Density-Functional Errors in Alkanes: A Real-Space Perspective

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Abstract

Density-functional theory (DFT) approximations are known to give systematic errors for isodesmic reaction energies of n-alkanes to form ethane. Several explanations have been proposed, involving both the exchange or correlation nature of the problem and its distance range (i.e., medium-range or long-range interactions). In this work, a new isodesmic reaction is defined to demonstrate that the reaction energy differences originate from localized interactions between contiguous CH2 units in the n-alkane, i.e., from 1,3 interactions. Furthermore, we introduce a real-space interpretation of the error based on changes in electron density, described by our recently developed Non-Covalent Interactions (NCI) method. The reduced density gradient has smaller values for noncovalent 1,3 interactions in n-alkane reactants compared to ethane products The gradient contribution to the exchange energy is consequently reduced, giving a constant energy bias against each propane unit in an n-alkane. Differences in exchange energy for grid points within the NCI regions are shown to be responsible for the reaction-energy errors. This is also demonstrated to be the source of error in Diels-Alder addition barrier heights obtained with GGA-based hybrid functionals.

Keywords

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