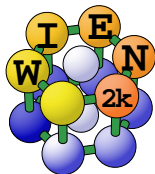


Methods available in WIEN2k for the treatment of exchange and correlation effects

F. Tran

Institute of Materials Chemistry
Vienna University of Technology, A-1060 Vienna, Austria

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Outline of the talk

- ▶ Introduction
- ▶ Semilocal functionals:
 - ▶ GGA and MGGA
 - ▶ mBJ potential (for band gap)
 - ▶ GLLB-SC
 - ▶ Input file case.in0
- ▶ Methods for van der Waals systems:
 - ▶ DFT-D3
 - ▶ Nonlocal functionals
- ▶ On-site methods for strongly correlated d and f electrons:
 - ▶ DFT+ U
 - ▶ On-site hybrid functionals
- ▶ Hybrid functionals

Total energy in Kohn-Sham DFT¹

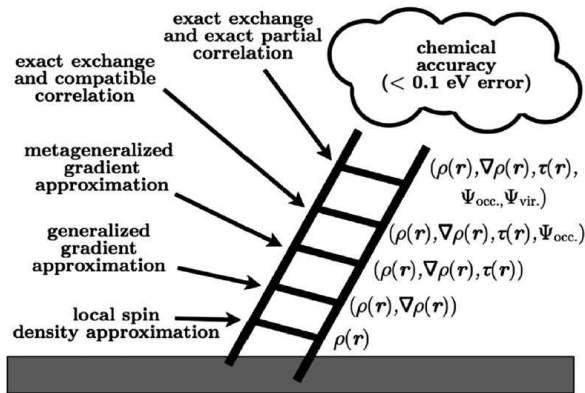
$$E_{\text{tot}} = \underbrace{\frac{1}{2} \sum_i \int |\nabla \psi_i(\mathbf{r})|^2 d^3 r}_{T_s} + \underbrace{\frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r'}_{E_{ee}} + \underbrace{\int v_{\text{en}}(\mathbf{r})\rho(\mathbf{r}) d^3 r}_{E_{en}} \\ + \underbrace{\frac{1}{2} \sum_{\substack{A,B \\ A \neq B}} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}}_{E_{nn}} + E_{\text{xc}}$$

- ▶ T_s : kinetic energy of the non-interacting electrons
- ▶ E_{ee} : repulsive electron-electron electrostatic Coulomb energy
- ▶ E_{en} : attractive electron-nucleus electrostatic Coulomb energy
- ▶ E_{nn} : repulsive nucleus-nucleus electrostatic Coulomb energy
- ▶ $E_{\text{xc}} = E_x + E_c$: exchange-correlation energy
Approximations for E_{xc} have to be used in practice
⇒ The reliability of the results depends mainly on E_{xc}

¹W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

Approximations for E_{xc} (Jacob's ladder¹)

$$E_{xc} = \int \epsilon_{xc}(\mathbf{r}) d^3r$$



The accuracy, but also the computational cost, increase when climbing up the ladder

¹ J. P. Perdew *et al.*, J. Chem. Phys. **123**, 062201 (2005)

Kohn-Sham Schrödinger equations

Minimization of E_{tot} leads to

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

Two types of \hat{v}_{xc} :

- ▶ Multiplicative: $\hat{v}_{\text{xc}} = \delta E_{\text{xc}} / \delta \rho = v_{\text{xc}}$ (KS method)
 - ▶ LDA
 - ▶ GGA
- ▶ Non-multiplicative: $\hat{v}_{\text{xc}} = (1/\psi_i) \delta E_{\text{xc}} / \delta \psi_i^* = v_{\text{xc},i}$ (generalized KS¹)
 - ▶ Hartree-Fock
 - ▶ LDA+ U
 - ▶ Hybrid (mixing of GGA and Hartree-Fock)
 - ▶ MGGA
 - ▶ Self-interaction corrected (Perdew-Zunger)

¹ A. Seidl *et al.*, Phys. Rev. B **53**, 3764 (1996)

Semilocal functionals: GGA

$$\epsilon_{xc}^{\text{GGA}}(\rho, \nabla\rho) = \epsilon_x^{\text{LDA}}(\rho) F_{xc}(r_s, s)$$

where F_{xc} is the enhancement factor and

$$r_s = \frac{1}{\left(\frac{4}{3}\pi\rho\right)^{1/3}} \quad (\text{Wigner-Seitz radius})$$

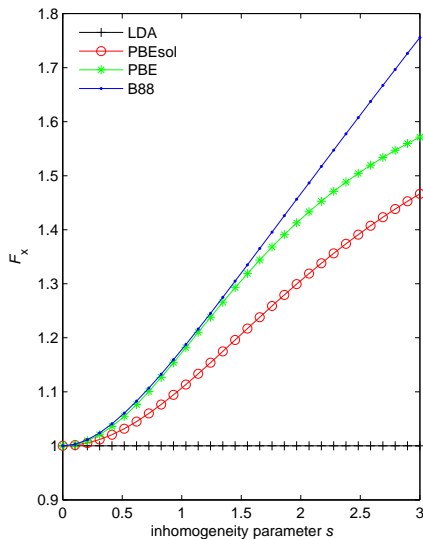
$$s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}} \quad (\text{inhomogeneity parameter})$$

There are two types of GGA:

- ▶ **Semi-empirical**: contain parameters fitted to accurate (i.e., experimental) data.
- ▶ **Ab initio**: All parameters were determined by using mathematical conditions obeyed by the exact functional.

Semilocal functionals: trends with GGA

$$\text{Exchange enhancement factor } F_x(\mathbf{s}) = \epsilon_x^{\text{GGA}} / \epsilon_x^{\text{LDA}}$$



good for atomization energy of molecules

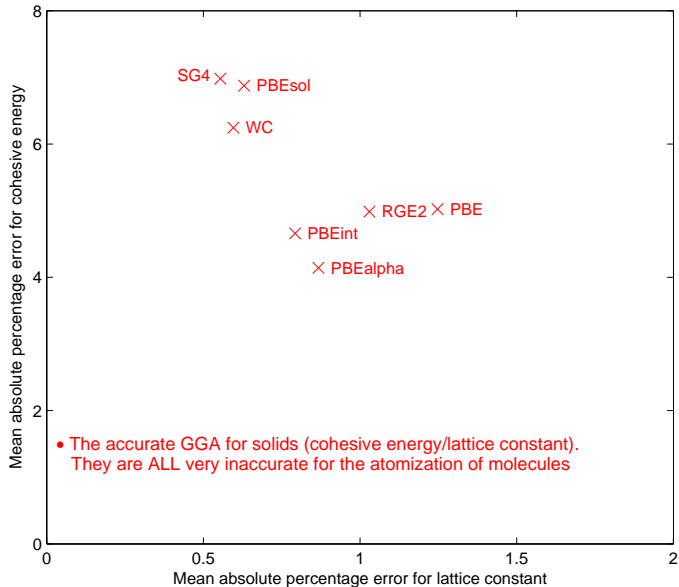
good for atomization energy of solids

good for lattice constant of solids

good for nearly nothing

Construction of an universal GGA: A failure

Test of functionals on 44 solids¹



¹ F. Tran *et al.*, J. Chem. Phys. **144**, 204120 (2016)

Semilocal functionals: meta-GGA

$$\epsilon_{xc}^{\text{MGGA}}(\rho, \nabla\rho, t) = \epsilon_{xc}^{\text{LDA}}(\rho) F_{xc}(r_s, s, \alpha)$$

- ▶ $\alpha = \frac{t-t_W}{t_{TF}}$
 - ▶ $\alpha = 1$ (region of constant electron density)
 - ▶ $\alpha = 0$ (in one- and two-electron regions very close and very far from nuclei)
 - ▶ $\alpha \gg 1$ (region between closed shell atoms)

⇒ MGGA functionals are more flexible

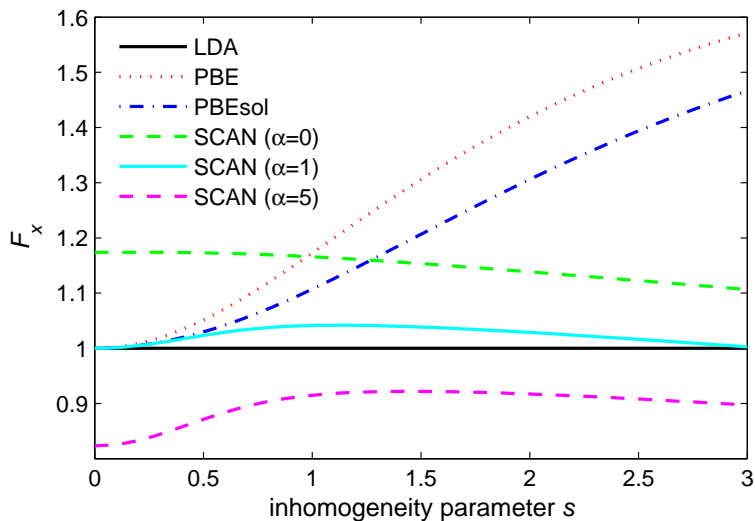
Example: **SCAN**¹ is

- ▶ as good as the best GGA for atomization energies of molecules
- ▶ as good as the best GGA for lattice constant of solids

¹J. Sun *et al.*, Phys. Rev. Lett. **115**, 036402 (2015)

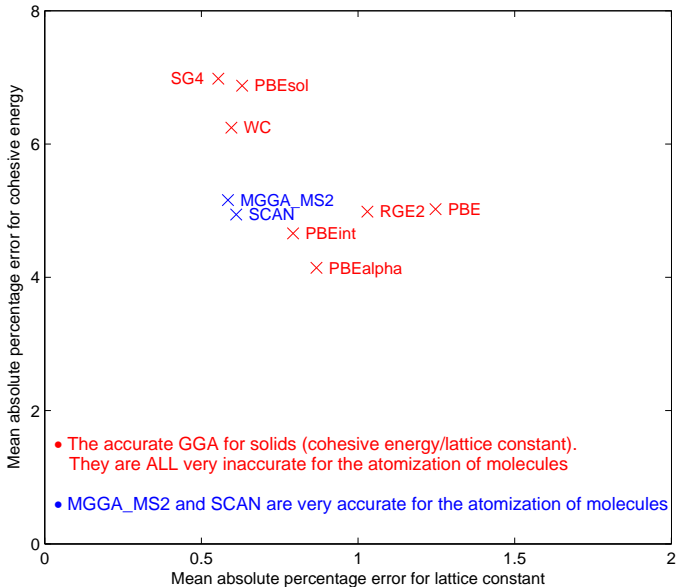
Semilocal functionals: meta-GGA

$$F_x(\mathbf{s}, \alpha) = \epsilon_x^{\text{MGGA}} / \epsilon_x^{\text{LDA}}$$



Semilocal functionals: MGGA_MS2 and SCAN

Test of functionals on 44 solids¹



¹ F. Tran *et al.*, J. Chem. Phys. **144**, 204120 (2016)

Semilocal potential for band gap: modified Becke-Johnson

- ▶ Standard LDA and GGA functionals underestimate the band gap
- ▶ Hybrid and *GW* are much more accurate, but also much more expensive

Semilocal potential for band gap: modified Becke-Johnson

- ▶ Standard LDA and GGA functionals underestimate the band gap
- ▶ Hybrid and *GW* are much more accurate, but also much more expensive
- ▶ A cheap alternative is to use the modified Becke-Johnson (mBJ) potential:¹

$$v_x^{\text{mBJ}}(\mathbf{r}) = c v_x^{\text{BR}}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{6}} \sqrt{\frac{t(\mathbf{r})}{\rho(\mathbf{r})}}$$

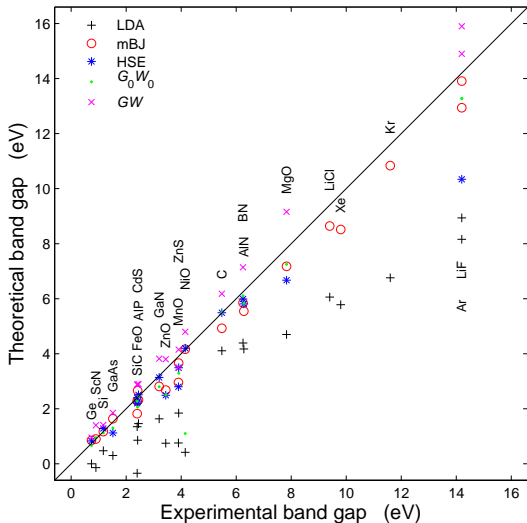
where v_x^{BR} is the Becke-Roussel potential, t is the kinetic-energy density and c is given by

$$c = \alpha + \beta \left(\frac{1}{V_{\text{cell}}} \int_{\text{cell}} \frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})} d^3r \right)^p$$

mBJ is a MGGA potential

¹ F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009)

Band gaps with mBJ: Reach the *GW* accuracy



See also F. Tran and P. Blaha, *J. Phys. Chem. A* **121**, 3318 (2017)

How to run a calculation with the mBJ potential?

1. `init_lapw` (choose LDA or PBE)
2. `init_mbj_lapw` (create/modify files)
 - 2.1 automatically done: `case.in0` modified and `case.inm_vresp` created
 - 2.2 `run(sp)_lapw -i 1 -NI` (creates `case.r2v` and `case.vrespsum`)
 - 2.3 `save_lapw`
3. `init_mbj_lapw` and choose one of the parametrizations:
 - 0: Original mBJ values¹
 - 1: New parametrization²
 - 2: New parametrization for semiconductors²
 - 3: Original BJ potential³
4. `run(sp)_lapw ...`

¹ F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009)

² D. Koller *et al.*, Phys. Rev. B **85**, 155109 (2012)

³ A. D. Becke and E. R. Johnson, J. Chem. Phys. **124**, 221101 (2006)

GLLB-SC potential

- ▶ GLLB-SC is a potential (no energy functional)¹:

$$V_{XC,\sigma}^{\text{GLLB-SC}} = 2\varepsilon_{X,\sigma}^{\text{PBEsol}} + K_X^{\text{LDA}} \sum_{i=1}^{N_\sigma} \sqrt{\varepsilon_{\text{H}} - \varepsilon_{i\sigma}} \frac{|\psi_{i\sigma}|^2}{\rho_\sigma} + V_{\text{C},\sigma}^{\text{PBEsol}}$$

- ▶ Leads to an **derivative discontinuity**:

$$\Delta = \int \psi_{\text{L}}^* \left[\sum_{i=1}^{N_{\sigma_{\text{L}}}} K_X^{\text{LDA}} (\sqrt{\varepsilon_{\text{L}} - \varepsilon_{i\sigma_{\text{L}}}} - \sqrt{\varepsilon_{\text{H}} - \varepsilon_{i\sigma_{\text{L}}}}) \frac{|\psi_{i\sigma_{\text{L}}}|^2}{\rho_{\sigma_{\text{L}}}} \right] \psi_{\text{L}} d^3r$$

Comparison with experiment: $E_{\text{g}} = E_{\text{g}}^{\text{KS}} + \Delta$

- ▶ Much better than LDA/GGA for band gaps
- ▶ Not as good as mBJ for strongly correlated systems²
- ▶ Seems interesting for electric field gradient²
- ▶ See user's guide for usage

¹ M. Kuisma *et al.*, *Phys. Rev. B* **82**, 115106 (2010)

¹ F. Tran, S. Ehsan, and P. Blaha, *Phys. Rev. Materials* **2**, 023802 (2018)

Input file case.in0: keywords for the xc-functional

The functional is specified at the 1st line of `case.in0`. Three different ways:

1. Specify a global keyword for E_x , E_c , v_x , v_c :
 - ▶ TOT `XC_NAME`
2. Specify a keyword for E_x , E_c , v_x , v_c individually:
 - ▶ TOT `EX_NAME1 EC_NAME2 VX_NAME3 VC_NAME4`
3. Specify keywords to use functionals from **LIBXC**¹:
 - ▶ TOT `XC_TYPE_X_NAME1 XC_TYPE_C_NAME2`
 - ▶ TOT `XC_TYPE_XC_NAME`

where *TYPE* is the family name: **LDA**, **GGA** or **MGGA**

¹ M. A. L. Marques *et al.*, *Comput. Phys. Commun.* **183**, 2272 (2012)
<http://www.tddft.org/programs/octopus/wiki/index.php/Libxc>

Input file case.in0: examples

▶ PBE:

TOT XC_PBE

or

TOT EX_PBE EC_PBE VX_PBE VC_PBE

or

TOT XC_GGA_X_PBE XC_GGA_C_PBE

▶ mBJ (with LDA for the xc-energy):

TOT XC_MBJ

▶ MGGA_MS2:

TOT XC_MGGA_MS 0.504 0.14601 4.0
 κ, c, b

All available functionals are listed in tables of the user's guide and in `$WIENROOT/SRC_lapw0/xc_funcs.h` for **LIBXC** (if installed)

Methods for van der Waals systems

Problem with semilocal and hybrid functionals:

- ▶ They do not include **London dispersion interactions** \implies Results are very often qualitatively wrong for van der Waals systems

Two types of dispersion terms added to the DFT total energy:

- ▶ Pairwise term (cheap)¹:

$$E_{c,\text{disp}}^{\text{PW}} = - \sum_{A < B} \sum_{n=6,8,10,\dots} f_n^{\text{damp}}(R_{AB}) \frac{C_n^{AB}}{R_{AB}^n}$$

- ▶ Nonlocal term (more expensive than semilocal)²:

$$E_{c,\text{disp}}^{\text{NL}} = \frac{1}{2} \int \int \rho(\mathbf{r}_1) \Phi(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2) d^3 r_1 d^3 r_2$$

¹S. Grimme, J. Comput. Chem. **25**, 1463 (2004)

²M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2004)

DFT-D3 pairwise method¹

► Features:

- Cheap
- C_n^{AB} depend on positions of the nuclei (via coordination number)
- Energy and forces (minimization of internal parameters)
- 3-body term available (more important for solids than molecules)

► Installation:

- Not included in WIEN2k
- Download and compile the DFTD3 package from <https://www.chemie.uni-bonn.de/pctc/mulliken-center/software/dft-d3/>
copy the `dftd3` executable in `$WIENROOT`

► Usage:

- Input file `case.indftd3` (if not present a default one is copied automatically by `x_lapw`)
- `run(sp)_lapw -dftd3 ...`
- `case.scfdftd3` is included in `case.scf`

¹ S. Grimme *et al.*, *J. Chem. Phys.* **132**, 154104 (2010)

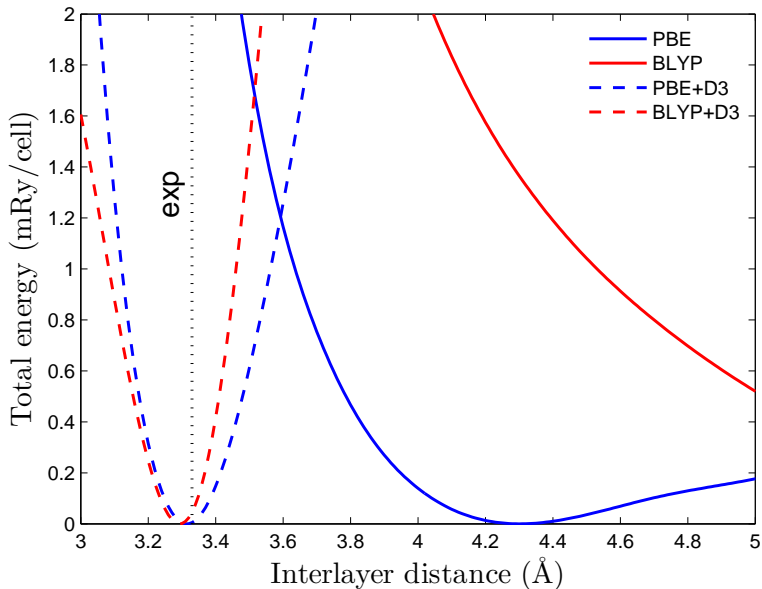
DFT-D3 method: input file case.indftd3

Default (and recommended) input file:

method	bj	damping function f_n^{damp}
func	default	the one in case.in0*
grad	yes	forces
pbc	yes	periodic boundary conditions
abc	yes	3-body term
cutoff	95	interaction cutoff
cnthr	40	coordination number cutoff
num	no	numerical gradient

* **default** will work for PBE, PBEsol, BLYP and TPSS. For other functionals, the functional name has to be specified (see dftd3.f of DFTD3 package)

DFT-D3 method: hexagonal BN¹



¹ F. Tran *et al.*, J. Chem. Phys. **144**, 204120 (2016)

Nonlocal vdW functionals

$$E_{c,\text{disp}}^{\text{NL}} = \frac{1}{2} \int \int \rho(\mathbf{r}_1) \Phi(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2) d^3 r_1 d^3 r_2$$

Kernels Φ proposed in the literature:

- ▶ **DRSLL**¹ (vdW-DF1, optB88-vdW, vdW-DF-cx0, ...):
 - ▶ Derived from ACFDT
 - ▶ Contains no adjustable parameter
- ▶ **LMKLL**² (vdW-DF2, rev-vdW-DF2):
 - ▶ Z_{ab} in DRSLL multiplied by 2.222
- ▶ **rVV10**^{3,4}:
 - ▶ Different analytical form as DRSLL
 - ▶ Parameters: $b = 6.3$ and $C = 0.0093$
- ▶ **rVV10L**⁵:
 - ▶ Parameters: $b = 10.0$ and $C = 0.0093$

¹ M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2004)

² K. Lee *et al.*, Phys. Rev. B **82**, 081101(R) (2010)

³ O. A. Vydrov and T. Van Voorhis, J. Chem. Phys. **133**, 244103 (2010)

⁴ R. Sabatini *et al.*, Phys. Rev. B **87**, 041108(R) (2013)

⁵ H. Peng and J. P. Perdew, Phys. Rev. B **95**, 081105(R) (2017)

Nonlocal vdW functionals in WIEN2k¹

► Features:

- Use the fast FFT-based method of Román-Pérez and Soler²:
 1. ρ is smoothed close to the nuclei (density cutoff ρ_c) $\rightarrow \rho_s$.
The smaller ρ_c is, the smoother ρ_s is.
 2. ρ_s is expanded in plane waves in the whole unit cell.
 G_{\max} is the plane-wave cutoff of the expansion.
- Most vdW functionals from the literature are available (see user's guide)

► Usage:

- Input file `case.innlvdw` (`$WIENROOT/SRC_templates`)
- `run(sp)_lapw -nlvdw ...`
- `case.scfnlvdw` is included in `case.scf`

¹F. Tran *et al.*, Phys. Rev. B **96**, 054103 (2017)

²G. Román-Pérez and J. M. Soler, Phys. Rev. Lett. **103**, 096102 (2009)

Nonlocal vdW functionals: the input file case.innlvdw

1	kernel type
-0.8491	parameters of the kernel
20	plane-wave expansion cutoff GMAX
0.3	density cutoff rhoc
T	calculation of the potential (T or F)

line 1 : “1” for DRSSL and LMKLL or “2” for rVV10

line 2 : “-0.8491” for DRSSL, “-1.887” for LMKLL or “6.3 0.0093” for rVV10

line 3 : Use $G_{\max} = 25$ or 30 in case of numerical noise

line 4 : Eventually repeat with larger ρ_c (e.g, 0.6)

line 5 : Potential is necessary only for forces. Save computational time if set to “F”

Strongly correlated electrons

Problem with semilocal functionals:

- ▶ They give qualitatively wrong results for solids which contain **localized 3d or 4f** electrons
 - ▶ The band gap is too small (zero in FeO!)
 - ▶ The magnetic moment is too small (zero in $\text{YBa}_2\text{Cu}_3\text{O}_6$!)
 - ▶ Wrong electronic configuration

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(Partial) solution to the problem:

- ▶ Combine semilocal functionals with **Hartree-Fock** theory:
 - ▶ DFT+ U
 - ▶ Hybrid

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 - ▶ DFT+ U
 - ▶ Hybrid

Even better:

- ▶ LDA+DMFT (DMFT codes using WIEN2k orbitals as input exist)

On-site DFT+ U and hybrid methods in WIEN2k

- ▶ For solids, the hybrid functionals are computationally **very expensive**.
- ▶ In WIEN2k the **on-site** DFT+ U ¹ and **on-site** hybrid^{2,3} methods are available. These methods are approximations of the Hartree-Fock/hybrid methods
- ▶ Applied only inside atomic spheres of selected atoms and electrons of a given angular momentum ℓ .

On-site methods → **As cheap as LDA/GGA**.

¹ V. I. Anisimov *et al.*, Phys. Rev. B **44**, 943 (1991)

² P. Novák *et al.*, Phys. Stat. Sol. (b) **243**, 563 (2006)

³ F. Tran *et al.*, Phys. Rev. B **74**, 155108 (2006)

DFT+ U and hybrid exchange-correlation functionals

The exchange-correlation functional is

$$E_{xc}^{\text{DFT}+U/\text{hybrid}} = E_{xc}^{\text{DFT}}[\rho] + E^{\text{onsite}}[n_{mm'}]$$

where $n_{mm'}$ is the density matrix of the correlated electrons

- ▶ For DFT+ U both exchange and Coulomb are corrected:

$$E^{\text{onsite}} = \underbrace{E_x^{\text{HF}} + E_{\text{Coul}}}_{\text{correction}} - \underbrace{E_x^{\text{DFT}} - E_{\text{Coul}}^{\text{DFT}}}_{\text{double counting}}$$

There are several versions of the double-counting term

- ▶ For the hybrid methods only exchange is corrected:

$$E^{\text{onsite}} = \underbrace{\alpha E_x^{\text{HF}}}_{\text{corr.}} - \underbrace{\alpha E_x^{\text{LDA}}}_{\text{d. count.}}$$

where α is a parameter $\in [0, 1]$

How to run DFT+ U and on-site hybrid calculations?

1. Create the input files:
 - ▶ `case.inorb` and `case.indm` for DFT+ U
 - ▶ `case.ineece` for on-site hybrid functionals (`case.indm` created automatically):
2. Run the job (can only be run with `runsp_lapw`):
 - ▶ LDA+ U : `runsp_lapw -orb ...`
 - ▶ Hybrid: `runsp_lapw -eece ...`

For a calculation without spin-polarization ($\rho_{\uparrow} = \rho_{\downarrow}$):
`runsp_c_lapw -orb/eece ...`

Input file case.inorb

LDA+ U applied to the 4*f* electrons of atoms No. 2 and 4:

```
1 2 0          nmod, natorb, ipr
PRATT,1.0      mixmod, amix
2 1 3          iatom, nlorb, lorb
4 1 3          iatom, nlorb, lorb
1             nsic (LDA+U(SIC) used)
0.61 0.07     U J (Ry)
0.61 0.07     U J (Ry)
```

nsic=0 for the AMF method (less strongly correlated electrons)

nsic=1 for the SIC method

nsic=2 for the HMF method

Review article : [E. R. Ylvisaker *et al.*, Phys. Rev. B **79**, 035103 \(2009\)](#)

Input file case.ineece

On-site hybrid functional PBE0 applied to the 4*f* electrons of atoms No. 2 and 4:

-12.0	2	emin, natorb
2	1 3	iatom, nlorb, lorb
4	1 3	iatom, nlorb, lorb
HYBR		HYBR/EECE
0.25		fraction of exact exchange

SCF cycle of DFT+ U in WIEN2k

lapw0	$\rightarrow v_{xc,\sigma}^{\text{DFT}} + v_{ee} + v_{en}$ (case.vspup(dn), case.vnsup(dn))
orb -up	$\rightarrow v_{mm'}^{\uparrow}$ (case.vorbup)
orb -dn	$\rightarrow v_{mm'}^{\downarrow}$ (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 -orb	$\rightarrow \rho_{\text{val}}^{\uparrow}$ (case.clmvalup), $n_{mm'}^{\uparrow}$ (case.dmatup)
lapw2 -dn -orb	$\rightarrow \rho_{\text{val}}^{\downarrow}$ (case.clmvaldn), $n_{mm'}^{\downarrow}$ (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 $n_{mm'}^{\sigma}$

Hybrid functionals

- ▶ **On-site** hybrid functionals can be applied only to localized electrons
- ▶ **Full** hybrid functionals are necessary (but expensive) for solids with delocalized electrons (e.g., in *sp*-semiconductors)

Hybrid functionals

- ▶ **On-site** hybrid functionals can be applied only to localized electrons
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Two types of full hybrid functionals available in WIEN2k¹:

- ▶ unscreened:

$$E_{xc} = E_{xc}^{\text{DFT}} + \alpha \left(E_x^{\text{HF}} - E_x^{\text{DFT}} \right)$$

- ▶ screened (short-range), $\frac{1}{|r-r'|} \rightarrow \frac{e^{-\lambda|r-r'|}}{|r-r'|}$:

$$E_{xc} = E_{xc}^{\text{DFT}} + \alpha \left(E_x^{\text{SR-HF}} - E_x^{\text{SR-DFT}} \right)$$

screening leads to faster convergence with **k**-points sampling

¹ F. Tran and P. Blaha, Phys. Rev. B **83**, 235118 (2011)

Hybrid functionals: technical details

- ▶ 10-1000 times more expensive than LDA/GGA
- ▶ **k**-point and MPI parallelization
- ▶ Approximations to speed up the calculations:
 - ▶ **Reduced k-mesh** for the HF potential. Example:
For a calculation with a $12 \times 12 \times 12$ **k**-mesh, the reduced **k**-mesh for the HF potential can be:
 $6 \times 6 \times 6$, $4 \times 4 \times 4$, $3 \times 3 \times 3$, $2 \times 2 \times 2$ or $1 \times 1 \times 1$
 - ▶ **Non-self-consistent** calculation of the band structure
- ▶ Underlying functionals for unscreened and screened hybrid:
 - ▶ LDA, PBE, WC, PBEsol, B3PW91, B3LYP
- ▶ Use **run_bandplothf_lapw** for band structure
- ▶ Can be combined with spin-orbit coupling

Hybrid functionals: input file case.inhf

Example for YS-PBE0 (similar to HSE06 from Heyd, Scuseria and Ernzerhof¹)

0.25	fraction α of HF exchange
T	screened (T, YS-PBE0) or unscreened (F, PBE0)
0.165	screening parameter λ
20	number of bands for the 2nd Hamiltonian
6	GMAX
3	lmax for the expansion of orbitals
3	lmax for the product of two orbitals
1d-3	radial integrals below this value neglected

¹ A. V. Krukau *et al.*, J. Chem. Phys. **125**, 224106 (2006)

Hybrid functionals: input file case.inhf

Example for YS-PBE0 (similar to HSE06 from Heyd, Scuseria and Ernzerhof¹)

0.25	fraction α of HF exchange
T	screened (T, YS-PBE0) or unscreened (F, PBE0)
0.165	screening parameter λ
20	number of bands for the 2nd Hamiltonian
6	GMAX
3	lmax for the expansion of orbitals
3	lmax for the product of two orbitals
1d-3	radial integrals below this value neglected

Important: The computational time will depend strongly on the number of bands, GMAX, lmax and the number of k-points

¹ A. V. Krukau *et al.*, J. Chem. Phys. **125**, 224106 (2006)

How to run hybrid functionals?

1. `init_lapw`
2. Recommended: `run(sp)_lapw` for the semilocal functional
3. `save_lapw`
4. `init_hf_lapw` (this will create/modify input files)
 - 4.1 adjust `case.inhf` according to your needs
 - 4.2 reduced **k**-mesh for the HF potential? Yes or no
 - 4.3 specify the **k**-mesh
5. `run(sp)_lapw -hf (-redklist) (-diaghf) ...`

SCF cycle of hybrid functionals in WIEN2k

lapw0 -grr

→ v_x^{DFT} (case.r2v), αE_x^{DFT} (:AEXSL)

lapw0

→ $v_{\text{xc}}^{\text{DFT}} + v_{\text{ee}} + v_{\text{en}}$ (case.vsp, case.vns)

lapw1

→ $\psi_{nk}^{\text{DFT}}, \epsilon_{nk}^{\text{DFT}}$ (case.vector, case.energy)

lapw2

→ $\sum_{nk} \epsilon_{nk}^{\text{DFT}}$ (:SLSUM)

hf

→ ψ_{nk}, ϵ_{nk} (case.vectorhf, case.energyhf)

lapw2 -hf

→ ρ_{val} (case.clmval)

lcore

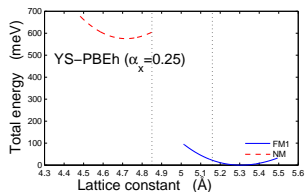
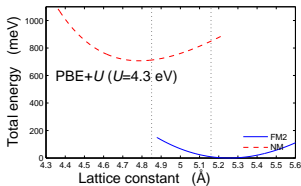
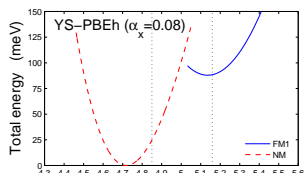
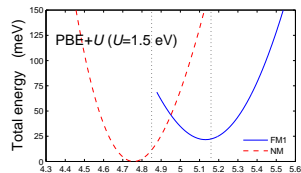
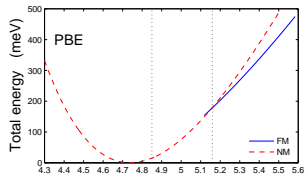
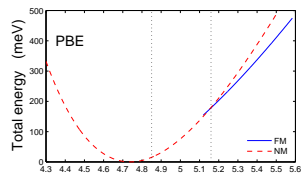
→ ρ_{core} (case.clmcor)

mixer

→ mixed ρ

Nonmagnetic and ferromagnetic phases of cerium¹

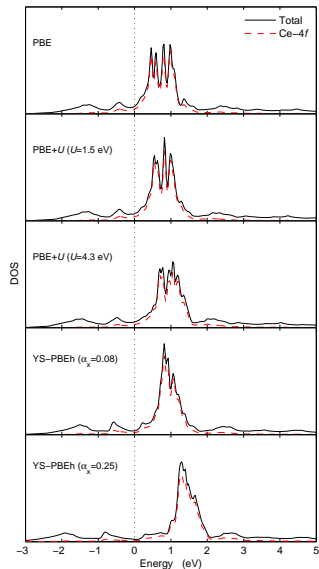
Small U (1.5 eV) or α_x (0.08) leads to correct stability ordering



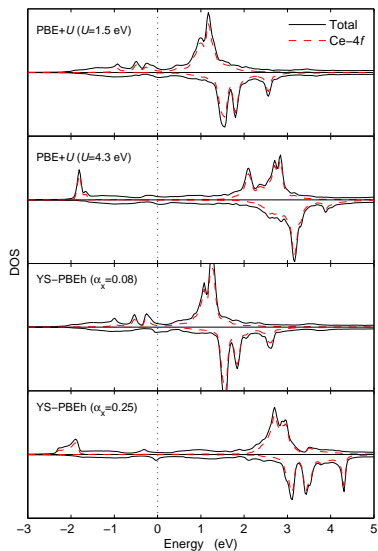
¹ F. Tran, F. Karsai, and P. Blaha, Phys. Rev. B **89**, 155106 (2014)

Nonmagnetic and ferromagnetic phases of cerium¹

NM: small sensitivity on U/α_x



FM: large sensitivity on U/α_x



¹ F. Tran, F. Karsai, and P. Blaha, Phys. Rev. B **89**, 155106 (2014)

Some recommendations

Before using a functional:

- ▶ read a few papers about the functional in order to know
 - ▶ for which properties or types of solids it is supposed to be reliable
 - ▶ if it is adapted to your problem
- ▶ figure out if you have enough computational resources
 - ▶ hybrid functionals and GW require (substantially) more computational resources (and patience)