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# Calculations of Alkane Energies Using Long-Range Corrected DFT Combined with Intramolecular van der Waals Correlation

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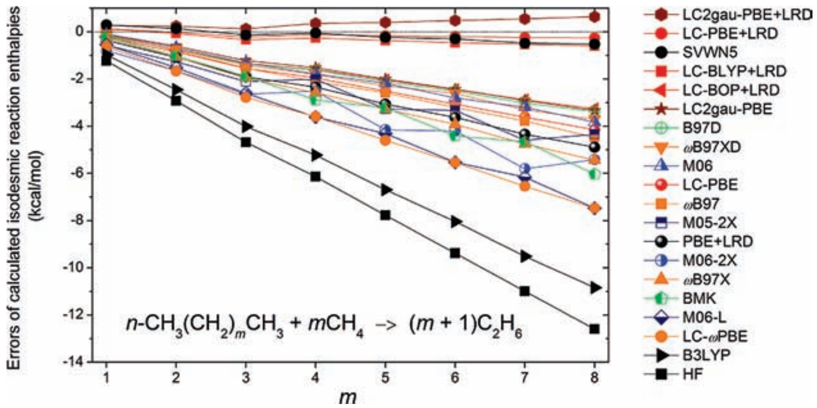
## ABSTRACT



**The isodesmic reaction enthalpies of *n*-alkanes to ethane, which have so far been known to give systematic errors in density functional theory (DFT) calculations, are successfully reproduced using long-range corrected (LC) DFT combined with a local response dispersion (LRD) method, which reveals that the failure of conventional DFT results from the lack of long-range exchange interactions in exchange functionals as well as intramolecular dispersion and medium-range electron correlations in correlation functionals.**

Density functional theory (DFT) is one of the best candidates for quantitatively calculating the chemical properties of real-size systems, such as those of nanomaterials and biomolecules, with both linear-scaling and parallelizing computational timing on next-generation supercomputers. However, many studies have thus far reported that DFT provides poor properties to large molecular systems.[1]

Contrary to our expectations, a simple isodesmic reaction[2] of alkanes is one of these systems. Redfern et al. calculated the reaction enthalpies of an isodesmic reaction

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

by using a hybrid B3LYP functional and found that it creates large errors in reaction enthalpy calculations.[3] The errors systematically become larger as the number of chain units in *n*-alkanes, *m* in eq 1, increases. Similar errors have been

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reported for other conventional pure generalized-gradient approximation (GGA), hybrid GGA, and meta-GGA functionals. However, a local density approximation (LDA) functional provided surprisingly accurate reaction enthalpies within an error of 1 kcal/mol even for decane ($m = 8$).[4]

Many studies have attempted to explain these systematic errors in the calculated isodesmic reaction enthalpies of *n*-alkanes. The errors were first attributed to the intramolecular dispersion interactions between 1,3-disposed methyl (methylene) groups, which have been called "protobranching stabilization"[4,5] and may be insufficiently provided by conventional local correlation functionals.[6] However, by careful analysis based on his special spin-component-scaled second-order Møller−Plesset perturbation (SCS-MP2)[7] method, Grimme suggested that the errors were due to the deficiency of medium-range electron correlation in DFT functionals.[8] Zhao and Truhlar agreed with this suggestion by Grimme and suggested that the hybrid meta-GGA M05-2x[9] functional excluding dispersion forces succeeds in providing more accurate isodesmic stabilization energies than the conventional dispersion-corrected functional.[10] Nevertheless, the error, −2.6 kcal/mol for *n*-octane ($m = 6$), is still too large to admit the problem is eliminated. By contrast, there have been reports that these serious systematic errors may result from the exchange fuctionals.[11] Especially, Brittain et al. very recently suggested that these serious systematic errors could be attributed to exchange functionals by comparing the results of the Hartree−Fock (HF) exchange + DFT correlation functional with those of the DFT exchange-correlation functional.[11b] Thus far, the origin of errors still remains open for discussion.

The long-range correction (LC) scheme[12] for exchange functionals is currently attracting the interest of many researchers. This is because the LC scheme has simultatneously solved several serious problems that previous DFT functionals have posed: e.g., the overestimation of linear and nonlinear optical properties of long-chain molecules,[1b,c,12] the poor description of van der Waals bonds,[1d,e] the underestimation of barrier heights,[13] and the underestimations of charge transfer and Rydberg excitation energies and the corresponding oscillator strengths in time-dependent DFT calculations.[1a] The LC scheme combines an exchange functional for the interelectronic short-range distance with the Hartree−Fock (HF) exchange integral for the long-range distance using the standard error function

$$\frac{1}{r_{12}} = \frac{1 - \mathrm{erf}(\mu r_{12})}{r_{12}} + \frac{\mathrm{erf}(\mu r_{12})}{r_{12}} \qquad (2)$$

where $r_{12} = | \mathbf{r}_1 - \mathbf{r}_2 |$ is the distance between electrons $\mathbf{r}_1$ and $\mathbf{r}_2$, and $\mu$ is a parameter controlling the proportion between HF and DFT exchange. Here, the term "long-range" does not necessarily mean that it is longer than "medium-range" mentioned above. The LC2gau method is LC-based, and modifies the LC scheme for the short-range exchange functional part by adding Gaussian attenuation to improve accuracies, especially in atomization energies and core excitation energies.[14] Considering that long-range exchange effects are significant for long-chain molecules contained in eq 1, it is reasonable to assume that the LC scheme may improve isodesmic reaction enthalpy energies.

We should also pay attention to the effect of intramolecular dispersion forces in isodesmic reaction calculations. To date, the LC scheme has been combined with the Anderson−Langreth−Lundqvist (ALL) dispersion functional[15] to calculate van der Waals and weak hydrogen bonds.[1d,e] However, since calculated systems have to be divided into the components in ALL functional calculations, it has been difficult to apply this dispersion functional to intramolecular van der Waals calculations.

Sato and Nakai very recently developed a local response dispersion (LRD) method,[16] which has enabled us to calculate the intramolecular dispersion forces with much less computational timing than that of the ALL-type dispersion functional.

LC and LC2gau calculations were performed using the Perdew−Burke−Ernzerhof (PBE)[17] functional (LC-PBE and LC2gau-PBE). The optimized $\mu$ value for ground states ($\mu$

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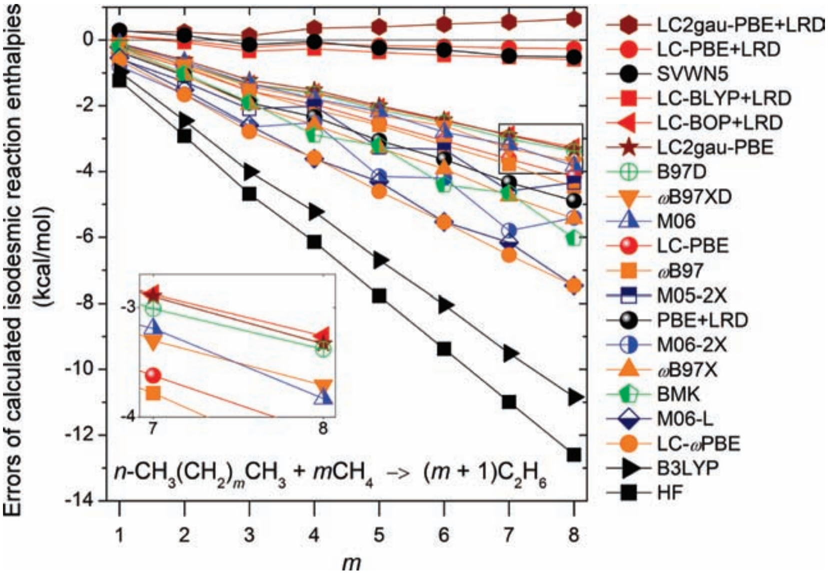

**Figure 1.** Errors in isodesmic reaction enthalpies of *n*-alkanes calculated using several DFT functionals from experimental values (0 K). All energies were calculated with geometries optimized by each method, followed by frequency calculations to obtain zero-point energy corrections. The 6-311+G(p,d) basis set was used in all calculations.

$= 0.47$ for BOP,[13] $\mu = 0.55$ for PBE,[18] and $\mu = 0.50$ for BLYP[18]) was used in the present calculations.[13] The parameters of LC2gau were used at the previously determined values using BOP.[14a] The parameters of LRD were taken from ref 16. Calculations using other recent LC functionals, i.e., LC-$\omega$PBE,[19] $\omega$B97,[20] and $\omega$B97X[20] ($\omega$B97XD),[21] were also carried out. To check what effect dispersion forces had, B97D[22] and $\omega$B97XD dispersion-corrected functionals were tested. In addition, Slater−Vosko−Wilk−Nusair (SVWN5)[23] LDA, M0x-series (M05-2x,[9] M06-2x,[24] M06,[24] and M06-L[25]), Boese−Martin for Kinetics (BMK)[26] hybrid meta-GGA functionals, B3LYP,[27] and the HF method were also examined. For comparison, the 6-311+G(d,p) basis set employed in previous related papers[4,10] was used in all calculations and zero-point vibrational corrections were taken into consideration after all geometry optimizations. Geometry optimizations and frequency calculations were performed using analytical derivatives for each method except for the LRD-applied functional, for which zero-point vibrational energies are obtained by numerically differentiating the analytical gradient.[28] The experimental values used in comparison were taken from NIST-JANAF tables for $n = 1-5$ and from ref 4 as the extrapolated values for $n = 6-10$.[29] All the calculated geometries of *n*-alkanes were set to be very symmetrical linear extended zigzag conformations ($T_d$ or $D_{3d}$ or $C_{2v}$ or $D_{2h}$).[29,30] The LC, LC2gau, and LRD calculations were carried out on a development version of the Gaussian03 program and the other calculations were done on the Gaussian09 program.[31]

Figure 1 has the calculated errors in the isodesmic reaction enthalpies in eq 1 in terms of the number of protobranching, *m*, for various functionals. The figure shows that LC-PBE+LRD and LC2gau-PBE+LRD yield surprisingly accurate isodesmic stabilization energies for *n*-alkanes. In contrast, all the other state-of-the-art functionals significantly underestimate the stabilization energies and the errors monotonically increase as *m* rises. Furthermore, the errors in all M0x-series and BMK functionals increase and decrease dependent on the odds and evens of *m*.

The figure also shows that even without the LRD dispersion functional, LC-PBE and LC2gau-PBE produce very small errors, which are much smaller than those of PBE+LRD excluding LC. This indicates that the lack of long-range interactions in exchange functionals is obviously one of the major causes for the underestimation of isodesmic reaction enthalpies and the contribution may be larger than that from

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(18) In the case of LC-PBE and LC-BLYP, the $\mu$ parameter was newly fitted with the same method as in case of LC-BOP (ref 13).

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the insufficient intramolecular dispersion interactions in correlation functionals.

From these results, we can infer that the deficiency of medium-range electron correlation in the DFT functionals is not the main origin of the systematic underestimation. Merely, it should be pointed out that LC+LRD yields very different errors for LC-BLYP+LRD and LC-BOP+LRD: these errors correspond to −0.36 and −3.26 kcal/mol for *n*-decane. The large discrepancy between the LC-BLYP+LRD and LC-BOP+LRD results suggests that these enthalpies greatly depend on the correlation functional used. Therefore, we assumed that the difference in correlation functionals may significantly affect the isodesmic reaction enthalpies, and medium-range electron correlation contained in conventional correlation functionals, where van der Waals effects are excluded, is a possible cause for the underestimation.

As shown in Figure 1, other LC functionals ($\omega$B97, $\omega$B97X, and LC-$\omega$PBE) provide poor enthalpies. This is mainly due to the lack of dispersion correlation. Actually, $\omega$B97XD, which is a correction of $\omega$B97X for dispersion effects, provides better enthalpies than $\omega$B97X does. However, even combining these LC functionals with a van der Waals correlation functional would provide worse enthalpies than LC-PBE+LRD ones, because the errors with these LC functionals are larger than LC-PBE ones. As previously mentioned, this discrepancy may result from the difference in correlation functionals.

In summary, we calculated the isodesmic reaction enthalpies of *n*-alkane to ethane and found that rather than the insufficiencies of intramolecular dispersion or medium-range electron correlations in correlation functionals, the lack of long-range exchange interactions in exchange functionals is the main origin for the errors in calculated enthalpies to monotonically increase as the number of chain units rises. Therefore, we concluded that a long-range correction is required for DFT exchange functionals to quantitatively reproduce the reaction diagrams of such long-chain systems.

On the basis of the poor enthalpies, it has been stated that "no available density functional is generally reliable for large molecules. Efforts to correct for DFT dispersion errors will not be sufficient...".[1i] We firmly believe that this study led to an answer to this statement. To make clear the large long-range exchange effects on the calculations of organic systems, we are now applying the LC scheme to other kinds of isomerization energy calculations, for which DFT has provided poor results.[1h−k,6b,8a]

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**Supporting Information Available:** The numerical energy tables related to Figure 1, the results calculated using other DFT functionals, and the geometries obtained from the LC-PBE+LRD. This material is available free of charge via the Internet at http://pubs.acs.org.

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