Beyond LDA and GGA: Hybrid Functionals

Muffin-tin Recipes, Jülich 2011 | Martin Schlipf
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Motivation

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

$\text{BaTiO}_3$
Self-interaction error

\[
\langle \phi_1 \phi_2 | \hat{V}_{coul} | \phi_1 \phi_2 \rangle - \langle \phi_1 \phi_2 | \hat{V}_{coul} | \phi_2 \phi_1 \rangle
\]

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

\[
\int \int d^3 r \, d^3 r' \frac{n_1(r) \, n_1(r')}{|r - r'|}
\]

delocalized state

localized state
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 $\lambda$ describes strength of interaction

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

d Energy derivative – eigenstates depend on $\lambda$

$$\frac{dE(\lambda)}{d\lambda} = \left\langle \varphi(\lambda) \right| V_{ee} + \frac{dV(\lambda)}{d\lambda} \left| \varphi(\lambda) \right\rangle$$

d Energy of full interacting system

$$E(\lambda = 1) - E(\lambda = 0) = \int_0^1 d\lambda \left\langle \varphi(\lambda) \right| V_{ee} \left| \varphi(\lambda) \right\rangle$$

$$- \int d^3r nV(\lambda = 0)$$
Exchange correlation energy

density functional theory $\Rightarrow$ functional design

$$E_{xc} = \int_0^1 d\lambda \langle \varphi(\lambda) | V_{ee} | \varphi(\lambda) \rangle - U_H(n) = \int_0^1 d\lambda E_{xc}(\lambda)$$
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 $\lambda$
Will it blend?
Becke 1993, JCP 98, p.1372 and p.5648

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

\[ E_{xc}^{\text{hyb}} = E_{xc}^{\text{GGA}} + \frac{1}{n}(E_{x}^{\text{HF}} - E_{x}^{\text{GGA}}) \Rightarrow a_0 = 0.25 \]

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 ⇒ only short-range HF
- separation of interaction ⇒ parameter $\omega$

\[
\frac{1}{r} = \frac{\text{erfc} \omega r}{r} + \frac{\text{erf} \omega r}{r}
\]

- 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?

\[ E_{x}^{\text{PBE,SR}} = \int d^3 r \ n(x) \epsilon_{x}^{\text{LDA}} F_{x}^{\text{PBE,SR}} \]

- integration over exchange hole \( J \)

\[ F_{x}^{\text{PBE,SR}} \propto \int dr \ r \ J_{\text{PBE}}^*(r) \text{erfc}(\omega r) \]

- additional term which reduces exchange


Summary: PBE0 and HSE06

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

non local energy is given as

\[
E_{x}^{NL} = \sum_{n,n'}^{\text{occ}} \left< \varphi_{n'} \varphi_n \right| V_{NL}^{\text{NL}} \left| \varphi_n \varphi_{n'} \right>
\]

PBE0 functional

\[
V_{NL}^{\text{PBE}}(r, r') = \frac{1}{|r - r'|}
\]

HSE functional

\[
V_{NL}^{\text{HSE}}(r, r') = \frac{\text{erfc}(\omega |r - r'|)}{|r - r'|}
\]
A generalized Kohn-Sham scheme

recollection: Kohn-Sham Scheme

\[
\sum_{G'} \langle \chi_G | H | \chi_{G'} \rangle \langle \chi_{G'} | \phi_n \rangle = \varepsilon_n \langle \chi_G | \phi_n \rangle
\]

\[
E_{\chi}^{\text{NL}} = \sum_{n,n'}^{\text{occ.}} \langle \phi_{n'} \phi_n | V_{\chi}^{\text{NL}} | \phi_{n'} \phi_n \rangle
\]

Resolution of the identity

\[
\sum_{G'} \sum_{n}^{\text{occ.}} \sum_{\text{occ.}} \langle \chi_{G'} \phi_n | V_{\chi}^{\text{NL}} | \phi_n \chi_{G'} \rangle \langle \chi_{G'} | \phi_n' \rangle
\]

\[
V_{\text{NL}}^{GG'}
\]
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

\[
V_{GG'}^{NL}(k) = \sum_{n} \sum_{q} \langle \chi_k G \varphi_n q | V^{NL} | \varphi_n q \chi_{kG'} \rangle
\]

- 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

\[ V_{GG'}^{NL}(k) = \sum_{n}^{\text{occ.}} \sum_{q}^{\text{BZ}} \langle \chi_k G \varphi_n q | V^{NL} | \varphi_n q \chi_{kG'} \rangle \]

- 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 $\rightarrow$ wavefunctions

$$V_{GG'} = \sum_{n} \langle \chi_{G} \varphi_{n} | V^{NL} | \varphi_{n} \chi_{G'} \rangle$$

wavefunction: eigenvector $\times$ basis function

$$|\varphi_{n}\rangle = \sum_{G} Z_{nG} |\chi_{G}\rangle \quad |\chi_{G}\rangle = \sum_{n} [Z_{nG}]^{-1} |\varphi_{n}\rangle$$

bands: important cutoff parameter in hybrid functionals

$$V_{nn'} = \sum_{m} \langle \varphi_{n} \varphi_{m} | V^{NL} | \varphi_{m} \varphi_{n'} \rangle$$
Auxiliary product basis

\[ V_{nn'} = \sum_{m}^{\text{occ.}} \langle \phi_{n} \phi_{m} | V^{NL} | \phi_{m} \phi_{n}' \rangle \]

idea: introduce an auxiliary basis

\[ 1 = \sum_{i} |M_i\rangle \langle M_i| \]

\[ V_{nn'} = \sum_{IJ}^{\text{occ.}} \sum_{m} \langle \phi_{n} | \phi_{m} M_{I} \rangle \langle M_{I} | V^{NL} | M_{J} \rangle \langle M_{J} \phi_{m} | \phi_{n}' \rangle \]

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

\[
M_I(r) = \begin{cases} 
  M_I(|r - R_a|) Y_{LM}(r - R_a) e^{i k R_a} & \text{muffin-tin} \\
  \frac{1}{\sqrt{\Omega}} e^{i (k + G)r} \Theta(r \in \mathbb{R}) & \text{interstitial}
\end{cases}
\]

- muffin-tin: \( I \rightarrow (a, L, M) \)
- interstitial: \( I \rightarrow G \)
- \( \Rightarrow \) mixed product basis
Cutoffs for mixed product basis

\[
M_l(r) = \begin{cases} 
M_l(|r - R_a|) Y_{LM} (r - R_a) e^{ikR_a} & \text{muffin-tin} \\
\frac{1}{\sqrt{\Omega}} e^{i(k+G)r} \Theta (r \in IR) & \text{interstitial}
\end{cases}
\]

- \(l_{cutm}\): angular moment cutoff in muffin-tin
  default 4, increase if \(f\)-states are used!

- \(g_{cutm}\): cutoff for interstitial planewaves
  default \(k_{\text{max}} - 0.5\), decrease for first guess calculation
Construction of muffin-tin functions

- **addition theorem** for spherical harmonics

\[
R_{lm}(r) Y_{lm}(\hat{r}) R_{l'm'}(r) Y_{l'm'}(\hat{r}) = \sum_{L=|l-l'|}^{l+l'} \sum_{M=-L}^{L} \hat{R}_{LM}(r) Y_{LM}(\hat{r})
\]

- several functions for every \(LM\)
- linear combination \(\hat{R} \Rightarrow \text{multipole-free} \ M_{ij}^{\text{mpf}}\)
- Coulomb matrix off-center elements vanish

\[
\langle M_{ij}^{\text{mpf}} | V^{NL} | M_{J} \rangle = 0 \quad I \neq J
\]

\(\Rightarrow\) sparse-matrix technique!
Nested self-consistency

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

activate nested self-consistency with $\text{imix} \geq 10$
Importance of the Γ point

- Fourier transformation of Coulomb potential

\[ \langle k + G \mid V^{NL} \mid k + G' \rangle = \frac{4\pi}{|k + G|^2} \delta(G - G') \]

- divergent for \( k + G \rightarrow 0 \)
- 3d-integral has finite limit
- explicit treatment of Γ point necessary
- gamma=t to use Γ point for k-point mesh
HSE functional: challenges

\[ v_{ij} = \left\langle M_i \left| V^{NL} \right| M_j \right\rangle \]

Naïve idea: replace non-local potential

\[
\frac{1}{|r - r'|} \quad \text{PBE0} \quad \rightarrow \quad \text{erfc}(\omega \frac{|r - r'|}{|r - r'|}) \quad \text{HSE}
\]

- sparse-matrix technique:
  multipole free ↔ Coulomb potential
- without sparse-matrix ⇒ significantly slower
HSE via Fourier transformation

\[ v(r) = \frac{1}{r} - \frac{\text{erfc}(\omega r)}{r} \]

**HSE = PBE0 – difference evaluated in reciprocal space**
Convergence of Fourier transformation

![Plot showing convergence of eigenvalues](image)

- **Gamma** (Γ)
- **Chi** (χ)

Convergence is observed as the number of G vectors increases. The eigenvalues decrease significantly, approaching values of 10^{-15}.
Convergence HSE06 vs. PBE0 for bulk silicon

<table>
<thead>
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<th>Γ → Γ</th>
<th>Γ → L</th>
<th>Γ → X</th>
</tr>
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<tr>
<td>4.1</td>
<td>3</td>
<td>2.1</td>
</tr>
<tr>
<td>4</td>
<td>2.9</td>
<td>1.3</td>
</tr>
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<td>2.6</td>
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<td>0.8</td>
</tr>
<tr>
<td>2.5</td>
<td>1.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Gap Energy in eV

Kpt-mesh is $n \times n \times n$
Parallelization scheme

\[ V_{nn'}(k) = \sum_{q} \sum_{m} \left\langle \phi_n k \phi m q \mid V^{NL} \mid \phi m q \phi n' k \right\rangle \]

- possible parallelization: \( k, q, m, \ldots \)
- every k-point needs different amount of time
- \( \Rightarrow \) parallelize 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

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

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
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