

# Computational Chemistry Research Unit

## 1. Unit members

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## 2. Research Activities

Electronic structure calculations are now indispensable not only for theoretical chemists, but also for experimental chemists to understand chemical phenomenon. Density functional theory (DFT) is a major tool to tackle chemical phenomenon theoretically. DFT efficiently calculate electronic structure with high accuracy, and its algorithm is suitable for parallel computing. DFT now plays an important role in applications of molecular science running on the K Computer. However, conventional DFT could not describe important properties such as van der Waals interaction and optical property, such as non-linear optics and charge-transfer excitation, which are essential for accurate calculations for large scaled molecular systems.

We have developed long-range corrected density functional theory (LC-DFT), which overcomes the drawbacks of conventional DFT mentioned above. Recently, we found that LC-DFT obtains accurate energies of highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO). The development of LC-DFT had a large impact in theoretical chemistry and the number of research based on LC-DFT is growing intensively. However, LC-DFT has yet difficulty in describing photochemical reactions. Photochemical process includes avoided crossing among electronic states, spin-forbidden transitions, and state transitions between high and low spins. These properties cannot be calculated accurately by LC-DFT so far.

The objective of our project is to establish LC-DFT to be a standard electronic structure theory by expanding its capability. We feature new developments of photo- and electro-chemical reaction theories and its high-speed computational algorithms for next-generation supercomputer "K", and the elucidations of significant reaction mechanisms and the designs of new functional materials in photo and electrochemistry. We also aim to increase reliability of electronic structure calculation by improving the accuracy of LC-DFT.

### 3. Research Results and Achievements

#### 3.1. Singularity-free hybrid functional with a Gaussian attenuating exact-exchange (Gau-PBE) in a plane-wave basis

Integrable singularity in the exact exchange calculations for hybrid density functionals, is an old and well-known problem in plane-wave basis widely used for electronic structure calculation of solid-state systems. We need to overcome this problem for accurate calculation of materials, because DFT using plane-wave basis is one of the major tools to tackle them. Recently, we developed a hybrid functional named Gau-PBE, which uses a Gaussian function as a modified Coulomb potential for the exact exchange in Gaussian-type-orbital software mainly used for electronic structure calculation of isolated molecules. We have further developed methods and efficient program for electronic structure calculation of solid-state systems. Our new method is

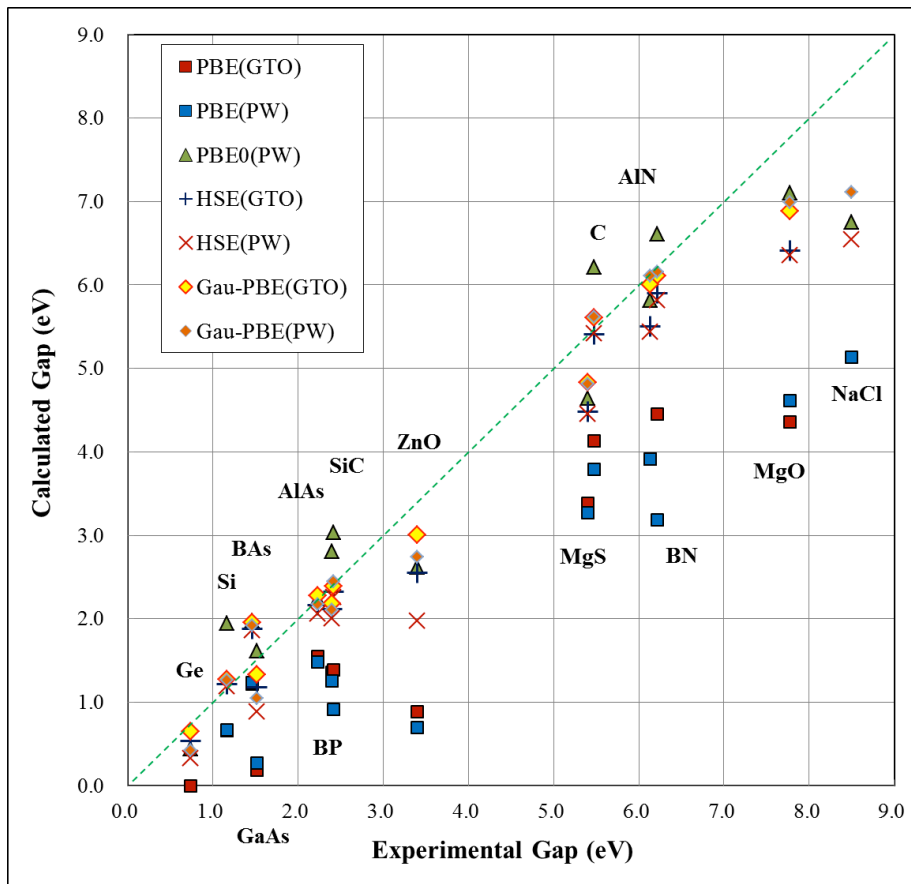


Figure 1. Calculated bandgap vs observed gap (Taken from J.-W. Song, G. Giorgi, K.Yamashita, K. Hirao, J. Chem. Phys., 138, 241101 (2013)).

implemented in a plane-wave-based software, Quantum ESPRESSO, widely used for electronic structure calculation of materials. We found the modified Coulomb potential of Gaussian function enables the exact exchange calculation in plane-wave basis to be singularity-free and, as a result, the Gau-PBE functional shows faster energy convergence on k and q grids for the

exact exchange calculations. Also, a tight comparison (same k and q meshes) between Gau-PBE, and two other well-known hybrid functionals, i.e. PBEo and HSEo6, indicates our new implemented functional as the least computational time consuming method (Figure 1). The Gau-PBE functional employed in conjunction with a plane wave basis provides bandgaps, an important property for material development, with higher accuracy than the PBEo and HSEo6 in agreement with bandgaps accurately calculated using Gaussian-type-orbitals. We found our new method promising for calculation of solid-state systems.

### 3.2. Long-range corrected density functionals combined with local response dispersion

Density functional theory, in general, underestimates the weak van der Waals type of intermolecular interactions. This is crucial in electronic structure calculation for large-sized molecular systems, which include the above weak interaction. We optimized parameters of the local response dispersion (LRD) method applied to the long-range corrected exchange-correlation functionals (LC-BOP12+LRD and LCgau-BOP+LRD) on the interaction energy for the complexes in the recently compiled S66 database. The new parameter optimization leads to highly accurate calculation for large systems. We found that calculation using our new parameter is comparable with the computationally demanding high-level wavefunction-based methods reported in Řezáč *et al.* (J. Chem. Theory Comput. 2011, 7, 2427). Our calculations with the S66 intermolecular complexes at equilibrium geometries suggest that LC-BOP12+LRD and LCgau-BOP+LRD are well-balanced and lower cost alternatives to the methods reported in the database. Further, critical test using the S66X8 database (with eight nonequilibrium points) and the HBC6 and NBC10 database shows LC+LRD method with newly optimized parameters is a promising candidate for dealing large molecular systems with such weak interactions.

### 3.3. Analysis of difference between intra- and inter-molecular charge transfer excitations in long-chained polyene

Charge transfer excitation plays an important role in various photochemical processes. It is still a challenge to describe charge transfer excitation for large-scaled molecular systems. For critical analysis of the performance of electronic structure calculation on charge transfer excitation, we performed intra- and inter-molecular charge transfer (CT) excitation calculations of  $\text{H}_2\text{N}-(\text{CH}=\text{CH})_n-\text{NO}_2$  (a) and its equidistant  $[\text{H}_2\text{N}-\text{H}\dots\text{H}-\text{NO}_2]$  complex (b) using EOM-CCSD ( $n=1-9$ ), time-dependent (TD) LC-DFT ( $n=1-10$ ). It was shown that LC-BOP and LCgau-BOP outperform all the tested DFT functionals on inter- and intra-CT excitation energy and oscillator strength, regardless of CT interaction distance (R). Decomposition of TD-DFT optical excitation energies of (a) and (b) into HOMO-LUMO gap and excitonic binding energy disclosed that HOMO-LUMO gap reduction resulting from delocalization of HOMO and LUMO through

bridged polyene conjugation is mainly responsible for the decreasing of intra-molecular CT excitation energy with polyene chain length, while inter-molecular CT increases linearly with  $-1/R$ , which is wholly due to the decrease in excitonic energy between HOMO and LUMO (Figure 2). The analysis provided wide understanding of charge transfer excitation and clues for further improvement of charge transfer excitation calculation. We found that success of exchange correlation functional on long-distanced intra-molecular CT calculations depends on correct descriptions of (1) Koopmans' energy of donor and acceptor and (2) excitonic energy between donor and acceptor, and (3) correct far-nucleus asymptotic behavior,  $-1/R$ . We found that LC scheme can satisfy (3), but needs an appropriate choice of long-range parameter able to satisfy (1) and (2). On the other hand, the pure, conventional hybrid, and screened hybrid functionals show near-zero intra- and inter-molecular excitonic energy regardless of  $R$ , which means optical band gap coincide with HOMO–LUMO gap. Therefore, we conclude that 100 % long-range Hartree–Fock exchange inclusion is indispensable for correct descriptions of intra-molecular CT excitations as well as inter-molecular CT. Our results indicate that bandgap calculation using conventional hybrids and screened hybrid functionals need reconsideration.

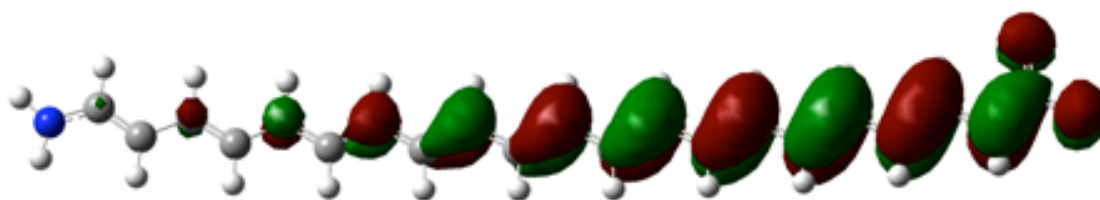


Figure 2. LUMO of  $\text{H}_2\text{N}-(\text{CH}=\text{CH})_{10}-\text{NO}_2$  obtained by LC-BOP (Taken from J.-W. Song, K. Hirao, *Theor. Chem. Acc.* 133, 1438(1-9) (2014)).

### 3.4. Path integral molecular dynamics simulation of hydrogen maleate anion based on range separated density functional theory

*Ab initio* path integral molecular dynamics (PIMD) simulation based on range separated DFT was performed to understand the nuclear quantum effect on the out-of-plane ring deformation of hydrogen maleate anion (Figure 3) and investigate the existence of a stable structure with ring deformation, which was suggested in experimental observation (Fillaux *et al.*, *Chem. Phys.* 1999, 120,

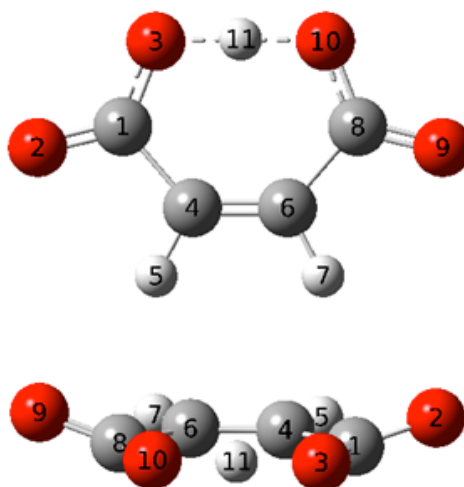


Figure 3. Hydrogen malonate anion and its ring-deformed structure.

387–403). The isotope effect and the temperature effect are studied as well. In our preliminary static calculation, we found that range separated DFT outperforms MP2 and conventional hybrid DFT. Thus, range separated DFT was used for our PIMD simulation. We first investigated the nuclear quantum effect on the proton transfer. In static calculation and classical *ab initio* molecular dynamics simulations, the proton in the hydrogen bond is localized to either oxygen atom. On the other hand, the proton is located at the center of two oxygen atoms in quantum *ab initio* PIMD simulations. The nuclear quantum effect washes out the barrier of proton transfer. We next examined the nuclear quantum effect on the motion of hydrogen maleate anion. Principal component analysis revealed that the out-of-plane ring bending modes have dominant contribution to the entire molecular motion. In quantum *ab initio* PIMD simulations, structures with ring deformation were the global minimum for the deuterated isotope at 300 K. We analyzed the out-of-plane ring-bending mode further and found that there are three minima along a ring distortion mode. We successfully found a stable structure with ring deformation of hydrogen maleate for the first time, to our knowledge, using theoretical calculation. The structures with ring deformation found in quantum simulation of the deuterated isotope allowed the proton transfer to occur more frequently than the planar structure. Static *ab initio* electronic structure calculation found that the structures with ring deformation have very small proton transfer barrier compared to the planar structure. We suggest that the “proton transfer driven” mechanism is the origin of stabilization for the structure with out-of-plane ring deformation.

#### 4. Schedule and Research Plans

In the next fiscal year, we will continue our effort to expand the capabilities of LC-DFT. We will develop the order- $N$  calculation algorithm of LC-DFT to calculate large molecular systems quantitatively with much less computational time. We will then apply this algorithm to excited state calculations on time-dependent density functional theory (TDDFT). We will also develop open-shell spin-orbit TDDFT to calculate molecular systems including metal atoms. Furthermore, we will develop a new method to calculate the nonadiabatic coupling among different electronic states, and carry out nonadiabatic coupling calculations based on TDDFT to reproduce photochemical reactions comprehensively. We are also planning to apply Gau-PBE and Gau-PBEh methods to solid-state calculations of real systems. We also aim to extend our TD-DFT based on LC-DFT to solid-state calculations as well.

#### 5. Publication, Presentation and Deliverables

(1) Journal Papers

[1] “Self-interaction correction in density functional theory” T.Tsuneda, K.Hirao, J.

- Chem. Phys., 140, 18A513 (1-13) (2014).
- [2] “Accurate Prediction of Hyperfine Coupling Constant in Muoniated and Hydrogenated Ethyl Radicals: Ab Initio Path Integral Simulation Study with Density Functional Theory Method”, K. Yamada, Y. Kawashima, M. Tachikawa, J. Chem. Theory. Comput., DOI: 10.1021/ct500027z
- [3] “What makes differences between intra- and inter-molecular charge transfer excitations of conjugated long-chained polyene?: EOM-CCSD and LC-BOP study” J.-W. Song, K. Hirao, Theor. Chem. Acc. 133, 1438(1-9) (2014).
- [4] “An *Ab Initio* Path Integral Molecular Dynamics Study of the Nuclear Quantum Effect on Out-of-plane Ring Deformation of Hydrogen” Y. Kawashima, M. Tachikawa, J. Chem. Theory Comp., 10, 153-163 (2014).
- [5] “Long-range correction for density functional theory”, T. Tsuneda, K. Hirao, Wiley Interdisciplinary Reviews: Computational Molecular Science, DOI: 10.1002/wcms.1178.
- [6] “Communication: Singularity-free hybrid functional with a Gaussian attenuating exact-exchange (Gau-PBE) in a plane-wave basis” J.-W. Song, G. Giorgi, K. Yamashita, K. Hirao, J. Chem. Phys., 138, 241101 (1-4) (2013).
- [7] “Three-dimensional Reference Interaction Site Model Self-consistent Field Study of the Solvation and Electronic Structures of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  in Aqueous Solution” S. Fujishige, Y. Kawashima, N. Yoshida, H. Nakano, J. Phys. Chem. A, 117, 8314-8322 (2013).
- [8] “Long-range corrected density functionals combined with local response dispersion: A promising method for weak interactions”, R. Kar, J.-W. Song, T. Sato, K. Hirao, J. Comput. Chem., 34, 2353-2359 (2013).
- [9] “Stochastic Search of Molecular Cluster Interaction Energy Surfaces with Coupled Cluster Quality Prediction. The Phenylacetylene Dimer”, M. A. Addicoat, Y. Nishimura, T. Sato, T. Tsuneda, S. Irle, J. Chem. Theory Comput., 9, 3848-3854 (2013).

## (2) Books

- [10] “Density Functional Theory in Quantum Chemistry” T. Tsuneda, Springer (2014).

## (3) Invited Talks

- [11] “Recent Advances in LC-DFT”, K. Hirao, 4th AICS International Symposium, Kobe, December 2-3 (2013).
- [12] “Recent Advances in LC-DFT”, K. Hirao, The 8th General Meeting of ACCMS-VO (Asian Consortium on Computational Materials Science – Virtual Organization), Sendai, November 7th (2013).

- [13] “Density functional theory for comprehensive orbital energy calculations”, T. Tsuneda, 2013 International Workshop on Computational Science and Engineering, National Taiwan University, Oct. 14-17 (2013).
- [14] “The K Computer and Recent Advances in DFT”, K. Hirao, 2013 International Workshop on Computational Science and Engineering, National Taiwan University, Oct. 14-17 (2013).
- [15] “DFT Exchange-Correlation Functionals and Correction”, T. Tsuneda, JACI Computational Chemistry Lectures, JACI, Tokyo, Sep. 13 (2013). (In Japanese)
- [16] “A Novel Analysis for Chemical Reaction Based on Orbital energies”, T. Tsuneda, Special Symposium in The 62th Annual Meeting of The Japan Society for Analytical Chemistry, Kinki University, Osaka, Sep. 10th (2013). (In Japanese)
- [17] “New World of Quantum Chemistry Lead by Long-Range Corrected Density Functional Theory”, T. Tsuneda, 18th Lecture for Research Group on Computational Polymer Science, Tokyo Institute of Technology, Aug. 7th (2013). (In Japanese)

(4) Posters and Presentations

- [18] “Configuration Search of Water Hexamer Anion: A Simulated Annealing Study”, Y. Kawashima, H. Nakano, T. Sato, K. Yagi, “Dynamical ordering and integrated functions” 2nd International Symposium, Campus Plaza Kyoto, Kyoto, Jan. 11-12 (2014). (Poster)
- [19] “The ring deformation of hydrogen maleate anion: A path integral molecular dynamics study”, Y. Kawashima, M. Tachikawa, 5th International Symposium on Theoretical Chemistry, Todai-ji National Center, Nara, Dec. 2-6, (2013). (Poster)
- [20] “Nuclear quantum effect on  $\text{OH}^-(\text{H}_2\text{O})_2$  with *ab initio* path integral molecular dynamics”, Y. Ogata, Y. Kawashima, K. Takahashi, M. Tachikawa, 3rd International Conference on Molecular Simulation, Kobe International Conference Center, Kobe, Nov. 18-20 (2013). (Poster)
- [21] “Quantum simulation for exotic molecules: Quantum Monte Carlo and Path Integral approach”, K. Koyanagi, Y. Kita, K. Yamada, Y. Kawashima, M. Tachikawa, 3rd International Conference on Molecular Simulation, Kobe International Conference Center, Kobe, Nov. 18-20 (2013). (Poster)
- [22] “Singularity-free hybrid functional with a Gaussian attenuating exact-exchange (Gau-PBE) in a plane-wave basis”ingularity G. Giacomo, K. Yamashita, K. Hirao, Sixth Asia-Pacific Conference of Theoretical and Computational Chemistry, Gyeongju Hilton Hotel, Gyeongju, Jul. 10-13 (2013). (Poster)
- [23] “The ring deformation of hydrogen maleate anion: A path integral molecular dynamics study”, Y. Kawashima, M. Tachikawa, Sixth Asia-Pacific Conference of Theoretical and Computational Chemistry, Gyeongju Hilton Hotel, Gyeongju, Jul. 10-13 (2013). (Poster)

- [24] “Theoretical investigation on the molecular and electronic structures of  $Ti(PC)_2$  and  $Ti(PC)_2^+$ ”, M. Sumimoto, Y. Kawashima, K. Hori, H. Fujimoto, The 7th Annual Meeting of Japanese Society for Molecular Science, Kyoto TERRSA, Kyoto, Sep. 24-27 (2013). (Poster in Japanese)
- [25] “*ab initio* path integral molecular dynamics study on the intramolecular hydrogen bond of hydrogen maleate”, Y. Kawashima, M. Tachikawa, The 7th Annual Meeting of Japanese Society for Molecular Science, Kyoto TERRSA, Kyoto, Sep. 24-27 (2013). (Poster in Japanese)
- [26] “Nuclear quantum effect on  $OH^-(H_2O)_2$  with *ab initio* path integral molecular dynamics”, Y. Ogata, Y. Kawashima, K. Takahashi, M. Tachikawa, The 7th Annual Meeting of Japanese Society for Molecular Science, Kyoto TERRSA, Kyoto, Sep. 24-27 (2013). (Poster in Japanese)
- [27] “A LC-DFT + vdW Study of the Diels-Alder Reactions and the Global Hardness Response Analysis”, R. K. Singh, T. Tsuneda, The 7th Annual Meeting of Japanese Society for Molecular Science, Kyoto TERRSA, Kyoto, Sep. 24-27 (2013).
- [28] “Chemical reaction path analysis based on orbital energies”, T. Tsuneda, The 7th Annual Meeting of Japanese Society for Molecular Science, Kyoto TERRSA, Kyoto, Sep. 24-27 (2013). (In Japanese)
- [29] “A New Theory for Quantitative Description of Core and Valence Orbital Energies”, A. Nakata, T. Tsuneda, 15th Annual Meeting of Theoretical Chemistry, May 15-17 (2013). (in Japanese)
- [30] “Theoretical Chemistry for Exotic Molecular Systems”, K. Koyanagi, Y. Kita, K. Yamada, Y. Kawashima, M. Tachikawa, 15th Annual Meeting of Theoretical Chemistry, May 15-17 (2013). (in Japanese)
- [31] “*ab initio* Path Integral Molecular Dynamics Simulation for Analysis on Low-Barrier Hydrogen Bond of Protonated Lysine”, Y. Ogata, M. Daido, Y. Kawashima, M. Tachikawa, 15th Annual Meeting of Theoretical Chemistry, May 15-17 (2013). (Poster in Japanese)

(5) Patents and Deliverables

- [32] Song *et al.* implemented the newly developed theory “GauPBE” in an open source plane-wave-based quantum chemistry software: “Quantum ESPRESSO”.  
<http://www.quantum-espresso.org/>