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

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Outline of the talk

- Introduction
- Semilocal functionals:
  - GGA
  - MGGA
- Methods for van der Waals systems:
  - DFT-D3
  - Nonlocal functionals
- Potentials for band gaps:
  - Modified Becke-Johnson
  - GLLB-SC
- On-site methods for strongly correlated d and f electrons:
  - DFT+U
  - On-site hybrid functionals
- Hybrid functionals

Total energy in Kohn-Sham DFT[1]

$$E_{\text{tot}} = \underbrace{\frac{1}{2}\sum_i \int |\nabla\psi_i(\mathbf{r})|^2\, d^3r}_{T_\text{s}} + \underbrace{\frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'}_{E_\text{ee}} + \underbrace{\int v_\text{en}(\mathbf{r})\rho(\mathbf{r}) d^3r}_{E_\text{en}}$$

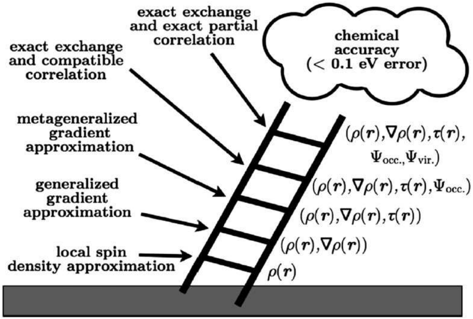
$$+ \underbrace{\frac{1}{2}\sum_{\substack{A,B\\ A\neq B}} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}}_{E_\text{nn}} + E_\text{xc}$$

- 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
- $E_\text{xc} = E_\text{x} + E_\text{c}$: exchange-correlation energy
  Approximations for E_xc have to be used in practice
  $\Longrightarrow$ The reliability of the results depends mainly on E_xc

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

Approximations for E_{xc} (Jacob's ladder[1])

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



When climbing up Jacob's ladder, the functionals are more and more

- sophisticated
- accurate (in principle)
- difficult to implement
- expensive to evaluate (time and memory)

[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 exchange-correlation potentials $\hat{v}_{\text{xc}}$:

- Multiplicative (rungs 1 and 2): $\hat{v}_{\text{xc}} = \delta E_{\text{xc}}/\delta\rho = v_{\text{xc}}$ (KS[1]):
  - LDA
  - GGA
- Non-multiplicative (rungs 3 and 4): $\hat{v}_{\text{xc}} = (1/\psi_i)\delta E_{\text{xc}}/\delta\psi_i^* = v_{\text{xc},i}$ (generalized KS[2]):
  - Hartree-Fock
  - LDA+U
  - Hybrid (mixing of GGA and Hartree-Fock)
  - MGGA
  - Self-interaction corrected (Perdew-Zunger)

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

[2] A. Seidl *et al.*, Phys. Rev. B **53**, 3764 (1996)

Semilocal functionals: GGA

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

where F_{xc} is the enhancement factor and

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

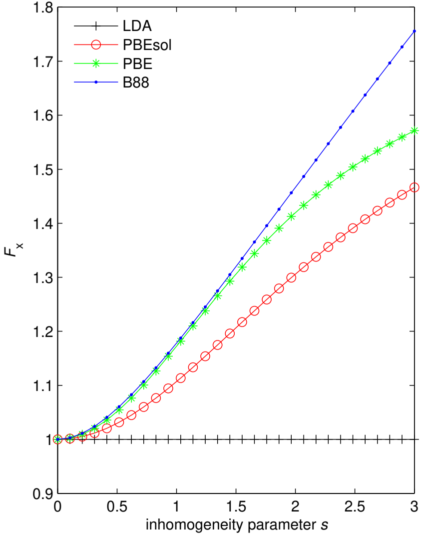
$$s = \frac{|\nabla\rho|}{2\left(3\pi^2\right)^{1/3}\rho^{4/3}} \qquad \text{(inhomogeneity parameter)}$$

$\sim$ 200 GGAs exist. They can be classified into two classes:

- 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

Exchange enhancement factor $F_{\mathrm{x}}(s) = \epsilon_{\mathrm{x}}^{\mathrm{GGA}} / \epsilon_{\mathrm{x}}^{\mathrm{LDA}}$



good for atomization energy of molecules

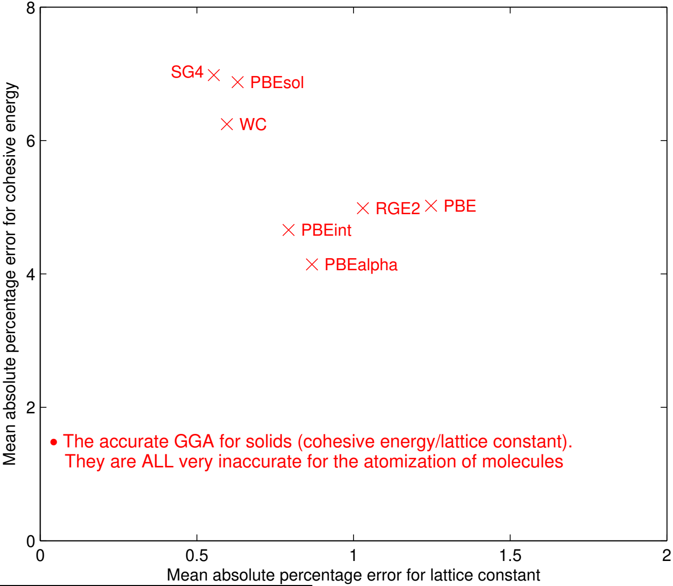
good for atomization energy of solids

good for lattice constant of solids

good for nearly nothing

Construction of an universal GGA: A failure

Test of functionals on 44 solids[1]



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

Semilocal functionals: meta-GGA

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

- $\alpha = \frac{t - t_{\rm W}}{t_{\rm TF}}$
  - $\alpha = 1$ (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)

$\Longrightarrow$ MGGA functionals are more flexible

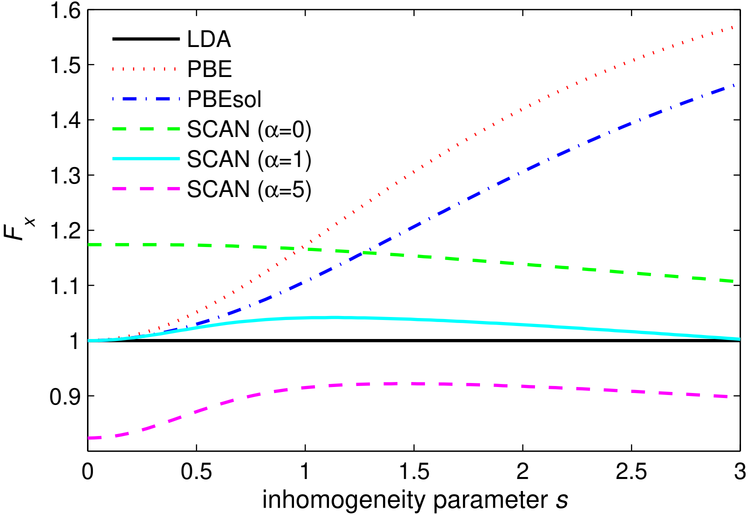
Example: SCAN[1] is

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

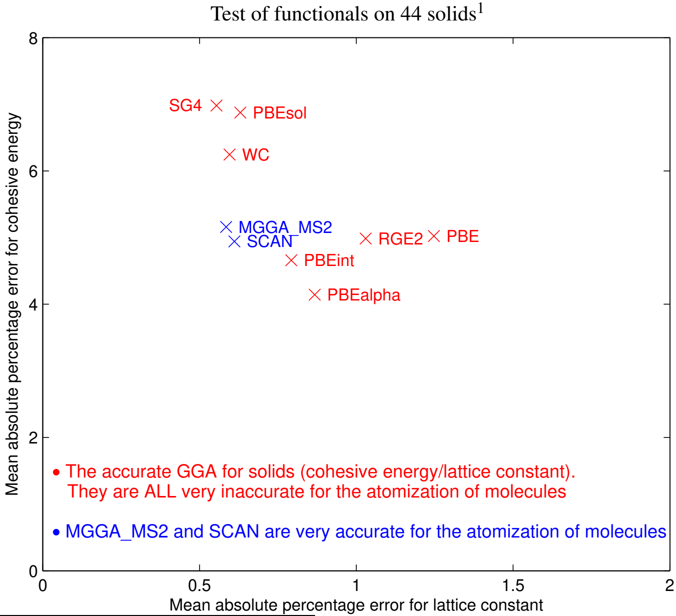
[1] J. Sun *et al.*, Phys. Rev. Lett. **115**, 036402 (2015)

Semilocal functionals: meta-GGA

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



Semilocal functionals: MGGA_MS2 and SCAN



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

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 $E_{\rm x}$, $E_{\rm c}$, $v_{\rm x}$, $v_{\rm c}$:
   - `TOT XC_`*NAME*
2. Specify a keyword for $E_{\rm x}$, $E_{\rm c}$, $v_{\rm x}$, $v_{\rm c}$ 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); S. Lehtola *et al.*, SoftwareX **7**, 1 (2018)
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 (Libxc keyword)

  `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` $\underbrace{0.504 \;\; 0.14601 \;\; 4.0}_{\kappa,c,b}$

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 $\Longrightarrow$ 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]:

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

- Nonlocal term (more expensive than semilocal)[2]:

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

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

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

DFT-D3 pairwise method[1]

- 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:

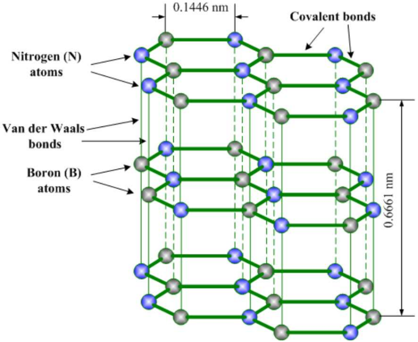
`method`	`bj`	damping function f_n^{damp}
`func`	`default`	the one in case.in0*
`grad`	`yes`	forces
`pbc`	`yes`	periodic boundary conditions
`abc`	`yes`	3-body term
`cutoff`	`95`	interaction cutoff
`cnthr`	`40`	coordination number cutoff
`num`	`no`	numerical gradient

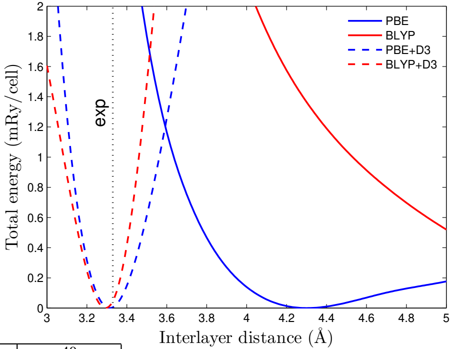
*default will work for PBE, PBEsol, BLYP and TPSS. For other functionals, the functional name has to be specified (see dftd3.f of DFTD3 package)

van der Waals interactions: hexagonal boron nitride

The GGA BLYP and PBE lead to too large interlayer distance and (nearly) no interlayer bonding

Adding the atom-pairwise correction D3[1] leads to good agreement with experiment





Interlayer binding energy (in meV/atom):

Experiment	40
PBE	2
BLYP	No binding
PBE-D3	41
BLYP-D3	58

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

Nonlocal vdW functionals

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

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 $C = 0.0093$
- DADE[5] (not tested on solids):

[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)

[6] M. Shahbaz and K. Szalewicz, Phys. Rev. Lett **122**, 213001 (2019)

Nonlocal vdW functionals in WIEN2k[1]

- Features:
  - Use the fast FFT-based method of Román-Pérez and Soler[2]:
    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.
  - Many of the 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

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

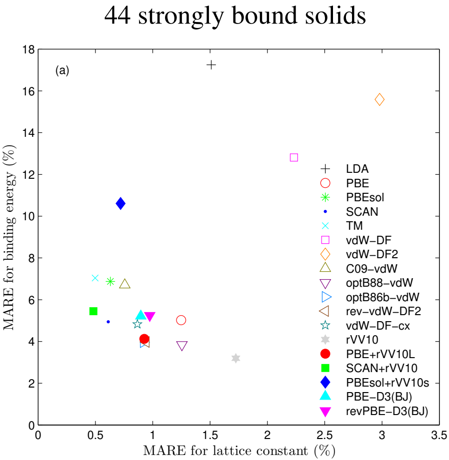
[2] G. Román-Pérez and J. M. Soler, Phys. Rev. Lett. **103**, 096102 (2009)

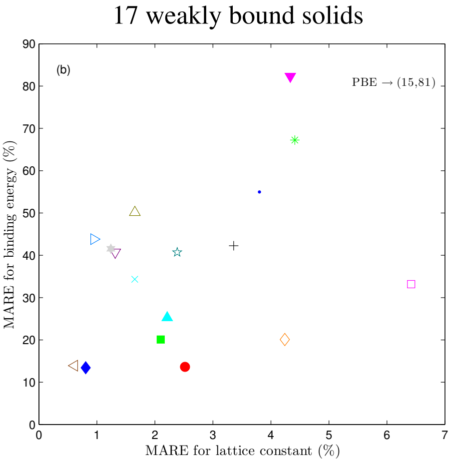
Nonlocal vdW functionals: the input file case.innlvdw

`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 DRSLL and LMKLL or “2” for rVV10(L)
line 2 : “-0.8491” for DRSLL, “-1.887” for LMKLL or “6.3 0.0093” for rVV10
line 3 : Use $G_{\mathrm{max}} = 25$ 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”

van der Waals interactions: tests on solids[1]





Conclusion: rev-vdW-DF2[2] is the best functional for solids

[1] F. Tran *et al.*, Phys. Rev. Materials **3**, 063602 (2019)

[2] I. Hamada, Phys. Rev. B. **89**, 121103(R) (2014)

Accurate band gaps with DFT: the modified Becke-Johnson potential

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

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- 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]

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

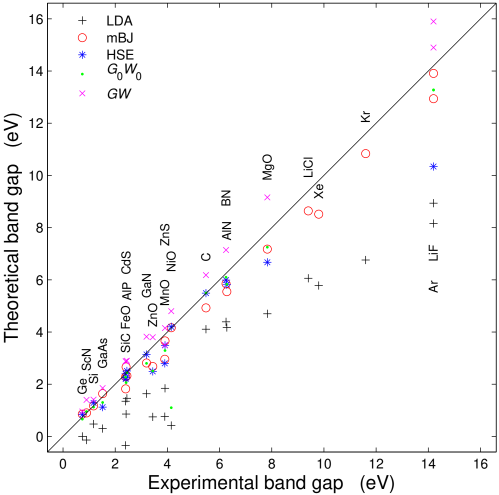
where $v_{\mathrm{x}}^{\mathrm{BR}}$ is the Becke-Roussel potential, t is the kinetic-energy density and c is given by

$$c = \alpha + \beta\left(\frac{1}{V_{\mathrm{cell}}}\int_{\mathrm{cell}}\frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})}d^3r\right)^{1/2}$$

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) (76 solids)

P. Borlido *et al.*, J. Chem. Theory Comput. **xx**, xxxx (2019) (472 solids)

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 values[1]
    - 1: New parametrization[2]
    - 2: New parametrization for semiconductors[2]
    - 3: Original BJ potential[3]
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 for band gaps

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

$$v_{\mathrm{xc},\sigma}^{\mathrm{GLLB\text{-}SC}} = 2\varepsilon_{\mathrm{x},\sigma}^{\mathrm{PBEsol}} + K_{\mathrm{x}}^{\mathrm{LDA}} \sum_{i=1}^{N_\sigma} \sqrt{\epsilon_{\mathrm{H}} - \epsilon_{i\sigma}} \frac{|\psi_{i\sigma}|^2}{\rho_\sigma} + v_{\mathrm{c},\sigma}^{\mathrm{PBEsol}}$$

- Leads to an derivative discontinuity:

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

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

- Much better than LDA/GGA for band gaps
- Not as good as mBJ for strongly correlated systems[2]
- Seems interesting for electric field gradient[2]
- 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)

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 $YBa_2Cu_3O_6$!)
  - Wrong electronic configuration

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(Partial) solution to the problem:

- Combine semilocal functionals with Hartree-Fock theory:
  - DFT+U
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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 $\rightarrow$ 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

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

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

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

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

  There are several versions of the double-counting term

- For the hybrid methods only exchange is corrected:

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

  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 $4f$ 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 $4f$ 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	$\rightarrow v_{\mathrm{xc},\sigma}^{\mathrm{DFT}} + v_{\mathrm{ee}} + v_{\mathrm{en}}$ (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	$\rightarrow \psi_{n\mathbf{k}}^{\uparrow}, \epsilon_{n\mathbf{k}}^{\uparrow}$ (case.vectorup, case.energyup)
lapw1 -dn -orb	$\rightarrow \psi_{n\mathbf{k}}^{\downarrow}, \epsilon_{n\mathbf{k}}^{\downarrow}$ (case.vectordn, case.energydn)
lapw2 -up -orb	$\rightarrow \rho_{\mathrm{val}}^{\uparrow}$ (case.clmvalup), $n_{mm'}^{\uparrow}$ (case.dmatup)
lapw2 -dn -orb	$\rightarrow \rho_{\mathrm{val}}^{\downarrow}$ (case.clmvaldn), $n_{mm'}^{\downarrow}$ (case.dmatdn)
lcore -up	$\rightarrow \rho_{\mathrm{core}}^{\uparrow}$ (case.clmcorup)
lcore -dn	$\rightarrow \rho_{\mathrm{core}}^{\downarrow}$ (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

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Two types of full hybrid functionals available in WIEN2k[1]:

- unscreened:

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

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

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

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 Ernzerhof[1])

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)

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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?

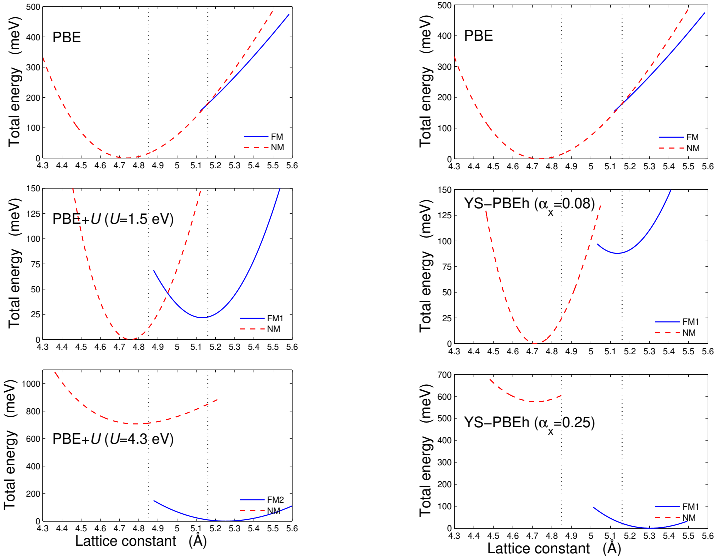
1. init_lapw
2. Recommended: run(sp)_lapw for the semilocal functional
3. save_lapw
4. init_hf_lapw (this will create/modify input files)
   4.1 adjust case.inhf according to your needs
   4.2 reduced **k**-mesh for the HF potential? Yes or no
   4.3 specify the **k**-mesh
5. run(sp)_lapw -hf (-redklist)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

SCF cycle of hybrid functionals in WIEN2k

lapw0 -grr	$\rightarrow v_{\mathrm{x}}^{\mathrm{DFT}}$ (case.r2v), $\alpha E_{\mathrm{x}}^{\mathrm{DFT}}$ (:AEXSL)
lapw0	$\rightarrow v_{\mathrm{xc}}^{\mathrm{DFT}} + v_{\mathrm{ee}} + v_{\mathrm{en}}$ (case.vsp, case.vns)
lapw1	$\rightarrow \psi_{n\mathbf{k}}^{\mathrm{DFT}}, \epsilon_{n\mathbf{k}}^{\mathrm{DFT}}$ (case.vector, case.energy)
lapw2	$\rightarrow \sum_{n\mathbf{k}} \epsilon_{n\mathbf{k}}^{\mathrm{DFT}}$ (:SLSUM)
hf	$\rightarrow \psi_{n\mathbf{k}}, \epsilon_{n\mathbf{k}}$ (case.vectorhf, case.energyhf)
lapw2 -hf	$\rightarrow \rho_{\mathrm{val}}$ (case.clmval)
lcore	$\rightarrow \rho_{\mathrm{core}}$ (case.clmcor)
mixer	$\rightarrow$ mixed ρ

Nonmagnetic and ferromagnetic phases of cerium[1]

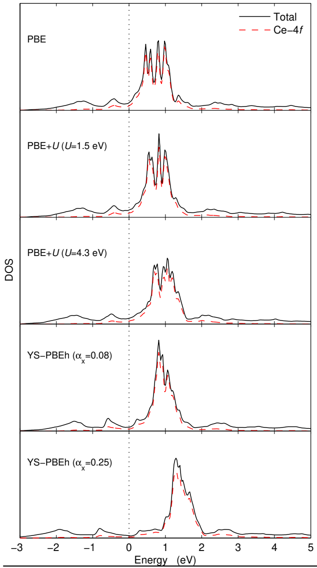
Small U (1.5 eV) or α_x (0.08) leads to correct stability ordering



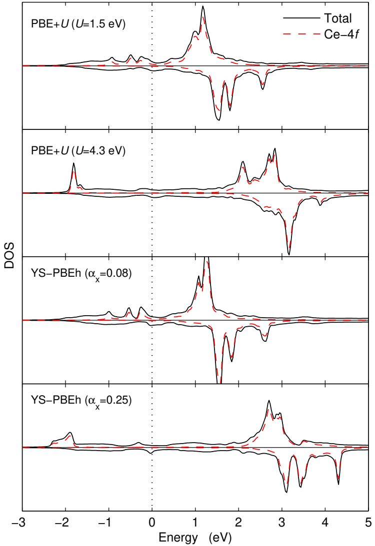
[1] F. Tran, F. Karsai, and P. Blaha, Phys. Rev. B **89**, 155106 (2014)

Nonmagnetic and ferromagnetic phases of cerium[1]

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 ressources
  - hybrid functionals and GW require (substantially) more computational ressources (and patience)