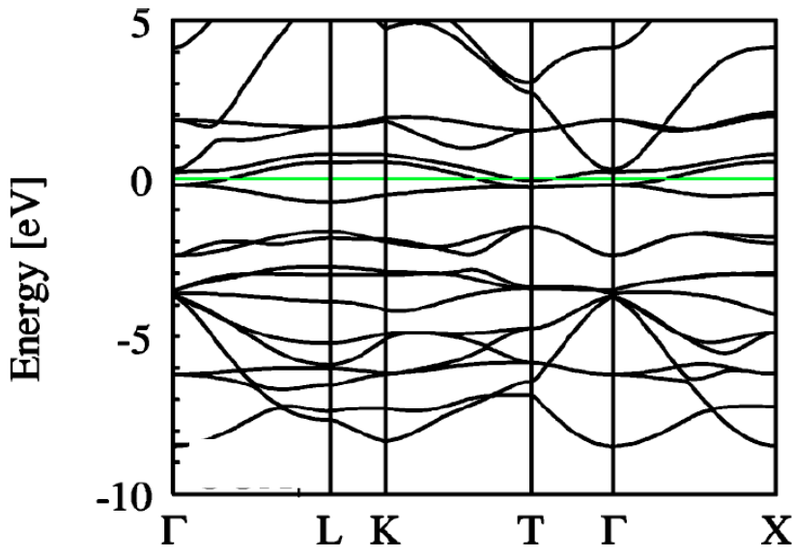
Martensite

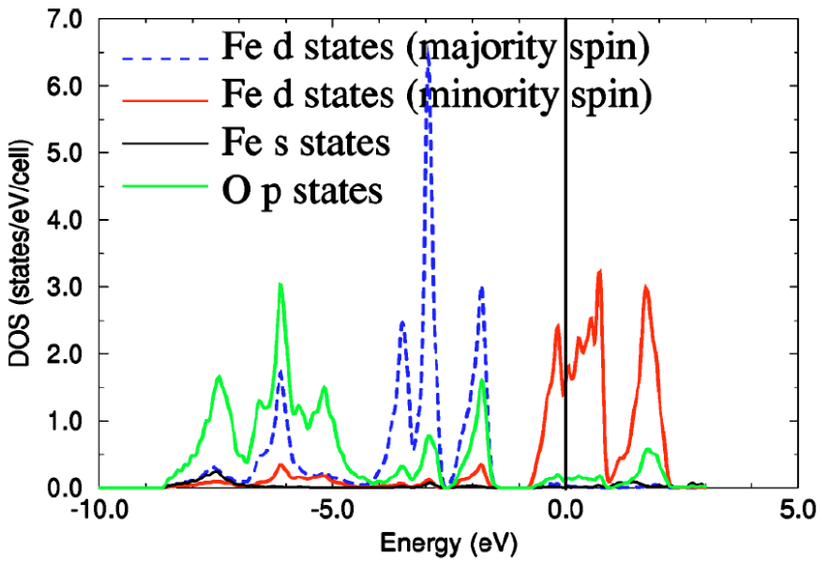




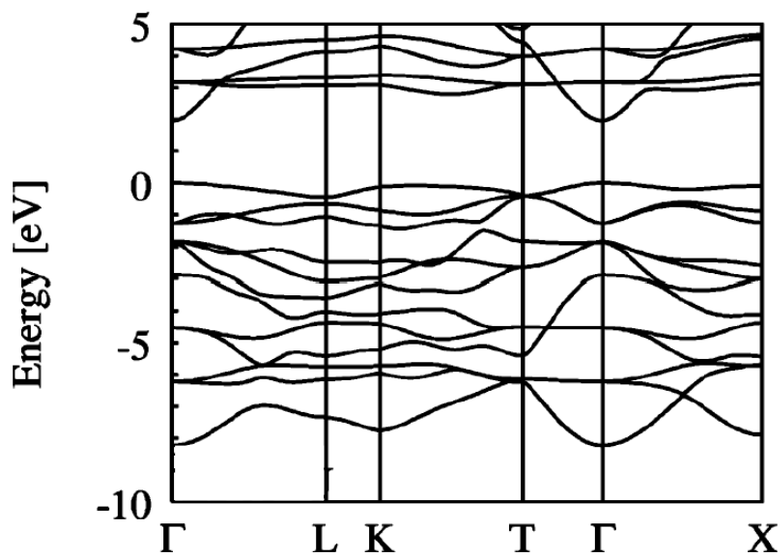
FeO: DFT and DFT+U

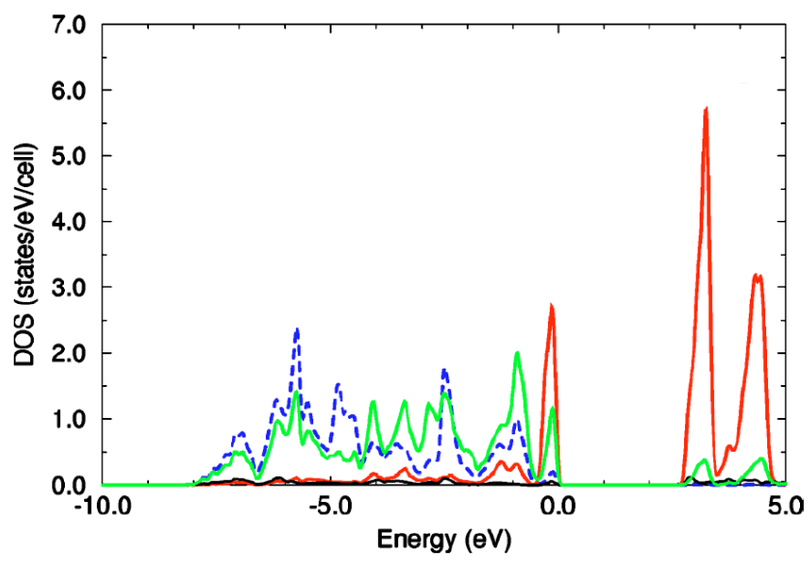
DFT





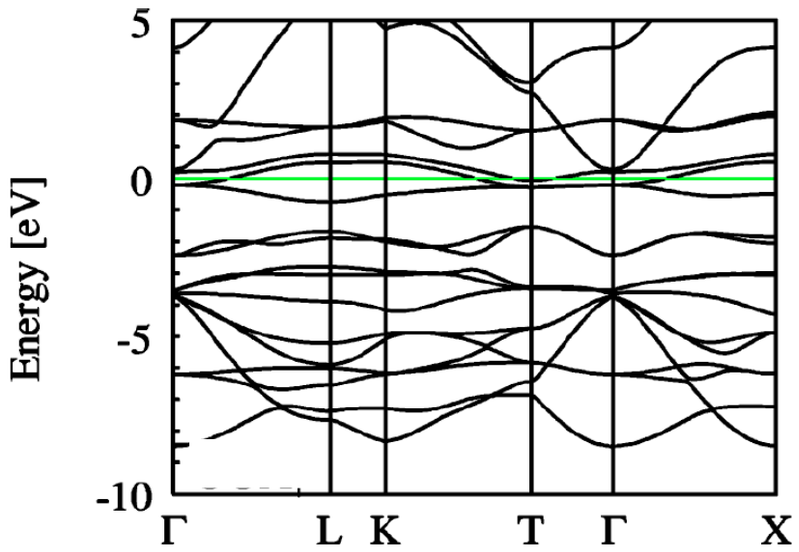
DFT+U





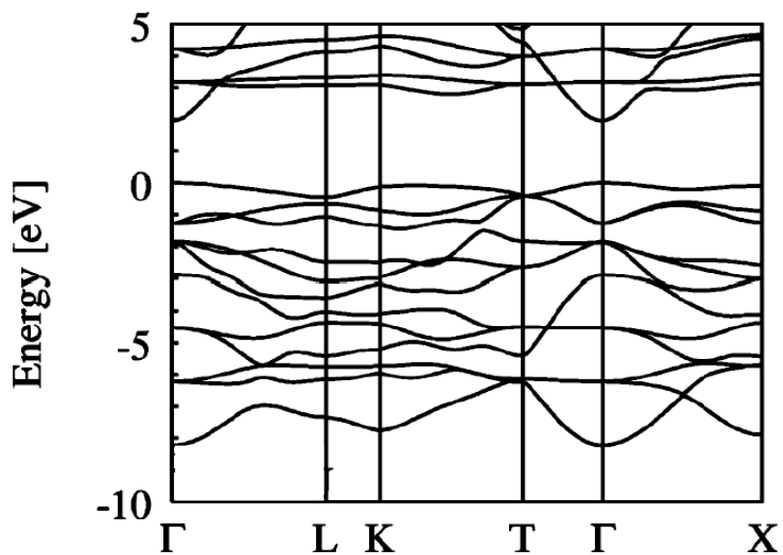
FeO: DFT and DFT+U

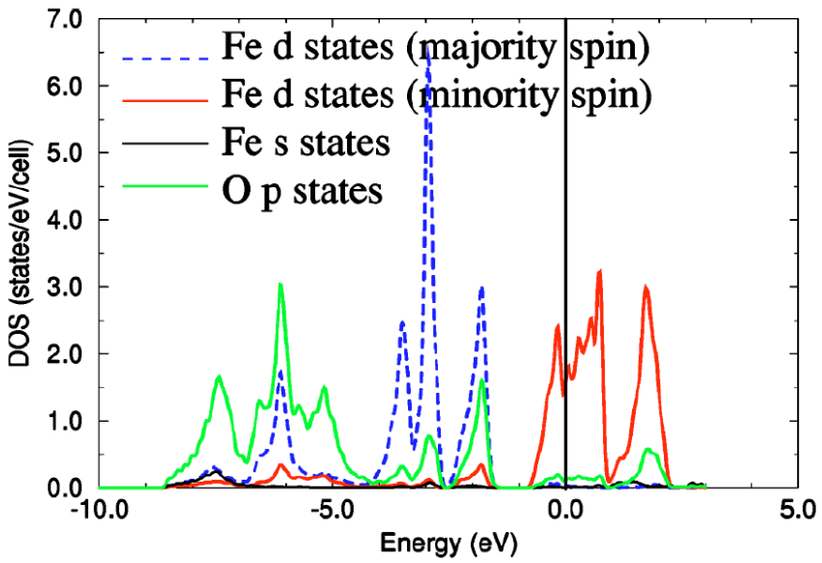
DFT

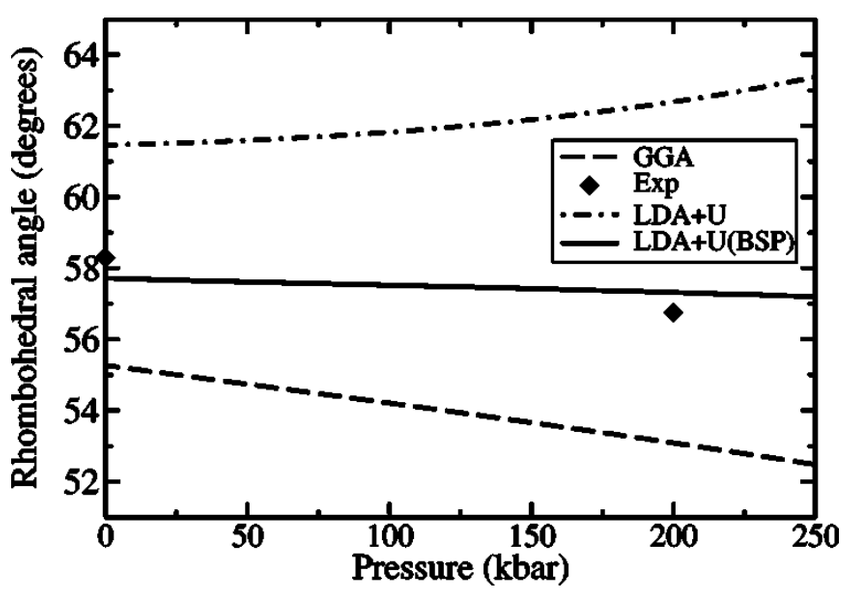


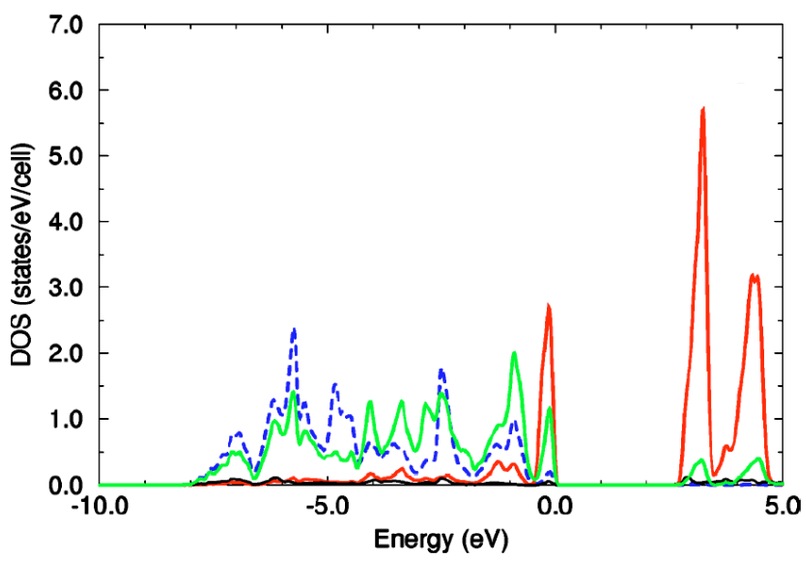
- ✓ Insulating character (Gap of right size)
- ✓ AFM ground state (AFII)
- ✓ Rhombohedral distortion

DFT+U



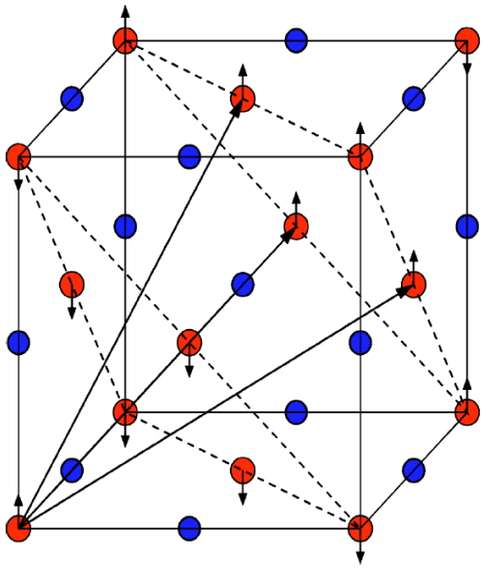


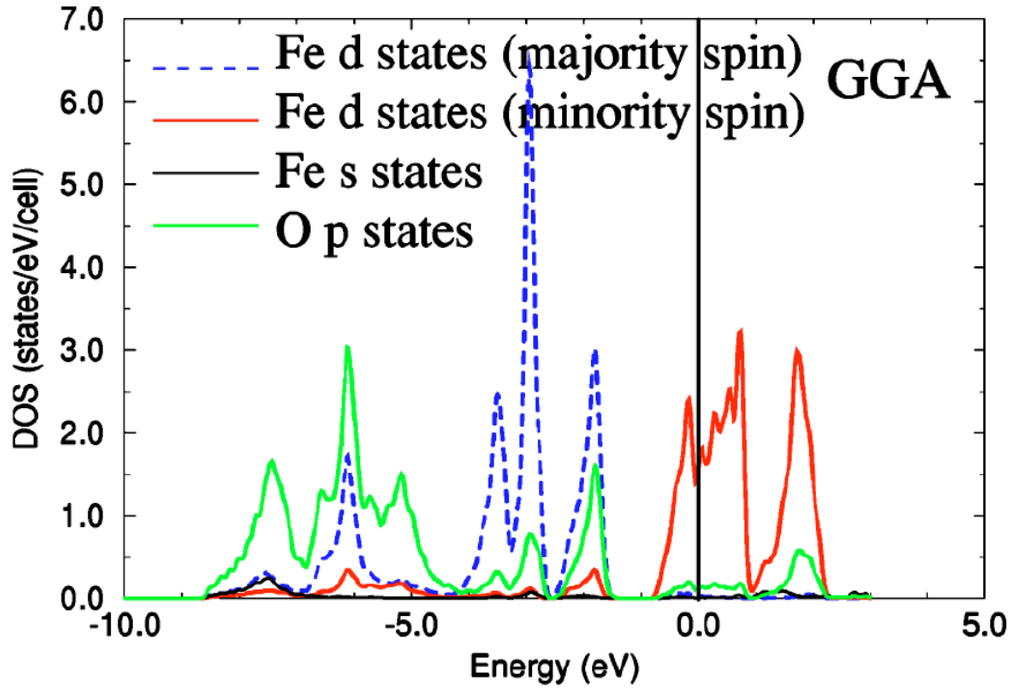




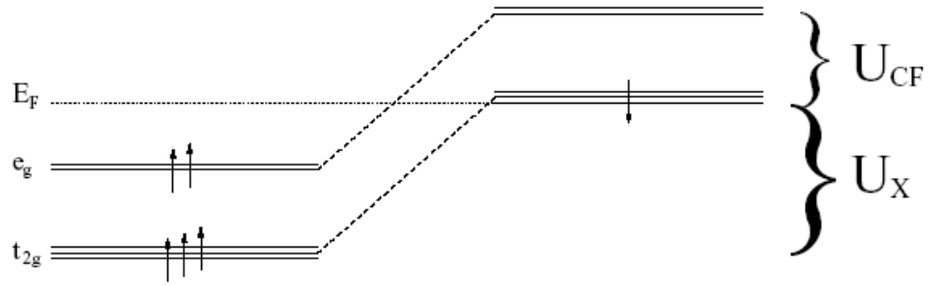
M. Cococcioni and S. de Gironcoli, *PRB* 71, 035105 (2005)

Orbital ordering: FeO



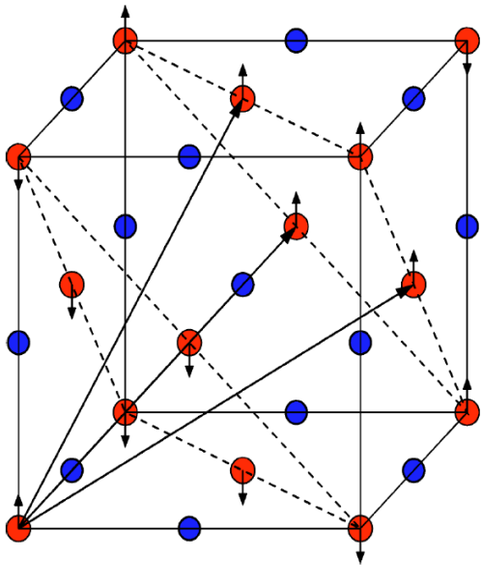


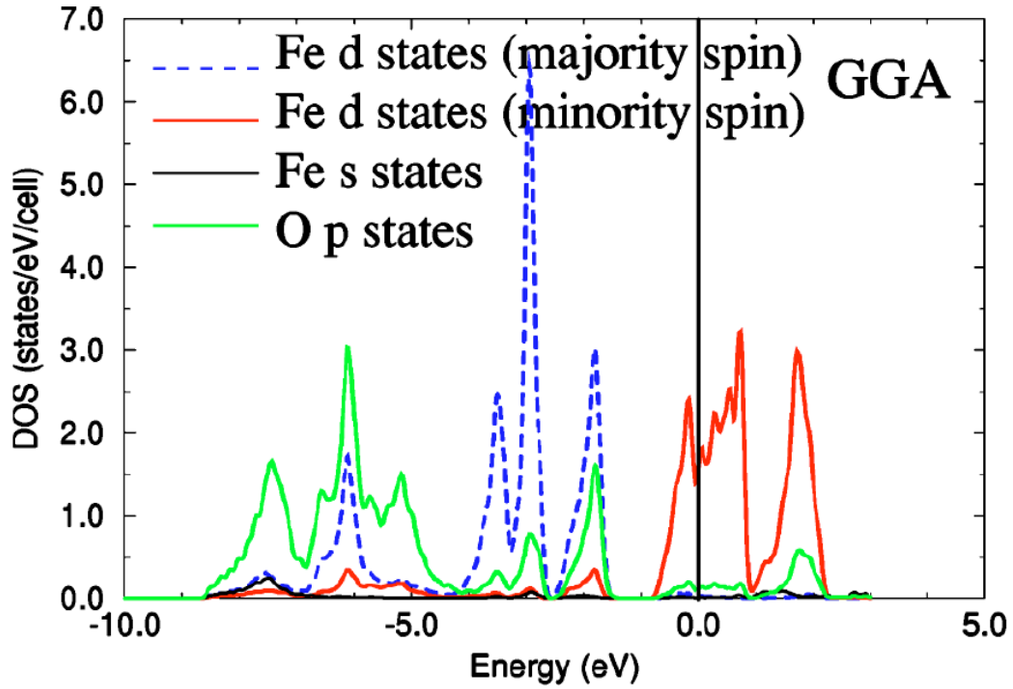
Fe^{2+}



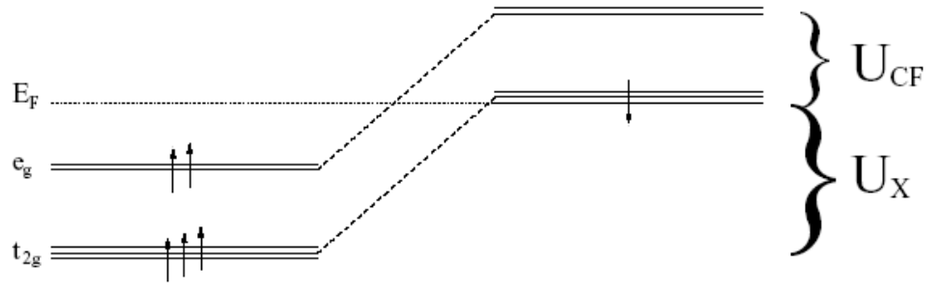
No gap: metallic ground state

Orbital ordering: FeO





Fe^{2+}



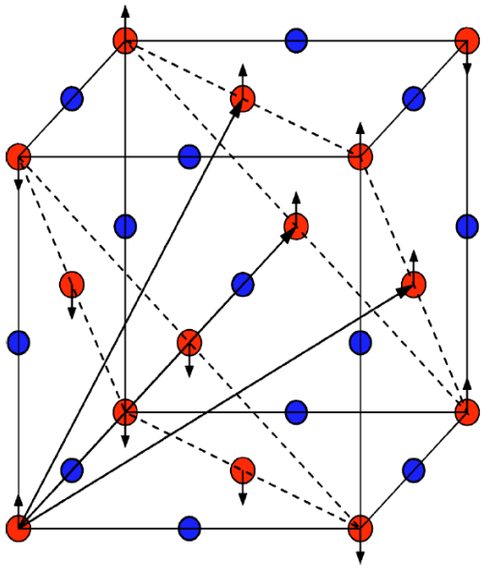
No gap: metallic ground state

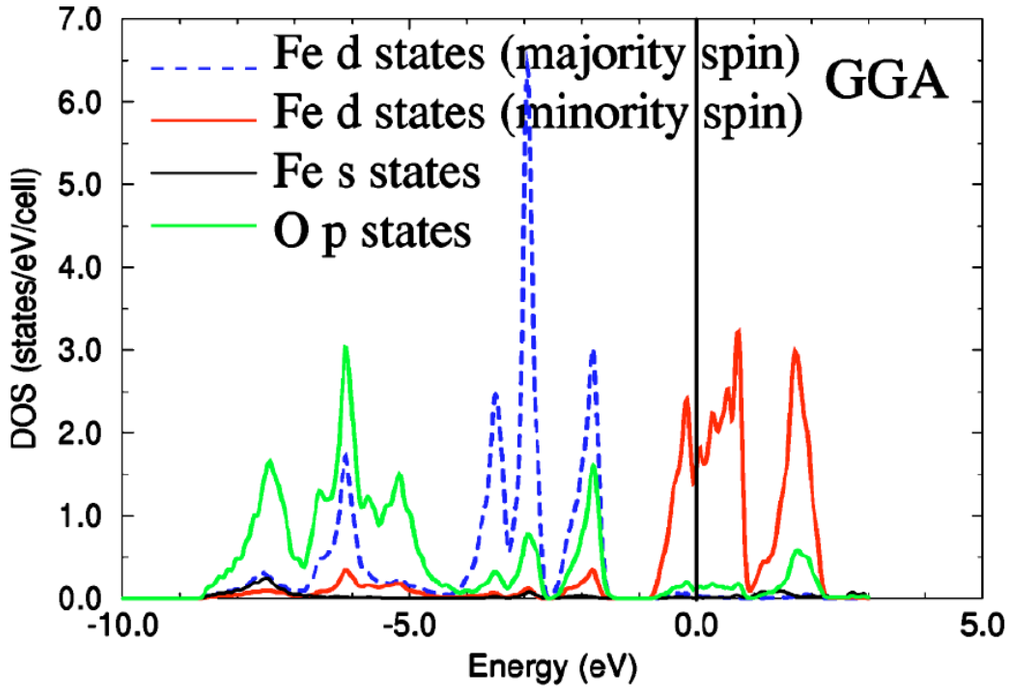
CF splitting

t_{2g} states (cubic)

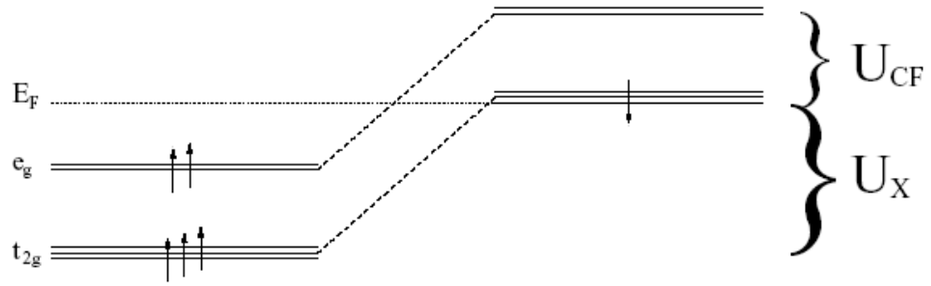
a_{1g} + $2e_g$ states (rhombohedral)

Orbital ordering: FeO





Fe^{2+}



No gap: metallic ground state

CF splitting

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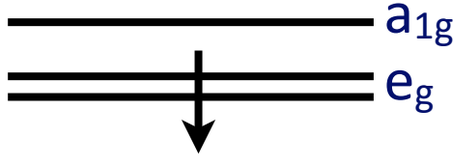
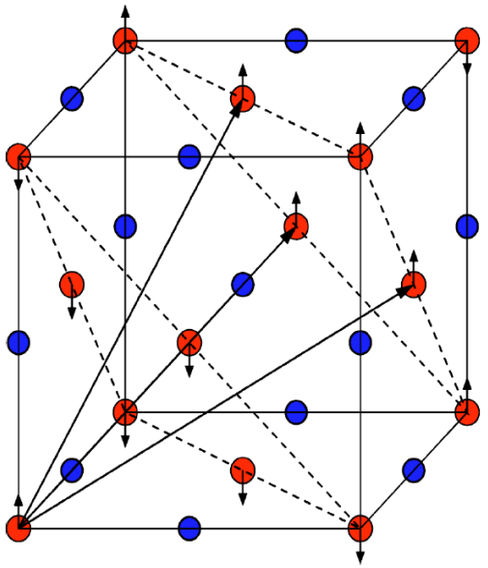
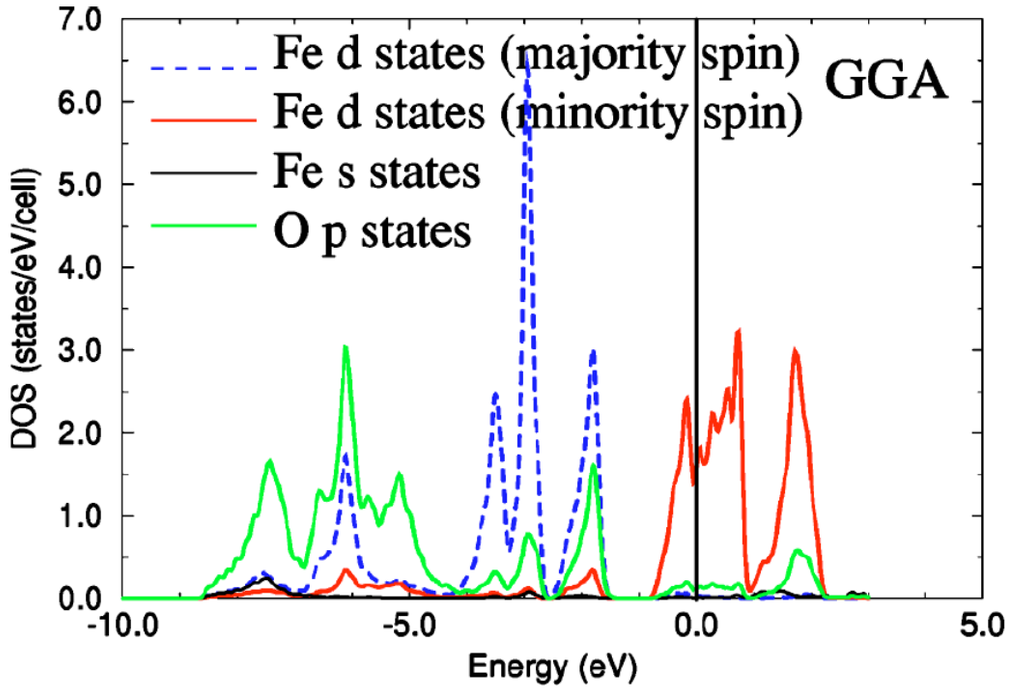
a_{1g} + $2e_g$ states (rhombohedral)

DFT solution (metallic)

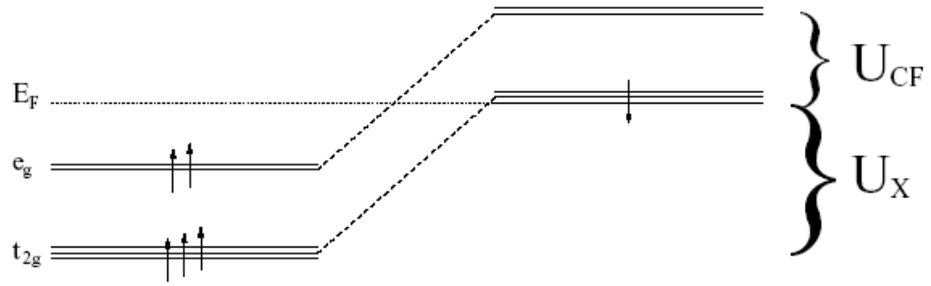


Orbital ordering: FeO





Fe^{2+}



No gap: metallic ground state

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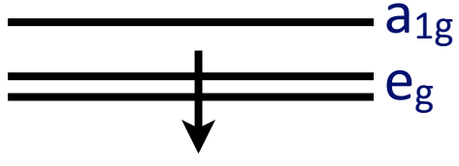
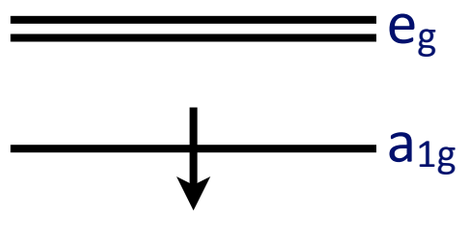
DFT solution (metallic)



DFT+U solution (insulator)



An orbital-ordered solution

An orbital-ordered solution

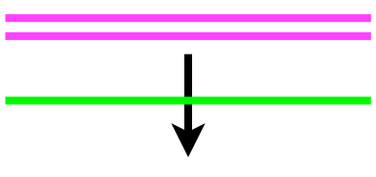
Can the metallic solution be understood as a combination of insulating ground states?

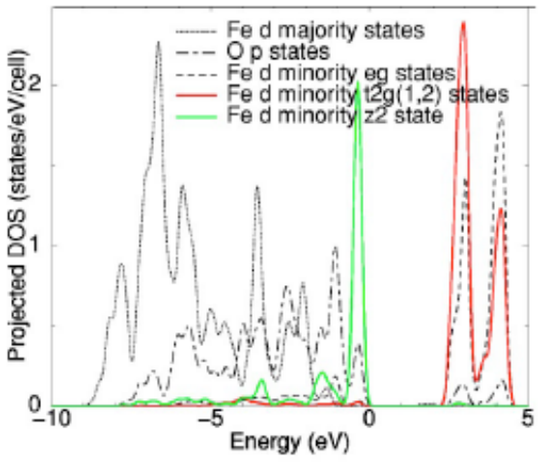
Would the “+U” correction stabilize the insulating GS?

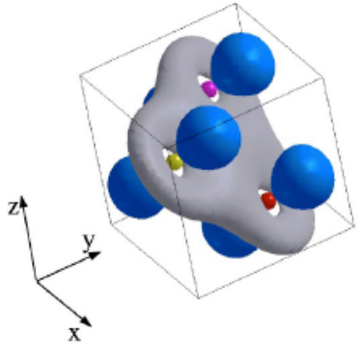
An orbital-ordered solution

Can the metallic solution be understood as a combination of insulating ground states?

Would the “+U” correction stabilize the insulating GS?



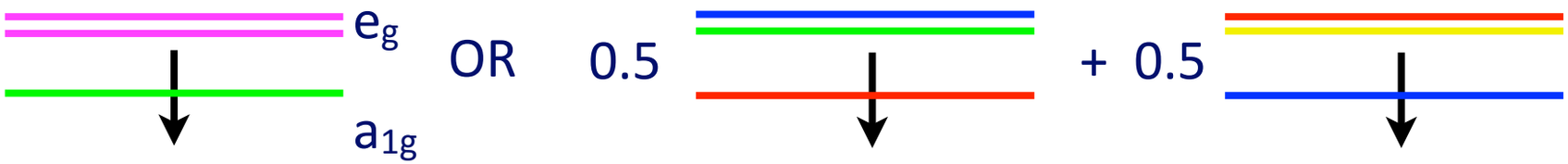


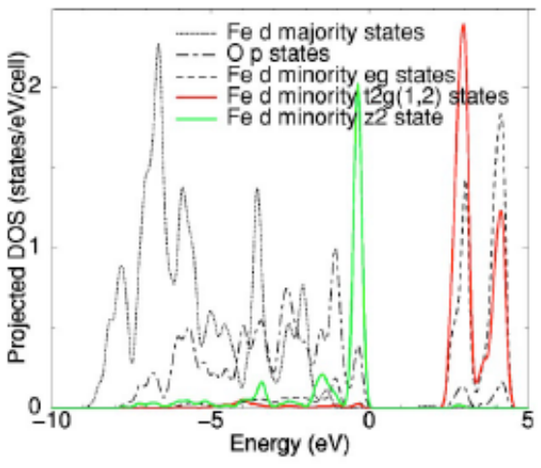


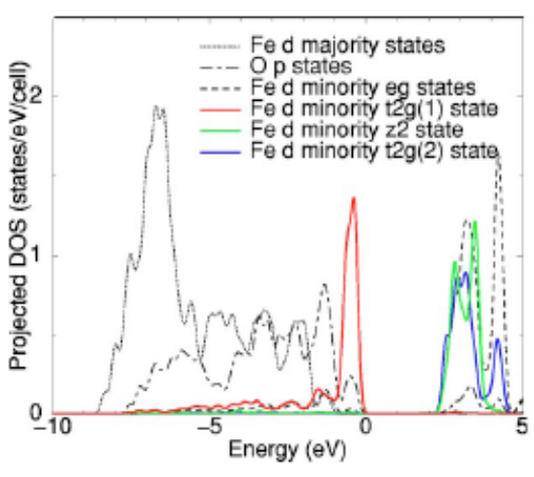
An orbital-ordered solution

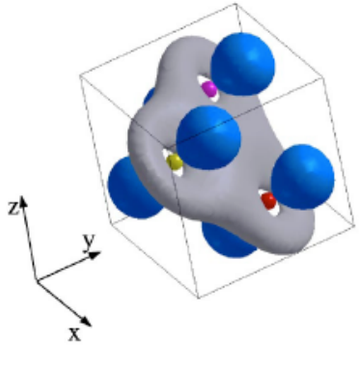
Can the metallic solution be understood as a combination of insulating ground states?

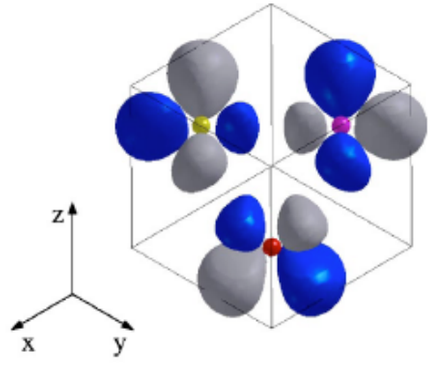
Would the “+U” correction stabilize the insulating GS?







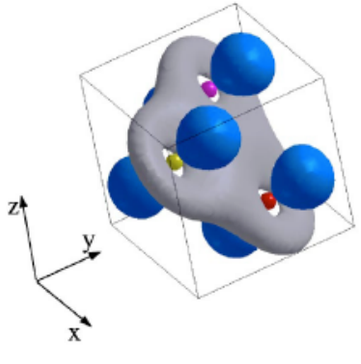


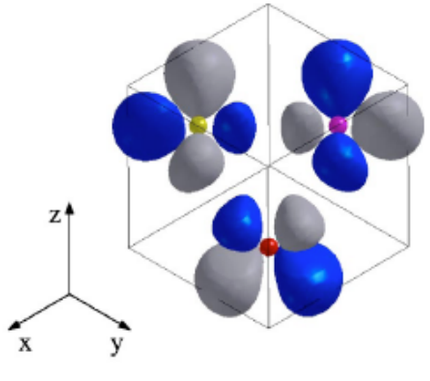


An orbital-ordered solution

Can the metallic solution be understood as a combination of insulating ground states?

Would the “+U” correction stabilize the insulating GS?





An orbital-ordered solution

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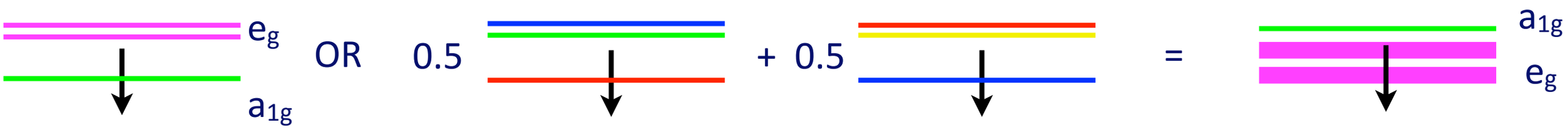
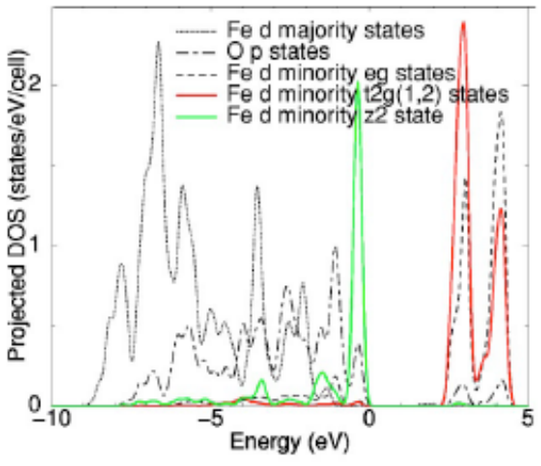
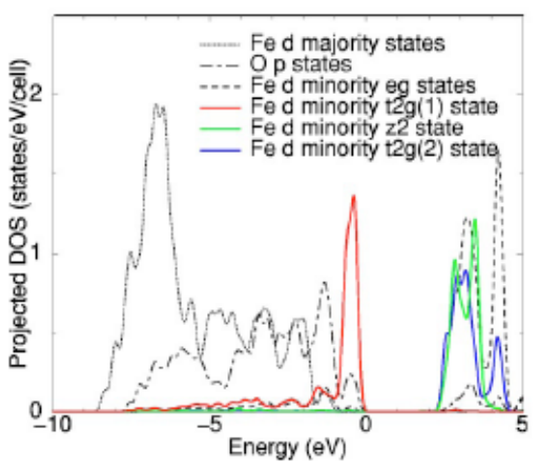
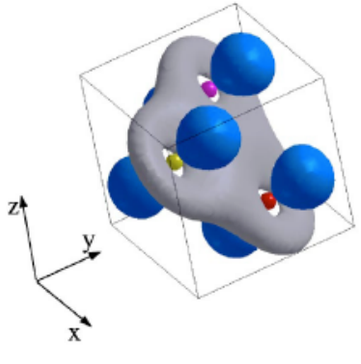


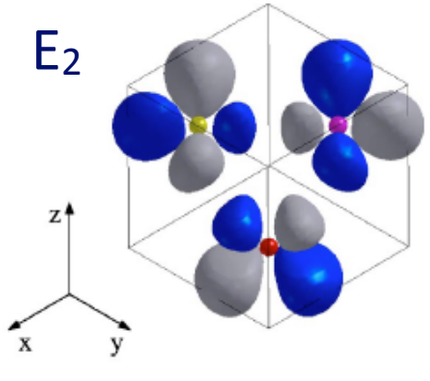




E_1



E_2



An orbital-ordered solution

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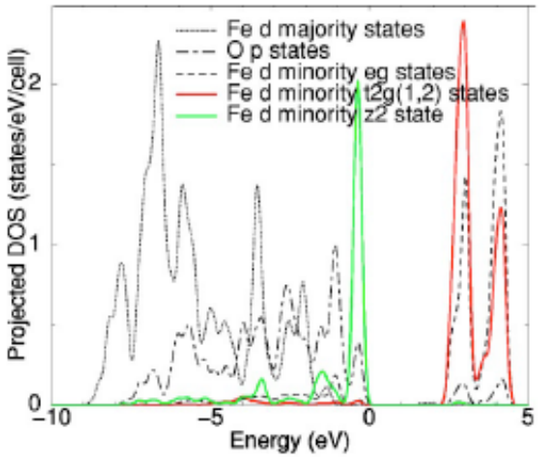
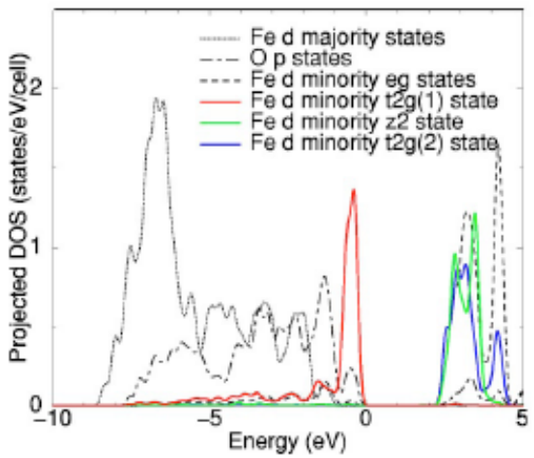
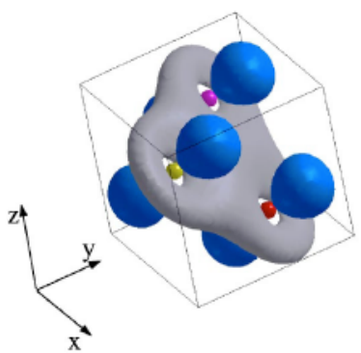


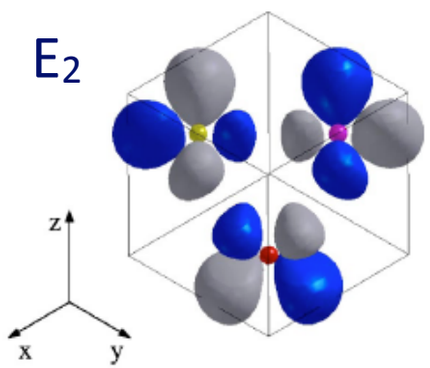


$E_1 > E_2$

E_1



E_2



An orbital-ordered solution

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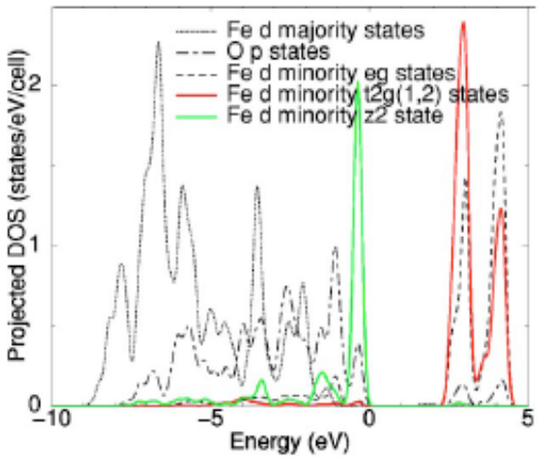

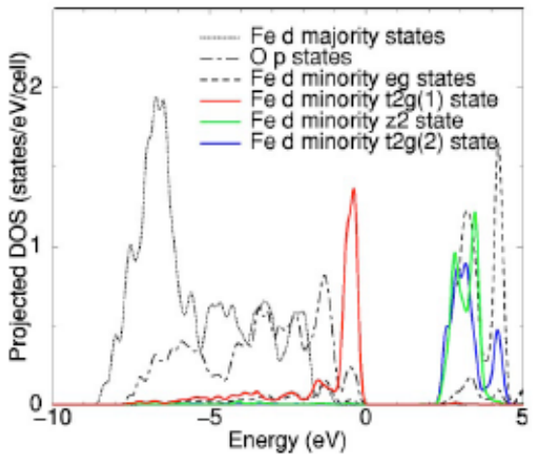

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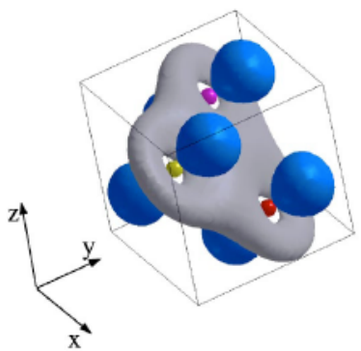

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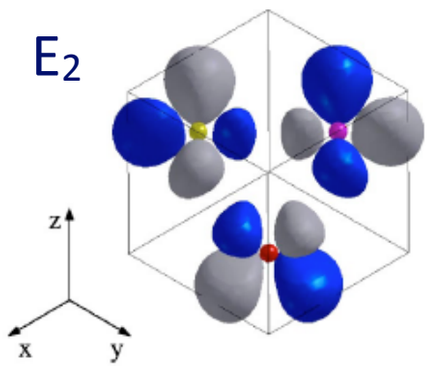

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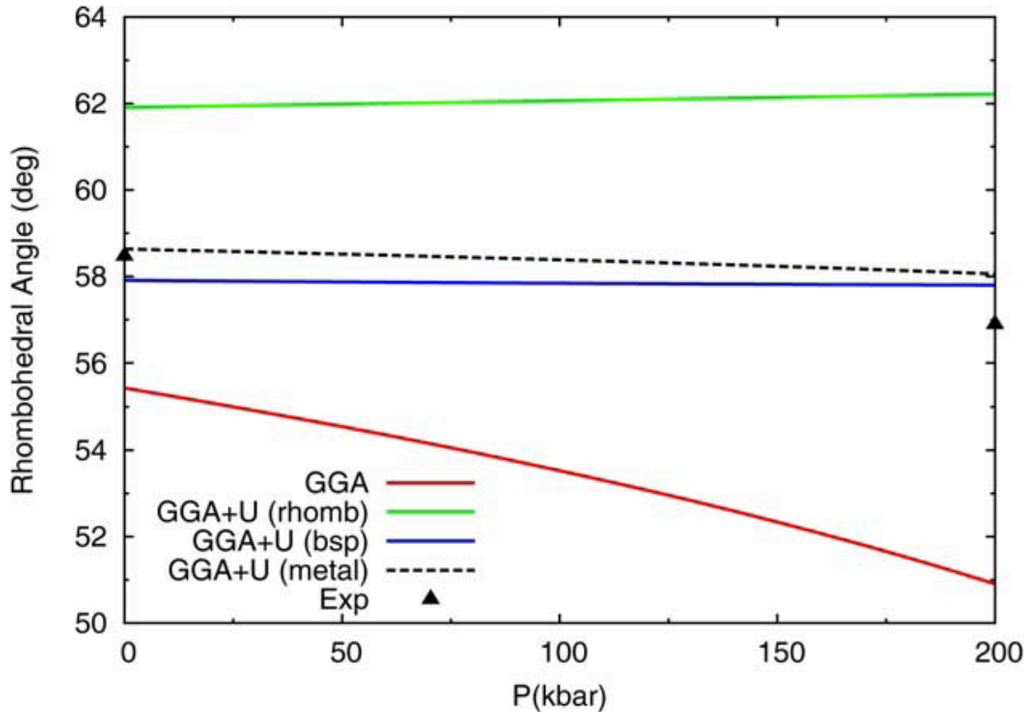
rhombohedral distortion vs P



Summary of the general theory part

- DFT+U is based on a correction shaped on the Hubbard model

- It helps improving the localization of charge and quantities that depend on it (e.g., magnetic interactions)

- It can be expected to work for non degenerate ground states

- Use with care in presence of degenerate ground states (e.g., FeO)

Computing U

The meaning of U

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

V. I. Anisimov, J. Zaanen, O. K. Andersen, PRB 44, 943 (1991)

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

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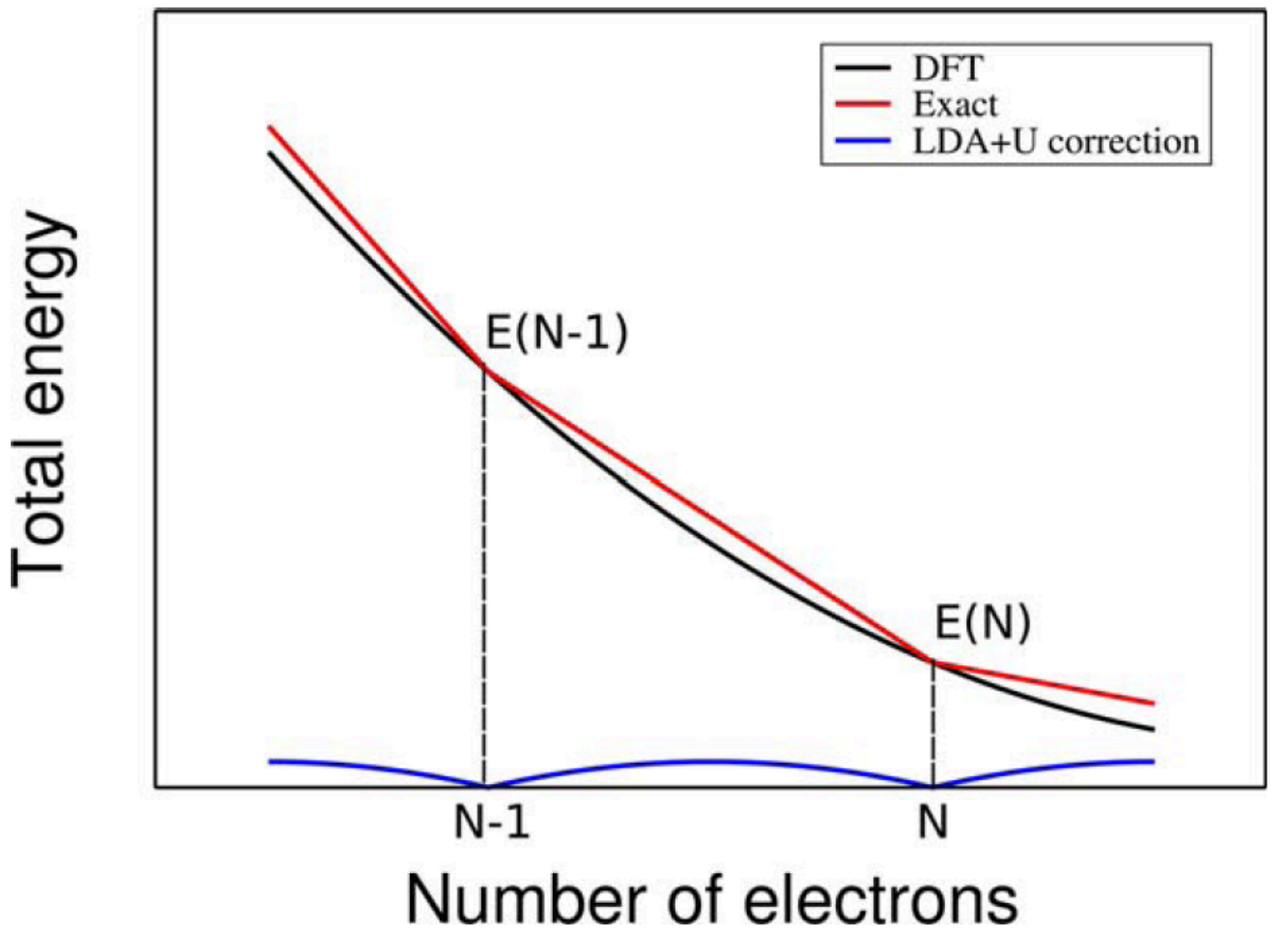

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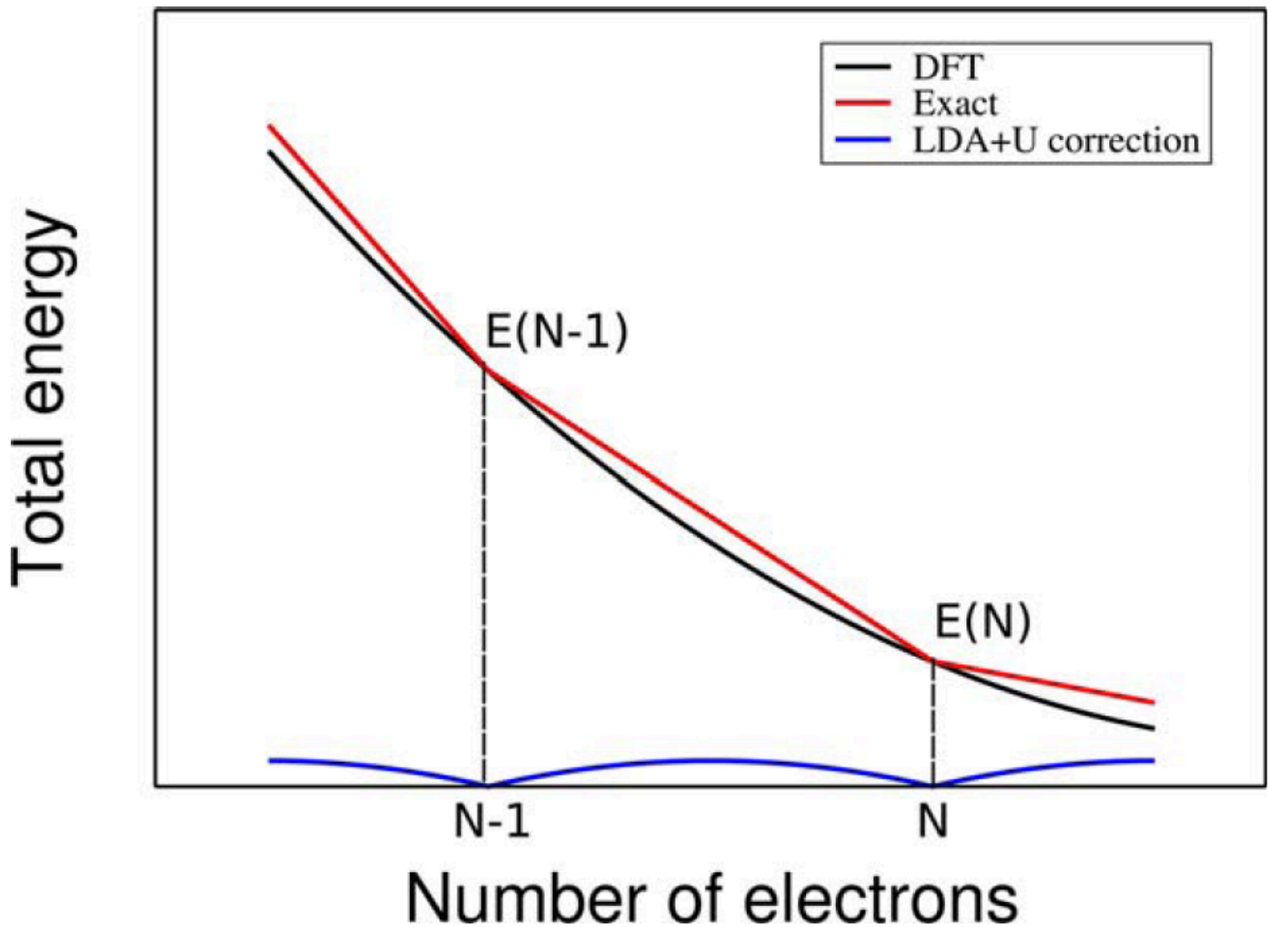

Hubbard U: spurious curvature of the energy...

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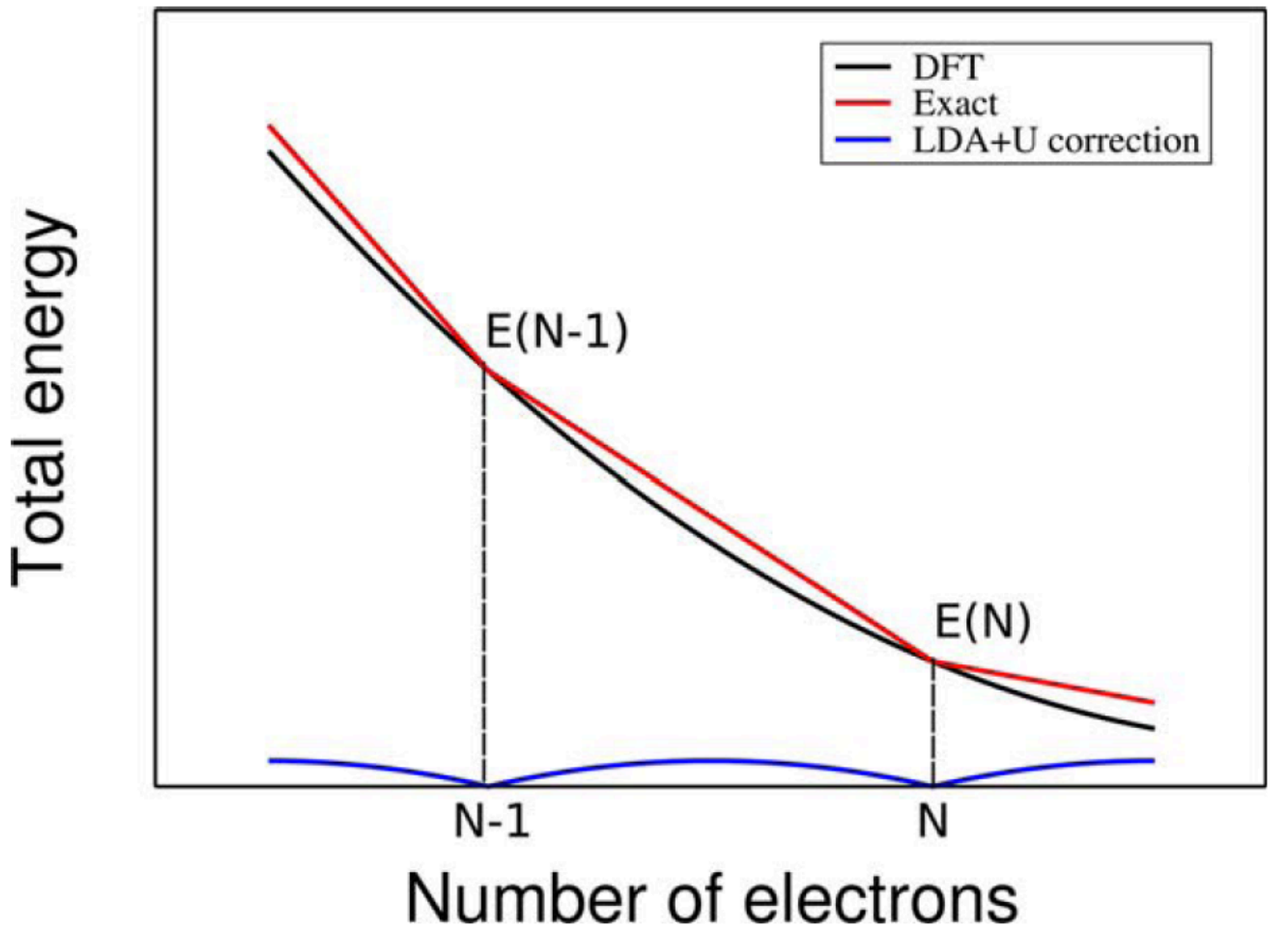

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... discontinuity of the xc functional

$$U \approx \Delta_{xc} = \Delta - \Delta_{KS}$$

Hubbard U from first-principles

- U corresponds to the spurious curvature of the energy to be eliminated

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M. Cococcioni and S. de Gironcoli, PRB 71, 35105 (2005)

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

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

A functional of the atomic occupations can be defined as:

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First and second derivatives can be easily obtained:

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

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

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Apply a perturbation to the potential acting on each Hubbard atom;
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$$V_{tot}|\psi^{\sigma}_{kv}\rangle = V_{KS}|\psi^{\sigma}_{kv}\rangle + \alpha^{I}\sum_{m}|\phi^{I}_{m}\rangle\langle\phi^{I}_{m}|\psi^{\sigma}_{kv}\rangle \;\Rightarrow\; \Delta n^{I}$$

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- Easy implementation in different computational schemes.

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

Overview of some extensions

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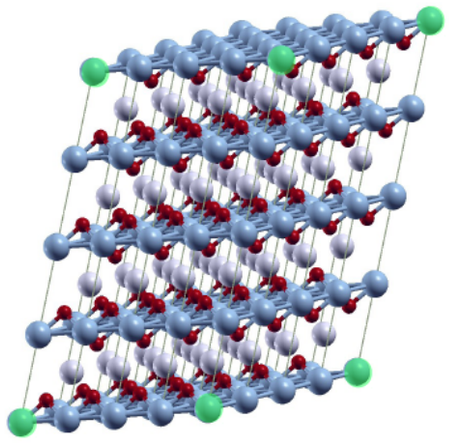
The calculation of U can be also made **consistent with the crystal structure** by performing a structural optimization after every calculation of U.

The cycle is interrupted when both structure and Hubbard parameters have converged.

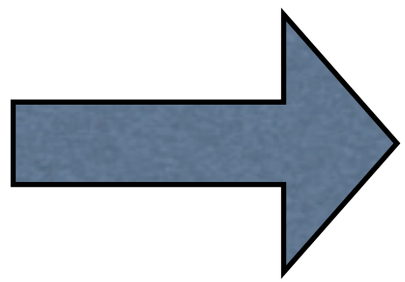
Automatic calculation of U

Calculation of the Hubbard U from Density Functional Perturbation Theory

finite differences in



Γ - point perturbation



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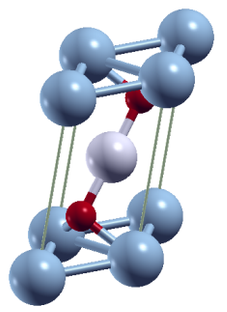

sum over monochromatic perturbations

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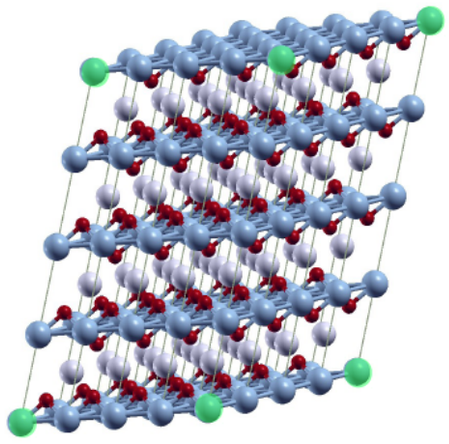

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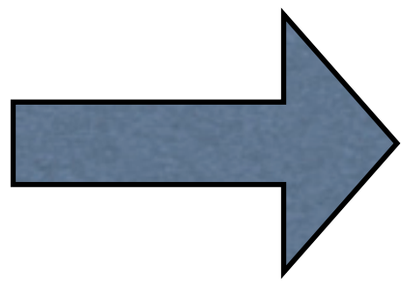

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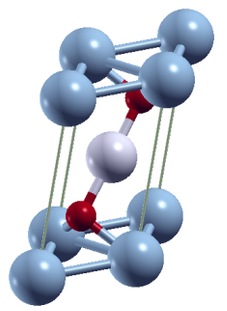

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$$V^I_{pert} = \alpha_I \sum_{m\mathbf{k}} |\phi^I_{m\mathbf{k}}\rangle\langle\phi^I_{m\mathbf{k}}|$$

Δn^I_{sc} read from output

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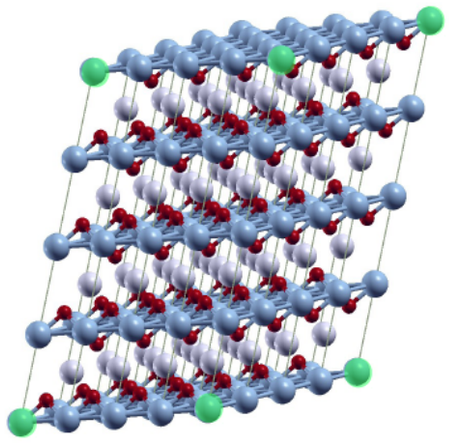

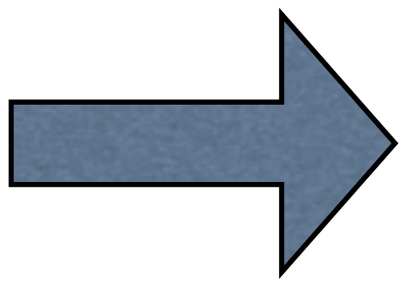

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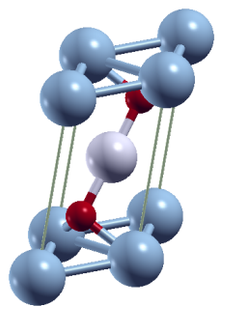

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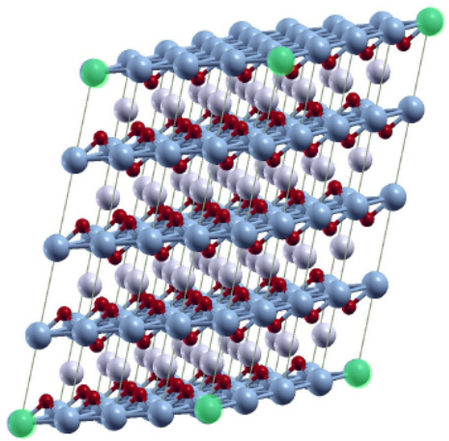

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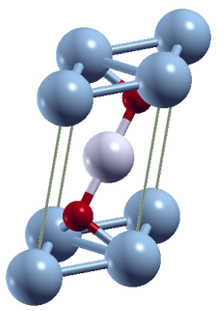

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Automation of the calculation and possible porting on “high-throughput” platforms

Extension of the method to closed-shell systems

DFT+U for covalent systems

DFT+U for covalent systems: Si e GaAs

$$U \approx \Delta_{xc} = \Delta - \Delta_{KS}$$

Can DFT+U improve the band gap estimate for band semiconductors?

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Can DFT+U improve the band gap estimate for band semiconductors?

	Si			GaAs		
	a (A)	B (GPa)	E_g (eV)	a (A)	B (GPa)	E_g (eV)
DFT	5.48	83.0	0.64	5.77	58.4	0.19
DFT+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

The DFT+U+V functional

DFT+U energy functional (from the Hubbard model)

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DFT+U+V energy functional (from the *extended* Hubbard model)

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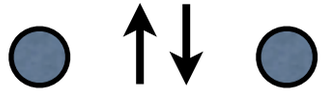

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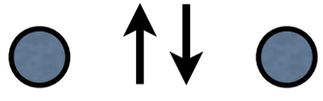

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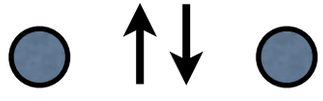
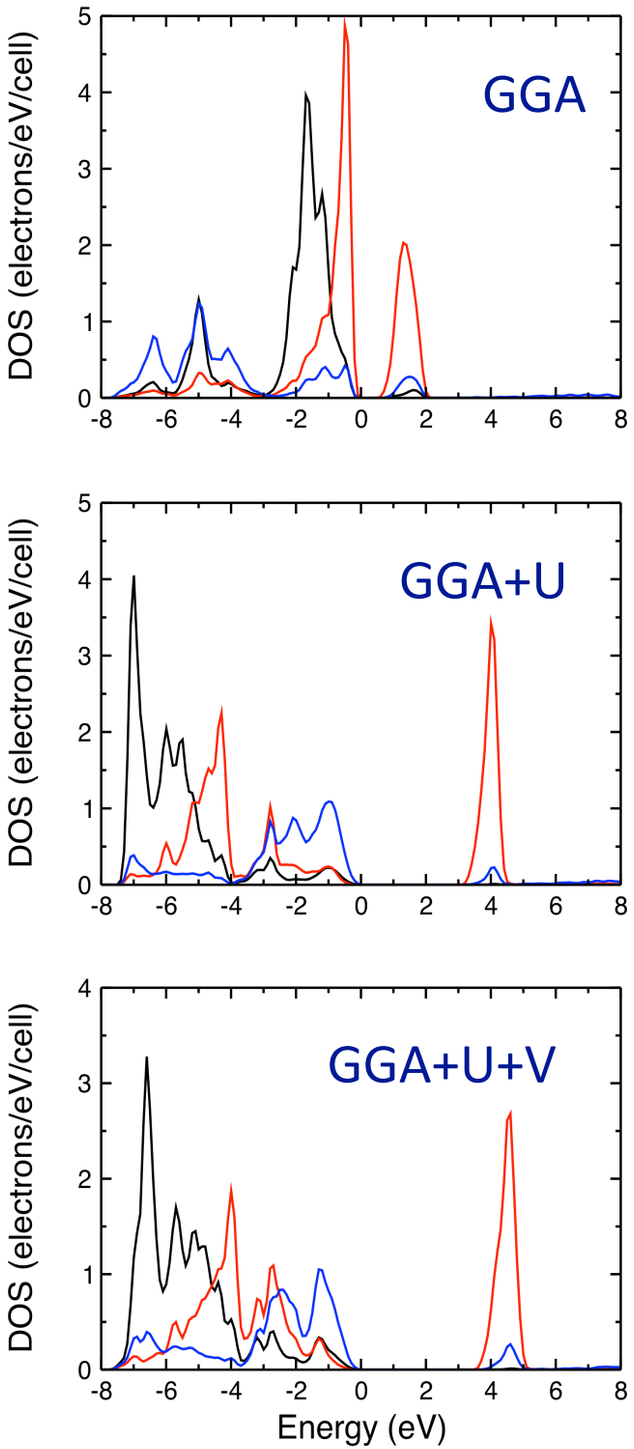


DFT+U+V can capture more general localization patterns and intermediate situations (e.g., TM magnetic impurities in semiconductors)

<u>*U* and *V* can be computed simultaneously</u> (at no extra cost)

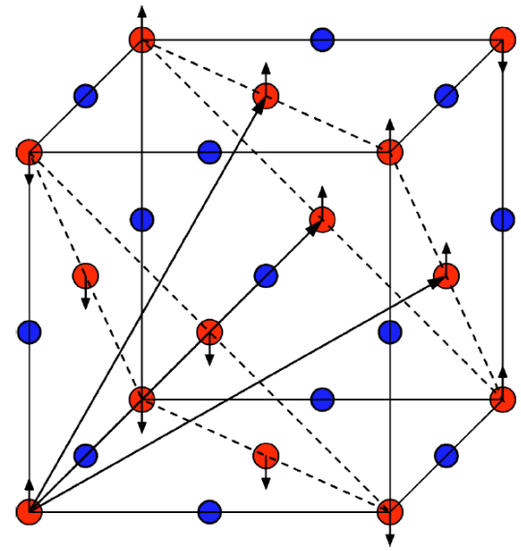
V. L. Campo Jr and M. Cococcioni, J. Phys.: Condens Matter 22 055602 (2010)

NiO



Typical TMO:

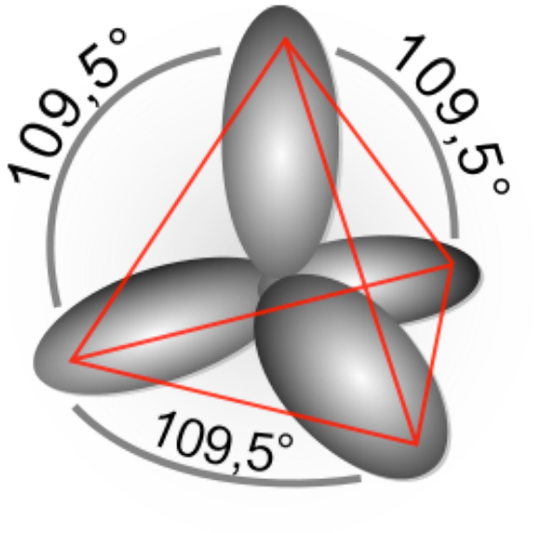
- Rock-salt structure
- AFII: rhombohedral symmetry
- Mott or Charge transfer insulator



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

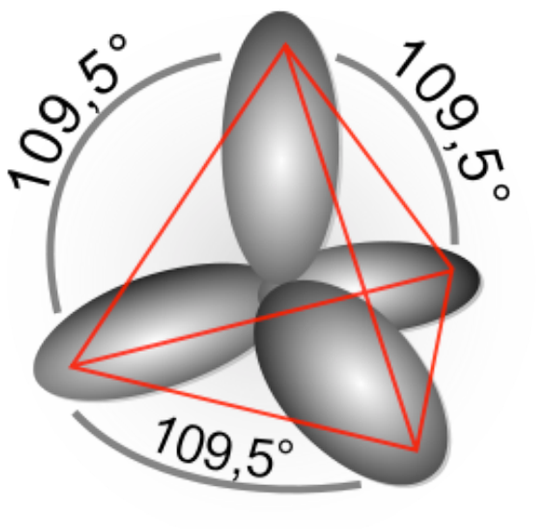
Electronic and structural properties of Si and GaAs

Electronic and structural properties of Si and GaAs



	U_{pp}	U_{ps}	U_{sp}	U_{ss}	V_{pp}	V_{ps}	V_{sp}	V_{ss}
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

Electronic and structural properties of Si and GaAs



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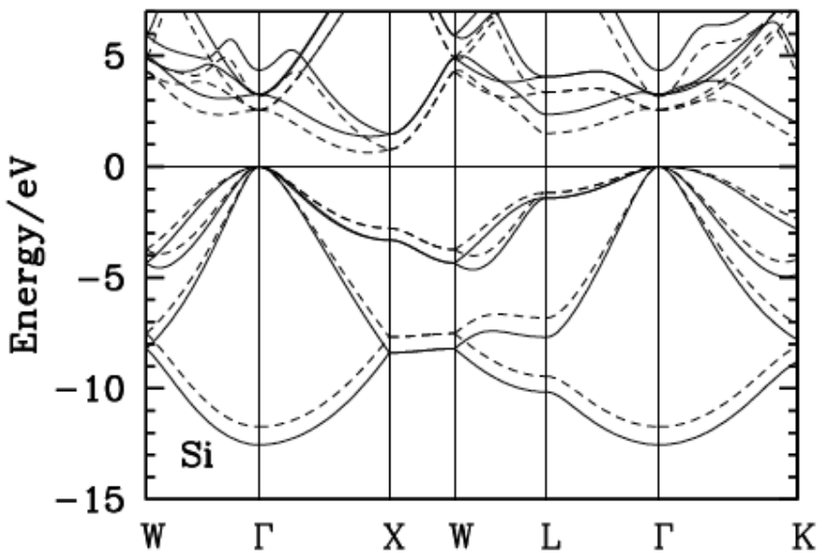
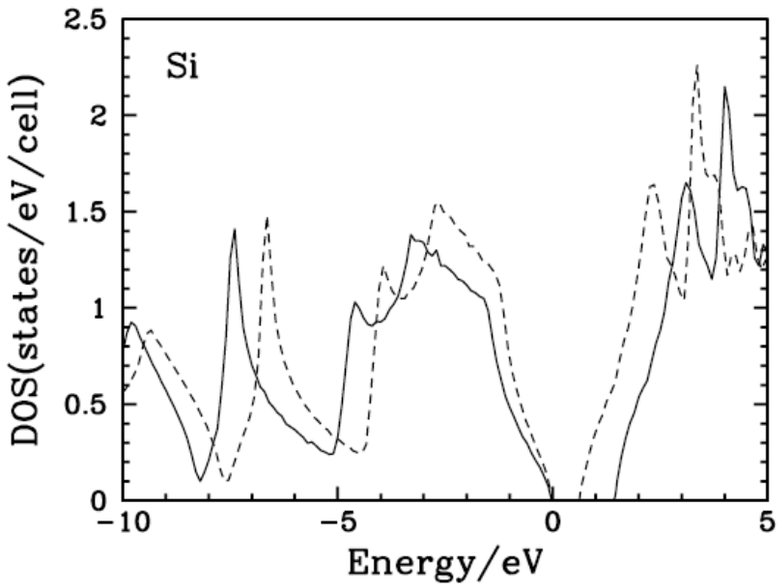
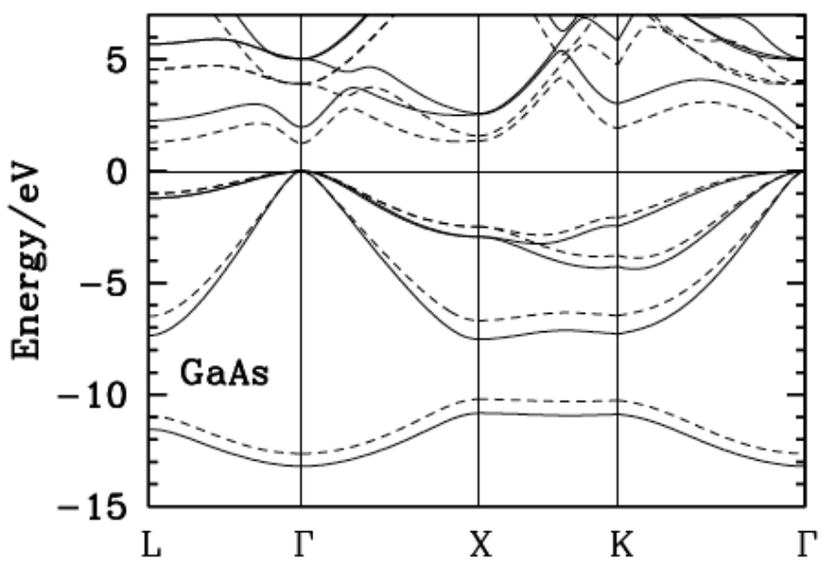
	Si			GaAs		
	a (A)	B (GPa)	E_g (eV)	a (A)	B (GPa)	E_g (eV)
DFT	5.48	83.0	0.64	5.77	58.4	0.19
DFT+U	5.36	93.9	0.39	5.74	52.6	0.00
DFT+U+V	5.37	102.5	1.36	5.65	67.5	0.90
Exp	5.43	98.0	1.12	5.65	75.3	1.42

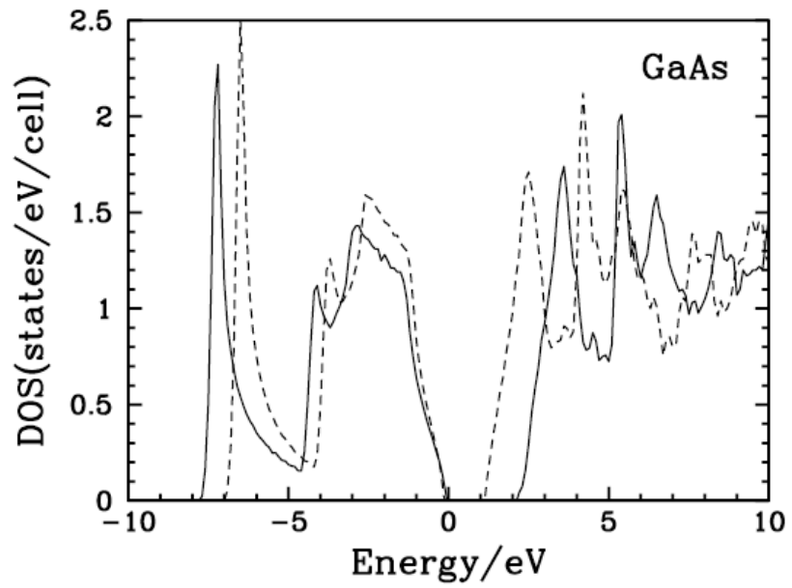
V. L. Campo Jr and M. Cococcioni, *J. Phys.: Condens Matter* 22, 055602 (2010)

DFT+U+V band structure of Si and GaAs









------- GGA ——— GGA+U+V

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

Voltage and formation energies of Li_xFePO_4

Method	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 3.5
DFT	-126	2.73
DFT+U	159	4.06
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e^- on Fe	$LiFePO_4$		$Li_{0.5}FePO_4$		$FePO_4$	
Method	2+	3+	2+	3+	2+	3+
DFT	6.22		6.11	6.08		5.93
DFT+U	6.19		6.19	5.68		5.65
DFT+U+V	6.22		6.22	5.77		5.76

Voltage and formation energies of Li_xMnPO_4

Method	F. E. (meV/FU)	Voltage (V)
Exp	> 0	~ 4.1
DFT	63	2.82
DFT+U	212	4.31
DFT+U+V	206	4.15

e^- on Mn	$LiMnPO_4$		$Li_{0.5}MnPO_4$		$MnPO_4$	
Method	2+	3+	2+	3+	2+	3+
DFT	5.30		5.19	5.17		5.11
DFT+U	5.19		5.11	5.05		4.96
DFT+U+V	5.23		5.22	4.99		4.99

DFT+U & DFT+U+V

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- Never use as a black-box :-((((

End

Questions?

Hands-on tutorial (afternoon session)

Aims:

- To compare DFT and DFT+U results (e.g., DOS)
- To understand electron localization in mixed-valence oxides
- To familiarize with the calculation of U using LRT (finite differences between supercell calculations)
- To study the convergence of U with the size of the supercell

Systems:

- NiO
- $Li_{0.5}FePO_4$
- $Li_{0.5}CoO_2$

DFT+U: energy functional and potential

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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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Potential

$$V_{DFT+U} = V_{DFT} + \sum_{I,\sigma} \frac{U^I}{2}\left(\delta_{mm'} - 2n^I_{mm'}\right)|\phi^I_m\rangle\langle\phi^I_{m'}|$$

The meaning of U

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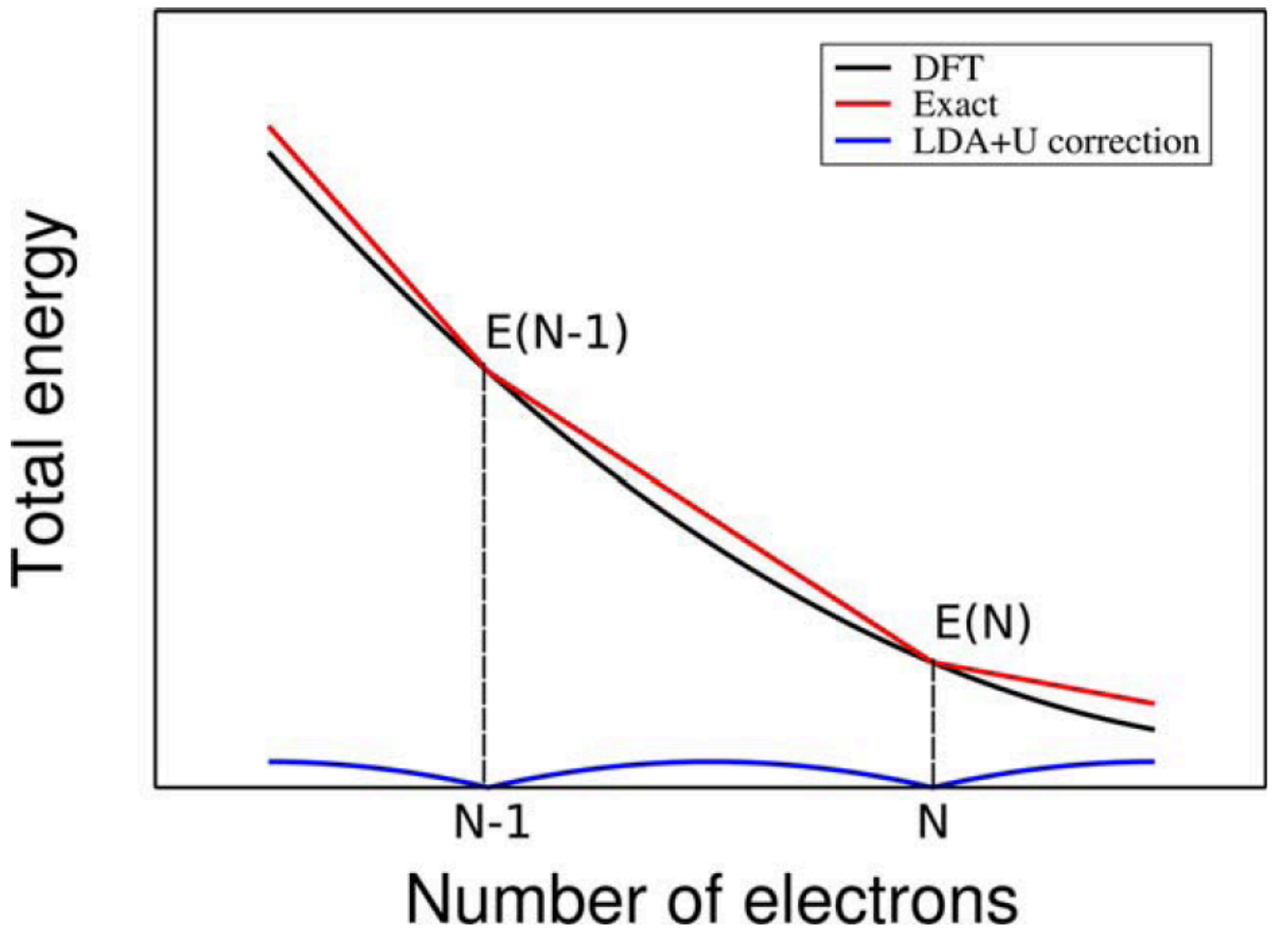

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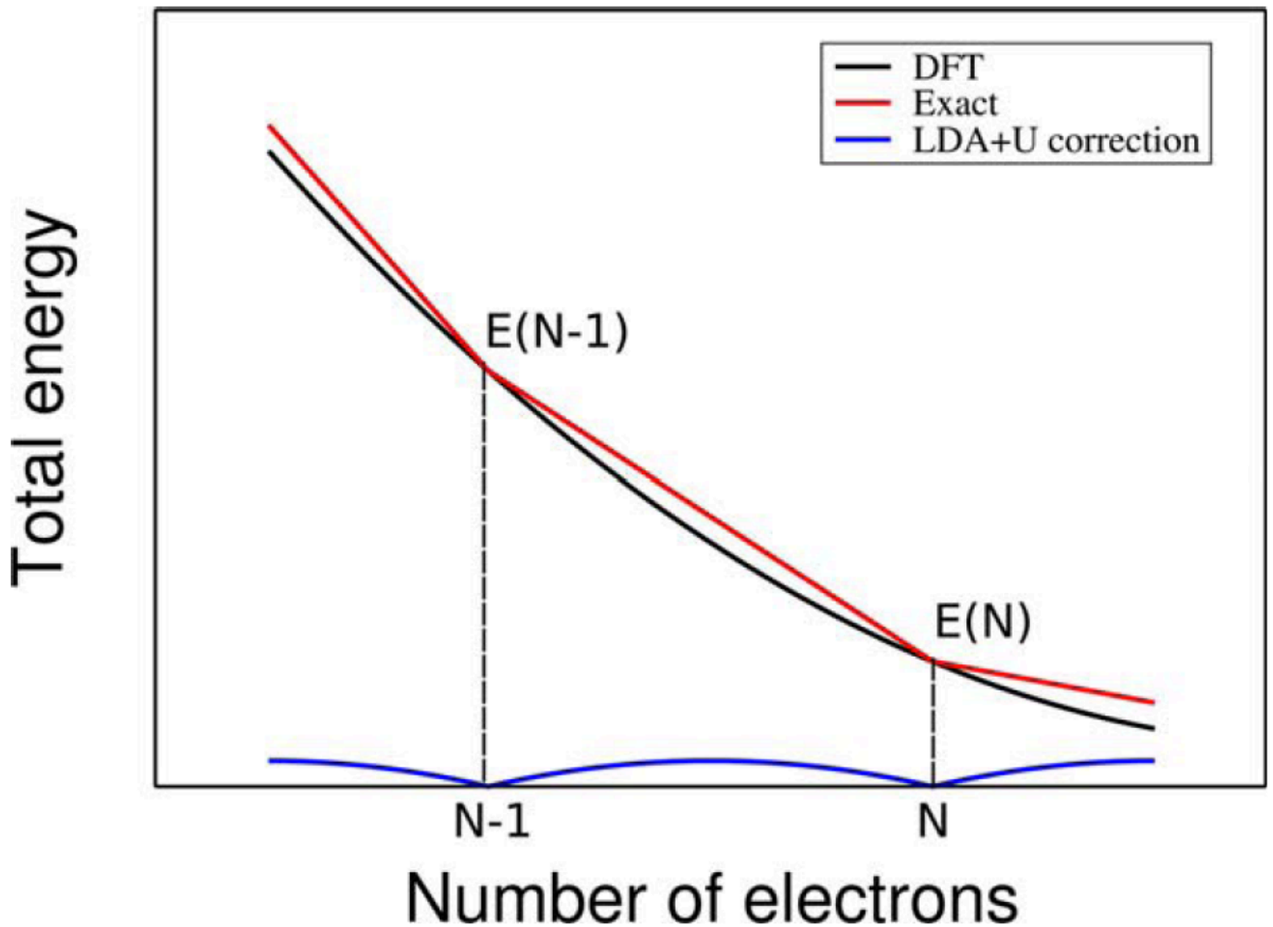

Hubbard U: spurious curvature of the energy...

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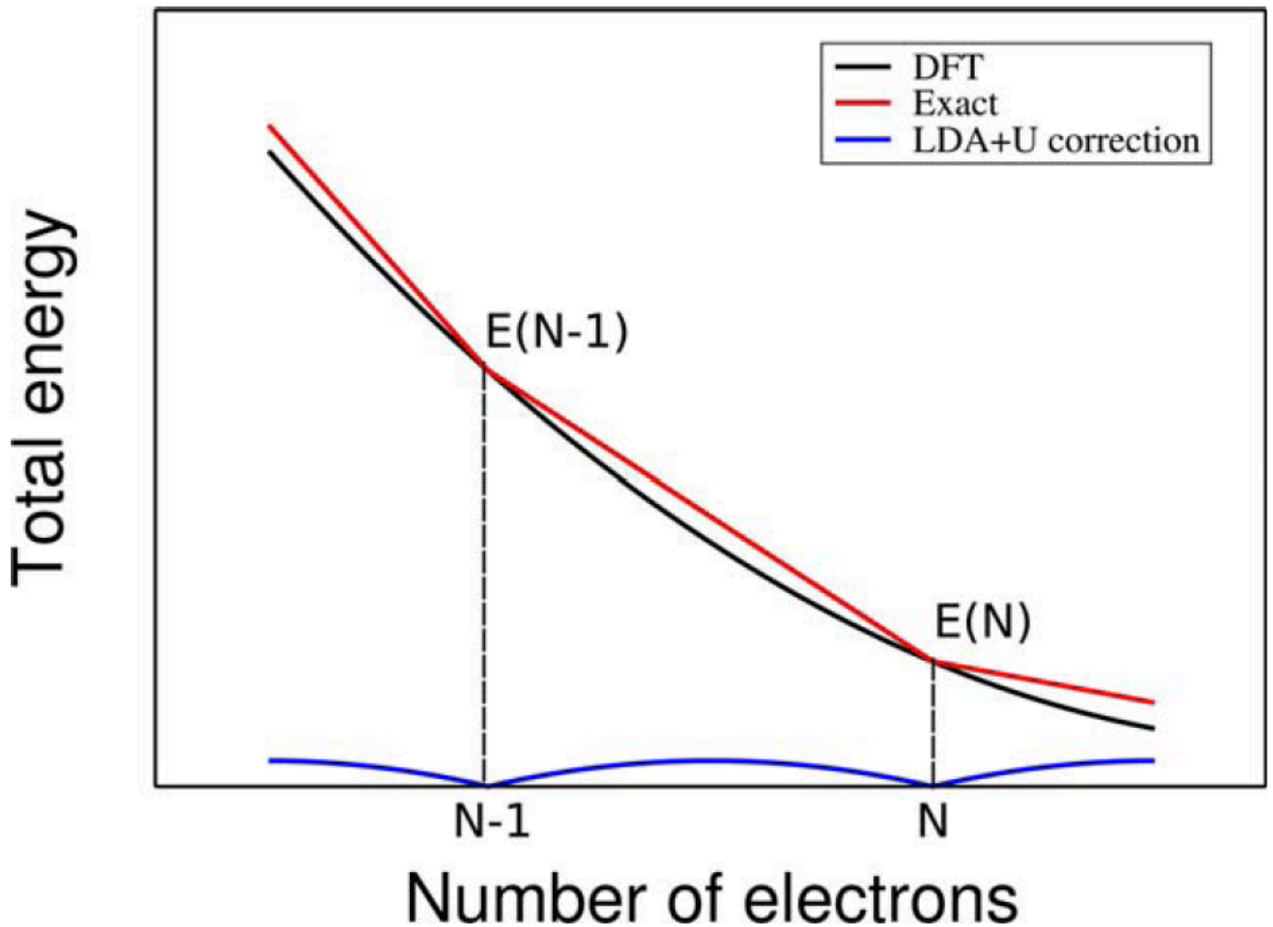


Hubbard U: spurious curvature of the energy...

$$U = \frac{d^2 E_{DFT}}{dn^2}$$

... discontinuity of the xc functional

$$U \approx \Delta_{xc} = \Delta - \Delta_{KS}$$

Hubbard U from first-principles

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

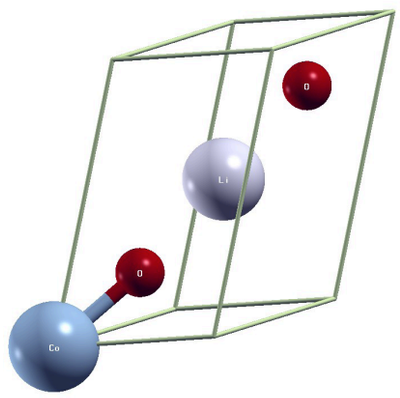
$$\chi^{IJ} = \frac{dn^I}{d\alpha^J} \qquad \chi_0^{IJ} = \frac{dn_0^I}{d\alpha^J}$$

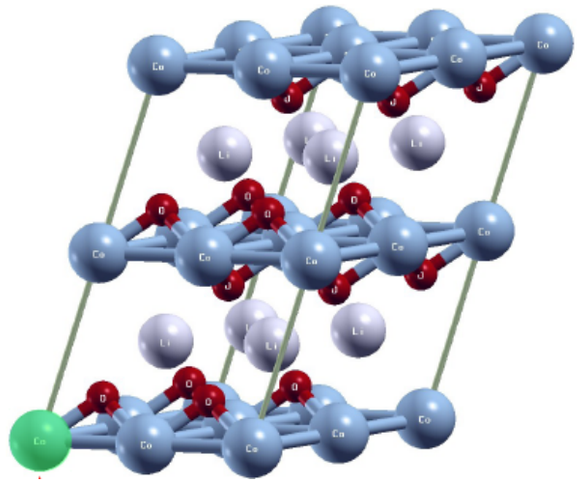
$$U^I = \left(\chi_0^{-1} - \chi^{-1}\right)_{II}$$

Some technical details

- The perturbation is applied in a supercell to avoid interactions with its periodic replica

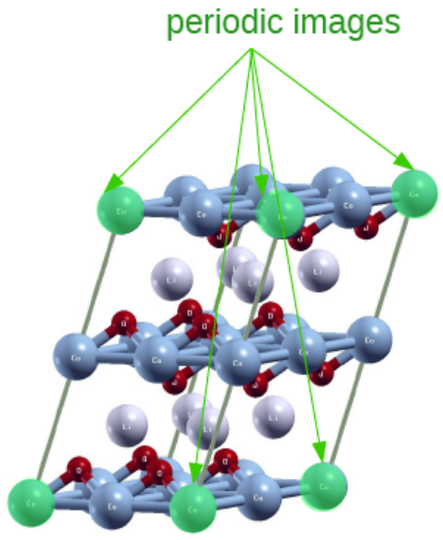
- The value of U should be converged with the size of the supercell

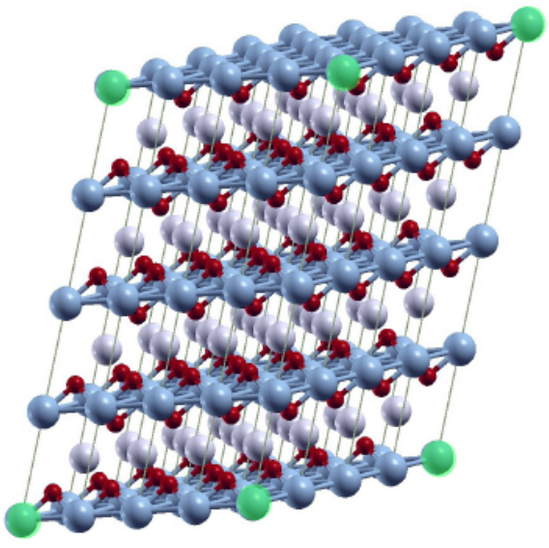




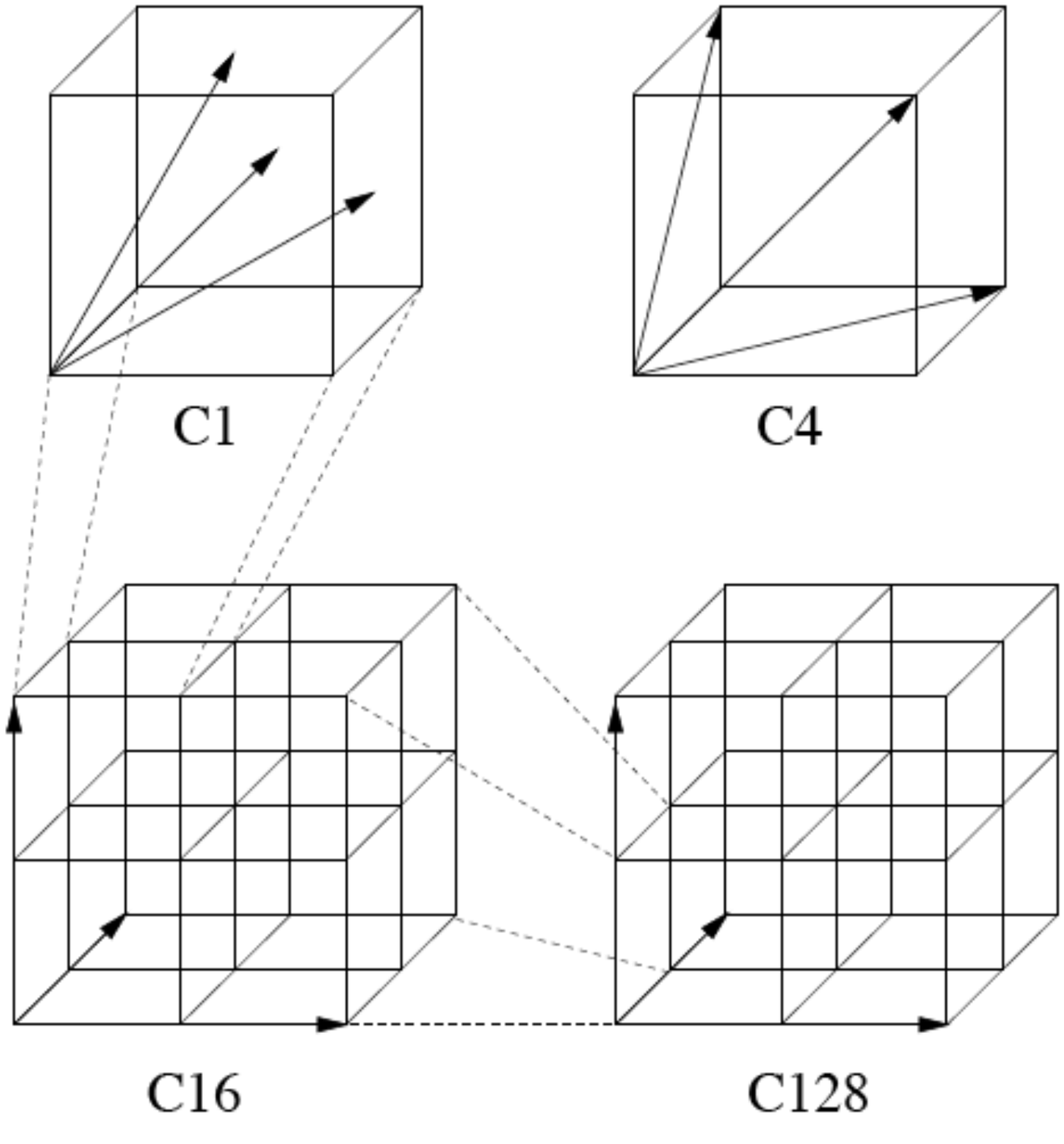
- The perturbation is applied on all the non-equivalent “Hubbard atoms”

- Often also non-Hubbard atoms and states are perturbed to evaluate the response of the “crystal bath” (charge reservoir)

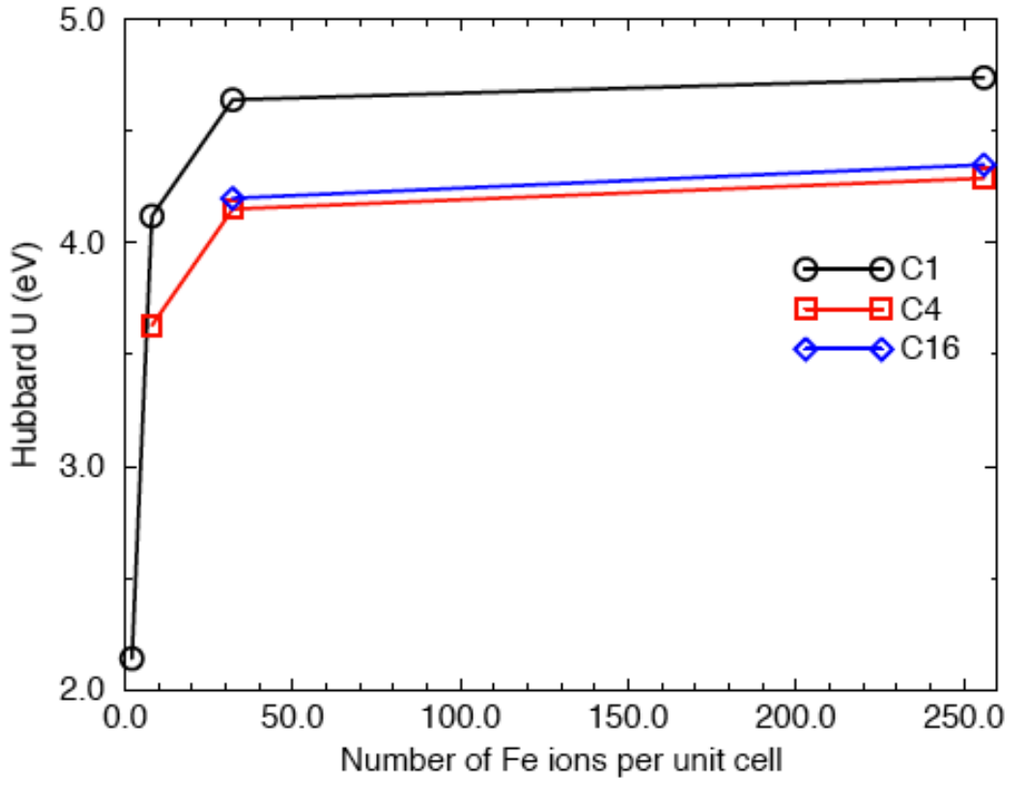




Isolated perturbations

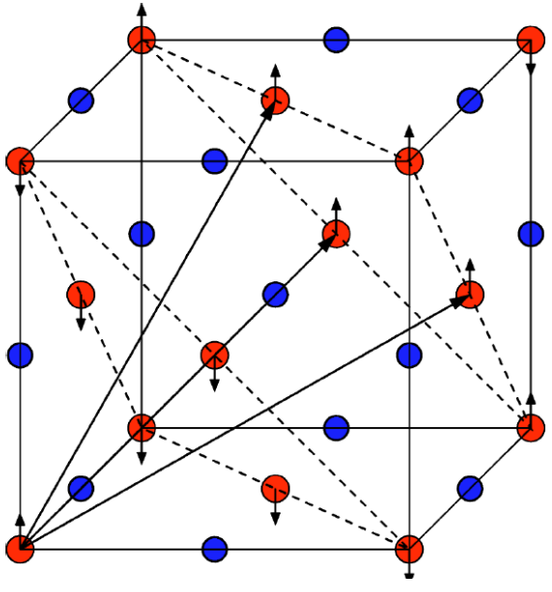


The U must be converged with the size of the supercell. Extrapolation also helpful



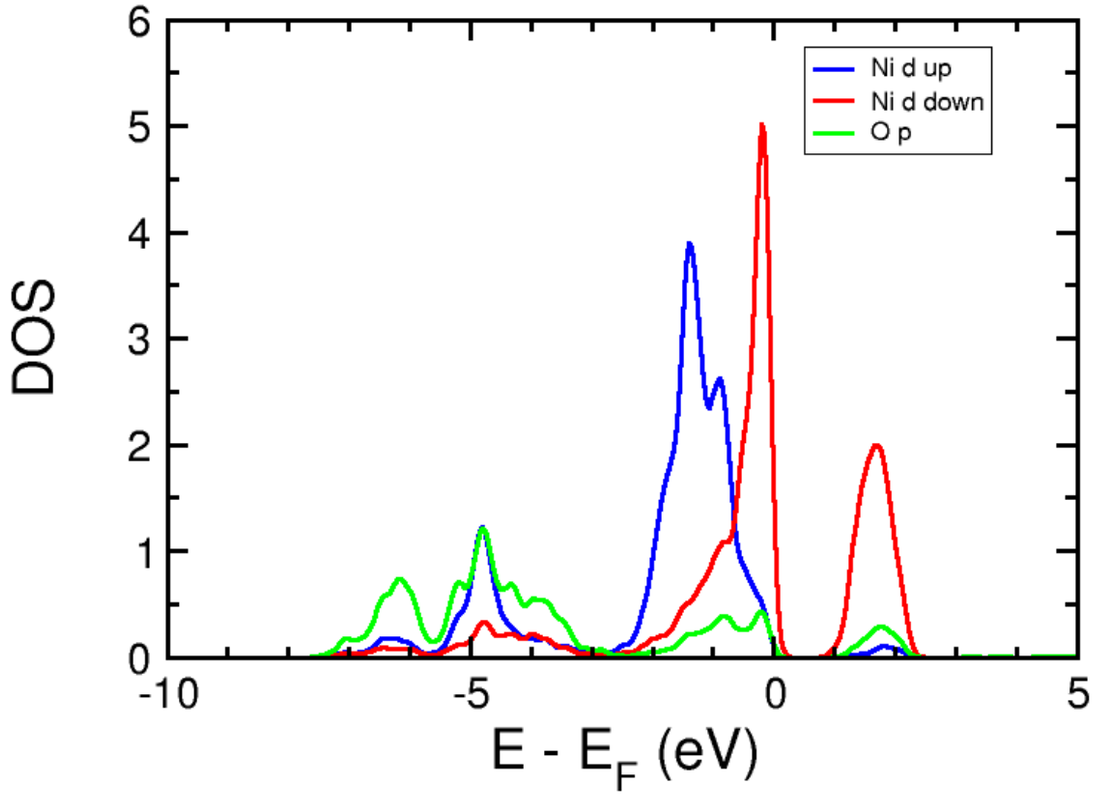
Potential shifts can be viewed as Γ- point perturbations for supercells.

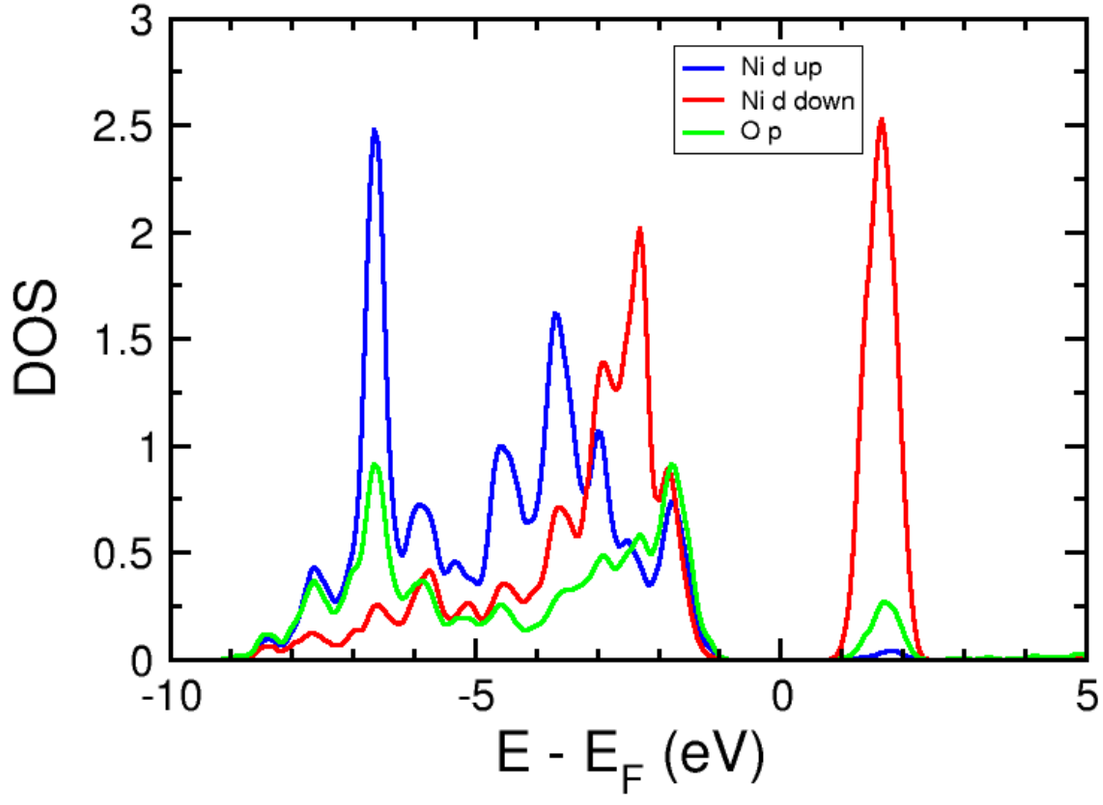
NiO



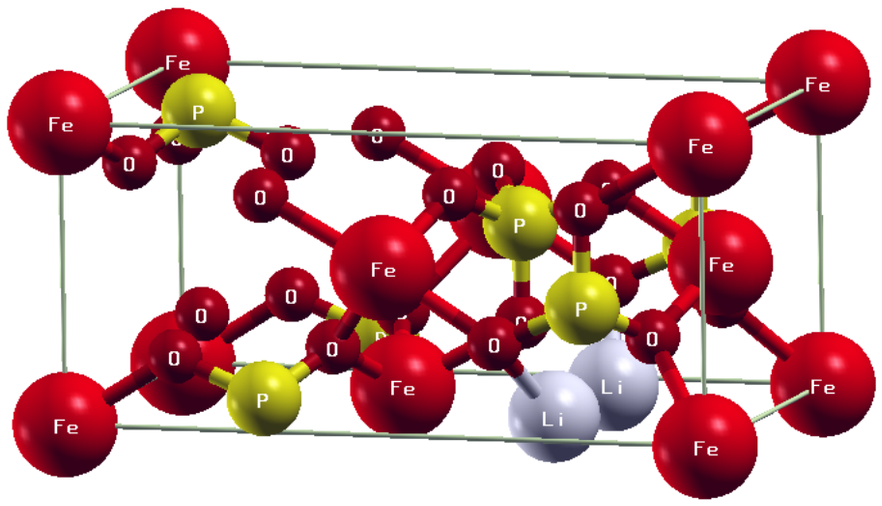
Aims:

- To study the effects of U (e.g., DOS)
- To compute U





$Li_{0.5}FePO_4$



Aims:

- To recognize mixed-valence ground states
- To study the role of U on enhancing electron localization and stabilizing charge disproportionation

Study the output (occupations)

```
atom    1   Tr[ns(na)] (up, down, total) =    4.98184
1.59590  6.57774

   spin  2
    eigenvalues:
  0.202  0.215  0.300  0.360  0.519
    eigenvectors:
  0.000  0.114  0.000  0.029  0.857
  0.000  0.695  0.000  0.261  0.044
  0.543  0.000  0.457  0.000  0.000
  0.000  0.191  0.000  0.709  0.099
  0.457  0.000  0.543  0.000  0.000
    occupations:
  0.479 -0.072  0.000 -0.068  0.000
 -0.072  0.266  0.000 -0.042  0.000
  0.000  0.000  0.247  0.000  0.048
 -0.068 -0.042  0.000  0.348  0.000
  0.000  0.000  0.048  0.000  0.255
```

$Li_{0.5}CoO_2$

Aims:

- To practice the calculation of U (on a mixed-valence material)
- To study the convergence of U with the size of the supercell used in the calculations