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REGULAR ARTICLE

An examination of density functional theories on isomerization energy calculations of organic molecules

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Abstract Long-range corrected (LC) density functional theories (DFTs) were applied to the isomerization energy calculations of organic molecules to make clear why conventional DFTs including B3LYP have given poor isomerization reaction energies. Combining with local response dispersion (LRD) method, we performed LC-DFT calculations for the benchmark set of isomerization reactions. Consequently, we found that LC-DFT + LRD methods give accurate reaction energies equivalent to up-to-date DFTs containing many semi-empirical parameters. This result indicates that long-range exchange and intramolecular dispersion correlation interactions, which have been neglected in conventional DFTs, play prominent roles in isomerization reactions. However, we also found that these interactions are not sufficient to give accurate isomerization energies especially for cyclization reactions. Considering that Gaussian-attenuated LC-DFTs (LCgau-DFTs) give better isomerization reaction energies than LC-DFTs, we suggested that the isomerization energies will be further improved by correcting the short-range part of exchange functionals in DFT with keeping the whole long-range exchange interactions.

Keywords Density functional theory (DFT) · Long-range correction (LC) · Isomerization energy

1 Introduction

Density functional theory (DFT) [1] has been the most efficient method in quantum chemistry to give electronic properties within chemical accuracy with much less CPU timings and basis set dependency than those of electron correlation wavefunction methods. These features seem to assure that DFT is promising especially in investigating large-system calculations. However, many studies have so far reported that DFT usually fails in accurately reproducing various properties, which are the characteristics of large systems, e.g., the overestimation of nonlinear optical properties of long-chain molecules [2, 3], the poor description of van der Waals and weak hydrogen bonds [4, 5], and the underestimation of charge transfer excitation energies and oscillator strengths in time-dependent DFT calculations [6]. These DFT problems, which are the characteristics of large systems, have been solved by applying the long-range correction (LC) scheme.

The long-range correction (LC) scheme was first developed by Savin for local density approximation exchange functional [7] and was then extended to general exchange functionals by Tsuneda and Hirao [8]. In this

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scheme, exchange functionals are divided into short- and long-range parts, and only the long-range part is then replaced with the long-range part of the Hartree–Fock (HF) exchange integral [8]. Consequently, besides the properties of large systems mentioned earlier, the LC scheme has solved various problems in DFT calculations such as underestimated reaction barrier heights [9]. In particular, it has recently been found that by using the LC scheme, DFT reproduces orbital energies quantitatively for the first time [10]. Following these remarkable features, a family of LC functionals has been developed [11–17]. LCgau functional is one of the LC functionals, in which the short-range HF exchange integral is included by incorporating a Gaussian attenuation with two parameters (a and k) in the original range separation using the error function with one parameter (μ) [13], and has consequently been shown to improve atomization energies and other thermochemical properties of small molecules, which LC-DFT has failed, probably by decreasing self-interaction errors [18], and these LC functionals have been applied to the calculations of various systems and have succeeded in providing new insights in investigating these systems.

Recently, we applied LC functionals to the isomerization enthalpy calculations of long-chain alkanes that conventional DFTs have failed to reproduce. Although alkanes are fundamental organic molecules containing only singly bonded C and H atoms, even state-of-the-art DFTs have been reported to have considerably overestimated the reaction enthalpies of isodesmic reactions.

$$n\text{-CH}_3(\text{CH}_2)_m\text{CH}_3 + m\text{CH}_4 \rightarrow (m+1)\text{C}_2\text{H}_6 \tag{1}$$

As the number of chain units (m) increases, the errors in the reaction enthalpies become larger for all types of DFTs [19]. LC functionals were applied to the isodesmic reaction enthalpy calculations by combining with local response dispersion (LRD) functional [20], which can reproduce intramolecular dispersion energies [21]. As a result, we found that the long-range exchange correction combined with intramolecular dispersion correlation clearly improves the increasing errors in the calculated reaction enthalpies. We also found that these errors considerably depend on the correlation functionals used. Following the previous studies on these reactions [22], we supposed that it is due to the medium-range correlation that is significant especially for 1,3-disposed methyl (methylene) groups, i.e. “protobranching pairs” [23]. In addition, it was reported that it is not easy to provide the isomerization energies between linear and branched alkanes using DFT. Based on these results, we have concluded that long-range exchange, intramolecular dispersion correlation, and medium-range correlation are all required to quantitatively reproduce chemical properties of large systems even for simple singly bonded systems.

In this study, we apply LC-DFTs combined with the LRD method to the calculations of the benchmark set of isomerization reactions in order to figure out why conventional DFTs have failed to reproduce these isomerization reaction energies. Here, we focus on the tautomeric reactions. Although tautomeric reactions attract attentions in drug design and have been discussed using DFT calculations, it is known that conventional DFTs have failed to reproduce these reaction energies [24]. Grimme and co-workers compiled a new benchmark set of the isomerization reactions of organic molecules to make clear that DFT poorly reproduces these isomerization energies [24]. This benchmark set contains a wide variety of isomerization reactions including cyclizations. By examining several conventional DFTs and ab initio perturbation theories on this benchmark set, they concluded that conventional hybrid generalized gradient approximation (GGA) functionals, including B3LYP functional, give poor isomerization energies and offer no advantages over pure GGA functionals. In their calculations, large errors of more than 4 kcal/mol are given for the reactions of long-chain molecules. We therefore suppose that these large errors are also due to the lack of long-range exchange and intramolecular dispersion correlation effects, similar to the isodesmic reaction enthalpies mentioned earlier. In this study, we therefore apply LC-DFT combined with LRD method to the benchmark set calculations of isomerization reaction enthalpies to make clear the reason why conventional DFTs poorly reproduce these isomerization reaction enthalpies.

2 Computational details

We performed LC-DFT calculations for the benchmark set of isomerization reactions. LC and LCgau schemes were applied to the Becke 1988 exchange [25] + one-parameter progressive (OP) [26] correlation functional (LC- and LCgau-BOP). We used the parameter $\mu = 0.47$ in LC-BOP calculations [9] and three fitted parameters ($\mu = 0.42$, $a = 0.011$, and $k = 18.0$) in LCgau-BOP calculations [10, 11]. Note that the parameters of LC and LCgau scheme are optimized to give minimal errors for the G2 set [27] atomization energies and reaction barrier heights. These LC functionals were combined with the LRD method, the parameters of which were taken from Ref. [20]. We also examined other LC functionals, LC-ωPBE [12], Coulomb-attenuating method (CAM)-B3LYP with $\alpha = 0.19$, $\beta = 0.46$, and $\mu = 0.33$ [11], which were fitted against the G2-1 set [27] atomization energies with μ fixed to 0.33, and CAM-B3PW91 [11, 28] in which Lee–Yang–Parr (LYP) [29] correlation functional of CAM-B3LYP is replaced with Perdew–Wang 1991 (PW91) one, to make clear the dependence on the short-range part of LC-DFT. For comparison, we also explored various types of functionals: BOP [26], hybrid B3LYP [30], B3PW91 [28] and Becke half-and-half LYP (BHHLYP) [31], hybrid meta-GGA Boese-Martin for kinetics enthalpies (BMK) [32], M05-2x [33] and M06-2x [34], and dispersion-corrected hybrid B97D functionals [35]. For the evaluations of all the functionals, geometry optimizations were performed and cc-pVTZ basis set was used, which has proven to be sufficient in the isomerization calculations by a previous study [24] and our preliminary test calculations. We also adopted the reaction energies that have been used as the experimental values of the benchmark set in previous studies. LC and LCgau calculations were performed on the development version of Gaussian09 program, and other calculations were executed on the official version of Gaussian09 program [36].

3 Results and discussions

Table 1 summarizes the mean errors in the calculated isomerization energies of the benchmark set, in which products are taken to have more localized electrons than those of reactants, and reactions are classified into cyclization, ring contraction, branching, atomic substitution, and hydrogen and methyl group transfer reactions as shown in Fig. 1. For analysis, the errors are classified into cyclization and other reactions in this table. The table clearly shows that LC-BOP and LCgau-BOP functionals obviously improve BOP results in both systems and give accurate isomerization energies except for cyclization reactions equivalent to the results of hybrid meta-GGAs containing many parameters. In particular, LC functionals combined with the LRD method correction (LC-BOP + LRD and LCgau-BOP + LRD) provide much lower mean absolute errors (MAEs) and root mean square errors (RMSs) than those of all other functionals except for cyclizations: MAEs are 0.85 and 0.93, and RMSs are 1.13 and 1.19 kcal/mol, respectively. For other LC functionals, it is interesting to note that LC-ωPBE and CAM-B3LYP show much different tendencies for cyclization and other reactions. Actually, in the CAM-B3LYP functional, the HF exchange integral is mixed at a fixed proportion ($\alpha = 0.19$) in the short-range part, and it is reduced for the long-range part by the proportion of 0.35 [$=1 - (\alpha + \beta)$]. Therefore, we suppose that the poor performance of CAM-B3LYP in the calculations of isomerizations except for cyclizations may be due to the insufficient long-range exchange interactions. In contrast, the LC-ωPBE functional containing long-range exchange interactions in full shows the worst performances in cyclization calculations, while it shows good performances for others. These results clearly indicate that long-range exchange plays a major role in isomerization energies.

Table 1 Mean signed errors (MSEs), mean absolute errors (MAEs) and root mean square errors (RMSs) in calculated isomerization energies of various types of DFT functionals for benchmark set of isomerization reactions in kcal/mol

Method	Total (34)			Cyclizations (10)			Others (24)		
	MSE	MAE	RMS	MSE	MAE	RMS	MSE	MAE	RMS
LC functionals									
LC-BOP	−0.96	1.60	2.19	−2.60	2.60	2.88	−0.28	1.18	1.82
LC-BOP + LRD	−0.87	1.39	1.86	−2.69	2.69	2.95	−0.11	0.85	1.13
LCgau-BOP	−0.97	1.46	1.89	−1.86	1.86	2.07	−0.60	1.30	1.81
LCgau-BOP + LRD	−0.88	1.23	1.55	−1.95	1.95	2.18	−0.44	0.93	1.19
LC-ωPBE	−1.59	2.26	3.22	−5.13	5.13	5.30	−0.11	1.06	1.74
CAM-B3LYP	−0.15	1.37	2.13	1.18	1.21	2.10	−0.70	1.44	2.14
CAM-B3PW91	−1.00	1.81	2.43	−3.02	3.12	3.30	−0.16	1.27	1.96
Other functionals									
BOP	0.22	3.58	4.94	5.39	5.39	6.14	−1.94	2.82	4.35
B3LYP	0.24	2.35	3.33	3.39	3.39	4.17	−1.07	1.92	2.92
B3PW91	−0.57	1.71	2.52	−0.65	1.61	2.02	−0.54	1.74	2.71
BHHLYP	0.21	1.61	2.61	1.85	1.85	3.04	−0.47	1.51	2.41
BMK	−0.70	1.28	1.76	−1.16	1.53	1.94	−0.51	1.17	1.67
M05-2x	−0.10	1.34	1.74	−0.76	1.92	2.20	0.17	1.09	1.51
M06-2x	−0.58	1.17	1.70	−1.12	1.86	2.32	−0.35	0.89	1.36
B97D	0.25	2.19	3.16	3.37	3.51	4.49	−1.05	1.65	2.41

The reactions consist of 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 of isomerization energy benchmark set, which are characterized as the reactions where a ring molecule is included only in one side

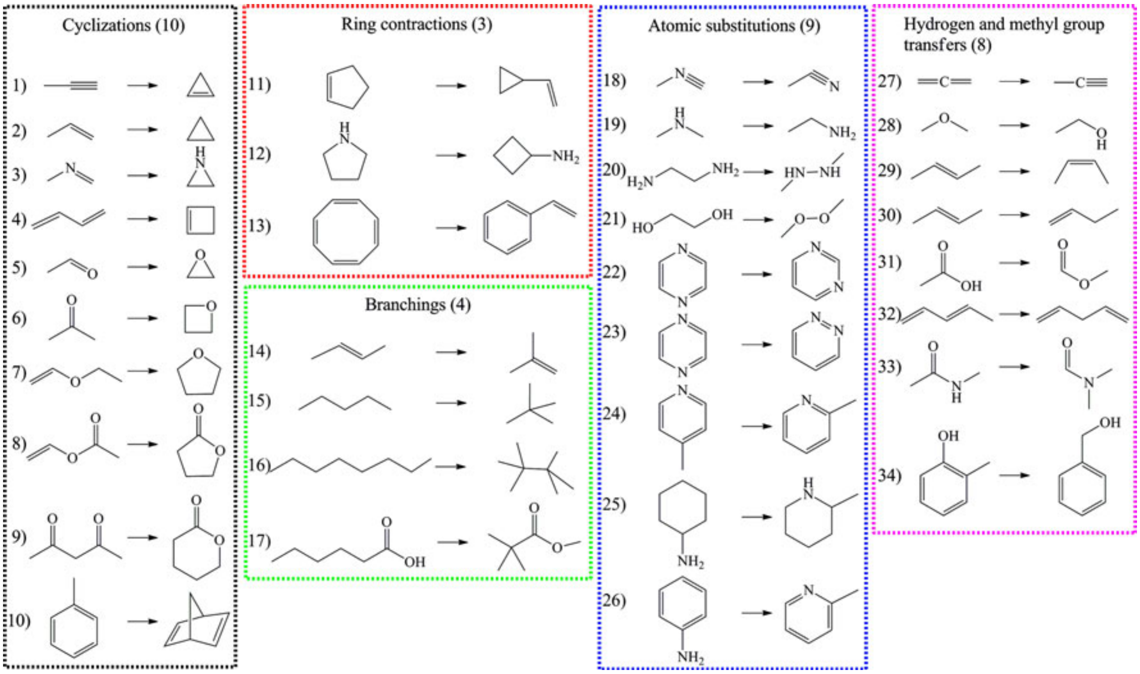

Fig. 1 Benchmark set of isomerization reactions tested in Ref. [24]. Reactions are classified into cyclization, ring contraction, branching, atomic substitution, and hydrogen and methyl group transformation reactions

On the other hand, compared with the LC-BOP and LC-ωPBE functionals, the LCgau-BOP functional which includes an additional short-range HF exchange shows improved results, especially in cyclization reaction calculations. Therefore, we suppose that short-range exchange is also crucial in cyclization isomerizations, and it should be improved by an appropriate approach, such as LCgau.

To figure out the reason for the significance of long-range exchange and intramolecular dispersion correlation, we next look into the errors for individual isomerization reactions. Figure 2 illustrates the signed errors in the calculated isomerization reaction energies. The figure shows that LC-BOP wholly improves the reaction energies of B3LYP and B3PW91 except for cyclization reactions. Its combination with LRD obviously reduces the errors, especially for branching reaction energies. These results support the significance of long-range exchange and intramolecular dispersion correlation interactions in isomerization reaction calculations. This figure also shows that an additional Gaussian HF exchange included in LCgau-BOP reduces the errors of LC-BOP results especially for the cyclization reactions, and consequently, LCgau-BOP + LRD gives the least RMS among all those functionals tested. Since the difference in LC-BOP and LCgau-BOP is mainly given in the short-range part, this indicates that the unimproved cyclization reaction energies stem from the short-range behaviors of exchange functionals. Actually, as mentioned earlier, these cyclization energies are well reproduced by CAM-B3LYP, in which the HF exchange integral is mixed in the short-range part. We therefore expect that the isomerization energies will be further improved by correcting the short-range part of LC-DFT.

Finally, let us compare the results of LC functionals to those of other up-to-date functionals. As shown in Fig. 1, LC functionals with the intramoleculer dispersion correlation correction give equivalent accuracies to the results of hybrid meta-GGA BMK, M05-2x, and M06-2x functionals, despite the former ones containing far fewer parameters than the latter ones. These accuracies have been found in the previous calculations including the isodesmic reactions of alkanes mentioned in Sect. 1 [21]. What we should notice is that other up-to-date functionals also tend to give inaccurate reaction energies for cyclization reactions. Fig. 2 shows that BMK and M06-2x functionals give large errors for cyclization reactions similarly to LC functionals. Nevertheless, these hybrid meta-GGA functionals provide small averaged errors for cyclizations, because these functionals give much less errors for oxygen heterocyclic reactions than those of LC functionals. Cyclization reactions are characterized by the strain to atoms constituting rings especially for small ring molecules. We suppose that this strain may cause short-range exchange interactions of core electrons, which cannot be accurately reproduced by conventional exchange functionals. These short-range exchange interactions can be corrected by mixing the HF exchange integral in the short-range exchange functionals.

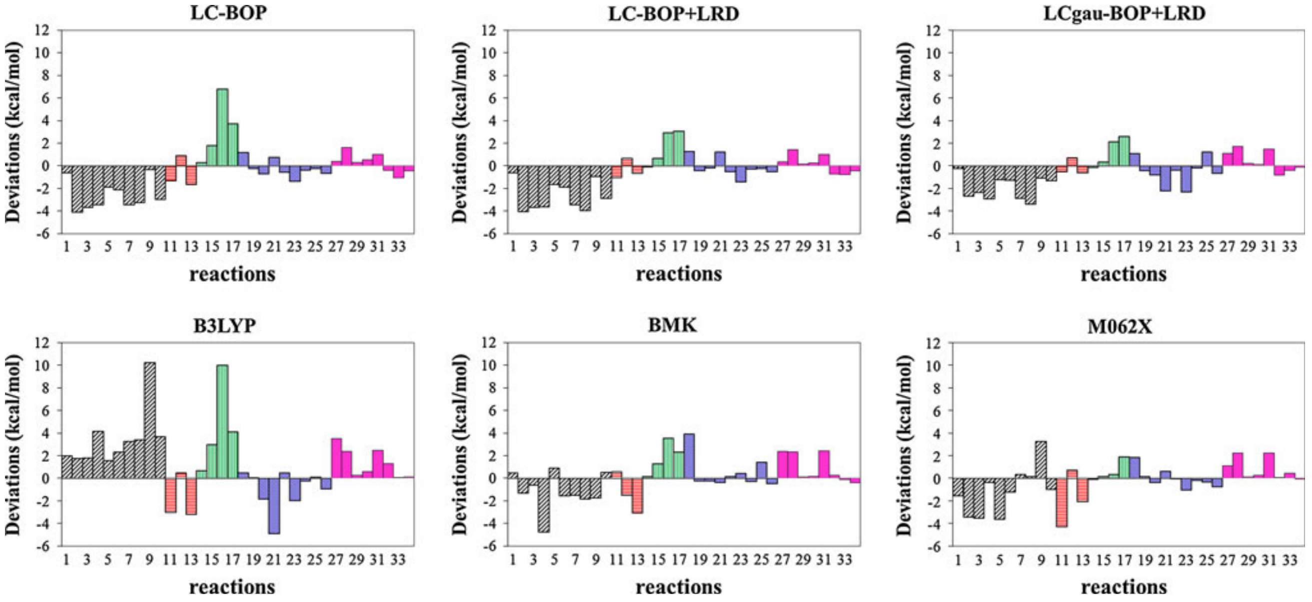

Fig. 2 Signed errors in the calculated individual isomerization reaction energies of various DFTs. Reaction numbers correspond to those in Fig. 1

However, considering the accurate cyclization reaction energies of CAM-B3LYP except for reaction no. 9 of large molecules (the error is 6.23 kcal/mol), cyclization reactions other than oxygen heterocyclic ones may not be corrected by a hybrid method mixing a fixed percentage of the HF exchange integral for the whole range of exchange interactions. Although B3PW91 seems to provide improved errors especially for cyclization reactions compared to B3LYP, CAM-B3PW91 shows worse results for cyclization reactions than CAM-B3LYP. This indicates that range-separated HF exchange plays a more crucial role in the calculations of cyclization reaction energies than correlation functional does.

4 Conclusions

In this study, we investigated why conventional DFTs including B3LYP have failed to reproduce the isomerization reaction energies of organic molecules. Using several types of long-range corrected (LC) DFTs and other up-to-date DFTs, we calculated the isomerization energies for the benchmark set of thirty-four isomerization reactions that Grimme suggested. As a result, we found that long-range exchange and intramolecular dispersion correlation interactions, which have usually been neglected in conventional DFTs, play major roles in isomerization reactions. This indicates that LC-DFT combined with local response dispersion (LRD) method is one of the promising DFTs to give accurate isomerization energies. However, we also found that even this combined method is not sufficient to reproduce cyclization reaction energies accurately. These cyclization energies were obviously improved by mixing the HF exchange integral in the short-range part of exchange functionals, such as LCgau-DFT. However, we should notice that the long-range exchange should not be reduced to correct the short-range part of exchange functionals. Actually, CAM-B3LYP, which decreases the long-range exchange of LC-DFT to mix the HF exchange integral in the short-range part, accurately reproduces cyclization reaction energies, but gives poorer reaction energies for other isomerizations. We therefore expect that the isomerization energies will be further improved by correcting the short-range exchange part of DFT with keeping the whole long-range exchange interactions.

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