

17. Computational Chemistry Research Unit

17.1. Unit members

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17.2. Research Activities

There are two major approaches in investigating the electronic structure theories of molecules: wavefunction methods and density functional theory (DFT). For more than 30 years, huge amount of efforts have been made to enhance wavefunction methods to become well-accepted state-of-the-art methodologies. Using the wavefunction methods, accurate results can be obtained for small systems. However, it is rather difficult to handle very large systems due to the steep N-dependence. Instead of the wavefunction methods, DFT has emerged as a powerful computational tool to study chemical systems for its simplicity, concept, and applicability to large systems. However, DFT has not reached such a mature stage as wave function methods.

One large drawback of DFT is that there is no means of systematically improving DFT energies. The accuracy is dictated by the exchange-correlation functional employed. DFT also fails to describe induced/response properties. The failures mainly arise from the wrong long-range behavior due to the local character of the approximate exchange-correlation functionals. So far, we have developed long-range corrected density functional theory (LC-DFT) to solve many problems found in conventional DFT. The development of LC-DFT had a large impact in theoretical chemistry and the number of research based on LC-DFT is growing intensively.

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

17.3. Research Results and Achievements

17.3.1. Long-range Corrected Functionals Satisfy Koopmans' Theorem

Recently, we found a new feature of long-range corrected density functional theory (LC-DFT): LC-DFT is the first and only method to give valence orbital energies quantitatively. Molecular orbitals provide us insights to clarify chemical processes as seen in frontier molecular orbital theory.

However, orbital energies have not been emphasized in investigating chemical processes, because there has never been a method that can quantitatively obtain orbital energies. LC-DFT is now going to change this situation.

In this project, we have shown that long-range corrected density functionals reproduce highly-accurate valence orbital energies beyond comparison to those of other methods. Figure 1 illustrates the HOMO-LUMO gaps of LC-DFT compared to the vertical electron affinities (EAs) minus vertical ionization potentials (IPs) that are calculated by CCSD(T)/6-311++G(3df,3pd) for 113 molecules. We found that molecular orbitals obtained by LC functionals almost meet the Koopmans' theorem, which establishes that HOMO and LUMO energies are identical to the minus corresponding IP and EA, respectively. We also showed that the valence orbital energies and HOMO-LUMO gaps of LC functionals are better than those of recently proposed ω M05-D [*J. Chem. Phys.* **136**, 154109 (2012)]. We have also decomposed the IP energies into the orbital, relaxation, and correlation energies. It is found that the LC-DFT inherently includes more relaxation effects than the Hartree-Fock method does and contains more correlation effects than conventional density functionals do.

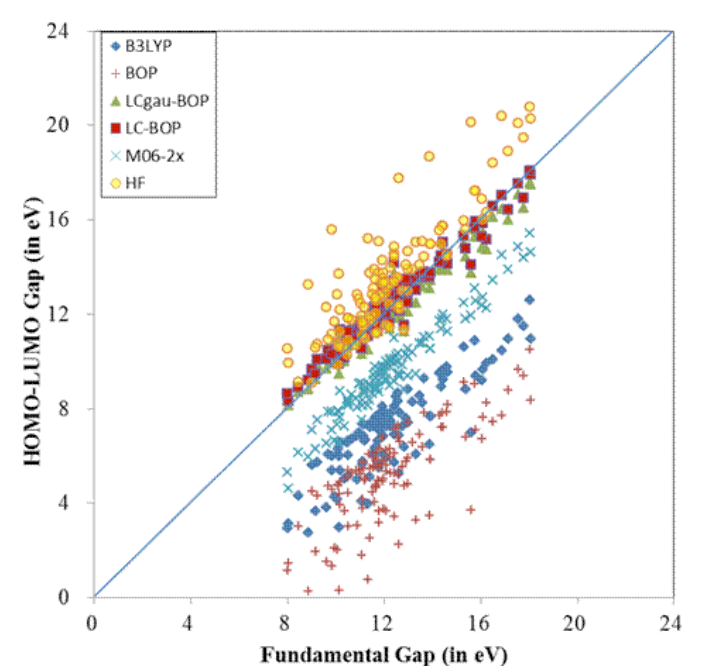


Fig. 1. Calculated HOMO-LUMO energy gap versus reference fundamental gap for 113 molecules. Reference fundamental gap are calculated using IP and EA calculated by CCSD(T). (Taken from R. Kar, J.-W. Song, K. Hirao, *J. Comput. Chem.*, 34, 958–964 (2013))

17.3.2. Improvement of LC-DFT functional performance on thermochemical properties

Various exchange and correlation functionals have been developed to enhance the applicabilities of DFT. One-parameter progressive (OP) correlation functional that we have previously developed is

a flexible correlation functional, which progressively depends on the exchange functional employed. In our previous study, long-range corrected exchange functionals and its Gaussian-attenuated functionals (LCgau) have been combined with the OP correlation functional. However, the parameter in the OP functional has not been optimized taking the exchange potential into account. We therefore examined to re-optimize the parameter.

The parameter of the OP correlation functional was optimized combining with the LC- and LCgau-applied Becke88 exchange functionals for atomization energies. As a result, we confirmed that the LC-BOP and LCgau-BOP functionals with the new parameter perform well in calculations of several properties compared to our previous calculations as shown in Fig. 2.

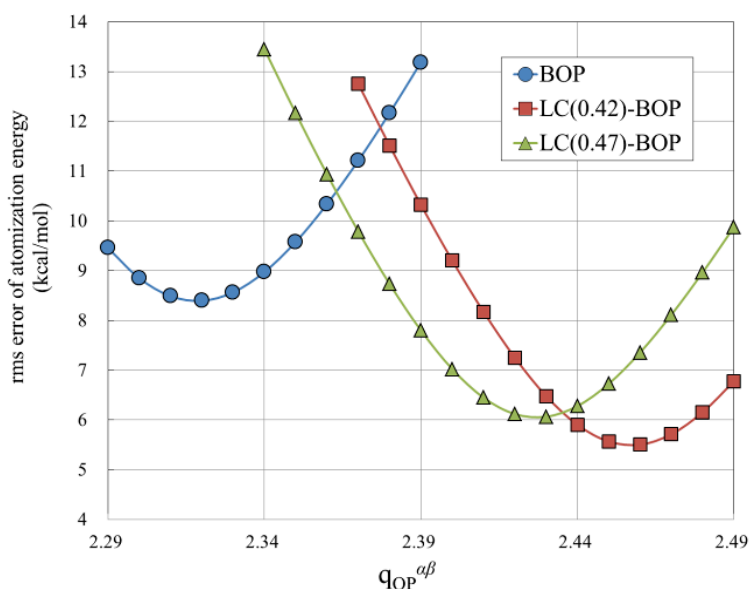


Fig. 2. The root mean square (rms) error of the G2 set atomization energies (148 molecules) depending on the μ parameter of the BOP functional and the LC-BOP functional with $\mu= 0.42$ and 0.47. (Taken from J.-W. Song, K. Hirao, Chem. Phys. Lett., 563, 15–19 (2013)).

17.3.3. The development of DFT functional applicable to solid states

To predict accurate band gaps by orbital energy gaps has been of substantial importance in developing new materials. However, conventional DFT functionals have been reported to give orbital energy gaps smaller than experimental band gaps for semi-conductors used in e.g. solar cells. Although several hybrid functionals such as Heyd-Scuseria-Ernzerhof (HSE) have been developed to make orbital energy gaps of semi-conductors close to band gaps, the computational cost of calculations using HSE is too demanding.

Recently, we developed a new functional for solid state band gap calculations, which is called Gau-PBE hybrid functional, that uses a Gaussian function as a modified Coulomb operator and is applied to Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. In the Gaussian-basis

calculations, the new functional is found to give much more accurate band gaps, described as orbital energy gaps, than those of HSE with much less computational time as shown in Fig. 3.

Moreover, we implemented our Gau-PBE functional in a periodic quantum chemistry software, Quantum ESPRESSO. It is well known that, in periodic calculations, hybrid functionals obtain orbital energy gaps close to the band gaps, but is too much time consuming. The new functional has no singularity problem in the Fock matrix calculations that is usually given in hybrid functional calculations. As a result, we confirmed that our new implemented functional as the most computational time saving method.

We also updated the Gau-PBE functional by adopting the Ernzerhof-Perdew exchange hole (EP) model to the DFT exchange part of PBE. The new functional is named Gau-PBEh. Applying the EP model to the DFT part of Gau scheme contributes to the improvement of the performance over atomization energies and solid state lattice constants. In addition, Gau-PBEh takes nearly the same computation time for band gap calculations as Gau-PBE, implying that less than 60% of the time taken in HSE hybrid DFT functional calculations.

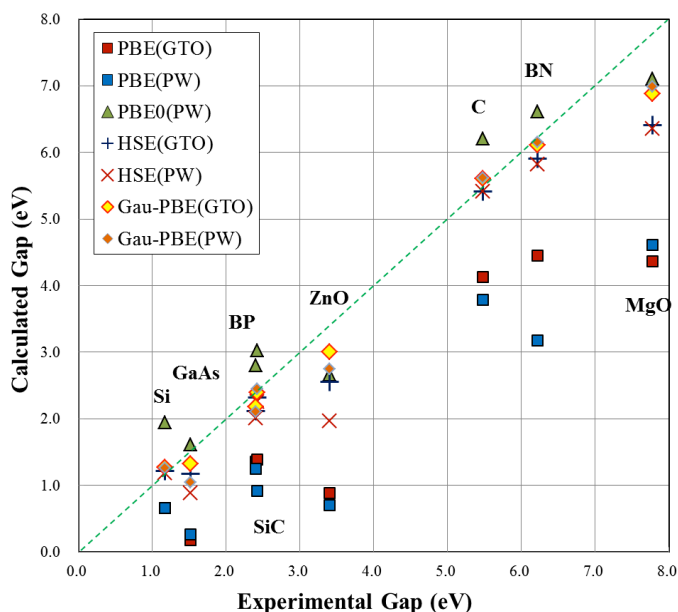


Fig. 3. A comparison of band gaps calculated using PBE, PBE0, HSE, and Gau-PBE vs experimental band gaps. The band gaps using both Gaussian-type-orbital and plane waves are presented. In plane wave calculations, $24 \times 24 \times 24 k/6 \times 6 \times 6 q$ is used. Only in ZnO, $8 \times 8 \times 8 k/4 \times 4 \times 4 q$ is used. (Taken from J.-W. Song, K. Yamashita, K. Hirao, J. Chem. Phys. 137, 244105 (2012))

17.3.4. LC-DFT application to Diels-Alder reactions

Diels-Alder reactions have been important target systems in quantum chemistry especially for chemical reactivity calculations. The empirical frontier molecular orbital theory has been used to interpret or to predict both the reaction rates and regioselectivities of the Diels–Alder reactions by

frontier (HOMO and LUMO) orbitals. The reactivities of the Diels–Alder reactions have been analyzed with global hardness, usually approximated as a half of the HOMO-LUMO gap. Recently, we found that LC-DFT reproduces HOMO-LUMO gap quantitatively. In this study, we seek the possibility of quantitative reaction analysis on the orbital energies of LC-DFT.

First, we calculated the Diels–Alder reaction enthalpies that have been poorly given by conventional functionals including B3LYP functional. As a result, it is found that the long-range correction drastically improves the reaction enthalpies. The barrier height energies were also computed for these reactions. Consequently, we found that dispersion correlation correction is also crucial to give accurate barrier height energies. It is, therefore, concluded that both long-range exchange interactions and dispersion correlations are essentially required in conventional functionals to investigate Diels–Alder reactions quantitatively. After confirming that LC-DFT accurately reproduces the orbital energies of the reactant and product molecules of the Diels–Alder reactions, the global hardness responses, the halves of HOMO-LUMO energy gaps, along the intrinsic reaction coordinates of two Diels–Alder reactions were computed as shown in Figure 4. We noticed that LC-DFT results satisfy the maximum hardness rule for overall reaction paths while conventional functionals violate this rule on the reaction pathways. Furthermore, our results also show that the HOMO-LUMO gap variations are close to the reaction enthalpies for these Diels–Alder reactions. Based on these results, we foresee quantitative reaction analysis on the orbital energies.

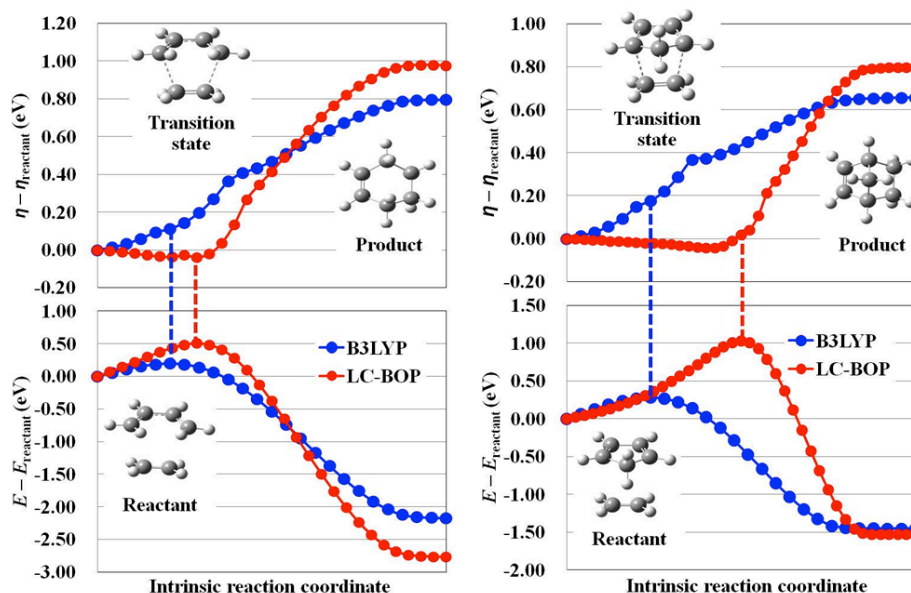


Fig. 4. Global hardness responses and total energies along the intrinsic reaction coordinates for the reactions of butadiene with ethylene a) and cyclopentadiene with ethylene b). Global hardness responses and total energies are set to be zero at the reactants. (Taken from R. K. Singh, T. Tsuneda, *J. Comput. Chem.* 34, 379–386 (2013))

17.4. Schedule and Future Plan

In the next fiscal year, we perform the following studies to expand the applicabilities of LC-DFT.

First, we are developing 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 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.

17.5. Publication, Presentation and Deliverables

(1) Journal Papers

1. J.-W. Song, K. Yamashita, K. Hirao, "Gaussian attenuation hybrid scheme applied to Ernzerhof-Perdew exchange hole model (Gau-PBEh)", *J. Chem. Phys.* 137, 244105 (2012).
2. K. Hirao, "The K Computer: User-Friendly", *Science* 338, 1149–1149 (2012).
3. K. Hirao, "Special Contribution Japan's K Computer Project", *FUJITSU Sci. Tech. J.* 48, 247–254 (2012).
4. R. Kar, J.-W. Song, K. Hirao, "Long-Range Corrected Functionals Satisfy Koopmans' Theorem: Calculation of Correlation and Relaxation Energies", *J. Comput. Chem.*, 34, 958–964 (2013).
5. R. K. Singh, T. Tsuneda, "Reaction Energetics on Long-Range Corrected Density Functional Theory: Diels-Alder Reactions", *J. Comput. Chem.* 34, 379–386 (2013).
6. J.-W. Song, K. Hirao, "Long-range corrected density functional theory with optimized one-parameter progressive correlation functional (LC-BOP12 and LCgau-BOP12)", *Chem. Phys. Lett.*, 563, 15–19 (2013).

(2) Review Articles and Books

1. T. Tsuneda, "Fundamentals of Density Functional Theory", (Kodansha) (2013). (in Japanese).
2. T. Tsuneda, " π -Stacking on Density Functional Theory: A Review", in π -Stacked Polymers and Molecules, edited by T. Nakano (Springer-Verlag) (2013).

(3) Invited Talks

1. K. Hirao, "Recent Advances in LC-DFT", "Electronic Structure Theory for Strongly Correlated Systems", Hotel La Torre, Palermo, Italy, May 30– Jun. 1 (2012).

2. K. Hirao, "Long-Range Corrected DFT Functional", University of Delaware, Newark, USA, Aug. 1–3 (2012).
3. T. Tsuneda, "Density Functional Theory for Chemistry", 52nd Summer School of Young Molecular Scientists' Association, University of Tokyo, Tokyo, Japan, Aug. 20–24 (2012). (In Japanese)
4. K. Hirao, "The K Computer and Science", Theory and Applications of Computational Chemistry (TACC2012), Pavia, Italy, Sep. 2–7(2012).
5. T. Tsuneda, "History and Recent Progress in Research on Orbital Energies", 24th Quantum Chemistry Seminar, Waseda University, Tokyo, Japan, Jan. 17 (2012). (In Japanese)
6. T. Tsuneda, "New Findings in Research on Orbital Energies", Supercomputer Workshop, Okazaki Conference Center, Okazaki, Japan, Jan. 22–23 (2013). (In Japanese)
7. K. Hirao, "Long-Range Corrected DFT Functionals", CRC International Symposium in Strasbourg "Chemical Theory for Complex Systems", University of Strasbourg, Strasbourg, France, Mar. 7–8 (2013).
8. T. Tsuneda, "Necessity of Long Range Correction in DFT for Dispersion Interaction Calculation", The 68th Annual Meeting of the Physical Society of Japan (Symposium), Hiroshima University, Higashi-Hiroshima, Japan, Mar. 26–29 (2012). (in Japanese)

(4) Posters and presentations

1. J.-W. Song, K. Hirao, "Which is Better: An Error Function or Gaussian Attenuation in Hybrid Density Functional Theory for Solid State Calculations?", The 14th International Congress of Quantum Chemistry, Boulder, USA, Jun. 25–30 (2012).
2. R. Kar, K. Hirao, "Do Long-Range Corrected Density Functionals Satisfy Koopmans' Theorem?", The 14th International Congress of Quantum Chemistry, Boulder, USA, Jun. 25–30 (2012).
3. A. Chutia, T. Tsuneda, "An examination of exchange-correlation functionals in solid-state calculations", 6th Annual Conference of the Molecular Science Society of Japan, University of Tokyo, Tokyo, Japan, Sep. 18–21 (2012).
4. R. K. Singh, T. Tsuneda, K. Miyake, M. Watanabe, " Theoretical Investigation of Proton Conductivity in Proton Exchange Membranes for Fuel Cells", 6th Annual Conference of the Molecular Science Society of Japan, University of Tokyo, Tokyo, Japan, Sep. 18–21 (2012).
5. J.-W. Song, K. Hirao, "An efficient hybrid DFT functional using a Gaussian attenuating HF exchange for band gap calculations of solid state materials", The 3rd AICS International symposium, Kobe, Japan, Feb. 28– Mar. 1 (2013).

(5) Patents and Deliverables

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