

## Exploring the Limits of Modern Density Functional Approximations for Interaction Energies

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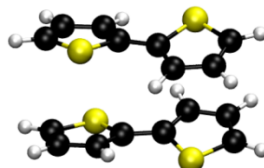
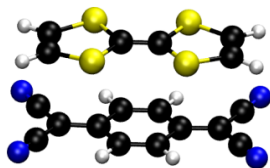
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**Abstract:** Standard density functional approximations fail to provide a consistent description of weak molecular interactions arising from small electron density overlaps. These intra- and intermolecular van der Waals interactions are responsible for many energetic and structural phenomena, such as host-guest chemistry, crystal packing of organic molecules, protein folding, pi-pi stacking of nucleic acids in DNA and supramolecular assemblies. A simple remedy to correct for the missing interactions is to add *a posteriori* an attractive energy term summed over all atom pairs in the system. For general applicability, the dispersion coefficients used in such corrections should depend on the electron density, and have no increase in computational cost. The density-dependent energy correction, dDsC, proposed herein, is constructed from density dependent dispersion coefficients,<sup>[1]</sup> and relies on a genuine damping function that accounts for charge-overlap effects.<sup>[2-4]</sup> The density dependence of both the dispersion coefficients and the damping function makes the approach particularly valuable for modeling redox reactions and charged species in general.

We will discuss general improvements obtained for standard and modern density functionals and present results for a broad variety of reaction energies and geometries. In addition, real-world applications featuring charge transfer complexes and charged radical  $\pi$ -dimers will be discussed. Those systems span the field of organic electronics, making their characterization of considerable interest. The electronic structure of charge transfer complexes is highly challenging. We demonstrate that standard density functionals fail to accurately describe interaction energies of charge-transfer complexes not only because of the missing long-range exchange, as generally assumed, but predominantly because of the ubiquitously present, yet neglected dispersion interactions.<sup>[5]</sup> While global hybrid functionals describe well the electronic structure of neutral charge-transfer complexes, long-range corrected exchange is required for the correct qualitative potential energy curve of cationic  $\pi$ -dimers. Accounting for dispersion *via* dDsC is strongly recommended in all cases. Our analysis reflects the delicate error cancellation between the delocalization error (overestimation of charge-transfer) and the missing long-range interactions.



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[2] S. N. Steinmann and C. Corminboeuf, *J. Chem. Theory Comput.* **2011**, 7, 3567.

[3] S. N. Steinmann and C. Corminboeuf, *J. Chem. Theory Comput.* **2010**, 6, 1990.

[4] S. N. Steinmann, M. D. Wodrich and C. Corminboeuf, *Theor. Chem. Acc.*, **2010**, 127, 429.

[5] S.N. Steinmann, C. Piemontesi, A. Delachat, C. Corminboeuf, *J. Chem. Theory Comput.*, doi 10.1021/ct200930x.