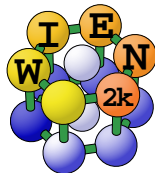# Methods available in WIEN2k for the treatment of exchange and correlation effects

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Outline of the talk

- Introduction
- Semilocal functionals:
  - GGA and MGGA
  - mBJ potential (for band gap)
  - Input file case.in0
- The DFT-D3 method for dispersion
- On-site methods for strongly correlated electrons:
  - DFT+U
  - Hybrid functionals
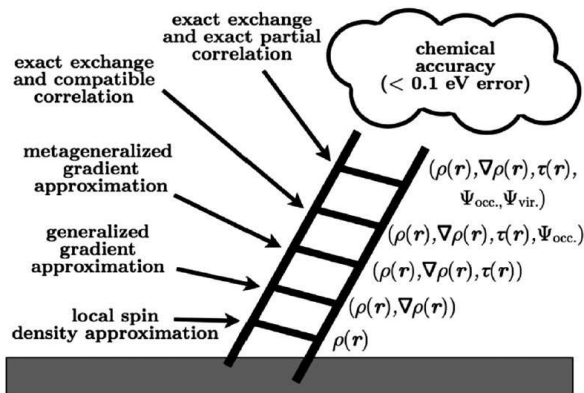- Hybrid functionals
- GW

Total energy in Kohn-Sham DFT [1]

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

$$\underbrace{\phantom{\frac{1}{2}\sum_i \int |\nabla\psi_i(\mathbf{r})|^2 d^3r}}_{T_{\mathrm{s}}} \quad \underbrace{\phantom{\frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r d^3r'}}_{E_{\mathrm{ee}}} \quad \underbrace{\phantom{\int v_{\mathrm{en}}(\mathbf{r})\rho(\mathbf{r})d^3r}}_{E_{\mathrm{en}}}$$

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

- T_{s} : kinetic energy of the non-interacting electrons
- E_{ee} : electron-electron electrostatic Coulomb energy
- E_{en} : electron-nucleus electrostatic Coulomb energy
- E_{nn} : nucleus-nucleus electrostatic Coulomb energy
- $E_{\mathrm{xc}} = E_{\mathrm{x}} + E_{\mathrm{c}}$: exchange-correlation energy
  Approximations for E_{xc} have to be used in practice
  $\implies$ 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])

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

exact exchange and exact partial correlation

exact exchange and compatible correlation

chemical accuracy (< 0.1 eV error)

metageneralized gradient approximation

$(\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r}), \tau(\boldsymbol{r}), \Psi_{occ.}, \Psi_{vir.})$

generalized gradient approximation

$(\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r}), \tau(\boldsymbol{r}), \Psi_{occ.})$

$(\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r}), \tau(\boldsymbol{r}))$

local spin density approximation

$(\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r}))$

$\rho(\boldsymbol{r})$

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)

The 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 $\hat{v}_{\text{xc}}$:

- 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 KS)
  - Hartree-Fock
  - LDA+U
  - Hybrid (mixing of GGA and Hartree-Fock)
  - MGGA
  - Self-interaction corrected (Perdew-Zunger)

Semilocal functionals: trends with 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

$$r_s = \frac{1}{\left(\frac{4}{3}\pi\rho\right)^{1/3}} \quad \text{(Wigner-Seitz radius)}$$
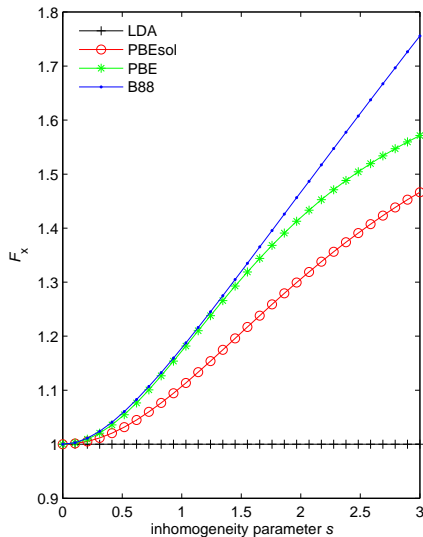
$$s = \frac{|\nabla\rho|}{2\left(3\pi^2\right)^{1/3}\rho^{4/3}} \quad \text{(inhomogeneity parameter)}$$

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: GGA

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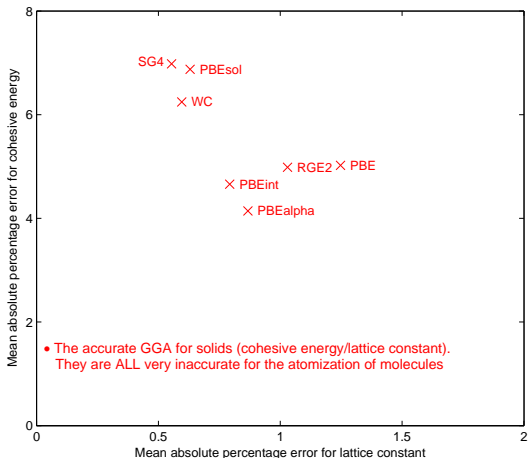

good for atomization energy of molecules

good for atomization energy of solids

good for lattice constant of solids

good for nothing

Construction of an universal GGA: A failure

Test of functionals on 44 solids[1]

Semilocal functionals: meta-GGA

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

where F_{xc} is the enhancement factor and

- $\alpha = \frac{t - t_{\mathrm{W}}}{t_{\mathrm{TF}}}$
  - $\alpha = 1$ where the electron density is uniform
  - $\alpha = 0$ in one- and two-electron regions
  - $\alpha \gg 1$ between closed shell atoms

$\implies$ MGGA functionals are more flexible

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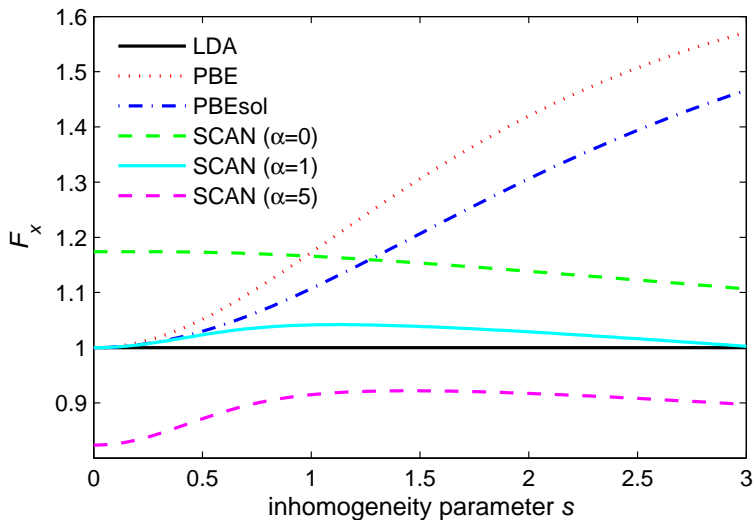
$\implies$ MGGA functionals are more flexible

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

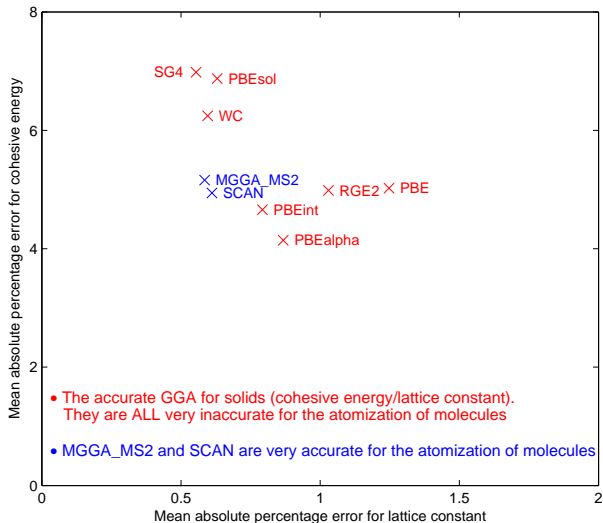[1] J. Sun *et al.*, Phys. Rev. Lett. **115**, 036402 (2015)

Semilocal functionals: meta-GGA

$$F_{\mathrm{x}}(s, \alpha) = \epsilon_{\mathrm{x}}^{\mathrm{MGGA}} / \epsilon_{\mathrm{x}}^{\mathrm{LDA}}$$

Semilocal functionals: MGGA_MS2 and SCAN

Test of functionals on 44 solids[1]

[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

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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]

$$v_{\mathrm{x}}^{\mathrm{mBJ}}(\mathbf{r}) = c\,v_{\mathrm{x}}^{\mathrm{BR}}(\mathbf{r}) + (3c - 2)\frac{1}{\pi}\sqrt{\frac{5}{6}}\sqrt{\frac{t(\mathbf{r})}{\rho(\mathbf{r})}}$$
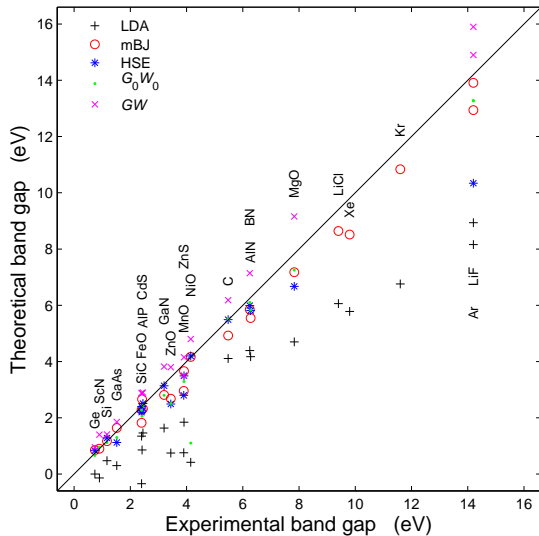
where $v_{\mathrm{x}}^{\mathrm{BR}}$ is the Becke-Roussel potential, t is the kinetic-energy density and c is given by

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

mBJ is a MGGA potential

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

Band gaps with mBJ

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 ...

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[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)

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 with keywords

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

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

Dispersion methods for DFT

Problem with semilocal functionals:

- They do not include London dispersion interactions
- Results are qualitatively wrong for systems where dispersion plays a major role

Two common dispersion methods for DFT:

- Pairwise term[1]:

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

- Nonlocal term[2]:

$$E_{c,disp}^{NL} = \frac{1}{2} \int \int \rho(\mathbf{r})\phi(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d^3r d^3r'$$

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

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

The DFT-D3 method[1] in WIEN2k

- **Features of DFT-D3:**
  - Very cheap (pairwise)
  - C_n^{AB} depend on positions of the nuclei (via coordination number)
  - Functional-dependent parameters
  - Energy and forces (minimization of internal parameters)
  - 3-body term
- **Installation:**
  - Not included in WIEN2k
  - Download and compile the DFTD3 package from
    http://www.thch.uni-bonn.de/tc/index.php
    copy the `dftd3` executable in $WIENROOT
  - input file case.indftd3 (if not present a default one is copied automatically)
  - run(sp)_lapw -dftd3 . . .
  - case.scfdftd3 is included in case.scf

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

The DFT-D3 method: the 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)

The DFT-D3 method: hexagonal BN[1]
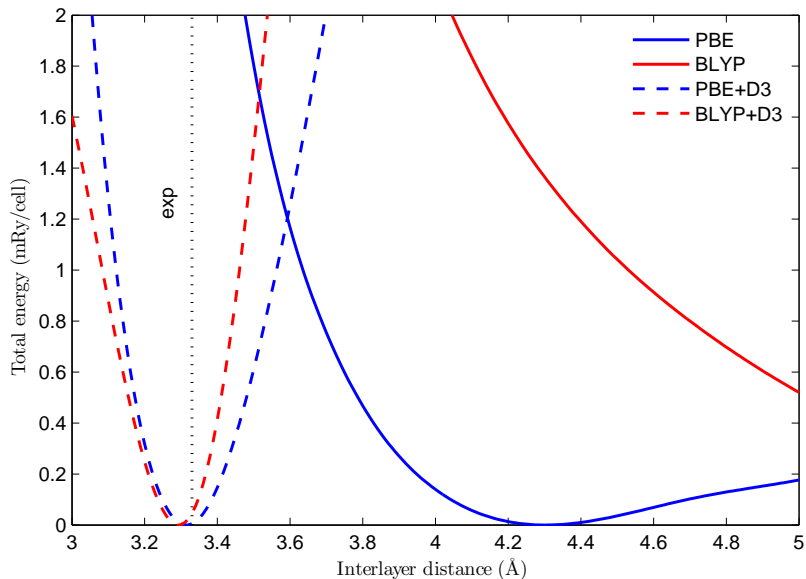
[1] F. Tran *et al.*, J. Chem. Phys. **144**, 204120 (2016)

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 or even absent like in Ge or FeO
  - The magnetic moments are too small
  - Wrong ground state

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Why?

- The strong on-site correlations are not correctly accounted for by semilocal functionals.

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(Partial) solution to the problem:

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

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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:

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

There are several versions of the double-counting term

- For the hybrid methods only exchange is corrected:

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

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

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	$\rightarrow v_{xc,\sigma}^{DFT} + v_{ee} + v_{en}$ (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	$\rightarrow \psi_{n\mathbf{k}}^{\uparrow}, \epsilon_{n\mathbf{k}}^{\uparrow}$ (case.vectorup, case.energyup)
lapw1 -dn -orb	$\rightarrow \psi_{n\mathbf{k}}^{\downarrow}, \epsilon_{n\mathbf{k}}^{\downarrow}$ (case.vectordn, case.energydn)

lapw2 -up	$\rightarrow \rho_{val}^{\uparrow}$ (case.clmvalup)
lapw2 -dn	$\rightarrow \rho_{val}^{\downarrow}$ (case.clmvaldn)

lapwdm -up	$\rightarrow n_{mm'}^{\uparrow}$ (case.dmatup)
lapwdm -dn	$\rightarrow n_{mm'}^{\downarrow}$ (case.dmatdn)

lcore -up	$\rightarrow \rho_{core}^{\uparrow}$ (case.clmcorup)
lcore -dn	$\rightarrow \rho_{core}^{\downarrow}$ (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)

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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), $\frac{1}{|\mathbf{r}-\mathbf{r}'|} \rightarrow \frac{e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$:

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

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

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[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 screend hybrid:
    - LDA
    - PBE
    - WC
    - PBEsol
    - B3PW91
    - B3LYP
- Use run_bandplothf_lapw for band structure

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)

Hybrid functionals: input file case.inhf

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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

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[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	$\rightarrow v_x^{\mathrm{DFT}}$ (case.r2v), $\alpha E_x^{\mathrm{DFT}}$ (:AEXSL)
lapw0	$\rightarrow v_{xc}^{\mathrm{DFT}} + v_{ee} + v_{en}$ (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

Calculation of quasiparticle spectra from many-body theory

- In principle the Kohn-Sham eigenvalues should be viewed as mathematical objects and not compared directly to experiment (ionization potential and electron affinity).
- The true addition and removal energies ϵ_i are calculated from the equation of motion for the Green function:

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{en}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right) + \int \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_i)\psi_i(\mathbf{r}')d^3r' = \epsilon_i\psi_i(\mathbf{r})$$

- The self-energy Σ is calculated from Hedin's self-consistent equations[1]:

$$\Sigma(1, 2) = i \int G(1, 4)W(1^+, 3)\Gamma(4, 2, 3)d(3, 4)$$

$$W(1, 2) = v(1, 2) + \int v(4, 2)P(3, 4)W(1, 3)d(3, 4)$$

$$P(1, 2) = -i \int G(2, 3)G(4, 2)\Gamma(3, 4, 1)d(3, 4)$$

$$\Gamma(1, 2, 3) = \delta(1, 2)\delta(1, 3) + \int \frac{\delta\Sigma(1, 2)}{\delta G(4, 5)} G(4, 6)G(7, 5)\Gamma(6, 7, 3)d(4, 5, 6, 7)$$

---

[1] L. Hedin, Phys. Rev. **139**, A769 (1965)

The GW and G_0W_0 approximations

- GW: vertex function Γ in Σ set to 1:

$$\Sigma(1,2) = i \int G(1,4)W(1^+,3)\Gamma(4,2,3)d(3,4) \approx iG(1,2^+)W(1,2)$$

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi} \int_{-\infty}^{\infty} G(\mathbf{r},\mathbf{r}',\omega+\omega')W(\mathbf{r},\mathbf{r}',\omega')e^{-i\delta\omega'}\,d\omega'$$

$$G(\mathbf{r},\mathbf{r}',\omega) = \sum_{i=1}^{\infty} \frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')}{\omega - \epsilon_i - i\eta_i} \qquad W(\mathbf{r},\mathbf{r}',\omega) = \int v(\mathbf{r},\mathbf{r}'')\epsilon^{-1}(\mathbf{r}'',\mathbf{r}',\omega)d^3r''$$

- G_0W_0 (one-shot GW):
  G and W are calculated using the Kohn-Sham orbitals and eigenvalues. 1st order perturbation theory gives

$$\epsilon_i^{GW} = \epsilon_i^{\text{KS}} + Z(\epsilon_i^{\text{KS}})\langle\psi_i^{\text{KS}}|\Re(\Sigma(\epsilon_i^{\text{KS}})) - v_{\text{xc}}|\psi_i^{\text{KS}}\rangle$$

A few remarks on *GW*

- *GW* calculations require very large computational ressources
- *G* and *W* depend on all (occupied and unoccupied) orbitals (up to parameter emax in practice)
- *GW* is the state-of-the-art for the calculation of (inverse) photoemission spectra, but not for optics since excitonic effects are still missing in *GW* (BSE code from R. Laskowski)
- *GW* is more accurate for systems with weak correlations

FHI-gap: a LAPW GW code[1]

- Based on the FP-LAPW basis set
- Mixed basis set to expand the GW-related quantities
- Interfaced with WIEN2k
- G_0W_0, GW_0 @LDA/GGA($+U$)
- Parallelized
- http://www.chem.pku.edu.cn/jianghgroup/codes/fhi-gap.html

[1] H. Jiang *et al.*, Comput. Phys. Comput. **184**, 348 (2013)

Flowchart of FHI-gap
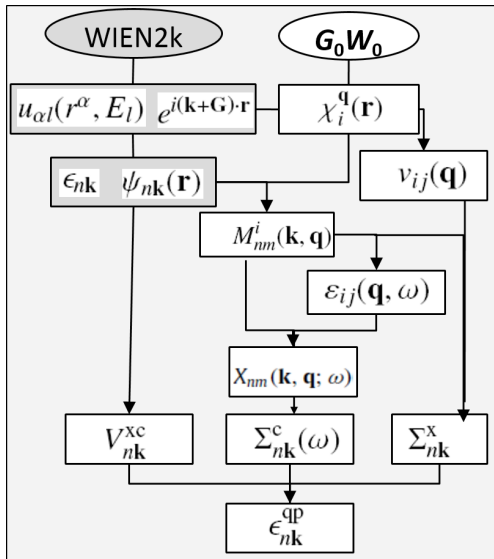
How to run the FHI-gap code?

1. Run a WIEN2k SCF calculation (in w2kdir)
2. In w2kdir, execute the script gap_init to prepare the input files for *GW*:

   gap_init -d <gwdir> -nkp <nkp> -s 0/1/2 -orb -emax <emax>

3. Eventually modify gwdir.ingw
4. Execute gap.x or gap-mpi.x in gwdir
5. Analyse the results from:
   5.1 gwdir.outgw
   5.2 the plot of the DOS/band structure generated by gap_analy

Parameters to be converged for a *GW* calculation

- Usual WIEN2k parameters:
  - Size of the LAPW basis set (RK_{max})
  - Number of **k**-points for the Brillouin zone integrations
- *GW*-specific parameters:
  - Size of the mixed basis set
  - Number of unoccupied states (emax)
  - Number of frequencies ω for the calculation of $\Sigma = \int GW d\omega$

Band gaps
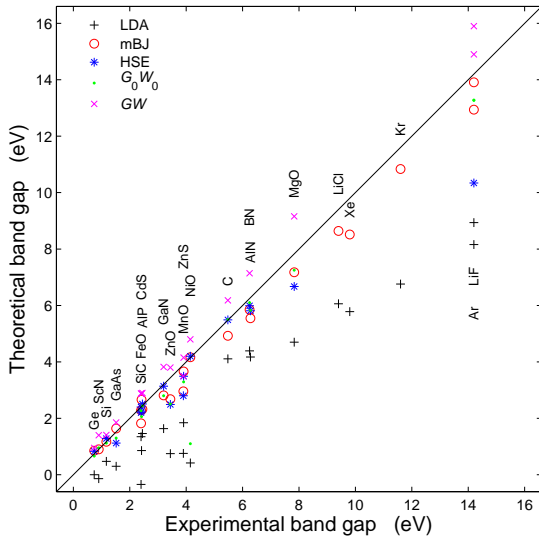
Some recommendations

Before using a method or a functional:

- ▶ Read a few papers concerning the method in order to know
  - ▶ why it has been used
  - ▶ for which properties or types of solids it is supposed to be reliable
  - ▶ if it is adapted to your problem
- ▶ Do you have enough computational ressources?
  - ▶ hybrid functionals and GW require (substantially) more computational ressources (and patience)