Computational Chemistry Research Unit

1. Team members

Kimihiko Hirao (Unit Leader)
Jong-Won Song (Research Scientist)
Yukio Kawashima (Research Scientist)
Takao Tsuneda (Senior Visiting Scientist)
Rahul Kar (Visiting Researcher)
Bun Chan (Visiting Researcher)

2. Research Activities

Electronic structure calculations are now indispensible for understanding chemical phenomenon even as for experimental chemists. Density functional theory (DFT) is a major tool to tackle chemical phenomenon. DFT efficiently calculates 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 charge-transfer excitation, which are essential for accurate calculations for large scaled molecular systems.

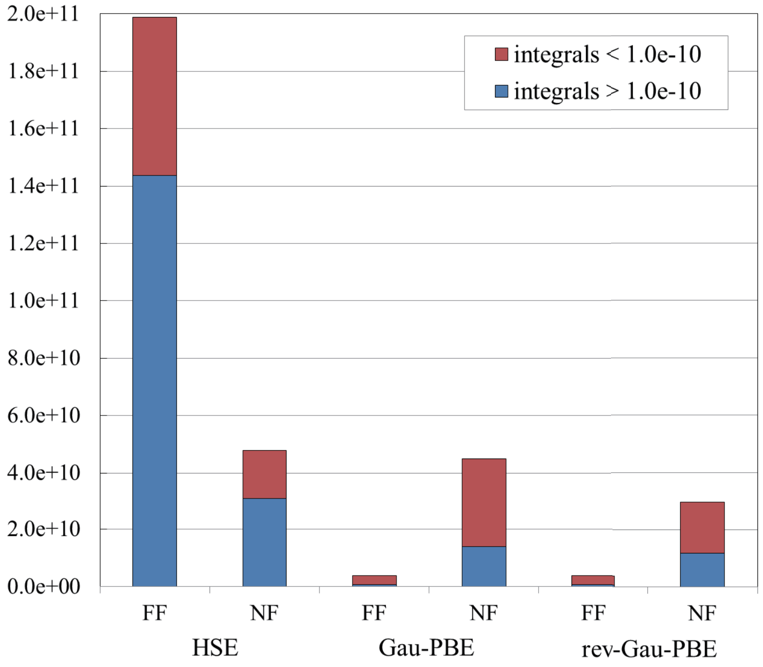
We have developed long-range corrected density functional theory (LC-DFT), which overcomes the drawbacks of conventional DFT mentioned above. LC-DFT also succeeded in describing induced/response properties. Recently, we found that LC-DFT obtains accurate energies of highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (HOMO). This indicates that prediction of chemical reactions can be done by LC-DFT calculations. The development of LC-DFT had a large impact in theoretical chemistry and the number of researches based on LC-DFT is growing intensively. However, LC-DFT has difficulty in describing photochemical reactions. Photochemical process includes avoided crossing among electronic states, spin-forbidden transitions, and states with high and low spins. These properties cannot be calculated accurately by LC-DFT. Moreover, the HF exact exchange, which remedies the shortcoming of the exchange functional in conventional DFT, requires large computational effort for real systems, which is the bottleneck for large-scale calculation.

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 using on 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. Efficient method of evaluation for Gaussian Hartree-Fock exchange operator for Gau-PBE functional

We previously developed an efficient screened hybrid functional called Gaussian-Perdew–Burke–Ernzerhof (Gau-PBE) [J. Chem. Phys. 135, 071103 (2011)] for large molecules and extended systems, which is characterized by the usage of a Gaussian function as a modified Coulomb potential for the HF exchange. In the previous researches, we found that the adoption of a Gaussian HF exchange operator considerably decreases the calculation time cost of periodic systems while improving the reproducibility of the band gaps of semiconductors. In our recent research, we presented a distance-based screening scheme tailored for the Gaussian HF exchange integral that utilizes multipole expansion for the Gaussian two-electron integrals. We found the new multipole screening scheme helps to save the time cost for the HF exchange integration by efficiently decreasing the number of integrals of, specifically, the near field region without incurring substantial changes in total energy. In our assessment on the periodic systems of seven semiconductors, the Gau-PBE hybrid functional with a new screening scheme has 1.56 times the time cost of a pure functional while the previous Gau-PBE was 1.84 times and HSE06 was 3.34 times.

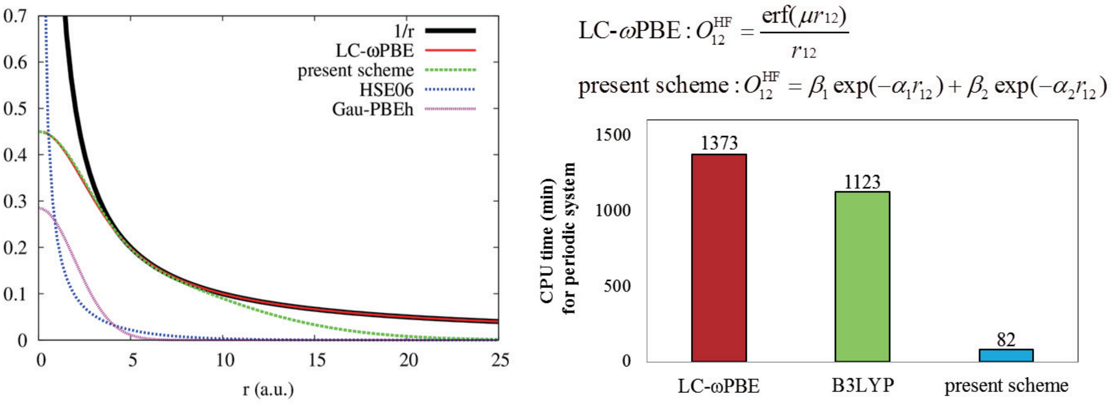


3.2. Long-Range Corrected Density Functional Theory with Linearly-Scaled Hartree-Fock

Figure 1 The numbers of calculated HF exchange integrals of HSE, Gau-PBE, and rev-Gau-PBE in C diamond. The numbers of integrals are decomposed into far-field (FF) and near-field (NF) and into integral sizes using the standard of 10^{-10}.

Exchange Using a Two-Gaussian Operator [LC-*ω*PBE(2Gau)]

Since the advent of hybrid functional in 1993, it has become a main quantum chemical tool for the calculation of energies and properties of molecular systems. Following the introduction of long-range corrected hybrid scheme for density functional theory a decade later, the applicability of the hybrid functional has been further amplified due to the resulting increased performance on orbital energy, excitation energy, non-linear optical property, barrier height, and so on. Nevertheless, the high cost associated with the evaluation of HF exchange integrals remains a bottleneck for the broader and more active applications of hybrid functionals to large molecular and periodic systems. In this research, we proposed a very simple yet efficient method for the computation of long-range corrected hybrid scheme. It uses a modified two-Gaussian attenuating operator instead of the error function for the long-range HF exchange integral. As a result, the two-Gaussian HF operator, which mimics the shape of the error function operator, reduces computational time dramatically and enables linear-scaling with system size, while maintaining the improved features of the long-range corrected density functional theory.



$$\text{LC-}\omega\text{PBE}: O_{12}^{\text{HF}} = \frac{\operatorname{erf}(\mu r_{12})}{r_{12}}$$

$$\text{present scheme}: O_{12}^{\text{HF}} = \beta_1 \exp(-\alpha_1 r_{12}) + \beta_2 \exp(-\alpha_2 r_{12})$$

Figure 2 Modified forms of the $1/r_{12}$ operator for the HF exchange contributions and timings (min) for C diamond in the LC-*ω*PBE, present scheme [LC-*ω*PBE(2Gau)], Gau-PBEh and HSE06 functionals.

3.3. Assessment of Density Functionals for the Estimation of Enthalpies of Formation, Barrier Heights, and Ionization Potentials of Selected C1-C5 Oxygenates

We assessed B3LYP, BHandHLYP, MPW3LYP, MPW1K, MPWB1K, BB1K, MPW1B95, BMK, LC-ωPBE, LC-BOP, LCgau-BOP, LC-BOP12, LCgau-B97 density functionals and the composite CBS-QB3 method for the enthalpies of formation for some selected oxygenates . Compared to experiment, BMK, LC-*ω*PBE, LC-BOP, LCgau-BOP, LC-BOP12, LCgau-B97, MPW195, MPW3LYP functionals and CBS-QB3 give root mean square errors (RMSE) in enthalpies of formation no greater than 4 kcal/mol, whilst MPW1K and BHandHLYP show much worse performance (RMSE of 20 - 40 kcal/mol). The B3LYP, MPWB1K and BB1K results fall between the two extremes. Energy barriers for the dominant paths in the unimolecular decomposition of simple esters (HCO2CH3, C2H5CO2C2H5), C1-C3 acids, and 1-butanol are reproduced well by CBS-QB3, BMK, BB1K, LCgau-B97, and PW1B95 (RMSE= 1- 2 kcal/mol), while other LC methods (LC-ωPBE, LC-BOP, LCgau-BOP, and LC-BOP12) show a deviation of up to 4 kcal/mol. For the ionization potentials, calculated from Koopman's theorem, all of the investigated LC-methods give good results compared to other DFT functionals with a maximum deviation of 0.4 eV, except for LCgau-B97, which has an RMSE of 0.7 eV.

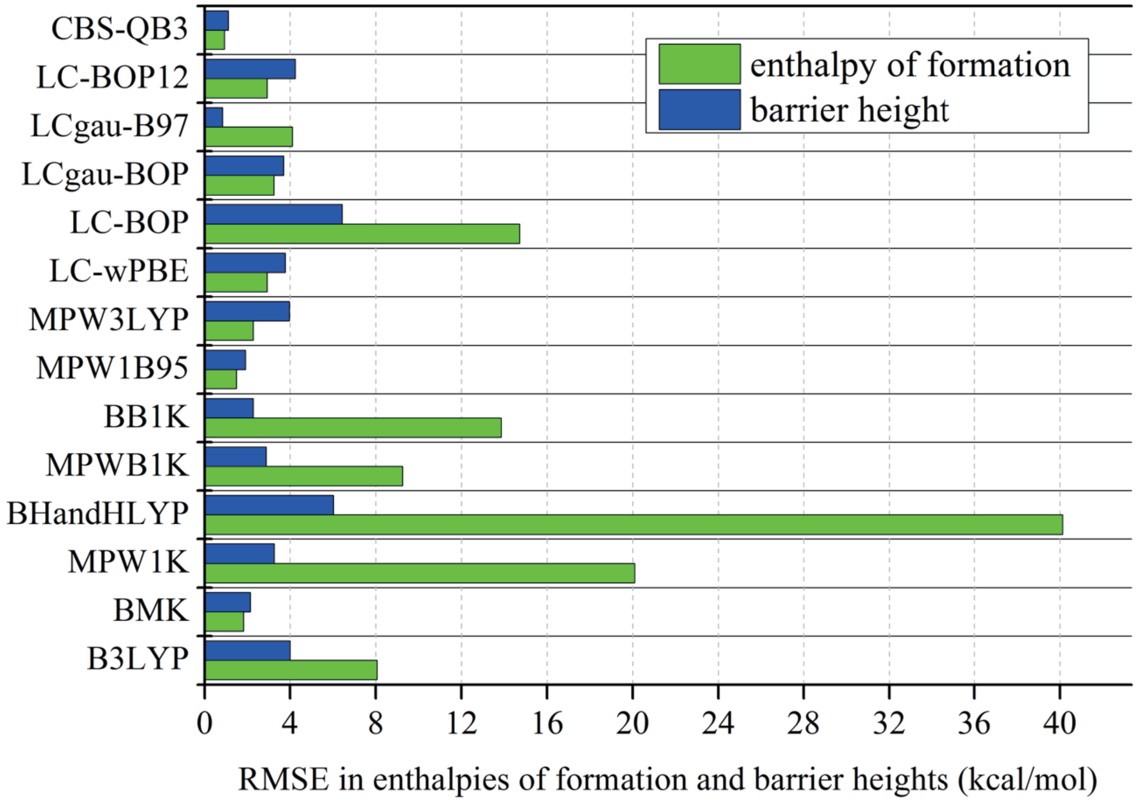


Figure 3 Plot of RMSE in enthalpies of formation and barrier heights for some oxygynates.

3.4. Molecules relevant for Organic Photovoltaics: A Range Separated Density Functional Study

Accurate determination of both fundamental and optical gap is necessary for designing molecules relevant for organic photovoltaics. In this research, we studied how range separated density functionals reproduce frontier orbital energies, HOMO (highest occupied molecular orbital) - LUMO (lowest unoccupied molecular orbital) gaps and optical gaps for molecules relevant for organic photovoltaics. Then, we considered 12 different range separated density functional for computing

HOMO energy, HOMO-LUMO gap and optical gap, which were then compared with available experimental and reported GW values. We found that the reproduction of desired photovoltaic properties primarily depends on range separation parameter. Moreover, the tested functionals are comparable with OT-BNL functional.

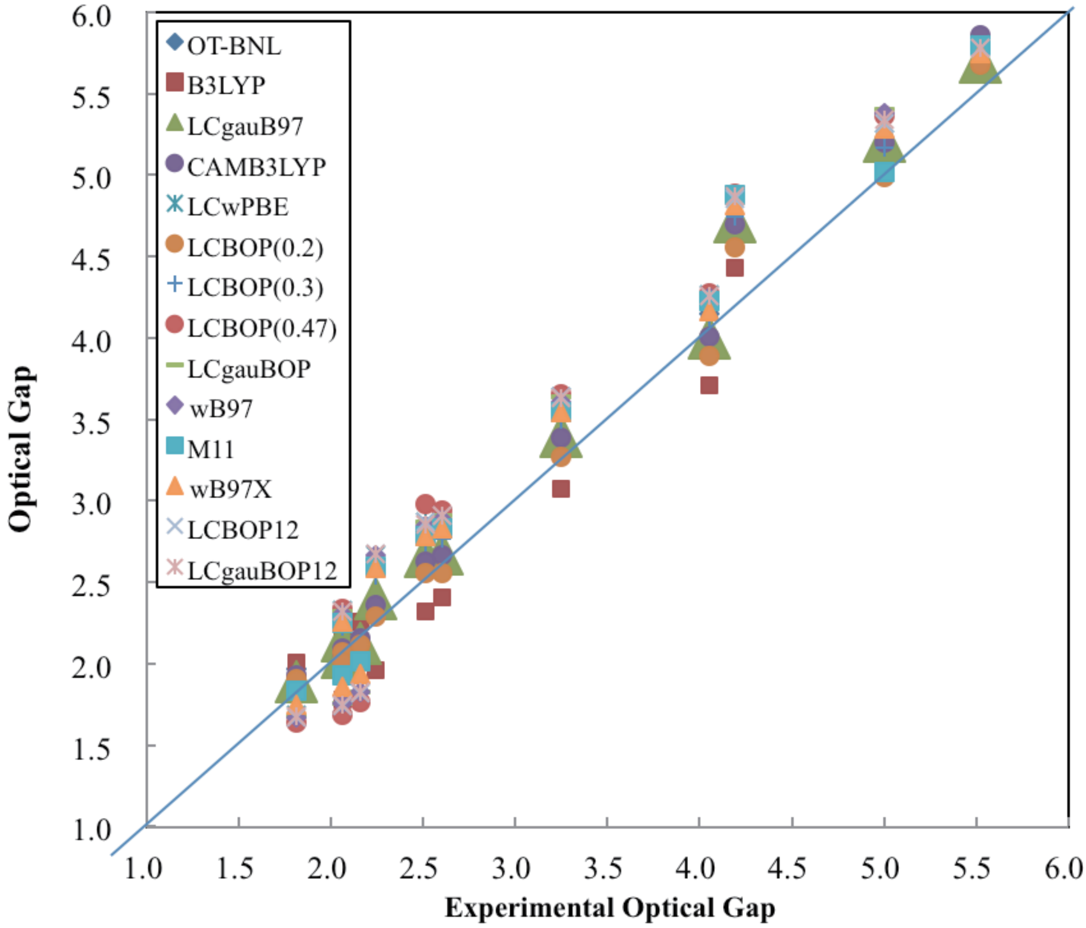


Figure 4 Plot of experimental optical gap versus optical gap (in eV) of large molecules using different rang-separated functionals.

3.5 An approach toward the complete range separation of non-hybrid exchange-correlational

Density functional theory (DFT) is arguably the most popular type of procedures among the various computational chemistry protocols, as these methods provide reasonable accuracy with good computational efficiency. DFT procedures contain an exchange component and a correlation component. Hybrid DFT procedures, which are now the most commonly used DFT, replace a proportion of the DFT exchange with Hartree Fock (HF) exchange. Many hybrid DFT methods are the so-called global hybrids, which have the same proportion of HF exchange throughout the entire system. However, short-range qualities in a system may have different requirements on the theoretical methods than long-range features. To this end, we previously developed a different type of hybrid DFT, the range-separated DFT (RS-DFT), which uses varying amounts of HF exchange for short-range and long-range interactions. Indeed, such a partition scheme often leads to an improved performance when compared with the typical global hybrids. Most commonly, in conjunction with the RS hybrid DFT exchange, the same correlation functional is used in RS-DFT procedures. Thus, a good performance across the board necessitates a good performance of the correlation functional in all ranges. This begs the question: would it be beneficial to also adopt range separation to the correlation component in an RS-DFT? In the present investigation, we will explore this issue. A different aspect regarding hybrid DFT is that the inclusion of HF exchange leads to an increase in computational cost, when compared with pure DFT procedures that do not have such a component. We thus find it desirable to first focus on pure functionals in the development of such a new DFT protocol. We emphasize that the objective of this study is to introduce a strategy that can complement existing techniques for DFT development, rather than devising the best-performing procedure using this new methodology.

In this study, we use a very simple scheme to achieve range separation of a total exchange–correlation functional. We have utilized this methodology to combine a short-range pure DFT functional with a corresponding long-range pure DFT, leading to a “Range-separated eXchange–Correlation” (RXC) scheme. By examining the performance of a range of standard exchange–correlation functionals for prototypical short- and long-range properties, we have chosen B-LYP as the short-range functional and PBE-B95 as the long-range counterpart. The results of our testing using a more diverse range of data sets, including S12L set of host-guest complexes shown in Figure 5, show that, for properties that we deem to be short-range in nature, the performance of this prescribed RXC-DFT protocol does resemble that of B-LYP in most cases, and vice versa. Thus, this RXC-DFT protocol already provides meaningful numerical results. Furthermore, we envisage that the general RXC scheme can be easily implemented in computational chemistry software packages. This study paves a way for further refinement of such a range-separation technique for the development of better performing DFT procedures.

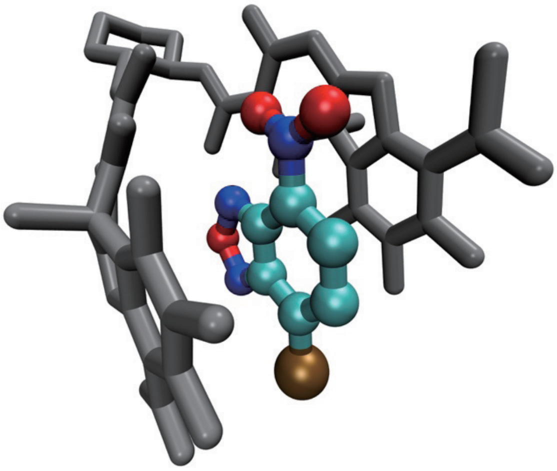


Figure 5. The largest host-guest system used for assessment in S12L set. Hydrogen atoms are omitted.

4. Schedule and Future Plan

In the next fiscal year, we will continue our effort to expand the capabilities of LC-DFT. First, we will develop the order-*N* calculation algorithm of LC-DFT to calculate large molecular systems quantitatively with much less computational time. We have gained insight on how to reduce the time-consuming exact exchange calculation and we will apply our knowledge to the algorithm development. 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, Gau-PBEh, and LC-DFT(2Gau) 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. “Relativistic Density Functional Theory”, *J. Comput. Chem. Jpn* **13**, 71-82 (2014).
2. “Towards the Complete Range Separation of Non-Hybrid Exchange–Correlation Functional” Bun Chan, J.-W. Song, Y. Kawashima, and K. Hirao, *J. Comput. Chem.* **36**, 871-877 (2015).
3. “Assessment of hybrid, meta-hybrid-GGA, and long-range corrected density functionals for the anstimation of enthalpies of formation, barrier heights, and ionisation potentials of selected C1–C5 xygenates” A. M. El-Nahas, J. M. Simmie, A. H. Mangood, K. Hirao, J.-W. Song, M. A. Watson, T. Taketsugu, and N. Koga, *Mol. Phys.* (Special Issue in Honour of Nicholas C. Handy) (2015) [**DOI:** 10.1080/ 00268976.2014.1002552].
4. “Is the structure of hydroxide dihydrate OH$^-$(H2O)$_2$? : An ab initio path integral molecular dynamics study” Y. Ogata, Y. Kawashima, K. Takahashi, M. Tachikawa, *Theo. Chem. Acc.* **134**, 1587 (2015).
5. “Theoretical study on the stability of double-decker type metal phthalocyanines, M(Pc)$_2$ and M(Pc)$_2^+$ (M = Ti, Sn and Sc): critical assessment on the performance of density functionals” M. Sumimoto, Y. Kawashima, K. Hori, H. Fujimoto, *Phys. Chem. Chem. Phys.* **17**, 6478-6483 (2015).
6. “Quantum simulation for muoniated and deuterated methyl radicals in implicit water solvent: combined ab initio path integral molecular dynamics and the polarizable continuum model simulation study” K. Yamada, Y. Kawashima, M. Tachikawa, *Mol. Sim.* [**DOI:** 10.1080/08927022.2014.938070].

7. ”Reactivity index based on orbital energies”, T. Tsuneda, R. K. Singh, *J. Comput. Chem.* **35**, 1093-1100 (2014).
8. “A new electron-nucleus correlation functional for multi-component density functional theory”, T. Udagawa, T. Tsuneda, M. Tachikawa, *Phys. Rev. A* **89**, 052519 (2014).
9. “Theoretical Investigation of Local Proton Conductance in Proton Exchange Membranes for Fuel Cells”, R. K. Singh, T. Tsuneda, K. Miyatake, M. Watanabe, *Chem. Phys. Lett.* **608**, 11-16 (2014).
10. “Chemical reaction analyses based on orbitals and orbital energies” T. Tsuneda, *Int. J. Quant. Chem.* **115**, 270-282 (2015).
11. “Theoretical Study of Isotope Enrichment Caused by Nuclear Volume Effect”, M. Abe, M. Hada, T. Suzuki, Y. Fujii, K. Hirao, *J. Comput. Chem. Jpn* **13**, 92-104 (2014).
12. “Theoretical Study on Reaction Mechanisms of Nitrite Reduction by Copper Nitrite Complexes: Towards Understanding and Controlling Possible Mechanisms of Copper Nitrite Reductase”, S Maekawa, T Matsui, K Hirao, Y Shigeta, *J. Phys. Chem. B* (2015) [**DOI:** 10.1021/acs.jpcb.5b01356].
13. “Long-Range Corrected Density Functional Theory with Linearly-Scaled Hartree-Fock Exchange Using a Two-Gaussian Operator [LC-ωPBE(2Gau)]” J.-W. Song, K. Hirao, *J. Phys. Chem. Lett.* submitted.
14. “Molecules relevant for Organic Photovoltaics: A Range Separated Density Functional Study” R. Kar, M. P. Borpuzari, J.-W. Song, K. Hirao, *Mol. Phys.* submitted.
15. “Efficient evaluation method for Hartree-Fock exchange of Gaussian operator for Gau-PBE functional” J.-W. Song, , K. Hirao, *J. Chem. Phys.* submitted.

(2) Books

1. “Density functional theory for Coordination Chemistry”, T. Tsuneda, Books from Japanese Society of Coordination Chemistry 10 “Quantum and computational chemistry for metal complex systems”, Ed. K. Yamaguchi, S. Sakaki, H. Masuda (2014)

(3) Invited Talks

1. “Present and Future Status of Quantum Chemistry”, T. Tsuneda, 3rd Frontier Chemistry Center (FCC) International Symposium, Hokkaido Univerisity, July 13-14 (2014).
2. “Looking Toward Quantum Chemistry on the Exascale”, T. Tsuneda, US-Japan Workshop on Exascale Applications, Gatlinburg, Tennessee, Sep. 5-6 (2014).
3. “Orbital energy gaps vs excitation energies for extended systems”, T. Tsuneda, 10th Triennial Congress of the World Association of Theoretical and Computational Chemists (WATOC 2014), Casa Piedra Santiago, Oct. 5-10 (2014).

4. “Relationship between excitation energies and orbital energy gaps for large systems”, T. Tsuneda, The 9th International Conference on Computational Physics (ICCP9), The National University of Singapore, Jan. 7-11 (2015).
5. “On the difference between band gaps and orbital energy gaps”, T. Tsuneda, A cluster of topical meeting on Current Trends in Condensed Matter Physics (CTCMP) 2015, National Institute of Science Education and Research (NISER), Bhubaneswar, Feb. 19-22 (2015).
6. “The present and the future of theoretical chemistry”, T. Tsuneda, 42nd Hokkaido University Theoretical Chemistry Seminar, Hokkaido University, Jun. 12 (2014). (In Japanese)
7. “The K Computer and Computational Chemistry”, K. Hirao, 102nd Indian Science Congress -Advances in Computation of Electronic Structure ACES-2015, University of Mumbai, Jan. 4 (2015).
8. “Quantum chemical approach to elucidate the mechanism of metabolism and UV protection”, Y. Kawashima, CBI Annual Meeting 2014 (Focused Session: Metabolomics and First-Principle Calculation: Prediction and Validation), Tower Hall Funabori, Tokyo, Oct. 29 (2014). (In Japanese)
9. “Towards large scale computing of path integral molecular dynamics simulation”, Y. Kawashima, The 12th Inamori Frontier Workshop: Large scale computing technology towards practical application, Kyushu Universtiy, Jan. 23 (2015). (In Japanese)
10. “Development of DFT functional applicable to large molecular and periodic systems” J.-W. Song, CJK-WTCC-II conference, Kobe, Jan. 20-23 (2015).

(4) Posters and presentations

1. “Tackling Nuclear Quantum Effect in Quantum Chemistry”, Y. Kawashima, XIXth International Workshop on Quantum Systems in Chemistry and Physics, Tamsui, Nov. 13 (2014).
2. ”Analysis of HF exact exchange in Long-Range Corrected Density functional Theory”, Y. Kawashima, K. Hirao, 17th Annual Meeting of Theoretical Chemistry, Nagoya University, May 22-24 (2014). (Poster in Japanese)
3. ”Theoretical Study of $OH^-(H_2O)_2$ Cluster Considering Nuclear and Thermal Fluctuation Effects”, Y. Ogata,Y. Kawashima, K. Takahashi, M. Tachikawa, 15th Annual Meeting of Theoretical Chemistry, Nagoya University, May 22-24 (2014). (In Japanese)
4. ”Analysis of HF exact exchange in Long-Range Corrected Density functional Theory Calculation of Physical Properties”, Y. Kawashima, K. Hirao, The 8th Annual Meeting of Japanese Society for Molecular Science, Hiroshima University, Sep. 21-24 (2014). (Poster in Japanese)

5. "Efficient evaluation of short-range Gaussian attenuation Hartree-Fock exchange for periodic systems and large molecules" J.-W. Song, K. Hirao, ICCMSE, Athens, Mar. 20-23 (2015).
6. "Efficient evaluation of short-range Gaussian attenuation Hartree-Fock exchange for periodic systems and large molecules" J.-W. Song, M. A. Watson, K. Hirao, Molecular Electronic Structure, Amasya, Sep. 1-5 (2014).
7. "Analysis of the difference in intra- and inter-molecular charge transfer employing long-range corrected density functional theory", J.-W. Song, K. Hirao, The 17th Theoretical Chemistry Symposium, Nagoya University, May22-24. (In Japanese)

(5) Patents and Deliverables

- None