

# Why are the Interaction Energies of Charge-Transfer Complexes Challenging for DFT?

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## S Supporting Information

**ABSTRACT:** The description of ground state charge-transfer complexes is highly challenging. Illustrative examples include large overestimations of charge-transfer by local and semilocal density functional approximations as well as inaccurate binding energies. It is demonstrated here 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 also as a result of the neglect of weak interactions. Thus, accounting for the missing van der Waals interactions is of key importance. These assertions, based on the evaluation of the extent of stabilization due to dispersion using both DFT coupled with our recent density-dependent dispersion correction (dDsC) and high-level *ab initio* computations, reflect the imperfect error-cancellation between the overestimation of charge-transfer and the missing long-range interactions. An in-depth energy decomposition analysis of an illustrative series of four small ambidentate molecules (HCN, HNC, HF, and ClF) bound together with  $\text{NF}_3$  provides the main conclusions, which are validated on a prototypical organic charge-transfer complex (i.e., tetrathiafulvalene-tetracyanoquinodimethane, TTF-TCNQ). We establish that the interaction energies for charge-transfer complexes can only be properly described when using well-balanced functionals such as PBE0-dDsC, M06-2X, and LC-BOP-LRD.

## INTRODUCTION

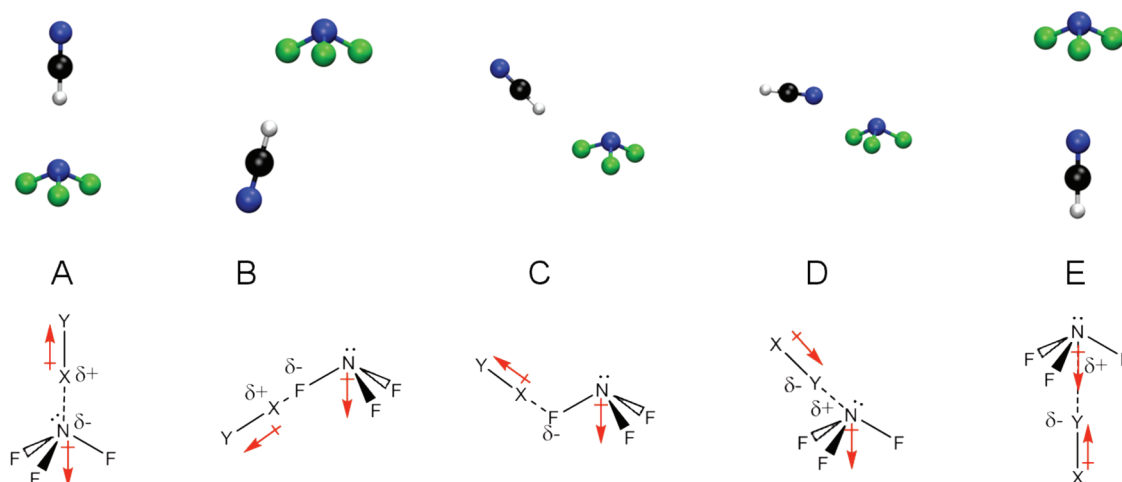
Charge-transfer (CT) complexes, as introduced by Mulliken, are species characterized by low-lying excited states (e.g., benzene $\cdots\text{I}_2$ ).<sup>1</sup> Since its introduction, Mulliken's original term has been extended beyond its original definition to generally designate donor–acceptor complexes of either ground or excited states. The ground state of reactive complexes between alkenes and dihalogens (e.g.,  $\text{C}_2\text{H}_4\cdots\text{F}_2$ ) are illustrative examples of the broader use of the term.<sup>2</sup> Currently, charge-transfer complexes span the field of organic electronics (e.g., organic solar cells or light-emitting diodes),<sup>3,4</sup> making them of considerable interest.

The origin of the binding interaction in ground-state charge-transfer complexes is controversial. Orbital interactions have been commonly invoked to explain the energies associated with CT complexes.<sup>1</sup> Although the importance of CT has been questioned,<sup>5,6</sup> it is still considered to be the primary source of binding—perhaps because CT is easily rationalized and visualized in terms of orbital interactions. The importance of van der Waals (vdW, especially London dispersion) forces in providing the correct qualitative descriptions of charge-transfer complexes has been known for some time<sup>7,8</sup> but remains largely overlooked. Alternatively, electrostatic interactions have also been suggested as the dominant forces in the formation of CT complexes.<sup>9</sup> Such complexes often show a strong dependence on the relative orientation of the monomers, a characteristic typically associated with orbital interactions. However, Hobza and co-workers<sup>10</sup> recently found that dispersion forces between nonspherical molecules have a stronger dependence on the relative orientation than hydrogen-bonded complexes. These findings question the use of orientation dependence for discriminating between interaction energy types.

The investigation of the ground state of CT complexes with approximate density functionals is very challenging. Note that “strong charge-transfer complex” refers herein to complexes affected by “strong” self-interaction (or the related delocalization) errors with common density functional approximations (charge-transfer excitation energies are highly problematic as well<sup>11–15</sup> but are not discussed herein; similarly, strong multireference electron–donor acceptor complexes such as TCNQ-TTF-TCNQ in an electric field<sup>16</sup> are also not the focus here). On one hand, “pure” density functionals (local density approximation, LDA, and generalized gradient approximation, GGA) tend to overestimate the binding energy of strong charge-transfer complexes,<sup>17,18</sup> while on the other hand, semilocal and hybrid functionals are unable to describe long-range dispersion interactions.<sup>19–22</sup> The overestimation of charge-transfer might somehow compensate for the neglect of dispersion energy, but the error cancellation is subtle: a given functional might be reasonably accurate for one system but quite wrong for another (e.g.,  $\text{F}_2$  is much more problematic in terms of CT, while  $\text{I}_2$  is more problematic in terms of neglected dispersion energy). In addition, error cancellation breaks down at longer intermolecular distances, as CT should fall off exponentially with distance, while dispersion decays as  $R^{-6}$ . Adding a sufficient amount of “exact” exchange suppresses the spurious charge transfer, while the dispersion energy can be recovered by explicitly adding the correct  $R^{-6}$  attractive form. On a more fundamental level, relying on error cancellation is always dangerous, as it could lead to a wrong qualitative interpretation of the origin of the binding energy. An intriguing

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**Figure 1.** Representations of the five binding modes for the example of  $\text{NF}_3 \cdots \text{HCN}$ , and the general scheme is shown below. Color code: white, hydrogen; black, carbon; blue, nitrogen; and green, fluorine. In the general interaction pattern:  $Y = \text{F}, \text{F}, \text{C}, \text{and N}$  for  $\text{ClF}$ ,  $\text{HF}$ ,  $\text{HNC}$ , and  $\text{HCN}$ , respectively. The red arrows represent the direction of the monomer molecular dipoles.

example is the organic CT complex investigated by Bredas and co-workers, for which “classic” density functionals were found to transfer more electron density than MP2, even though the DFT complex is bound less strongly than with (SCS-)MP2.<sup>23</sup> An alternative study examines the inaccurate DFT treatment of the interaction energy between a Lewis acid and a bulky transition metal complex. The authors attribute the error to the missing long-range exchange prior to recommending higher percentages of “exact” exchange for the description of the dative bond between Pt and Al.<sup>24</sup> In both cases, M06-2X performs well with respect to CCSD(T). These studies, however, did not address the apparent contradiction between the actual under-binding and the expected overbinding by semilocal density functional approximations. In fact, the performance does not correlate with the percentage of “exact” exchange, which is noted only in passing and without making a link to the importance of weak interactions.<sup>23</sup> The very good performance of M06-2X can indeed be attributed to the improved description of weak interactions<sup>25</sup> rather than to the large amount of nonlocal exchange (*vide infra*).

In a previous study,<sup>26</sup> we demonstrated that the errors of standard density functionals for relative energies of saturated hydrocarbons are due to a combination of over-repulsiveness in the short-range and the ubiquitous missing dispersion interactions. Adding *a posteriori* an atom pairwise correction energy term to standard density functionals not only conveniently accounts for weak interactions<sup>27–30</sup> for intermolecular complexes but also dramatically improves the performance for various reaction and interaction energies involving saturated hydrocarbons.<sup>27,30–32</sup> The recently developed density dependent dispersion correction dDSC<sup>29,30,33</sup> is pertinent for systems for which density rearrangements (charge transfer, polarization) might influence the interaction energy.

In the present work, the comparison of uncorrelated (HF) and correlated *ab initio* computations suggests that the interaction energy of closed-shell neutral charge-transfer complexes is dominated by weak electron correlation (i.e., vdW interactions) and not by the charge-transfer interaction energy itself. In line with these realizations, dispersion corrected HF and density functional approximations are shown to describe interaction energies substantially better than their standard counterparts. Further analysis based on energy

decompositions indicates that the challenge for density functional approximations resides mostly in the description of the monomers (i.e., the self-interaction errors introduced by semilocal approximations, which affect the monomer, can lead to dramatic failures in the presence of a second molecule) and less in the strength of the actual charge-transfer interaction. We further demonstrate that only specific functionals achieve a consistent binding energy curve for typical vdW and charge-transfer complexes by providing an adequate description of the monomers, including a sufficient amount of “exact exchange” (to avoid over-repulsiveness at short and spurious charge transfers at long intermolecular distances) and accounting for weak interactions.

The performance of various density functionals and the role of CT are evaluated on an illustrative series of four small ambidentate molecules (HCN, HNC, HF, and ClF) bound together with  $\text{NF}_3$ . Five different geometries are considered for each of the small molecules (see Figure 1).<sup>34</sup> These systems are particularly well suited for our purpose: depending on the orientation and relatively small electronic changes (e.g., HCN vs HNC), the binding energy and the relative importance of different components is substantially different. The broad range of interactions characterizing this series of small molecular complexes is representative of conventional applications involving charge-transfer complexes and thus valuable for gaining insight into larger related complexes that are typically targeted in chemical applications. In this respect, the crucial role of dispersion interactions, determined by these small model compounds, is further established on a typical cofacial organic complex of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).<sup>23</sup>

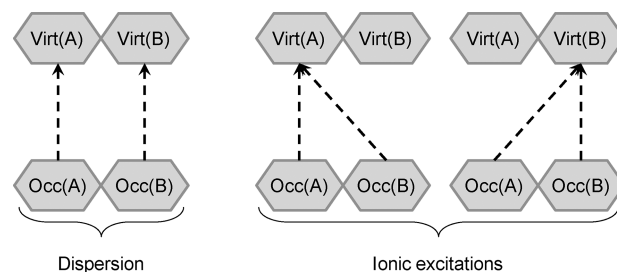
**Theoretical Background, Methods, and Computational Details.** Studies on typical strong CT complexes<sup>17,18</sup> (e.g.,  $\text{C}_2\text{H}_4 \cdots \text{F}_2$ ) demonstrate that semilocal DFT exchange suffers from failures (i.e., overbinding), which can be reduced by increasing the amount of nonlocal “exact” exchange. In particular, BHHLYP has been recurrently qualified as the best performing standard functional for geometries, interaction energies, and properties of charge-transfer complexes in general.<sup>18,35–38</sup> The need for “exact” exchange is often rationalized by invoking the wrong asymptotic potential in semilocal density functionals, which is corrected in global

hybrid variants according to the percentage of “exact” exchange. Since the asymptotic potential is only partially corrected in global hybrid functionals, systems with a relatively small HOMO–LUMO gap (e.g., NaCl at long interatomic distances<sup>39</sup> as well as TTF-TCNQ, *vide infra*) can still be affected by spurious charge transfer. Alternatively, long-range corrected exchange functionals<sup>40,41</sup> possess the correct form in the asymptotic region. Two particular flavors ( $\omega$ B97X-D<sup>42</sup> and LC-BOP-LRD<sup>43,44</sup>) are tested here. LC-BLYP<sup>45</sup> and LC- $\omega$ PBE08<sup>46–48</sup> are only briefly discussed in the Supporting Information, since we<sup>30</sup> and others<sup>45</sup> noticed difficulties arising from combining them with a dispersion correction. In any case, the asymptotic potential, which is the central quantity improved by the long-range corrected functionals, is designed to better describe charge-transfer at large distances, where overlap effects are negligible and qualitative (and relative) errors of semilocal functionals are therefore most pronounced (*vide infra*). For most systems of chemical interest, however, the charge-transfer in the ground state vanishes at long intermolecular distances. Thus, we argue that when standard functionals underbind, instead of overbind, improving the treatment of weak van der Waals interactions is more critical than increasing the amount of “exact” exchange. Around equilibrium, the overestimation of CT interaction with semilocal functionals can be “damped” by admixing a suitable amount of (mainly repulsive) HF exchange, resulting in seemingly accurate intermolecular distances and interaction energies. Nevertheless, the improvement originates from labile error cancellation between the (overestimated) CT and missing<sup>19–22</sup> dispersion (*vide infra*).

The importance of charge transfer for interaction energies is generally assessed on the basis of energy decomposition analysis (EDA). Akin to other useful chemical concepts (e.g., atomic charge and aromaticity), interaction energy components (e.g., electrostatic, charge-transfer, dispersion) are, nevertheless, noumena, i.e., unobservables. Thus, they can be quantified by computational means—but not in a unique manner.<sup>49</sup> Although conceptually arbitrary, energy decomposition analysis is a powerful method for a quantitative interpretation, which is not accessible from total interaction energies. In particular, such analysis provides valuable insight into the “inner workings” of density functional approximations. Ultimately, EDA may help in further understanding functional performance and guide development aimed to go beyond or improve error cancellation. Perturbation theory can be considered as the most ambitious approach, as the interaction energy is computed directly, i.e., without any self-consistent treatment of the dimer.<sup>50–53</sup> Interaction energies based on natural bond orbitals (NBO) extract the charge-transfer interaction from the density matrix of the dimer.<sup>54</sup> The best known family of EDAs based on a combination of monomer and dimer computations is related to the energy decomposition of Morokuma<sup>55</sup> and to its numerous refinements.<sup>56–59</sup> The separation between charge-transfer and polarization is generally challenging, as it tends to vanish in the complete basis set (CBS) limit and is even undefined in the perturbation approach.<sup>6,50</sup> The scheme based on the block localized wave function (BLW) from Mo and co-workers<sup>60,61</sup> provides a well-behaved and insightful energy decomposition analysis including the separation between polarization and CT.<sup>62,63</sup> Closely related alternatives have advised a real-space partitioning<sup>64</sup> or abandoning the separation altogether.<sup>65</sup> The localized orbitals variant of MP2 (LMP2) represents a special case that splits the correlation energy into

dispersion interactions and ionic contributions (see Scheme 1).<sup>66</sup>

**Scheme 1. Relevant Terms Associated with the Double Excitation Classification in LMP2<sup>a</sup>**



<sup>a</sup>Each arrow indicates the excitation of one electron. Dispersion interactions are excitations of one electron of monomer A into one of its virtual orbitals coupled to a corresponding excitation in monomer B (“induced dipole...induced dipole” interaction). “Ionic” excitations are excitations from monomer B into the virtual space of monomer A coupled with an excitation of one electron of A into its virtual space (and the ones with A and B flipped around).

With the goal of gaining insight into the origin of the failure of standard density functionals to describe binding energies, four energy decomposition schemes are applied herein: symmetry adapted perturbation theory (SAPT);<sup>53</sup> BLW,<sup>62</sup> which distinguishes polarization from charge-transfer; the scheme of Su and Li,<sup>65</sup> which separates terms arising from the exchange and the correlation functional; as well as LMP2, which is used to distinguish ionic from dispersion-type interactions.<sup>66</sup>

The following subsections give a qualitative overview of each of these EDA schemes along with the details of the computational settings. As we do not provide the (mathematical/physical) definitions associated with each scheme, the interested reader is referred to original works and reviews for BLW,<sup>62,67,68</sup> LMOEDA,<sup>65</sup> SAPT,<sup>53</sup> and LMP2.<sup>66,69</sup> Note that NBO,<sup>54</sup> which emphasizes charge-transfer, turned out to be completely inadequate for the complexes studied herein: first, stronger charge-transfer interactions are found for HF than for LDA, in disagreement with previous, independent assessments, and second, the charge transfer is too long-ranged for CIF-A (e.g., 1 kcal mol<sup>−1</sup> at a distance of 5 Å, where the interaction energy is about 0.1 kcal mol<sup>−1</sup>). More details are given in the Supporting Information.

The geometries for the NF<sub>3</sub> complexes correspond to minima at the MP2/aug-cc-pVTZ level and are taken from ref 34. The geometry of TTF-TCNQ was optimized at the B97-dDsC/def2-TZVP level of theory. Nonequilibrium geometries are constructed from equilibrium structures by varying the intermolecular distance (i.e., “unrelaxed” potential energy profiles) and can be found in the Supporting Information.

**BLW.** The BLW formalism<sup>61,62</sup> (also known in Q-Chem as “absolutely localized molecular orbitals”, ALMO<sup>63</sup>), which serves to separate the polarization energy from the charge-transfer interaction, can be seen as the simplest variant of valence bond theory. The distinction between polarization and charge-transfer energy is stable with respect to the basis set, provided that only a few diffuse functions are used: in the CBS limit, the polarization includes all CT terms already.

With BLW-EDA, the interaction energy is defined as:



$$E_{\text{int}} = \Delta E_{\text{FRZ}}^{\text{BLW}} + \Delta E_{\text{pol}}^{\text{BLW}} + \Delta E_{\text{CT}}^{\text{BLW}}$$

Akin to the other schemes, the interaction energy is computed with respect to the monomers in the geometry they adopt in the dimer, i.e., excluding the deformation energy. The first term,  $\Delta E_{\text{FRZ}}^{\text{BLW}}$ , sometimes denoted Heitler–London (HL; especially in the context of BLW at the HF level<sup>70</sup>) or “steric” energy  $\Delta E_{\text{s}}$ ,<sup>67</sup> corresponds to the energy difference between the monomers and the dimer composed of (frozen) monomer densities. In line with Head-Gordon and co-workers,<sup>63</sup> we refer to this term as the “frozen energy”,  $\Delta E_{\text{FRZ}}^{\text{BLW}}$ . The frozen energy contains both the electrostatic energy and the Pauli repulsion (due to the antisymmetrization of the product of monomer wave functions). The density dependent dispersion correction dDsC<sup>30</sup> essentially alters this term.<sup>67</sup> The polarization energy  $\Delta E_{\text{pol}}^{\text{BLW}}$  is the difference between the energy of the “frozen” monomers and the variationally optimized localized state (i.e., the BLW state). Finally,  $\Delta E_{\text{CT}}^{\text{BLW}}$  accounts for all of the delocalization energy between the monomers. The delocalization energy is affected by the basis set superposition error and is therefore BSSE corrected. The sum of polarization and charge transfer is denoted as  $\Delta E_{\text{POLCT}}^{\text{BLW}}$ .

BLW-EDA computations (applying the algorithm of Gianinetti et al.<sup>71</sup>) were performed in a development version of Q-Chem<sup>72</sup> using the 6-311+G\*\* basis set and tight convergence criteria (max DIIS error < 10<sup>−8</sup>), integral thresholds (10<sup>−12</sup>), and grid settings (99/590 Euler–MacLaurin–Lebedev<sup>73,74</sup>). The BSSE correction was computed without the dispersion correction. Identical settings were applied for ωB97X-D computations.

**LMOEDA.** The EDA scheme of Su and Li<sup>65</sup> is implemented under the acronym LMOEDA in GAMESS<sup>75</sup> (but does not rely on localized molecular orbitals) and decomposes the DFT interaction energy as follows:

$$E_{\text{int}} = \Delta E_{\text{ele}}^{\text{LMO}} + \Delta E_{\text{ex}}^{\text{LMO}} + \Delta E_{\text{rep}}^{\text{LMO}} + \Delta E_{\text{pol}}^{\text{LMO}} + \Delta E_{\text{disp}}^{\text{LMO}}$$

where “LMO” is used herein to distinguish the energy contributions of the LMOEDA scheme from those of the other EDAs.

Together,  $\Delta E_{\text{ele}}^{\text{LMO}} + \Delta E_{\text{ex}}^{\text{LMO}} + \Delta E_{\text{rep}}^{\text{LMO}}$  is closely related to  $E_{\text{FRZ}}^{\text{BLW}}$  but differs in that only the contributions from the exchange functional are included. The “polarization” energy,  $\Delta E_{\text{pol}}^{\text{LMO}}$ , contains the exchange-functional contributions to the energy difference between the dimer and the (anti-symmetrized) product of the monomer wave functions. When compared to BLW-EDA,  $\Delta E_{\text{pol}}^{\text{LMO}}$  corresponds to  $\Delta E_{\text{POLCT}}^{\text{BLW}}$  minus all contributions associated with the correlation functional. The contributions rooted in the correlation functional (i.e., the difference in “correlation energy” between the monomer and the dimer) are collected into  $\Delta E_{\text{disp}}^{\text{LMO}}$ .

LMOEDA computations are performed in GAMESS<sup>75</sup> using the 6-311+G\*\* basis set and an ultrafine Euler–MacLaurin<sup>73</sup>/Lebedev<sup>74</sup> integration grid of 99/590 and 150/1202 for the M06 family of functionals and tight (10<sup>−12</sup>) integration thresholds. Identical settings were adopted for LC-BOP-LRD<sup>43,44</sup> computations.

**SAPT.** SAPT<sup>53</sup> is an *ab initio* method that computes the interaction energy between molecules based on perturbation theory. To facilitate the discussion, we divide the various interaction energy terms into three main classes (frozen energy, polarization/charge-transfer in analogy to the BLW energy decomposition, and dispersion energy, the most interesting component at the SAPT level) and two correlation corrections

(one for the frozen energy and one for the polarization/charge-transfer):

$$E_{\text{int}}^{\text{SAPT}} = E_{\text{FRZ}}^{\text{SAPT}} + \epsilon_{\text{FRZ}} + E_{\text{POLCT}}^{\text{SAPT}} + \epsilon_{\text{POLCT}} + E_{\text{DISP}}^{\text{SAPT}}$$

The difference between HF and SAPT first-order interaction ( $E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} = E_{\text{FRZ}}^{\text{SAPT}}$ ) plus second-order induction(-exchange) ( $E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)}$ ) energies is given by  $\delta\text{HF}$ .<sup>76,77</sup> The consideration of  $E_{\text{FRZ}}^{\text{SAPT}}$  rather than that of the individual electrostatic and exchange terms seems preferable to us, given that the exchange accounts for the antisymmetrization of the wave function, which is neglected when computing the electrostatic energy. We define  $E_{\text{POLCT}}^{\text{SAPT}}$  as the sum of the second order induction(-exchange) energy and  $\delta\text{HF}$ , the latter being dominated by corrections to the induction energy. Our notation also emphasizes that polarization and charge-transfer are not separable within SAPT. The dispersion interaction ( $E_{\text{DISP}}^{\text{SAPT}}$ ) is given by the sum of second-order dispersion(-exchange) ( $E_{\text{disp}}^{(20)} + E_{\text{disp-exch}}^{(20)}$ ) and the higher order correction terms ( $E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)}$ ). The intramolecular correlation corrections to the first-order interaction energy ( $\epsilon_{\text{FRZ}}$ ) are obtained from the sum of the exchange correction  $\epsilon_{\text{exch}}^{(1)}$  (CCSD) with that for the electrostatics,  $E_{\text{elst,resp}}^{(12)} + E_{\text{elst,resp}}^{(13)}$ . Finally, the correction to the induction energy due to the intramolecular correlation  $\epsilon_{\text{POLCT}}$  is given by  $E_{\text{ind}}^{(22)} + E_{\text{exch-ind}}^{(22)}$ .

SAPT computations are performed with SAPT 2008.2,<sup>78</sup> interfaced to GAMESS,<sup>75</sup> using the dimer centered aug-cc-pVTZ<sup>79</sup> basis set and frozen core orbitals.

Reference interaction energies are obtained at the counterpoise corrected CCSD(T)-F12b/VTZ-F12<sup>80–82</sup> level of theory in Molpro2010.1,<sup>83</sup> where the df-LMP2<sup>66</sup>/VTZ-F12 and BCCD/VTZ-F12 computations are also performed. Note that the basis set will not be indicated further and the F12b will be dropped for clarity.

The reference interaction energies for the larger TTF-TCNQ complex are computed according to

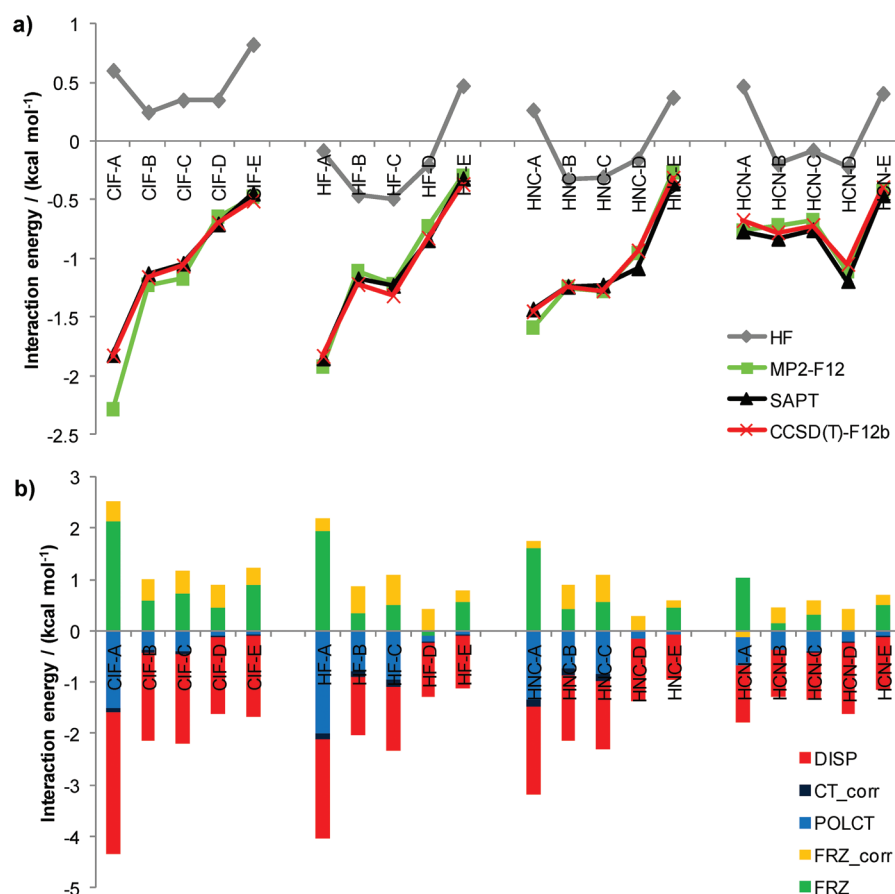
$$\Delta E(\text{CCSD(T)*}) = \Delta E(\text{HF/AVQZ}) + \Delta E(\text{df-MP2/CBS}) + \delta\text{CCSD(T)6-31G*}(0.25)$$

The complete basis set extrapolation is carried out with aug-cc-pVTZ and aug-cc-pVQZ (AVTZ and AVQZ, respectively) according to the Helgaker scheme,<sup>84</sup> and the higher-order correlation correction  $\delta\text{CCSD(T)}/6-31\text{G*}(0.25)$  corresponds to the difference between MP2 and CCSD(T) in the 6-31G\*(0.25) basis set.<sup>85,86</sup> Similarly, MP2.5\*,<sup>87</sup> which is computationally less expensive than CCSD(T)\* and therefore applicable to larger systems, refers to MP2/CBS + 0.5(MP3-MP2)/6-31G\*(0.25). The asterisk is used to indicate that the composite approach is used to obtain the CBS estimate.

All computations used the Molpro2010.1 defaults for auxiliary basis sets and technical parameters.

## RESULTS AND DISCUSSION

The following discussion is divided into five sections aimed at deciphering the physical origin of the interaction energies in CT complexes and assessing the performance of various density functional approximations. Robust *ab initio* and SAPT computations first serve to determine the nature of the interaction energy for 20 NF<sub>3</sub>-based complexes and to benchmark DFT methods. The second section contains a detailed analysis of the interaction energy profiles of two representative complexes connecting the source of the binding energy to the DFT performance. The third section provides



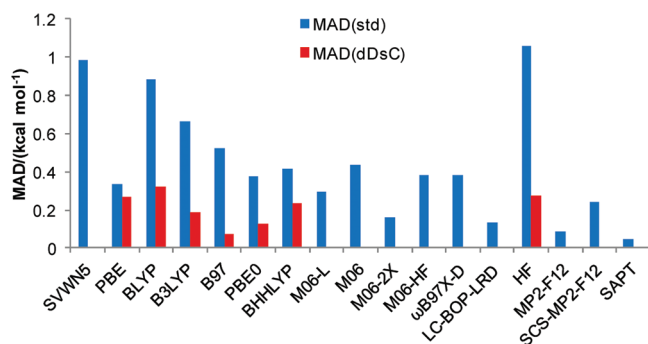
**Figure 2.** (a) Total interaction energy for the 20 complexes studied for wave function methods. (b) SAPT energy decomposition analysis for the complexes.

further insights into the error cancellation by interpreting the individual terms derived from the energy decomposition schemes at both the DFT and *ab initio* levels. The excellent performance of M06-2X is finally scrutinized prior to validating the overall conclusions on a prototypical organic charge-transfer complex, TTF-TCNQ.

**General Trends.** At the CCSD(T) level of theory, arrangement A (Figure 1) is the lowest lying minimum for three out of the four amphiphile molecules (ClF, HF, and HNC) with ClF forming the strongest complex among the series (see Figure 2a). HCN binds NF<sub>3</sub> not only the weakest but also with a different preferred arrangement (i.e., D). Both the most strongly bound complex (i.e., ClF-A) and the weakly bound lowest-lying minima (i.e., HCN-D) will be extensively analyzed throughout this study. Whereas half of the complexes are unbound at the HF level, MP2 is in a close agreement with CCSD(T) (MAD = 0.08 kcal mol<sup>-1</sup>), indicating that higher-order correlations are of minor importance. MP2 has an appreciable error only for the strongest charge-transfer complex (ClF-A). For these complexes, spin-component scaled MP2<sup>88</sup> gives a higher MAD (0.24 kcal mol<sup>-1</sup>) than regular MP2. The SAPT level provides an *ab initio* energy decomposition, including some higher-order correlations. The sum of the interaction components agrees remarkably well with CCSD(T) (MAD = 0.05 kcal mol<sup>-1</sup>). SAPT identifies arrangement A as most favorable for charge-transfer ( $E_{\text{POLCT}}^{\text{SAPT}}$ ). According to Figure 2b, the contributions of electron correlation to electrostatics and exchange ( $\epsilon_{\text{FRZ}}$ ) are small and the correction to polarization ( $\epsilon_{\text{POLCT}}$ ) even smaller. Electrostatic interactions

( $E_{\text{FRZ}}^{\text{SAPT}}$ , mainly dipole–dipole interactions) are most important in arrangement D, which is in line with the picture of the two interacting dipoles (see Figure 1). The correlation correction  $\epsilon_{\text{FRZ}}$  is, however, positive, and overall the dipole–dipole interactions are unable to overcome the Pauli repulsion. The major difference between HF and CCSD(T) is thus related to dispersion, confirming that HF adequately describes charge transfer. The arrangements for which HF captures some binding (e.g., HF-C or HNC-B) do not correspond to the most strongly bound complexes at the CCSD(T) level, revealing the dramatic failure of HF in correctly predicting trends. The failure is due to the dominance of  $E_{\text{DISP}}^{\text{SAPT}}$  over  $E_{\text{FRZ}}^{\text{SAPT}} + E_{\text{POLCT}}^{\text{SAPT}}$ , even in the case of the strongest CT complex (i.e., ClF-A).

The mean absolute deviations (MAD) for the DFT approximations are given in Figure 3. The systematic overbinding of LDA is coincidentally on the same order of magnitude as the underbinding at the HF level (MAD of 0.98 kcal mol<sup>-1</sup> and 1.05 kcal mol<sup>-1</sup>, respectively). As can be seen, the rest of the density functionals perform better than these two extremes, but their performance does not necessarily correlate with the amount of “exact” exchange admixture (e.g., the MAD varies more between two GGAs, i.e., BLYP and PBE, than between a GGA and a hybrid-GGA, i.e., PBE and PBE0, see Table 1). In contrast, the density dependent dispersion correction<sup>30,33</sup> systematically improves all of the methods tested, lowering the MADs to the range between 0.32 kcal mol<sup>-1</sup> (BLYP-dDsC) and 0.07 kcal mol<sup>-1</sup> (B97-dDsC). Surprisingly, the long-range corrected functional  $\omega$ B97X-D<sup>42</sup> does not outperform PBE0 or BHHLYP for the NF<sub>3</sub>



**Figure 3.** Mean absolute deviation (MAD) over the 20 complexes studied. Benchmark values are obtained at the CCSD(T)-F12b/VTZ-F12 level. “dDsC” denotes the use of the dDsC dispersion correction to the corresponding functional.

**Table 1.** Description of Density Functionals, Their Mean Absolute Deviation (MAD) and Mean Signed Deviation (MSD) from CCSD(T)-F12b/VTZ-F12 for the 20 NF<sub>3</sub> Complexes

type	functional name	% “exact” exchange	MAD (MSD)/ (kcal mol <sup>-1</sup> )
LDA	SVWN5	0.0	0.98 (−0.98)
GGA	PBE	0.0	0.34 (0.22)
	BLYP		0.88 (0.88)
	M06-L	0.0	0.29 (0.21)
hybrid-GGA	B97	19.43	0.52 (0.52)
	B3LYP	20	0.66 (0.66)
	PBE0	25	0.38 (0.38)
	BHHLYP	50	0.41 (0.41)
	M06	27	0.43 (0.43)
hybrid-meta-GGA	M06-2X	54	0.16 (0.09)
	M06-HF	100	0.38 (0.31)
long-range corrected	LC-BOP-LRD	depends on	0.13 (−0.09)
	ωB97X-D	interelectronic distance	0.38 (0.38)

complexes. However, LC-BOP-LRD<sup>43,44</sup> and the highly parametrized hybrid-meta GGA functional M06-2X<sup>25</sup> give excellent results (MAD = 0.13 and 0.16 kcal mol<sup>-1</sup>, respectively).

Dispersion clearly has a major influence on the interaction energies of the studied complexes, rationalizing the poor performance of both HF and standard density functionals. According to SAPT, the charge-transfer plays an obvious role for the most strongly bound complex arrangements (e.g., A).

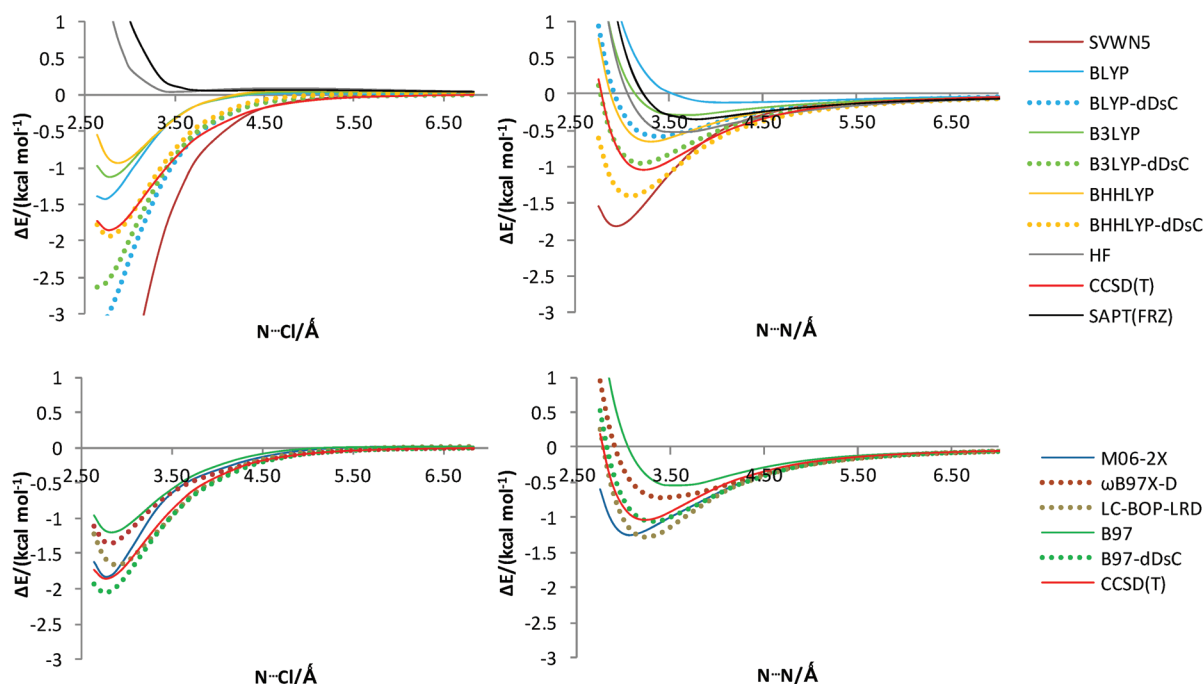
**Relationships between the Nature of Binding Energies and DFT Performance.** Interaction energy profiles for the two extreme examples, CIF-A (the most strongly bound NF<sub>3</sub> complex investigated herein) and HCN-D (the minimum energy arrangement for HCN), provide insights into both the origin of the binding energy and the relative functional performance.

The comparison of the rather flat HF profile of CIF-A with the  $E_{\text{FRZ}}^{\text{SAPT}}$  curve (corresponding to HF without polarization/CT) indicates that the charge-transfer reduces the molecular repulsion, without actually providing any binding. Hence, for CIF-A, adding a fraction “exact” exchange does not improve the interaction energy (see B3LYP and BHHLYP as compared to BLYP). In such a case, the typical overestimation of the binding energy by the semilocal functionals is only visible when the

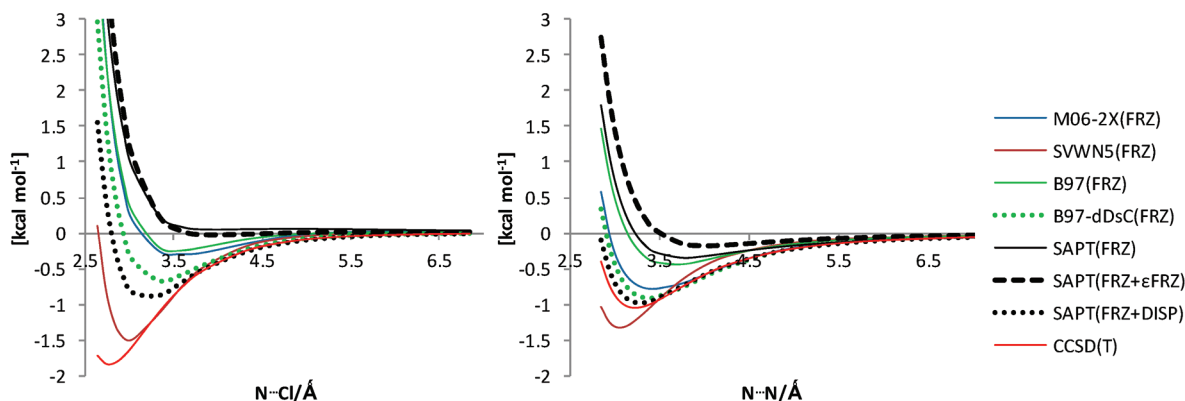
dispersion interactions are accounted for. Adding a high amount of “exact” exchange indeed offers a significant improvement for BHHLYP-dDsC as compared to B3LYP-dDsC and BLYP-dDsC, which overestimate the binding significantly. Thus, the achievement of an accurate description is highly challenging. Interestingly, the difference between the performances of three functionals is amplified after the inclusion a dispersion correction (dDsC and other schemes).<sup>89</sup> It is, however, beyond the scope of a *posteriori* dispersion corrections to overcome the underlying inadequacies of typical functionals to account for charge-transfer. As is well-known, BLYP is more repulsive than BHHLYP for vdW complexes and needs a stronger correction for dispersion in these systems. In contrast, the pure GGA functional is too attractive for charge-transfer complexes and thus should be corrected less in the medium-range. The bottom line is that standard GGA should clearly not be used, as only more sophisticated and well-balanced functionals, such as B97-dDsC, PBE0-dDsC, M06-2X, and LC-BOP-LRD, are sufficiently robust to provide a consistent treatment for these different types of interactions and deliver a good overall performance. Note that we call “well-balanced” functionals those that provide a nearly optimal, yet subtle, interplay between (i) self-interaction error, (ii) over-repulsiveness in the short-range, and (iii) dispersion. CIF-A is, nevertheless, an example for which any kind of error compensation is very difficult, even around the equilibrium distance.

In contrast to the strong charge-transfer complex (i.e., CIF...A), HCN...D is bound even at the Hartree–Fock level, which stresses the importance of dipole–dipole interactions in the arrangement of this complex (see Figure 1). On the other hand, BLYP (which is known to be repulsive for van der Waals complexes) underbinds HCN-D significantly when compared to CCSD(T), corroborating that weak interactions play a role as well (see Figure 2). While the few complexes in which CT is most important might be overly stabilized at the standard DFT-dDsC level (e.g., CIF-A with BLYP-dDsC, Figure 4), the dispersion correction is fundamentally important as it lowers the overall MAD of DFT-dDsC when compared with uncorrected-DFT for all other complexes. M06-2X gives an energy profile in close agreement with that of CCSD(T), indicating that the monomer density overlap is non-negligible in the probed region and provides a reasonable description if a suitable parametrization is chosen. The physical reason for the performance of M06-2X is, however, difficult to assess at this stage due to its complex functional form (see more details later). In contrast, the influence of dispersion interactions in B97-dDsC can be evaluated directly. In line with our recent benchmarking over a broad variety of reaction energies,<sup>30</sup> B97-dDsC shows excellent performance, even in these contrasting and challenging cases.

**The Energy Decomposition.** *i. The Frozen Term.* The electrostatic attraction (described as the most important interaction in related complexes<sup>90</sup>) is in most cases dominated by the exchange-repulsion ( $E_{\text{FRZ}}^{\text{SAPT}} = E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)}$ ) is thus mostly positive in Figures 2b and 5).  $E_{\text{FRZ}}^{\text{SAPT}}$  is therefore of minor importance for the overall stabilizing interaction energy around the equilibrium. Intramolecular correlation influences the electrostatics and exchange only to a minor extent ( $E_{\text{FRZ}}^{\text{SAPT}}$  is very similar to  $E_{\text{FRZ}}^{\text{SAPT}} + \epsilon_{\text{FRZ}}$ ). One might expect  $E_{\text{FRZ}}^{\text{SAPT}}$  to be similar to the DFT frozen-density interaction energy counterparts, but the latter generally give more attractive profiles. As suggested in ref 67, the dispersion interaction in (dispersion



**Figure 4.** Total interaction energy profiles and  $E_{\text{FRZ}}^{\text{SAPT}}$  for ClF-A (left) and HCN-D (right). Top: standard functionals (for PBE and PBE0, see Supporting Information). Bottom: modern functionals (see Supporting Information for other long-range corrected functionals).



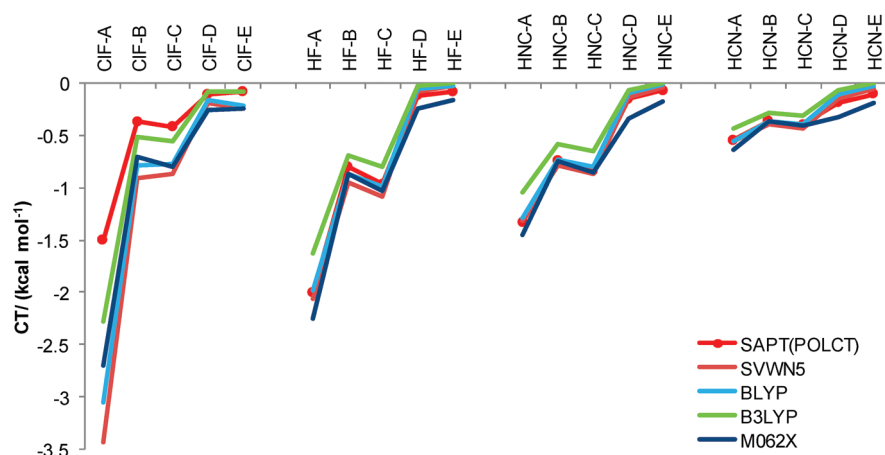
**Figure 5.** Interaction energy contributions for ClF-A (left) and HCN-D (right). For density functionals,  $\Delta E_{\text{FRZ}}^{\text{BLW}}$  is shown (see Supporting Information for more functionals). For SAPT, three partial sums are shown:  $E_{\text{FRZ}}^{\text{SAPT}}$ ,  $E_{\text{FRZ}}^{\text{SAPT}} + \epsilon_{\text{FRZ}}$ , and  $E_{\text{FRZ}}^{\text{SAPT}} + E_{\text{DISP}}^{\text{SAPT}}$ . CCSD(T)-F12b/VTZ-F12 is given as the reference total interaction energy profile.

corrected) DFT approaches is best assigned to the frozen density (Heitler–London or “steric”) term (see refs 91 and 92 for a similar discussion addressing hydrogen bonded systems). Surprisingly, LDA is overly attractive even when compared to the combination of  $E_{\text{FRZ}}^{\text{SAPT}}$  with the dispersion energy,  $E_{\text{DISP}}^{\text{SAPT}}$ ! Given the absence of charge transfer in the frozen term, the explanation for the strong binding at the LDA level is not trivial. After correcting the asymptotic region of the LDA exchange correlation potential with the LB94 model<sup>93</sup> (the energy is evaluated with the SPW92 functional), it becomes evident that the incorrect form of long-range potential already affects the frozen term or in other words the density of the superimposed monomers (e.g.,  $\Delta E_{\text{FRZ}}^{\text{BLW}} = -0.82$  and  $0.37$  kcal mol<sup>−1</sup> for LDA and LDA/LB94 respectively at the equilibrium structure for ClF-A). LDA leads to substantial attractive energy contributions when adding the two monomer densities together. The fluorine atoms, which carry many electrons in a small volume, are affected by a large self-interaction error and

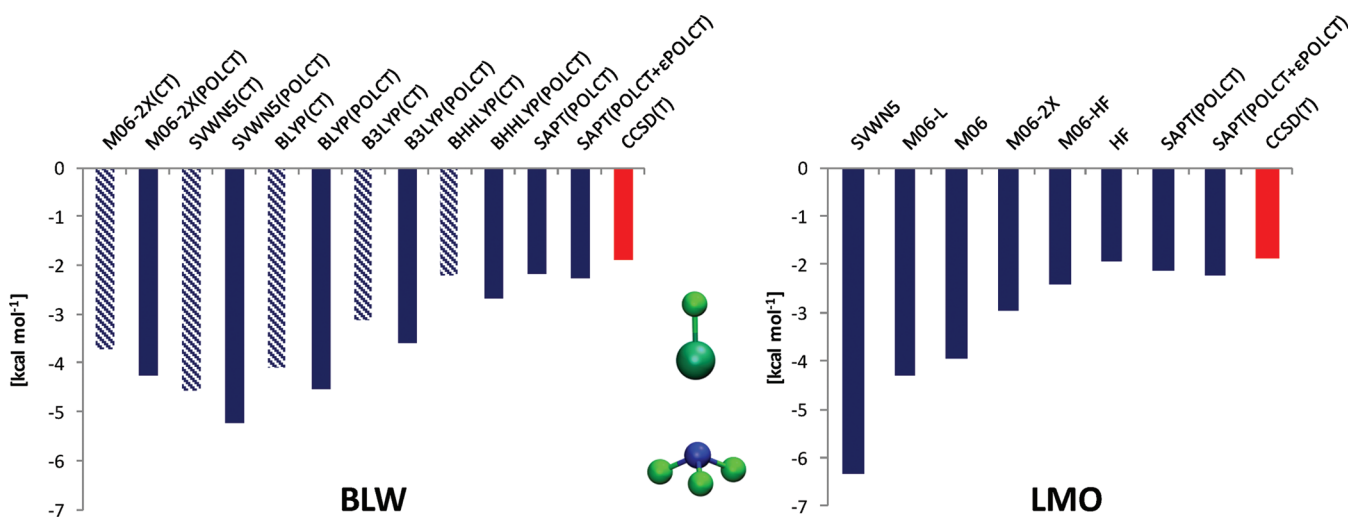
characterized by a diffuse density. The association of two excessively diffuse densities (i.e., LDA monomers) describing the monomers is therefore at the origin of the too attractive LDA energy. The error in the exchange-correlation potential does not only affect CT interactions but clearly causes qualitatively incorrect behaviors for monomers and their superposition: the frozen term of most density functionals represents only about 60% of that of SAPT ( $E_{\text{FRZ}}^{\text{SAPT}}$ ; see Supporting Information for the corresponding linear regression). In fact, this “lack of repulsiveness” has been overlooked in the literature as it is partially compensated by the missing dispersion energy in standard density functionals and might result in relatively reasonable total interaction energies.<sup>94</sup>

The difficulties of standard density functionals for describing the interaction between two frozen monomer densities are partly due to the imperfect description of the individual monomer densities (i.e., self-interaction error) along with the approximated energy expression, which might account for





**Figure 6.** Charge-transfer terms from BLW  $\Delta E_{CT}^{BLW}$  for selected functionals compared to SAPT ( $E_{POLCT}^{SAPT}$ ).



**Figure 7.** Polarization and charge-transfer terms for ClF-A from BLW (left) and  $\Delta E_{pol}^{LMO}$  (right), compared among different functionals and to SAPT ( $\Delta E_{POLCT}^{SAPT}$  and  $\Delta E_{POLCT}^{SAPT} + \epsilon_{POLCT}$ ). For BLW,  $\Delta E_{CT}^{BLW}$  and  $\Delta E_{POLCT}^{BLW}$  are shown; CCSD(T)-F12b/VTZ-F12 is given to indicate the (total) interaction strength at the chosen (equilibrium) distance.

(overlap) dispersion interactions. Thus, we expect weakly interacting systems characterized by significant self-interaction (halogenated molecules and dihalogens) to be more problematic than typical vdW complexes for dispersion corrected density functionals.

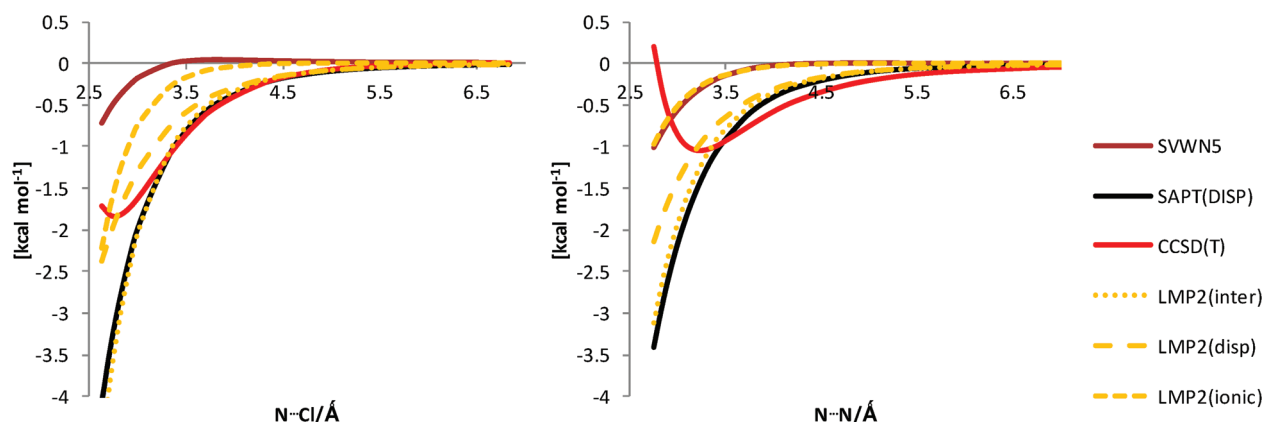
*ii. The CT Terms.* For ClF-A, only about 50% of the full binding energy is lost when CT is excluded (see Figure 5). The minimum of  $E_{FRZ}^{SAPT} + E_{DISP}^{SAPT}$  is rather flat and located at an increased intermolecular distance compared to CCSD(T). Such a profile indicates that the two monomers approach more closely due to the charge transfer (already seen in Figure 4 for the Hartree–Fock interaction energy) with the dispersion energy providing more stability. In contrast, the minimum for HCN-D is dominated by dispersion.

According to SAPT, there is less CT in ClF-A than in HF-A (1.5 and 2.0 kcal mol<sup>-1</sup>, respectively); however, all density functionals tested herein show the opposite trend (see Figure 6). In other words, the difficulties with treating CT complexes do not exclusively correlate with the extent of charge transfer, as a stronger CT is not systematically overestimated to a greater extent.  $\Delta E_{CT}^{BLW}$  is higher for ClF-A than for HF-A but respectively over- and underestimated when compared to the  $E_{POLCT}^{SAPT}$  value. The charge transfer in other ClF arrangements is

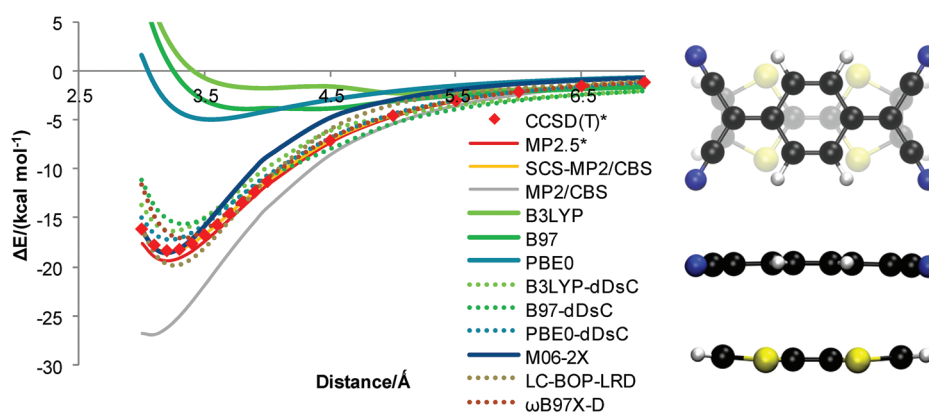
overestimated, while for the other complexes the  $\Delta E_{CT}^{BLW}$  compares well to  $E_{POLCT}^{SAPT}$  (see the Supporting Information for all least-squares parameters between the two, excluding the ClF complexes). Among the entire series, the description of the ClF complexes is clearly most tricky: the  $\Delta E_{CT}^{BLW}$  values are substantially larger than those of other complexes and that of  $\Delta E_{POLCT}^{SAPT}$  (see Figure 7). This ClF peculiarity highlights the importance of the self-interaction errors occurring between nonbonded halogen atoms that are considerably smaller in the other complexes.

**The Particular Case of M06-2X.** The charge-transfer term of M06-2X is surprisingly large and much closer to LDA than to BHLYP (e.g., Figures 6 and 7, for ClF-A), even though CT is expected to correlate with the amount of “exact” exchange (~50% for BHLYP and M06-2X but zero for LDA). The LMOEDA analysis of the M06 functional family delivers a term (i.e.,  $\Delta E_{pol}^{LMO}$ ) closely related to  $\Delta E_{POLCT}^{BLW}$  (the energy difference between the frozen monomers and the optimized dimer density) but that depends only on the exchange-functional. Unlike  $\Delta E_{POLCT}^{BLW}$ ,  $\Delta E_{pol}^{LMO}$  displays the expected behavior: LDA exhibits the larger  $\Delta E_{pol}^{LMO}$ , which is increasingly reduced at the M06-L, M06-2X, and M06-HF levels, respectively. Knowing that (i) the “dispersion-like” interactions proper to M06-2X do





**Figure 8.**  $\Delta E_{\text{disp}}^{\text{LMO}}$  from LDA compared to  $E_{\text{DISP}}^{\text{SAPT}}$  and the dispersion contribution in LMP2. CCSD(T)-F12b/VTZ-F12 is given to indicate the interaction strength.



**Figure 9.** Interaction energy of cofacial TTF-TCNQ computed at various levels of theory. Top and side views of the complex are given on the right-hand side.

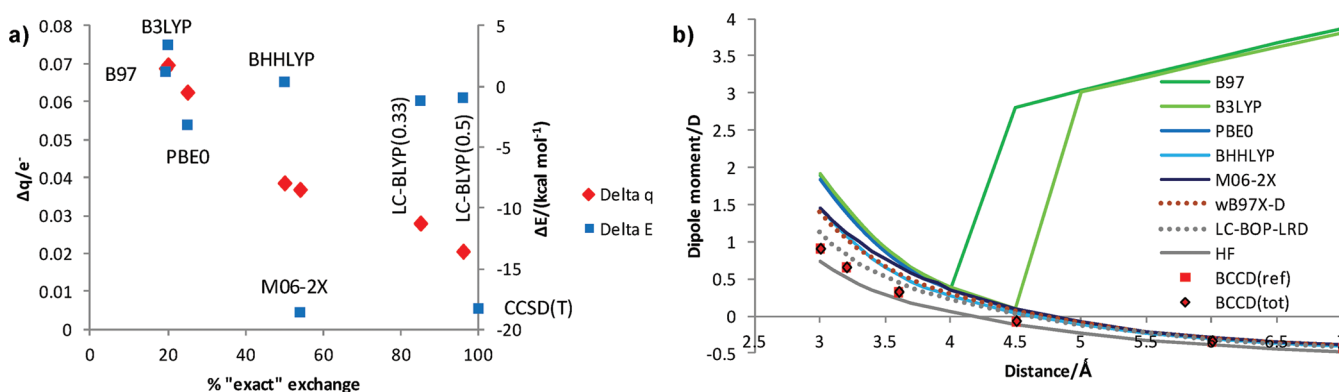
not transpire in the frozen energy (see Figure 5, the frozen energy for M06-2X is small compared to  $E_{\text{FRZ}}^{\text{SAPT}} + E_{\text{DISP}}^{\text{SAPT}}$ ) but that (ii) the total interaction energy is reasonably accurate, the missing interaction energy must be recovered in polarization/charge-transfer terms. From comparing the BLW and LMOEDA interaction energy components, it follows that M06-2X compensates the repulsion introduced by “exact” exchange by a correlation functional that gives rise to terms that resemble charge transfer (errors) in classical density functional approximations.

Around equilibrium, the depiction of M06-2X is relatively reasonable:  $\sim 40\%$  (and  $\sim 20\%$ ) of  $\Delta E_{\text{DISP}}^{\text{SAPT}}$  for ClF-A (and HCN-D) originates from the ionic terms<sup>95</sup> according to LMP2 (see Figure 8). While resembling charge transfer,<sup>96</sup> the ionic contributions should be interpreted as the “non-dispersive” component of the “mysterious” medium-range correlation.<sup>97</sup> The LMP2 decomposition shows that the dispersion energy of SAPT is equivalent to two components (see also ref 69): one, which is the classical  $\sim R^{-6}$  dependent long-range dispersion, and a shorter ranged component that should decay exponentially. The exponential decay could in principle be recovered by suitably parametrized functionals, which rationalizes the good performance of M06-2X.

In summary, the treatment of CT by standard density functionals is highly problematic when two diffuse densities interact (e.g., halogens...halogens, halogens...alkenes). The success of M06-2X relies on a significant fraction of medium range correlation that adjusts itself to the interaction type. On

the other hand, properly balanced combinations such as B97-dDsC, PBE0-dDsC, and LC-BOP-LRD represent a very reliable alternative to high parametrization

**A Prototype Organic Charge-Transfer Complex.** As mentioned earlier, the role played by vdW interactions in the stabilization of the prototype organic charge-transfer complex, TTF-TCNQ, has not yet been discussed (see ref 23). Akin to the  $\text{NF}_3$  complexes considered throughout this study and to the terthiophene-TCNQ assembly (see ref 98), the charge-transfer energy for TTF-TCNQ is surely overestimated by standard DFT methods, even though the minimum is too shallow. Our present analysis suggests that standard hybrid density functionals with a dispersion correction would provide the most reasonable results for interaction energies. Figure 10 confirms that the three standard hybrid density functionals tested (B3LYP, PBE0, and B97) together with dDsC lead to interaction energies that agree closely with reference values. Long-range and dispersion corrected functionals ( $\omega$ B97X-D and LC-BOP-LRD) also perform well for this organic charge-transfer complex. M06-2X correctly describes the region around the equilibrium, but at longer distances the interaction energy falls off too quickly, illustrating that the correct long-range physics are missing. In such cases, the inclusion of a dispersion correction can improve M06-2X as well.<sup>99</sup> In contrast to the  $\text{NF}_3$  complexes, SCS-MP2 gives closer agreement with higher-level correlation methods than classical MP2 for TTF-TCNQ. Note that the apparent overbinding obtained for M06-2X and  $\omega$ B97X-D in ref 23 is slightly biased, due to the too small basis



**Figure 10.** (a) Charge-transfer (according to BLW/ALMO; red diamonds, referring to the left axis) and interaction energy (blue squares, referring to the right axis) at the equilibrium distance ( $\sim 3.2 \text{ \AA}$ ) of TTF-TCNQ. (b) Molecular dipole moment in z direction of TTF-TCNQ as a function of the distance. The z axis points from TCNQ to TTF. Due to the computational expense, only a few points at the BCCD/6-31G\*(0.25) reference level are included. Note that these are closed-shell singlet computations. The spurious charge-transfer of B3LYP and B97 at longer distances can lead to a lower lying open-shell singlet solution, which enhances the charge transfer even further.

set employed in the reference SCS-MP2 interaction profile. While interaction energies do not clearly correlate with the fraction of "exact" exchange, the overestimation of charge-transfer and related properties (such as dipole moments) increase monotonically with decreasing the percentage of "exact" exchange (see Figure 10a). From the point of view of interaction energy (Figure 9) B3LYP-dDsC and B97-dDsC seem reasonable choices. In contrast, the analysis of dipole moments (which are not affected by the dispersion correction in the current implementation) reveals a serious break down of these functionals at longer ( $>4.0 \text{ \AA}$ ) distances (Figure 10b), a feature which is nearly invisible in the interaction energy profile. At these larger intermolecular distances, the B3LYP and B97 HOMO–LUMO gap collapses, resulting in a spurious charge transfer (see Figure S7 for density differences). This unphysical behavior is strongly dependent on the intermolecular distance and on the planarity of the monomers' geometry (see Figure S9). The more pronounced orbital overlap at shorter distances or, alternatively, the inclusion of a larger amount of nonlocal exchange (e.g., PBE0) prevents this unphysical behavior. Interestingly, the limiting amount of "exact" exchange is roughly the same ( $\sim 20\%$ ) as that necessary for a successful geometry optimization of alkynyl radicals.<sup>100</sup> The change of sign in the profile of the molecular dipole moment (Figure 10b) can be rationalized by the gradual decrease of the charge transfer with increasing intermolecular distance, which goes in the opposite direction as the sum of the molecular dipole moments that are aligned and amount to  $\sim -0.6 \text{ D}$  in the z direction (from TCNQ to TTF) at the BCCD/6-31G\*(0.25) level.

The challenge for common DFT approximations to describe charge-transfer complexes is connected to both the lack of dispersion interactions resulting in inaccurate binding energies and the overestimated charge transfer, which, depending on the percentage of "exact" exchange and the intermolecular distances, can lead to erroneous values for density-based properties (e.g., dipole moments). Stressing the role of dispersion interactions in CT complexes, of course, does not imply that electrostatics and/or charge-transfer interactions are unimportant for the description of binding energy. As mentioned above, dispersion bound complexes show a strong dependence on the relative orientation.<sup>10</sup> This dependence might reflect not only the loss of contact area but also the

enhancement of dispersion through electrostatic and charge-transfer interactions, which may allow the monomers to approach one another more closely in one binding mode as opposed to another. In many cases, dispersion interactions are, however, responsible for most of the stabilization energy, and the use of noncorrected standard density functionals is therefore precluded, as they might lead to erroneous conclusions about the nature of the binding. The inclusion of *a posteriori* dispersion correction such as dDsC represents an inexpensive and broadly applicable method (as compared to LMP2 and SAPT) to appropriately describe charge-transfer complexes and to provide qualitative insight into the ubiquitous importance of dispersion interactions.

## CONCLUSIONS

The description of charge-transfer complexes is highly challenging for standard density functionals. On the basis of an illustrative series of  $\text{NF}_3$ -based complexes, we have demonstrated that the stabilization of most CT complexes arises essentially from dispersion interactions, with relative orientations and intermolecular distances being dictated by electrostatics and charge-transfer interactions. Despite the illustrative overestimation of the charge-transfer interactions by common density functionals, the use of a dispersion correction is crucial in providing an accurate description of interaction energies. Highly parametrized functionals such as M06-2X also describe such systems well, due to the substantial density overlap in the intermolecular distances of interest. However, because of the lack of an explicit dispersion term, individual interaction energy components (e.g., charge-transfer) cannot be easily interpreted. Due to the subtle interplay of monomer description, overestimation of charge transfer, and neglect of dispersion interactions, only certain well balanced dispersion corrected density functionals provide excellent results; in particular, LC-BOP-LRD and PBE0-dDsC are confirmed to be broadly applicable. The validity of these observations for rationalizing the DFT binding energy of real-world charge-transfer complexes has been verified on a typical cofacial TTF-TCNQ organic complex. Importantly, the description of the density at distances longer than equilibrium necessitates, even in the ground state, more than 20% of "exact" exchange to prevent spurious charge transfer, a failure that is not directly noticeable in the interaction energy profile itself.

## ■ ASSOCIATED CONTENT

## ■ Supporting Information

Brief discussions on long-range corrected functionals and the charge-transfer from natural bond analysis (NBO) are provided. All geometries and interaction energy contributions for all functionals tested herein are listed. This material is provided free of charge via the Internet at <http://pubs.acs.org>

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## Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811–824.
- (2) Dubois, J. E.; Garnier, F. *Tetrahedron Lett.* **1965**, *6*, 3961–3968.
- (3) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338.
- (4) Walzer, K.; Maennig, B.; Pfeiffer, M.; Leo, K. *Chem. Rev.* **2007**, *107*, 1233–1271.
- (5) Stone, A. J.; Price, S. L. *J. Phys. Chem.* **1988**, *92*, 3325–3335.
- (6) Stone, A. J.; Misquitta, A. J. *Chem. Phys. Lett.* **2009**, *473*, 201–205.
- (7) Banthorpe, D. V. *Chem. Rev.* **1970**, *70*, 295–322.
- (8) Prissette, J.; Seger, G.; Kochanski, E. *J. Am. Chem. Soc.* **1978**, *100*, 6941–6947.
- (9) Karthikeyan, S.; Sedlak, R.; Hobza, P. *J. Phys. Chem. A* **2011**, *115*, 9422–9428.
- (10) Rezac, J.; Riley, K. E.; Hobza, P. *J. Chem. Theory Comput.* **2011**, *7*, 3466–3470.
- (11) Dreuw, A.; Weisman, J. L.; Head-Gordon, M. *J. Chem. Phys.* **2003**, *119*, 2943–2946.
- (12) Köhn, A.; Hättig, C. *J. Am. Chem. Soc.* **2004**, *126*, 7399–7410.
- (13) Rappoport, D.; Furche, F. *J. Am. Chem. Soc.* **2004**, *126*, 1277–1284.
- (14) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- (15) Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2004**, *120*, 8425–8433.
- (16) Geskin, V.; Stadler, R.; Cornil, J. *Phys. Rev. B* **2009**, *80*, 085411.
- (17) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Am. Chem. Soc.* **1995**, *117*, 1141–1142.
- (18) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Phys. Chem.* **1996**, *100*, 12265–12276.
- (19) Kristyan, S.; Pulay, P. *Chem. Phys. Lett.* **1994**, *229*, 175–180.
- (20) Perez-Jorda, J. M.; Becke, A. D. *Chem. Phys. Lett.* **1995**, *233*, 134–137.
- (21) Hobza, P.; Sponer, J.; Reschel, T. *J. Comput. Chem.* **1995**, *16*, 1315–1325.
- (22) Zhang, Y.; Pan, W.; Yang, W. *J. Chem. Phys.* **1997**, *107*, 7921–7925.
- (23) Sini, G.; Sears, J. S.; Bredas, J.-L. *J. Chem. Theory Comput.* **2011**, *7*, 602–609.
- (24) Tsukamoto, S.; Sakaki, S. *J. Phys. Chem. A* **2011**, *115*, 8520–8527.
- (25) Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (26) Steinmann, S. N.; Wodrich, M.; Corminboeuf, C. *Theor. Chem. Acc.* **2010**, *127*, 429–442.
- (27) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (28) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
- (29) Steinmann, S. N.; Corminboeuf, C. *J. Chem. Theory Comput.* **2010**, *6*, 1990–2001.
- (30) Steinmann, S. N.; Corminboeuf, C. *J. Chem. Theory Comput.* **2011**, *7*, 3567–3577.
- (31) Wodrich, M. D.; Jana, D. F.; Schleyer, P. v. R.; Corminboeuf, C. *J. Phys. Chem. A* **2008**, *112*, 11495–11500.
- (32) Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670–6688.
- (33) Steinmann, S. N.; Corminboeuf, C. *J. Chem. Phys.* **2011**, *134*, 044117.
- (34) Blanco, F.; Alkorta, I.; Rozas, I.; Solimannejad, M.; Elguero, J. *Phys. Chem. Chem. Phys.* **2011**, *13*, 674–683.
- (35) Garcia, A.; Elorza, J. M.; Ugalde, J. M. *THEOCHEM* **2000**, *501–502*, 207–214.
- (36) Karpfen, A. *Theor. Chem. Acc.* **2003**, *110*, 1–9.
- (37) Liao, M.-S.; Lu, Y.; Scheiner, S. *J. Comput. Chem.* **2003**, *24*, 623–631.
- (38) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415–432.
- (39) Dutoi, A. D.; Head-Gordon, M. *Chem. Phys. Lett.* **2006**, *422*, 230–233.
- (40) Savin, A.; Flad, H.-J. *Int. J. Quantum Chem.* **1995**, *56*, 327–332.
- (41) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 3540–3544.
- (42) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
- (43) Sato, T.; Nakai, H. *J. Chem. Phys.* **2009**, *131*, 224104.
- (44) Sato, T.; Nakai, H. *J. Chem. Phys.* **2010**, *133*, 194101.
- (45) Kamiya, M.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2002**, *117*, 6010–6015.
- (46) Henderson, T. M.; Janesko, B. G.; Scuseria, G. E. *J. Chem. Phys.* **2008**, *128*, 194105.
- (47) Rohrdanz, M. A.; Martins, K. M.; Herbert, J. M. *J. Chem. Phys.* **2009**, *130*, 054112.
- (48) Weintraub, E.; Henderson, T. M.; Scuseria, G. E. *J. Chem. Theory Comput.* **2009**, *5*, 754–762.
- (49) The molecular Hamiltonian only contains the kinetic energy and the electrostatic attraction (electron-nuclei) and repulsion (electron–electron, nuclei-nuclei), which are, moreover, connected by the virial theorem.
- (50) Murrell, J. N.; Randic, M.; Williams, D. R. *Proc. R. Soc. London, Ser. A* **1965**, *284*, 566–581.
- (51) Daudey, J. P.; Claverie, P.; Malrieu, J. P. *Int. J. Quantum Chem.* **1974**, *8*, 1–15.
- (52) Hayes, I. C.; Stone, A. J. *Mol. Phys.* **1984**, *53*, 83–105.
- (53) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887–1930.
- (54) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.
- (55) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236–1244.
- (56) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325–340.
- (57) Ziegler, T.; Rauk, A. *Theor. Chem. Acc.* **1977**, *46*, 1–10.
- (58) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W. *J. Chem. Phys.* **1984**, *80*, 4378–4386.
- (59) Stevens, W. J.; Fink, W. H. *Chem. Phys. Lett.* **1987**, *139*, 15–22.
- (60) Stoll, H.; Wagenblast, G.; Preuß, H. *Theor. Chem. Acc.* **1980**, *57*, 169–178.
- (61) Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687–1697.
- (62) Mo, Y.; Gao, J.; Peyerimhoff, S. D. *J. Chem. Phys.* **2000**, *112*, 5530–5538.
- (63) Khaliullin, R. Z.; Cobar, E. A.; Lochan, R. C.; Bell, A. T.; Head-Gordon, M. *J. Phys. Chem. A* **2007**, *111*, 8753–8765.
- (64) Wu, Q.; Ayers, P. W.; Zhang, Y. *J. Chem. Phys.* **2009**, *131*, 164112.



- (65) Su, P.; Li, H. *J. Chem. Phys.* **2009**, *131*, 014102.
- (66) Schuetz, M.; Rauhut, G.; Werner, H.-J. *J. Phys. Chem. A* **1998**, *102*, 5997–6003.
- (67) Steinmann, S. N.; Corminboeuf, C.; Wu, W.; Mo, Y. *J. Phys. Chem. A* **2011**, *115*, 5467–5477.
- (68) Mo, Y.; Song, L.; Lin, Y. *J. Phys. Chem. A* **2007**, *111*, 8291–8301.
- (69) Langlet, J.; Caillet, J.; Bergès, J.; Reinhardt, P. *J. Chem. Phys.* **2003**, *118*, 6157–6166.
- (70) Mo, Y.; Bao, P.; Gao, J. *J. Phys. Chem. Chem. Phys.* **2011**, *13*, 6760–6775.
- (71) Gianinetti, E.; Raimondi, M.; Tornaghi, E. *Int. J. Quantum Chem.* **1996**, *60*, 157–166.
- (72) Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; DiStasio, R. A., Jr.; Lochan, R. C.; Wang, T.; Beran, G. J. O.; Besley, N. A.; Herbert, J. M.; Lin, C. Y.; Voorhis, T. V.; Chien, S. H.; Sodt, A.; Steele, R. P.; Rassolov, V. A.; Maslen, P. E.; Korambath, P. P.; Adamson, R. D.; Austin, B.; Baker, J.; Byrd, E. F. C.; Dachsel, H.; Doerksen, R. J.; Dreuw, A.; Dunietz, B. D.; Dutoi, A. D.; Furlani, T. R.; Gwaltney, S. R.; Heyden, A.; Hirata, S.; Hsu, C.-P.; Kedziora, G.; Khalliulin, R. Z.; Klunzinger, P.; Lee, A. M.; Lee, M. S.; Liang, W.; Lotan, I.; Nair, N.; Peters, B.; Proynov, E. I.; Pieniazek, P. A.; Rhee, Y. M.; Ritchie, J.; Rosta, E.; Sherrill, C. D.; Simmonett, A. C.; Subotnik, J. E.; Woodcock, H. L., III; Zhang, W.; Bell, A. T.; Chakraborty, A. K.; Chipman, D. M.; Keil, F. J.; Warshel, A.; Hehre, W. J.; Schaefer, H. F., III; Kong, J.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3172–3191.
- (73) Murray, C. W.; Handy, N. C.; Laming, G. J. *Mol. Phys.* **1993**, *78*, 997–1014.
- (74) Lebedev, V. I.; Laikov, D. N. *Dokl. Math.* **1999**, *59*, 477–481.
- (75) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (76) Jeziorska, M.; Bogumil, J.; Jiri, C. *Int. J. Quantum Chem.* **1987**, *32*, 149–164.
- (77) Moszynski, R.; Heijmen, T. G. A.; Jeziorski, B. *Mol. Phys.* **1996**, *88*, 741–758.
- (78) Bukowski, R.; Cencek, W.; Jankowski, P.; Jeziorska, M.; Jeziorski, B.; Lotrich, V. F.; Kucharski, S.; Misquitta, A. J.; Moszyński, R.; Patkowski, K.; Podeszwa, R.; Rybak, S.; Szalewicz, K.; Williams, H. L.; Wheatley, R. J.; Wormer, P. E. S.; Zuchowski, P. S. *SAPT 2008.2*.
- (79) Thom, H.; Dunning, J. J. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (80) Adler, T. B.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2007**, *127*, 221106.
- (81) Peterson, K. A.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 084102.
- (82) Yousaf, K. E.; Peterson, K. A. *J. Chem. Phys.* **2008**, *129*, 184108.
- (83) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. *Molpro2010.1*; University College Cardiff Consultants Limited: Cardiff, UK, 2010.
- (84) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639–9646.
- (85) Kroon-Batenburg, L. M. J.; van Duijneveldt, F. B. *THEOCHEM* **1985**, *121*, 185–199.
- (86) Hobza, P.; Sponer, J. *Chem. Rev.* **1999**, *99*, 3247–3276.
- (87) Pitoňák, M.; Neogrády, P.; Černý, J.; Grimme, S.; Hobza, P. *ChemPhysChem* **2009**, *10*, 282–289.
- (88) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095–9102.
- (89) The same amplification is found with -D3 and especially with the -D3(BJ) dispersion correction, see Supporting Information.
- (90) Munusamy, E.; Sedlak, R.; Hobza, P. *ChemPhysChem* **2011**, *12*, 3253–3261.
- (91) Langlet, J.; Berges, J.; Reinhardt, P. *THEOCHEM* **2004**, *685*, 43–56.
- (92) Langlet, J.; Berges, J.; Reinhardt, P. *Chem. Phys. Lett.* **2004**, *396*, 10–15.
- (93) van Leeuwen, R.; Baerends, E. J. *J. Phys. Rev. A* **1994**, *49*, 2421–2431.
- (94) See Supporting Information for a related discussion on long-range corrected functionals.
- (95) These percentages are about  $\pm 10\%$  accurate, as they depend on the basis set and localization procedure.
- (96) The “true” charge-transfer is associated with single-electron excitations, while the ionic terms correspond to two-electron excitations and not to the “correlation corrections” for the single excitations. Evidence is provided by the BCCD reference (which includes all charge-transfer contributions) that gives even less interaction energy compared to HF, see Supporting Information.
- (97) Zhao, Y.; Truhlar, D. G. *Org. Lett.* **2006**, *8*, 5753–5755.
- (98) Arago, J.; Sancho-Garcia, J. C.; Orti, E.; Beljonne, D. *J. Chem. Theory Comput.* **2011**, *7*, 2068–2077.
- (99) Marom, N.; Tkatchenko, A.; Rossi, M.; Gobre, V. V.; Hod, O.; Scheffler, M.; Kronik, L. *J. Chem. Theory Comput.* **2011**, *7*, 3944–3951.
- (100) Oyeyemi, V. B.; Keith, J. A.; Pavone, M.; Carter, E. A. *J. Phys. Chem. Lett.* **2012**, *3*, 289–293.