

Project Title:

Rigorous higher-order DFT

Name: ○Bun Chan (Nagasaki University), Takahito Nakajima (RIKEN),
Michio Katouda (RIKEN), Yukio Kawashima (RIKEN), Kimihiko Hirao (RIKEN)

Laboratory at RIKEN: Computational Molecular Science Research Team

1. Background and Aim

Density functional theory (DFT) is the most prominent technique in computational chemistry. With computational resource support from RIKEN, we have in the past few years developed advanced DFT methods using rigorous fundamental physical principles. This includes the formulation of an improved “screened-exchange” (SX) procedure (that we named HSEB) based on the widely used HSE06 method. The results have now been published.

As a continuation of this line of work, we have extended our study to the use of a more sophisticated SX equation. Thus, while HSEB provides independent treatment of short- and long-range inter-electronic interactions, our latest work is based on the “HISS” equation, which contains an additional mid-range term. The added flexibility would by itself already lead to an enhancement in the accuracy. More importantly, chemical properties are largely controlled by mid-range inter-electronic interactions. Thus, dedicated treatment of these interactions should lead to a significant improvement.

2. System Usage and Methodologies

The developmental work in this project employs customized Gaussian program on Hokusai. As with our previous DFT developments, we have tested the new methods with a large set of thermochemical and kinetic data. These include, for example, atomization energies (W4/08, G2HoF, G3HoF), intermolecular interactions (HB16, WI9, S22), ionization energies (G2IE), electron affinities (G2EA), reaction energies (RR49), and reaction barriers (DBH24 and PR8). The large amount of computations required in this project alone has

consumed a significant portion of the assigned computer time on Hokusai.

Our strategy for the derivation of the new method is based mainly on two considerations, namely maximizing accuracy while at the same time minimize computational cost. This leads us to the two major design features for the new method; they are the inclusion of maximum amount of accurate but computationally demanding “Hartree–Fock” exchange (HFX) and a rapid decay to zero HFX in the long range.

Thorough analysis of the dependence of the accuracy on several other adjustable parameters in the new method leads to the formulation of the reHISS exchange functional, which has a maximum HFX of 30% occurring at an inter-electronic distance of 2.4 Å. The variation in HFX also suggests an important inter-electronic distance range of 1–4 Å for chemical properties. To arrive at a complete DFT procedure, we have paired the reHISS exchange functional with several “correlation” functional, including a revised “B97c” functional previously developed and used in the HSEB method.

3. Significant Results

Our assessment study shows that the reHISSB-D method, which uses the revised B97c correlation functional plus a correction for dispersion effects, to be the most accurate (see the table below for examples of average errors). The finding of the revised-B97c-based method to be the most accurate is also consistent with previous comparison between HSE06 and HSEB. Importantly, the reHISSB-D method appears to yield a more consistent accuracy across different chemical properties.

	HISS	reHISSP	reHISSB-D
E3	24.3	19.0	16.2
W4/08	25.5	14.3	10.8
G3HoF	17.0	20.3	12.2
S22	7.9	9.6	7.3

In order to further validate the reHISSB-D method and compare it with related DFT methods, we have expanded the E3 database of thermochemical quantities to the E4 set, which contains over a thousand data points. Encouragingly, the results continue to support the robustness of reHISS. See for example key results below, which includes additional chemical properties namely bond dissociation energies (BDE262), isomerization energies (C24ISO), proton-exchange kinetics (CEPX33) and molecular vibrational frequencies (LF10).

	HISS	reHISSB-D
E4	24.4	16.8
E3	24.3	16.2
BDE262	20.6	16.9
C24ISO	14.1	3.2
CEPX33	12.1	7.8
LF10	4.6	3.8

4. Concluding Remarks

We have in this project employed knowledge gained from previous ACCC-supported investigations to formulate a more accurate SX-DFT procedure using the flexible HISS equation, and we term the new method reHISSB-D. Through our extensive assessment, we have demonstrated the improved accuracy and robustness of reHISSB-D in comparison with existing SX-DFT methods. We are now in the process of preparing a manuscript for publication. In addition to the main investigation into DFT, previously developed methodologies within this project have been used in other computational chemistry applications, with the results detailed in the list of publications.

5. Prospect for Future Research

In accordance with our previous successful approach, we have in this initial phase formulated the reHISSB-D as a proof-of-principle method rather than a fully optimized one. Thus, further tuning of the procedure will lead to an improved SX-DFT. The simplicity of the mathematical form of reHISSB-D enables straightforward inclusion of higher-order terms into a refined procedure. Future developments in this direction will also enable an even stronger adhesion to the physical principles of DFT, which would in turn further enhance the robustness of the resulting method.

Furthermore, other potential directions include the use of advanced “dispersion corrections” and the incorporation of additional ingredients such as the “kinetic energy density” that have already been demonstrated to improve accuracy, notably in the very recently developed ω B97M-V method, which offers superior accuracy but its formulation is somewhat computationally demanding.

While it is important to pursue better accuracy in a refined DFT, another significant avenue to follow is thus to further improve the computational efficiency. One of the significant scientific findings during the course of formulating reHISS is the identification of the important inter-electronic distance range for the computation of general chemical properties. This knowledge would enable us to reduce the reliance on the computationally demanding HFX for distances outside of this critical range. To this end, the “2Gau” approach of Dr Hirao would enable a partitioning scheme that is more efficient than the one used in reHISS.

These will build on the collaboration between Dr Chan at Nagasaki University and Prof Nakajima, Prof Hirao, Dr Katouda and Dr Kawashima at RIKEN AICS, and the provision of computational resources from RIKEN ACCC.

Fiscal Year 2017 List of Publications Resulting from the Use of the supercomputer

[Publication]

1. Correlation Functional in Screened-Exchange Density Functional Theory Procedures. Chan, B.; Kawashima, Y.; Hirao, K. *J. Comput. Chem.* **2017**, *38*, 2307.
2. Use of Low-Cost Quantum Chemistry Procedures for Geometry Optimization and Vibrational Frequency Calculations: Determination of Frequency Scale Factors and Application to Reactions of Large Systems. Chan, B. *J. Chem. Theory Comput.* **2017**, *13*, 6052.
3. Watson–Crick Base Pair Radical Cation as a Model for Oxidative Damage in DNA. Feketeova, L.; Chan, B.; Khairallah, G. N.; Steinmetz, V.; Maitre, P.; Radom, L.; O’Hair, R. A. J. *J. Phys. Chem. Lett.* **2017**, *8*, 3159.

[Oral presentation at an international symposium]

1. *20th Annual Meeting of Theoretical Chemistry Society*, 2017, Kyoto (oral presentation).
2. *The 8th Asian Pacific Conference of Theoretical and Computational Chemistry (APCTCC8)*, 2017, Mumbai (invited oral presentation).