

# Orbital energies in DFT

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# Contents

## 1. DFT in Quantum Chemistry

Present status of DFT in Quantum Chemistry  
Kohn-Sham equation & its problems

## 2. Long-range corrected (LC) DFT

Problems that LC-DFT has solved  
LC-DFT & its derivatives  
Chemical reaction calculations  
Van der Waals calculations  
Nonlinear optical property calculations  
Excited state calculations

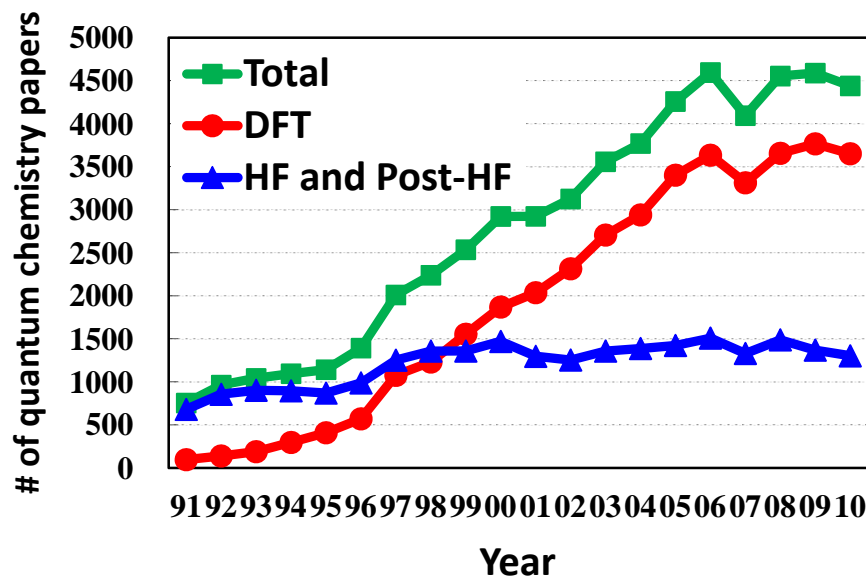
## 3. Orbital energies

Molecular orbitals  
Orbital energies  
Orbital energy calculations by LC-DFT  
Why LC-DFT reproduces orbital energies?  
Chemical reactions vs orbital energies

# 1. DFT in Quantum Chemistry

# DFT in Quantum Chemistry

In the field of QC, DFT studies are hardly found in the beginning of 1990's but rapidly increases to become the main stream at present.

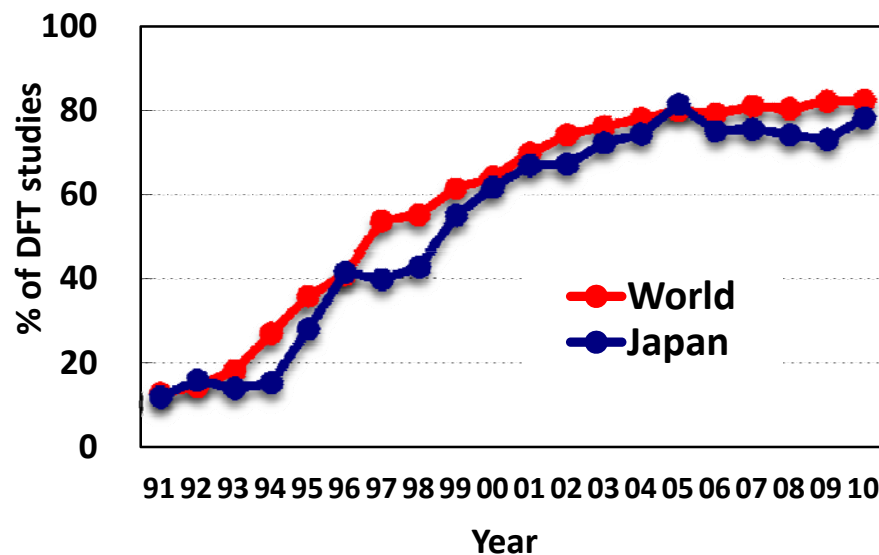


Number of related papers published in electric journals of chemistry

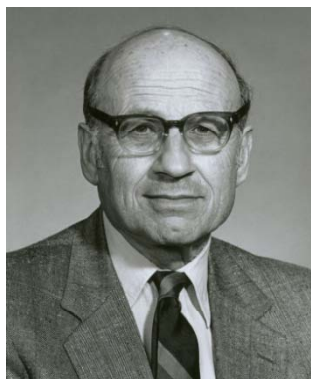
DFT-related papers pull up the number of QC papers.

The percentage of DFT-related papers in QC papers

At 2010, DFT-related papers are **more than 80%** of QC papers, and are supposed to be **more than 90%** as far as applications go.



# DFT & its problems



Walter Kohn  
 Nobel prize winner  
 for chemistry in 1998

## Kohn-Sham equation

$$\hat{F} \varphi_i = \left[ \hat{h} + 2\hat{J} + \frac{\delta E_{xc}}{\delta \rho}[\rho] \right] \varphi_i = \varepsilon_i \varphi_i$$

$$E = h + 2J + E_{xc}[\rho]$$

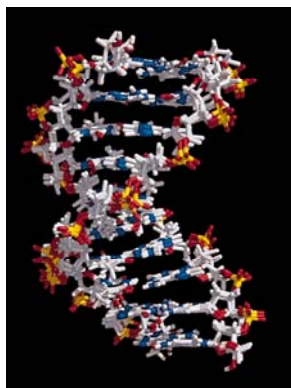
Orbital (band) energy  
 Orbital (band)

The exchange-correlation energy is expressed as a functional of density  $E_{xc}[\rho]$ .

**This simple method reproduces accurate properties with much less computational time than conventional ones.**

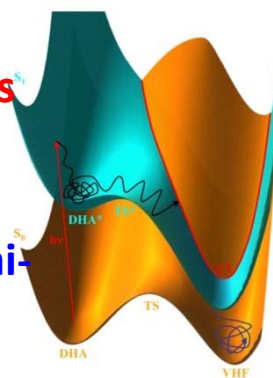
## Significant problems that DFTs have faced in QC calculations

### Large systems



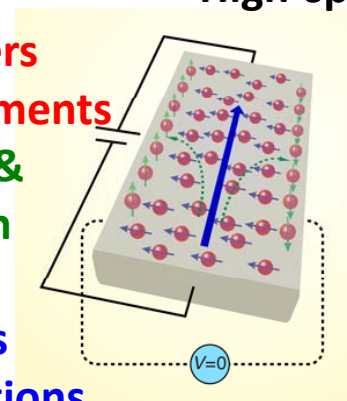
VdW bonds  
 Optical properties of long-chain molecules  
 Band gaps of semiconductors & insulators

### Photochemical reactions



Charge transfers  
 Transition moments  
 Nonadiabatic & Spin-forbidden transitions  
 State crossings  
 Bond dissociations

### High-spin systems



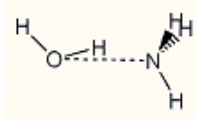
Magnetic properties  
 Spin-orbit splittings  
 Diradicals

## 2. Long-range corrected (LC) DFT

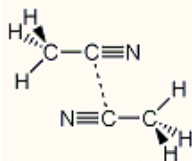
# DFT problems which LC has solved

## Van der Waals calculations

Hydrogen bond complexes



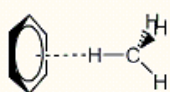
Dipole-dipole complexes



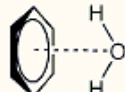
Stacking complexes



Dispersion complexes



Dipole-induced dipole complexes

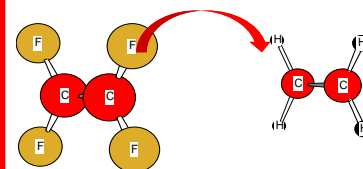


Long-range correction (LC) scheme

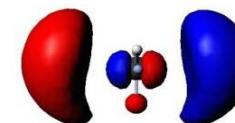
LC scheme has solved or improved serious DFT problems in various chemical property calculations.

## Excited state calculations

Charge transfers

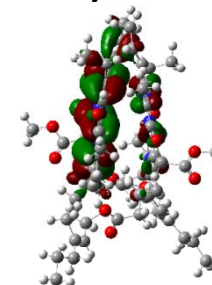


Rydberg excitations

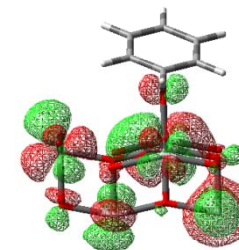


Photochemistries of large systems

Photosynthesis

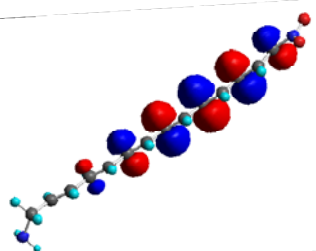


Photocatalysis



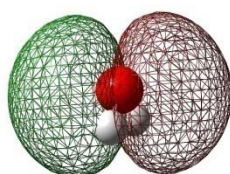
Optical property calculations

Long-chain polyenes



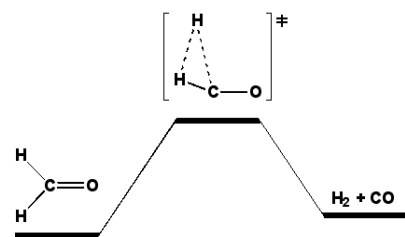
Orbital energy calculations

Orbital energies



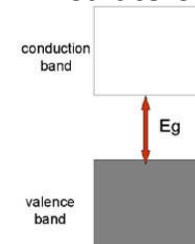
Chemical reaction calculations

Reaction barrier heights



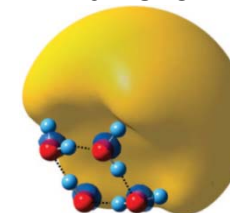
Solid state calculations

Band gaps of insulators

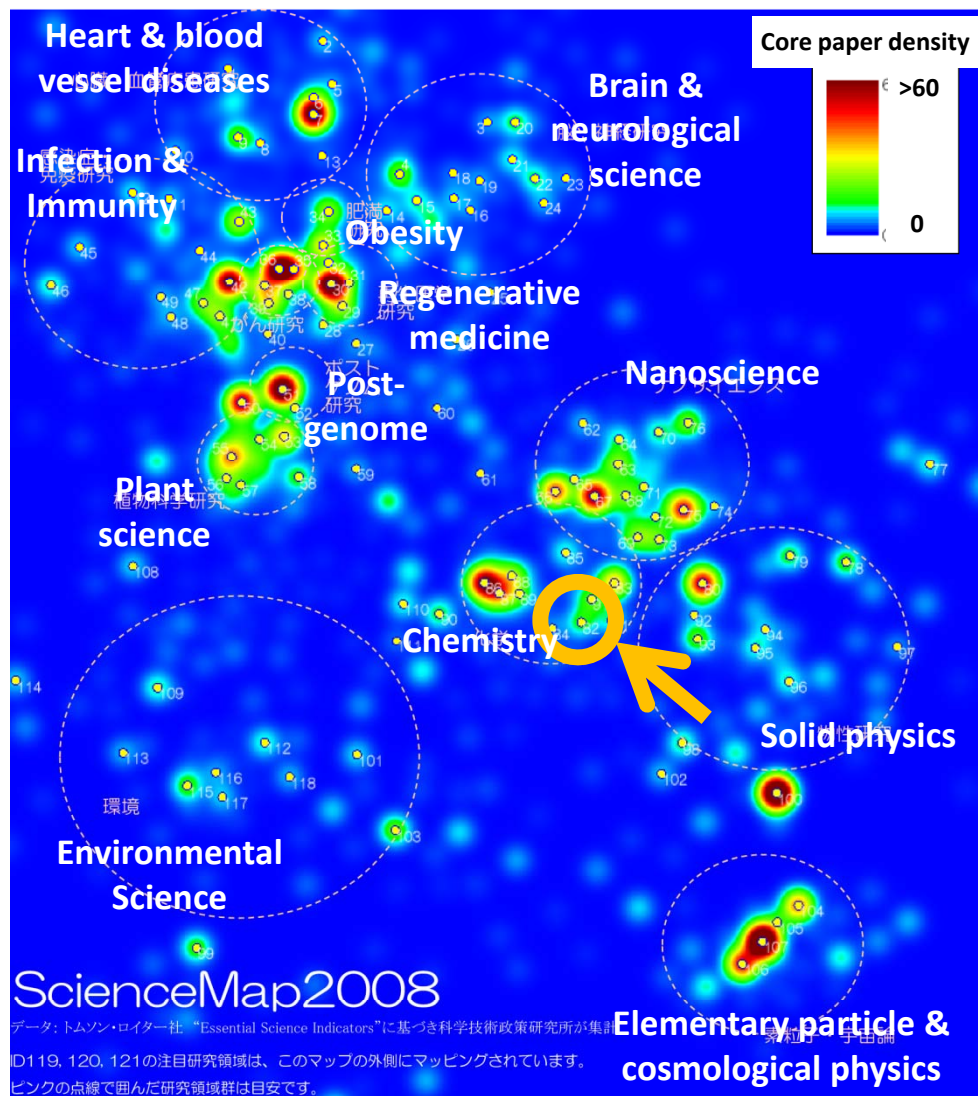


Cluster calculations

Water cluster anions



# The status of LC-DFT in Science



## Citations of LC-related papers (TT)

**1270** citations/21 papers (ISI Web of Science, Sep. 10, 2011)

## Scientific impact of LC-related papers

According to "**ScienceMap 2008**" (Ministry of Education, Culture, Sports, Science and Technology, Japan, 2010), **LC-related papers form a new research area of highest 1% citations in science.**

LC-DFT is available on the official version of **Gaussian09 & GAMESS programs.**

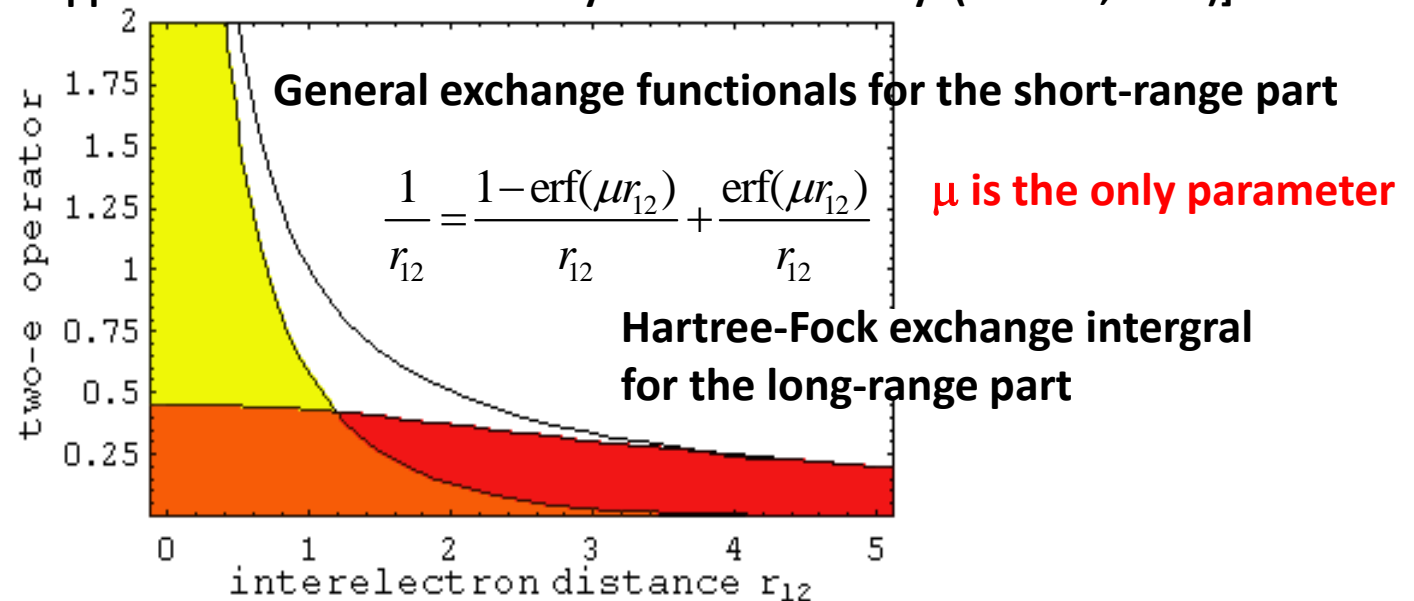




# Long-range correction (LC) scheme

**The correction for the long-range part of general exchange functionals.**

[H. Iikura, T. Tsuneda, T. Yanai and K. Hirao, J. Chem. Phys. 115, 3540, 2001; A. Savin, in 'Recent Developments and Applications of Modern Density Functional Theory' (Elsevier, 1996)]



Functionals base on LC scheme

**CAM-series** [T. Yanai, D.P. Tew, & N.C. Handy, Chem. Phys. Lett. 91, 551, 2004.]

**LC- $\omega$ PBE** [O. A. Vydrov, J. Heyd, A. V. Krukau, & G. E. Scuseria, J. Chem. Phys. 125, 074206, 2006.]

**LCgau-series** [J.-W. Song et al., J. Chem. Phys. 127, 154109, 2007.]

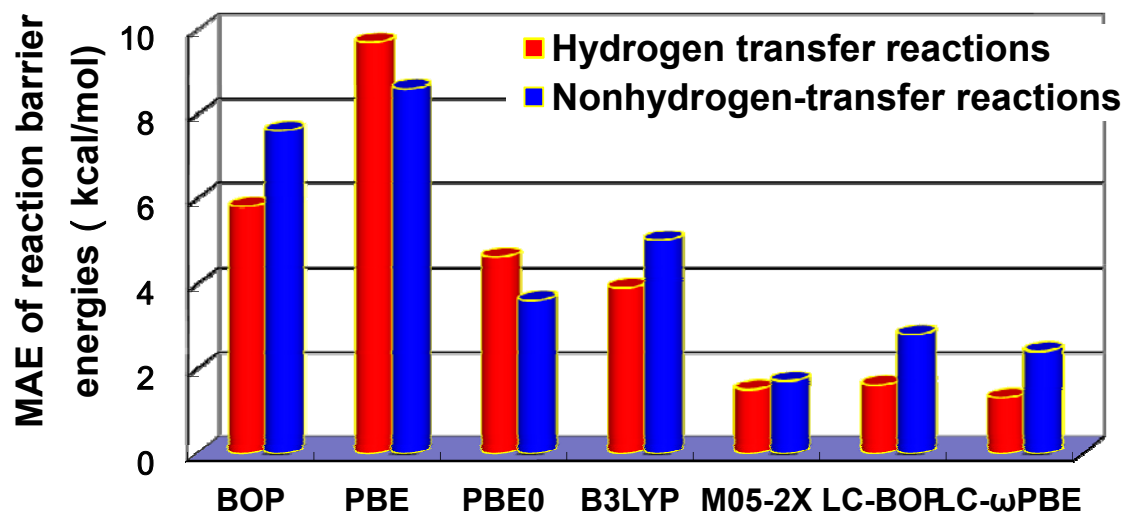
**MCY-series** [A. J. Cohen, P. Mori-Sanchez, & W. Yang, J. Chem. Phys. 126, 191109, 2007.]

**BNL** [E. Livshits & R. Baer, Phys. Chem. Chem. Phys., 9, 2937, 2007.]

**$\omega$ B97-series** [J.-D. Chai & M. Head-Gordon, J. Chem. Phys. 128, 084106, 2008.]

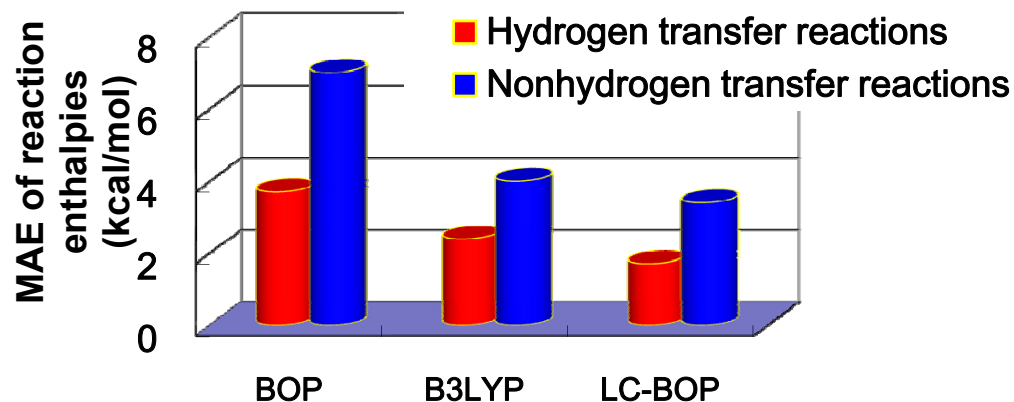
# Chemical reactions of small molecules

Figs. Mean absolute deviations in calculated reaction barriers & reaction enthalpies for Truhlar's benchmark set (78 chemical reactions).

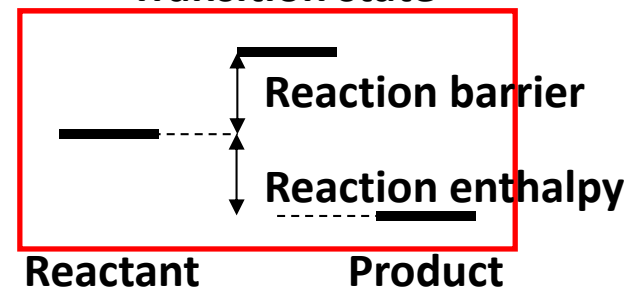


## Reaction enthalpies

LC scheme drastically improves reaction barriers with also modifying reaction enthalpies.



## Transition state



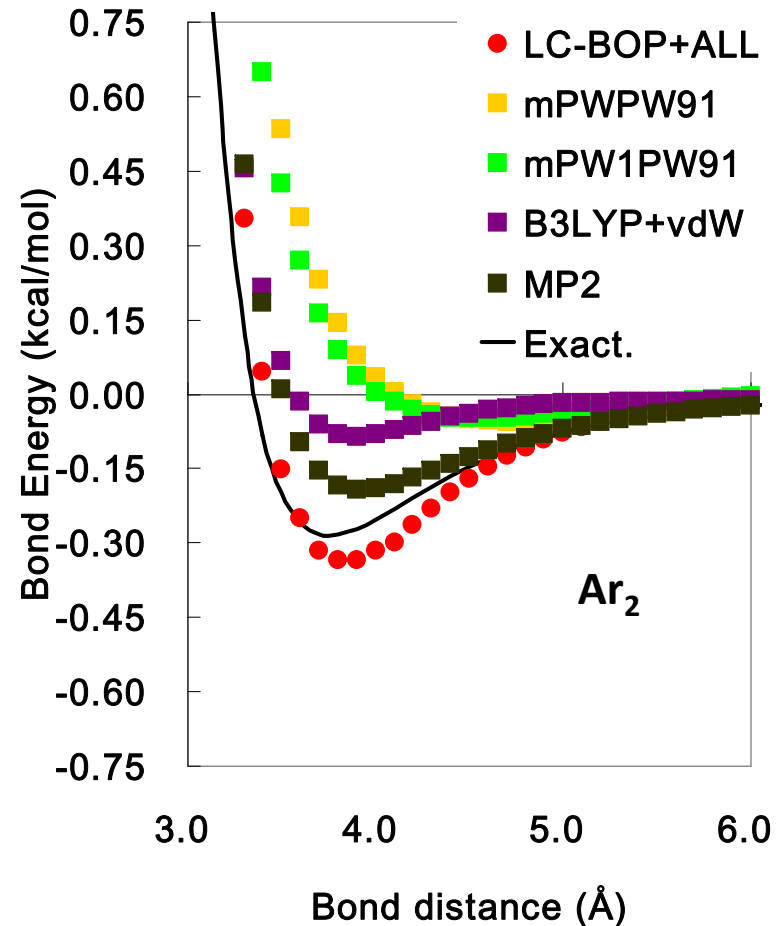
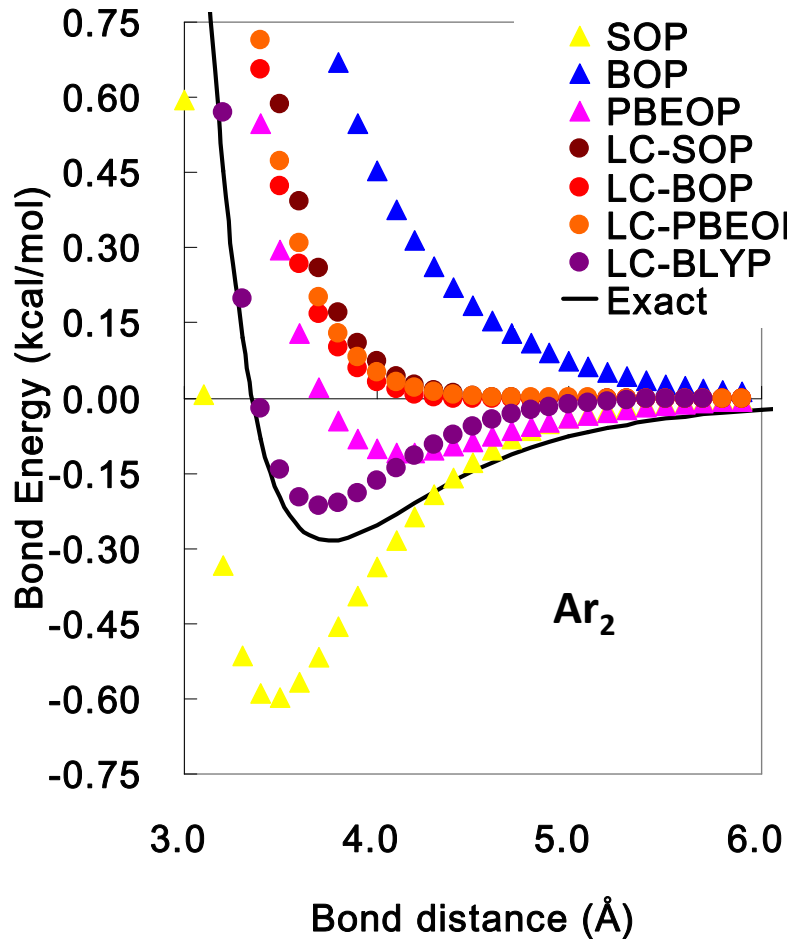
## Reaction barrier energies

[J. Song, T. Hirose, T. Tsuneda, and K. Hirao, J. Chem. Phys. 126, 154105, 2007; O. A. Vydrov and G. E. Scuseria, J. Chem. Phys. 125, 234109, 2006.]

# Van der Waals bonds

Combining LC-DFT with a dispersion functional ALL was applied to the calculations of van der Waals bonds.

[M. Kamiya, T. Tsuneda and K. Hirao, J. Chem. Phys. 117, 6010, 2002.]



# Van der Waals and weak hydrogen bonds

[T. Sato, T. Tsuneda and K. Hirao, J. Chem. Phys. 126, 234114, 2007.]

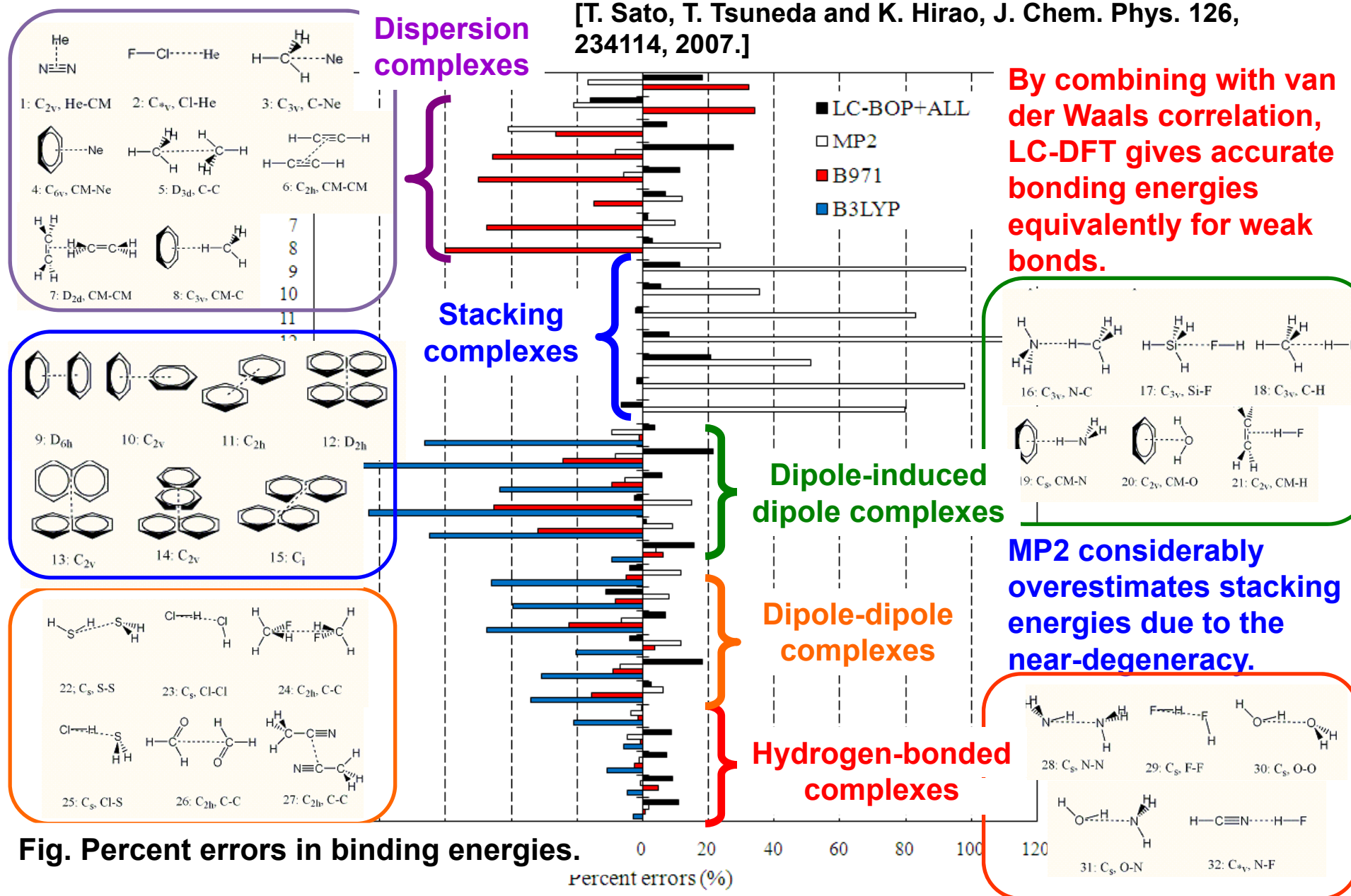
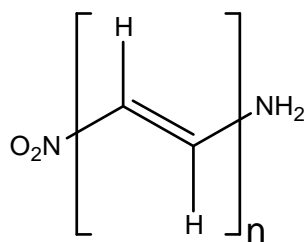
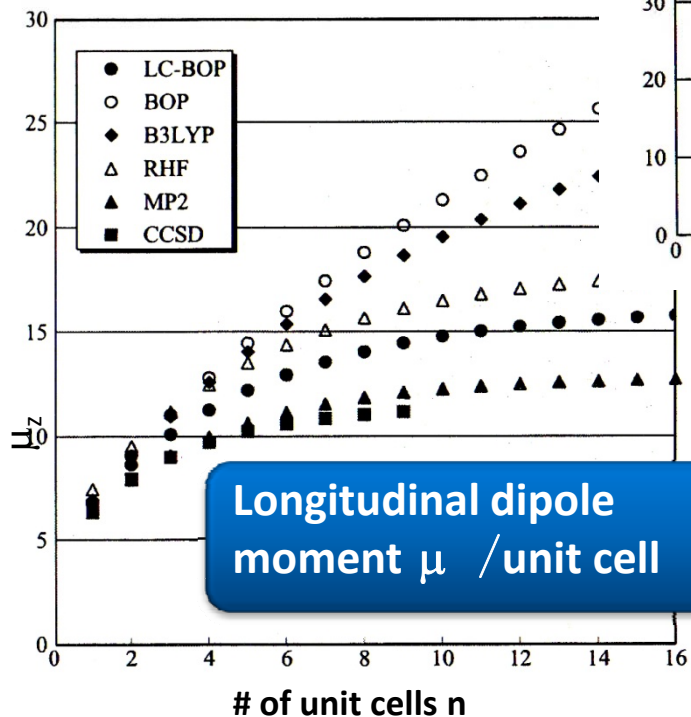


Fig. Percent errors in binding energies.

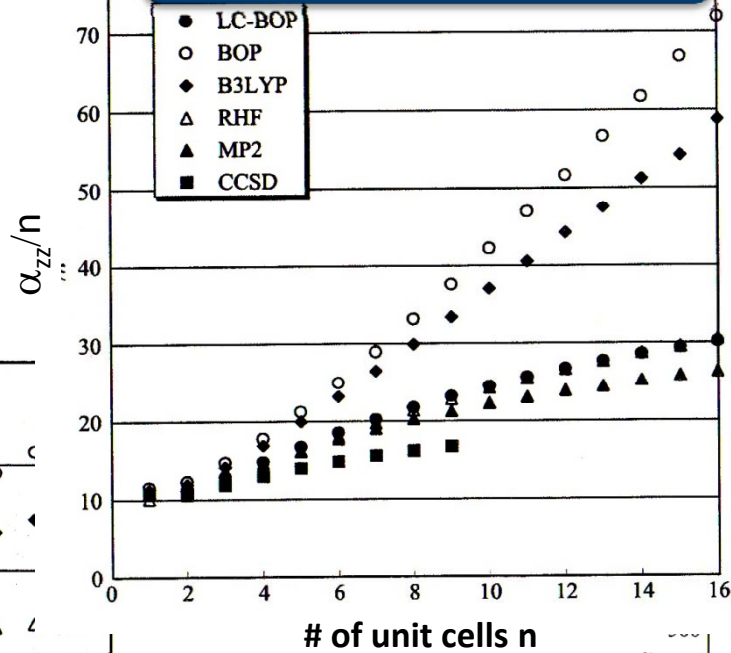
# Optical response properties of long-chain polyenes



$\alpha,\omega$ -nitro,amino-polyacetylene

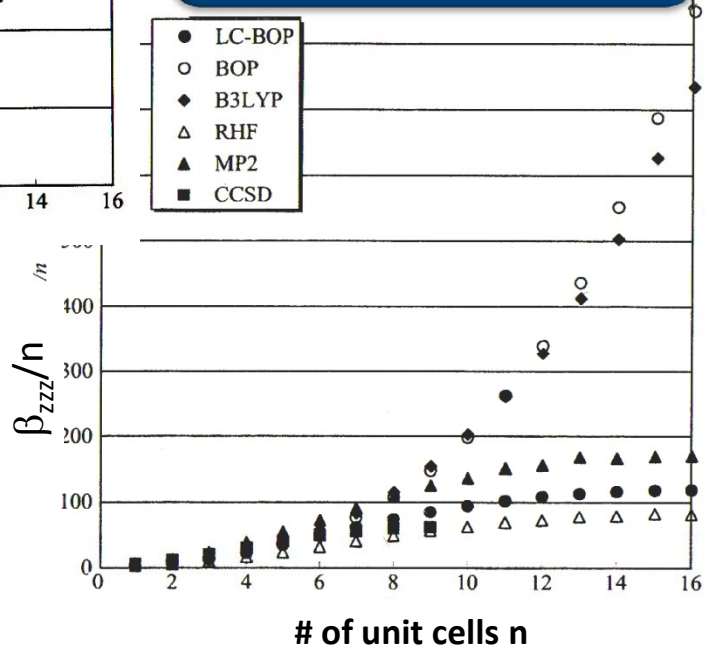


**Longitudinal polarizability  $\alpha_{ZZ}$  / unit cell**



[M. Kamiya, H. Sekino, T. Tsuneda, and K. Hirao, J. Chem. Phys. 122, 234111, 2005.]

**Longitudinal hyperpolarizability  $\beta_{ZZZ}$  / unit cell**

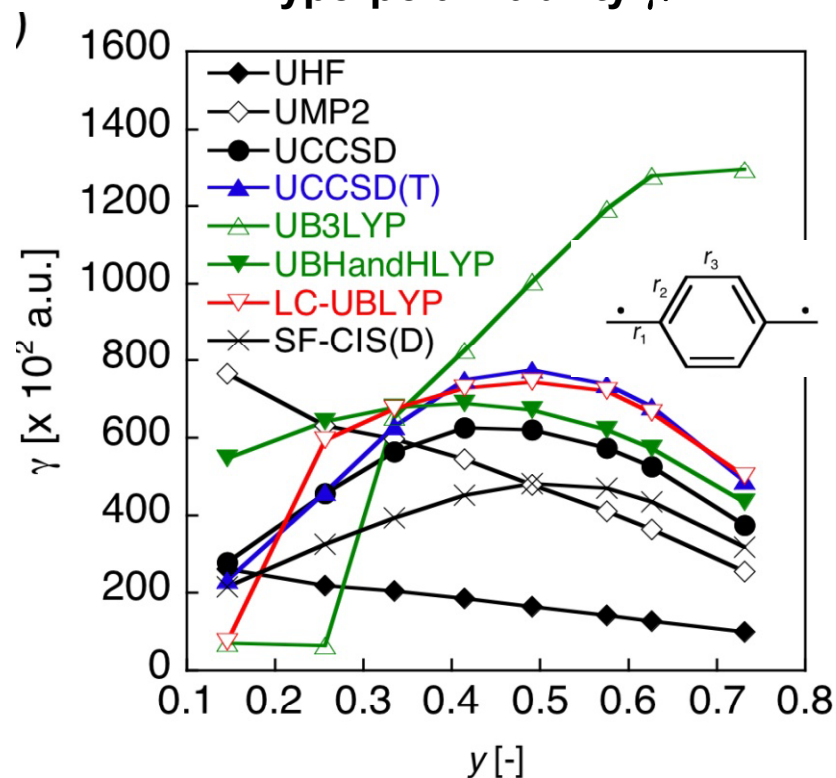


**LC scheme solve the overestimations of optical properties in conventional DFTs.**

# Second hyperpolarizabilities of diradicals

[R. Kishi, S. Bonness, K. Yoneda, H. Takahashi, M. Nakano, E. Botek, B. Champagne, T. Kubo, K. Kamada, K. Ohta, and T. Tsuneda, J. Chem. Phys. 132, 094107, 2010.]

Fig. Diradical character dependence of second hyperpolarizability  $\gamma$ .



$$y = 1 - \frac{2T}{1+T^2}, \quad T = \frac{n_{\text{HOMO}} - n_{\text{LUMO}}}{2}$$

Closed shell  $\rightarrow y=0$ , Diradical  $\rightarrow y=1$

**LC-UBLYP quantitatively reproduces second hyperpolarizabilities of diradicals.**

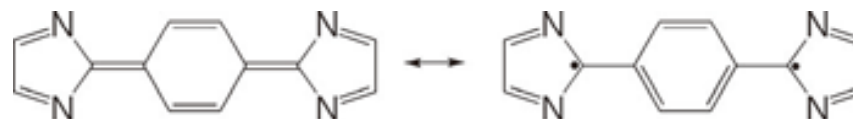


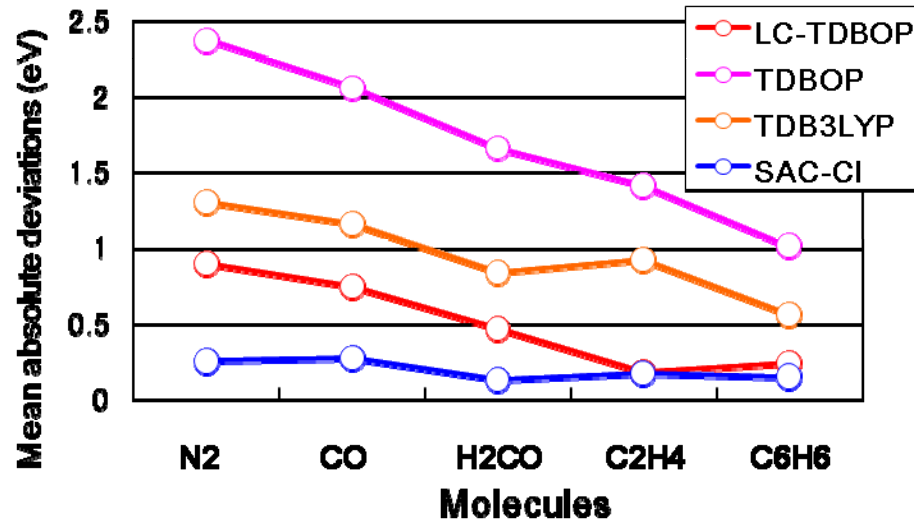
Table. Second hyperpolarizabilities of 1,4-bis-imidazol-2-ylidenecyclohexa-2,5-diene (BI2Y)  $\gamma$  ( $\times 10^2$  a.u.).

Method	6-31G	6-31G*+p
UHF	1736	2002
UMP2	9387	9962
UCCSD	4474	-
UCCSD(T)	5244	-
UBLYP	-129	-298
UB3LYP	-377	-472
LC-UBLYP	4310	6019

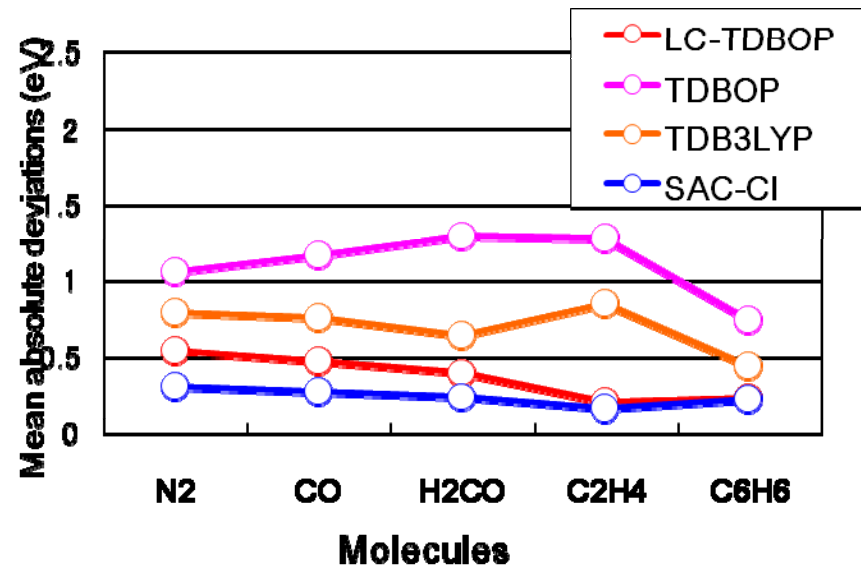


# Electronic spectra in TDDFT

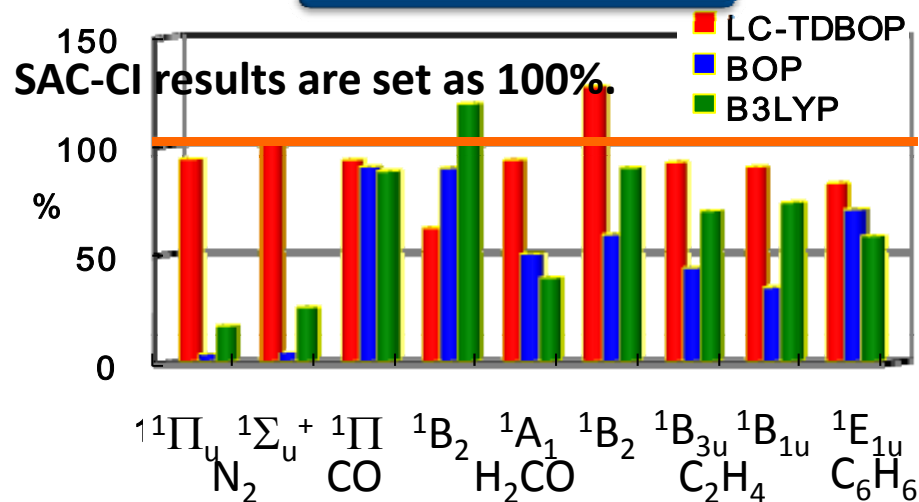
Rydberg excitation energies



Valence & Rydberg excitation energies



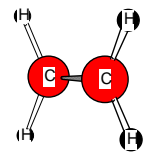
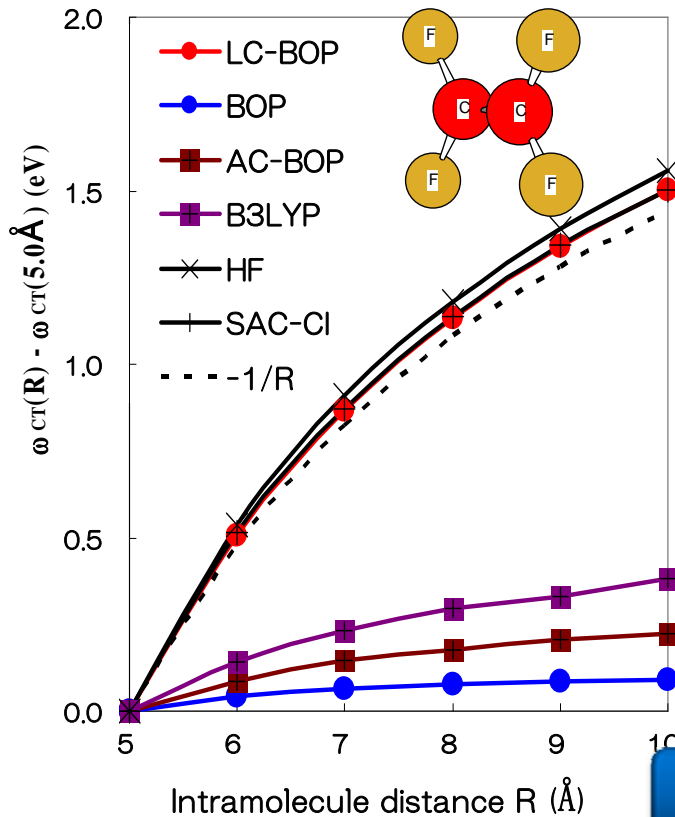
Oscillator strengths



**LC scheme drastically improves Rydberg excitation energies & oscillator strengths underestimated in time-dependent DFT.**

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

# Charge transfer excitations in TDDFT

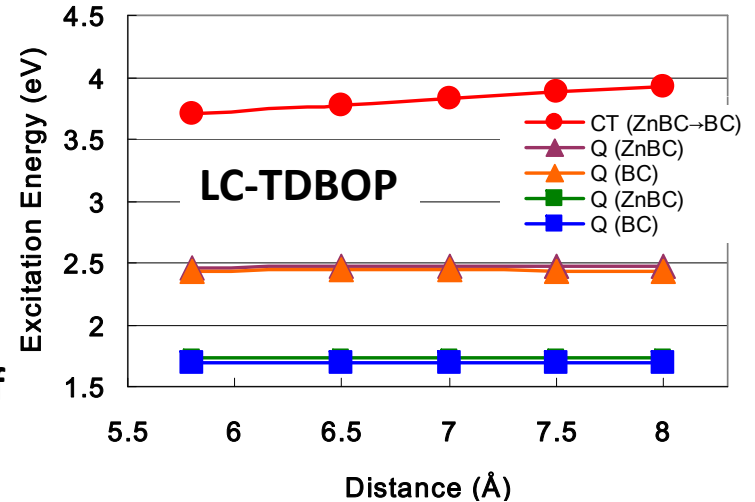
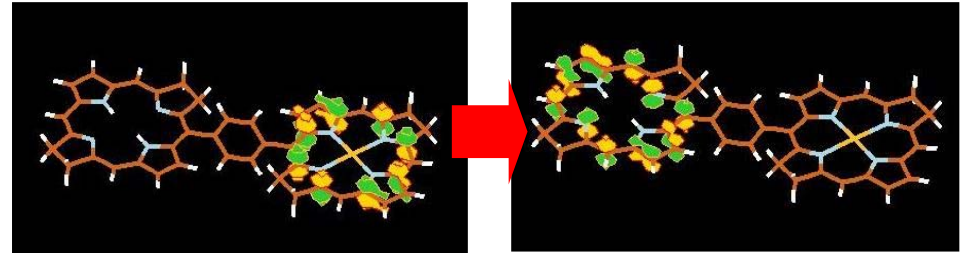


CT energies

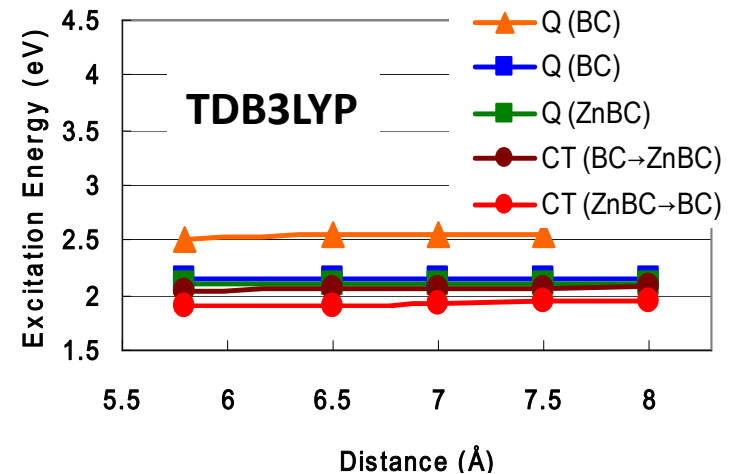
Fig. CT energies of ethylene-tetrafluoroethylene.

Fig. The lowest excitation energies of Zn-bacteriochlorin-bacteriochlorin.

Dissociation limit



TDB3LYP



	Exp.	LC-TDBOP	TDB3LYP	SAC-CI
$E_{CT}(R=\infty)$	12.5	12.43	7.42	14.43

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



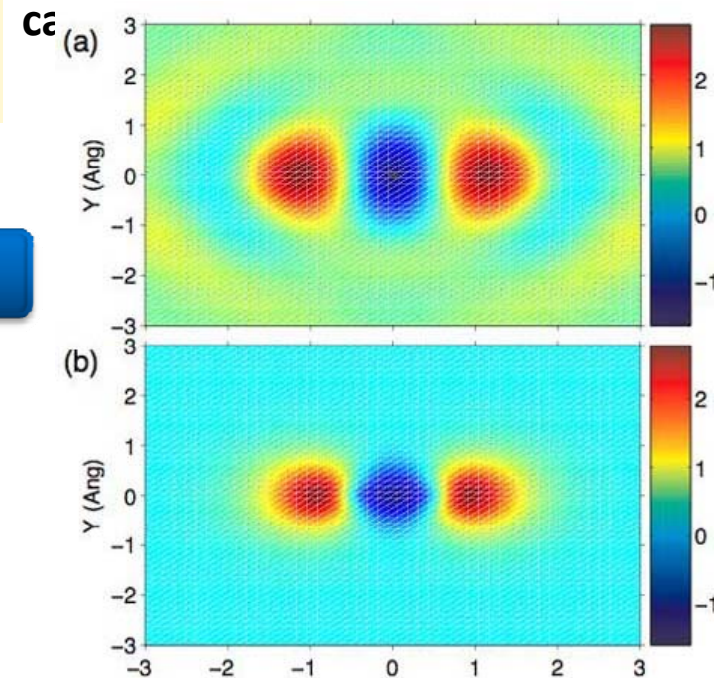
## 3. Orbital energies

# Molecular orbitals

## Molecular orbitals

MOs are expressed as a linear combination of atomic orbitals.

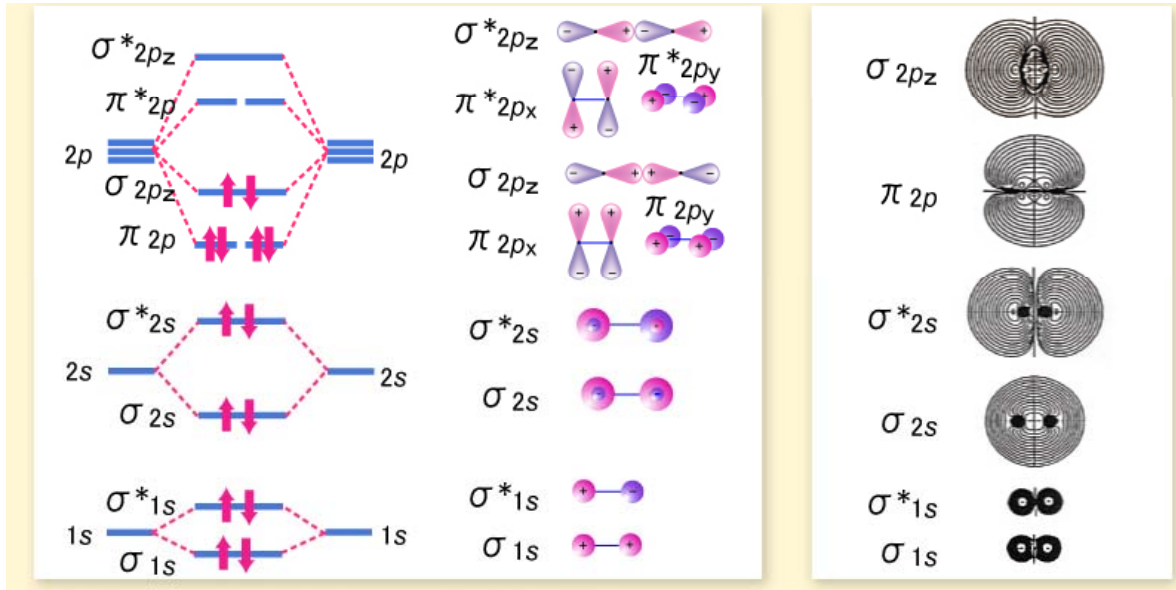
MOs have been taken as unobservable (unphysical) due to the free orbital rotation (unitary transformation) in HF



## Molecular orbital imaging

MO imaging of  $N_2$  molecule.  
 (a) experimental, (b) QC calculation. [Itatani et al., Nature, 432, 867, 2004.]

By experimental observations, MOs take increasing attentions in the field of QC.



# Reaction analyses on molecular orbitals

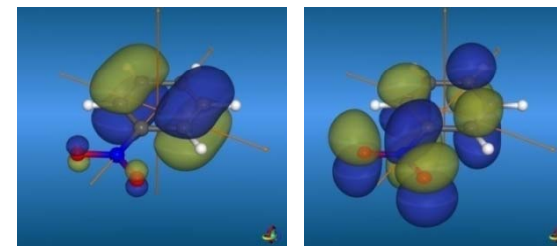
## Frontier orbital theory (1952)



K. Fukui

- Substitution reactions of aromatic compounds :
- (1) **Electrophilic** reactions target **HOMO density**.
  - (2) **Nucleophilic** reactions target **LUMO density**.
  - (3) **Radical** reactions proceed as **the sum of (1) & (2)**.

Electronic distribution of frontier orbitals of nitrobenzene.



HOMO

LUMO

## Woodward-Hoffmann rule (1965)



R. B. Woodward

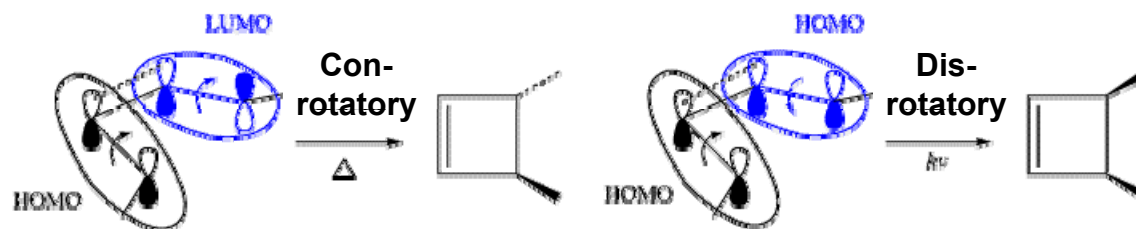


R. Hoffmann

Woodward & Hoffmann succeeded to explain experimental results by MO symmetry.

MOs are usually used in experiments to analyze and design chemical reactions.

Cyclization  
(Ring-closing)  
reactions

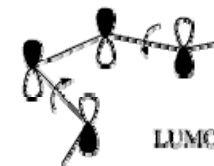


*n* Rules

Woodward-Hoffmann rule



HOMO



LUMO

# Reaction analyses on orbital energies

## Koopmans' theorem

Without SCF (orbital rotation), Hartree-Fock calculations give **occupied orbital energies as minus corresponding IP & unoccupied orbital energies as minus corresponding EA.**

No conventional theory including DFT satisfies this theorem.

Fukui function: HOMO & LUMO densities

## Maximum hardness rule

Fukui functions of *p*-Cl-benzonitrile oxide.

[A. Ponti & G. Molteni, Chem. Eur. J., 1156, 2006.]

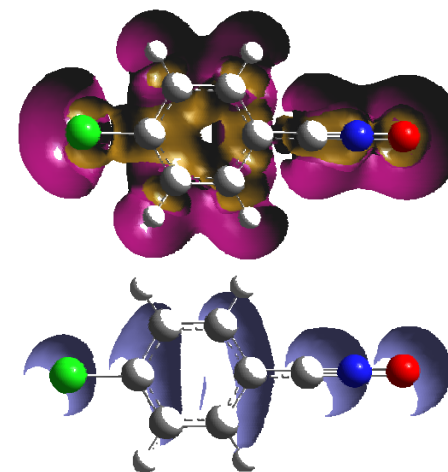
A reaction index using orbital energies.

As HOMO-LUMO gaps increasing, molecules become stabilized.

⇒ **Reactions proceed to increase HOMO-LUMO gaps.**

Global hardness:

$$\eta = \frac{1}{2} \left[ \frac{\partial^2 E}{\partial N^2} \right]_v = \frac{1}{2} \left[ \frac{\partial \mu}{\partial N} \right]_v \quad \longrightarrow \quad \eta \approx \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2}$$

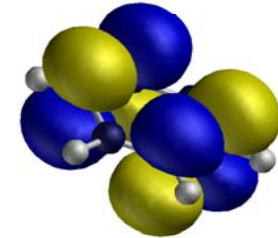


# Conditions for reproducing orbital energies

Many studies have been reported to identify the cause why orbital energy gaps are usually underestimated especially on the context of band gaps.

Kohn-Sham equation:

$$\left( \hat{h} + \hat{J} + v_{xc} \right) \phi_i = \varepsilon_i \phi_i$$



Poor orbital energy gaps are originated from **the discontinuity of exchange-correlation potentials** [Perdew, Parr, Levy, & Balduz, Phys. Rev. Lett. 49, 1691, 1982.]

$$\Delta_{xc} = v_{xc}^{n+\Delta n} - v_{xc}^{n-\Delta n} = \text{const.} > 0 \quad \Longrightarrow \quad \Delta_{xc} = \{ \text{IP} - \text{EA} \} - \{ \varepsilon_{n+1}(n) - \varepsilon_n(n) \}$$

$\Rightarrow$  For  $\Delta_{xc}=0$ , **HOMO & LUMO energies correspond to minus IP & EA, respectively.**  
[Perdew & Levy, Phys. Rev. B 56, 1602, 1997; Casida, Phys. Rev. B 59, 4694, 1999.]

$\Delta_{xc}$  is attributed to **the energy deviation of outermost orbital energies.**  
[Sham & Schlüter, Phys. Rev. B 32, 3883, 1985.]

$$\Delta_{xc} = \varepsilon_{n+1}(n+1) - \varepsilon_{n+1}(n)$$

**Orbital energies are not varied for outermost orbitals.**

# Koopmans' Ionization Potentials

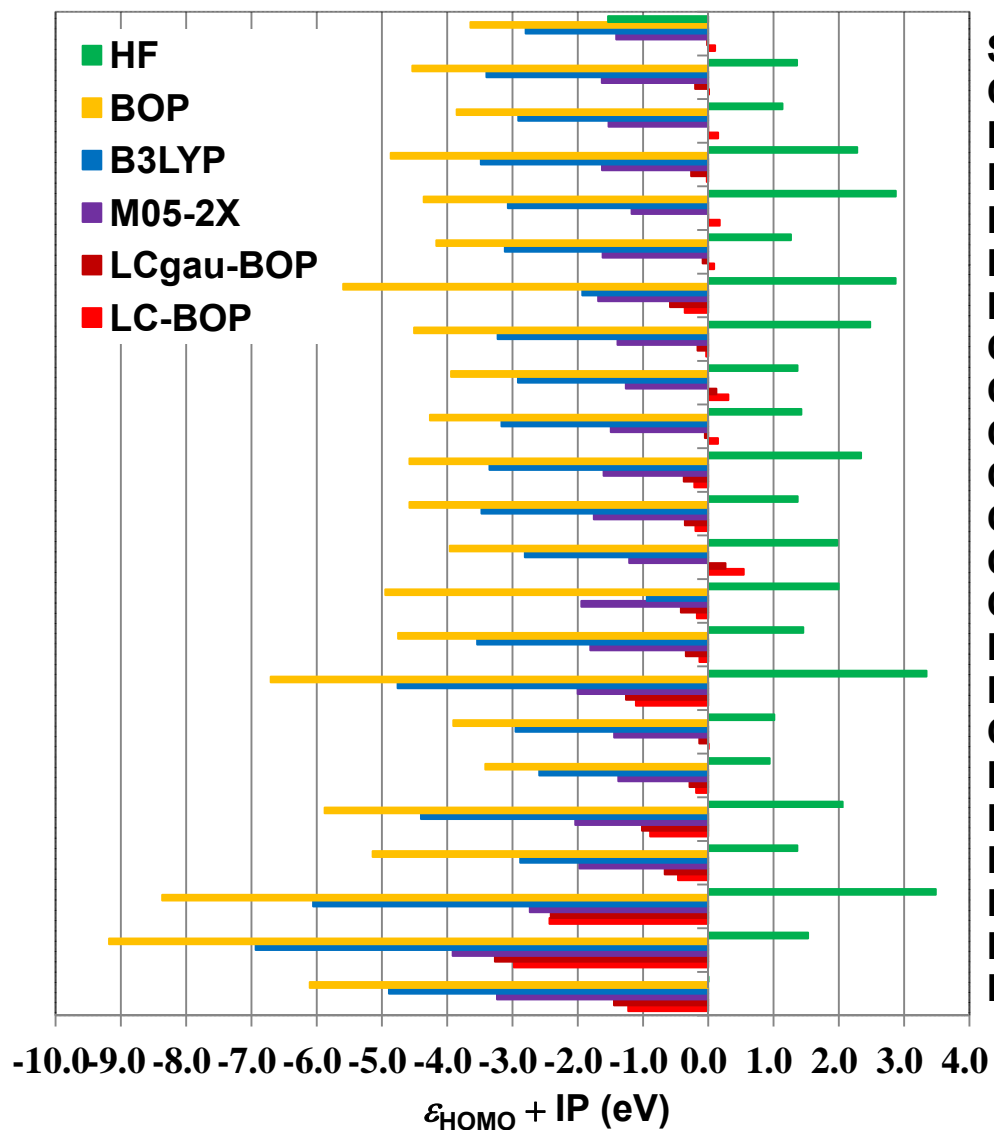


Fig. Deviations of HOMO energies from the minus vertical IPs ( $\epsilon_{\text{HOMO}} + \text{IP}$ ) with aug-cc-pVQZ basis set.

LC-DFT calculations give  $\epsilon_{\text{HOMO}}$  close to  $-\text{IP}$  except for H, He & Ne atoms.

The  $\epsilon_{\text{HOMO}}$  of other functionals are significantly lower than  $-\text{IP}$ .

LC-DFT approximately satisfies Koopmans' theorem.

The  $\epsilon_{\text{HOMO}}$  of HF are larger than  $-\text{IP}$ .  
 $\Rightarrow$  HF does not obey Koopmans' theorem when the orbital relaxation is not neglected.

Method	MAE
LC-BOP	0.266
LCgau	0.332
M05-2X	1.600
B3LYP	3.087
BOP	4.580
HF	1.823

# Koopmans' Electron Affinities

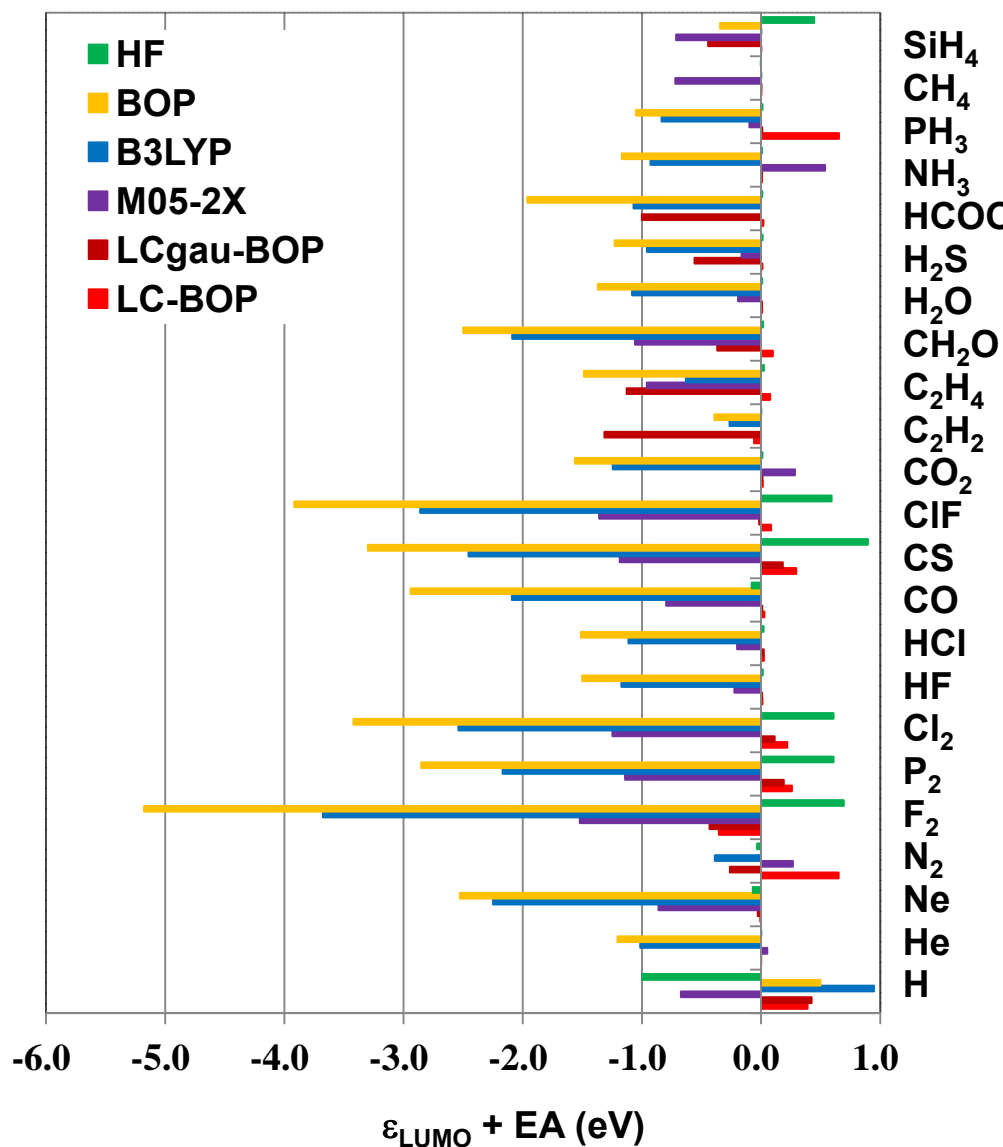


Fig. Deviations of LUMO energies from the minus vertical EAs ( $\epsilon_{\text{LUMO}} + \text{EA}$ ) with aug-cc-pVQZ basis set.

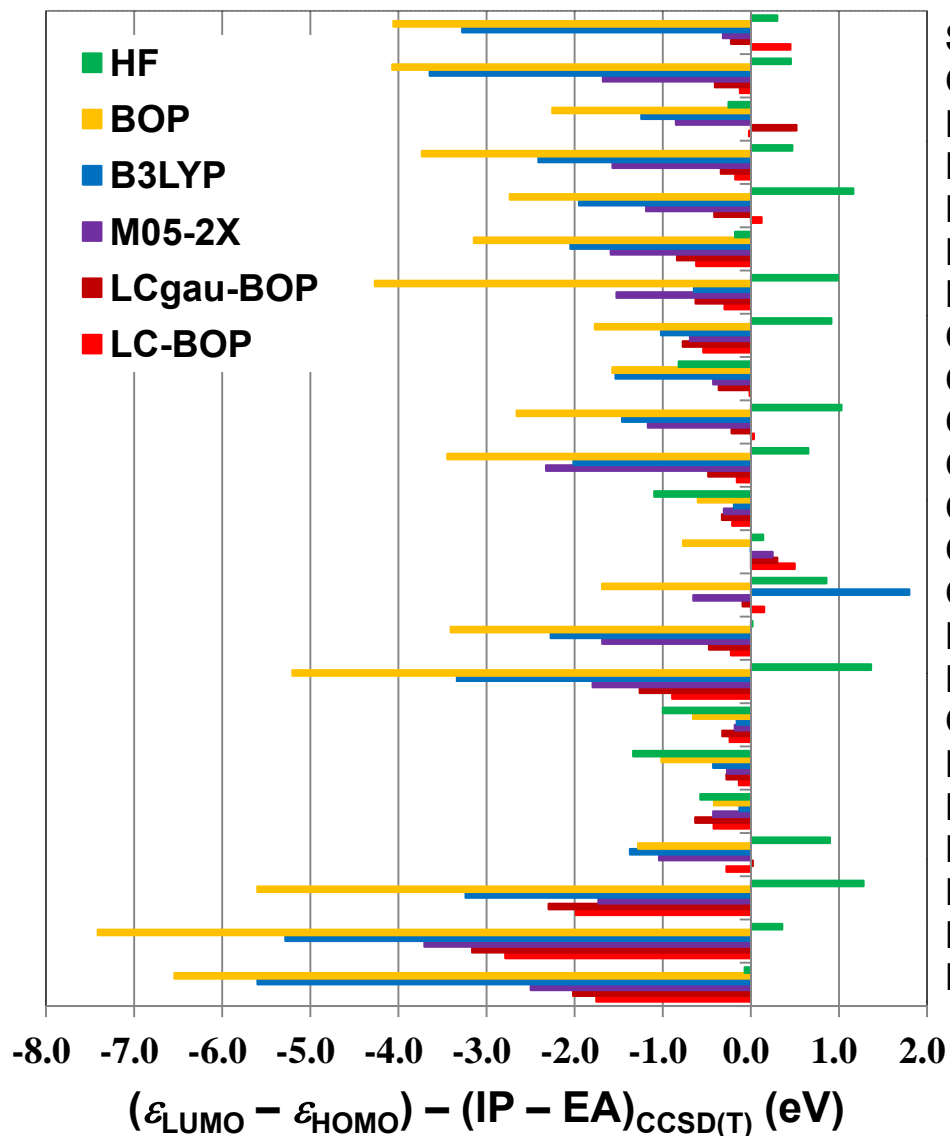
The  $\epsilon_{\text{LUMO}}$  of LC-DFT calculations are very close to  $-\text{EA}$  for all systems.

The  $\epsilon_{\text{LUMO}}$  of other functionals are considerably lower than  $-\text{EA}$ .

LC functionals satisfy Koopmans' theorem even for LUMO.

Method	MAE
LC-BOP	0.142
LCgau	0.115
M05-2X	0.618
B3LYP	1.370
BOP	2.116
HF	0.287

# HOMO-LUMO gaps



SiH<sub>4</sub> CH<sub>4</sub> PH<sub>3</sub> NH<sub>3</sub> HCOOH H<sub>2</sub>S H<sub>2</sub>O CH<sub>2</sub>O C<sub>2</sub>H<sub>4</sub> C<sub>2</sub>H<sub>2</sub> CO<sub>2</sub> ClF CS CO HCl HF Cl<sub>2</sub> P<sub>2</sub> F<sub>2</sub> N<sub>2</sub> Ne He H

Fig. Deviations of HOMO-LUMO gaps from the IP – EA values given by CCSD(T)/CCSD/aug-cc-pVQZ.

The gaps of LC functionals are very close to IP – EA of CCSD(T) except for H, He & Ne atoms.

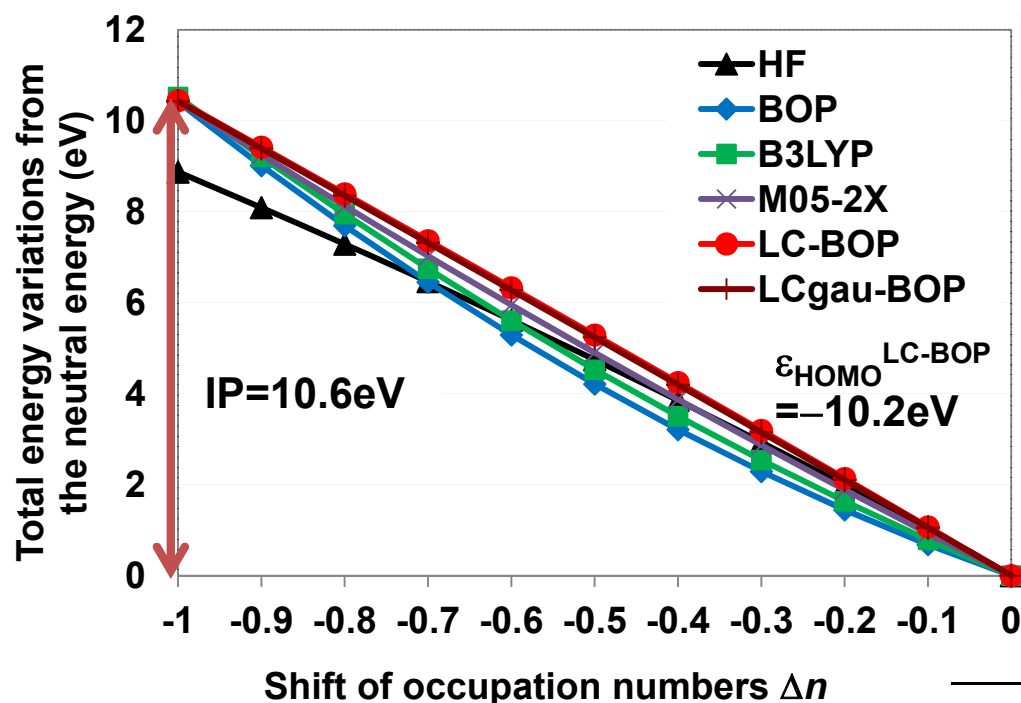
For other functionals, the HOMO-LUMO gaps are significantly underestimated for most molecules.

LC functionals quantitatively reproduces orbital energies except for H, He & Ne atoms.

Method	MAE
LC-BOP	0.282
LCgau	0.447
M05-2X	0.997
B3LYP	1.439
BOP	2.514
HF	0.727



# Fractional occupations to cation



## Energies of fractionally-occupied systems

Fig. Total energies of  $C_2H_4$  calculated for varying occupation numbers of HOMO to  $C_2H_4^+$  cation.

Only LC functionals give total energies very close to a straight line, while other functionals give curved lines.

Table. Orbital energies of  $C_2H_4$  &  $C_2H_4^+$  compared to the total energy gradients.

## Janak's theorem

All functionals nearly satisfy Janak's theorem:

$$\mu = \partial E / \partial n_i = \varepsilon_i$$

To make  $\partial E / \partial n(0)$  identical to  $-IP$ , a straight line should be given for the energy.

$\varepsilon_{HOMO}$  of the neutrals should be identical to  $\varepsilon_{LUMO}$  of the cations.

= Sham-Schlüter's argument

Method	$C_2H_4^+$		$C_2H_4$	
	$\varepsilon_{LUMO}$	$\partial E / \partial n(-1)$	$\partial E / \partial n(0)$	$\varepsilon_{HOMO}$
LC-BOP	-10.22	-10.17	-10.71	-10.68
B3LYP	-13.48	-13.46	-7.59	-7.60
BOP	-14.40	-14.39	-6.43	-6.45
HF	-7.71	-7.61	-10.11	-10.22
M05-2X	-11.92	-11.67	-9.17	-9.16
LCgau	-10.37	-10.33	-10.53	-10.56

# Fractional occupations to anion

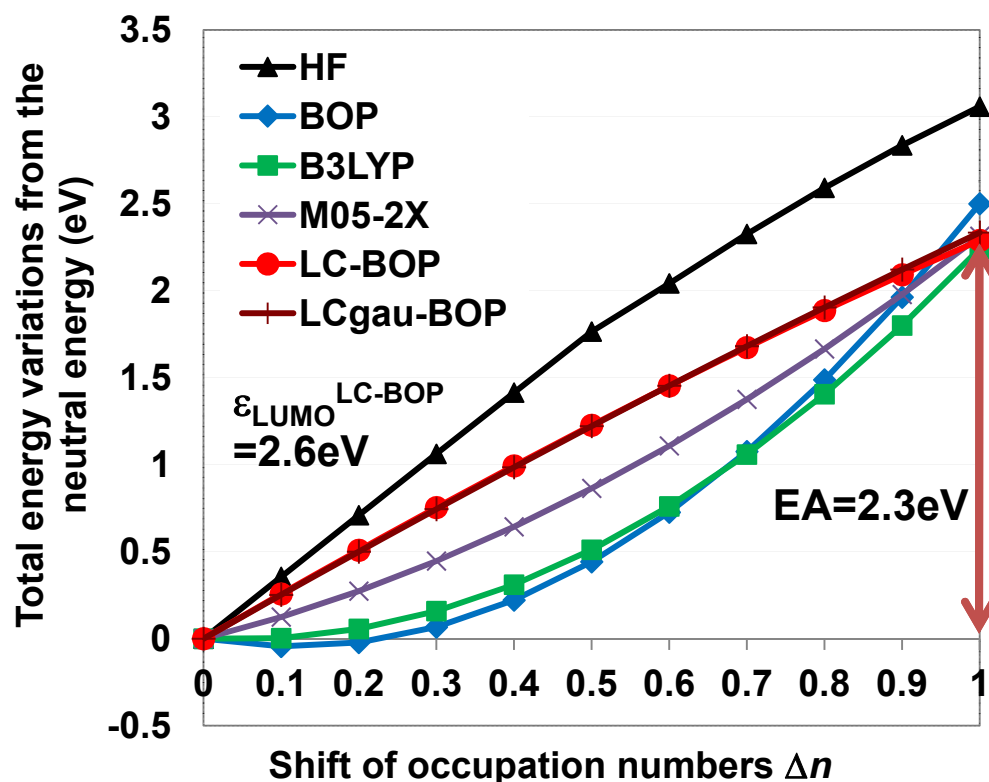


Fig. Total energies of  $\text{C}_2\text{H}_4$  calculated for varying occupations of HOMO to  $\text{C}_2\text{H}_4^-$  anion.

For anions, similar curves are given.

LC functionals always give  $\partial^2 E / \partial n^2$  close to zero.

Table. Orbital energies of  $\text{C}_2\text{H}_4$  &  $\text{C}_2\text{H}_4^-$  compared to the total energy gradients.

This also backs up that LC functionals satisfy Koopmans' theorem approximately.

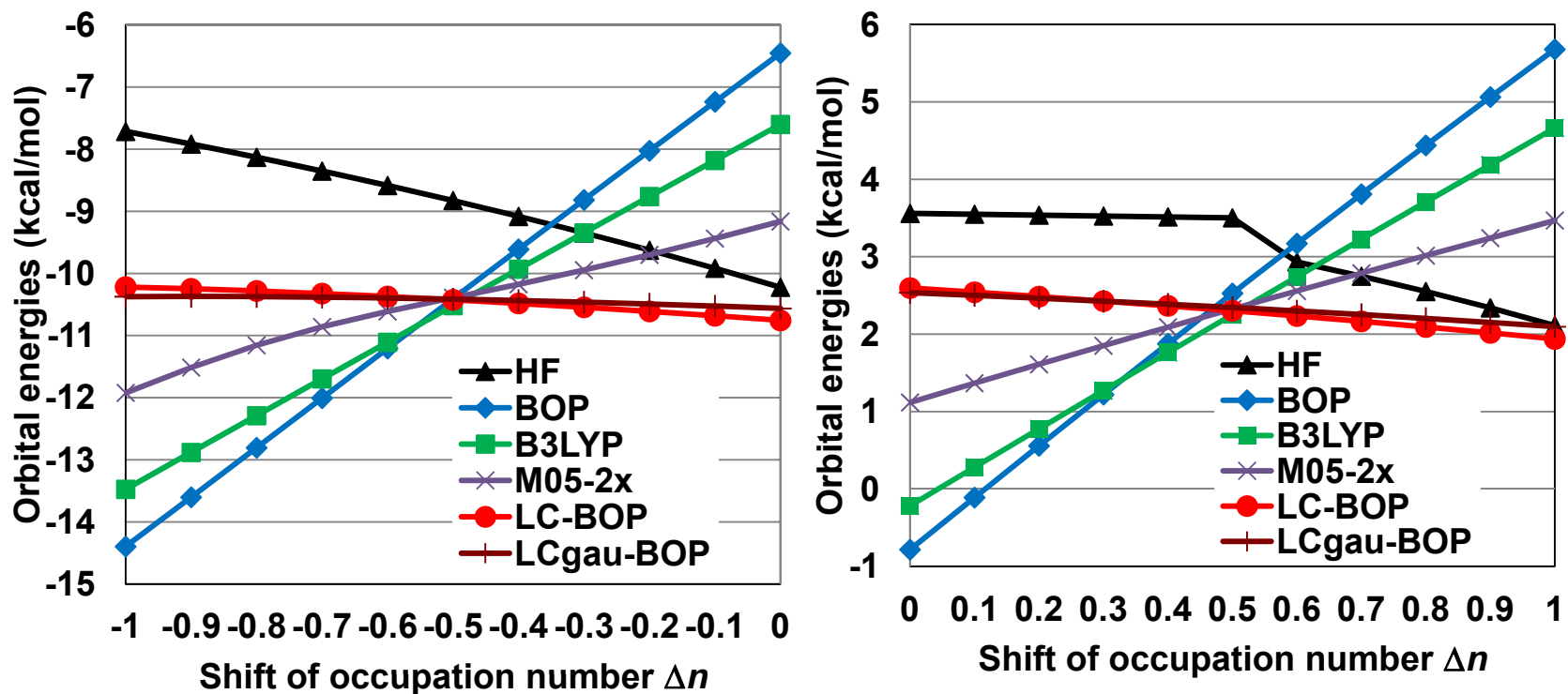
Hybrid B3LYP & pure GGA BOP provide negative orbital energies for  $\text{C}_2\text{H}_4$ .

$\epsilon_{\text{LUMO}}$  of neutrals should also be identical to  $\epsilon_{\text{HOMO}}$  of the anions.

Method	$\text{C}_2\text{H}_4$		$\text{C}_2\text{H}_4^-$	
	$\epsilon_{\text{LUMO}}$	$\partial E / \partial n(0)$	$\partial E / \partial n(1)$	$\epsilon_{\text{HOMO}}$
LC-BOP	2.60	2.62	1.97	1.94
B3LYP	-0.22	-0.20	4.69	4.66
BOP	-0.78	-0.72	5.74	5.68
HF	3.56	3.95	2.23	2.11
M05-2X	1.12	1.15	3.49	3.47
LCgau	2.54	2.56	1.97	2.10

# Orbital energies for fractional occupations

Fig. Orbital energies of  $C_2H_4$  calculated for varying occupation numbers of HOMO to  $C_2H_4$  for  $-1 < \Delta n < 0$  (left) and for  $0 < \Delta n < 1$  (right).



**LC functionals give almost constant orbital energies for fractional occupations.**

**Other functionals provide positive gradients raising  $\epsilon$  as increasing electrons.**

**HF gives negative gradients lowering  $\epsilon$  due to the lack of electron correlation.**

# Orbital energy derivatives

## Orbital energy derivative

The derivative of the orbital energy in terms of the fractional occupation:

$$\frac{\delta \varepsilon_i}{\delta n_i} = \iint \phi_i^*(\mathbf{r}) \phi_i^*(\mathbf{r}') \left[ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}}{\delta \rho} \right] \phi_i(\mathbf{r}) \phi_i(\mathbf{r}') d^3 \mathbf{r} d^3 \mathbf{r}'$$

Only the discrepancy in the self-interaction through the sum of Coulomb and exchange-correlation potential derivative  $dv_{xc}/d\rho$  directly affects the dependence of orbital energies on fractional occupations.

## Coulomb self-interaction potential

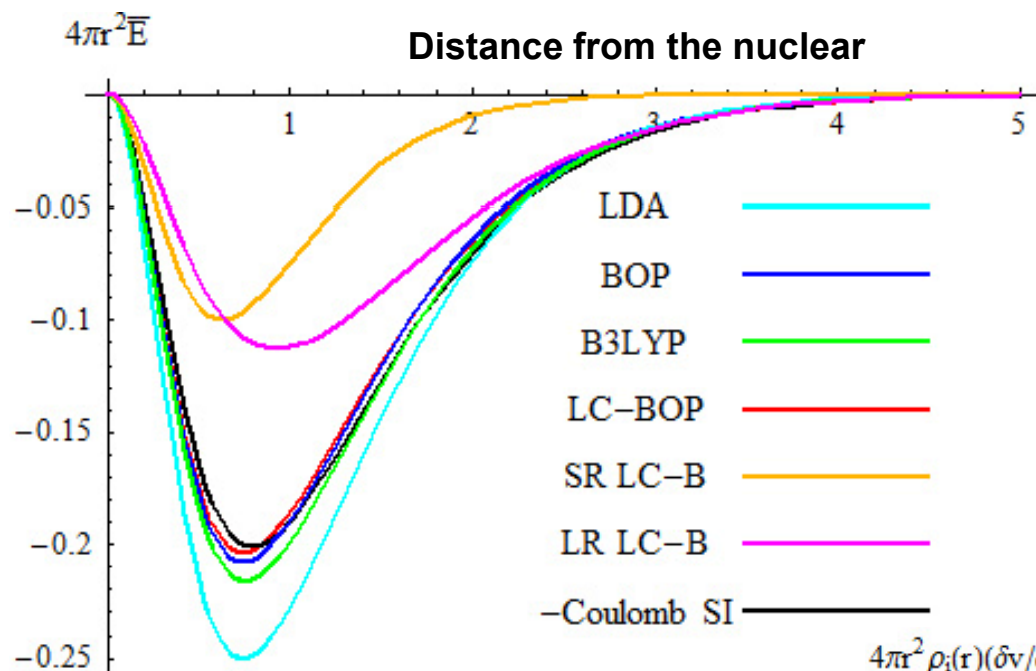
A normalized Gaussian-type function:  $\phi_i(\mathbf{r}) = \sqrt{\frac{\zeta_i}{\pi}} \exp(-\zeta_i r^2)$

⇒ The Coulomb self-interaction potential approximated:

$$\begin{aligned} \hat{j}^{\text{sl}} &= \left( \frac{\zeta_i}{\pi} \right) \int \frac{\exp[-2\zeta_i (r^2 + r_{12}^2 + 2rr_{12} \cos \theta)]}{r_{12}} d^3 \mathbf{r}_{12} \\ &= r^{-1} \exp(-2\zeta_i r^2) \int_0^\infty r_{12}^{-1} \exp[-2\zeta_i r_{12}^2] \sinh[4\zeta_i r r_{12}] dr_{12} \end{aligned}$$

This form gives the accurate Coulomb energy for H atom.

# Self-interaction energies



Exchange self-interaction energy

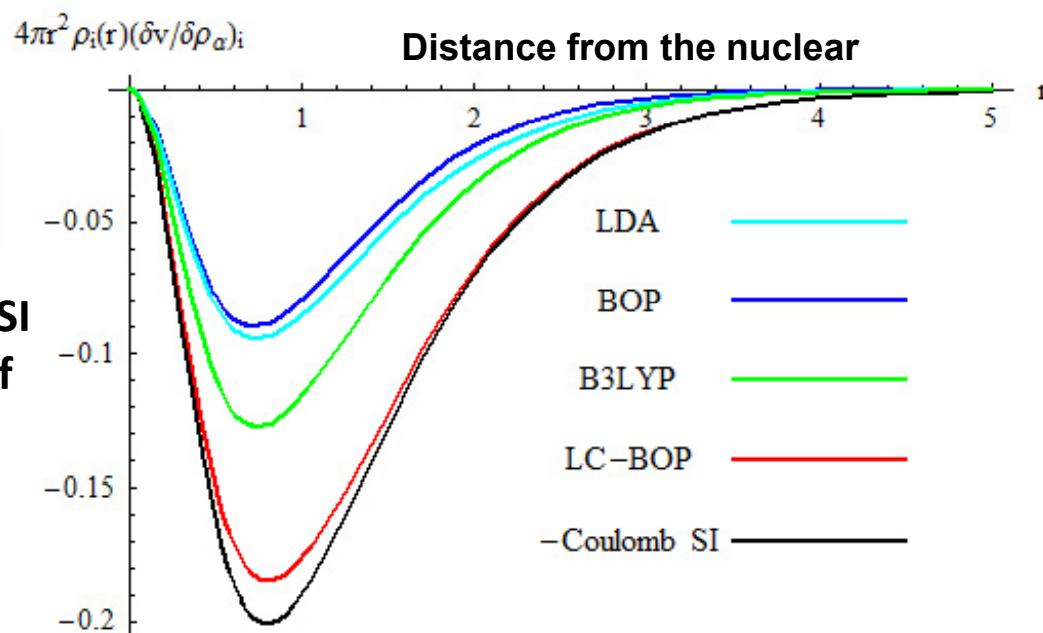
Fig. The integral kernels of the exchange functional SI energies of HOMO of H atom.

The exchange functional SI energies are cancelled out with the Coulomb SI energy for all functionals but LDA.

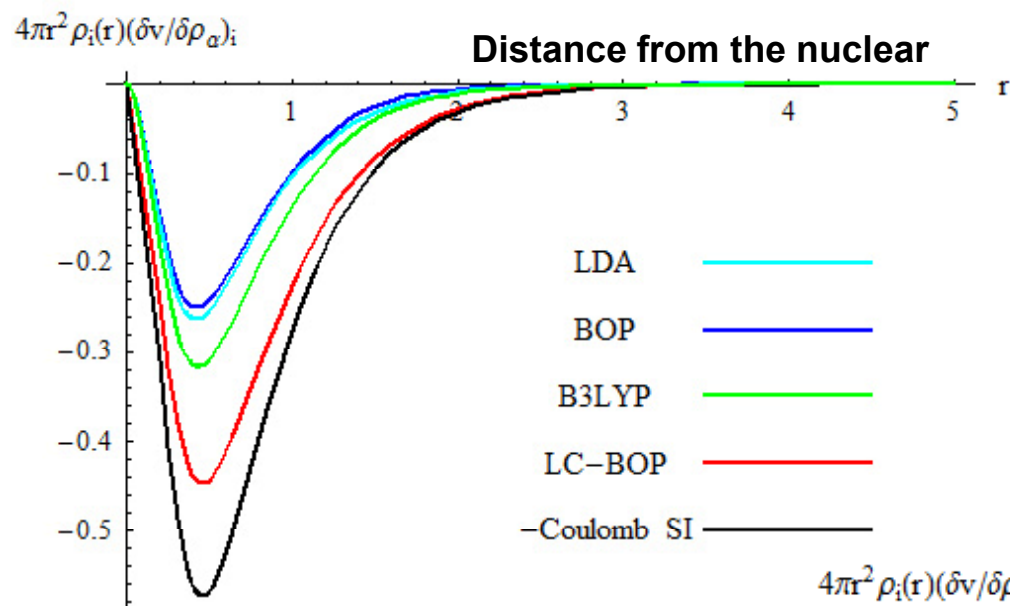
Exchange self-interaction energy through potential derivative

Fig. The integral kernels of the exchange SI energies through the  $dv_x/d\rho$  of HOMO of H atom.

Only LC-DFT gives a reasonable exchange SI energy even through  $dv_x/d\rho$ .



# Why orbital energy reproducibilities are different?



Poorly-given  $\epsilon_{\text{HOMO}}$  or He atom

Fig. The integral kernels of the exchange SI energies through the  $dv_x/d\rho$  for the HOMO of He atom.

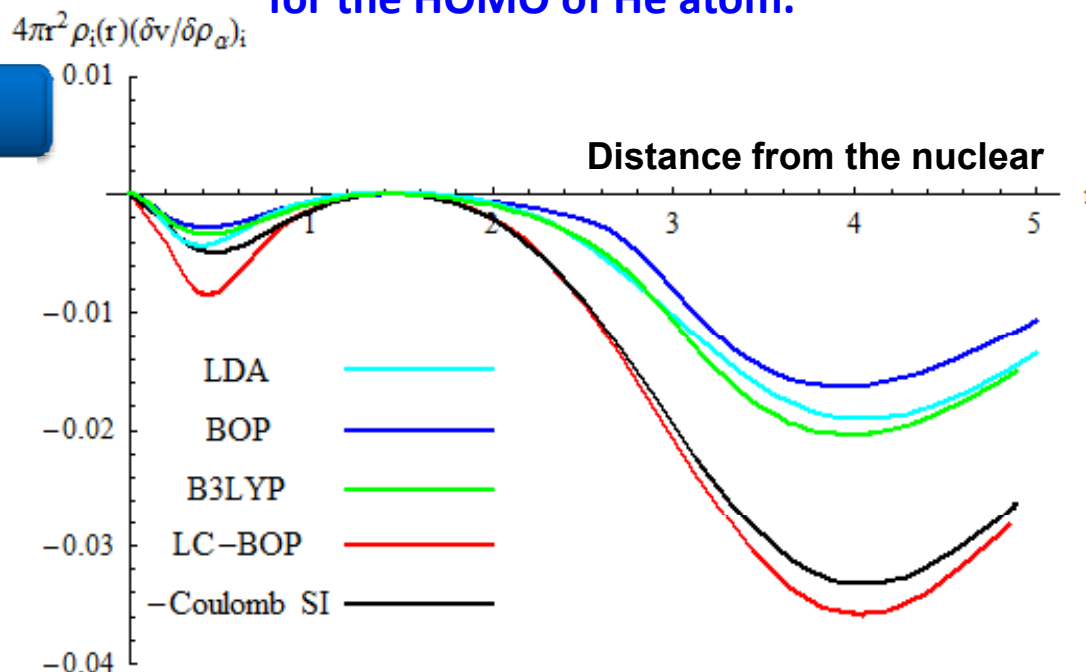
Even LC-BOP slightly underestimates the exchange SI energy through  $dv_x/d\rho$  for the HOMO of He atom.

Accurately-given  $\epsilon_{\text{LUMO}}$  or He atom

Fig. The integral kernels of the exchange SI energies through the  $dv_x/d\rho$  of the LUMO of He atom.

$$\epsilon_{\text{LUMO}} = -EA = 2.653 \text{ eV}$$

Only for LC-BOP, the SI error is cancelled out even for the exchange SI through the potential derivative.



# Conclusions

## Long-range corrected (LC) DFT

Applicabilities of LC-DFT are reviewed.

LC-DFT has solved or improved various chemical properties that conventional DFTs have poorly given: van der Waals bonds, charge transfers, optical properties, reaction barriers and enthalpies, and so on.

## Orbital energies

LC-DFT also enables us to calculate orbital energies quantitatively for the first time. To reproduce orbital energies quantitatively by DFT, self-interaction energies through the potential derivatives should be excluded in exchange functionals. LC may be the best strategy to remove the self-interaction energies. LC-DFT suggests a new reaction analysis based on orbital energies.

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