Usage Report for Fiscal Year 2018

Project Title: Development of new long-range corrected density functional theory

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1. Background and purpose of the project, relationship of the project with other projects

Over the two decades, research has demonstrated that long-range corrected (LC) density functional theory (DFT) can improve the problematic behaviors of the conventional DFT functionals that arise with regards to several key chemical properties. These improvements can be achieved by the inclusion of the Hartree-Fock (HF) exchange integral at long-range inter-electronic distance using a modified two-electron HF exchange operator with an error function,

$$O^{\mathrm{HF}}(r_{12}) = \frac{\mathrm{erf}(\mu r_{12})}{r_{12}}. \quad (1)$$

Here, the modified exchange operator, OHF, is defined through the decomposition of the Coulomb operator, 1/r12, of the exchange energy as

$$\frac{1}{r_{12}} = O^{\mathrm{HF}}(r_{12}) + \left[\frac{1}{r_{12}} - O^{\mathrm{HF}}(r_{12})\right]_{\mathrm{DFT}} \quad (2)$$

where $r_{12} = | r_1 - r_2 |$ is the distance between electrons r_1 and r_2 and μ is a parameter that controls the inclusion ratio between HF and DFT exchange dependent on r12.

In order to accelerate long-range corrected HF DFT calculations, we recently developed a modified LC-DFT functional, named LC-DFT(2Gau), with the accelerated evaluation of long-range HF exchange integrals, which utilizes a two-electron HF operator consisting of two Gaussian functions, instead of the error function operator of Eqn. (1) as

$$O^{\mathrm{HF}}_{LC-DFT(2Gau)}(r_{12}) = \beta_S e^{-\alpha_S r_{12}^2} + \beta_L e^{-\alpha_L r_{12}^2}. \quad (3)$$

In the two-electron HF operator of Eqn. (3), the first one of two Gaussian functions, which has a set of two parameters, α_S and β_S, is used to mimic the short-range region of the HF exchange operator, while the other Gaussian function with α_L and β_L covers the long-range HF exchange region of LC-DFT.

The OP correlation functional is a unique correlation functional, in that its functional form includes the generalized gradient approximation factor of the combined exchange functional and a semi-empirical parameter, $q_{\mathrm{OP}}^{\alpha\beta}$, which determines the correlation length and is also dependent on the combined exchange functional.

In this project, we attempted to extend the LC scheme with 2Gau to more general cases of exchange correlation functionals, such as Becke88 exchange (B88) + LYP correlation functionals and B88 + OP correlation functionals (LC-BLYP and LC-BOP) with various values of range separation parameter (μ) in order to activate the applicability of the LC-DFT(2Gau) scheme.

2. Specific usage status of the system and calculation method

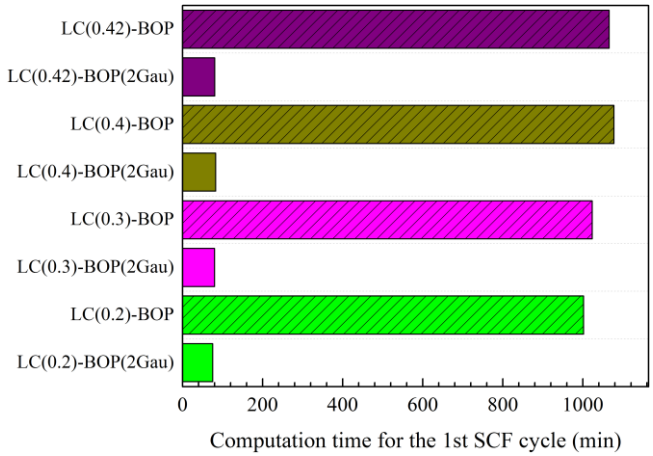
In this project, we used 0.2% of gwmpc (7,014 hour), 0.9% of gwacsg (548 hour) and more than 19.0% of bwmpc (557,185 hour) for this project and other researches which will be submitted to publications.

3. Result

We assessed LC-BOP(2Gau) functionals with the optimal parameter set of αS, βS, and $q_{\mathrm{OP}}^{\alpha\beta}$ with the atomization energies of the G3 set, the reaction barrier height of the HTBH38/04 and NHTBH38/04 sets, and the HOMO energies of 113 molecules. The statistical data of calculated results using LC-BOP(2Gau) and LC-BOP show that the atomization energies of the G2 and G3 sets, the reaction barrier heights, and the HOMO energies calculated using LC-BOP(2Gau) do not deviate from those of LC-BOP. The results also show that using

long-range Gaussian parameters (αL=0.18 and βL=0.006) to LC-BOP(2Gau) with μ values other than 0.4 is successful when performing calculations of the tested chemical properties. As a result, LC-BOP(2Gau) seems to reproduce the results of LC-BOP well in all the tested calculations.

Additionally, we examined the efficiency of the two-Gaussian operator corresponding to several μ values on the computational time by recording the time cost for the first SCF cycle of the periodic diamond system of carbon as done in the previous report. Figure 2 shows computational time taken for LC-BOP with μ=0.2, 0.3, 0.4, and 0.42 and its corresponding LC-BOP(2Gau) to complete the first cycle using single core computations of CPU. The ratios for LC-BOP(2Gau) to LC-BOP are noticeably small at 0.075~0.078:1 in any cases of μ value, which indicates that the short-range HF Gaussian function is nearly not responsible for the computational cost and time cost of LC-BOP(2Gau) functionals corresponding to various μ values have little difference on time cost.



4. Conclusion

LC-BOP [or LC-BOP(2Gau)] with optimal parameters, in particular, provides errors on thermochemical energies that are 3~5 times smaller than LC-BLYP [or LC-BLYP(2Gau)] and, moreover, LC-BOP [or LC-BOP(2Gau)] provides low errors on thermochemical energies compared with LC-ωPBE [or LC-ωPBE(2Gau)] and LC-BLYP [or LC-BLYP(2Gau)] even in small μ values. We expect that LC-DFT(2Gau) with various μ values presented here can be more widely applied to periodic systems and large molecules and that the insights obtained from this study can be used to improve LC-DFT functionals and develop new range-separation functionals.

5. Schedule and prospect for the future

From the next fiscal year, we will extend the application of LC-DFT to Pt and Rh metal surface for the calculations of adsorption energy. To perform these calculations, we will utilize Crystal17 software where our LC-DFT(2Gau) method is implemented.

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Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. “Accelerated Long-Range Corrected Exchange Functional Using a Two-Gaussian Operator Combined with One-Parameter Progressive Correlation Functional [LC-BOP(2Gau)]” J.-W. Song and K. Hirao, J. Comput. Chem. 40, 105 (2019).

[Oral presentation]

1. “Development of DFT functional applicable to large molecular and periodic systems” J.-W. Song, CJK-WTCC4 (2019), Nanjing, China. [invited]
2. “Development of DFT functional applicable to large molecular and periodic systems” J.-W. Song, 23RD INTERNATIONAL WORKSHOP ON QUANTUM SYSTEMS IN CHEMISTRY, PHYSICS, AND BIOLOGY (2018), Kruger Park, South Africa.
3. “Development of DFT functional applicable to large molecular and periodic systems” J.-W. Song, 49th Conference for Korean Society for Imaging Science and Technology (2018), Deagu, Korea. [invited]

[Poster presentation]

1. “Photophysical property calculations of Carbon Nano Belt using Long-range Corrected DFT” Dae-Hwan Ahn and Jong-Won Song, 14th Korea-Japan Symposium on Frontier Photoscience (2018), GIST Gwangju, Korea.
2. “Pyrene Boronic Acid, 'On-off' Sensing System with High Selectivity to Hg2+ ion: Long-range Corrected DFT method” Bhattarai Komala and Jong-Won Song, 14th Korea-Japan Symposium on Frontier Photoscience (2018), GIST Gwangju, Korea.
3. “UV/vis Absorption Spectra of Syn and Anti Pyrene by LC-BOP/TD-DFT” Nizam Udin and Jong-Won Song, 14th Korea-Japan Symposium on Frontier Photoscience (2018), GIST Gwangju, Korea.
4. “Importance fo van der Waals descriprions on accurate isomerization energy calculations of thiourea compounds: LCgau-BOP+LRD method” Dae-Hwan Ahn and Jong-Won Song, 23RD INTERNATIONAL WORKSHOP ON QUANTUM SYSTEMS IN CHEMISTRY, PHYSICS, AND BIOLOGY (2018), Kruger Park, South Africa.
5. “Quantum chemical investigations of intermolecular binding energies between Carbon Nano Tube and aromatic molecules” Dae-Hwan Ahn and Jong-Won Song, 23RD INTERNATIONAL WORKSHOP ON QUANTUM SYSTEMS IN CHEMISTRY, PHYSICS, AND BIOLOGY (2018), Kruger Park, South Africa.
6. “Importance of van der Waals descriprions on accurate isomerization energy calculations of thiourea compounds:LCgau-BOP+LRD method” Dae-Hwan Ahn and Jong-Won Song, 2018 The 2018 Yeungnam regional Conference of Korean Chemical Society (2018), Deagu, Korea.
7. “DFT calculation studies on accurate isomerization energy calculations of thiourea compounds” Dae-Hwan Ahn and Jong-Won Song, 49th Conference for Korean Society for Imaging Science and Technology (2018), Deagu, Korea.