

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 the workhorse of modern computational chemistry owing to its reasonable accuracy and good computational efficiency. With computational resource support from RIKEN, we have in the past few years developed advanced DFT methods. We have demonstrated the applicability of these methods for a wide range of thermochemical properties of a diverse collection of chemical systems.

Most of the past efforts on validating new and existing DFT methods, including our research, focus on systems of organic chemistry. This is due to several factors. First, DFT, by design, can be expected to be quite accurate for organic species, but it is less so for other systems. Second, to formulate a good DFT method would necessitate accurate reference data for the “training”; while such data is abundant for organic molecules, it is sparse for other types of species.

As material science becomes an increasingly important field of chemistry due to the demand for technological advances, there is an urgency for the adaptation of DFT for non-organic systems. As noted above, a prerequisite for the development of advanced DFT is reliable reference data for the training and validation of new methods. Thus, we digress from direct DFT development to the provision of accurate thermochemical quantities for non-organic main-group species and some transition-metal systems. Such data will then form the foundation for the expansion of the scope of highly reliable DFT computations.

2. Specific usage status of the system and calculation method

This project employs the Gaussian and Q-chem programs on Hokusai, as well as a wide range of standard quantum chemistry software packages such as Molpro, MRCC, 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, with which accurate reference data can be obtained, to a vast collection of over 200 DFT methods at the other end, with which a baseline for comparison with our methods can be established, and insights into the fundamentals of a reliable DFT for non-organic systems can be revealed.

Our initial focus is on heavy main-group species such as tin and iodine compounds that are of relevance to materials and biological sciences in addition to fundamental physical significance. We also investigated coinage metal systems for which highly accurate thermochemical quantities can be straightforwardly computed using standard high-level quantum chemistry methods. Limited amount of highly accurate reference data is also available from literature for atoms and small molecular systems, which we use to develop and validate new high-level protocols for our systems of interest.

The molecular properties that we have examined include the fundamentals such as heat of formation, ionization energy, electronic affinity, proton affinity, isomerization energy, and ligand binding energy. These properties have also been the focus of many previous assessment studies on organic chemistry, and we have also used such data for the formulation of our advanced DFT. Thus, the use of these

properties would enable a direct comparison of the performances of a DFT method on organic and non-organic chemistries.

3. Result

The thermochemical properties of heavy main-group elements are known to be uniquely affected by substantial relativistic effects. To accurately account for these, we have surveyed a wide range of high-level wavefunction methods, and we have found that the use of the ‘‘CASSCF’’ method with a ‘‘minimal active space’’ to be the most cost-effective means for their calculations.

As with accurate computation of organic systems, adequate account of the dynamic and static correlation effects is critical. We apply our experience in the formulation of high-level ‘‘composite methods’’ for organic chemistry, and extend the widely used Wn and our WnX protocols to heavy main-group species, by combining the optimal protocol with the CASSCF relativistic corrections.

Our investigation also reveals an important modification to Wn that is necessary for accurate calculation of heavy elements, namely the inclusion of ‘‘inner-shell’’ correlation effects at the highest level, rather than as a correction with a lower-level method.

With the validated composite method (Wn -P34), we have obtained highly accurate energies for nearly 100 heavy main-group species. These data are used to assess the reliability of lower-cost methods; we find our previously developed G4(MP2)-XK composite protocol, and our SCANh DFT method, are the best choice in their respective class of methods.

For coinage-metal systems, i.e., copper (Cu), silver (Ag), and gold (Au), we have developed a series of methods, termed W1X-G0, CM1, and CM3, using the same strategy. The CM1 and CM3 methods are analogous to the W1-P34 and W3-P34 methods. For the coinage-metal systems, the requirement for the inclusion of inner-shell correlation effects is computationally highly demanding. Thus, to enable the calculation of systems that are sized reasonably close to actual materials, we have further developed

the lower-cost W1X-G0 method based on our previous WnX composite protocols for organic systems.

We again use these cost-effective and highly accurate methods to compute reliable reference data for the assessment of lower-cost methods, leading to our CUAGAU-2 data set that contains more than 130 species from small molecules to clusters that begin to resemble bulk materials systems.

Our assessment of lower-cost methods shows that some modern and widely used DFT methods (MN15, ω B97M-V) are inadequate for systems that resemble bulk materials. This observation is significant because they show poor accuracies despite them being some of the best methods for organic chemistry and even molecular transition-metal species. These results show that our new accurate data sets would be indispensable for DFT developments. Overall, our achievements are summarized below.

method	system	accuracy
W1-P34	heavy main group	high
W3-P34	heavy main group	maximum
W1X-G0	Cu, Ag, Au	good
CM1	Cu, Ag, Au	high
CM3	Cu, Ag, Au	maximum
G4(MP2)-XK	main group	reasonable
SCANh	general	qualitative

data set	system
P34	heavy main group molecule
CUAGAU-2	Cu, Ag, Au molecule and cluster

4. Conclusion

We have developed a series of composite protocols to expand the scope of highly accurate computational thermochemistry beyond organic systems. The thus obtained data are used to assess modern DFT methods, with the results showing the importance of including non-organic systems in DFT developments.

5. Schedule and prospect for the future

Our future investigations will involve further expansion of our data sets to reach a critical number of data points. This would guarantee an unbiased data set, which would be a prerequisite for the development of reliable DFT methods.

Fiscal Year 2021 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. Assessment and Development of DFT with the Expanded CUAGAU-2 Set of Group-11 Cluster Systems. Chan, B. *Int. J. Quantum Chem.* **2021**, *211*, e26453.
2. Re-Examining the Electronic Structure of Fluorescent Tetra-Silver Clusters in Zeolites. Chan, B. *Phys. Chem. Chem. Phys.* **2021**, *23*, 1984.
3. Hydride Affinities for Main-Group Hydride Reductants: Assessment of Density Functionals and Trends in Reactivities. Chan, B.; Luo, Y.; Kimura, M. *J. Phys. Chem. A* **2021**, *125*, 835.
4. Polycyclic Aromatic Hydrocarbons: From Small Molecules Through Nano-Sized Species Towards Bulk Graphene. Chan, B.; Karton, A. *Phys. Chem. Chem. Phys.* **2021**, *23*, 17713.
5. Accurate Heats of Formation for Polycyclic Aromatic Hydrocarbons: A High-Level Ab Initio Perspective. Karton, A.; Chan, B. *J. Chem. Eng. Data* **2021**, *66*, 3453.
6. Accurate Thermochemistry for Main-Group Elements up to Xenon with the Wn-P34 Series of Composite Methods. Chan, B. *J. Chem. Theory Comput.* **2021**, *17*, 5704.
7. Accurate Quantum Chemical Prediction of Gas-Phase Anion Binding Affinities and Their Structure-Binding Relationships. Sandler, I.; Sharma, S.; Chan, B.; Ho, J. *J. Phys. Chem. A* **2021**, *125*, 9838.

[Oral presentation]

1. *International Chemical Congress of Pacific Basin Societies (Pacifichem, Symposium – Computation Quantum Chemistry: Synergism Between Theory and Experiment)*, 2021, Honolulu (invited oral presentation).
2. *International Chemical Congress of Pacific Basin Societies (Pacifichem, Symposium – From Homogeneous to Heterogeneous Catalysis: A Computational Perspective)*, 2021, Honolulu (invited oral presentation).
3. *24th Annual Meeting of Theoretical Chemistry Society*, 2021, Sapporo (oral presentation).