Chapter 16

Computational Chemistry Research Unit

16.1 Members

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16.2 Research Activities

Electronic structure calculations are now indispensible for understanding chemical phenomena. Density functional theory (DFT), which is simple, conceptual, and applicable to large systems, has emerged as a powerful computational tool to tackle molecular electronic structures. 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.

16.3 Research Results and Achievements

16.3.1 Long-Range Corrected Density Functional Theory with Linearly-Scaled Hartree-Fock Exchange Using a Two-Gaussian Operator

Hybrid density functionals have become a main quantum chemical tool for the calculation of energies and properties of molecular systems since its development in 1993. The Hartree-Fock (HF) exchange introduced in hybrid functionals remedy the shortcomings of density functional theory (DFT). Development of long-range corrected hybrid scheme for density functional theory, which follows a decade later, widened the applicability of the hybrid functional further. The introduction of the error function HF exchange operator in DFT calculation 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 remain as a bottleneck for the broader and more active applications of hybrid functionals to large molecular and periodic systems. 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 (e.g., about 14 times acceleration in C diamond calculation using periodic boundary condition) and enables lower scaling with system size, while maintaining the improved features of the long-range corrected density functional theory.

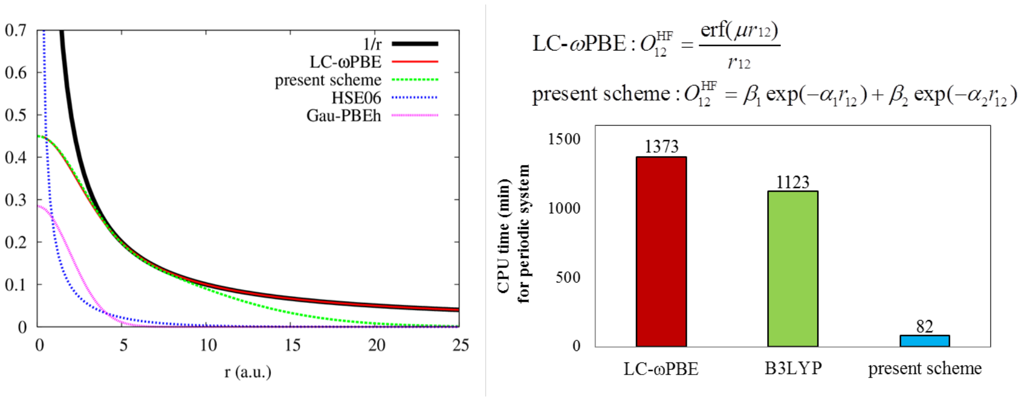

Figure 16.1: Functions of the HF exchange operator (left) and CPU time comparison of the new proposed method vs conventional methods (right).

16.3.2 Development of efficient algorithm for Gaussian Hartree-Fock exchange operator

Hybrid density functionals have succeeded in increasing the accuracy of density functional theory (DFT) by including Hartree-Fock (HF) exchange. Nowadays, most electronic structure calculations for isolated systems employ hybrid density functionals. Inclusion of HF exchange lead to improvement of electronic structure calculations for extended systems as well. The accuracy of bandgap, which is a major factor determinig electronic conductivity in extended systems, increased dramatically. However, the computational cost of HF exchange inhibits the use of hybrid density functionals for electronic structure calculations for extended or large-scale systems. We previously developed an efficient screened hybrid functional called Gaussian-Perdew–Burke–Ernzerhof (Gau-PBE) [Song et al., J. Chem. Phys. 135, 071103 (2011)], which is characterized by the usage of a Gaussian function as a modified Coulomb potential for the Hartree-Fock (HF) exchange. 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 bandgaps of semiconductors compared to previously developed well-known methods. We present a distance-based screening scheme here that is tailored for the Gaussian HF exchange integral that utilizes multipole expansion for the Gaussian two-electron integrals. We found the new multipole screening scheme saves the computational cost for the HF exchange integration by efficiently decreasing the number of integrals of 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 is 1.2 times faster than our previous implementation, and 2.1 times faster than the well-known HSE06 method.

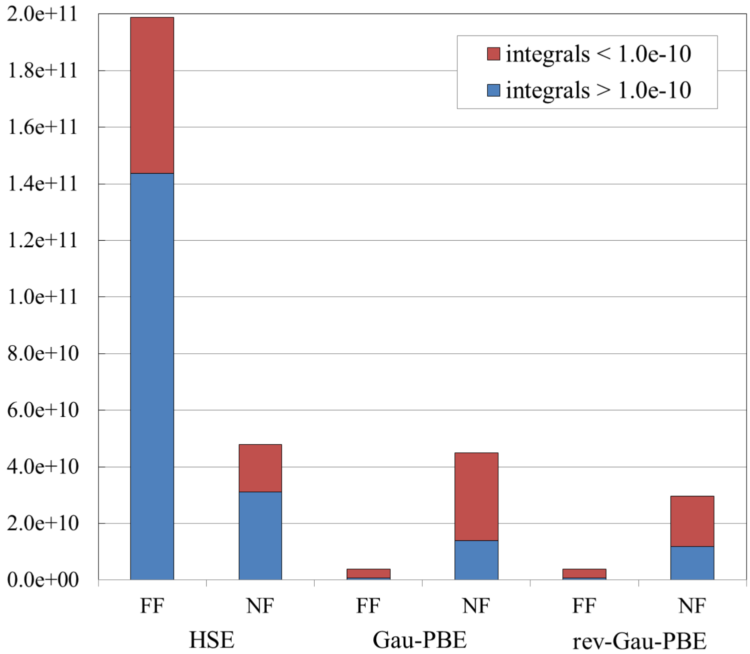

Figure 16.2: The numbers of calculated HF exchange integrals of HSE, Gau-PBE, and rev-Gau-PBE in C diamond.

16.3.3 Critical Assessment of Same-Spin Correlation in OP Correlation Functional

In the present study, we have investigated two significant features of the OP correlation functional, namely the incorporation of the exchange functional into itself, and the inclusion of only opposite-spin (OS) effects. To explore the latter feature, we have compared OP with B95 and a new functional introduced in the present study – the OPB method that combines OP with the same-spin (SS) component of B95. In general, we find that B95 and OPB perform comparably. Our comparisons of the various Density Functional Theory (DFT) procedures suggest that the incorporation of a meta-GGA (e.g., TPSS) into OP and OPB does not necessarily lead to a chemically more accurate procedure than the use of a related GGA (e.g., PBE). An important finding is the more notable (and somewhat more consistent) improvement in performance with the incorporation of SS correlation, particularly for longer-range chemical properties. Nonetheless, on average across our test sets of over 800 systems, the difference between the performances of OP versus B95 or OPB is not exceedingly large. By drawing a parallel between these DFT methods and the wavefunction scaled-MP2-type methods, we reason that one can further develop the OP functional, and perhaps a wider range of correlation functionals by combining it with the technique of range separation.

16.3.4 Probing Fullerene Formation by Supercomputers

Fullerenes are nano-sized carbon materials studied intensively due to its to its wide applicability such as a silver bullet for HIV, cosmetics, and superconductive devices. However, its precise value of "heat of formation", which is a fundamental property to understand how materials form and change, was not yet known. We have carried out large-scale computational quantum chemistry calculations on the K computer with NTChem software to obtain heats of formation for C_{60} and some higher fullerenes with the DSD-PBE-PBE/cc-pVQZ double-hybrid density functional theory method. Our best estimated values are 2520.0 ± 20.7 (C_{60}), 2683.4 ± 17.7 (C_{70}), 2862.0 ± 18.5 (C_{76}), 2878.8 ± 13.3 (C_{78}), 2946.4 ± 14.5 (C_{84}), 3067.3 ± 15.4 (C_{90}), 3156.6 ± 16.2 (C_{96}), 3967.7 ± 33.4 (C_{180}), 4364 (C_{240}) and 5415 (C_{320}) kJ/mol. Using the convergence behavior for the calculated per-atom heats of formation, we obtained the formula $\Delta_f H$ per carbon = $722\text{n}^{-0.72}$ + 5.2 kJ/mol (n = the number of carbon atoms), which enables an estimation of $\Delta_f H$ for higher fullerenes more generally. A slow convergence to the graphene limit is observed, which we attribute to the relatively small proportion of fullerene carbons that are in “ low-strain” regions. We further propose that it would take tens, if not hundreds, of thousands of carbons for a fullerene to roughly approach the limit. Such a distinction may be a contributing factor to the discrete properties between the two types of nanomaterials. During the course of our study, we also observe a fairly reliable means for the theoretical calculation of heats of formation for medium-sized fullerenes. This involves the use of isodesmic-type reactions with fullerenes of similar sizes to provide a good balance of the chemistry and to minimize the use of accompanying species.

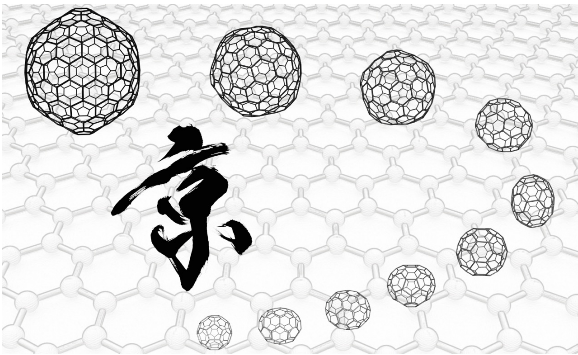

Figure 16.3: Illustration of fullerene systems calculated on the K computer.

16.4 Schedule and Future Plan

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 develop methods for solid-state calculations.

16.5 Publications

Journal Articles

[1] Bun Chan et al. “From C_{60} to Infinity: Large-Scale Quantum Chemistry Calculations of the Heats of Formation of Higher Fullerenes”. In: *J. Am. Chem. Soc.* 138 (2016), p. 1420.

[2] Bun Chan et al. “Performance of the OP correlation functional in relation to its formulation: Influence of the exchange component and the effect of incorporating same-spin correlations”. In: *J. Comput. Chem.* 37 (2016), p. 1306.

[3] Rahul Kar et al. “Molecules relevant for Organic Photovoltaics: A Range Separated Density Functional Study”. In: *Mol. Phys. (Special Issue in Honour of Sourav Pal)* 113 (2015), p. 2930.

[4] Yudai Ogata et al. "Theoretical vibrational spectra of $OH^{-}(H_2O)_2$: the effect of quantum distribution and vibrational coupling". In: *Phys. Chem. Chem. Phys.* 17 (2015), p. 25505.

[5] Jong-Won Song and Kimihiko Hirao. "Efficient method of evaluation for Gaussian Hartree-Fock exchange operator for Gau-PBE functional". In: *J. Chem. Phys.* 143 (2015), p. 024102.

[6] Jong-Won Song and Kimihiko Hirao. "Long-Range Corrected Density Functional Theory with Accelerated Hartree-Fock Exchange Using a Two-Gaussian Operator [LC-ωPBE(2Gau)]". In: *J. Chem. Phys.* 113 (2015), p. 2930.

[7] Takao Tsuneda. "Chemical reaction analyses based on orbitals and orbital energies". In: *Int. J. Quantum Chem. (Special Issue on Theoretical Chemistry in Japan)* 115 (2015), p. 270.

[8] Takao Tsuneda, Raman K. Singh, and Ayako Nakata. "Relationship between orbital energy gaps and excitation energies for long-chain systems". In: *J. Comput. Chem.* 37 (2016), p. 1451.

[9] Sara Watanabe et al. "Effects of a microhydration on an adenine-thymine pair". In: *Theo. Chem. Acc.* 134 (2015), p. 84.

Conference Papers

[10] Jong-Won Song and Kimihiko Hirao. "Long-range Corrected Density Functional Theory with Linearly-Scaled HF exchange". In: *AIP Conf. Proc., 1702, 090062.* Vol. 1702. 2015, p. 090062.

Invited Talks

[11] Kimihiko Hirao. *Range separated DFT functional.* Workshop on "Advances in Electronic Structure Theory". Paris, France. Apr. 2015.

[12] Kimihiko Hirao and Jong-Won Song. *Recent Advances in Long-range Corrected (LC) DFT.* The Seventh Asia-Pacific Conference of Theoretical and Computational Chemistry APCTCC7. Kaoshiung, Taiwan. Jan. 2016.

[13] Yukio Kawashima. *Highly accurate calculations of large-scale fullerenes with NTChem and Supercomputers (in Japanese).* 5th NTChem Workshop. Tokyo, Japan. Mar. 2016.

[14] Takao Tsuneda. *Reaction analyses based on orbital energies.* The Seventh Asia-Pacific Conference of Theoretical and Computational Chemistry APCTCC7. Kaoshiung, Taiwan. Jan. 2016.

[15] Takao Tsuneda. *Reconsideration of chemical reactivity indices.* The 6th Japan-Czech-Slovak International Symposium on Theoretical Chemistry (JCS-2015). Bratislava, Slovakia. Oct. 2015.

[16] Takao Tsuneda. *Theoretical investigation on local proton conductance in proton exchange membranes.* EMN meeting on Membranes. Dubai, UAE. Apr. 2016.

[17] Takao Tsuneda. *Theoretical Investigations on Band Gaps of Extended Systems.* The 36th Progress in Electromagnetics Research Symposium (PIERS 2015). Prague, Czech Republic. July 2015.

Posters and Presentations

[18] Yukio Kawashima and Kimihiko Hirao. *Fast Algorithm Development for LC-DFT (in Japanese).* The 9th Annual Meeting of Japan Society for Molecular Science. Tokyo, Japan. Sept. 2015.

[19] Jong-Won Song and Kimihiko Hirao. *Accelaration of LC-DFT employing Gaussian functions (in Japanese).* The 18th Theoretical Chemistry Symposium. Osaka, Japan. May 2015.

[20] Jong-Won Song et al. *Adsorption energy calculations using long-range corrected density functional theory between CO and metal system (in Japanese).* The 9th Annual Meeting of Japan Society for Molecular Science. Tokyo, Japan. Sept. 2015.

[21] Takao Tsuneda. *Exciton Binding Energies for Extended Systems (in Japanese).* Workshop on Theoretical Chemistry for Condensed Systems. Okinawa, Japan. Mar. 2016.

[22] Takao Tsuneda. *The effect of long-range exact exchange and two-electron excitation in excited states of extended systems (in Japanese)*. Symposium on Recent Advances in Quantum Chemistry: Quantum chemical simulation on large-scale complex systems. Kobe, Japan. Mar. 2016.

[23] Takao Tsuneda. *Theoretical study on fuel cells: proton exchange membranes (in Japanese)*. The 7th Symposium of Elements Strategy Initiative for Catalysts and Batteries: Interplay Between Experimental and Theoretical Studies. Kyoto, Japan. Sept. 2015.

[24] Takao Tsuneda. *Theory of Orbitals and Its Energies (in Japanese)*. The 5th Quantum Chemistry School. Okazaki, Japan. Nov. 2015.