Lecture 12 DFT: GGA and Beyond

Generalized gradient approximation; hybrid functionals

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The DFT formalism separates the energy functional into manageable components

- Ground-state energy functional as sum of kinetic energy, electron-electron Coulomb, and electron-nuclei Coulomb $E_0[\rho] = T[\rho] + E_{ee}[\rho] + E_{Ne}[\rho]$
 - $E_{\text{Ne}}[\rho]$ known exactly: $-\sum_{A} \int \frac{\rho(\mathbf{r})Z_{A}}{|\mathbf{r}_{A}-\mathbf{r}|} d\mathbf{r}$
 - *T*[ρ] from Kohn-Sham, noninteracting reference system with Slater-determinant wavefunction
 - $E_{ee}[\rho]$ given as classical contribution + correction for exchⁱange, correlation, and self-interaction $1 \int \int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) d\mathbf{r}_2 d\mathbf{r}$

$$egin{aligned} rac{1}{2} \int \int rac{
ho(\mathbf{r}_1)
ho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{ ext{XC}}[
ho] \ &\equiv J[
ho] + E_{ ext{XC}}[
ho] \end{aligned}$$

 $-\sum_i ig\langle arphi_i | rac{1}{2}
abla^2 | arphi_i ig
angle$

 $ho({f r})=\sum n_i |\phi_i({f r})|^2$

The XC functional is the focus of DFT developments

• The XC hole provides a framework $E_{\rm XC}[\rho] = \frac{1}{2} \int \int \frac{\rho(1)\bar{h}_{\rm XC}(1,2)}{r_{12}} d1d2$

$$h_{
m XC}(1,2) = rac{
ho_2(1,2)}{
ho(1)} -
ho(2)$$

 $ar{h}$ includes KE correction (adiabatic connection)

- Local density approximation provides a starting point $E_{\rm XC}^{\rm LDA}[\rho] = \int \rho(1) \varepsilon_{\rm XC}(\rho(1)) d1$
 - Uniform electron gas as reference
 - Coulomb correlation treated by fitting of Monte Carlo data for interacting uniform electron gas, as a function of density
 - Exchange treated by simple hole model, yields a $\rho^{4/3}$ dependence

The performance of LDA in application is mixed

• Overbinding tendency

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- LDA good description between bonded atoms, but inaccurate between them at nonbonded separations
- More of an effect on energy than on the geometry
 - Density between atoms is more homogeneous
 → LDA good
 - not so for separated atoms
 - Good description of geometry
 - Bad description of energy
- Generally underestimates exchange energy and overestimates correlation energy

Atomization Energy Error (kcal/mol)

Method	Mean err	MAE
HF	-158.9	158.9
X LDA	-23.6	35.0
XC LDA	82.9	82.9
	accuracy	precision (if accurate)

LDA is a crude approximation, so why does it work as well as it does?

- It retains many of the required features of the exchange hole
 - Sum rules: $\int h_X(1,2)d2 = -1$ $\int h_C(1,2)d2 = 0$
 - Behavior at zero interelectronic distance: $h_X(\mathbf{r}_1, \mathbf{r}_1) = -\rho(\mathbf{r}_1)$
 - $-h_{\rm X} \le 0$ everywhere

The LDA is the first term in an expansion of ε_{XC} . The natural next step is to include the gradient

• Gradient expansion approximation (GEA)

$$E_{ ext{XC}}^{ ext{GEA}}[
ho] = \int
ho(1)arepsilon_{ ext{XC}}(
ho(1))ig\{1+\mu_{ ext{XC}}(
ho(1))s^2+\mathcal{O}(s)^4ig\}d1$$

- Does not perform as well as might be expected
- Extension does not retain the required features of h_X that supported the performance of LDA



Generalized Gradient Approximation includes gradient while enforcing required hole behaviors

- $h_{\rm X}$ set to zero anywhere it becomes positive
- Truncate exchange and correlation holes to enforce sum rules

• GGA form:
$$E_{\rm XC}^{\rm GGA}[
ho] = \int
ho(1) \varepsilon_{\rm XC}^{\rm GGA}(
ho(1),
abla
ho(1)) d1$$
 Often will extend to show separate dependence on $ho^{\alpha},
ho^{\beta}$ and their gradients

- Again, sum exchange and correlation: $E_{\rm XC}^{\rm GGA} = E_{\rm X}^{\rm GGA} + E_{\rm C}^{\rm GGA}$
- Formulation from physical models is not as fruitful as for LDA

, ρ^{β} and their gradients

- Semi-empirical methods work well, but there are many targets
 - Properties: total energy, structural properties, atomization energy, charge density, bulk modulus,...
 - Substances: molecules, extended solids, insulators, conductors,...

The GGA functional is constructed by adding a gradient term to the LDA

- Primary focus is on improving exchange, because it is generally larger than the correlation correction ...as suggested by the sum rules: $\int h_X(1,2)d2 = -1 \int h_C(1,2)d2 = 0$
- Starting from LDA, we write

$$E_{
m X}^{
m GGA}[
ho] = E_{
m X}^{
m LDA}[
ho] - \sum_{\sigma} \int F(s_{\sigma})
ho_{\sigma}^{4/3}(1) d1 \qquad s_{\sigma} \equiv rac{|
abla
ho_{\sigma}|}{
ho_{\sigma}^{4/3}}$$

Functional of reduced gradient

- GEA would have $F(s) = \beta s^2$

Becke introduced a functional in 1988 that had a huge impact

- Some requirements of *F*(*s*)
 - Even function of s (expansion starts at s^2)
 - Specific limiting behavior at $r \rightarrow \infty$
- Becke proposed

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$$F^B(s) = rac{eta s^2}{1+6eta s \sinh^{-1}s}$$

Parameter β = 0.0042 fit to exact exchange energies for 6 noble-gas atoms
"B88" exchange functional



Becke's exchange functional has good accuracy at less cost than wavefunction methods

A−H + B' → A' + B−H

TABLE IV. Mean error (ME) and mean absolute error (MAE), in kcal/mol, for 148 atomization energies of the G2/97 test set⁴⁰ and 41 hydrogen-atom-transfer (HAT) reaction barriers of Lynch and Truhlar¹¹¹ (computed using LDA orbitals). See text for explanation of the acronyms.

The strong performance of the B88 functional (with LYP correlation) led GAUSSIAN to include DFT in its distribution for the first time in 1992

A. Becke, "Perspective: Fifty years of density-functional theory in chemical physics", *J. Chem. Phys.* **140**, 18A301 (2014); doi: 10.1063/1.4869598

	G2/97(ME)	G2/97(MAE)	HAT(ME)	HAT(MAE)	
Atomization energies H-atom transfer					
HF	-158.9	158.9	22.4	22.4	
HFS (X-only LDA)	-23.6	35.0	-12.8	13.0	
LDA	82.9	82.9	-17.8	17.8	
B86+PBE	5.4	8.0	-7.9	7.9	
B86b+PBE	11.5	12.6	-8.7	8.7	
B88+PBE	5.5	8.1	- 7.6	7.6	
PW86+PBE	5.7	8.7	-7.9	7.9	
revPW86+PBE	3.1	7.7	- 7.6	7.6	
PBE+PBE	16.3	16.9	- 9.5	9.5	
BR+B88c(BR)	- 5.9	9.0	- 5.6	5.7	
B3PBE	1.1	3.2	- 3.7	3.8	
PBE0	1.9	4.4	- 3.6	3.6	
B05	0.9	2.6	0.2	1.2	
B13	0.8	3.8	0.9	1.8	

GGA correlation is somewhat less important than exchange, but has received attention

- The effect of parallel-spin electrons in the uniform electron gas LDA is not the same as in low-*Z* atoms
 - E.g, $E_{\rm C}$ for the H-atom is zero (only one electron)
 - Suggests attenuating LDA correlation by half or more in light atoms
- Self-correlation correction requires consideration of the kinetic-energy density, $\tau_{\sigma} = \sum_{i} |\nabla \varphi_{i\sigma}|^2$, along with ρ and $\nabla \rho$

– Functionals incorporating τ_{σ} are called "meta-GGA"

Functionals beyond GGA rely on the idea of an *adiabatic connection* to the HF reference

• Two exact expressions for the energy functional

 $E[
ho] = T[
ho] + E_{
m Ne}[
ho] + J[
ho] + E_{
m ncl}[
ho]$

 $E[
ho]=T_0[
ho]+E_{
m Ne}[
ho]+J[
ho]+E_{
m XC}[
ho]$

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- The Slater-determinant reference has no correlation
- It is consistent with a system having no Coulomb interaction
- We can connect T_0 to T by integrating an "adiabatic" path that turns on interactions
 - Path Hamiltonian: $H_{\lambda} = \left(-rac{1}{2}
 abla^2 + v_{\lambda}
 ight) + rac{\lambda}{2}\sum_{i
 eq j}rac{1}{|\mathbf{r}_i \mathbf{r}_j|}$
 - $\lambda = 0$ is noninteracting reference, $\lambda = 1$ is fully interacting target
 - v_{λ} is whatever external potential keeps $\rho(\mathbf{r})$ constant on path ("adiabatic")

The net result of applying the adiabatic connection is a reinterpretation of $h_{\rm XC}$

$$egin{aligned} E[
ho] &= T_0[
ho] + E_{ ext{Ne}}[
ho] + J[
ho] + J[
ho] + E_{ ext{XC}}[
ho] \ E_{ ext{XC}}[
ho] &= rac{1}{2} \int \int rac{
ho(1)ar{h}_{ ext{XC}}(1,2)}{r_{12}} d1d2 \end{aligned}$$

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• Coupling-strength integrated exchange-correlation hole $\bar{h}_{\rm XC}(1,2) = \int_0^1 h_{\rm XC}^{\lambda}(1,2) d\lambda$

- Sum rules and other requirements for $h_{\rm XC}$ still apply

• The $\lambda = 0$ limit of the integrand is of interest $h_{\text{XC}}^{\lambda=0}(1,2) = h_{\text{X}}^{\lambda=0}(1,2) = -\frac{2}{\rho(1)} \left| \sum_{i} \varphi_{i}^{*}(1)\varphi_{i}(2) \right|^{2}$ noninteracting \Rightarrow no correlation

The localized UEG exchange model differs a lot from the non-local behavior at $\lambda = 0$

• The noninteracting $(\lambda = 0)$ hole is delocalized



- Electron correlation ($\lambda = 1$) has the effect of localizing that hole
- $\bar{h}(1,2)$ has contributions from both limits
- A strategy would be to combine these in some fashion

In 1993, Becke proposed a "hybrid" combination of functionals from different regimes of λ

$$\bullet \quad E_{\mathrm{XC}} = E_{\mathrm{XC}}^{\mathrm{LDA}} + a(E_{\mathrm{X}}^{\mathrm{exact}} - E_{\mathrm{X}}^{\mathrm{LDA}}) + b\Delta E_{\mathrm{X}}^{\mathrm{B88}} + c\Delta E_{\mathrm{C}}^{\mathrm{PW91}}$$

a, b, c parameters fit to atomization-energy data

PW: Perdew-Wang

- *a* = 0.20, *b* = 0.72, *c* = 0.81
- Exact exchange is the $\lambda = 0$ value
- $-\Delta$ indicates the GGA correction to LDA
 - Attenuated by *b* and *c* because use of exact exchange reduces their importance
- This is referred to as the B3PW91 functional
- Hybrid functionals require a HF calculation $\rightarrow N^4$ scaling again

Replacing PW91 with LYP correlation functional yielded the most popular functional to date

$$E_{ ext{XC}}^{ ext{B3LYP}} = E_{ ext{X}}^{ ext{LDA}} + a(E_{ ext{X}}^{ ext{exact}} - E_{ ext{X}}^{ ext{LDA}}) + b\Delta E_{ ext{X}}^{ ext{B88}} + (1-c)E_{ ext{C}}^{ ext{LDA}} + cE_{ ext{C}}^{ ext{LYP}}$$

- Slight difference because LYP is meant to replace LDA, not correct it
- Uses same *a*, *b*, *c* parameters as
 B3PW91
- Development of hybrids is the first time functionals were developed by fitting to molecular, and not just atomic data
 - The fitting of functionals has proliferated greatly ⁽³⁾

	G2/97(ME)	G2/97(MAE)	HAT(ME)	HAT(MAE	
	Atomizati	on energies	H-atom	H-atom transfer	
HF	-158.9	158.9	22.4	22.4	
HFS (X-only LDA)	-23.6	35.0	-12.8	13.0	
LDA	82.9	82.9	-17.8	17.8	
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B05	0.9	2.6	0.2	1.2	
B13	0.8	3.8	0.9	1.8	

→ A' + B-H

The self-interaction is not handled exactly in any of the functionals

- Consider a hydrogen atom
- Classical Coulomb repulsion is not zero, even though there's no electron-electron interaction $J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$
- Correction would require exactly cancelled by $E_{\rm XC}$: $J = -E_{\rm XC}$

- There's no guarantee this happens

					,
Functional	E _{tot}	J[p]	$E_X[\rho]$	$E_{C}[\rho]$	$J[\rho] + E_{XC}[\rho]$
SVWN	-0.49639	0.29975	-0.25753	-0.03945	0.00277
BLYP	-0.49789	0.30747	-0.30607	0.0	0.00140
B3LYP	-0.50243 -	- 0.30845	-0.30370^{a}	-0.00756	-0.00281
BP86	-0.50030	0.30653	-0.30479	-0.00248	-0.00074
BPW91	-0.50422	0.30890	-0.30719	-0.00631	-0.00460
HF	-0.49999	0.31250	-0.31250	0.0	0.0

Table 6-2. Energy components $[E_h]$ of various functionals for the hydrogen atom.(Hartrees)

^a Includes 0.06169 E_h from exact exchange.

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Koch & Holthausen, p.86

B3LYP rules them all (as of 2007)

Occurrence of functionals in titles/abstracts of publications



Total

S.F.Sousa, P. A.Fernandes, and M.J. Ramos "General Performance of Density Functionals", *J. Phys. Chem. A*, **111**, 10439 (2007). DOI: 10.1021/jp0734474

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B3LYP **B3P86** B3PW91 BH&LYP BLYP BP86 BPW91 ■ HCTH mPW1K PBE TPSS □ Others







A. Becke, "Perspective: Fifty years of density-functional theory in chemical physics", *J. Chem. Phys.* **140**, 18A301 (2014); doi: 10.1063/1.4869598

Summary

- We've covered a wide range of topics in relation to DFT
 - HK theorems
 - KS approach to KE
 - Electron density
 - Fermi and Coulomb correlation/holes
 - Local density approximation
 - Generalized gradient approximation, Meta-GGA
 - Hybrid functionals
- What is left?
 - Many topics: excited states, spin polarization, time-dependence...
 - New developments focus on locality vs nonlocality of exchange and correlation
 - Focus has been on intra-molecular interactions, but *inter*molecular is of great interest to us
 - DFT as presented so far is quite poor at this, due to inability to handle vdW dispersion interactions
 - We'll return to this later
 - Basis sets

Suggested Reading/Viewing

- Koch & Holthausen
 - Sec. 6.2, 6.5, 6.6
- A. Becke, "Perspective: Fifty years of density-functional theory in chemical physics", *J. Chem. Phys.* **140**, 18A301 (2014); doi: 10.1063/1.4869598
- Cramer
 - Video 5.06: <u>https://www.youtube.com/watch?v=VNoVpwhM-Yw</u>
 - Video 5.07: <u>https://www.youtube.com/watch?v=CzyR2lRgVtQ</u>