Usage Report for Fiscal Year 2019

Project Title:

Development of new long-range corrected density functional theory

Name: Jong-Won Song

Laboratory at RIKEN: Computational Molecular Science Research Team

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

For decades, van der Waals forces have been investigated with a particular interest in supramolecular, structural biology, and surface science to provide a fundamental and theoretical understanding of the physicochemical causes for noncovalent interactions. However, although many quantum chemical computational methods have been routinely used to estimate the van der Waals forces, it was reported that some conventional density functional theory (DFT) functionals have still provided poor calculations.

Since the discovery of carbon nanotubes (CNTs) in the 1990s, quantum chemistry calculations were performed using MP2 and DFT, using the local density approximation (LDA) and generalized gradient approximation (GGA), but it was known to be inadequate in describing dispersive forces like the van der Waals force.

We have previously reported that developed long-range corrected (LC)- and LC including Gaussian attenuation (LCgau)-DFT+ local response dispersion (LRD) functionals can accurately calculate inter-and intra-molecular weak interactions. Additionally, B3LYP with D3 functional is also known to calculate well intermolecular weak interactions. Therefore, in this project, we will apply the B3LYP-D3 and LCgau-BOP+LRD functionals able to estimate the van der Waals interactions on the CNT complex and alkylthiourea compound.

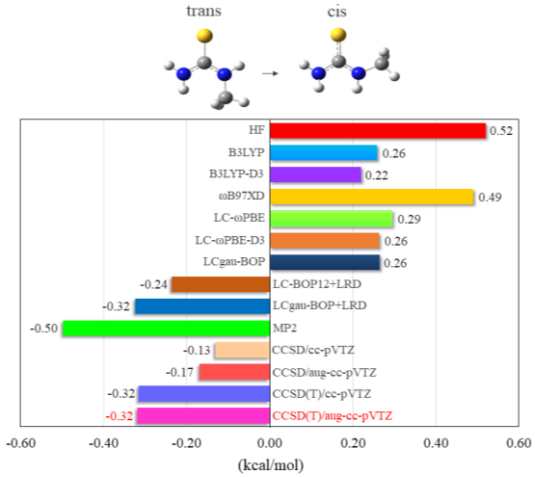
2. Specific usage status of the system and calculation method

We performed LC-DFT calculations for the isomerization reactions of thiourea derivatives. The LC and LCgau schemes were applied to the Becke 1988 exchange + one-parameter progressive (OP) correlation functional (LC-BOP12 and LCgau-BOP). We used the usual three fitted parameters (μ=0.42, a=0.011, and k=18.0) in LCgau-BOP calculations. The LCgau-BOP functional was combined with the original LRD method, and the LC-BOP12 functional, which utilizes a new parameter set of range separation and one parameter for OP correlation functional, was combined with the LRD method with newly optimized parameters. We also adopted the B3LYP with D3 weak interaction functional to obtain intermolecular binding energies on the CNT systems.

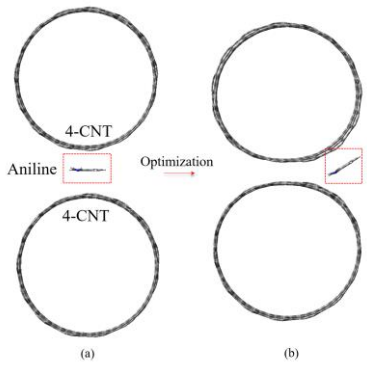
3. Result

We found that all the tested electron correlation methods of CCSD(T), CCSD, and MP2 predict that the cis isomer is more stable than the trans isomer in methylthiourea and all the DFT functionals seem to have severe systematic errors on methylthiourea isomerization energy. Moreover, van der Waals correction for DFT functionals in ωB97XD, LC-ωPBE-D3, and B3LYP-D3 does not seem to improve these systematic errors. The van der Waals correction using D3 seems to improve isomerization energies to a slight extent when we compare the isomerization energies between B3LYP and B3LYP-D3 or between LC-ωPBE and LC-ωPBE-D3. However, LC-BOP12+LRD, which includes both weak interaction and long-range exchange corrections, computes that the energy of cis-methylthiourea is more stable than that of

trans-methylthiourea, in agreement with the CCSD(T) prediction. Therefore, LC-BOP+LRD and LCgau-BOP+LRD are also expected to accurately calculate intramolecular weak interactions between the alkyl group and the S atom in thiourea compounds.



All aromatic molecules such as aniline, benzophenone, and diphenylamine were found to exhibit strong intermolecular binding energies with the inner surface of the CNT, rather than the outer surface. Hydrogen bonding between two aromatic molecules that include N and O atoms is shown to further stabilize the intermolecular adsorption process. Therefore, when benzophenone and diphenylamine were simultaneously allowed to interact with a CNT, the aromatic molecules were expected to preferably enter the CNT. Furthermore, additional calculations of the intermolecular adsorption energy for aniline adsorbed on a graphene surface showed that the concavity of graphene-like carbon sheet is in proportion to the intermolecular binding energy between the graphene-like carbon sheet and the aromatic molecule.



4. Conclusion

We found that B3LYP-D3, LC-ωPBE-D3, and ωB97XD, known for their good descriptions of weak interaction calculations, fail to reproduce the isomerization reaction energies of the molecules that include the S atom. In contrast, LC- and LCgau-BOP+LRD functionals provide isomerization reaction energies that are very close to those produced by highly accurate wave function methods. These results show that accurate description of the intramolecular weak interaction between the alkyl group and the S atom, unlike the case of urea, is significant to reproduce correct energy of molecules with alkyl group and S atom.

We found that the intermolecular binding energies obtained consistently show that all the aromatic molecules of aniline, benzophenone, and diphenylamine preferentially bind to the inside of the CNT rather than to the outer surface and aromatic molecules, such as benzophenone and diphenylamine, are likely to be preferably adsorbed on the inner surface of the CNT, to optimize binding energies.

5. Schedule and prospect for the future

Recently, we reported in a previous study that a simple yet efficient method for the computation of a long range corrected (LC) hybrid scheme [LC-DFT(2Gau)], which uses a modified two Gaussian attenuating operator instead of the error function for the long-range HF exchange integral, reproduces well the thermochemical and frontier orbital energies of LC-BOP with a lower time cost. We hope to apply LC-DFT(2Gau) functional to adsorption energy calculations between metal surface (Cu, Pt, Ph, etc) and CO molecule with Gaussian16 and NTChem. We also hope to develop a combined functional of van der Waals and LC scheme with variable range separation parameter, which can be applied to fluorescence calculations.

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Fiscal Year 2019 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. "Application of Accelerated Long-range Corrected Exchange Functional to Periodic Boundary Condition Systems: CO Adsorption on Cu(111) Surface" Kenji Mishima, Masanori Kaneko, Jong-Won Song,* Hiroki Kawai, Koichi Yamashita, and Kimihiko Hirao, *J. Chem. Phys. in revision* (2020).
2. "Excitation energies expressed as orbital energies of KS-DFT with LC functionals" Kimihiko Hirao, Bun Chan, Jong-Won Song, Kamala Bhattarai, and Subrata Tewary, *J. Compt. Chem.* in revision (2020).
3. "Predicting whether aromatic molecules would prefer to enter a carbon nanotube — A density functional theory study" Dae-Hwan Ahn, Chiyoung Park, and Jong-Won Song,* *J. Compt. Chem.* in press (2020).
4. "Importance of van der Waals descriptions on accurate isomerization energy calculations of thiourea compounds: LCgau-BOP+LRD method" Dae-Hwan Ahn, Takeshi Sato, Jong-Won Song,* and Kimihiko Hirao, *J. Phys. Chem. A* **123**, 7034-7041 (2019).
5. "A Density Functional Theory Based Scheme to Compute the Redox Potential of a Transition Metal Complex: Applications to Heme Compound" Matsui Toru* and Jong-Won Song,* *Molecules* **24**, 819 (2019).

[Oral presentation]

1. "Fluorescence calculations with Long-range Corrected Density Functional Theory" J.-W. Song, 25RD INTERNATIONAL WORKSHOP ON QUANTUM SYSTEMS IN CHEMISTRY, PHYSICS (2019), Ukraine.
2. "Development of DFT functional applicable to large molecular and periodic systems" J.-W. Song, International symposium of 3rd university(Saga-Daegu-Soochow) (2019), Saga, Japan (invited)

[Poster presentation]

1. "Study on spectrum of Carbon Nano Belt(CNB) using Long-range Corrected DFT" Dae-Hwan Ahn and Jong-Won Song, 51th Conference for Korean Society for Imaging Science and Technology (2019), Busan, Korea.
2. "Study on absorption and fluorescence spectra of Pyrene Excimer using Long-range Corrected density functional theory" Kmla Bhattarai and Jong-Won Song, 51th Conference for Korean Society for Imaging Science and Technology (2019), Busan, Korea.
3. "Reproduction of photophysical properties for carbon nanobelt(CNB) using long-range corrected DFT calculation" Dae-Hwan Ahn and Jong-Won Song, International Conference on Advanced Imaging (2019), Chiba, Japan.
4. "Quantum chemical calculation of UV/Vis Absorption Spectrum of Pyrene Excimers using Long-range Corrected DFT method" Kmla Bhattarai and Jong-Won Song, International Conference on Advanced Imaging (2019), Chiba, Japan.
5. "Fluorescence calculation of exciplex state of magnetic field effect (MFE) peptoid using density functional theory" Dae-Hwan Ahn and Jong-Won Song, 124th General Meeting of the Korean Chemical Society (2019), Changwon, Korea.
6. "ab initio quantum chemical computational study on Hg2+ ion selectivity of tetraphenylethylene- bis (thiophene-2-ylmethyl)amine" Dae-Hwan Ahn and Jong-Won Song, 52th Conference for Korean Society for Imaging Science and Technology (2019), Busan, Korea.