Project Title:

Rigorous higher-order DFT

Name: ○Bun Chan , Jong-Won Song , Yukio Kawashima , Kimihiko Hirao

Laboratory at RIKEN: Computational Chemistry Research Unit, AICS

1. Background and Aim

Density functional theory (DFT) is the most prominent technique in computational chemistry. DFT typically has two components: the exchange and the correlation functionals. This project aims to develop an advanced form of DFT based on an important consideration: the rigorous incorporation of higher-order terms into the correlation functional through the exchange. This is a simple yet physical concept, first proposed by the project mentor Prof Hirao, to maintain a balance between the exchange and correlation functionals. However, such an idea has never been applied together with higher-order exchange functionals, and as a result its true potential is yet to be exploited. This project intends to close this gap.

2. Usage of RICC and Methodologies

The developmental work in this project employs customized Gaussian program on the RICC. To include higher-order effects into the correlation functional in a balanced manner, we use the exchange functional TPSS in conjunction with the OP correlation functional. This is due to the unique property of OP of explicitly incorporating the exchange component into itself. The choice of the TPSS exchange functional is due to its close connection with the somewhat lower-order PBE functional, which has been previously incorporated into OP.

This choice of the OP functional also leads to another important consideration, namely the treatment of electron correlations of different nature. In general, two types of electron correlations are considered in quantum chemistry procedures. They are the correlations between electron pairs of opposite spin (OS) and same spin (SS). Due to the implicit treatment of SS electronic interactions by the exchange functional, it was argued in the formulation of the OP functional that an explicit SS correlation component was not warranted, and as a result such an element is not included in OP. On the other hand, many of the most accurate correlation functionals do include such a component.

We therefore, in this project, also investigate the effect of adding SS correlation into OP. We accomplish this by incorporating the SS term from the B95 correlation functional. The B95 correlation functional is chosen in this case based on existing knowledge of its superior performance for the treatment of interactions between SS electrons. Our new method constructed in this manner is termed the OPB correlation functional.

The resulting methods have been tested on 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 BDE261), and reaction barriers (DBH24 and PR8). The large amount of computations required in this project has consumed more than 57,000 hours of computer time on the RICC.

3. Significant Results

Our benchmark studies have compared TPSS-OP-type and TPSS-OPB-type methods with a wide range of related DFT procedures based on the alternative exchange and correlation functionals. These include the B88 and PBE exchange and B95 correlation functionals. It shows that, while the incorporation of the physically more sound TPSS exchange functional into OP and OPB may lead to improved total energies, it does not necessarily yield more accurate values for chemical properties (see the table below for average errors).

	PBE12 -OP	PBEh42 -B95	PBEh36 -OB
W4/08	18.3	19.2	19.7
G2/97' Δ_fH	16.7	15.3	16.0
G3/99' Δ_fH	28.6	22.8	23.1
G2/97 IE	29.5	16.7	18.5
G2/97 EA	12.0	16.2	16.8
G2/97 PA	3.0	6.5	6.1
ADD	20.6	13.0	15.5
ABS	12.1	8.5	9.4
DBH24	21.1	5.8	10.4
PR8	9.5	4.5	8.2
HB16	1.6	1.5	2.0
WI9/04	1.7	0.7	0.7
S22	15.6	5.9	6.0
BDE261	26.3	8.7	8.9
CEPX33	9.3	10.3	15.1

Regarding the effect of the addition of explicit SS correlation effects, our comparison shows that such a modification leads to a significantly improved performance for OPB over that of OP. In particular, because SS interactions are typically longer-range in nature, OPB outperforms OP most notably for properties such as intermolecular interactions. Overall, our extensive benchmark study also reveals two DFT procedures, namely PBEh42-B95 and PBEh36-OPB, are quite accurate and robust for a wide range of chemical applications.

4. Concluding Remarks

We have in this project examined the concept of

incorporating higher-order terms into the correlation functional through the exchange component. We find that, while this approach is theoretically rigorous, it does not necessarily lead to superior performance over standard DFT procedures. In contrast, our investigation into the addition of same-spin effects into an opposite-spin-only correlation functional leads to a significant improvement in the accuracy. Through our extensive assessment, we have also identified several existing DFT methods that are fairly robust and accuacry, and they can therefore find applications in a wide range of chemical problems. Our results are already published. They also suggest directions for further development of advanced DFT methods.

5. Prospect for Future Research
During the course of this investigation, it becomes apparent that there exist conceptual similarities between the OPB functional and the wavefunction counterpart MP2. Thus, both methods include explicit treatments for OS and SS electron correlation effects. In the case of MP2, the use of separate empirical scaling for the two components leads to the more accurate SCS-MP2 procedure. The incorporation of the range-separation technique further enables the removal of the SS component (the MOS-MP2 procedure) without a significant compromise on the performance.

Further development on DFT can be guided by such knowledge. Thus, the application of range separation to the OP and OPB functionals can lead to improved accuracy for a wide range of chemical properties. This course of action also resonates with our previous findings in the development of the RXC-DFT-type of functionals. As such, development in this direction would unit our knowledge. It would leveage the skills that we built, and lead to the development of advanced DFT methods in a productive manner.

These investigations will be undertaken in an expanded project. It will build on the collaboration between Dr Chan at the University of Sydney and Prof Hirao, Dr Song and Dr Kawashima at RIKEN AICS, and the generous provision of computational resources from the RICC of RIKEN

Fiscal Year 2015 List of Publications Resulting from the Use of the supercomputer

[Publication]

1. Towards the Complete Range Separation of Non-Hybrid Exchange–Correlation Functional. Chan, B.; Song, J.-W.; Kawashima, Y.; Hirao, K. *J. Comput. Chem.* **2015**, *36*, 871.

2. From C_{60} to Infinity: Large-Scale Quantum Chemistry Calculations of the Heats of Formation of Higher Fullerenes. Chan, B.; Kawashima, Y.; Katouda, M.; Nakajima, T.; Hirao, K. *J. Am. Chem. Soc.* **2016**, *138*, 1420.

3. Performance of the OP Correlation Functional in Relation to Its Formulation: Influence of the Exchange Component and the Effect of Incorporating Same-Spin Correlations. Chan, B.; Song, J.-W.; Kawashima, Y.; Hirao, K. *J. Comput. Chem.* Accepted.

[Oral presentation at an international symposium]

1. *International Chemical Congress of Pacific Basin Societies (Pacifichem)*, 2015, Honolulu (invited oral presentation).

2. *Novel Computational Methods for Quantitative Electronic Structure Calculations*, 2015, Kobe (poster and oral presentations).

3. *International Congress of Quantum Chemistry*, 2015, Beijing (poster presentation).