

Lecture 7 - Exchange-correlation functionals

XC functionals

Functionals in
DFT

Functional
classes

LDA

GGA

Hybrid

Asymptotically
Corrected

Numerical
integration

- ρ -dependent functionals.
- Gradient corrected and hybrid functionals.
- Asymptotically corrected functionals.
- Numerical integration of functionals and its derivatives.

Energy Evaluation in DFT

XC functionals

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Numerical integration

- Energy E is a functional of density $\rho(\vec{r})$:

$$E = F_{\text{HK}}[\rho(\vec{r})]$$

- Traditionally partitioned as:

$$E = T[\rho(\vec{r})] + V_{\text{ext}}[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{\text{exc-corr}}[\rho(\vec{r})]$$

$$V_{\text{ext}}[\rho(\vec{r})] = \int \rho(\vec{r}) v(\vec{r}) d\vec{r}$$

$$J[\rho(\vec{r})] = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

- Kinetic energy $T[\rho(\vec{r})]$ and non-classical e-e interaction $E_{\text{exc-corr}}[\rho(\vec{r})]$ are tricky.

Kohn-Sham Approximation

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Numerical integration

Introduce orbitals $\varphi_i(\vec{r})$, $\rho(\vec{r}) = \sum_i^N |\varphi_i(\vec{r})|^2$ and compute the kinetic energy as:

$$T_s = \langle \Phi_s | \hat{T} | \Psi_s \rangle, \quad \Phi_s = |\varphi_1 \dots \varphi_N|$$

The exchange and correlation functional collects all “difficult” parts:

$$E_{xc}[\rho] = F_{HK}[\rho] - T_s - J[\rho]$$

- 1 Exchange
- 2 Corellation
- 3 $T[\rho] - T_s[\rho]$

Local Density Approximation

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Numerical integration

$$E_{\text{xc}}[\rho(\vec{r})] = \int E(\rho(\vec{r}), \dots) d\vec{r}$$

- ρ -dependent functionals $E_{\text{xc}}^{\text{LDA}}(\rho)$
- Gradient corrected functionals $s = \frac{1}{(24\pi^2)^{1/3}} \frac{\nabla\rho(\vec{r})}{\rho^{4/3}(\vec{r})}$:
 - standard** For $s \rightarrow 0$: $E_{\text{xc}}^{\text{LDA}}(\rho)$ For $0 \leq s \leq 1$ behaves as s^4
 - modified** For $s \rightarrow 0$: around $1.05 E_{\text{xc}}^{\text{LDA}}(\rho)$. For $0 \leq s \leq 1$ behaves as s^2

Exchange and Correlation Functionals

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Numerical
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- The exchange and correlation formally estimated separately:

$$E_{xc} = E_x + E_c$$

- Some combination works better, some work worse: Error cancellation.

ρ -dependent Functionals

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Numerical integration

$$E_{\text{xc}} = \int E_{\text{xc}}(\rho(\vec{r}))d\vec{r} \quad (1)$$

- Commonly used in solid-state physics because of its simplicity.
- Slater exchange $E = E_{\alpha} + E_{\beta}$

$$E_{\sigma} = -\frac{3}{4} \left(\frac{6}{\pi} \right)^{1/3} \rho_{\sigma}^{4/3} \quad (2)$$

- Example: PZ81 correlation.
- Example: VWN correlation. Two variants present, usually denoted as VWN3 and VWN5. VWN5 is the more accurate approximation of correlation energy for the testing set.

LDA approximation works relatively well for systems with smooth density.

Gradient Corrected Functionals

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Numerical integration

- Locality of DFT makes it simple and efficient – and inaccurate. . .
- Add some non-locality by including density gradient dependence (or s).

$$E_{\text{xc}} = \int E_{\text{xc}}(\rho(\vec{r}), s) d\vec{r} = \int E_{\text{xc}}^{\text{LDA}}(\rho) F(s) d\vec{r}$$
$$s = \frac{1}{(24\pi^2)^{1/3}} \frac{|\nabla\rho(\vec{r})|}{\rho^{4/3}(\vec{r})}$$

- Improved ground state geometries.
- Atomization energies improved by order of magnitude.
- Examples: BLYP, PW91, PBE.

Hybrid functionals: B3LYP, PBE0

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Numerical integration

- Becke(88) is only slightly better than Dirac exchange.
- ... but HF exchange is exact by definition!
- take 80% of Dirac, 20% of HF, 72% of Becke(88) correction.
- ... and 19% of VWN and 81% of LYP.
- → get B3LYP!

$$E_{\text{B3LYP}} = 0.2E_{\text{HFexchange}} + 0.8E_{\text{Slater}} + 0.72E_{\text{B88}} + 0.19E_{\text{VWN3}} + 0.81E_{\text{LYP}}$$

- PBE0: PBE with 25% of exact HF exchange.

OPTX: Optimal Exchange

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Numerical
integration

- Modern exchange functional by Handy and Cohen.
- Designed to reproduce the Hartree-Fock (HF) energies of the 18 first and second row atoms.
- Two empirical parameters.
- “modified” GGA: $\lim_{s \rightarrow 0} F(s) \approx 1.05$ instead of 1.
- Originally combined with LYP correlation (OLYP).
- Gets very good barriers when used with LAP3 correlation functional (E. I Proynov, S. Sirois, and D.R. Salahub), also for “difficult” systems.

X3LYP: Modern Hybrid Functional

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Numerical integration

- Also uses a form for an exact exchange energy (X. Xiu, W. A. Goddard III): Improves description of exchange interaction for large values of s .
- a “modified” GGA: Similarly to OPTX, disturbs the low s limit (1.07 instead of 1).
- Good description of Heat of formation, electron affinity, and excitation energies from s to d orbitals for transition metal atoms.

Functional	ΔH	IP	EA	PA	H-Ne	TM ΔE
B3LYP	0.13	0.168	0.103	0.06	0.38	0.25
O3LYP	0.18	0.139	0.107	0.05	0.06	0.49
X3LYP	0.12	0.154	0.087	0.07	0.11	0.22

Asymptotically Corrected Functionals

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Numerical integration

- 1 True exchange potential has to fulfill number of conditions: Scaling, asymptotic behavior, translational and rotational invariance.
- 2 Problem: eigenvalue of the highest occupied KS orbital: ionization potential. LDA wrong by eg. 5eV.
- 3 Negative ions have positive HOMO energy with LDA.
- 4 Most of the DFT potentials have incorrect asymptotic behavior \rightarrow unphysically diffuse density in outer regions.
- 5 Local functionals cannot account for effects occurring during charge-transfer (CT).

Asymptotically Corrected Functionals, cont.

XC functionals

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Numerical
integration

LB94

- Fulfills functional constraints by construction.
- Major problems reproducing potential generated by inner-valence electrons.

AC

- Asymptotic Correction ionization potential feedback scheme.
- *ad hoc*.

LC,CAM-B3LYP

- exact HF exchange at long distances.
- Difficult to get all the properties right.

LC: Long-range Corrected

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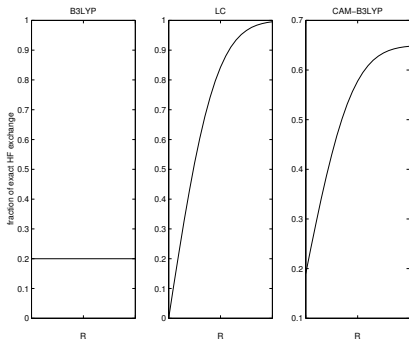
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Hybrid

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Numerical integration

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}$$



LC functional partitions exchange into short and long range terms switching between them smoothly using an $\text{erf}(r)$ function. Short range-exchange interactions are estimated with help of mostly (0.81) DFT potential while long range interactions are treated as mostly (0.65-0.8) exact HF exchange.

Short-range Exchange

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Numerical integration

Replace ordinary form of exchange functional K_σ :

$$E_x = -\frac{1}{2} \sum_{\sigma} \int \rho_{\sigma}^{4/3} K_{\sigma} d^3\vec{r}$$

with K_{σ}^{as}

$$K_{\sigma}^{\text{as}} = K_{\sigma} \left\{ 1 - \frac{8a_{\sigma}}{3} \left[\sqrt{\pi} \operatorname{erf} \left(\frac{1}{2a_{\sigma}} \right) + 2a_{\sigma}(b_{\sigma} - c_{\sigma}) \right] \right\}$$

$$a_{\sigma} = \frac{\mu K_{\sigma}^{1/2}}{6\sqrt{\pi}\rho^{1/3}}$$

$$b_{\sigma} = \exp \left(-\frac{1}{4a_{\sigma}^2} \right) - 1$$

$$c_{\sigma} = 2a_{\sigma}^2 b_{\sigma} + \frac{1}{2}$$

Straightforward implementation numerically unstable.

Long-range Exchange

XC functionals

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Numerical integration

The long-range part of the exchange interaction expressed with HF exchange integral:

$$\begin{aligned} g_{pqrs} &= \int \int b_p(\vec{r}_1) b_q(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} b_r(\vec{r}_2) b_s(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\ &\rightarrow \int \int b_p(\vec{r}_1) b_q(\vec{r}_1) \frac{\alpha + \beta \operatorname{erf}(\mu r_{12})}{r_{12}} b_r(\vec{r}_2) b_s(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \end{aligned}$$

- Evaluation cost similar to B3LYP.

LC Deficiencies

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Numerical
integration

- Plain long-range-corrected (LC) functional describes very well CT systems, but. . .
- does not work well for more standard energy calculations (same mistake as LB94).
- Mean absolute error in the atomization energies of 52 molecules increases from 2.5 kcal/mol (B3LYP) to 9.5 kcal/mol (LC-BOP).

CAM-B3LYP Design

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Numerical
integration

- B3LYP – probably the most successful functional so far.
- it has a number of deficiencies:
 - polarizabilities of long chains.
 - excitation using TD-DFT for Rydberg states.
 - charge transfer (CT) excitations.
- Reasons understood: long range exchange potential behaves like $-0.2r^{-1}$ instead of $-r^{-1}$.

CAM-B3LYP is meant to address these deficiencies.

Polarizabilities of Alkene Chains

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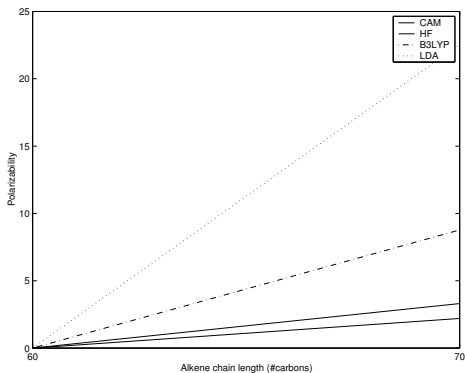
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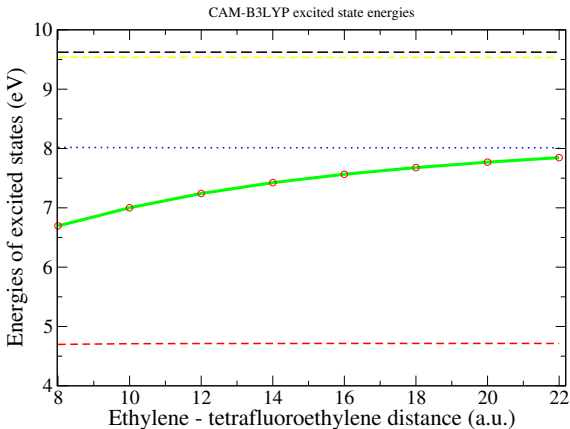


Normalized alkene polarizabilities as a function of chain length.

CAM-B3LYP gets the trend right (close to HF). LDA too steep. B3LYP is in the middle.

Model CT Systems

- Model ethylene - tetrafluoroethylene system.
- Fact: CT excitation energy varies like $-R^{-1}$.
- CAM-B3LYP gives CT state with a correct trend.



Singlet Excitation Energies: AF295

- LDA (SVN5) cannot describe nonlocal excitations properly.
- GGA (BLYP) does not improve on it.
- CAM-B3LYP provides much better estimation of non-local excitation energy.

State	LDA	BLYP	CAM-B3LYP
1	2.08	2.11	3.90
2	2.12	2.15	4.02
3	2.81	2.80	4.40
4	2.81	2.80	4.51
5	3.06	3.08	4.52
6	3.19	3.22	4.78
7	3.23	3.25	4.80
8	3.26	3.26	4.87
9	3.27	3.28	4.88
10	3.30	3.33	4.91

Other Properties with CAM-B3LYP

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Numerical integration

- G2 test set (short bonds): CAM-B3LYP \approx B3LYP
- CAM-B3LYP improves long-range interactions: better description of molecules with long bonds and reaction barriers.

Reaction	B3LYP	CAM-B3LYP	Expt
$\text{CH}_3 + \text{H}_2$	9.6	10.0	12.1
$\text{CH}_4 + \text{OH}$	2.9	4.2	6.7
$\text{CH}_3 + \text{H}_2\text{O}$	14.7	16.5	19.6
$\text{OH} + \text{H}_2$	1.4	2.4	5.1

6-311+G(3df,2p) basis set; kcal/mol

Coulomb Attenuated Method: Summary

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Numerical
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- CAM-B3LYP: a improvement on the long-range-corrected (LC) exchange functional of Yanai.
- provides as accurate description of charge-transfer systems as LC...
- ... without sacrificing other properties (atomization energies).

Self-interaction

XC functionals

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Numerical integration

$$E[\rho] = T[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho]$$

Consider a 1-electron system. $J[\rho] + E_{xc}[\rho]$ is strictly 0, also in Hartree-Fock but not in DFT. Simplest correction:

$$J[\rho] = \frac{N-1}{2N} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

- Does not work well in practice.
- Other schemes exist. Explicit orbital dependence as in $T[\rho]$.
- Theoretically satisfactory SIC exist – but a practical implementation is difficult.

Omitted XC Functionals

XC functionals

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Omitted because of time limits:

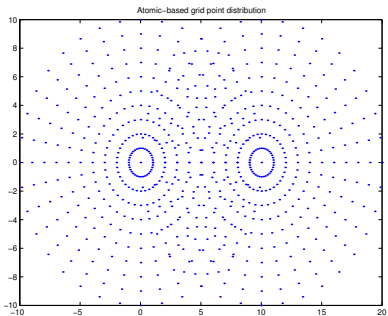
TPSS a non-empirical meta-GGA functional. Has a hybrid version.

HCTH highly parametrized functionals (15 parameters).

KT3 functional optimized for NMR properties.

Atomic Grid with Weight Adjustment

- Atomic grids were the first ones created.
 - ↑ experience from atomic integration can be utilized.
- adaptive grids possible but not always easy.
 - ↓ space partitioning (weight adjustment) can be time-consuming making it difficult to generate grids on the fly (although it is doable under certain conditions).



Multi-scale Cubatures

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- Use cartesian grid of variable density and cubatures to integrate within the smallest cubes.
 - ↑ experience from multidimensional, multi-scale integration of other problems can be used.
 - ↑ relatively easy to implement adaptive, generated on the fly grids.
 - ↓ such schemes are still very new and not extensively tested. Problem with integrating other quantities than the one the cubature was tuned for.