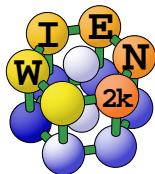


LDA+ U in WIEN2k

F. Tran

Institute of Materials Chemistry
Vienna University of Technology

15th WIEN2k workshop, 26-29 March 2008, Vienna



Kohn-Sham total-energy functional

The total energy is given by

$$E_{\text{KS}} = T_s + E_{\text{xc}} + V_{\text{ee}} + V_{\text{en}} + V_{\text{nn}}$$

- ▶ T_s : kinetic energy
- ▶ $E_{\text{xc}} = E_x + E_c$: exchange-correlation energy
- ▶ V_{ee} : electron-electron electrostatic Coulomb energy
- ▶ V_{en} : electron-nucleus electrostatic Coulomb energy
- ▶ V_{nn} : nucleus-nucleus electrostatic Coulomb energy

The variational principle

The variational principle

$$\frac{\delta E_{\text{KS}}}{\delta \psi_i^*(\mathbf{r})} = \frac{\delta}{\delta \psi_i^*(\mathbf{r})} \left(\sum_{ij} \epsilon_{ij} \left(\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d^3r - \delta_{ij} \right) \right)$$

leads to the Kohn-Sham equations:

$$\left(-\frac{1}{2} \nabla^2 + \hat{v}_{\text{eff}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

where

$$\hat{v}_{\text{eff}}(\mathbf{r}) = \hat{v}_{\text{xc}}(\mathbf{r}) + v_{\text{ee}}(\mathbf{r}) + v_{\text{en}}(\mathbf{r})$$

Exchange-correlation potential

Depending on the choice for E_{xc} , \hat{v}_{xc} can be **orbital-independent**:

$$\hat{v}_{xc} = v_{xc} \quad (\text{e.g., LDA, GGA})$$

or **orbital-dependent**:

$$\hat{v}_{xc} = v_{xc,i} \quad (\text{e.g., meta-GGA, Hartree-Fock, LDA+}U)$$

Exchange-correlation functionals available in WIEN2k

- ▶ LDA (PW92 for correlation)
- ▶ GGA (PBE, WC, PBEsol, AM05, etc.)
- ▶ Meta-GGA (e.g., TPSS) (not self-consistent)
- ▶ LDA+ U , GGA+ U , meta-GGA+ U (on-site)
- ▶ Approximate Hartree-Fock (on-site)
- ▶ Approximate hybrid functionals (PBE0, B3PW91, etc.) (on-site)

When do LDA and GGA fail?

For many solids and properties, LDA and GGA functionals are good enough to be useful, but there are particular cases where they give very bad results.

For instance, LDA and GGA are not able to describe correctly:

- ▶ The geometry and energetics of van der Waals complexes. The reason is that the **dispersion interaction** is not included in LDA and GGA.
- ▶ The electronic and magnetic structures of strongly correlated systems. One of the reasons is that LDA and GGA are not **self-interaction free**.

The self-interaction error

The electron-electron electrostatic Coulomb energy

$$V_{ee} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$

contains the interaction of an electron with itself (the self-interaction):

$$\sum_{i=1}^N \frac{1}{2} \int \int \frac{|\psi_i(\mathbf{r})|^2 |\psi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$

In principle, this self-interaction should be removed by the exchange energy. For instance, for **one-electron systems** one should have

$$V_{ee} + E_x = 0 \quad (\text{and also } E_c = 0)$$

This is what is done in Hartree-Fock theory, but not in LDA and GGA.

(Partially) self-interaction free functionals

- ▶ Hartree-Fock
- ▶ Kohn-Sham exact exchange (EXX, OEP)
- ▶ Self-interaction corrected LDA ¹ (there are several variants)
- ▶ LDA+ U (there are several variants)

Interesting recent papers about self-interaction:

- ▶ Mori-Sánchez *et al.*, J. Chem. Phys. **125**, 201102 (2006)
- ▶ Ruzsinszky *et al.*, J. Chem. Phys. **126**, 104102 (2007)

¹Perdew and Zunger, Phys. Rev. B **23**, 5048 (1981)

LDA+ U

The idea of LDA+ U is to remove (partially) the self-interaction error present in LDA in a **cheap way**:

Remove the self-interaction error only for the electrons of a given angular momentum ℓ and type of atom.

For instance:

- ▶ 3d electrons in transition-metal oxides
- ▶ 4f electrons in rare-earth oxides
- ▶ 5f electrons in actinide oxides

LDA+ U exchange-correlation functional

The LDA+ U exchange-correlation functional is

$$E_{\text{xc}}^{\text{LDA}+U} = E_{\text{xc}}^{\text{LDA}}[\rho^\sigma] + E^U[n_{m_i m_j}^\sigma]$$

where

$$E^U[n_{m_i m_j}^\sigma] = E_{\text{ee}}[n_{m_i m_j}^\sigma] - E_{\text{dc}}[n_{m_i m_j}^\sigma]$$

and $n_{m_i m_j}^\sigma$ is the occupation matrix.

E_{ee} is an Hartree-Fock-type term and E_{dc} is the double-counting term.

The mathematical expression of E_{dc} depends on the version of LDA+ U .

LDA+ U exchange-correlation potential

The variational principle leads to

$$\frac{\delta E_{\text{xc}}^{\text{LDA}}}{\delta \psi_{\mathbf{nk}}^{\sigma*}(\mathbf{r})} = \int \frac{\delta E_{\text{xc}}^{\text{LDA}}}{\delta \rho^{\sigma}(\mathbf{r}')} \frac{\delta \rho^{\sigma}(\mathbf{r}')}{\delta \psi_{\mathbf{nk}}^{\sigma*}(\mathbf{r})} d^3 r' = \int \underbrace{\frac{\delta E_{\text{xc}}^{\text{LDA}}}{\delta \rho^{\sigma}(\mathbf{r}')}}_{v_{\text{xc},\sigma}^{\text{LDA}}(\mathbf{r}')} \frac{\partial \rho^{\sigma}(\mathbf{r}')}{\partial \psi_{\mathbf{nk}}^{\sigma*}(\mathbf{r})} \delta(\mathbf{r}-\mathbf{r}') d^3 r' = v_{\text{xc},\sigma}^{\text{LDA}}(\mathbf{r}) \psi_{\mathbf{nk}}^{\sigma}(\mathbf{r})$$

and

$$\frac{\delta E^U}{\delta \psi_{\mathbf{nk}}^{\sigma*}(\mathbf{r})} = \sum_{m_1, m_2} \underbrace{\frac{\partial E^U}{\partial n_{m_1 m_2}^{\sigma}}}_{v_{m_1 m_2}^{\sigma}} \frac{\delta n_{m_1 m_2}^{\sigma}}{\delta \psi_{\mathbf{nk}}^{\sigma*}(\mathbf{r})} = \sum_{m_1, m_2} v_{m_1 m_2}^{\sigma} \hat{P}_{m_1 m_2} \psi_{\mathbf{nk}}^{\sigma}(\mathbf{r}) = \hat{v}_{\sigma}^U \psi_{\mathbf{nk}}^{\sigma}(\mathbf{r})$$

The LDA+ U exchange-correlation potential is

$$\hat{v}_{\text{xc},\sigma}^{\text{LDA}+U} = v_{\text{xc},\sigma}^{\text{LDA}}(\mathbf{r}) + \hat{v}_{\sigma}^U$$

The different versions of LDA+ U

- ▶ Original around mean field ²
- ▶ Around mean field ³
- ▶ Atomic limit (also called fully localized limit) ⁴
- ▶ Interpolation between AMF and AL ⁵
- ▶ Version of Seo ⁶ (better self-interaction correction)

²Anisimov *et al.*, Phys. Rev. B **44**, 943 (1991)

³Czyżyk and Sawatzky, Phys. Rev. B **49**, 14211 (1994)

⁴Anisimov *et al.*, Phys. Rev. B **48**, 16929 (1993)

⁵Petukhov *et al.*, Phys. Rev. B **67**, 153106 (2003)

⁶Seo, Phys. Rev. B **76**, 033102 (2007)

Atomic limit version of LDA+U

$$E_{\text{xc}}^{\text{LDA}+U} = E_{\text{xc}}^{\text{LDA}}[\rho^\sigma] + E_{\text{ee}}[n_{m_i m_j}^\sigma] - E_{\text{dc}}[n_\ell^\sigma]$$

$$E_{\text{ee}}[n_{m_i m_j}^\sigma] = \frac{1}{2} \sum_{\sigma} \sum_{m_1, m_2, m_3, m_4}^{\ell} [n_{m_1 m_2}^{\sigma} n_{m_3 m_4}^{-\sigma} \langle m_1 m_3 | v_{\text{ee}}^{\text{S}} | m_2 m_4 \rangle + n_{m_1 m_2}^{\sigma} n_{m_3 m_4}^{\sigma} (\langle m_1 m_3 | v_{\text{ee}}^{\text{S}} | m_2 m_4 \rangle - \langle m_1 m_3 | v_{\text{ee}}^{\text{S}} | m_4 m_2 \rangle)]$$

$$E_{\text{dc}}[n_\ell^\sigma] = U \frac{n_\ell (n_\ell - 1)}{2} - J \sum_{\sigma} \frac{n_\ell^\sigma (n_\ell^\sigma - 1)}{2}$$

Very often, U and J are treated as adjustable parameters, but there exist a few procedures to calculate U and J (see Aryasetiawan *et al.*⁷ and references therein).

⁷Phys. Rev. B **74**, 125106 (2006)

SCF cycle of LDA+ U in WIEN2k (runsp_lapw -orb)

lapw0	$\rightarrow v_{xc,\sigma}^{\text{LDA}} + v_{ee} + v_{en}$ (case.vspup(dn), case.vnsup(dn))
orb -up	$\rightarrow v_{m_1 m_2}^{\uparrow}$ (case.vorbup)
orb -dn	$\rightarrow v_{m_1 m_2}^{\downarrow}$ (case.vorbdn)
lapw1 -up -orb	$\rightarrow \psi_{nk}^{\uparrow}, \epsilon_{nk}^{\uparrow}$ (case.vectorup, case.energyup)
lapw1 -dn -orb	$\rightarrow \psi_{nk}^{\downarrow}, \epsilon_{nk}^{\downarrow}$ (case.vectordn, case.energydn)
lapw2 -up	$\rightarrow \rho_{\text{val}}^{\uparrow}$ (case.clmvalup)
lapw2 -dn	$\rightarrow \rho_{\text{val}}^{\downarrow}$ (case.clmvaldn)
lapwdm -up	$\rightarrow n_{m_1 m_2}^{\uparrow}$ (case.dmatup)
lapwdm -dn	$\rightarrow n_{m_1 m_2}^{\downarrow}$ (case.dmatdn)
lcore -up	$\rightarrow \rho_{\text{core}}^{\uparrow}$ (case.clmcorup)
lcore -dn	$\rightarrow \rho_{\text{core}}^{\downarrow}$ (case.clmcordn)
mixer	\rightarrow mixed ρ^{σ} and $n_{m_1 m_2}^{\sigma}$

A few remarks on LDA+ U in WIEN2k

- ▶ Any GGA and meta-GGA functionals can be used instead of LDA: GGA+ U and meta-GGA+ U (choose another number in case.in0)
- ▶ Calculation with several angular momenta ℓ on the same atom is possible (s, p, d, f)
- ▶ runsp_c_lapw -orb : spin-unpolarized LDA+ U calculation
- ▶ runsp_lapw -orbcc : LDA+ U calculation with fixed case.vorbup(dn) ($v_{m_1 m_2}^\sigma$)

Results for antiferromagnetic MnO ($U = 6.04$ and $J = 0$ eV)

a : lattice constant (Å)

B : bulk modulus (GPa)

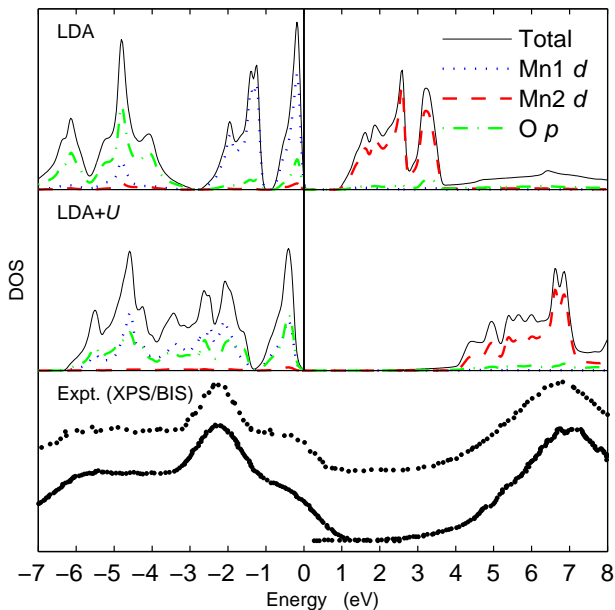
M : magnetic moment (μ_B)

Δ_{fund} : fundamental band gap (eV)

Δ_{opt} : optical band gap (eV)

	a	B	M	Δ_{fund}	Δ_{opt}
LDA	4.32	184	4.19	0.8	1.0
LDA+ U	4.40	174	4.50	1.9	2.5
Expt.	4.445	151–162	4.58–4.79	3.9	2.0

DOS of antiferromagnetic MnO



Results for antiferromagnetic CoO ($U = 6.88$ and $J = 0$ eV)

a : lattice constant (Å)

B : bulk modulus (GPa)

M : total magnetic moment (μ_B)

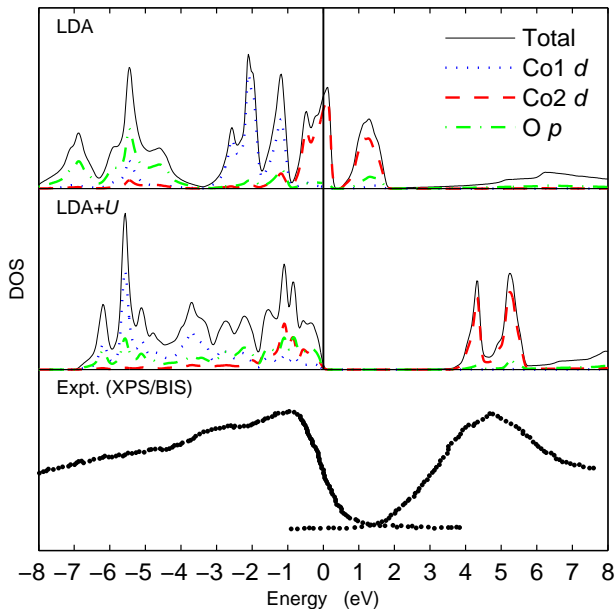
M_ℓ : orbital magnetic moment (μ_B)

Δ_{fund} : fundamental band gap (eV)

Δ_{opt} : optical band gap (eV)

	a	B	M	M_ℓ	Δ_{fund}	Δ_{opt}
LDA	4.11	250	2.53	0.17	0.0	0.0
LDA+ U	4.20	212	3.48	0.79	2.7	3.6
Expt.	4.254	180	3.35–3.98		2.5	2.7

DOS of antiferromagnetic CoO



Interesting references for the concepts of LDA+ U

- ▶ Anisimov *et al.*, J. Phys.: Condens. Matter **9**, 767 (1997):
Review
- ▶ Lechermann *et al.*, Phys. Rev. B **69**, 165116 (2004):
Comparison of AMF and FLL versions of LDA+ U for Fe-Al systems
- ▶ Cococcioni and de Gironcoli, Phys. Rev. B **71**, 035105 (2005):
Ab initio calculation of U
- ▶ Kasinathan *et al.*, Phys. Rev. B **74**, 195110 (2006):
Comparison of LDA+ U , SIC-LDA, pseudo-SIC-LDA, and hybrid for MnO

Total energy, force, and stress

- ▶ The total energy E is a function of the lattice parameters a , b , c , angles α , β , and γ , and positions of the nuclei \mathbf{R}_l :

$$E = E(a, b, c, \alpha, \beta, \gamma, \mathbf{R}_1, \mathbf{R}_2, \dots)$$

- ▶ The force \mathbf{F}_l on nucleus l is given by

$$\mathbf{F}_l = -\nabla_l E$$

The equilibrium positions of the \mathbf{R}_l are reached when $\mathbf{F}_l = 0$ for all nuclei l

- ▶ The stress of the unit cell is given by

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \frac{dE}{d\epsilon_{\alpha\beta}}$$

The equilibrium values for a , b , c , α , β , and γ are reached when $\sigma_{\alpha\beta} = 0$

Force in WIEN2k

- ▶ The force formalism for LAPW basis set was developed by Soler and Williams⁸ and Yu *et al.*⁹
- ▶ The formalism of Yu *et al.* was implemented by Kohler *et al.* in WIEN2k¹⁰
- ▶ Madsen *et al.*¹¹ adapted the formalism for APW+lo basis set

⁸Phys. Rev. B **40**, 1560 (1989)

⁹Phys. Rev. B **43**, 6411 (1991)

¹⁰Comput. Phys. Commun. **94**, 31 (1996)

¹¹Phys. Rev. B **64**, 195134 (2001)

The total force

The total force acting on atom α is given by

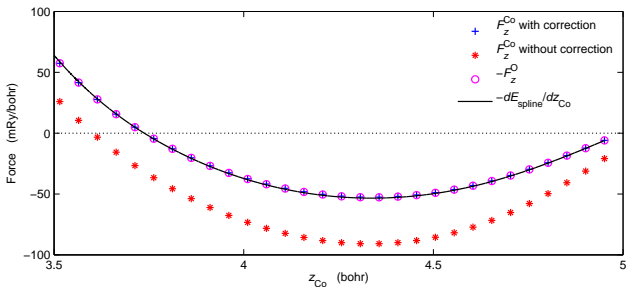
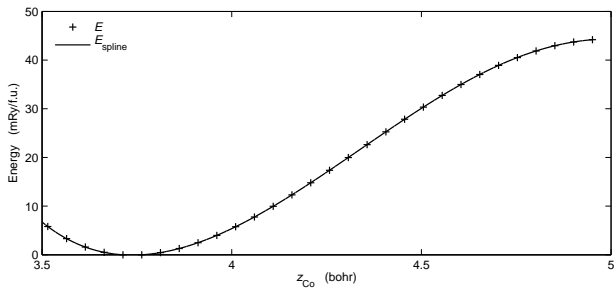
$$\mathbf{F}_{\alpha} = \mathbf{F}_{\alpha}^{\text{HF}} + \mathbf{F}_{\alpha}^{\text{IBS}}$$

- ▶ $\mathbf{F}_{\alpha}^{\text{HF}}$ is the electrostatic force (also called Hellmann-Feynman force)
- ▶ $\mathbf{F}_{\alpha}^{\text{IBS}}$ is the force which arises due to the use of an atom-position-dependent and incomplete basis set (IBS) (also called Pulay force)

The Pulay force

- ▶ In general, the calculation of the Pulay force $\mathbf{F}_{\alpha}^{\text{IBS}}$ is not trivial and, in addition, with the FP-(L)APW+lo basis set the discontinuity of the derivatives of the basis functions leads to a contribution to $\mathbf{F}_{\alpha}^{\text{IBS}}$.
- ▶ The formula for $\mathbf{F}_{\alpha}^{\text{IBS}}$ depends on the type of exchange-correlation functional. The implementation in WIEN2k (based on Yu and Singh formulation) works only for LDA and GGA.
- ▶ Recently, the force formulation was adapted to work with LDA+ U and hybrid functionals and it has been implemented in WIEN2k.
- ▶ The calculation of the Pulay force is activated by replacing TOT by FOR in case.in2 (first line)

Force with LDA+ U : wurtzite CoO



Force with LDA+ U : hexagonal Ce_2O_3

