

# **AICS CAFÉ:**

## **Development of new DFT functional applicable to large systems**

RIKEN AICS

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**2012. 06. 01.**

# What is Quantum Chemistry?

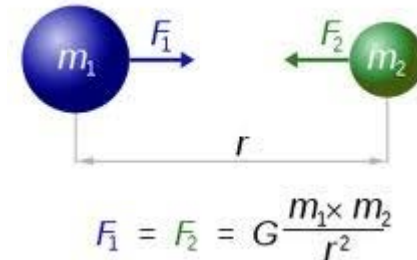
- Visible system

( m, cm, g, ... )



Classical mechanics (Newton's law)

$$F = m \frac{d^2x}{dt^2}, \dots$$



- Invisible system

( $10^{-10}\text{m} = 1\text{\AA}$ , ....)



Quantum mechanics

Schrodinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E \psi(\mathbf{r})$$

# Schrodinger Equation

$$H(r)\Psi(r) = E\Psi(r)$$

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \Psi(r) = E\Psi(r)$$

$$\text{where } \nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(r) + V(r)\Psi(r) = E\Psi(r)$$

$$\text{and } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- The solution of Schrodinger equation is wave function ( $\Psi$ ).
- Quantum Chemistry is to solve Schrodinger equation of molecule or solid.
- Exact wave function ( $\Psi$ ) of some system (if we can know) provides many pragmatic chemical information of matter, such as energy, structure, spectrum, color, dipole moment, (hyper-)polarizability....



**Erwin Schrodinger**

# Schrodinger Equation

- The Schrodinger equation for the hydrogen atom can be solved exactly.
- $|\Psi| \times |\Psi|$  means an electron density ( $\rho$ ) of the system.
- The concept of orbital.
- However, Schrodinger equation is **nonlinear 2<sup>nd</sup> differential equation**. It is impossible to solve it exactly if the system has more than 2 electrons (H atom, He<sup>+</sup>, H<sub>2</sub><sup>+</sup>).
- To solve the Schrodinger equation of general system, inevitably we should use some approximations.
- One of the most important approximation methods is Hartree-Fock approximation.

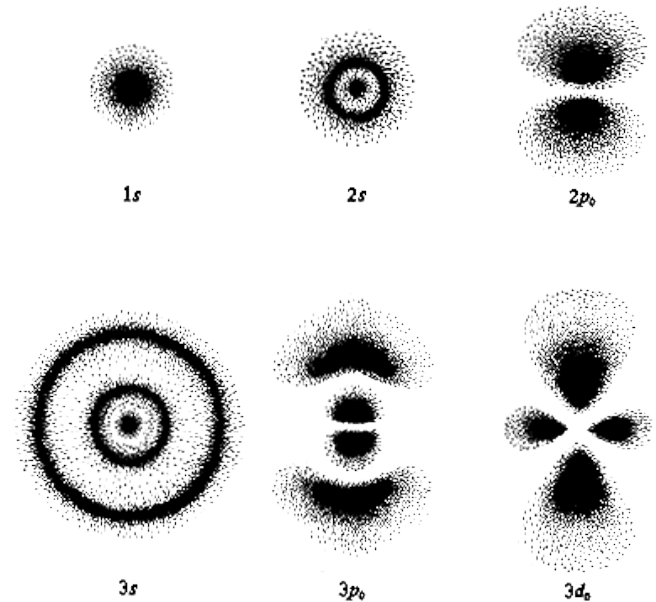


Figure 6-12. Probability density plots of some hydrogen atomic orbitals. The density of the dots represents the probability of finding the electron in that region.  
© 1983 University Science Books; "Quantum Chemistry" by Donald A. McQuarrie

# Hartree-Fock (HF) method

$$\Psi_0 = \Psi_{\text{HF}} = \Psi^{\text{SD}}(r_1, r_2, \dots, r_N) = (N!)^{-1/2} \begin{vmatrix} \Phi_1(x_1) & \Phi_2(x_1) & \dots & \Phi_N(x_1) \\ \Phi_1(x_2) & \Phi_2(x_2) & \dots & \Phi_N(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \Phi_1(x_N) & \Phi_2(x_N) & \dots & \Phi_N(x_N) \end{vmatrix}$$

$$\langle \Phi_i | \Phi_j \rangle = \delta_{ij}$$

**FC=SCε**

$$H = \underbrace{-\sum_{i=1}^N \frac{1}{2} \nabla_i^2}_{T_e} - \underbrace{\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2}_{T_n} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}}_{V_{en}} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}}_{V_{nn}}$$

**Born-Oppenheimer Approximation** →  $T_n=0$ ,  $V_{nn}=ct$

$$H_{elec} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

- Hartree Product [ $\Psi(r_1, r_2) = \phi(r_1) \phi(r_2)$ ] or Slater determinant  
→ no interaction between electrons.
- One electron problem – one electron feels other electrons' charge in an average way.
- No considering of electron correlation.
- HF method is a non-linear self-consistent field method.
- Two electron integration is the most expensive part.
- Koopman's theorem → HOMO energy = – Ionization potential,  
LUMO energy = – Electron affinity

# Why Quantum Chemistry?

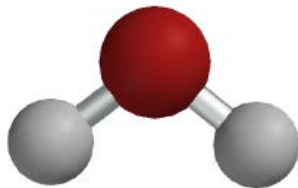
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- If only we can get the exact or accurate solution of Schrodinger equation, we can expect all the properties of matters without experiment in principle!
- The basic mathematical quantum chemistry study to solve Schrodinger equation **by hand** has reached the **limitation**.
- But recent development of computational system like K computer enables us to access to the solution of Schrodinger equation of real molecules and solids.

# Hartree-Fock method

- HF approximation excludes electron correlation  
(correlation energy = exact energy – HF energy)
- The HF energy accounts for more than 99% of the energy, but ...

Ex) atomization energy of water molecule



| Energy            | H <sub>2</sub> O | 2 H + O    | $\Delta E$ |
|-------------------|------------------|------------|------------|
| $E_{\text{HF}}$   | -76.057770       | -75.811376 | 0.246393   |
| $E_{\text{CCSD}}$ | -76.337522       | -75.981555 | 0.355967   |

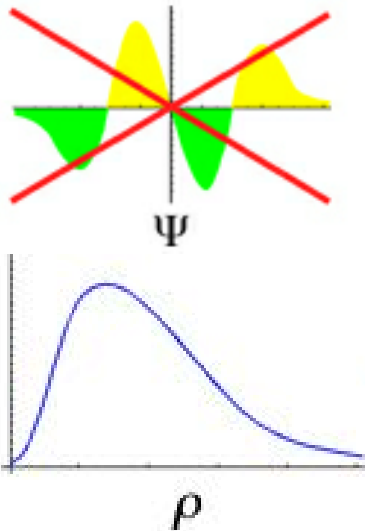
The neglect of the correlation energy in the atomization energy of water makes a **30% error!**

- So, it is not enough only to use Hartree-Fock method to get the energy of systems.
- However, electron correlation methods, such as CCSD, CCSD(T), CCSDT, show high order of system size as  $O(N^{6\sim 8})$

cf) HF as  $O(N^4)$

# Hohenberg-Kohn Theorem

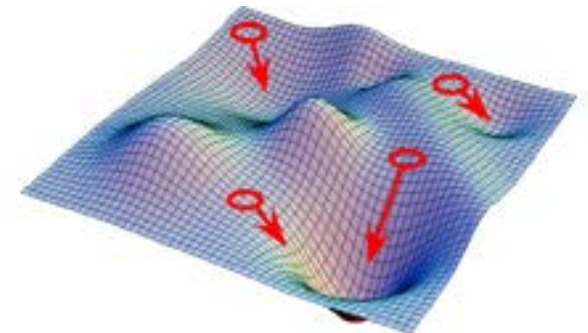
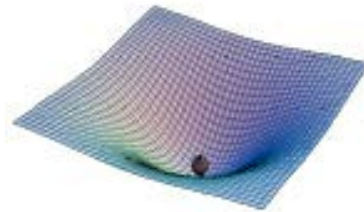
1. The ground state of electronic energy is determined completely by the electron density.



2. Variational principle:  
For a trial density  $\tilde{\rho}(r)$  such that  $\tilde{\rho}(r) \geq 0$

$$\text{and } \int \tilde{\rho}(r) dr = N,$$

$$E_0 \leq E_v[\tilde{\rho}].$$





# Kohn-Sham Equation

- Kohn-Sham Equation (introduction of orbital to DFT)

calculate the kinetic energy under the assumption of non-interacting electrons (same as HF)

$$T_s = (-1/2) \sum_{i=1}^N \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) dv$$
$$\int \rho(r) = N \quad \left[ -\frac{1}{2} \nabla^2 + \int \frac{\rho(r_2)}{r_{12}} dr_2 + v_{xc}(r_1) - \sum_{A=1}^M \frac{Z_A}{r_{1A}} \right] \varphi_i = \varepsilon_i \varphi_i$$
$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \quad \rho(r) = \sum_i |\varphi_i(r)|^2$$
$$v_{xc}(r) = \frac{\delta E_{xc}(\rho)}{\delta \rho}$$

- Let's simply write Kohn-Sham energy as

$$E_{\text{DFT-KS}}[\rho] = T_s[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

# Density Functional Theory (DFT; 密度汎関数)

$$E_{\text{DFT-KS}}[\rho] = T_s[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

- Hohenberg-Kohn Theorem
- Kohn-Sham equation

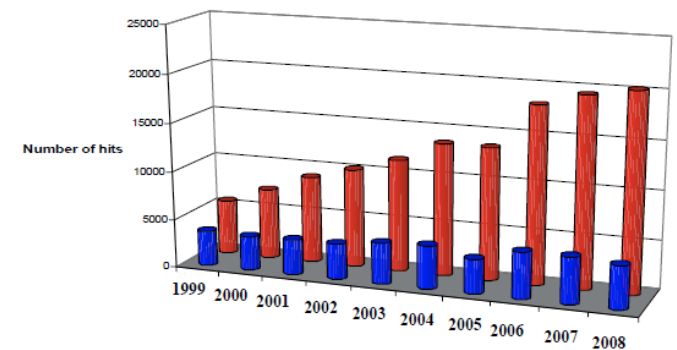


Exact exchange-correlation functional is not know yet.



A variety of functionals have been proposed till now.

- $O(N^{3\sim 4})$  is expected.
- Low dependency on the size of basis set.
- includes correlation energy.
- We expect DFT to be applied to **real-size biochemical systems** and **nanomaterials** using parallelizing and linear-scaling techniques.



References from SciFinder® database for "Quantum Chemistry" and "Density Functional Theory" (last 10 years).

# Conventional DFT functionals

□ **Pure DFT**: only uses electron density in expressing  $E_x$  and  $E_c$

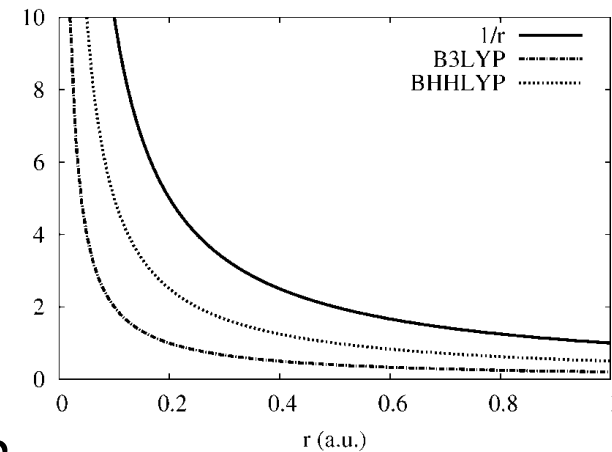
BOP: Becke88 Exchange + One Parameter (OP) correlation

BLYP: Becke88 Exchange + LYP correlation

□ **Hybrid DFT**: uses electron density and HF exchange integral

$$E_{DFT-KS} = T_s + E_{ne} + J + E_x + E_c$$

$$E_{xc}^{\text{hybrid}} = (1 - a_0) E_x^{\text{DFT}} + a_0 E_x^{\text{HF}} + E_c$$



$$\text{B3LYP: } E_{xc}^{\text{B3LYP}} = (1 - a_0) E_x^{\text{Becke88}} + a_0 E_x^{\text{HF}} + E_c^{\text{LYP}}; a_0 = 0.2$$

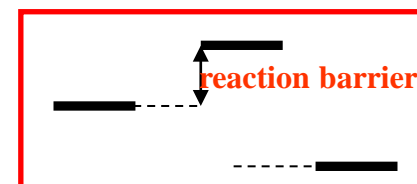
$$\text{BHHLYP: } E_{xc}^{\text{BHHLYP}} = (1 - a_0) E_x^{\text{Becke88}} + a_0 E_x^{\text{HF}} + E_c^{\text{LYP}}; a_0 = 0.5$$

# The problem of DFT

## The underestimation of reaction barrier height

Calculated reaction barrier height (kcal/mol)

| Reaction  | BOP  | B3LYP | Exp. |
|---|------|-------|------|
| $\text{CH}_3\text{F} + \text{H} \rightarrow \text{CH}_2\text{F} + \text{H}_2$       | 3.4  | 5.9   | 9.0  |
| $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$                       | 4.7  | 7.5   | 11.4 |
| $\text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2$     | 2.8  | 4.9   | 7.3  |
| $\text{CH}_3\text{Cl} + \text{Cl}^- \rightarrow \text{Cl}^- + \text{CH}_3\text{Cl}$ | -3.8 | -2.1  | 2.9  |
| $\text{CH}_3\text{Br} + \text{Br}^- \rightarrow \text{Br}^- + \text{CH}_3\text{Br}$ | -5.5 | -3.9  | 1.7  |
| $1,2,4,5\text{-C}_2\text{N}_4\text{H}_2 \rightarrow \text{N}_2 + 2\text{HCN}$       | 27.3 | 39.7  | 51.8 |
| $\text{H}_2\text{O} + \text{OH} \rightarrow \text{OH} + \text{H}_2\text{O}$         | -2.0 | 3.8   | 8.6  |
| $\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}$                        | 4.9  | 3.5   | 8.1  |
| $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$              | -    | 1.3   | 4.7  |
| $\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$              | 0.7  | -3.2  | 1.4  |

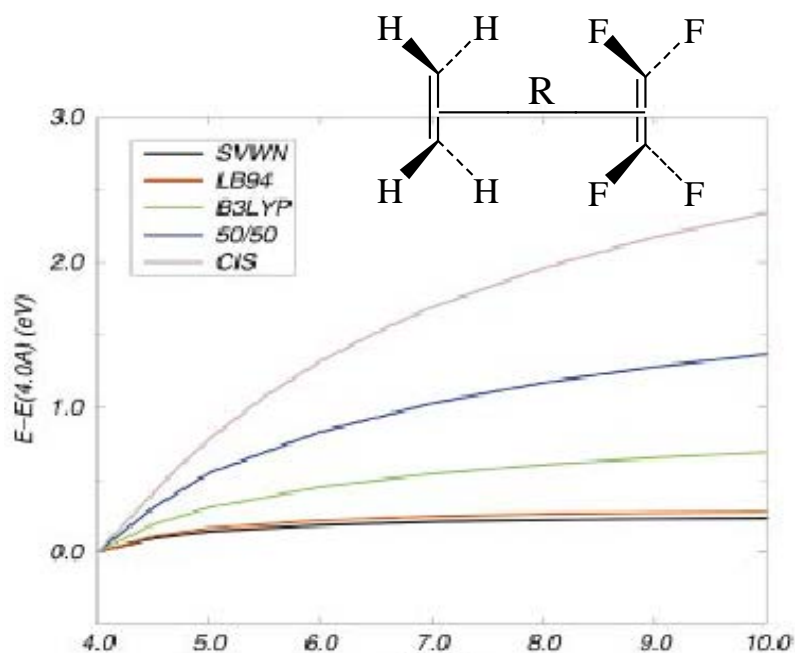


Pure (-3~10kcal/mol) and hybrid DFT (-3~5kcal/mol) underestimate reaction barrier height

Self-interaction error of conventional DFT

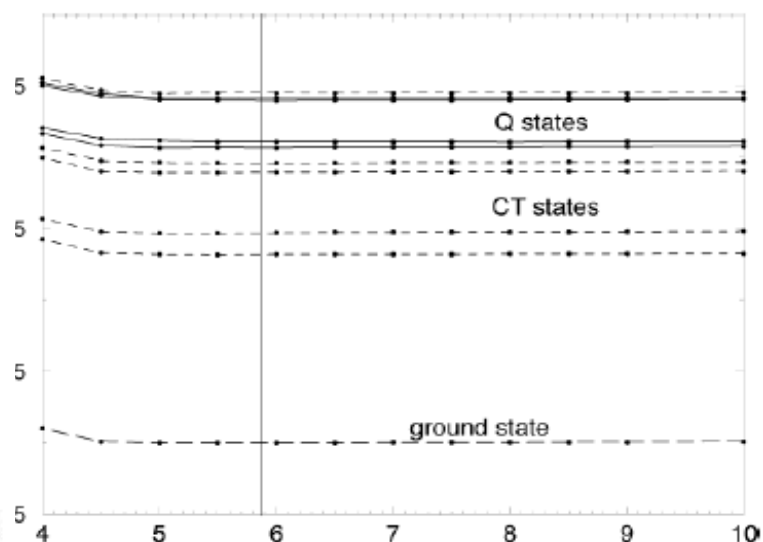
# The problem of DFT

## The underestimation of charge transfer and Rydberg excitation energy



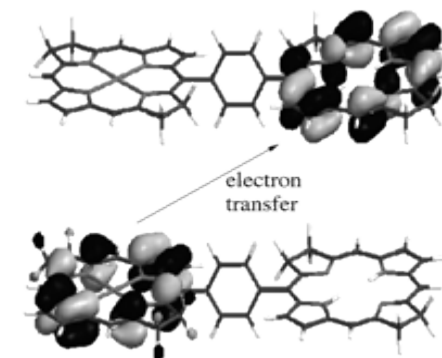
Dreuw, Weisman, and Head-Gordon,  
JCP, 119, 2943 (2003).

Charge transfer excitations of  
 $\text{C}_2\text{F}_4 \rightarrow \text{C}_2\text{H}_4$



Dreuw and Head-Gordon,  
JACS, 126, 4007 (2004).

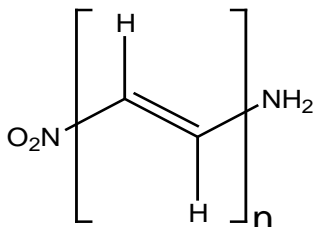
Charge transfer excitations of  
 $\text{ZnBc} \rightarrow \text{Bc}$



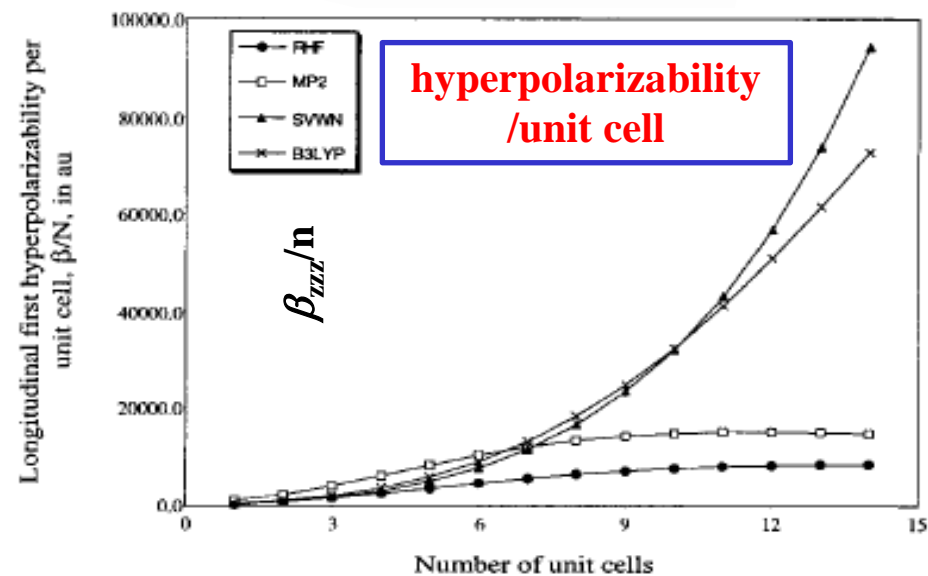
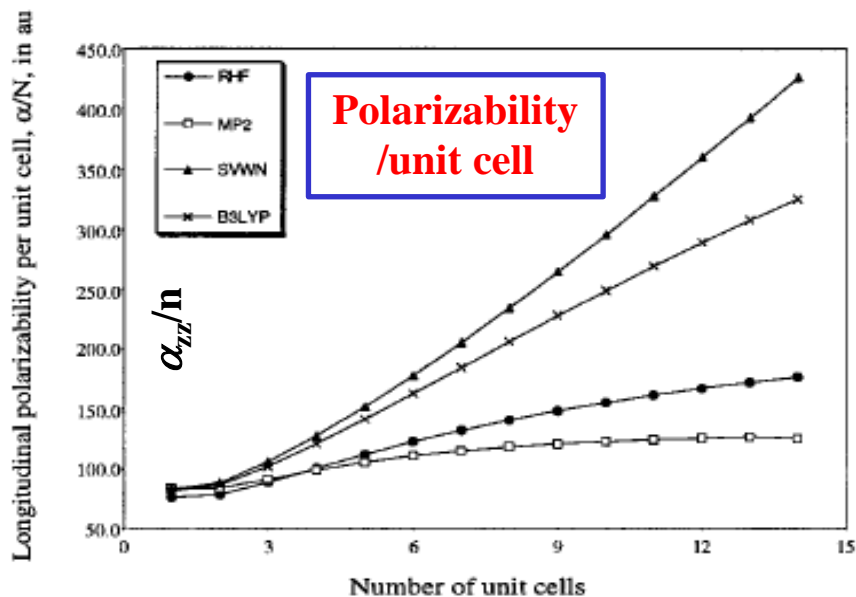
**CT states should be located  
higher than Q states.**

# The problem of DFT

## The overestimation of linear and nonlinear optical property



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



Conventional DFT functionals overestimate polarizability and hyperpolarizability.



# The problems of the DFT

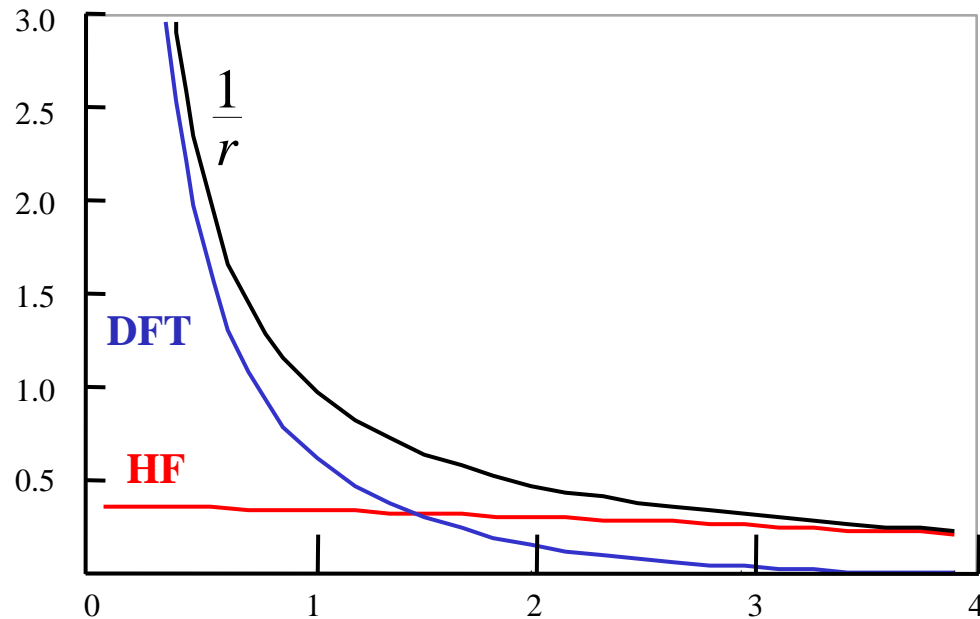
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- the underestimation of **reaction barrier heights**
- the underestimation of **charge transfer** and **Rydberg excitation energies** and the corresponding **oscillator strengths**
- the overestimation of **linear and nonlinear polarizabilities and hyperpolarizabilities** of long-chain molecules
- the poor description of **van der Waals bondings**
- the underestimation of **alkane energies**

**All are the inter-electronic long-range properties!**

# Long-range Corrected DFT

$$E_{DFT}[\rho] = T_s[\rho] + E_{ne}[\rho] + J[\rho] + E_x[\rho] + E_c[\rho]$$



$$\frac{1}{r_{12}} = \underbrace{\frac{1 - \text{erf}(\mu r_{12})}{r_{12}}}_{\text{short-range: DFT}} + \underbrace{\frac{\text{erf}(\mu r_{12})}{r_{12}}}_{\text{long-range: HF}}$$

short-range: DFT long-range: HF

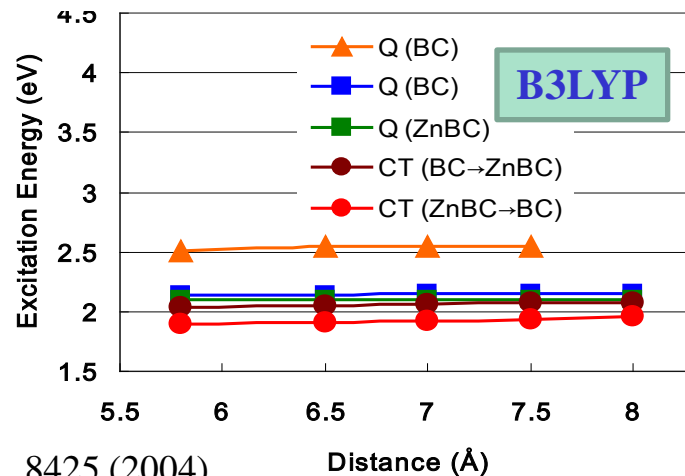
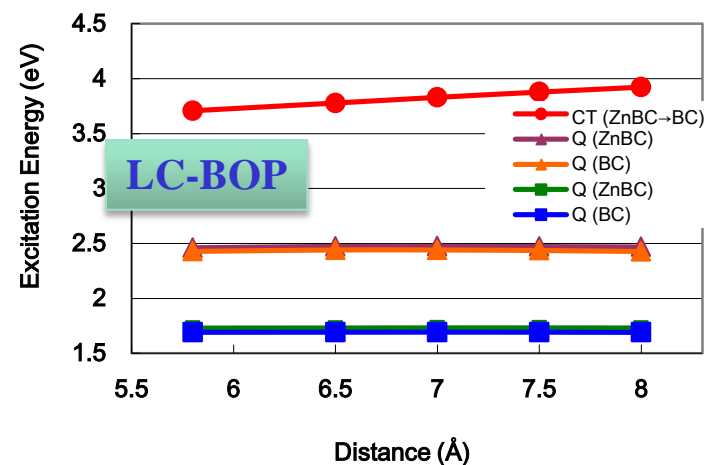
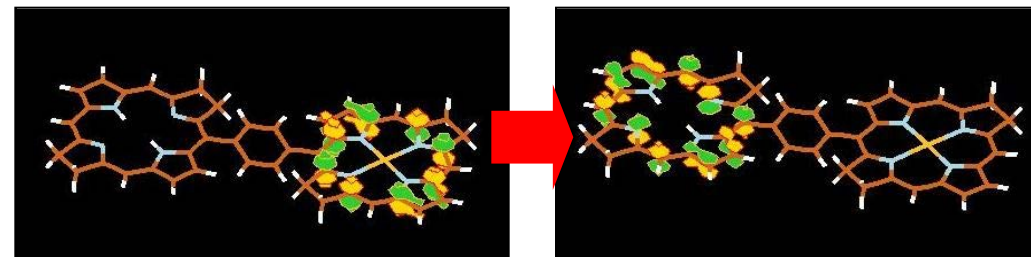
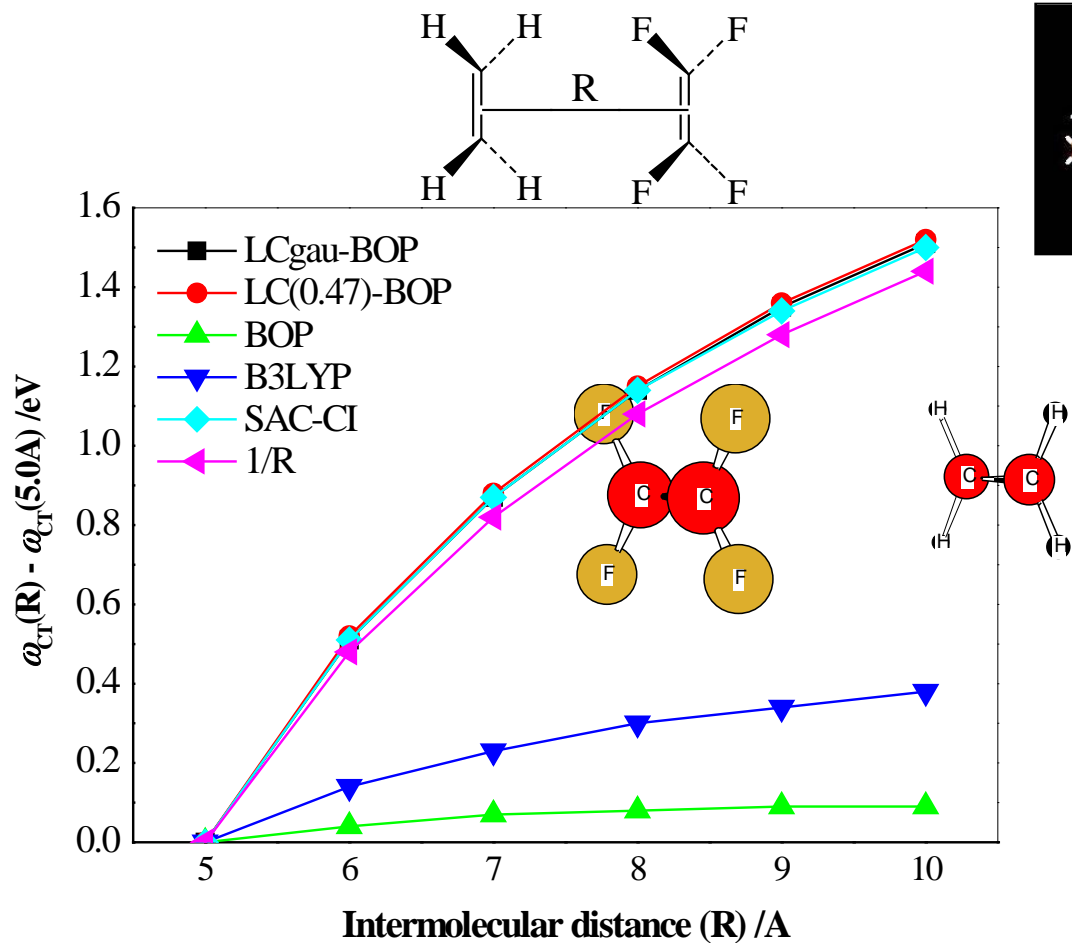
The only parameter  $\mu$  was determined using atomization energy error of G2 set(148 molecules) and the critical problems above were clearly solved.

H. Iikura, T. Tsuneda, T. Yanai, and K. Hirao, J. Chem. Phys. **115**, 3540 (2001).

J.-W. Song, T. Hirose, T. Tsuneda, and K. Hirao, J. Chem. Phys. **126**, 154105 (2007).



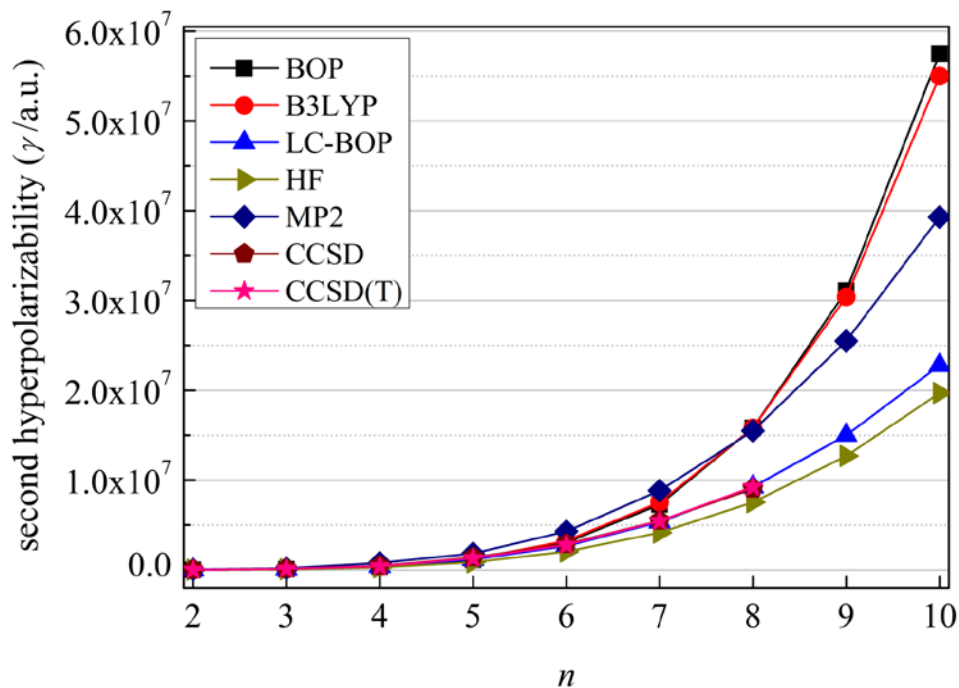
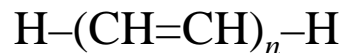
# Charge transfer calculations using LC-TDDFT



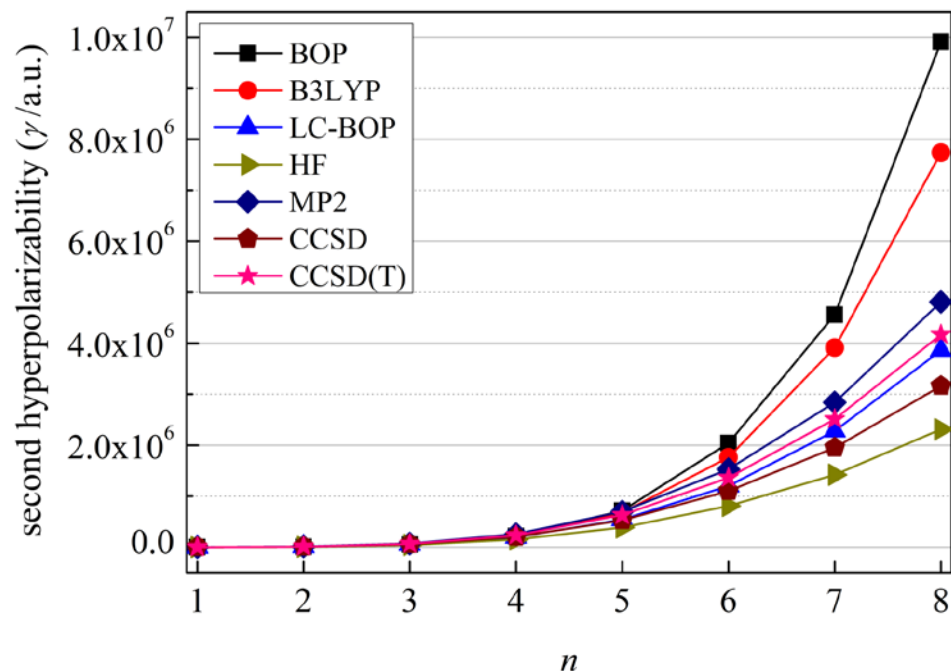
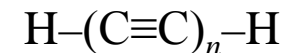
|                    | Exp. | LC-BOP | B3LYP | SAC-CI |
|--------------------|------|--------|-------|--------|
| $E_{CT}(R=\infty)$ | 12.5 | 12.43  | 7.42  | 14.43  |

# Nonlinear optical property calculation of polyene and polyene using LC-DFT

polyene

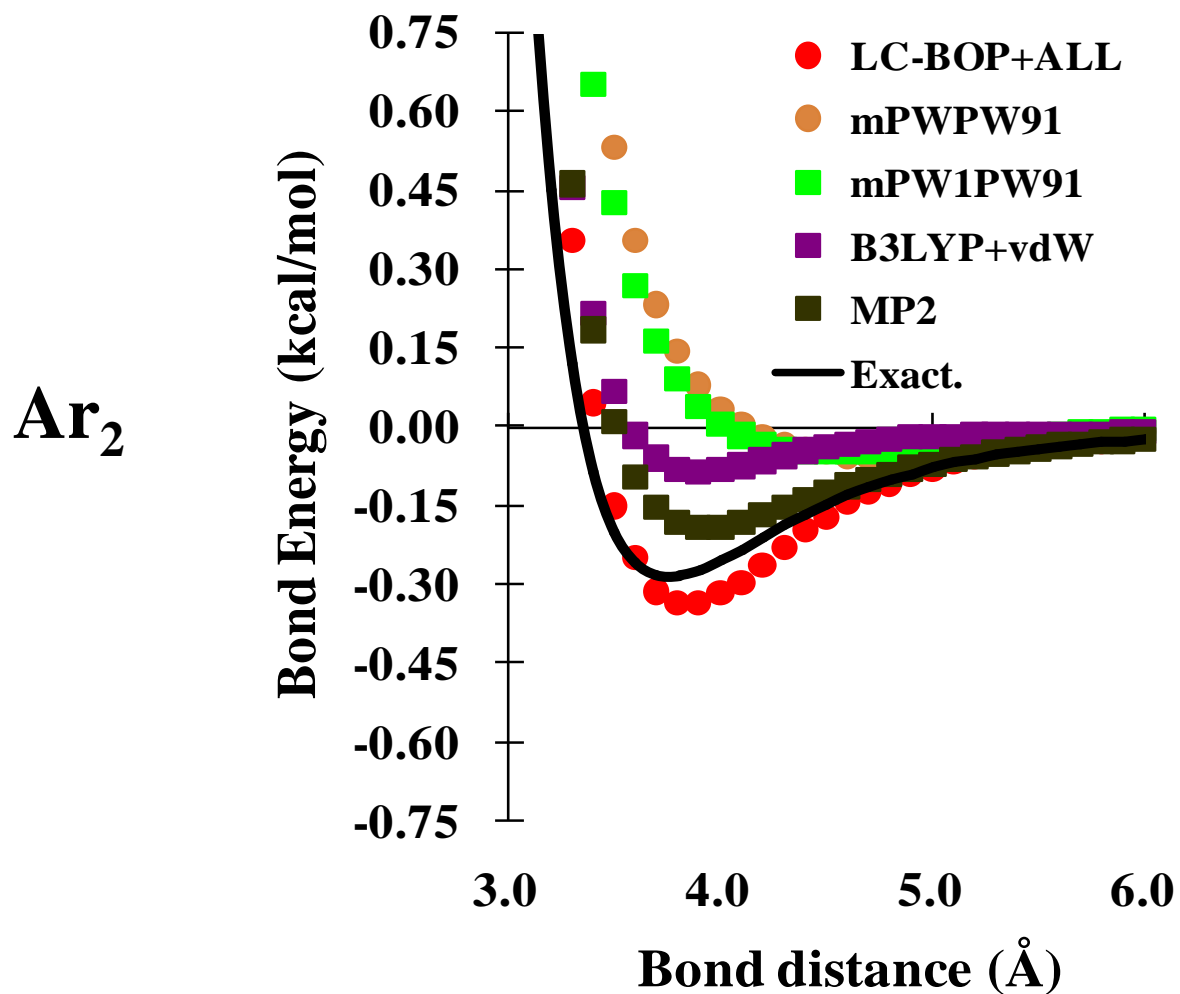


polyene



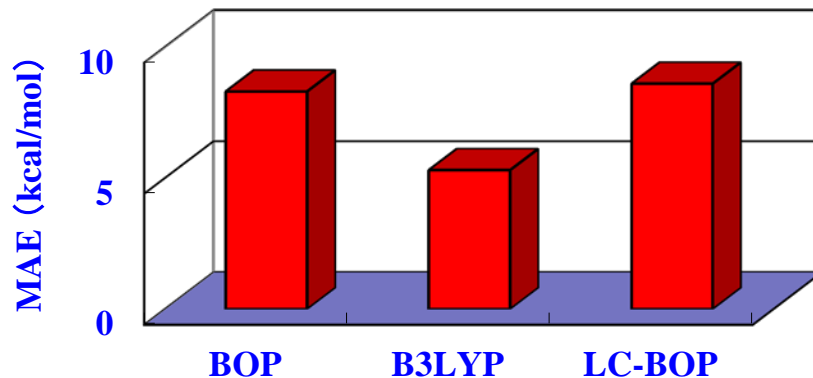
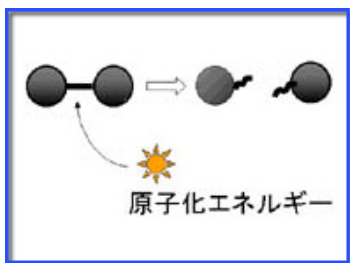
LC( $\mu=0.47$ )-BOP provides very near  $\gamma$  values of CCSD(T) in polyynes and polyenes.

# LC-DFT + ALL (C/R<sup>6</sup>) calculations on van der Waals force

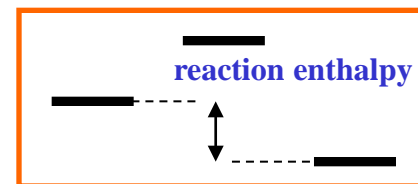


# Reaction barrier height and reaction enthalpy calculation with LC-DFT

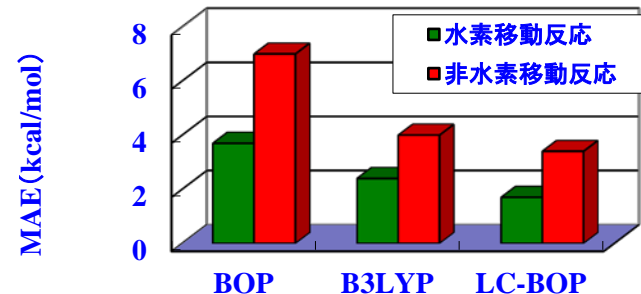
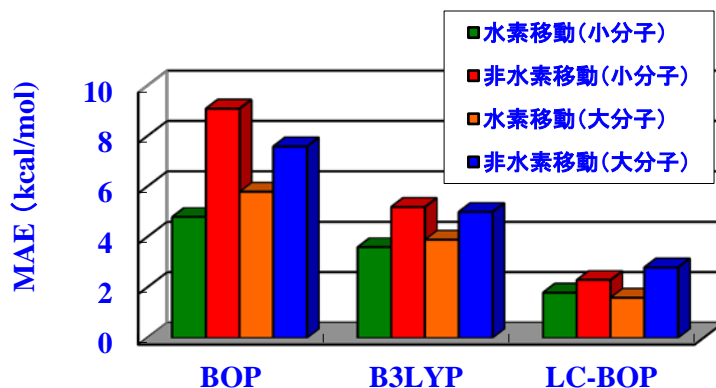
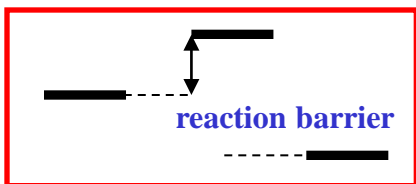
The error of atomization energy



The error of reaction enthalpy



The error of barrier height



# Ionization Potentials (Koopmans' theorem)

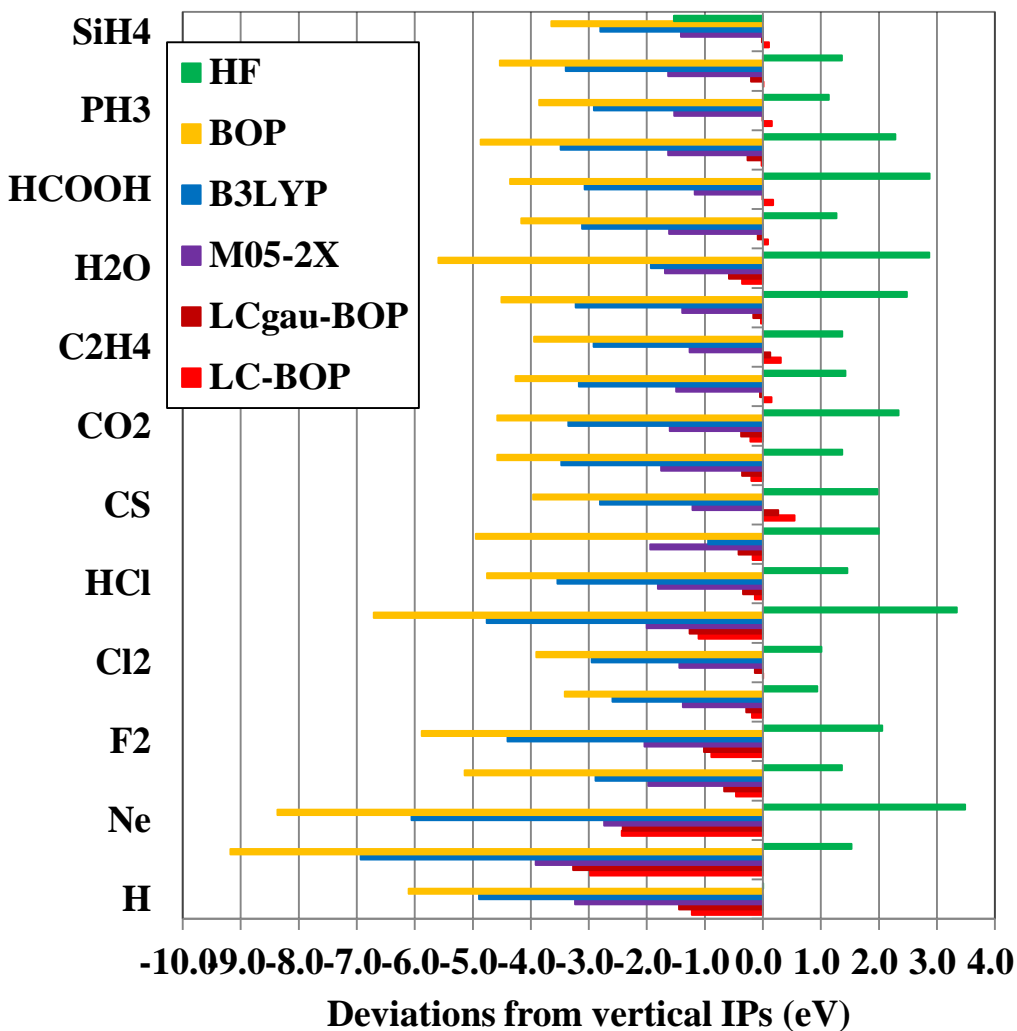


Fig. Deviations of orbital energies from the vertical IPs given by each method with aug-cc-pVQZ basis set ( $e_{\text{HOMO}} + \text{IP}$ ).

LC calculations give orbital energies are very close to vertical IPs.

LC-DFT approximately satisfies Koopmans' theorem.

Orbital energies calculated by other DFT functionals significantly underestimate the vertical IPs.

HF orbital energies overestimates vertical IPs.  $\Rightarrow$  HF violates Koopmans' theorem due to the orbital relaxation effects after removing an electron.

# Electron Affinities

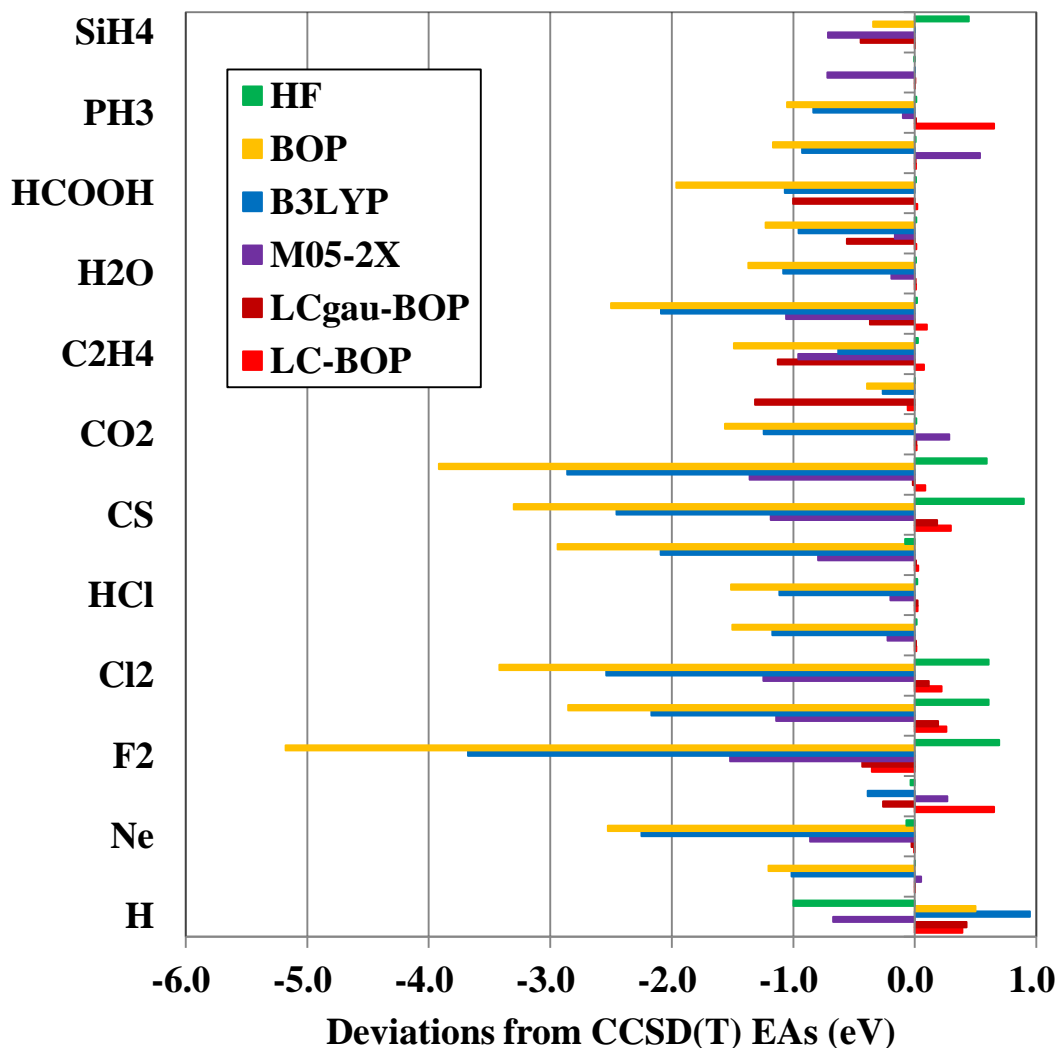


Fig. Deviations of LUMO energies from the vertical EAs given by each method with aug-cc-pVQZ basis set ( $\epsilon_{\text{LUMO}} - \text{EA}$ ).

LC-BOP orbital energies are very close to vertical EAs for all systems.

LC-BOP also satisfies Koopmans' theorem even for LUMO.

Orbital energies given by other DFT functionals underestimate vertical EAs, although the deviations are smaller than those of HOMO energies.

HF orbital energies give accurate vertical IPs due to small orbital relaxation effects.  
 $\Leftrightarrow$  Koopmans' theorem is not applicable to virtual orbitals.

# The problem to be solved of LC-DFT

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Hartree-Fock exchange integral – how to decrease the cost

How to apply LC-DFT to solid state calculation

Test and application to various systems, such as transition metal complex...