Usage Report for Fiscal Year 2019

Project Title:

Rigorous higher-order DFT

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

Density functional theory (DFT) is a widely used quantum chemistry technique for the modeling of chemical reactions. With computational resource support from RIKEN, we have in the past few years developed advanced DFT methods. We show that these methods, when compared with methods on which they are based, have improved accuracies for a wide range of main-group molecular thermochemical properties. At the same time, they have reduced requirements on computational resources.

We aim to further develop our DFT methods for an even more diverse set of systems and properties. Notably, we intend to extent the applicability to transition metals, and to nano and materials systems. In this regard, a critical obstacle is the lack of reliable reference data with which the accuracies of new DFT methods can be assessed. Filling this gap is by-no-means straightforward, because transition-metal systems are notorious for their difficulty to be treated by even some of the most reliable quantum-chemistry methods.

To tackle this challenge, we have taken a careful approach by first examining systems that are known to be straightforwardly treatable with standard high-level quantum chemistry methods. The insights that we will gain from these systems will then be applied to generate additional reliable reference data, with which advanced DFT methods with wider applicability can then be developed.

２. Specific usage status of the system and calculation method

This project employs the Gaussian program on Hokusai, as well as the a wide range of standard quantum chemistry software packages such as Molpro, Q-Chem and Orca. These tools enable us to access a diverse range of quantum chemistry methodologies, from highly accurate coupled-cluster methods at the one end and a vast collection of over 200 DFT methods at the other end.

Limited amount of reference data for transition-metal chemistry are available from literature. We have selected some of the most reliable ones for assessing representative DFT methods. The data set that we used comprises heavy transition metals, which, in contrast to light transition metals, are mostly free from complications associated with “multi-reference characters”.

To further expand the diversity of existing data for transition-metals, which contains only molecular properties, we have used the high-level CCSD(T) complete-basis-set method to compile a systematic collection of reaction energies for group-11 transition metal clusters. With these new data, we have evaluated the accuracy of DFT methods for the modeling of systems that are relevant to nano and materials chemical applications of transition metals.

The large amount of computations required in these projects has consumed a significant portion of the assigned computer time on Hokusai. Overall, we have in FY2019 dedicated most of our resources toward the compilation of highly accurate reference data for representative transition-metal clusters.

３. Result

We have collected a total of 151 highly reliable literature reference data (termed the TMC151 set) for transition-metal bond energies, reaction energies, and barrier heights. Using these data, we have examined a total of 35 DFT methods that cover the entire range of 12 existing classes of functionals.

Among these methods, we find that, in an overall manner, the ωB97M-V and the MN15 methods to be the most accurate for the TMC151 set. Significantly, these two methods have also been previously found to be the most accurate for main-group molecular properties. In particular, the ωB97M-V method has been developed with only main-group molecular input data. Its relatively good accuracy for molecular transition-metal systems suggests that carefully chosen main-group data may be sufficient for initial development of DFT methods for both main-group and transition-metal molecular systems.

Nonetheless, while ωB97M-V and MN15 are the most accurate DFT methods for both main-group and transition-metal molecular species, our results also show that transition metals are, on average, more challenging (average error ~15 kJ mol^{-1}) for these two methods when compared with their outstanding accuracies for main-group chemistry (average error ~5 kJ mol^{-1}). Other important theoretical insights include the significant role of having a flexible proportion of exact exchange in the DFT method, as well as the critical role of dispersion interactions in these systems. Notably, these observations further support the use of the functional form of our previously published reHISSB-D method.

In a follow-up study, we have compiled a set of 60 structural data and thermochemical properties (bond energies, ionization potentials, isomerization energies and complexation energies) for clusters of Cu, Ag and Au (the CUAGAU set), for which the CCSD(T) method that we use are known to be highly reliable. The assessment of DFT methods with the CUAGAU set shows that, for clusters that resemble extended systems, the functionals ωB97M-V and MN15, which are developed for molecular species, do not outperform other DFT methods as much as they do for molecular systems. In some cases, ωB97M-V even lags behind much simpler methods such as B97-D3BJ. The comparison between the ωB97M-V and B97-D3BJ methods again suggest that the form of our reHISSB-D method may provide a route to a functional that is universally applicable to both main-group and transition metals, and to both molecular and materials systems.

４. Conclusion

Our previously developed DFT method already has near-optimal accuracy and computational efficiency for main-group molecular thermochemical properties. In order to further expand the applicability of the method, we are now in the process of gathering and producing reliable reference data for molecular and cluster transition-metal species, which will then be used for further training our DFT method.

At present, we have obtained a small but diverse and statistically significant number of accurate thermochemical data from either the literature or from our own high-level quantum chemistry computations. The results has revealed several important factors, such as an delicate balance of the proportion of Hartree–Fork exchange in different regions of inter-electronic interactions, and the critical role of dispersion forces in many transition-metal chemistries. Significantly, the results have validated the functional form of our DFT method to be optimal for further development.

５. Schedule and prospect for the future

Our objective in the near future is to further strengthen and expand our data sets for larger systems, as well as to cover elements for which the accuracy of routine high-level methodologies have yet to be firmly established. We will tackle these challenges with state-of-the-art techniques such as local as well as high-order coupled-cluster methods.

These will build on the collaboration between Dr Chan at Nagasaki University and Prof Nakajima and Prof Hirao at RIKEN R-CCS, with the provision of computational resources from RIKEN ISC.

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

[Paper accepted by a journal]

1. Benchmark Study of DFT and Composite Methods for Bond Dissociation Energies in Argon Compounds. Yu, L. J.; Dale, S. G.; Chan, B.; Karton, A. *Chem. Phys.* **2020**, *531*, 110676.
2. G4(MP2)-XK: A Variant of the G4(MP2)-6X Composite Method with Expanded Applicability for Main-Group Elements up to Radon. Chan, B.; Karton, A.; Raghavachari, K. *J. Chem. Theory Comput.* **2019**, *15*, 4478.
3. The CUAGAU Set of Coupled-Cluster Reference Data for Small Copper, Silver, and Gold Compounds and Assessment of DFT Methods. Chan, B. *J. Phys. Chem. A* **2019**, *123*, 5781.
4. Assessment of DFT Methods for Transition Metals with the TMC151 Compilation of Data Sets and Comparison with Accuracies for Main-Group Chemistry. Chan, B.; Gill, P. M. W.; Kimura, M. *J. Chem. Theory Comput.* **2019**, *15*, 3610.
5. A Simple Model for Relative Energies of All Fullerenes Reveals the Interplay between Intrinsic Resonance and Structural Deformation Effects in Medium-Sized Fullerenes. Chan, B.; Kawashima, Y.; Dawson, W.; Katouda, M.; Nakajima, T.; Hirao, K. *J. Chem. Theory Comput.* **2019**, *15*, 1255.

[Oral presentation]

1. *The 9th Asian Pacific Conference of Theoretical and Computational Chemistry (APATCC2019)*, 2019, Sydney (invited oral presentation).