Beyond LDA and GGA: Hybrid Functionals

Muffin-tin Recipes, Jülich 2011 | Martin Schlipf
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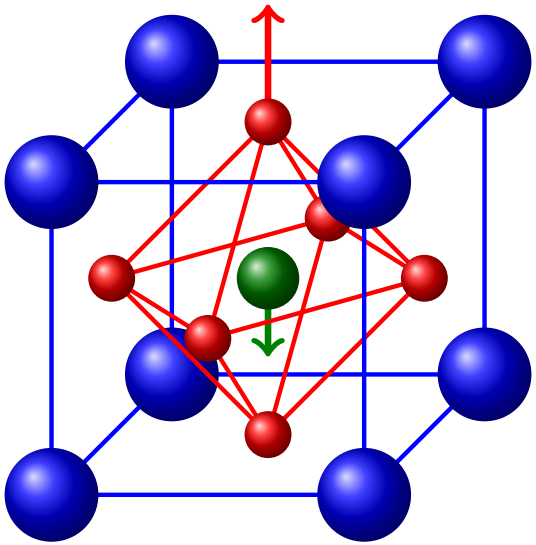
Motivation



$BaTiO_3$

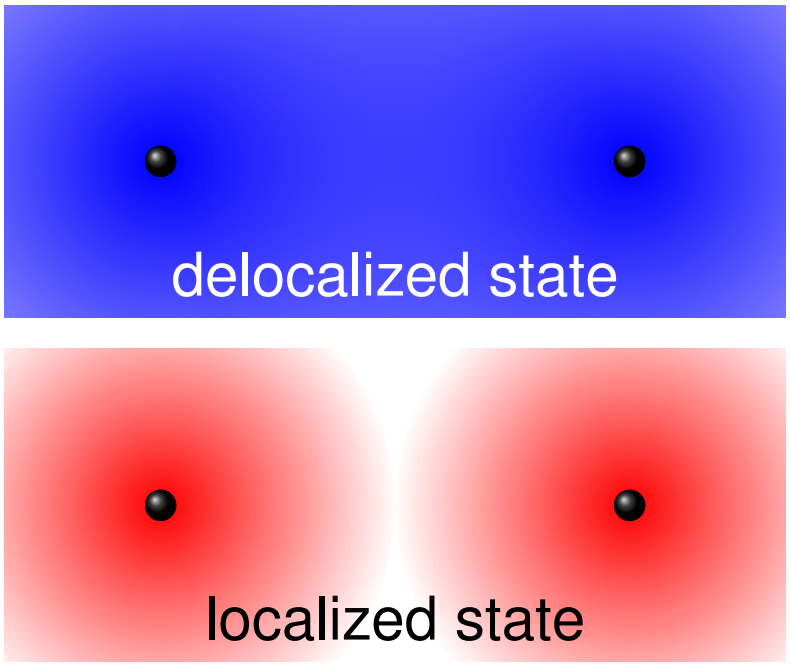
- oxide materials
- band transition $<$ experiment
- pseudo Jan-Teller effect
- ferroelectric distortion

Self-interaction error

$$\underbrace{\left\langle \phi_1\,\phi_2 \left| \hat{V}_{\text{coul}} \right| \phi_1\,\phi_2 \right\rangle}_{\text{Coulomb}} - \underbrace{\left\langle \phi_1\,\phi_2 \left| \hat{V}_{\text{coul}} \right| \phi_2\,\phi_1 \right\rangle}_{\text{Exchange}}$$

- self-interaction $\phi_1 = \phi_2$
- terms cancel in HF theory
- LDA or GGA $\Rightarrow$ finite error

$$\iint \mathrm{d}^3 r\, \mathrm{d}^3 r' \, \frac{n_1(\boldsymbol{r})\, n_1(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$



Overview

Introduction: Hybrid Functionals
- Adiabatic connection formula
- Development of hybrid functionals
- The PBE0 and the HSE functional

Implementation in FLAPW

How to use Hybrid Functionals in `fleur`

Adiabatic connection formula

Parameter λ describes strength of interaction

$$\mathcal{H} = T + \lambda V_{\mathrm{ee}} + V(\lambda)$$

energy derivative – eigenstates depend on λ

$$\frac{\mathrm{d}E(\lambda)}{\mathrm{d}\lambda} = \left\langle \varphi(\lambda) \left| V_{\mathrm{ee}} + \frac{\mathrm{d}V(\lambda)}{\mathrm{d}\lambda} \right| \varphi(\lambda) \right\rangle$$

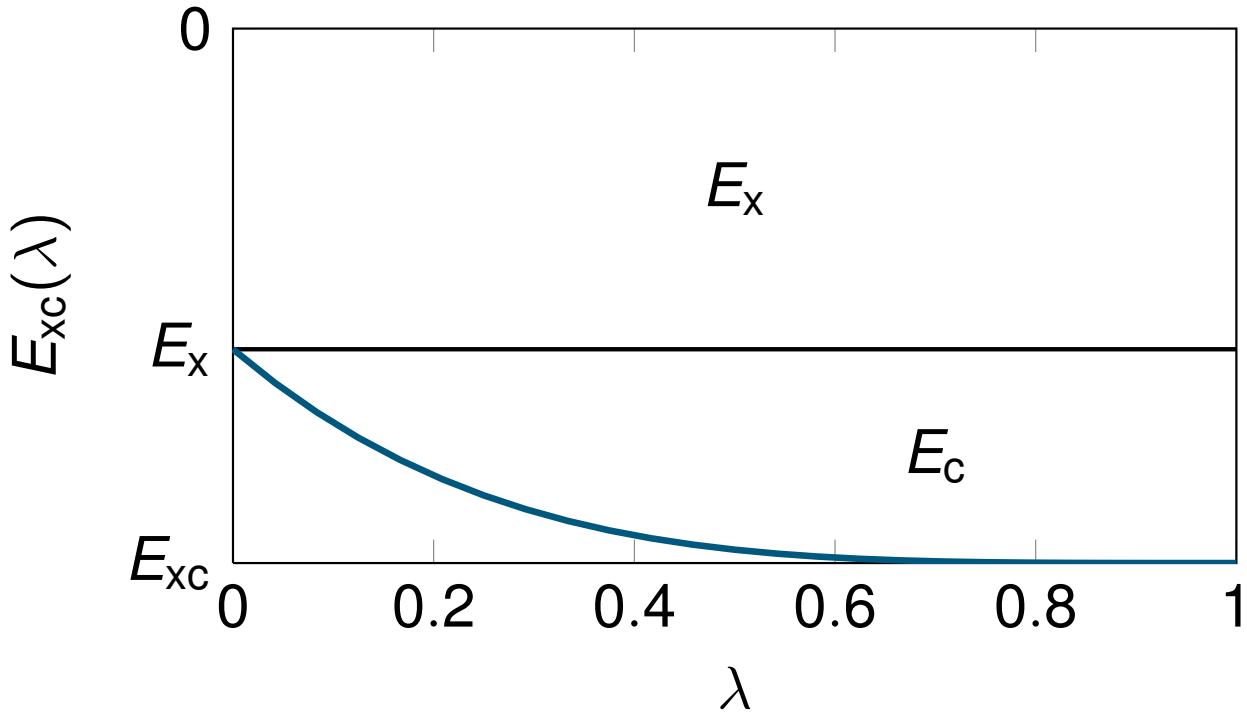
energy of full interacting system

$$E(\lambda = 1) - E(\lambda = 0) = \int_0^1 \mathrm{d}\lambda \, \langle \varphi(\lambda) \, | V_{\mathrm{ee}} | \, \varphi(\lambda) \rangle - \int \mathrm{d}^3 r \, n V(\lambda = 0)$$

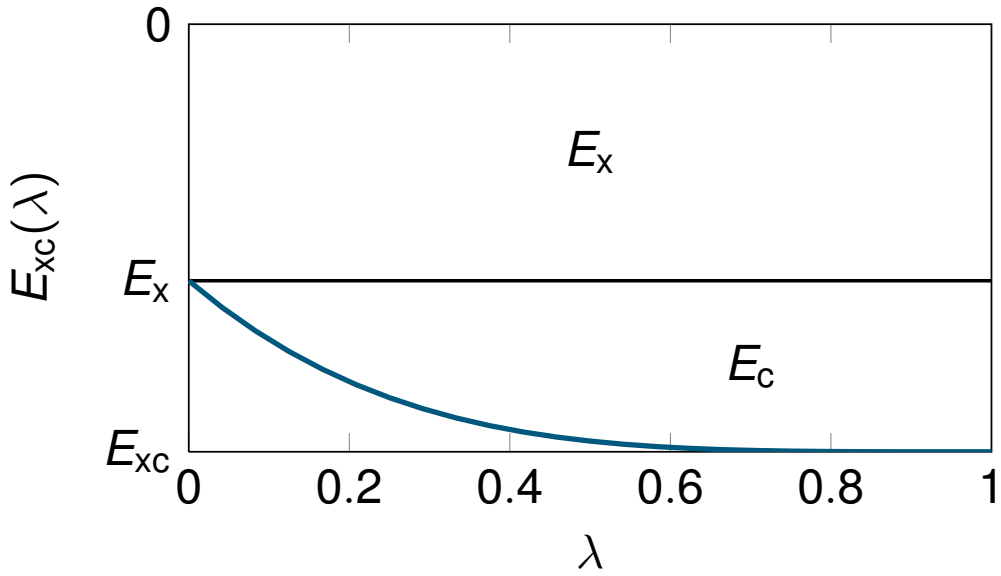
Exchange correlation energy

density functional theory $\Rightarrow$ functional design

$$E_{\mathrm{xc}} = \int_0^1 \mathrm{d}\lambda \, \langle \varphi(\lambda) | V_{\mathrm{ee}} | \varphi(\lambda) \rangle - U_{\mathrm{H}}(n) = \int_0^1 \mathrm{d}\lambda \, E_{\mathrm{xc}}(\lambda)$$



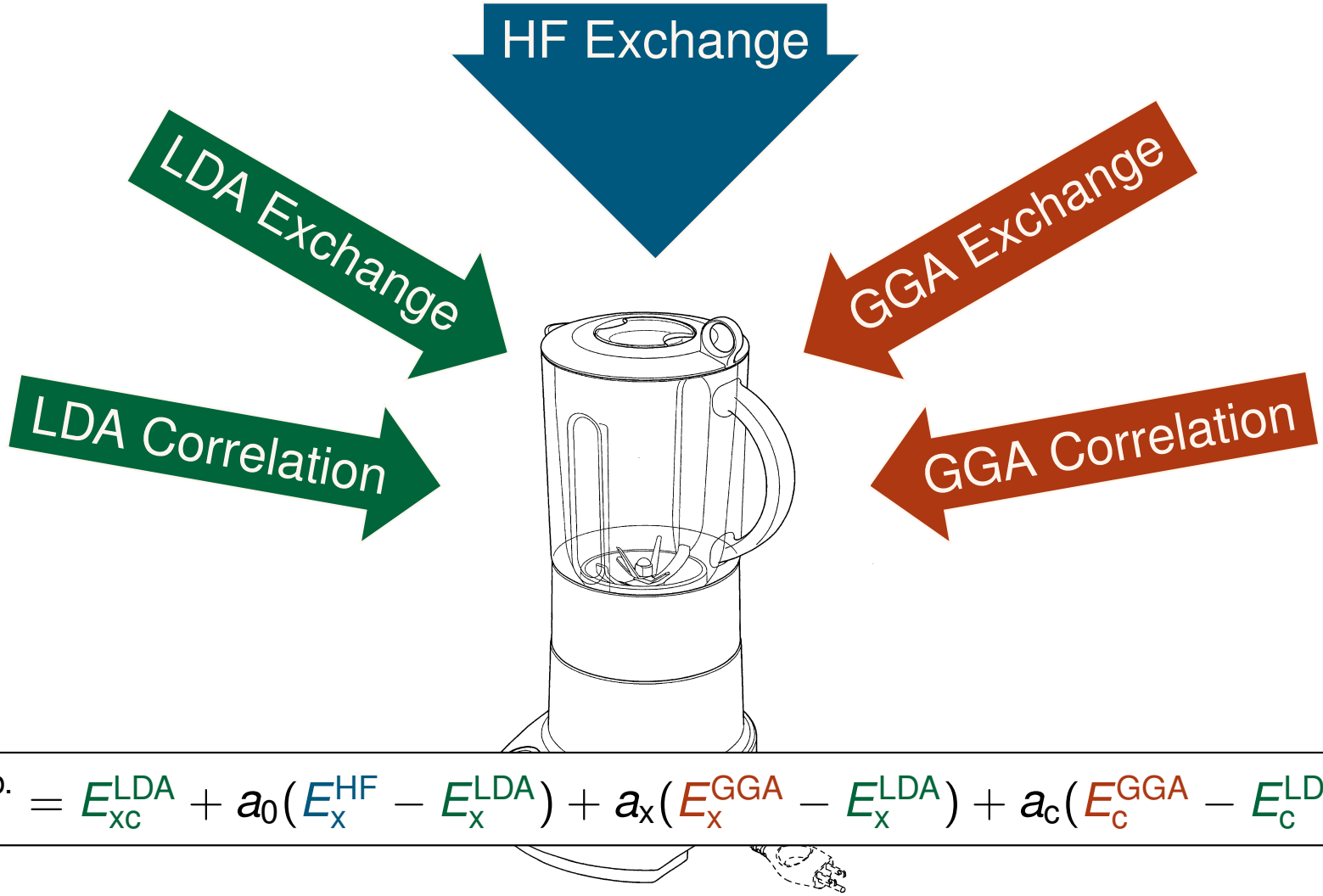
Brief review



- for the non-interacting system only exchange
- Hartree-Fock is exact solution for $\lambda = 0$
- observation in simple materials: DFT improves for large λ

Will it blend?

Becke 1993, JCP 98, p.1372 and p.5648



$$E_{xc}^{hyb.} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA})$$

Constructing a simpler hybrid functional

Becke 1996, JCP 104, p.1040

$$E_{xc}^{hyb.} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA})$$

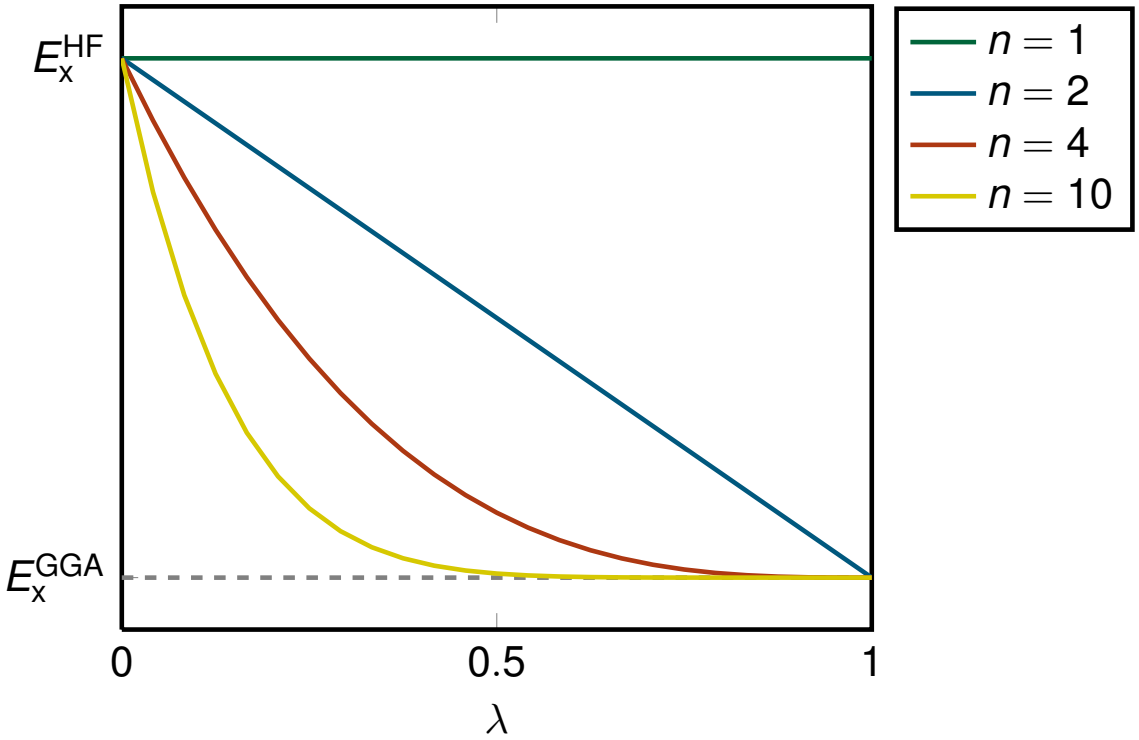
- empirical values: $a_0 = 0.20$, $a_x = 0.72$, $a_c = 0.81$
- simplification: $a_x = 1 - a_0$, $a_c = 1$

$$E_{xc}^{hyb.} = E_{xc}^{GGA} + a_0(E_x^{HF} - E_x^{GGA})$$

- only one parameter $a_0 = 0.16$ or 0.28

The PBE0 functional

Perdew, Burke, Ernzerhof, 1996, JCP 105, p.9982



$$E_{xc}^{hyb} = E_{xc}^{GGA} + \frac{1}{n}(E_x^{HF} - E_x^{GGA}) \quad \Rightarrow \quad a_0 = 0.25$$

comparison with Møller-Plesset perturbation theory

Discussion of the PBE0 functional

- computational expensive long-ranged interaction
- bandgaps improved, but typically too large
- correlation effects screen long-range interaction
- long-range is small, expensive, inconsistent

The HSE functional

concept of a faster hybrid functional

- idea: long-range correlation cancel exchange
  $\Rightarrow$ only short-range HF
- separation of interaction $\Rightarrow$ parameter ω

$$\frac{1}{r} = \underbrace{\frac{\operatorname{erfc} \omega r}{r}}_{\text{SR}} + \underbrace{\frac{\operatorname{erf} \omega r}{r}}_{\text{LR}}$$

- treat only short-range part with non-local functional
- $\omega = 0.11$ optimized to experimental data set (HSE06)

The local part

- short-range PBE exchange?

$$E_{\mathrm{x}}^{\mathrm{PBE,SR}} = \int \mathrm{d}^3 r \, n \, \epsilon_{\mathrm{x}}^{\mathrm{LDA}} \, F_{\mathrm{x}}^{\mathrm{PBE,SR}}$$

- integration over exchange hole J

$$F_{\mathrm{x}}^{\mathrm{PBE,SR}} \propto \int \mathrm{d}r \, r \, J^{\mathrm{PBE}}(r) \, \mathrm{erfc}(\omega r)$$

- additional term which reduces exchange

Summary: PBE0 and HSE06

$$E_{\mathrm{xc}} = E_{\mathrm{xc}}^{\mathrm{PBE}} + a_0 \left(E_{\mathrm{x}}^{\mathrm{NL}} - E_{\mathrm{x}}^{\mathrm{loc}} \right)$$

non local energy is given as

$$E_{\mathrm{x}}^{\mathrm{NL}} = \sum_{n,n'}^{\mathrm{occ.}} \left\langle \varphi_{n'} \varphi_n \left| V^{\mathrm{NL}} \right| \varphi_n \varphi_{n'} \right\rangle$$

PBE0 functional

$$V^{\mathrm{NL}}(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

HSE functional

$$V^{\mathrm{NL}}(\boldsymbol{r}, \boldsymbol{r}') = \frac{\mathrm{erfc}(\omega\,|\boldsymbol{r} - \boldsymbol{r}'|)}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

A generalized Kohn-Sham scheme

recollection: Kohn-Sham Scheme

$$\sum_{\boldsymbol{G}'} \langle \chi_{\boldsymbol{G}} | \mathcal{H} | \chi_{\boldsymbol{G}'} \rangle \langle \chi_{\boldsymbol{G}'} | \varphi_n \rangle = \varepsilon_n \langle \chi_{\boldsymbol{G}} | \varphi_n \rangle$$

$$E_{\mathrm{x}}^{\mathrm{NL}} = \sum_{n,n'}^{\mathrm{occ.}} \left\langle \varphi_{n'} \varphi_n \left| V^{\mathrm{NL}} \right| \varphi_n \varphi_{n'} \right\rangle$$

Resolution of the identity

$$\sum_{\boldsymbol{G}'} \underbrace{\sum_{n}^{\mathrm{occ.}} \left\langle \chi_{\boldsymbol{G}} \varphi_n \left| V^{\mathrm{NL}} \right| \varphi_n \chi_{\boldsymbol{G}'} \right\rangle}_{V^{\mathrm{NL}}_{\boldsymbol{G}\boldsymbol{G}'}} \langle \chi_{\boldsymbol{G}'} | \varphi_{n'} \rangle$$

Overview

Introduction: Hybrid Functionals

Implementation in FLAPW

- General concepts
- Details of implementation

How to use Hybrid Functionals in `fleur`

Betzinger *et al.*, PRB **81** (2010), 195117

Computational complexity

$$V^{\mathrm{NL}}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{k}) = \sum_{n}^{\mathrm{occ.}} \sum_{\boldsymbol{q}}^{\mathrm{BZ}} \left\langle \chi_{\boldsymbol{k}\boldsymbol{G}} \varphi_{n\boldsymbol{q}} \middle| V^{\mathrm{NL}} \middle| \varphi_{n\boldsymbol{q}} \chi_{\boldsymbol{k}\boldsymbol{G}'} \right\rangle$$

- six-dimensional integral
- #k-points^2 $\times$ #basis functions^2 $\times$ #occ. states
- comparison (local DFT): #k-points $\times$ #basis functions^2
- typically: 1 - 2 order of magnitude slower

Using symmetry to enhance execution speed

$$V^{\mathrm{NL}}_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{k}) = \sum_{n}^{\mathrm{occ.}} \sum_{\boldsymbol{q}}^{\mathrm{BZ}} \left\langle \chi_{\boldsymbol{k}\boldsymbol{G}} \varphi_{n\boldsymbol{q}} \middle| V^{\mathrm{NL}} \middle| \varphi_{n\boldsymbol{q}} \chi_{\boldsymbol{k}\boldsymbol{G}'} \right\rangle$$

- Outer k-point loop: Full symmetry of crystal
- Inner q-point loop: Reduced symmetry of current k-point
- Every k-point different execution time
- without spin-orbit coupling $\Rightarrow$ time reversal symmetry

Basis functions $\longrightarrow$ wavefunctions

$$V_{\boldsymbol{G}\boldsymbol{G}'} = \sum_{n}^{\text{occ.}} \left\langle \chi_{\boldsymbol{G}} \varphi_n \middle| V^{\text{NL}} \middle| \varphi_n \chi_{\boldsymbol{G}'} \right\rangle$$

wavefunction: eigenvector $\times$ basis function

$$|\varphi_n\rangle = \sum_{\boldsymbol{G}} z_{n\boldsymbol{G}} \, |\chi_{\boldsymbol{G}}\rangle \qquad |\chi_{\boldsymbol{G}}\rangle = \sum_{n}^{\text{bands}} \left[z_{n\boldsymbol{G}}\right]^{-1} |\varphi_n\rangle$$

`bands`: important cutoff parameter in hybrid functionals

$$V_{nn'} = \sum_{m}^{\text{occ.}} \left\langle \varphi_n \varphi_m \middle| V^{\text{NL}} \middle| \varphi_m \varphi_{n'} \right\rangle$$

Auxiliary product basis

$$V_{nn'} = \sum_{m}^{\text{occ.}} \left\langle \varphi_n \varphi_m \left| V^{\text{NL}} \right| \varphi_m \varphi_{n'} \right\rangle$$

idea: introduce an auxiliary basis $1 = \sum_I |M_I\rangle \langle M_I|$

$$V_{nn'} = \sum_{IJ} \sum_{m}^{\text{occ.}} \langle \varphi_n | \varphi_m M_I \rangle \left\langle M_I \left| V^{\text{NL}} \right| M_J \right\rangle \langle M_J \varphi_m | \varphi_{n'} \rangle$$

Advantages:

- matrix evaluated once
- only overlap integrals in every SCF

Mixed product basis

which auxiliary basis in FLAPW?

- keep accuracy of FLAPW function
- easy construction from FLAPW basis

$$M_I(\boldsymbol{r}) = \begin{cases} M_I(|\boldsymbol{r}-\boldsymbol{R}_a|)\, Y_{LM}(\widehat{\boldsymbol{r}-\boldsymbol{R}_a})\, e^{i\boldsymbol{k}\boldsymbol{R}_a} & \text{muffin-tin} \\ \frac{1}{\sqrt{\Omega}}\, e^{i(\boldsymbol{k}+\boldsymbol{G})\boldsymbol{r}}\, \Theta(\boldsymbol{r}\in \mathrm{IR}) & \text{interstitial} \end{cases}$$

- muffin-tin: $I \to (a, L, M)$ interstitial: $I \to \boldsymbol{G}$
- $\Rightarrow$ mixed product basis

Cutoffs for mixed product basis

$$M_l(\boldsymbol{r}) = \begin{cases} M_l(|\boldsymbol{r} - \boldsymbol{R}_a|)\, Y_{LM}(\widehat{\boldsymbol{r} - \boldsymbol{R}_a})\, e^{i\boldsymbol{k}\boldsymbol{R}_a} & \text{muffin-tin} \\ \frac{1}{\sqrt{\Omega}}\, e^{i(\boldsymbol{k}+\boldsymbol{G})\boldsymbol{r}}\, \Theta(\boldsymbol{r} \in \mathrm{IR}) & \text{interstitial} \end{cases}$$

- `lcutm`: angular moment cutoff in muffin-tin

  default 4, increase if *f*-states are used!

- `gcutm`: cutoff for interstitial planewaves

  default `kmax` - 0.5, decrease for first guess calculation

Construction of muffin-tin functions

- addition theorem for spherical harmonics

$$R_{lm}(r)\,\mathrm{Y}_{lm}(\hat{\boldsymbol{r}})\,R_{l'm'}(r)\,\mathrm{Y}_{l'm'}(\hat{\boldsymbol{r}}) = \sum_{L=|l-l'|}^{l+l'} \sum_{M=-L}^{L} \hat{R}_{LM}(r)\,\mathrm{Y}_{LM}(\hat{\boldsymbol{r}})$$

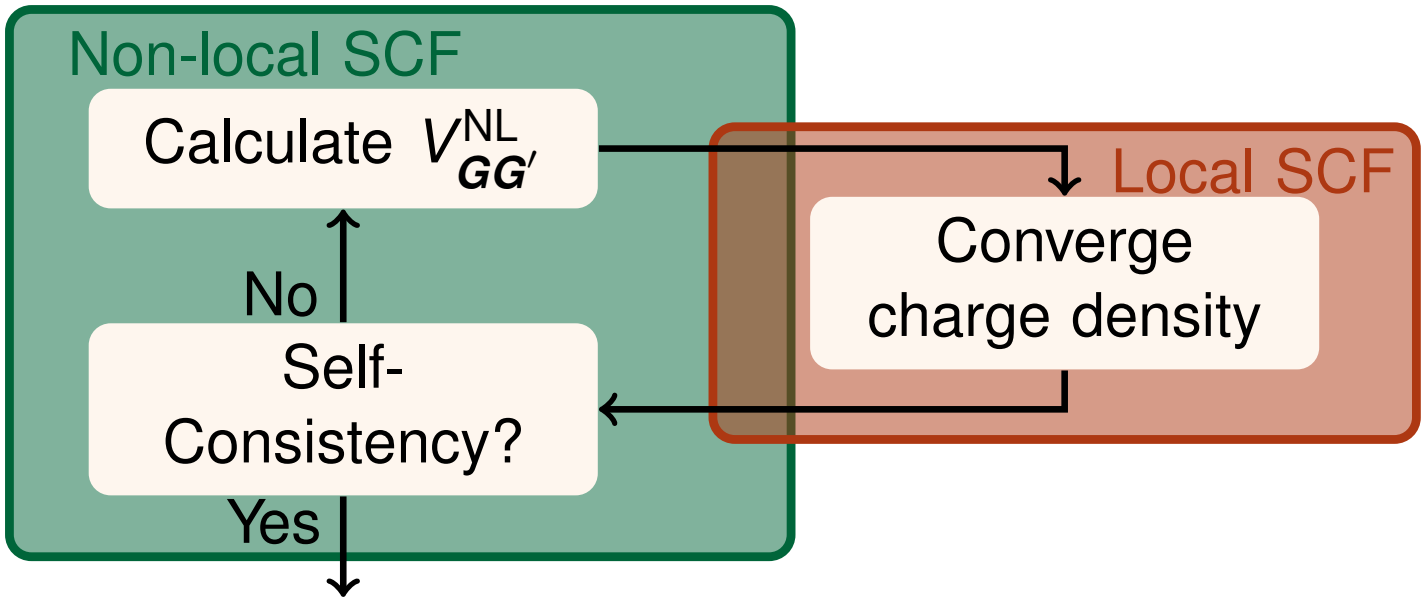
- several functions for every LM
- linear combination $\hat{R} \Rightarrow$ multipole-free M_I^{mpf}
- Coulomb matrix off-center elements vanish

$$\left\langle M_I^{\mathrm{mpf}} \middle| V^{\mathrm{NL}} \middle| M_J \right\rangle = 0 \qquad I \neq J$$

$\Rightarrow$ sparse-matrix technique!

Nested self-consistency

- non-local potential more expensive
- idea: converge in separate loops



activate nested self-consistency with `imix` ≥ 10

Importance of the Γ point

- Fourier transformation of Coulomb potential

$$\left\langle \boldsymbol{k}+\boldsymbol{G}\left|V^{\mathrm{NL}}\right|\boldsymbol{k}+\boldsymbol{G}'\right\rangle = \frac{4\pi}{|\boldsymbol{k}+\boldsymbol{G}|^2}\delta(\boldsymbol{G}-\boldsymbol{G}')$$

- divergent for $\boldsymbol{k}+\boldsymbol{G}\rightarrow\boldsymbol{0}$
- 3d-integral has finite limit
- explicit treatment of Γ point necessary
- `gamma=t` to use Γ point for k-point mesh

HSE functional: challenges

$$v_{IJ} = \left\langle M_I \left| V^{\mathrm{NL}} \right| M_J \right\rangle$$

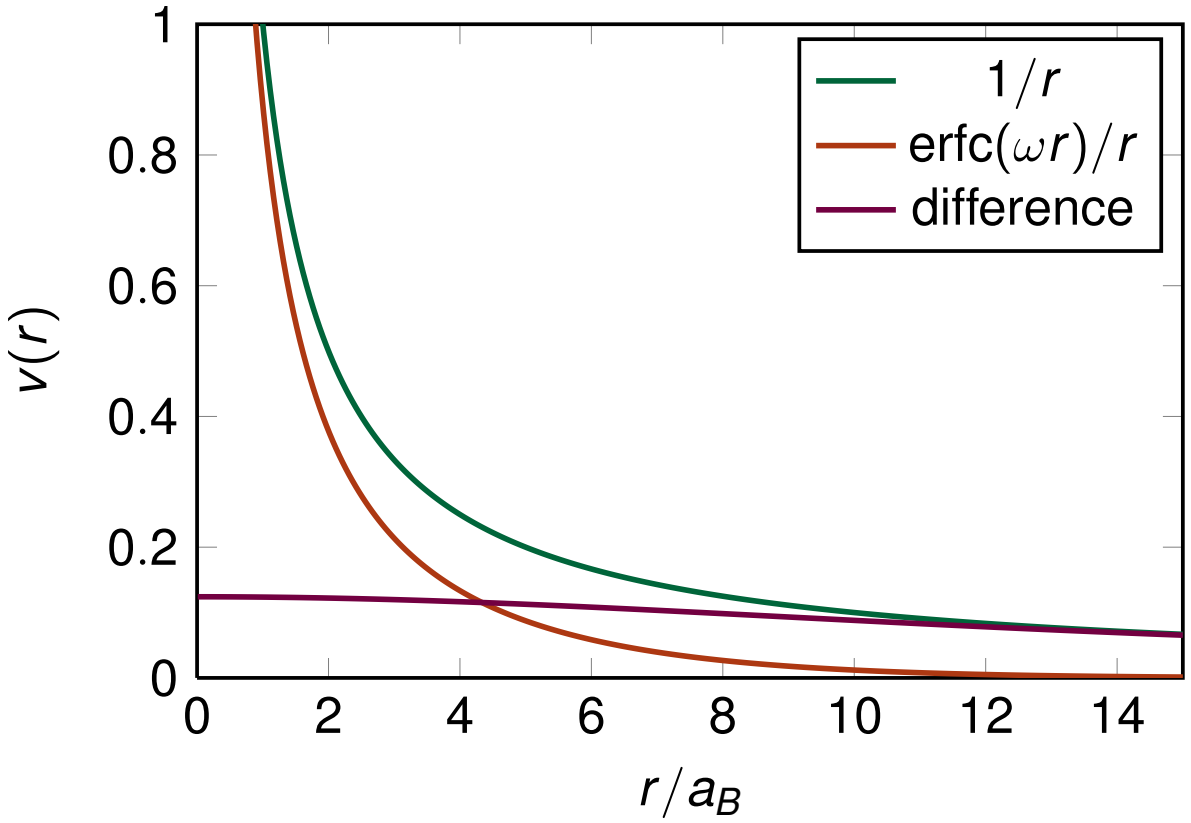
Naïve idea: replace non-local potential

$$\underbrace{\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}}_{\text{PBE0}} \longrightarrow \underbrace{\frac{\operatorname{erfc}(\omega\,|\boldsymbol{r} - \boldsymbol{r}'|)}{|\boldsymbol{r} - \boldsymbol{r}'|}}_{\text{HSE}}$$

- sparse-matrix technique:

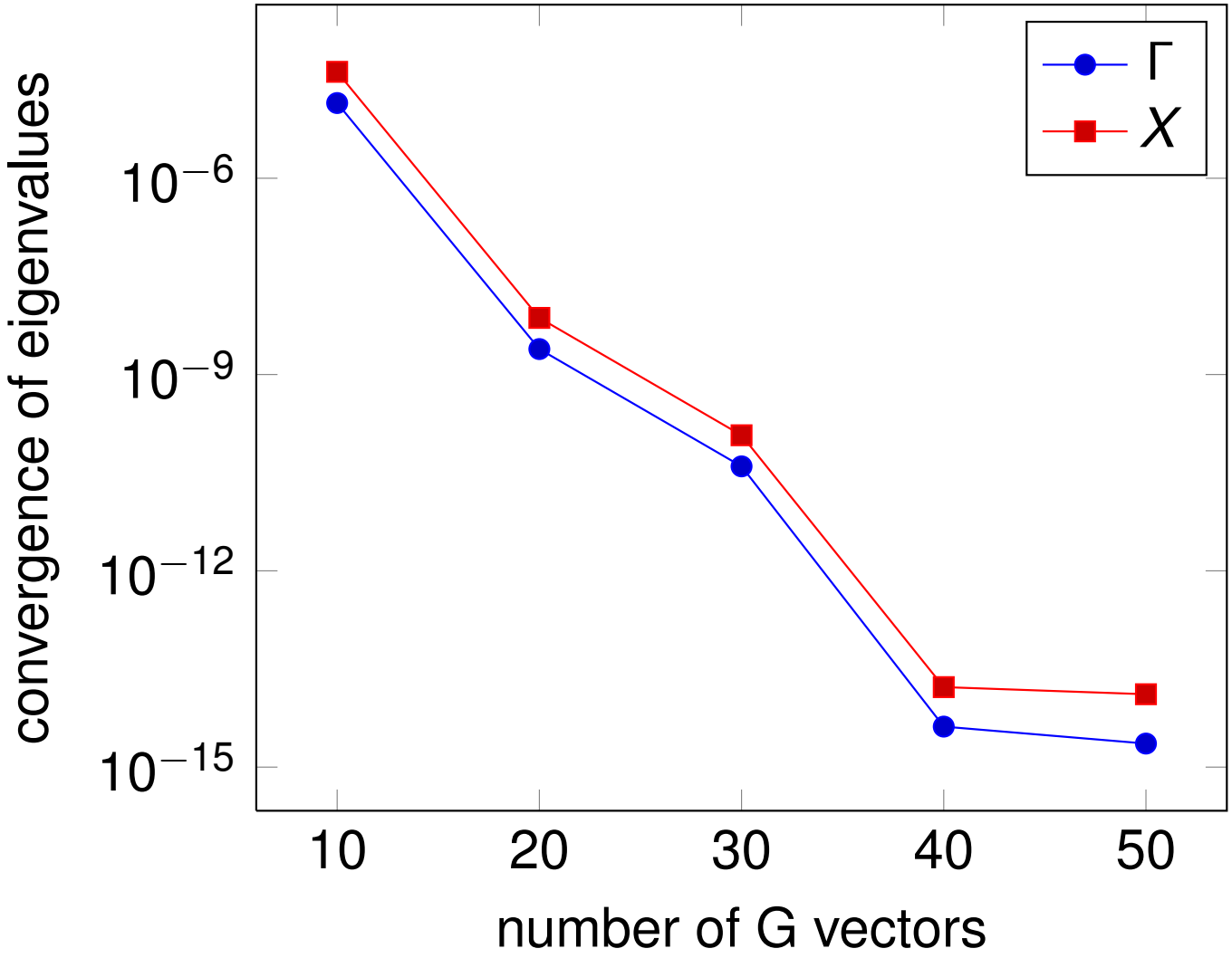
  multipole free $\leftrightarrow$ Coulomb potential
- without sparse-matrix $\Rightarrow$ significantly slower

HSE via Fourier transformation

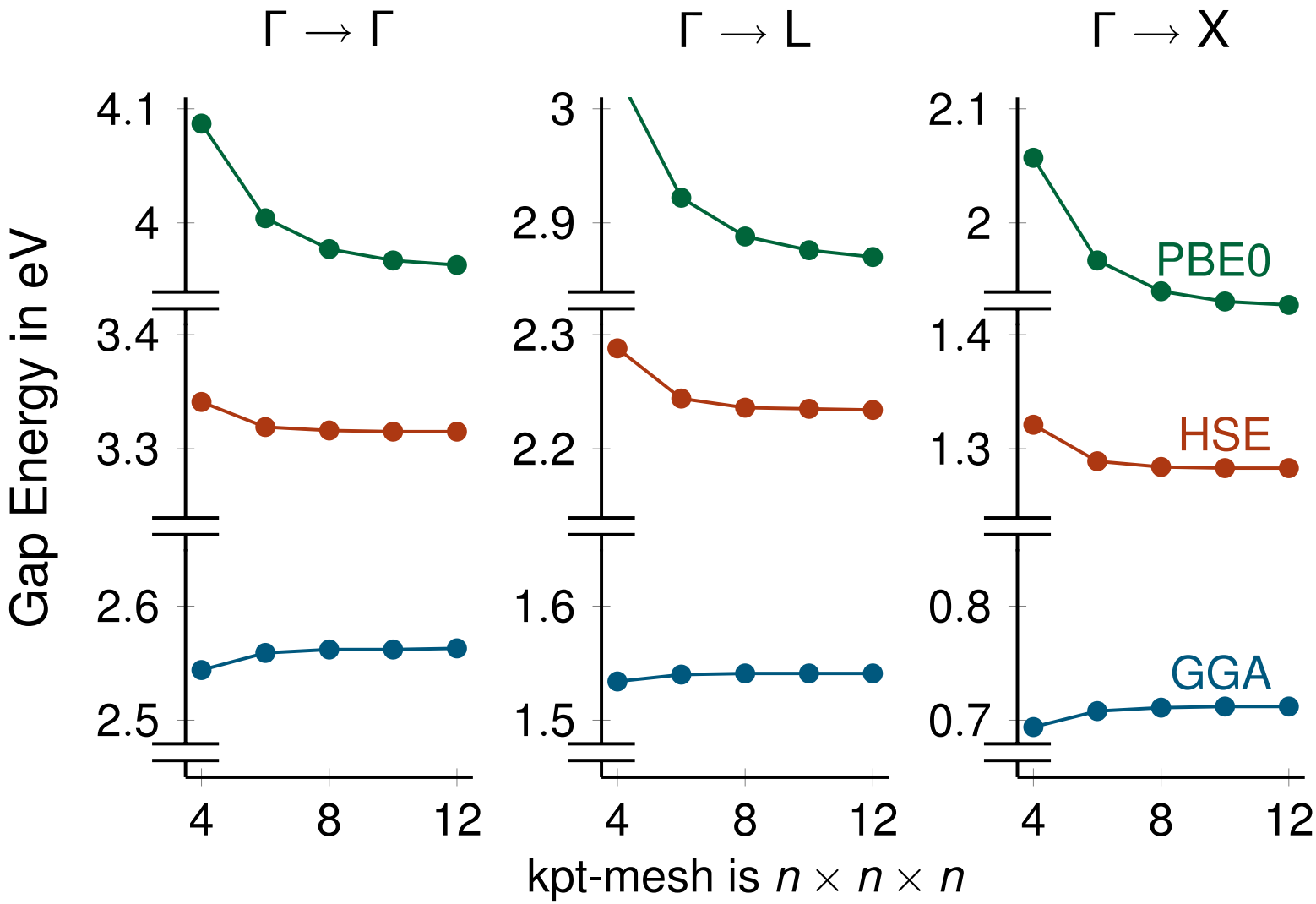


HSE = PBE0 − difference evaluated in reciprocal space

Convergence of Fourier transformation



Convergence HSE06 vs. PBE0 for bulk silicon



Parallelization scheme

$$V_{nn'}(\boldsymbol{k}) = \sum_{\boldsymbol{q}}^{\mathrm{BZ}} \sum_{m}^{\mathrm{occ.}} \left\langle \varphi_{n\boldsymbol{k}} \varphi_{m\boldsymbol{q}} \middle| V^{\mathrm{NL}} \middle| \varphi_{m\boldsymbol{q}} \varphi_{n'\boldsymbol{k}} \right\rangle$$

- possible parallelization: $\boldsymbol{k}$, $\boldsymbol{q}$, m, ...
- every k-point needs different amount of time
- $\Rightarrow$ parellelize over tasks = $\#k \times \#q(k)$
- not all k-points done by same amount of processes

```
HF: kpt 3 was done by rank 1 and 1 more
```

Overview

Introduction: Hybrid Functionals

Implementation in FLAPW

How to use Hybrid Functionals in `fleur`

Generate input file for hybrid functionals

- specify `&input hybrid = t /`
- additional `inp_hyb` file generated
- use `inp` for PBE calculation
- use `inp_hyb` for PBE0 or HSE calculation

New input file

```
07|hse    non-relativi
08|gcutm= 3.10000,...,bands= 64
13| 2,force =F,lcutm= 4,...,nlo= 0,llo=
18|vchk=F,cdinf=F,pot8=T,gw=0,numbands= 70
28|itmax= 15,maxiter= 25,imix=17,...
37|nkpt=   64,nx= 4,ny= 4,nz= 4,gamma=T
```

- `hse` or `pbe0` - hybrid functional
- `bands` - cutoff for basis function representation
- `numbands` - eigenvalues calculated in diagonalization
- `itmax` - counts only outer cycles

Recipe: how to calculate with PBE0/HSE

1. increase `numbands` sufficiently
2. converge PBE calculation
   (copy all files to new folder)
3. rename `inp_hyb` to `inp`
4. set `numbands` to same value as in PBE
5. converge calculation with PBE0 or HSE

Files - generated by or for hybrid functionals

- `mixbas` - mixed product basis (for restart)
- `coulomb1` - Coulomb matrix for all k-points
- `cmt,z` - wavefunction coefficients in MT and IR
- `olap` - overlap of LAPW basis
- `potx` - local correction due to hybrid functional
- `vr0` - spherical MT potential

Conclusion

- adiabatic connection motivate hybrid functionals
- PBE0 and HSE: hybrid functionals for solids
- implementation in FLAPW: mixed product basis
- convergence of number of `bands` important

Outlook

- faster calculation by k-point interpolation
- more efficient parallelization scheme
- merge hybrid functionals with other features

- screening derived from electronic density
- correlation in random phase approximation