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
  - Keywords
- The DFT-D3 method for dispersion
- On-site methods for strongly correlated electrons:
  - DFT$+U$
  - Hybrid-DFT
- Hybrid functionals
- *GW*

Total energy in Kohn-Sham DFT [1]

$$\begin{aligned} E_{\mathrm{tot}} &= \underbrace{\frac{1}{2}\sum_i \int |\nabla\psi_i(\mathbf{r})|^2\, d^3r}_{T_{\mathrm{s}}} + \underbrace{\frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d^3r d^3r'}_{E_{\mathrm{H}}} + \underbrace{\int v_{\mathrm{nuc}}(\mathbf{r})\rho(\mathbf{r})d^3r}_{V_{\mathrm{en}}} \\ &\quad + \underbrace{\frac{1}{2}\sum_{\substack{A,B\\A\neq B}} \frac{Z_A Z_B}{|\mathbf{R}_A-\mathbf{R}_B|}}_{V_{\mathrm{nn}}} + E_{\mathrm{xc}} \end{aligned}$$

- T_{s} : kinetic energy of non-interacting electrons
- E_{H} : electron-electron electrostatic Coulomb energy
- V_{en} : electron-nucleus electrostatic Coulomb energy
- V_{nn} : nucleus-nucleus electrostatic Coulomb energy
- $E_{\mathrm{xc}} = E_{\mathrm{x}} + E_{\mathrm{c}}$: exchange-correlation energy
  Problem with E_{xc}:
  the exact form of E_{c} is too complicated to be useable $\Longrightarrow$
  approximations have to be used in practice

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

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

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

1. Local density approximation (LDA): $\epsilon_{\mathrm{xc}} = f\left(\rho\right)$
2. Generalized gradient approximation (GGA): $\epsilon_{\mathrm{xc}} = f\left(\rho, \nabla\rho\right)$
3. Meta-GGA: $\epsilon_{\mathrm{xc}} = f\left(\rho, \nabla\rho, \nabla^2\rho, t\right),\; t = \frac{1}{2}\sum_i \left|\nabla\psi_i\right|^2$
4. The use of occupied orbitals (e.g., Hartree-Fock)
5. The use of unoccupied orbitals (e.g., RPA)

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

The one-electron Schrödinger equations

Minimization of E_{tot} leads to

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

Two ways of calculating $\hat{v}_{\mathrm{xc}}$:

- $\hat{v}_{\mathrm{xc}} = \delta E_{\mathrm{xc}}/\delta\rho = v_{\mathrm{xc}}$ (KS method)
- $\hat{v}_{\mathrm{xc}} = (1/\psi_i)\delta E_{\mathrm{xc}}/\delta\psi_i^* = v_{\mathrm{xc},i}$ (generalized KS [1], e.g., HF)

Remarks:

- If E_{xc} is an explicit functional of ρ (LDA and GGA), then both possibilities lead to the same potential v_{xc}.
- MGGA (with t) and hybrid functionals are usually implemented in the generalized KS method.

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

Semilocal functionals: GGA

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

where F_{xc} is the enhancement factor and

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

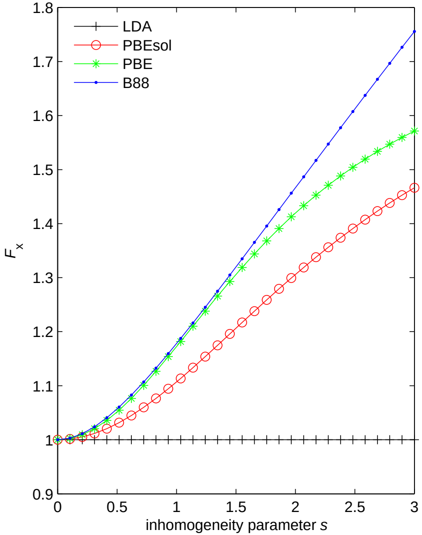
$$s = \frac{|\nabla\rho|}{2\left(3\pi^2\right)^{1/3}\rho^{4/3}} \quad \text{(inhomogeneity parameter)}$$

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

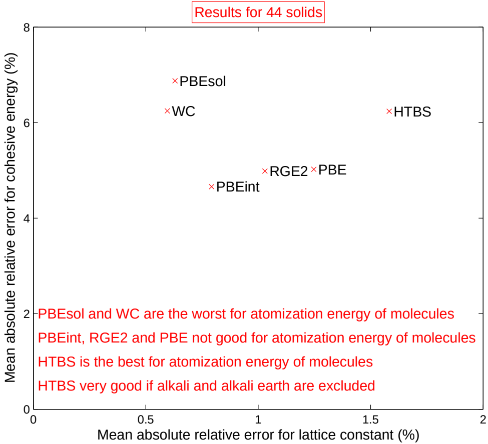
good for atomization energy of solids

good for lattice constant of solids

exact for homogeneous electron gas

Construction of an universal GGA: A failure (up to now)

Attempts: RGE2[1], PBEint[2], HTBS[3]



Results for 44 solids

PBEsol and WC are the worst for atomization energy of molecules

PBEint, RGE2 and PBE not good for atomization energy of molecules

HTBS is the best for atomization energy of molecules

HTBS very good if alkali and alkali earth are excluded

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[1] A. Ruzsinszky *et al.*, J. Chem. Theory Comput. **5**, 763 (2009)

[2] E. Fabiano *et al.*, Phys. Rev. B **82**, 113104 (2010)

[3] P. Haas *et al.*, Phys. Rev. B **83**, 205117 (2011)

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

$\Longrightarrow$ MGGA functionals are more flexible

Example: MGGA_MS2[1] is

- as good as the best GGA for atomization energies of molecules
- as good as the best GGA for lattice constant of solids
- maybe not too bad for van der Waals systems

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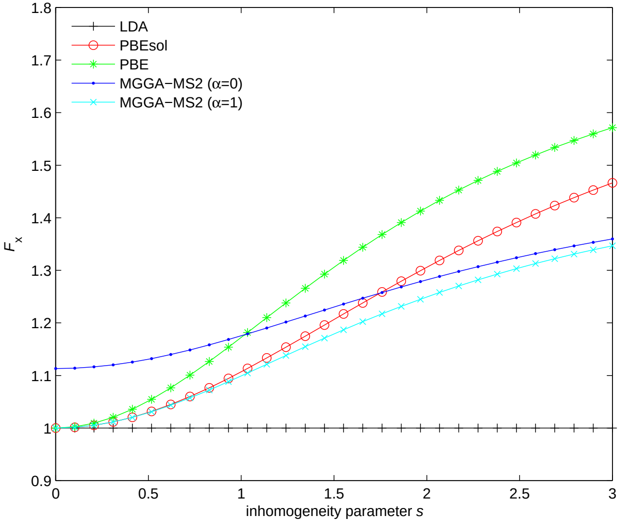
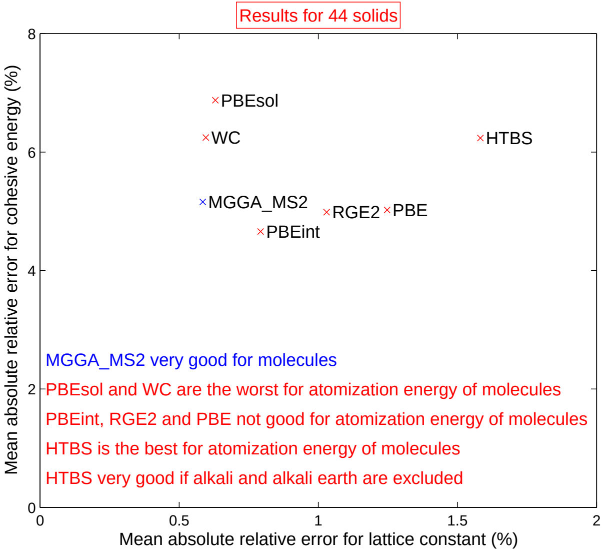
[1] J. Sun *et al.*, Phys. Rev. Lett. **111**, 106401 (2013)

Semilocal functionals: meta-GGA

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



Semilocal functionals: MGGA_MS2



MGGA_MS2 very good for molecules

PBEsol and WC are the worst for atomization energy of molecules

PBEint, RGE2 and PBE not good for atomization energy of molecules

HTBS is the best for atomization energy of molecules

HTBS very good if alkali and alkali earth are excluded

Semilocal functionals: modified Becke-Johnson potential

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

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

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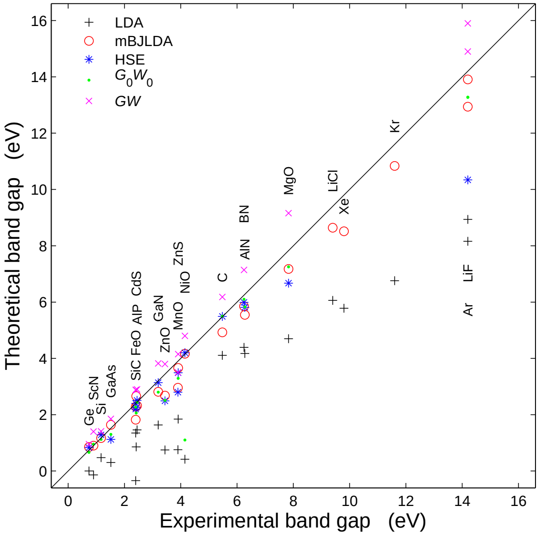
[1] F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009)

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. Eventually: edit case.inm and choose PRATT with small mixing factor smaller than 0.1
5. 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 first line of case.in0. Three possibilities:

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

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[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 `inputpars.f` and `vxclm2.f` (`SRC_lapw0` directory) 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]:

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

- Nonlocal term[2]:

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

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[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
  - run(sp)_lapw -dftd3 . . .

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

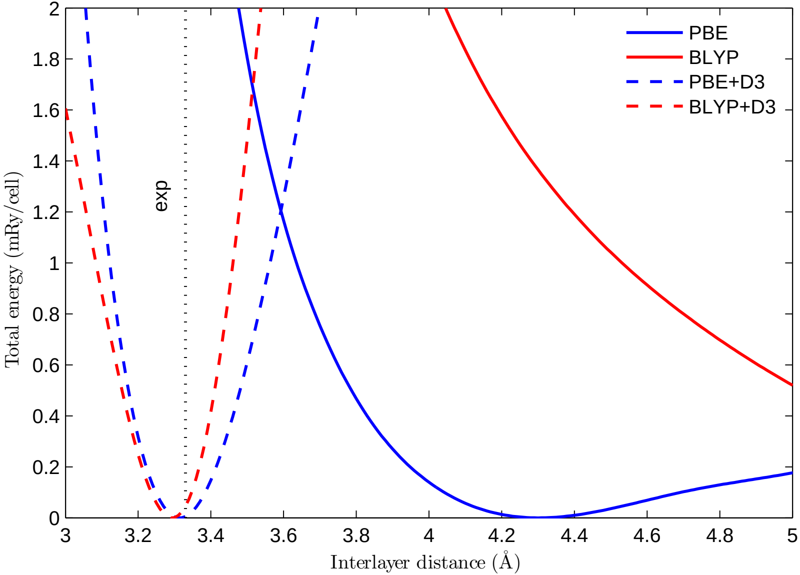
The DFT-D3 method: the input file case.indftd3

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



Strongly correlated electrons

Problem with semilocal functionals:

- They give qualitatively wrong results for solids which contain localized 3*d* or 4*f* electrons
  - The band gap is too small or even absent like in FeO
  - The magnetic moments are too small
  - Wrong ground state

Why?

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

(Partial) solution to the problem:

- Combine semilocal functionals with Hartree-Fock theory:
  - 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] 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.

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

[2] P. Novák *et al.*, Phys. Stat. Sol. (b) **243**, 563 (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 $\rightarrow v^{\mathrm{DFT}}_{\mathrm{xc},\sigma} + v_{\mathrm{ee}} + v_{\mathrm{en}}$ (case.vspup(dn), case.vnsup(dn))

orb -up $\rightarrow v^{\uparrow}_{mm'}$ (case.vorbup)

orb -dn $\rightarrow v^{\downarrow}_{mm'}$ (case.vorbdn)

lapw1 -up -orb $\rightarrow \psi^{\uparrow}_{n\mathbf{k}}, \epsilon^{\uparrow}_{n\mathbf{k}}$ (case.vectorup, case.energyup)

lapw1 -dn -orb $\rightarrow \psi^{\downarrow}_{n\mathbf{k}}, \epsilon^{\downarrow}_{n\mathbf{k}}$ (case.vectordn, case.energydn)

lapw2 -up $\rightarrow \rho^{\uparrow}_{\mathrm{val}}$ (case.clmvalup)

lapw2 -dn $\rightarrow \rho^{\downarrow}_{\mathrm{val}}$ (case.clmvaldn)

lapwdm -up $\rightarrow n^{\uparrow}_{mm'}$ (case.dmatup)

lapwdm -dn $\rightarrow n^{\downarrow}_{mm'}$ (case.dmatdn)

lcore -up $\rightarrow \rho^{\uparrow}_{\mathrm{core}}$ (case.clmcorup)

lcore -dn $\rightarrow \rho^{\downarrow}_{\mathrm{core}}$ (case.clmcordn)

mixer → mixed ρ^{σ} and $n^{\sigma}_{mm'}$

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)

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

- unscreened:

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

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

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

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

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 $\rightarrow v_{\mathrm{x}}^{\mathrm{DFT}}$ (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

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:

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

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

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

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

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

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

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[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

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

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

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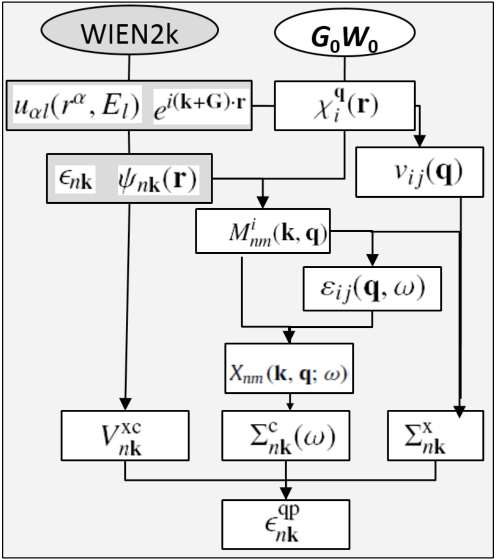
[1] H. Jiang *et al.*, Comput. Phys. Comput. **184**, 348 (2013)

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*:

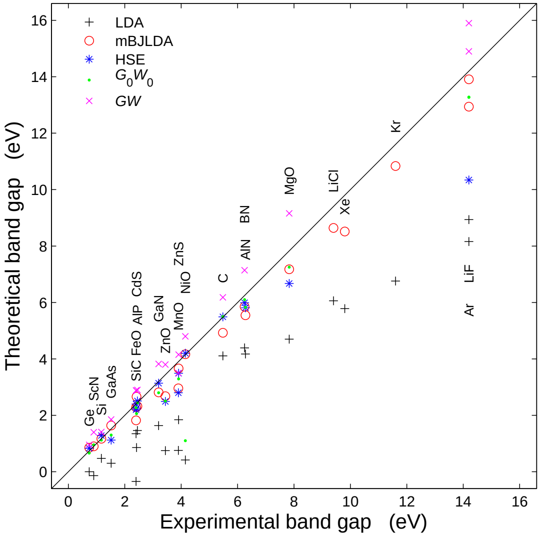
```
gap_init -d <gwdir> -nkp <nkp> -s 0/1/2 -orb -emax <emax>
```

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 $\Sigma = \int GWd\omega$

Band gaps



+ LDA
○ mBJLDA
✳ HSE
• G_0W_0
× *GW*
Theoretical band gap (eV)
Experimental band gap (eV)
0
2
4
6
8
10
12
14
16
Ge
Si
ScN
GaAs
SiC
FeO
AlP
CdS
ZnO
GaN
MnO
NiO
ZnS
C
AlN
BN
MgO
LiCl
Xe
Kr
LiF
Ar

Thank your for your attention!