# Minimizing Density Functional Failures for Non-Covalent Interactions Beyond van der Waals Complexes

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CONSPECTUS: Kohn−Sham density functional theory offers a powerful and robust formalism for investigating the electronic structure of many-body systems while providing a practical balance of accuracy and computational cost unmatched by other methods. Despite this success, the commonly used semilocal approximations have difficulties in properly describing attractive dispersion interactions that decay with R^{-6} at large intermolecular distances. Even in the short to medium range, most semilocal density functionals fail to give an accurate description of weak interactions. The omnipresence of dispersion interactions, which are neglected in the most popular electronic structure framework, has stimulated intense developments during the past decade.

In this Account, we summarize our effort to develop and implement dispersion corrections that dramatically reduce the failures of both inter- and intramolecular interaction energies. The proposed schemes range from improved variants of empirical atom pairwise dispersion correction (e.g., dD10) to robust formulations dependent upon the electron density. Emphasis has been placed on introducing more physics into a modified Tang and

Toennies damping function and deriving accurate dispersion coefficients. Our most sophisticated and established density-dependent correction, dDsC, is based on a simple generalized gradient approximation (GGA)-like reformulation of the exchange hole dipole moment introduced by Becke and Johnson. Akin to its empirical precursor, dDsC dramatically improves the interaction energy of a variety of standard density functionals simultaneously for typical intermolecular complexes and shorter-range interactions occurring within molecules. The broad applicability and robustness of the dDsC scheme is demonstrated on various representative reaction energies, geometries, and molecular dynamic simulations. The suitability of the a posteriori correction is also established through comparisons with the more computationally demanding self-consistent implementation. The proposed correction is then exploited to identify the key factors at the origin of the errors in thermochemistry beyond van der Waals complexes. Particular focus is placed on charge-transfer and mixed-valence complexes, which are relevant to the field of organic electronics. These types of complexes represent insightful examples for which the delocalization error may partially counterbalance the missing dispersion. Our devised methodology reveals the true performance of standard density functional approximations and the subtle interplay between the two types of errors. The analysis presented provides guidance for future functional development that could further improve the modeling of the structures and properties of molecular materials. Overall, the proposed state-of-the-art approaches have contributed to stress the crucial role of dispersion and improve their description in both straightforward van der Waals complexes and more challenging chemical situations. For the treatment of the latter, we have also provided relevant insights into which type of density functionals to favor.
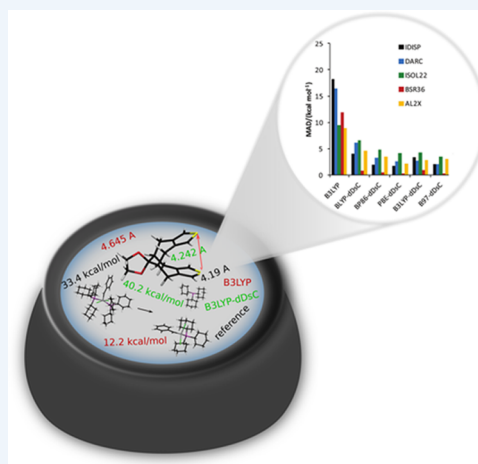
■ INTRODUCTION

Myriad structural and electronic phenomena in chemistry,[1] biology,[2,3] and materials science are governed by van der Waals interactions. These interactions have profound implications in all aspects of our everyday life, ranging from the practicality of Post-it Notes to the crispiness of French fries,[4] as well as in DNA intercalators used in chemotherapeutic treatment.[5] Examples more relevant to the present Account include molecular recognition processes,[6,7] binding energies of charge-transfer complexes,[8] and interactions within simple hydrocarbons.[9] The accurate modeling of these omnipresent weak non-covalent interactions today is ubiquitous. From the computational perspective, conventional semilocal and hybrid

density functional approximations offer the best cost−accuracy ratio. Nonetheless, they suffer from serious shortcomings: on the one hand, they are unable to properly describe attractive dispersion interactions that decay with R^{-6} at large intermolecular distances,[10−13] while on the other hand, they overstabilize electron-delocalized structures (i.e., delocalization error).[14] The interplay between these two shortcomings is rather subtle and somewhat limits the applicability of density

functional theory (DFT)-based methods to a narrower range of situations encountered in chemistry. Recent activity in our laboratory includes addressing the inability of density functional approximations to provide the correct $-C_6/R^6$ dependence (i.e., dispersion). Over the past few years, we have devised damped atom pairwise dispersion corrections (eq 1),

$$E_{disp} = -\sum_{i=2}^{N_{at}}\sum_{j=1}^{i-1}\sum_{n=3}^{5} \underbrace{f_{2n}(bR_{ij})}_{\text{damping function}} \frac{\overbrace{C_{2n}^{ij}}^{\substack{\text{dispersion}\\\text{coefficients}}}}{R_{ij}^{2n}} \tag{1}$$

which result in a balanced description of both inter- and intramolecular weak interactions.[15−19] In addition, the proposed schemes have been exploited to reveal the "true" performance of standard DFT approximations and identify the origin of their errors in challenging systems that go beyond typical van der Waals complexes.[8,9,20] This Account summarizes our recent efforts concerning these two directions.

TOWARD A UNIFIED INTER- AND INTRAMOLECULAR DENSITY-DEPENDENT DISPERSION CORRECTION

Despite their ability to provide computationally efficient access to many ground-state properties for relatively large-scale systems, conventional DFT approximations are intrinsically unable to accurately describe nonlocal dispersion forces.[10−13] The most obvious failures are cases for which van der Waals interactions dominate the total binding energy, but these ubiquitous interactions occur between and within all molecules. Various approaches to tackle this problem have been proposed in the literature. Here, we aim to summarize our schemes and perspectives based on a posteriori atom pairwise dispersion corrections.[14−20] It is not meant to be a comprehensive review of the accurate treatment of dispersion interactions, which has been the subject of several excellent recent review articles (see e.g., refs 21 and 22). In particular, the most prevalent alternative density-dependent [e.g., Becke and Johnson's exchange hole dipole moment (XDM) dispersion model,[23] Tkatchenko and Scheffler's vdW-TS approach,[24] and Sato and Nakai's local response theory[25]] and geometry-dependent (Grimme's D3[26]) atom pairwise dispersion corrections will not be discussed herein.

Our original motivation for improving the DFT treatment of weak non-covalent interactions started when we and others[27−31] demonstrated that most functionals systematically underestimate the bond separation reaction energy of propane and larger alkanes as well as energy differences of hydrocarbon isomerization reactions. A better description of medium-range correlation, a source of error in alkanes identified by Grimme,[27] was shown to improve the energies dramatically.[32] In 2008, we realized that a reparametrized dispersion correction has the ability to remove systematic error associated with alkane thermochemistry.[33] The empirical dispersion corrections typically available at the time were devised for intermolecular interactions but failed to achieve a sufficient correction at shorter ranges, where intramolecular interactions take place.[9,33] Thus, we introduced an empirical atom pairwise dispersion correction specifically tailored for weak intramolecular interactions characteristics of alkanes. In contrast to the "intermolecular schemes" (i.e., typical DFT-D),[34,35] the so-called "Intra" correction successfully improved alkane thermochemistry but significantly overbound intermolecular com-

plexes such as those in the representative S22 test set.[33] We overcame this problem by building more physics into our model through the construction of a sophisticated damping function capable of providing enough correction at short distances without deteriorating the description of longer-range intermolecular interactions.[15] Our initial model, dD10, was empirical in the sense that the parameters were fixed for each element and independent of the system environment. However, dD10 went beyond standard schemes by improving the description of medium-range nonbonded interactions through the inclusion of higher-order contributions (C_8/R^8 and C_{10}/R^{10}) and a physically motivated Tang and Toennies damping function[36] that was modified and fine-tuned at covalent bond distances to minimize double-counting effects.

Interestingly, the dD10 empirical variants show a minimum between 2.3 and 2.6 Å for the carbon−carbon interaction, a distance corresponding roughly to the 1,3 C−C (or 1,5 H···H) distance in propane (e.g., 2.536 Å/4.792 au) (Figure 1). With
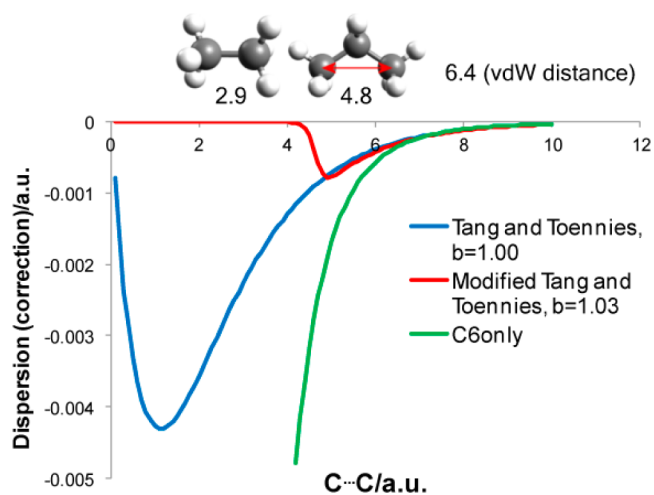

Figure 1. Dispersion energy correction curves for the C···C dispersion interaction vs the C···C distance. The value $a = 1.45$ was employed in our modified Tang and Toennies damping function used in the PBE-dD10 combination (given in red). The green curve corresponds to C_6/R^6.

only two parameters (a and b), nonempirical generalized gradient approximation (GGA) functionals corrected with dD10 were shown to perform well on reaction energies featuring both intra- and intermolecular interactions.

Building on the momentum of dD10, we took the idea one step further and proposed a general dispersion correction that depends on the electron density of the molecule while also preserving the simplicity of a sum over atom pairs. Our resulting density-dependent dispersion correction, dDsC,[16−18] uses nonempirical dispersion coefficients that are based on a simple and computationally inexpensive GGA-like reformulation[17] of the XDM introduced by Becke and Johnson.[23] The dominant Hirshfeld[37] partitioning scheme provides a realistic distribution of the dispersion coefficients among the atoms. In addition, instead of employing the traditionally used damping functions,[24,25,34,38−40] one exploits Hirshfeld atomic overlaps and charges to detect overlapping regions in the extended Tang and Toennies[36] damping function, which constitutes a significant asset in the treatment of intramolecular interactions, polarized systems, or charged species. In short, the dDsC dispersion correction attempts to improve the XDM model by

introducing a more sophisticated damping function that depends on the electron density along with proposing a simplified GGA-like expression for the XDM. dDsC possesses two parameters that are fitted to each functional separately.

The robust performance of the scheme was demonstrated through comprehensive benchmarking on a variety (over 340) of reaction energies featuring both inter- and intramolecular interactions.[18] The broad applicability of dDsC beyond model systems was also illustrated by addressing various chemical questions involving chemosensors,[6,7] water splitting or oxygen reduction catalysts,[41,42] cleavage of peptide $N-C_\alpha$ backbones,[43] and the course of dimerization reactions of carbon-rich compounds.[44] Our overall experience has demonstrated that dDsC adjusts very well to a given functional and provides highly robust performance when mixed interactions, including challenging reaction energies, are considered. More recently, dDsC was also found to improve significantly upon the original XDM method for large supramolecular complexes.[45] A relevant aspect of the latter study was that the good performance of most dispersion-accounting methods for small complexes also applies to large supramolecular systems after inclusion of a three-body energy correction term. All together, we frequently rely upon the dDsC scheme, which is now implemented in three quantum-chemical software codes (ADF, GAMESS-US, and Q-Chem).

The introduction of the density dependence offers the possibility of a correction that not only depends on the electron density but also influences the density through the Fock matrix. The self-consistent implementations could be especially relevant for ab initio molecular dynamics simulations, which might benefit from the accessibility of exact analytical gradients, as well as for low-IR-frequency modes. Still, the dispersion correction schemes are generally applied in a post-SCF manner under the assumption that the influence on the density is weak. In the case of the Becke and Johnson's XDM, Kong and co-workers[46] demonstrated that the perturbative approach is a suitable approximation for computing interaction energies, geometries, and even harmonic frequencies. Similar conclusions were drawn in the context of the local response dispersion (LRD) approach[47] and for van der Waals functionals.[48–50] The self-consistent implementation of the dDsC scheme[51] essentially confirmed these observations, as exemplified by the negligible influence of the correction on the dipole moment of the tetrathiafulvalene (TTF)–tetracyanoquinodimethane (TCNQ) donor–acceptor complex (Figure 2).

The reasonable quality of the approximated dDsC gradients along with the importance of accounting for dispersion in Born–Oppenheimer molecular dynamics (MD) was also demonstrated through the MD trajectories of a highly flexible dithiacyclophane characterized by several low-lying minima featuring both $\pi\pi$-stacked and open conformations. More specifically, we demonstrated that the energy is essentially conserved in the microcanonical (*NVE*) ensemble. The energy fluctuation amplitudes obtained with the post-SCF dDsC approach and the approximated gradients are larger than those computed with noncorrected PBE (the standard deviations are equal to 0.06 and 0.32 kcal mol^{-1} for PBE and PBE-dDsC, respectively), but the energy drift is negligible (less than 0.05 kcal mol^{-1}), justifying the use of the post-SCF process (Figure 3). However, it is worth noting that, as one expects, the $\pi\pi$-stacked conformation is not stabilized at the non-dispersion-corrected PBE level and persists only in the PBE-dDsC trajectory. This qualitative difference stresses the necessity of
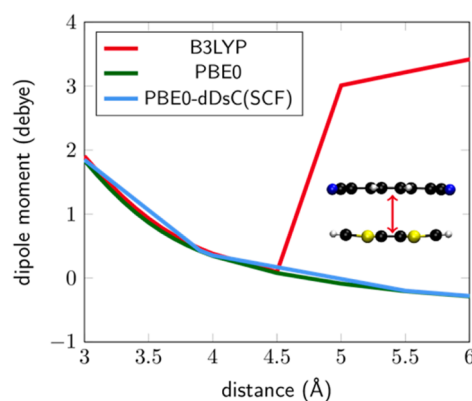

Figure 2. TTF–TCNQ dipole moments computed at the B3LYP, PBE0, and PBE0-dDsC(SCF) levels with the 6-311+G** basis set. The complex was optimized at the B97-dDsC/def2-TZVP level. Nonequilibrium geometries were constructed from equilibrium structures by varying the intermolecular distance (i.e., "unrelaxed" potential energy profiles).

adding a post-SCF dispersion correction as opposed to neglecting the crucial role of dispersion.

The atom pairwise dispersion corrections introduced above offer robust performance and delivers reliable energies and geometries. However, relevant improvements such as the incorporation of many-body terms,[52] the inclusion of anisotropy,[53] the development of state-specific corrections (i.e., binding energies of excited states), and the expansion to "fast" electronic structure approaches[54] are the current focus of the community. Actually, the inherent advantages of dDsC (i.e., density dependence and robust treatment of both intra- and intermolecular interactions) can easily be adapted to other electronic structure methods capable of producing molecular structures and energetics at dramatically reduced computational cost compared with the DFT framework. Toward our objective of modeling nanowires of π-conjugated oligomers,[55,56] our attention has been drawn to the self-consistent charge density functional tight-binding approach (SCC-DFTB, or DFTB for conciseness), which can provide valuable insight for systems involving over 1000 atoms if one accounts for dispersion. We recently devised a correction analogous to dDsC that can be combined with DFTB. The density dependence of dDsC is replaced by a dependence on Mulliken charges (vide infra), which are readily available from the self-consistent DFTB computations. Furthermore, the Hirshfeld-based "bond index" formulated in our original damping function is here simplified into a dependence on atom pair distances and atom sizes. Thus, the related dDMC correction[57] (where MC stands for Mulliken charges) has similar characteristics as dDsC and offers a promising alternative to other dispersion corrections suitable for DFTB. Unfortunately, a critical issue inherent to the DFTB parametrization that causes spurious binding in simulations of non-covalent interactions featuring sulfur atoms[55] (Figure 4) has currently impeded the efficiency and application of SCC-DFTB-dDMC on molecular organic electronics.

◼ THE DIAGNOSIS OF DENSITY FUNCTIONAL APPROXIMATIONS BEYOND TYPICAL VAN DER WAALS COMPLEXES

Our experience and interest in the properties of π-conjugated systems over the last 10 years initiated a related aspect of our research, emphasized here. The objective was to exploit the
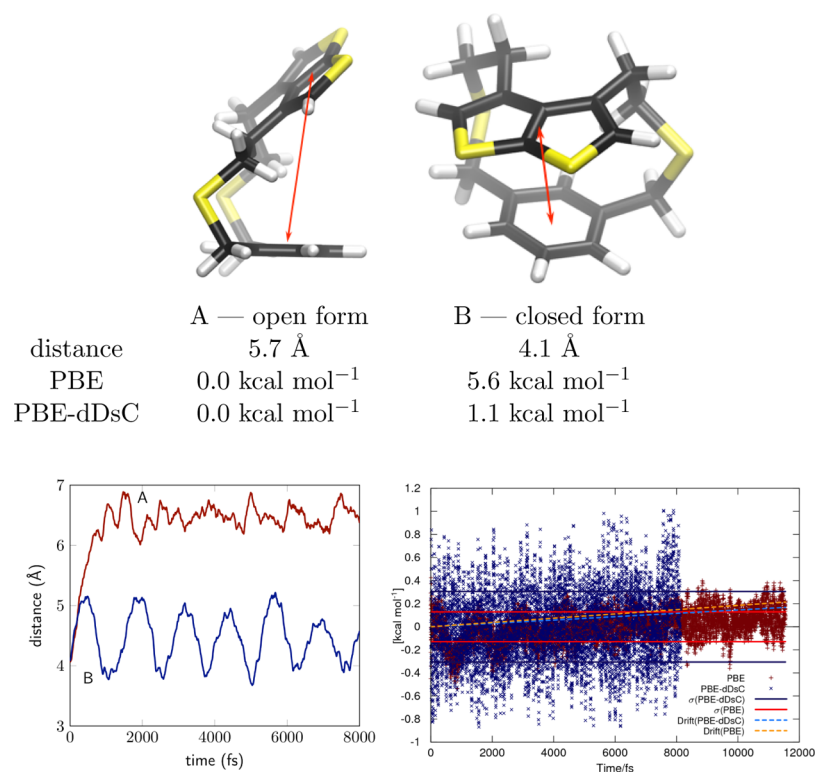
Figure 3. *NVE Born−Oppenheinmer molecular dynamics simulations performed with noncorrected and dispersion-corrected PBE functionals on a closed conformer (B) of a dithiacyclophane displayed at the top. The graphs at the bottom represent the measured distances (in Å) between the barycenter of the benzene ring and the middle of the bond of the thienothiophene (left) and the energy profiles of the MD simulations (right).*
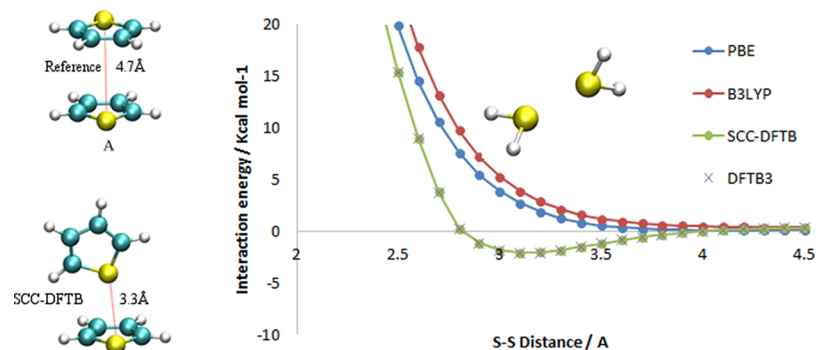

Figure 4. (left) Reference geometry of the antiparallel thiophene dimer[20] and the spurious DFTB3-optimized geometry obtained using the MIO set of parameters. (right) Interaction energy profiles of the H_2S dimer (right) at the DFT and DFTB levels. The SCC-DFTB and DFTB3 computations were performed using the MIO parameters. DFT energies were computed at the PBE/6-31G* and B3LYP/6-31G* levels. As illustrated by the DFT computations, the H_2S dimer should not be bound in the absence of a dispersion correction.

schemes described above to identify the key factors responsible for the errors of conventional density functional approximations beyond van der Waals complexes, more specifically in complexes and properties relevant to the field of organic electronics. Our analysis was primarily based on the realization that the true functional performance can be assessed only after a proper treatment of dispersion interactions. Until recently, the successful applications of DFT to molecules and materials have profited, to some extent, from the neglect of dispersion interactions thanks to fortuitous error compensations between two deficiencies rooted in unrelated approximations.[8] As an example, the overestimation of binding energies of some charge-transfer complexes arising from in the delocalization error can appear to be attenuated at the equilibrium distance if weak long-range attractive interactions are not properly considered. Such compensation is dangerous as it could lead to the wrong diagnostic regarding the main origin of the error of standard functional approximations.[8,58] In this regard, the performance of DFT-dDsC in describing ground-state charge-transfer complexes[8] attracted our attention, as the general assumption was that standard density functionals fail to accurately describe interaction energies of charge-transfer complexes because of the missing long-range exchange[59] with no deep consideration of the role played by long-range correlation. The extent of stabilization due to dispersion was evaluated using both DFT coupled with dDsC and high-level ab initio computations on a set of illustrative charge-transfer complexes that bind more or less strongly and on a typical cofacial TTF−TCNQ organic complex.[8]
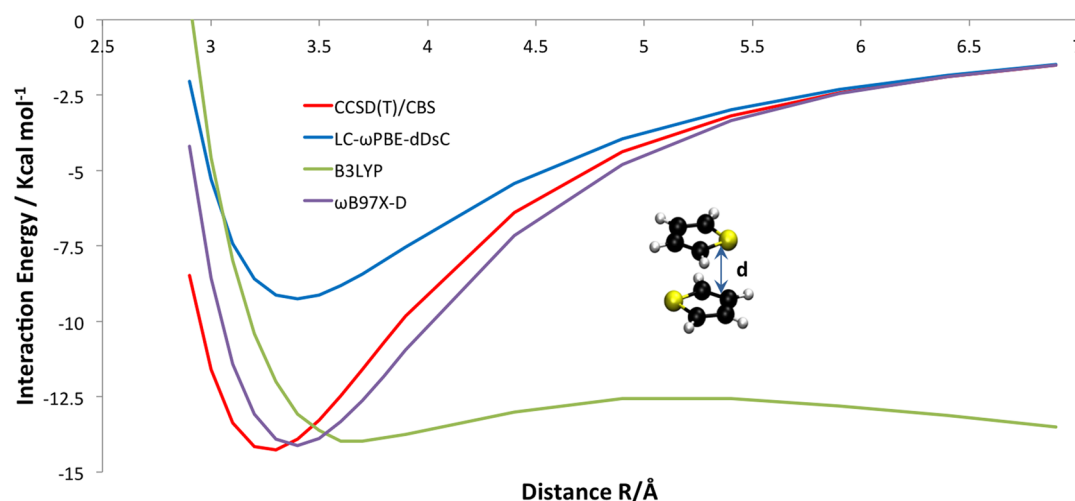
Figure 5. Interaction energy profiles for the radical cation dimer of thiophene (antiparallel) at three DFT levels compared with the profile estimated using CCSD(T)/CBS.[20]

A relevant outcome of this study was that the performance of functional approximations does not necessarily correlate with the amount of "exact" exchange admixture, as is commonly assumed. Instead, we demonstrated that standard density functionals fail to accurately describe the binding energies of typical charge-transfer complexes specifically as a result of the neglect of weak interactions. This conclusion was supported by the Hartree−Fock results, which never provide enough binding, along with the expected overestimation of the binding energy by semilocal functionals that is only visible when accounting for dispersion.

In the context of ground-state charge-transfer complexes, we recommended the use of "well-balanced" functionals that account for dispersion and incorporate a reasonable amount of exact exchange as opposed to assessing the performance of a given functional by neglecting dispersion. The latter alternative is especially dangerous because subtle error cancellations are system-dependent and break down at longer intermolecular distances (charge transfer should fall off exponentially with distance, while dispersion decays as R^{-6}). At the complex equilibrium distance, accurate binding energies can be achieved with M06-2X or with the combination of dDsC with standard global hybrids. At longer distances, however, global hybrids with less than 25% exact exchange are affected by a serious breakdown (i.e., spurious charge transfer) that is nearly invisible in the interaction energy profile but is clearly evident when the dipole moments are computed (see B3LYP in Figure 2). These realizations could have implications when non-covalent interactions are analyzed using energy decomposition schemes[60] and clearly should discourage achieving fortunate agreement through higher-level methods that neglect physically important contributions (e.g., dispersion). Getting the right answer for the right reason should remain the primary objective.

Global hybrid functionals corrected for dispersion might properly describe the electronic structure and binding energy of neutral ground-state charge-transfer complexes and pure dispersively bound systems, but they fail for the more challenging radical cation π-dimers.[20] The latter systems, which represent the simplest models of hole-carrier states in organic functional units, were represented by our illustrative Orel26rad test set featuring 26 radical cation model

compounds, with a special emphasis placed on the potential energy curves of sulfur- and oxygen-containing heterocycles (e.g., thiophene and furan dimers). This challenging Orel26rad database can serve as a valuable test set to develop improved functional schemes and assess their performance. Our analysis of Orel26rad reflects the highly delicate cancellation of the delocalization error affecting these fractionally charged systems and the missing long-range correlation (Figure 5).[20] Non-dispersion-corrected global hybrids give seemingly reasonable binding energies for (thiophene)$_2^+$ and (furan)$_2^+$ because the missing dispersion compensates for the systematic over-estimation of binding energies associated with the delocalization error. However, the incorrect behavior and spurious barrier toward dissociation into one charged and one neutral monomer point to a serious pitfall. The correct asymptotic form is achieved with long-range-corrected exchange functionals, but all of the dispersion-corrected combinations of the latter (e.g., LC-ωPBE-dDsC, LC-BOP-LRD) severely underestimate the interaction energies at the equilibrium distance because of the lack of a nondispersive fraction of correlation. From the perspective of simulating molecular organic electronics, the deficiency affecting the Orel26rad systems could lead to serious consequences, particularly in ab initio molecular dynamic trajectories, for which the reproduction of both equilibrium and nonequilibrium distances is important. Notwithstanding the fact that the performance of the dispersion-corrected range-separated functionals is generally disappointing, ωB97X-D from Chai and Head-Gordon[40] represents an insightful exception providing considerably more binding at the equilibrium distance without deteriorating the description of the neutral analogues. The major difference between the ωB97X-D functional and the more conventional range-separated hybrid functionals is the joint fitting of the exchange−correlation functional together with the dispersion correction parameters.

Chai pursued the same strategy while introducing the more sophisticated ωB97X-D3 and ωM06-D3 variants.[61] Thus, we are interested in exploiting our Orel26 database to achieve an improved description of radical cation π-dimers through optimization of a dDsC-corrected range-separated functional specifically devised to allow for an optimal degree of consistency between the minimization of the delocalization error and the dispersion correction. In comparison with

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standard parametrizations, this functional would have the advantage of exploiting the density information twice: once for the dispersion correction and a second time for the improved description of all other exchange and correlation effects. We expect such an approximation to provide accurate results for the challenging Orel26rad test set and other mixed-valence dimer models of organic electronics precursors. Alternatives involving new parameters of the local response dispersion method applied to the long-range-corrected exchange functional could be of interest as well.

CONCLUSIONS

This Account has summarized our recent achievements and state-of-the-art approaches that have contributed to revealing the critical importance of dispersion not only between neutral molecules but also beyond van der Waals situations. We introduced and validated original atom pairwise dispersion corrections that dramatically reduce the failure of both inter- and intramolecular interaction energies. In particular, our most established density-dependent correction, dDsC, dramatically improves the interaction energies and geometries of a variety of standard density functionals simultaneously for typical van der Waals complexes and shorter-range interactions occurring *within* molecules. These corrections were then exploited to identify key factors responsible for errors of conventional density functional approximations in increasingly challenging compounds relevant to the field of organic electronics. The main emphasis was placed on charge-transfer complexes and radical cation π-dimers. Numerous successful applications of DFT on related molecules and materials have profited to some extent from the neglect of dispersion interactions thanks to fortuitous error compensations with the overestimation of binding energies that arise from overdelocalization of charges. The dDsC scheme is ideally suited to demonstrate the subtle interplay between long-range correlation and the delocalization error. We formulated recommendations regarding which error types and interactions dominate these compounds, how to attenuate these errors, and how to improve the next generation of DFT functionals accordingly.

The reported developments and analysis address lingering difficulties in describing ground-state interaction energies of van der Waals complexes and beyond. However, we consider the binding energies and nature of low electronically excited states as a highly stimulating and relevant upcoming challenge.

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Notes

The authors declare no competing financial interest.

Biography

Clemence Corminboeuf was appointed Tenure Track Assistant Professor and Sandoz Family Foundation Chair at the Ecole Polytechnique Fédéral de Lausanne in 2007. She earned her Ph.D. from the University of Geneva, followed by postdoctoral stays at New York University and the University of Georgia. Her research is essentially built upon the framework of Kohn–Sham density functional theory. Her group has been involved in the development and application of innovative methods to accurately describe and analyze non-covalent interactions. She has coauthored more than 80 publications. In 2010, she was the silver medalist of the European Young Chemist Award. In 2012, she was awarded an ERC Starting Grant, and she received the Werner Prize of the Swiss Chemical Society in 2014.

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