1.2. Density Functional Theory

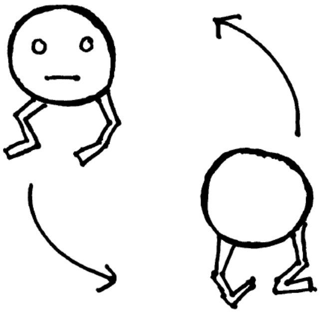
Motivation

Reminder:

Hartree-Fock:	computationally cheap not very accurate
post-HF:	Considerable computational effort potentially very accurate

Physical Reason:

HF:	Electrons interact with an **average** potential generated by the other electrons No instantaneous repulsion (no Coulomb correlation)
post-HF:	Electrons avoid each other (are correlated) Linear combination of Slater determinants, many coefficients to optimize
Idea:	It would be convenient to reduce the number of variables to optimize



Electrons moving through the density swerve to avoid one another, like shoppers in a mall.

J. P. Perdew, A. Ruzsinszky, L. A. Constantin, J. Sun and G. b. I. Csonka, *J. Chem. Theory Comput.*, **2009**, *5*, 902-908.

General idea

Ψ Can the problem be described by a simpler function? ρ

Wave function-based methods

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,....,\mathbf{r}_N)=\det[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)...\psi_N(\mathbf{r}_N)]$$

Complex mathematical object that depends on 4 * N variables: N = electrons, 3 spatial and 1 spin variable each

DFT

$$\rho(\mathbf{r})=\sum_{i=1}^{N}\left|\psi_i(\mathbf{r})\right|^2$$

Function of only 3 variables x, y, z

This chapter

Chapter 1.2

General idea

Hohenberg and Kohn (1964):

A unique/universal functional of the electron density exists

The functional delivers the **exact** electronic energy, formally:

kinetic energy

electron-nuclei interaction

electron-electron interaction

$$E[\rho]=\underbrace{\int\rho(\mathbf{r})v_{ne}d\mathbf{r}}_{\text{system dependent}}+\underbrace{T[\rho(\mathbf{r})]+E_{ee}[\rho(\mathbf{r})]}_{\text{universal}}$$

ρ(r) contains all the information of a wave function for computing observables.

Chapter 1.2

What is a functional?

A functional is like a function - just not quite...

A function relates one scalar quantity to another, e.g.,

$$y = f(x) \quad = \quad x^2$$
$$x = 2 \quad \rightarrow \quad y = 4$$

A functional relates a function to a scalar quantity and is denoted *F*[*f*(*x*)], e.g.,

$$y = F[f(x)] \quad = \quad \int_{-\infty}^{\infty} f(x)$$

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad \rightarrow \quad y = 1$$

Functionals and functional derivatives are central to DFT development
but not the topic of this course.

Chapter 1.2

Advanced level

Kohn-Sham DFT (I)

In Hohenberg-Kohn DFT, **2 necessary functionals are unknown**:

- the kinetic energy
- the exchange-correlation functional

The kinetic energy is a very large portion of the energy.

→ the relative errors must be small for this term.

So far, best solution is the “trick” of **Kohn-Sham** (1965):

The kinetic energy of a single Slater determinant is easy to compute:

\# of occupied orbitals

2nd derivatives: $\nabla^2 = \left(\frac{\partial^2}{\partial x^2}, \frac{\partial^2}{\partial y^2}, \frac{\partial^2}{\partial z^2} \right)$

$$T_s = \sum_{i=1}^{N} \left\langle \psi_i \left| -\frac{1}{2} \nabla_i^2 \right| \psi_i \right\rangle$$

1-electron orbitals

Theorem:

There exists a Slater determinant, which has the exact ground state ρ(r)

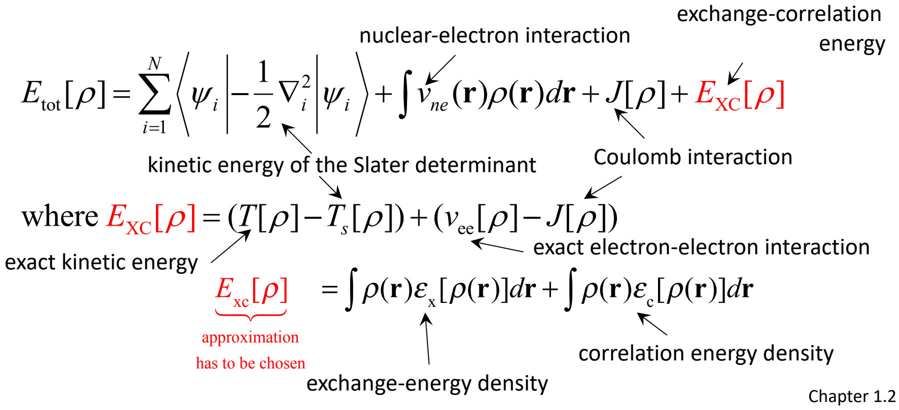
Chapter 1.2

Advanced level

Kohn-Sham DFT (II)

Theorem: There exists a Slater determinant, which has the exact ground state ρ(r)

- Compute the kinetic energy of this determinant
- **Approximate only the difference** between the exact and this kinetic energy
- Combine all the unknown stuff into one functional and call it exchange-correlation



exchange-correlation energy

nuclear-electron interaction

$$E_{\text{tot}}[\rho]=\sum_{i=1}^{N}\left\langle\psi_i\left|-\frac{1}{2}\nabla_i^2\right|\psi_i\right\rangle+\int v_{ne}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}+J[\rho]+E_{\text{XC}}[\rho]$$

kinetic energy of the Slater determinant

Coulomb interaction

$$\text{where } E_{\text{XC}}[\rho]=(T[\rho]-T_s[\rho])+(v_{\text{ee}}[\rho]-J[\rho])$$

exact electron-electron interaction

exact kinetic energy

$$\underbrace{E_{\text{xc}}[\rho]}_{\substack{\text{approximation}\\ \text{has to be chosen}}}=\int\rho(\mathbf{r})\varepsilon_{\text{x}}[\rho(\mathbf{r})]d\mathbf{r}+\int\rho(\mathbf{r})\varepsilon_{\text{c}}[\rho(\mathbf{r})]d\mathbf{r}$$

correlation energy density

exchange-energy density

Advanced level

Kohn-Sham DFT (III)

Kohn-Sham have re-introduced one-electron functions
The resulting **equations are no harder to solve than HF**

The theory is exact, but the universal functional is unknown

→ **Approximations to the exchange-correlation functional**
Variational principle applies, but only "inside" one E_{xc} approximation

Exchange and correlation are important for chemical applications: "nature's glue"

Reasonable approximations are possible!

Even the simplest (local density approximation, Slater functional) is better than HF

Disadvantage:
No systematic improvement possible:
→ there is no "road-map" towards the exact functional
Right answer for the right reason? - Most likely not, but error cancellation

Why is DFT so successful?

As cheap as Hartree-Fock

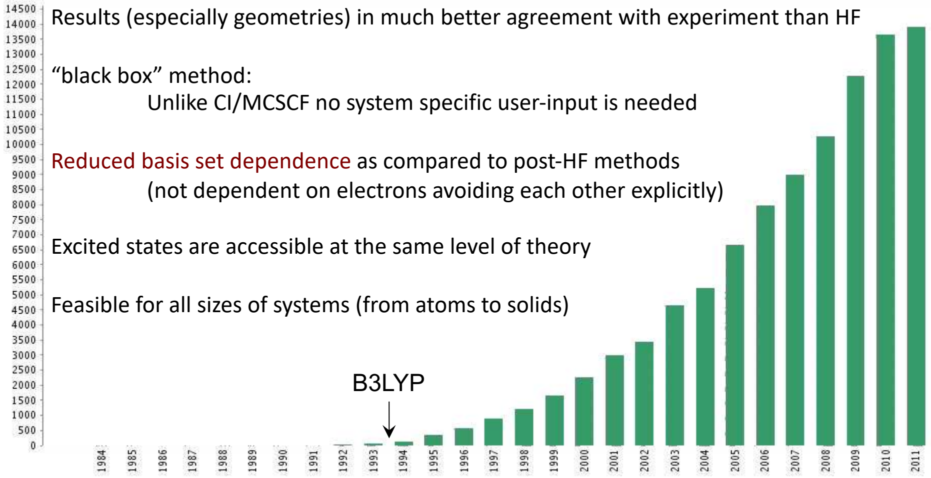
Results (especially geometries) in much better agreement with experiment than HF

“black box” method:
Unlike CI/MCSCF no system specific user-input is needed

Reduced basis set dependence as compared to post-HF methods
(not dependent on electrons avoiding each other explicitly)

Excited states are accessible at the same level of theory

Feasible for all sizes of systems (from atoms to solids)

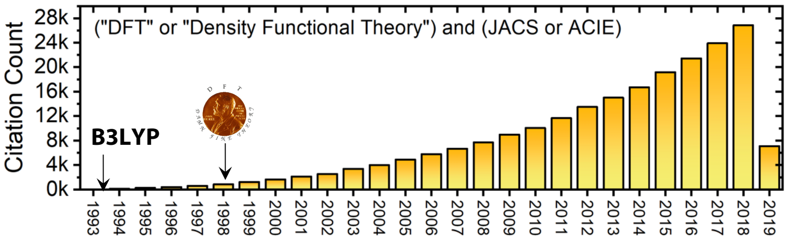


Citations of JACS and Angewandte DFT papers over years

Chapter 1.2

Why is DFT so successful?

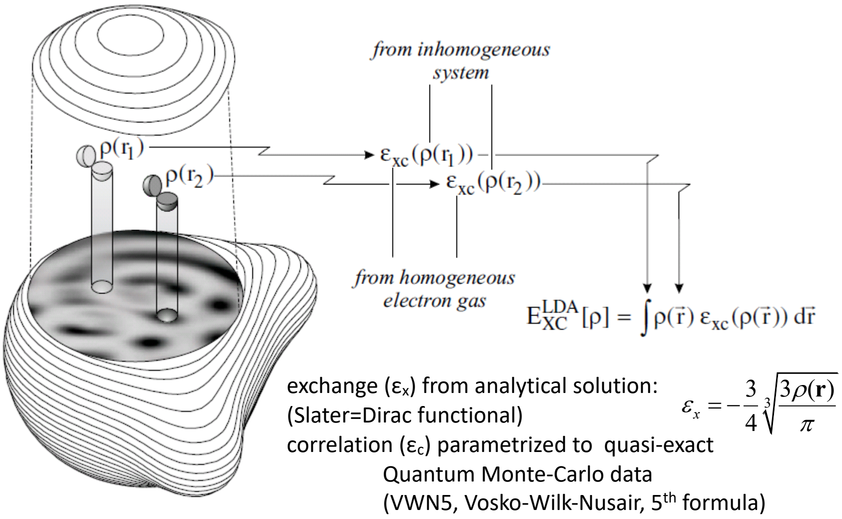
- **Lower computational cost**
- **Good agreement with experiment**
- **From atom to solids**



Chapter 1.2

How does LDA perform?

LDA is the simplest density functional approximation



$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r})\,\varepsilon_{xc}(\rho(\vec{r}))\,d\vec{r}$$

exchange (ε_x) from analytical solution:
(Slater=Dirac functional)

$$\varepsilon_x = -\frac{3}{4}\sqrt[3]{\frac{3\rho(\mathbf{r})}{\pi}}$$

correlation (ε_c) parametrized to quasi-exact
Quantum Monte-Carlo data
(VWN5, Vosko-Wilk-Nusair, 5th formula)

W. Koch and M. C. Holthausen, A Chemist's Guide to Density Functional Theory

Chapter 1.2

How well does LDA perform?

Surprisingly well!
Geometries are fairly accurate

Table 8-1. Basis set dependence of SVWN-optimized C-C/C-H bond lengths [Å].

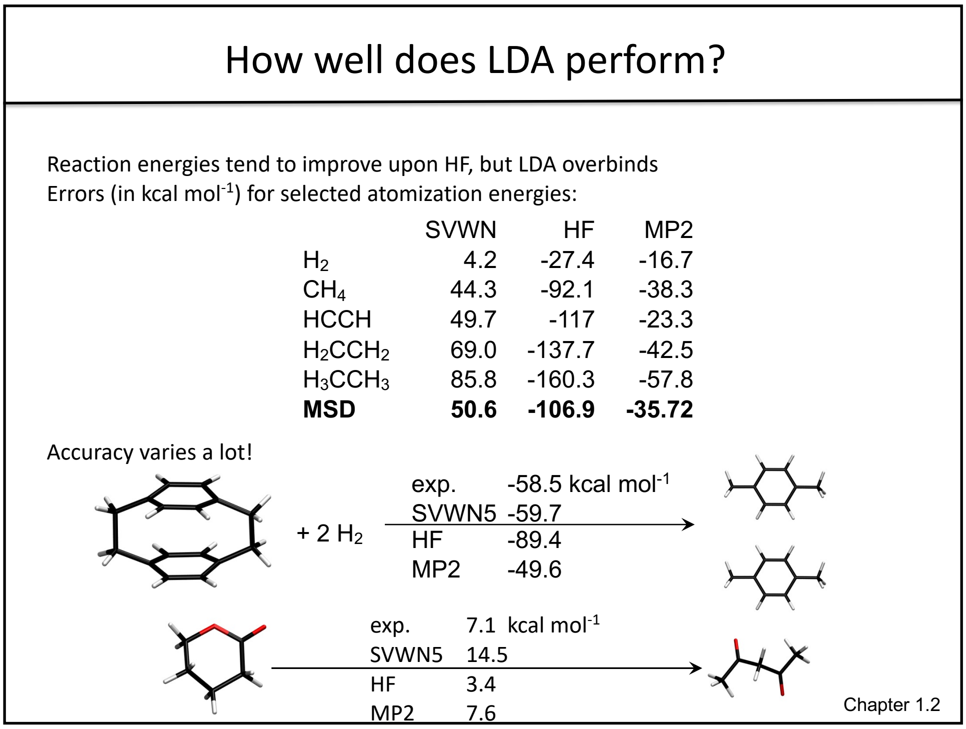
Bond	6-31G(d,p)	6-311++G(d,p)	Limit[a]	Experiment
H-H	— /0.765	— /0.765	— /0.765	— /0.741
$H_3C\text{-}CH_3$	1.513/1.105	1.510/1.101	1.508/1.100	1.526/1.088
$H_2C{=}CH_2$	1.330/1.098	1.325/1.094	1.323/1.093	1.339/1.085
$HC{\equiv}CH$	1.212/1.078	1.203/1.073	1.203/1.074	1.203/1.061

Bond lengths for neutral hexacarbonyl complexes of Cr, Mo, and W in O_h symmetry [Å].

	$Cr(CO)_6$		$Mo(CO)_6$		$W(CO)_6$	
Method	$R_{M\text{-}C}$	$R_{C\text{-}O}$	$R_{M\text{-}C}$	$R_{C\text{-}O}$	$R_{M\text{-}C}$	$R_{C\text{-}O}$
SVWN	1.866	1.145	2.035	1.144	2.060	1.144
B3LYP	1.921	1.155	2.068	1.155	2.078	1.156
MP2/ECP	1.862	1.154	2.031	1.152	2.047	1.153
Experiment	1.914	1.141	2.063	1.145	2.058	1.148

W. Koch and M. C. Holthausen, A Chemist's Guide to Density Functional Theory

Chapter 1.2



How well does LDA perform?

Reaction energies tend to improve upon HF, but LDA overbinds
Errors (in kcal mol^{-1}) for selected atomization energies:

	SVWN	HF	MP2
H_2	4.2	-27.4	-16.7
CH_4	44.3	-92.1	-38.3
HCCH	49.7	-117	-23.3
H_2CCH_2	69.0	-137.7	-42.5
H_3CCH_3	85.8	-160.3	-57.8
MSD	**50.6**	**-106.9**	**-35.72**

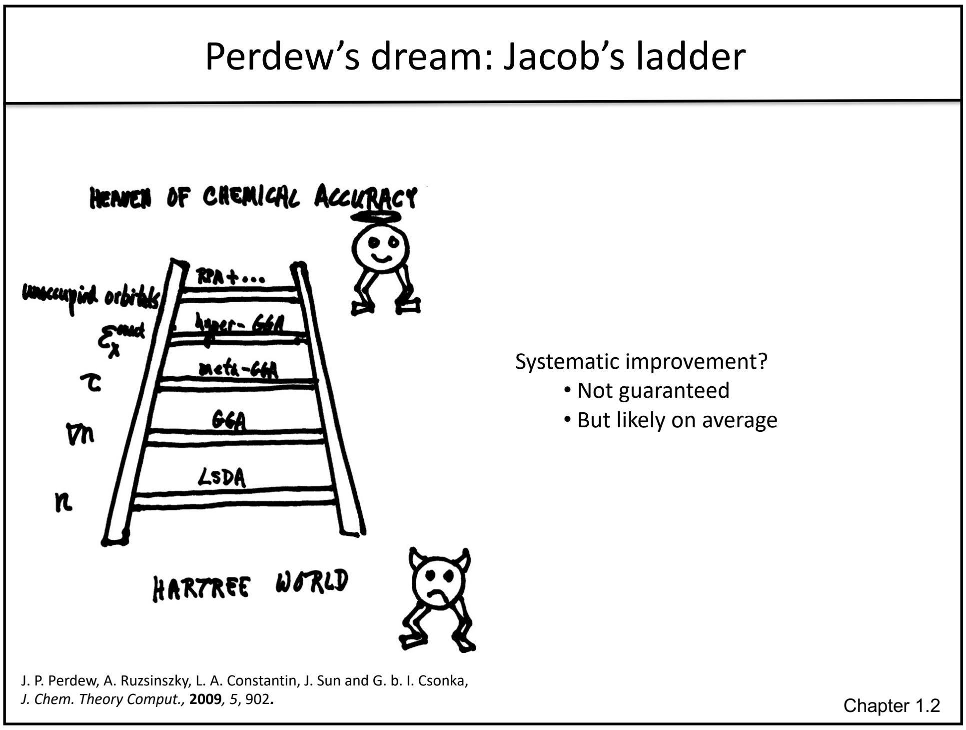
Accuracy varies a lot!

+ 2 H_2

exp.	-58.5 kcal mol^{-1}
SVWN5	-59.7
HF	-89.4
MP2	-49.6

exp.	7.1 kcal mol^{-1}
SVWN5	14.5
HF	3.4
MP2	7.6

Chapter 1.2



Perdew's dream: Jacob's ladder

Systematic improvement?

- Not guaranteed
- But likely on average

J. P. Perdew, A. Ruzsinszky, L. A. Constantin, J. Sun and G. b. I. Csonka, *J. Chem. Theory Comput.*, **2009**, *5*, 902.

Chapter 1.2

How to improve upon LDA?

LDA (=SVWN) a very crude approximation (*i.e.*, local)
The incorporation of the following information should offer improvements:

- The gradient of the density
  GGA (Generalized Gradient Approximation)
- The second derivatives (Laplacian or the kinetic energy density) $\tau = \frac{1}{2}\sum_{i}^{N} |\nabla \psi_i|^2$
  meta-GGAs
  semi-local density functionals: GGAs and meta-GGAs

Hartree-Fock exchange is fully non-local
Including some percentage of this “exact” exchange
Hybrid functionals

All these ingredients can be introduced with more or less empiricism:

> Whether the underlying, universal functional dependence is obtained from purely theoretical arguments (very difficult!), or from fits to experimental data (much more practical!), is entirely irrelevant. Information on the ‘‘shape’’ of the Kohn–Sham functional, revealed by *whatever means, is of fundamental value and utility. In short,* the object we are trying to fit is *known to exist*.
> A. Becke, JCP **1997**, *107*, 8554.

→ Plethora of functionals

Chapter 1.2

The world of acronyms (I)

General rule (except for hybrid functionals):
The name of the functional is divided into two components: Exchange-Correlation functional
Numbers are often indicative of the development year - but not always.

LDA: SVWN5 is the most common.

S	Slater Exchange
VWN5	Vosko, Wilk, Nusair, 5th formula

GGA: There are many. The most important are: BLYP, BP86, PBE

B	(aka B88): Becke’s exchange from 1988
LYP	Lee-Yang-Parr correlation from 1988
P86	Perdew’s correlation functional from 1986
PBE	Perdew, Burke, Ernzerhof exchange and correlation from 1996

meta-GGA: TPSS, M06-L
Tao, Perdew Staroverov, Scuseria exchange and correlation (2003)
M06-L Minnesota functional from the 2006 family developed by Truhlar

Chapter 1.2

The world of acronyms (II)

hybrid-GGA functionals

B3LYP: Becke, 3 parameters with LYP correlation (a=0.2, b=0.72, c=0.19)

$$E_{xc}^{B3LYP} = aE_x^{HF} + (1-a)E_x^{S} + bE_x^{B88} + cE_c^{VWN} + (1-c)E_c^{LYP}$$

PBE0 (aka PBE1PBE): a= 0.25

$$E_{xc}^{PBE0} = aE_x^{HF} + (1-a)E_x^{PBE} + E_c^{PBE}$$

hybrid-meta-GGA functionals (aka hyper-GGAs):

TPSSh: a=0.1

$$E_{xc}^{TPSSh} = aE_x^{HF} + (1-a)E_x^{TPSS} + E_c^{TPSS}$$

M06, M06-2X (M05, M05-2X):

Truhlar's Minnesota functionals, which contain ~30 empirically fitted parameters

M06: Supposedly an all-round functional, 27% "exact" exchange E_x^{HF}

M06-2X: 54% "exact" exchange (2X=2*exchange from M06)

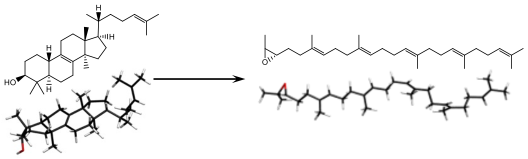
Improved description of main-group thermochemistry and weak interactions

M06-family: very sensitive to the numerical integration grid used in computations.
Precise (as opposed to accurate) computations become rather expensive compared to B3LYP.

How well do (hybrid-)GGAs perform?

GGAs generally improve over LDA for reaction energies (with exceptions), but geometries are generally similar

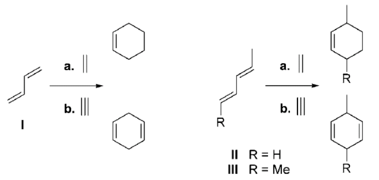
Hybrid-GGAs improve over LDA and are used **extensively** even nowadays especially for thermochemistry and frequencies, but **problems remain**

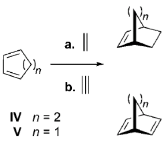


Benchmark: 74.5 kcal mol^{-1}; B3LYP: 18.9 kcal mol^{-1} → Error > 50 kcal mol^{-1}

Highly empirical meta-GGA hybrid functionals such as M06-2X are performing well for organic chemistry problems.

How well does M06-2X perform?

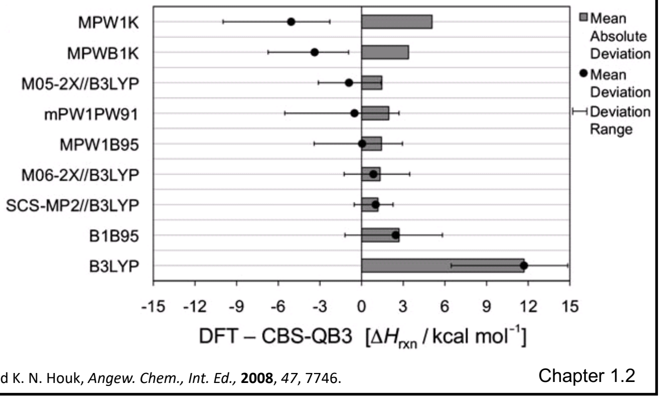




Diels-Alder reactions are among the most studied reactions

B3LYP used to be the most popular but still suffers from severe errors for reaction energies

The more recent M06-2X offers considerable improvements



S. N. Pieniazek, F. R. Clemente and K. N. Houk, *Angew. Chem., Int. Ed.*, **2008**, *47*, 7746.

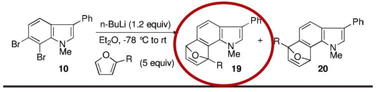
Chapter 1.2

Selected Applications of M06-2X

A more exotic example:
Stereoselectivity of a Cycloaddition

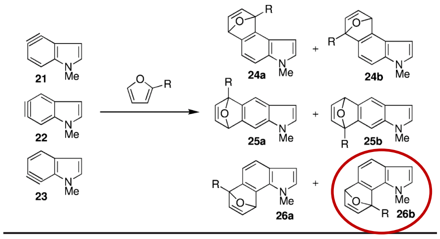
Table 1: experimental results
Table 2: M06-2X results

Table 1. Regioselective 6,7-Indolyne Cycloadditions with 2-Substituted Furans



entry	furan, R	**19**	**20**	yield, %
1	Me	80	20	89
2	Et	84	16	90
3	*i*-Pr	94	6	88
4	*t*-Bu	98	2	91
5	Ph	>99	<1	92
6	SO_2Ph	<1	>99	83

Table 2. $\Delta G^\ddagger$ Values in kcal/mol for the Reaction of Indolynes with Substituted Furans



entry	aryne	furan, R	$\Delta G^\ddagger$ (**a**)	$\Delta G^\ddagger$ (**b**)
1	**21**	H	10.5	
2	**22**	H	10.0	
3	**23**	H	8.7 (8.4)[a]	
4	**21**	*t*-Bu	6.3	7.3
5	**22**	*t*-Bu	6.9	6.1
6	**23**	*t*-Bu	7.0 (8.0)	[b]
7	**23**	Me	9.2 (9.4)	7.5 (7.8)
8	**23**	Et	9.0 (9.4)	7.8 (8.2)
9	**23**	*i*-Pr	9.7 (10.3)	7.6 (8.2)

A. N. Garr, D. Luo, N. Brown, C. J. Cramer, K. R. Buszek and D. VanderVelde, *Org. Lett.*, **2009**, *12*, 96.

Chapter 1.2

Advanced level

Common problems

The theory is exact.
Density functional approximations suffer from 3 severe shortcomings:

1. **Missing dispersion interactions** : *e.g.*, **DNA base pairs or benzene dimers will not bind.**
   → *can be incorporated easily (@LCMD)*

2. **Self-interaction / Delocalization errors**
   One electron should not interact with itself but it does in many approximations: **the density spreads out too much, fractional charges get stabilized =** Errors in charge-transfer excitations
   → *can be corrected with more sophisticated functional approximations*

3. **Static correlation error: Wrong dissociation behaviour *e.g.*, H_2, spin-unpolarized**

   → *No general correction.*

How to improve upon hybrid-GGAs?

Add one or several more ingredients:

For problem 1 (missing dispersion interactions):

Atom pairwise Dispersion correction
Semi-local exchange-correlation functionals miss long-range dispersion = van der Waals interactions ~C_6/R^6
C_6: dispersion coefficient, R: intermolecular distance

For problem 1 and more…
Perturbation theory, *i.e.*, non-local correlation
"Double hybrid" functionals add second-order perturbation theory correlation (like MP2 for Hartree-Fock)

For problem 2 (self-interaction error):
Long-range corrected exchange
Instead of a constant fraction of "exact" exchange
Non-local exchange depends on the interelectronic distance r_{12}

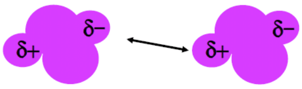
Chapter 1.2

Dispersion correction

Standard density functionals cannot account for long-range correlation (= dispersion)
- semi-local information is not sufficient for non-overlapping densities

Easy solution: **Add an atom pair wise dispersion correction**

London-dispersion
or
van der Waals
interactions:
induced dipole ··· induced dipole



# of atoms

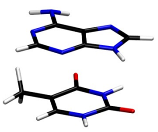
atom-pair specific
dispersion coefficient

$$E_{disp} = -\sum_{i=2}^{N_{at}} \sum_{j=1}^{i-1} f_d(R_{ij}) \frac{C_6^{ij}}{R_{ij}^6}$$

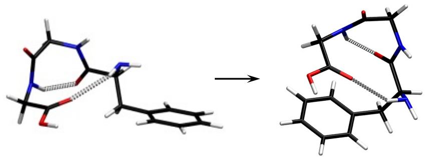
damping function

interatomic distance

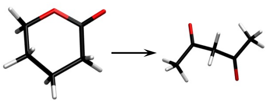
Dispersion correction



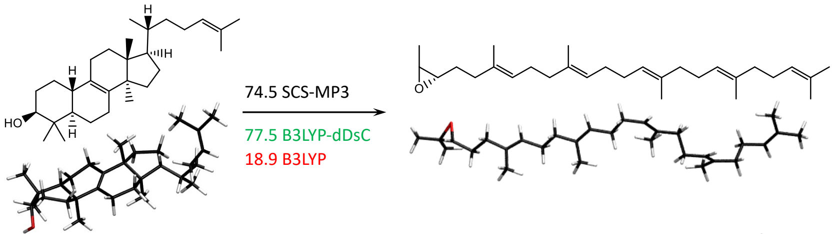
Dissociation energy:
11.7 CCSD(T)
10.9 B3LYP-dDsC
-1.9 B3LYP



-3.1 CCSD(T)
-1.6 B3LYP-dDsC
4.3 B3LYP



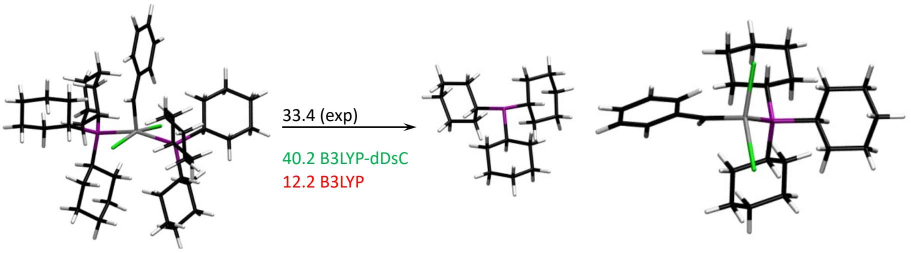
7.1 CCSD(T)
6.4 B3LYP-dDsC
2.7 B3LYP



74.5 SCS-MP3
77.5 B3LYP-dDsC
18.9 B3LYP

Dispersion correction

Grubb's 1st generation olefin-metathesis catalyst

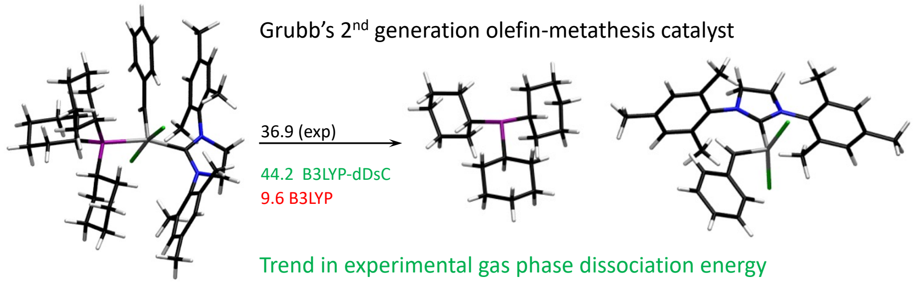


33.4 (exp)

40.2 B3LYP-dDsC

12.2 B3LYP

Grubb's 2nd generation olefin-metathesis catalyst



36.9 (exp)

44.2 B3LYP-dDsC

9.6 B3LYP

Trend in experimental gas phase dissociation energy
only reproducible when accounting for weak interactions

Advanced level

Long-range correction for the exchange

Classical hybrid functionals (aka global hybrids): fixed percentage of "exact" exchange

Long-range corrected functionals

percentage of "exact" exchange **depends on interelectronic distance** r_{12}.

→ Electrons far apart interact by non-local exchange

Electrons close to each other interact by local (DFT) exchange

→ Improved balance between needed long-range physics and DFT exchange

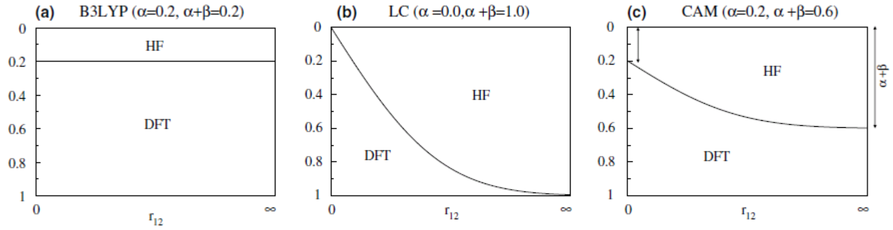
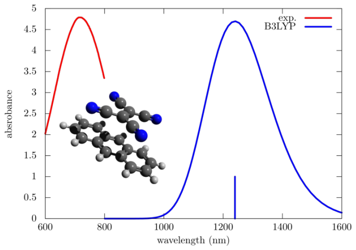


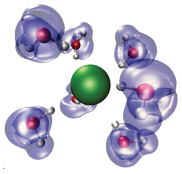
Fig. 2. Schematic plots of the contributions to exchange from r_{12}^{-1}, apportioned into DFT and HF, for: (a) B3LYP, (b) LC, and (c) CAM.

T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, **2004**, *393*, 51.

Overestimation of Electron Flow

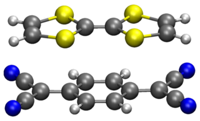


Charge transfer excitations are too low



Charges overly disperse

Cohen, A. J.; Mori-Sanchez , P.; Yang W. *Science* **2008**, *321*, 792.



Cumulenes are overly stabilized

=C= ⟶ ≡C—

-1.4 kcal mol^{-1} CCSD(T)/CBS
+2.0 kcal mol^{-1} B3LYP

DFT **overbinds**

Woodcock, H. L.; Schaefer, H. F.; Schreiner, P. R. *JPC A* **2002**, *106*, 11923.

Charge-transfer excitations

The accurate description of excited states is generally very demanding
The electronic structure changes considerably as compared to ground state.

- Often multi-reference problems
- Within DFT: Usually not treated self-consistently

→ Additional approximations, additional errors

Time-dependent DFT (TD-DFT) is a convenient framework
Exact in principle, approximated in practice
An electronic excitation is related to:

Response of the ground-state to a periodical perturbation (electric field)

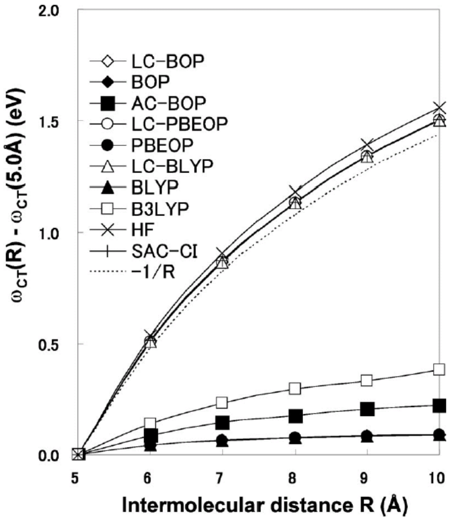
Practical approximation:
Adiabatic linear-response time dependent DFT

- Local in time (no dependence on preceding time evolution)
- No dependence on perturbation frequency

Due to self-interaction errors, charge-transfer excitations are particularly difficult
→ Long-range corrected functionals improve description

Chapter 1.2

Charge-transfer excitations



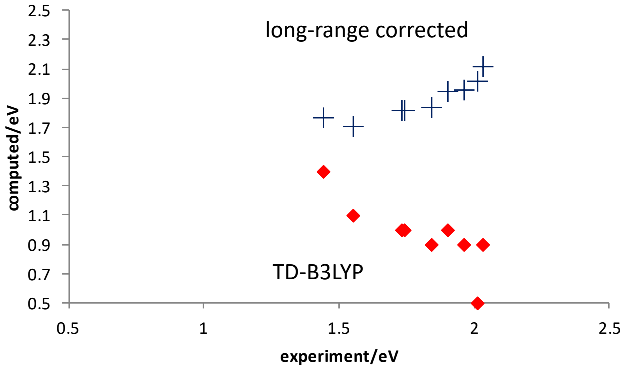
The lowest charge transfer excitation energy of ethylene–tetrafluoroethylene dimer for the long intermolecular distance calculated by TDDFT employing various types of functionals. For all methods, the excitation energy at 5.0 Å is set to zero.

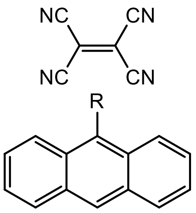
Non-local exchange is necessary for correct long-range charge transfer

Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai and K. Hirao, *J. Chem. Phys.*, **2004**, *120*, 8425.

Charge-transfer excitations

Charge-transfer excitations of anthracene derivatives -TCNE





Asymptotic non-local exchange is necessary for correct trends of charge transfer excitations

T. Stein, L. Kronik and R. Baer, *J. Am. Chem. Soc.* **2009**, *131*, 2818.

The World of Acronyms (III)

Long-range corrected (LC) functionals
LC-BLYP, LC-BOP, LC-ωPBE, CAMB3LYP
LC-B: long-range corrected Becke 88 exchange
OP: One parameter progressive correlation functional (Hirao, 1999)
LC-ωPBE: Long-range corrected PBE exchange with PBE correlation
CAMB3LYP: Coulomb-attenuating method in the spirit of B3LYP

$$E_{xc}^{\text{CAM-B3LYP}} = \alpha E_x^{HF} + (1-\alpha)E_x^{B88} + \beta(E_x^{LR-HF} + E_x^{SR-B88}) + cE_c^{VWN} + (1-c)E_c^{LYP}$$
$$\text{where } \alpha = 0.19, \beta = 0.46 \text{ and } c = 0.19$$

Double hybrids
B2PLYP (Grimme, 2006)

$$E_{xc}^{\text{B2PLYP}} = aE_x^{HF} + (1-a)E_x^{B88} + bE_c^{PT2} + (1-b)E_c^{LYP} \text{ where } a = 0.53 \text{ and } b = 0.27$$

many others out now, no “standard” yet,
differ by i) parameters and ii) by spin-component scaling

Dispersion correction
in general: DFT-D (e.g., B3LYP-D), but different flavours are often indicated:
B3LYP-D3 (Grimme 2010)
B3LYP-dDsC (LCMD 2011)

Chapter 1.2

The Notion of Accuracy

Accuracy *versus* Precision

Precision: the degree to which a particular computation approaches the exact result that should have been obtained with the specified method and basis set *(e.g. the integration grid when using M06-2X).*

Accuracy: absolute theoretical accuracy set *(e.g. GGA are more accurate that LDA; CCSD(T) is more accurate than Hartree-Fock).*

Hoffmann, Schleyer, Schaefer *Angew. Chem. Int Ed.* **2008**, *47*, 7164.

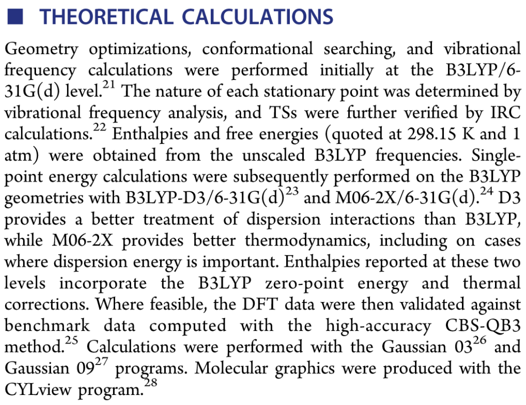
Take home message

DFT is very successful and useful if you know its limit!

Chapter 1.2

Mini Quiz 2

1. As a computational organic chemist, which functional will you rather choose if you need to compute
   - (a) Energy barriers
   - (b) Charge transfer excitations
   - (c) Conformation energies
2. Why did hybrid functionals become so popular within the field of organic chemistry?
3. Why is LDA hardly used to address questions in organic chemistry?
4. When should one not use DFT?



THEORETICAL CALCULATIONS

Geometry optimizations, conformational searching, and vibrational frequency calculations were performed initially at the B3LYP/6-31G(d) level.[21] The nature of each stationary point was determined by vibrational frequency analysis, and TSs were further verified by IRC calculations.[22] Enthalpies and free energies (quoted at 298.15 K and 1 atm) were obtained from the unscaled B3LYP frequencies. Single-point energy calculations were subsequently performed on the B3LYP geometries with B3LYP-D3/6-31G(d)[23] and M06-2X/6-31G(d).[24] D3 provides a better treatment of dispersion interactions than B3LYP, while M06-2X provides better thermodynamics, including on cases where dispersion energy is important. Enthalpies reported at these two levels incorporate the B3LYP zero-point energy and thermal corrections. Where feasible, the DFT data were then validated against benchmark data computed with the high-accuracy CBS-QB3 method.[25] Calculations were performed with the Gaussian 03[26] and Gaussian 09[27] programs. Molecular graphics were produced with the CYLview program.[28]

Now, you should be able to better understand the paragraph above.