Project Title:

Unlocking the True Potential of Range-Separation in Density Functional Theory

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1. Background and Aim

Range separation is one of the most promising techniques in modern density functional theory (DFT) development. With DFT itself being the major driver of computational chemistry, further refinement of range separation will undoubtedly have an important impact on the field of computational chemistry. Most of the widely-used DFT methods consist of two parts, namely the exchange and correlation components. As of today, range separation only applies to the exchange term, i.e., half of any given DFT method, thus limiting the potential of range separation. This is the issue that this project aims to address, which is to apply range separate to the entirety of DFT.

2. Usage of RICC and Methodologies

The developmental work in this project employs customized Gaussian program on the RICC. Thorough benchmarking of exchange and correlation components in DFT methods has been conducted to determine the optimal method in different ranges. We use atomization energies as a probe for short-range effects and intermolecular interactions to evaluate the long-range behaviors.

The most accurate total exchange–correlation DFT in the short range is then combined with the best method in the long range using range separation. Our method is analogous to the conventional range-separation for exchange, i.e., it applies the standard error function to the Coulomb operator: $1/r = \text{erf}(1-r)/r + \text{erf}(r)/r$. However, in our strategy, this technique is used to operate on the total exchange–correlation DFT, using a partitioning scheme based on the fraction of the exchange component.

The resulting method has been tested on a large set of thermochemical and kinetic data. These include, in addition to atomization energies (W4/08) and intermolecular interactions (S22), ionization energies (G2IE), electron affinities (G2EA), bond strengths (BDE261), reaction energies (RR49), and barriers for five types of reactions (DBH24 and PR8). The large amount of computations required in this project has so far consumed more than 22,000 hours of computer time on the RICC.

	B-LYP	PBE-B95	RXC-DFT
W4/08	25.6	70.9	29.4
S22	18.2	6.7	11.1
G2IE	30.9	25.6	31.5
G2EA	27.0	24.8	29.2
BDE261	31.4	16.5	31.9
RR49	19.4	14.9	16.4
DBH24	34.7	39.1	33.0
PR8	13.5	24.8	12.4

3. Significant Results

Our preliminary benchmark studies have pointed to the B-LYP method being the most appropriate exchange–correlation DFT for short-range chemical properties. They indicate that the PBE-B95 method is the best long-range procedure among the DFTs tested. Our new method (RXC-DFT) has a performance that resembles B-LYP for short-range chemical properties, and it is similar to PBE-B95 in the long range (see table above for mean absolute deviations in kJ mol^{-1} for the various chemical properties). For most medium-range properties, RXC-DFT has a performance that is in between those of B-LYP and PBE-B95.

These observations are entirely consistent with our expectation and supports our range-separating protocol used in RXC-DFT. We also find that in cases where the new method excels, it has a performance that is better than even more rigorous DFT methods such as B3-LYP, but at a much lower cost in terms of computational resources consumption. Importantly, the simplicity in its formulation can lead to the straightforward implementation of the method into other computational chemistry software packages.

4. Concluding Remarks

We have in this project employed the range separation technique that has originally been developed for half of any DFT method, namely the exchange component, to the entirety of it, i.e., the total exchange–correlation DFT. The protocol that we used (RXC-DFT) employs existing algorithms and is therefore easily implemented in computational software packages that already support the widely-used range-separation method for exchange.

Our results are predictable due to the simple formulation of RXC-DFT, such that the outcomes for short-range properties are influenced by the short-range component, and vice versa for long-range effects. A manuscript has been submitted for publication. Significantly, the promising results have laid the groundwork for further development of RXC-DFT in the future.

5. Prospect for Future Research

During the course of this investigation, it becomes apparent that there are multiple courses that one can further take to advance the general RXC-DFT strategy. These include (1) the use of a more flexible mathematical expression rather than the error function for the range separation, (2) further exploration of the dependence of the performance for short- and long-range properties on a wider range of the exchange–correlation DFTs, (3) elucidation of the physical fundamentals behind the observations in 2 above, (4) construction of new exchange–correlation DFTs and tailor them to the performance of short- or long-range effects, and combined them in the refined RXC-DFT determined in 1 above, and (5) further broadening of the scope of RXC-DFT by incorporating additional features such as corrections for dispersion interactions, exact exchange, and additional correlation effects from higher-order methods such as MP2.

These individual 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 2014 List of Publications Resulting from the Use of RICC

[Publication]

1. Chan, B.; Song, J.-W.; Kawashima, Y.; Hirao, K., Towards the Complete Range Separation of Non-Hybrid Exchange–Correlation Functional. *J. Comput. Chem.* in press (manuscript ID: JCC-14-0655.R1).