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n-Alkane Isodesmic Reaction Energy Errors in Density Functional Theory Are Due to Electron Correlation Effects

Stefan Grimme

Organisch-chemisches Institut, Westfälische Wilhelms Universität Münster,
Corrensstr. 40, 48149 Münster, Germany

grimmes@uni-muenster.de

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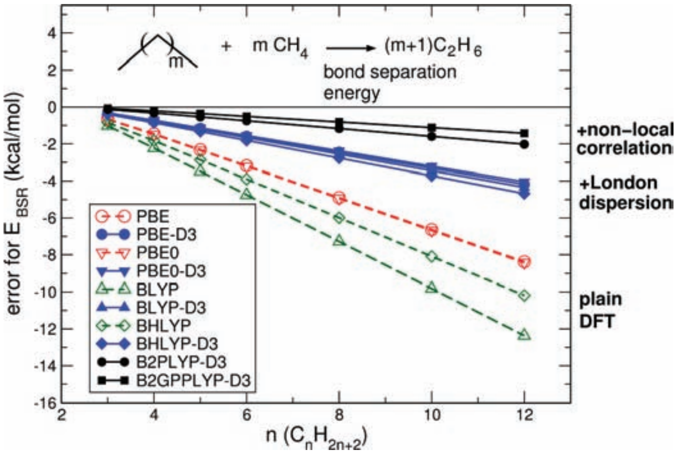
ABSTRACT



The isodesmic reaction energies of *n*-alkanes to ethane, which have so far been known to give systematic errors in standard DFT calculations, are successfully reproduced by SCS-MP2 and dispersion-corrected double-hybrid functionals. The failure of conventional DFT is not due to the lack of long-range exchange interactions but results from an inaccurate account of medium-range electron correlation that is attractive for 1,3-interactions (proto-branching). Highly accurate CCSD(T)/CBS data are provided that are recommended in thermochemical benchmarks.

Alkanes are at the heart of organic chemistry and understanding their electronic structure and interactions is a must for quantum chemistry. In a recent letter in this journal Song, Tsuneda, Sato, and Hirao (STSH) published quantum chemical calculations for alkane isodesmic reaction energies using a long-range corrected (LC) density functional theory (DFT) combined with corrections for intramolecular van der Waals (vdW) effects by an atomic response dispersion model (LRD).[1] The considered bond separation reaction (BSR, with associated energy E_{BSR}) is

$$CH_3(CH_2)_mCH_3 + mCH_4 \rightarrow (m + 1)C_2H_6 \qquad (1)$$

which has been proposed originally by Redfern et al.[2] to uncover errors of popular DFT approximations like B3LYP for large molecules. This and similar reactions of hydrocarbons[3] have recently attracted a lot of interest in the theoretical community. They are related to the problem of many DFT approaches to inconsistently describe the energies of small and large molecules. Because DFT is the "natural" theory for large systems, it is of fundamental and also of practical interest to understand (and ultimately improve) its performance. The problem is also related to the well-known and intensively discussed problem of DFT with vdW interactions[4] that appears here in an intramolecular form.

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In their work, STSH reported “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.” This conclusion is based on the much better performance of their dispersion-corrected LC-PBE and LC2Gau-PBE methods compared to standard and standard-dispersion-corrected functionals. Brittain et al.[3g] also attribute the errors for hydrocarbon reaction energies to the exchange functional.

It is shown here that this conclusion is in conflict with the results of wave function and dispersion-corrected (global hybrid) GGA calculations for (neutral) alkane isodesmic reactions. Overwhelming evidence is presented in favor of the original viewpoint that it is a medium-range correlation effect (that originally has been introduced for the strongly related alkane branching[5] and proto-branching problems[6]). That long-range exchange effects are important here is also not sensible from a chemical point of view. In the considered reaction short-range exchange errors in the covalent CC and CH bonds should cancel out because the number and types of bonds on the left and right side of eq 1 is the same. Because of the saturated character of alkanes (an atomic-orbital-based density matrix is sparse and local) the proposed long-range effects are difficult to understand. According to common knowledge, the chemical and physical properties of alkanes are additive, which implies a rather short-ranged nature of the electronic interactions. It will also be shown here that a small but significant part of the deviations between DFT and experimental data is rooted in the harmonic approximation used by STSH to compute the zero point vibrational energy (ZPVE) and enthalpic contributions (H298).

STSH used experimental enthalpies of formation in eq 1 to derive the corresponding reaction enthalpy. These are compared to theoretical values in which the ZPVE data have been computed in the vibrational harmonic approximation using only one (the fully zigzag) conformer. It is not entirely clear if the data always consistently correspond to 0 or 298 K. We will take here standard enthalpies of formation (i.e., 298 K) from the NIST database[7] and use the term energy (or E_{BSR}) to indicate plain electronic energy values without any vibrational or thermal contributions.

As we have pointed out recently[8] the standard approach to compute ZPVE/H298 is problematic for two reasons. First, longer alkanes include effects of thermally populated higher-lying conformations that are usually neglected (and which is unknown experimentally for larger alkanes in the gas phase). Second, the harmonic approximation neglects varying anharmonic vibrational contributions to the ZPVE+H298 corrections which accumulates for large m (up to a few kcal/mol[8,9]). Hence we prefer to compare theoretical isodesmic reaction energies at the very accurate CCSD(T) estimated basis set limit (CBS) with the corresponding DFT values for the same fixed set of (optimized) nuclear coordinates (single-point energies). Our here described very extensive CCSD(T)/CBS computations (based on aug-cc-pVTZ/QZ extrapolations including core-correlation effects) lead to the most accurate reference data known for larger n-alkanes. The remaining errors are estimated to be less than about 1% of E_{BSR} (<0.2−0.3 kcal/mol for larger m) which is also much less than the typical error for the experimental heats of formation. Our recommended E_{BSR} value for $m = 1$ of 2.16 kcal/mol compares very well with that from the highly accurate W4 protocol (2.20 kcal/mol[10]).

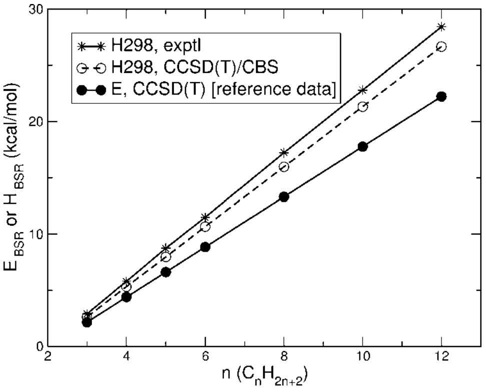

Figure 1. Comparison of isodesmic bond separation standard enthalpies H_{BSR} from experimental data (NIST database) and from harmonically corrected CCSD(T)/CBS calculations for n-alkanes. The CCSD(T)/CBS energy values proposed here as reference are also given.

In Figure 1 the experimental and theoretical enthalpies from CCSD(T) energies augmented with PBE/SV(P)[11] derived harmonic ZPVE+H298 corrections are shown. It is seen that the deviations linearly increase with m, which is

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not due to error of the CCSD(T)/CBS computations but reflects the inappropriateness of the ZPVE/H298/single-conformer approach as mentioned above. The difference is about 2 kcal/mol for the largest system considered, which is definitely non-negligible when DFT errors of 2−10 kcal/mol are to be discussed. In the following we will only consider ZPVE-exclusive CCSD(T)/CBS data as reference and report deviations (errors) DFT-CCSD(T)/CBS. In passing we note that use of our recommended reference data also would lead to a reduction of DFT errors in the work of STSH.

Turning now to the basic question for the reason of the DFT errors, we will first consider wave function based approaches. All of the following results have been obtained in single-point calculations using the very large def2-QZVP Gaussian AO basis sets[12] that provide results close to the limit. The Hartree−Fock (HF) method represents the perfect starting point for an analysis because the exchange interactions are treated exactly (variationally optimal for one Slater-determinant) and no Coulomb correlation is included. In Figure 2 (left) the errors for E_{BSR} with respect to the CCSD(T)/CBS reference data are shown. Negative values indicate an underestimation of the BSR energy (alkane chain stability). As it is seen, HF errors are negative ranging from −1.3 (for propane) to −14 kcal/mol (for $m = 12$). Qualitatively similar HF results can be found in refs 1 and 3b. Note that the relative error is always about 60% of E_{BSR}, which means that there is a constant error per CH_2 group. This also holds for the DFT results (see below).

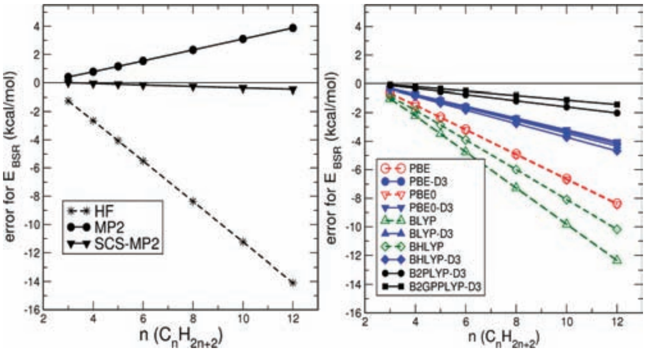

Figure 2. Errors for E_{BSR} using wave function based (left) and DFT methods (right). The methods dubbed “-D3” (colored black and blue) include a long-range dispersion correction.

When (Coulomb) electron correlation is included using perturbation theory (MP2), the HF errors are strongly reduced but MP2 overshoots. MP2 is known to “over-correlate” many chemical systems on the medium electron length scale and has been improved in this respect by the so-called spin-component scaling (SCS-MP2[13]) approach. Here we see that SCS-MP2 errors are extremely small (<0.5 kcal/mol; <3% of E_{BSR}) which clearly demonstrates that medium-range correlation (a term coined in ref 5) is the source of the HF problem. If one accepts the wave function based definition of the correlation energy with the HF energy as the basic quantity, the answer to our question is very clear: the underestimation of alkane stability is a correlation and not an exchange energy problem.

The separation of correlation and exchange effects is not so clear in DFT, and the question remains why many current (and necessarily approximate) density functionals provide rather large errors for E_{BSR} as pointed out correctly in ref 1. In order to clarify this we have tested as examples two basically different GGA forms (PBE[11a] and BLYP[14]) and their corresponding global hybrid variants (PBE0[15] and BHLYP[16]). All in all we thus consider two functionals without (short- and long-range) exact exchange (PBE, BLYP), one with 25% percent nonlocal Fock-exchange admixture (PBE0) and BHYLP with 50%. If there would be any effect of nonlocal exchange on the investigated thermochemical property, it should show up by strongly varying errors for the three functional classes. As pointed out previously, however, long-range intramolecular dispersion type interactions also influence our reaction[5] because a large molecule with many of such interactions is fragmented into many smaller systems. A pragmatic solution for this problem is to add a damped, atom pairwise energy correction of the form C_6R^{-6} to the DFT energy (DFT-D[17] method). Compared to previous approaches of similar type, DFT-D is applicable with unmodified functionals in a standardized form and therefore has meanwhile become a widely used tool in quantum chemistry. Very recently we published a basic revision of the correction termed DFT-D3[18] which is basically *ab initio* in character, provides higher accuracy and a more clear separation of long- and short-range effects. This correction is used here and the corresponding results are indicated by an appended “-D3” to the functional name. Note, that we can not recommend to use “exotic” combinations of various exchange and GGA components for our analysis (e.g., 100% Fock-exchange+GGA correlation) but instead rely on functionals that perform reasonably not only for this special thermochemical problem.

The results are shown in Figure 2, right. Without long-range dispersion correction the BLYP and BHLYP functionals yield similar errors and PBE and PBE0 are very close to each other. This already indicates that exchange effects are not important. For $m = 8$ ($n = 10$) we can also compare our PBE-D3 result (error of −3.3 kcal/mol for E_{BSR}) with the corresponding PBE-LRD enthalpy error reported by STSH of −5 kcal/mol. Thus, about 30% of the error discussed by STSH can be attributed to the use of inappropriate reference values.

The absolute DFT errors (especially for BLYP and BHLYP) are similar to HF. In contrast, note the improvement

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of the results when DFT-D3 is applied. All four density functionals, independent of the amount of included Fock exchange now yield not only smaller but very similar errors such that the curves (shown in blue) are hardly distinguishable. This definitely excludes nonlocal Fock-exchange as a decisive factor for the investigated property. This result is in line with the view of Zhao and Truhlar that standard density functionals do not account correctly for medium range correlation.[19] The opposing (but similar to those of STSH) conclusions in ref 3g do not apply in our opinion as mainly charged or open-shell systems (for which the self-interaction/delocalization error plays an important role[20]), branched alkanes and DFT without dispersion corrections have been investigated. None of our DFT-D3 curves shows artificial oscillatory behavior for odd/even *m* as reported by STSH for the M06 class of functionals.

The added DFT-D3 correction is constructed such that it provides a correct description of noncovalent interactions. This is achieved by an asymptotically correct long-range treatment and a short/medium-range correction (of C_8R^{-8} form) for the different "repulsiveness" of the various functionals.[18] What is missing in DFT-D3 with standard density functionals is an accurate treatment of medium-range correlation effects. These can be included by nonlocal correlation functionals[21] (see, for example,. the good results with so-called double-hybrid functionals B2PLYP[21] and B2GPPLYP[22] shown in Figure 2 with black symbols) or more empirically by refitting together with inclusion of new terms.[23]

The DFT based conclusion is in perfect agreement with the results from the wave function methods. It also supports ideas that consider (medium-range) 1,3-interactions in organic chemistry as being basically attractive (proto-branching model[6]). Our total proto-branching increment is 2.23 kcal/mol for $m = 1$ (methyl⋯methyl), which is very similar to the value of 2.16 kcal/mol from the slope derived for $CH_2 \cdots CH_2$ (the corresponding $m = 1$ enthalpy value used in the literature[3b] is 2.8 kcal/mol). From the slope of the HF-error curve a total stabilizing correlation energy increment of 1.4 kcal/mol per protobranch (CH_2 group) can be estimated. This value contains a "simple" component that is captured by DFT-D3 and a more complicated medium-range contribution that can not be consistently calculated by an atom pairwise approach.[24] It can be estimated from the remaining DFT-D3 errors, which are about 0.4 kcal/mol per CH_2 unit. So according to these considerations, about 30% of the total correlation stabilization of a CH_2 group in alkanes results from truly nonlocal medium-range correlation effects with the neighboring groups. Future approximations of the exchange-correlation energy should accurately account for these in order to yield reliable predictions of the thermodynamics of large molecules. The (rather nonempirical) double-hybrid density functionals already approach closely the desired accuracy (absolute errors <2.0 kcal/mol; <9% of E_{BSR}), which confirms previous conclusions.[10]

In summary we find no indications for energetically significant long-range exchange effects in alkanes. Short-range exchange effects cannot be entirely excluded but seem to be relatively small. Stabilizing 1,3-type interactions are mainly due to nonlocal electron correlation effects as pointed out some years ago.[5] The obvious success of the LC treatment in reference[1] is not understandable by simple reasoning and can tentatively be attributed to error compensation between the LC (exchange) and short-range GGA (exchange + correlation) treatment.

Acknowledgment. This work was supported by the Deutsche Forschungs-gemeinschaft in the framework of the SFB 858.

Supporting Information Available: Details of the calculations, energy components of the CCSD(T)/CBS reference values, ZPVE+H298 corrections and Cartesian coordinates of the alkanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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