Potential energy surfaces of Charge Transfer states

Balázs Kozma[a], Romain Berraud-Pache[b], Attila Tajti[a] and Péter G. Szalay[a]

[a]ELTE Eötvös Loránd University, Institute of Chemistry, Laboratory of Theoretical Chemistry, P. O. Box 32, H-1518, Budapest 112, Hungary; [b]Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany

ABSTRACT
In this paper the potential energy curves of CT states and their interaction with local ones have been investigated. Besides the global view of these curves, special attention has been paid to the region of the crossing and the infinite separation limit. It was found that triple excitations are needed to accurately describe potential energy surfaces of CT states. Among the cheaper variants, both STEOM-CCSD and CCSD(T)(a)* methods are promising in this respect. The somewhat larger error of CCSD for CT states can be explained by its size extensivity error and the overestimation of the asymptotic excitation energy. Second order approximations are not advantageous for the error cancellation, in fact CC2 is much worse for CT states than any other method investigated here. The results also show that the location of the (avoided) crossings of local and CT states depend very much on the accurate description of the CT states. Failure to describe this topology might affect dynamics, and a warning, in particular in case of CC2, should be issued if CT states play a role in the physics of the problem.

1. Introduction

In a recent study we have established a benchmark set for testing the performance of various excited state methods on the vertical excitation energies of Charge Transfer (CT) type electronic states[1]. This test set contains bimolecular complexes with low lying CT states and the benchmark excitation energies have been obtained by high level Coupled Cluster (CC) methods EOM-CCSDT and EOM-CCSDT-3. The paper also discusses the performance of other CC methods, including CC2-LR, EOM-CCSD(2), EOM-CCSD, STEOM-CCSD, as well as EOM-CCSD(T)(a)* and CC3-LR.

During the course of this work[1], the classification of states as of either CT or local nature, turned out to be problematic in many cases. In these situations a strong interaction and a nearby crossing of CT and local states were identified as the cause of this difficulty. This issue hampered the comparison of different methods if the geometry

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Email: tat@chem.elte.hu
Email: szalay@chem.elte.hu
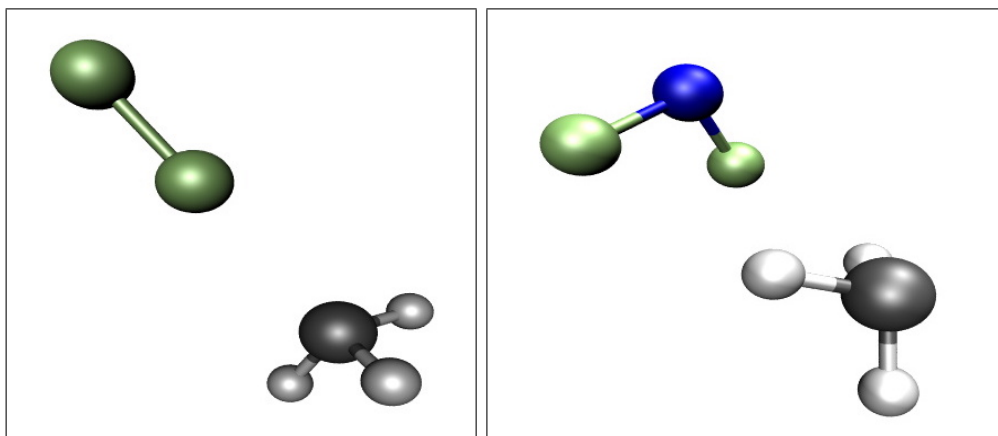
Figure 1. Equilibrium structures of the ammonia–fluorine and the ammonia–oxygen-difluoride complexes taken from Ref. [1]

used was in between the "crossing-ponts" for the respective methods. Therefore, in Ref. [1] an additional study was warranted to obtain information on how the different methods describe the surfaces near these crossings, and how different are the surfaces of CT states overall.

Most previous works investigating the performance of quantum chemical methods on CT states focused primarily on the long-range behavior of the potential energy curves. The most often used systems were the tetrafluoroethylene–ethylene (C_2F_4–C_2H_4) and ammonia–fluorine (NH_3–F_2) complexes [2–6], but the Be–C_2 complex was also investigated [5, 7]. Concerning TDDFT results, it was found [2, 3] that the various functionals can provide very different potential curves. For CC methods, the importance of triple excitations have been outlined by Nooijen and Bartlett [7] and later by Dutta et al. [5].

In this paper we present benchmark results on the potential energy curves of CT and local states of bimolecular complexes, with the focus on the crossing region, i.e. where the CT and local states become nearly degenerate, but we also investigate the long range region since the asymptotic behavior is also an important indicator on the quality of CT potential curves. As the highest level method, and therefore as benchmark, the EOM-CCSDT method will be used, and the performance of various CC ansätze investigated in our previous paper [1] is discussed in detail.

2. Computational details

We have chosen two systems from Ref. [1] for the present study. One is the ammonia–fluorine complex which has been often used in CT benchmarks [4, 5]. The second system is the ammonia–oxygen-difluoride complex where we first encountered the assignment problem associated with the "crossing" of local and CT states. Both examples are small enough to perform even CCSDT level calculations. The structures for the points of the curves were defined by the separation of the centers of mass of the individual subsystems, aligned according to the reference geometries presented in Ref. [1] and its supporting information. The equilibrium structures are also shown on Figure 1.

For the calculation of excited state potential energy curves of these bimolecular complexes, including those of the CT states, several variants of Coupled-Cluster methods were used. As the standard approximation, the inclusion of the CCSD (Coupled-

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Cluster Singles and Doubles)[8] model is vital, the corresponding methods for excited states being EOM-CCSD [9–11] (Equation of Motion Coupled-Cluster with Singles and Doubles) and CCSD-LR [12, 13] (CCSD Linear Response) (no distinction between EOM and LR will be made here since these two give the same excitation energy, so for our purpose they are equivalent). From the many methods that are approximations of CCSD, we will test the popular CC2 [14] approach, as well as EOM-CCSD(2)[15] (second order approximation to Equation-of-Motion Coupled Cluster Singles and Doubles, also known as EOM-MBPT(2)[16]). The STEOM-CCSD (Similarity Transformed Equation-of-Motion Singles and Doubles) [7, 17, 18] of Nooijen and coworkers includes also only single and double excitations explicitly but represents an improvement over CCSD due to the implicit inclusion of connected triple excitations. For more details see e.g. Refs. [7, 19]. In our previous study [1] we have found that it indeed behaves similarly to triples methods in many respects.

From the high accuracy methods that explicitly account for connected triple excitations (the so-called triples methods), the EOM-CCSDT [20] (EOM Coupled-Cluster with Singles, Doubles and Triples) calculations can be considered as benchmark here. Three approximate triples methods have also been included in the present study: the iterative EOM-CCSDT-3 [21], and CC3 [22] methods, as well as the recent, non-iterative EOM-CCSD(T)(a)* technique of Matthews and Stanton[23].

Calculations of IP and EA have been perfomed using the continuum orbital technique described in Ref. [24].

Except for STEOM-CCSD, all calculations have been performed using the CFOUR [25, 26] program package. STEOM-CCSD calculations were done with the Orca 4.2 [27] program. The process of selecting the active space for both the occupied and virtual spaces in the STEOM-CCSD calculation has already been made automatic using a process based on configuration interaction singles (CIS) state-averaged densities.[28] In the present study, the default value (0.01) is used for both the occupied (OTHRESH) and virtual (VTHRESH) active space selection thresholds. The active space was kept the same along the potential energy curve, using the largest space the above procedure suggested.

The cc-pVDZ basis set of Dunning and co-workers[29] was used in all calculations. In Ref. [1] it was shown that from the benchmarking point of view, cc-pVDZ gives results very similar to cc-pVTZ. On the other hand, the absence of diffuse basis functions that are normally required to accurately describe non-covalent complexes is motivated by the experience that the appearance of Rydberg states in the presence of small-exponent functions highly complicates the interpretation of the results. These states tend to interact with the valence and CT type ones, often resulting in states of intricately mixed character in which the description of the Rydberg component varies greatly among the methods. The main objective of this study being the comparison of how different methods provide the CT surfaces, instead of achieving the best absolute accuracy, a basis set lacking diffuse functions is a more favorable choice.

The characterization of the different electronic states along the potential energy curve is possible using the numerical descriptors of Plasser and co-workers[30, 31]. These quantities, obtained from the population analysis of the one-particle density matrix, are available in CFOUR for CCSD and CC2 methods. While the *Charge Transfer (CT) character* (ω_{CT}) measures the CT nature of the state ranging from zero to one, the *average position* (ω_{POS}), defined as the mean of the *hole* (ω_{POSi}) and the *particle* (ω_{POSf}) positions, provides the *average exciton position*. For a system consisting of two fragments this ranges from 1 to 2, with $\omega_{POS} \approx 1.5$ results being typical for CT, as well as completely delocalized (one-to-one mixed) Frenkel and charge resonance states.

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Similarly, ω_{PR} is the arithmetic mean of ω_{PRi} and ω_{PRf}, the *participation ratios* of the fragments in the hole and particle orbitals, respectively. Thus, $\omega_{PR} \approx 1$ holds for both clear CT and local excitations, while in a two-component system, $\omega_{PR} \approx 2$ is seen for completely delocalized Frenkel-type excitations and charge resonance states[30].

The descriptors were calculated with the TheoDORE program and libwfa library of Plasser et al. [32–35] at the CC2 and CCSD levels, with the help of our in-house CFOUR[25] / libwfa interface.

3. Results and discussion

3.1. *Ammonia–fluorine system*

On Figure 2 the potential energy curves of the ammonia–fluorine complex calculated at different levels of theory are shown. Five electronic states are considered here: the 1^1E (black curve) and 2^1E (red curve) are essentially local excitations on fluorine, the 2^1A_1 and 3^1A_1 (blue and magenta curves) correspond to a local excitation on ammonia, and the CT state, while the 3^1E (green curve) states is another local excitation on ammonia.

The figure also shows the $-\frac{e^2}{R}$ (with e being the unit charge) function, the theoretical potential curve of two interacting charges with the same asymptotic value as that of the CT curve obtained with the respective method (see below).

The first observation is that the curve of the CT state shows a very pronounced distance dependence, driven by the $1/R$ decay of the interaction of two ions. For this reason, the curve of the CT state crosses with several other curves, but for symmetry reasons, interaction with only the blue curve is observable. This interaction and the resulting avoided crossing will be discussed in detail below, representing the core of this communication. The slight energy decrease for the green curve at short distances, most probably due to another avoided crossing possibly with another CT state, will not be investigated in this study.

The curves for the triples methods are fairly similar, they hardly can be distinguished one from the other. The CCSD and CCSD(2) figures are also quite similar and their differences to the triples curves consist only in the smaller gap between the 2^1E and 2^1A_1 curves and a slightly higher asymptotic limit of the CT energy curve. The former difference can be explained by the relatively large double excitation contribution in the 2^1E state, which is not well described by the singles-doubles methods. (Note that for this reason this state was not included in our test set in Ref. [1].) The discrepancy of the asymptotic limit will be discussed in detail below.

Among the investigated methods, only the CC2 curves show a striking qualitative difference to the other figures. The overestimation of the red 2^1E curve is not a surprise considering the high double excitation contribution. On the other hand, the CT curve is considerably too low, its limiting value is below that of the 3^1E state. This underestimation has a considerable influence on the crossing of the 2^1A_1 and 3^1A_1 states which happens at a much longer intermolecular distance. It is also CC2 where the most significant deviation of the CT curve and the simplified charge attraction curve can be observed: a damped interaction between the two fragments is seen already at large distances. This observation will be discussed together with other discrepancies later.

On Figure 3 the crossing region of the potential energy curves of the 2^1A_1 and 3^1A_1 states are shown. At first look, the CCSDT, CCSDT-3 and CC3 curves are very similar,
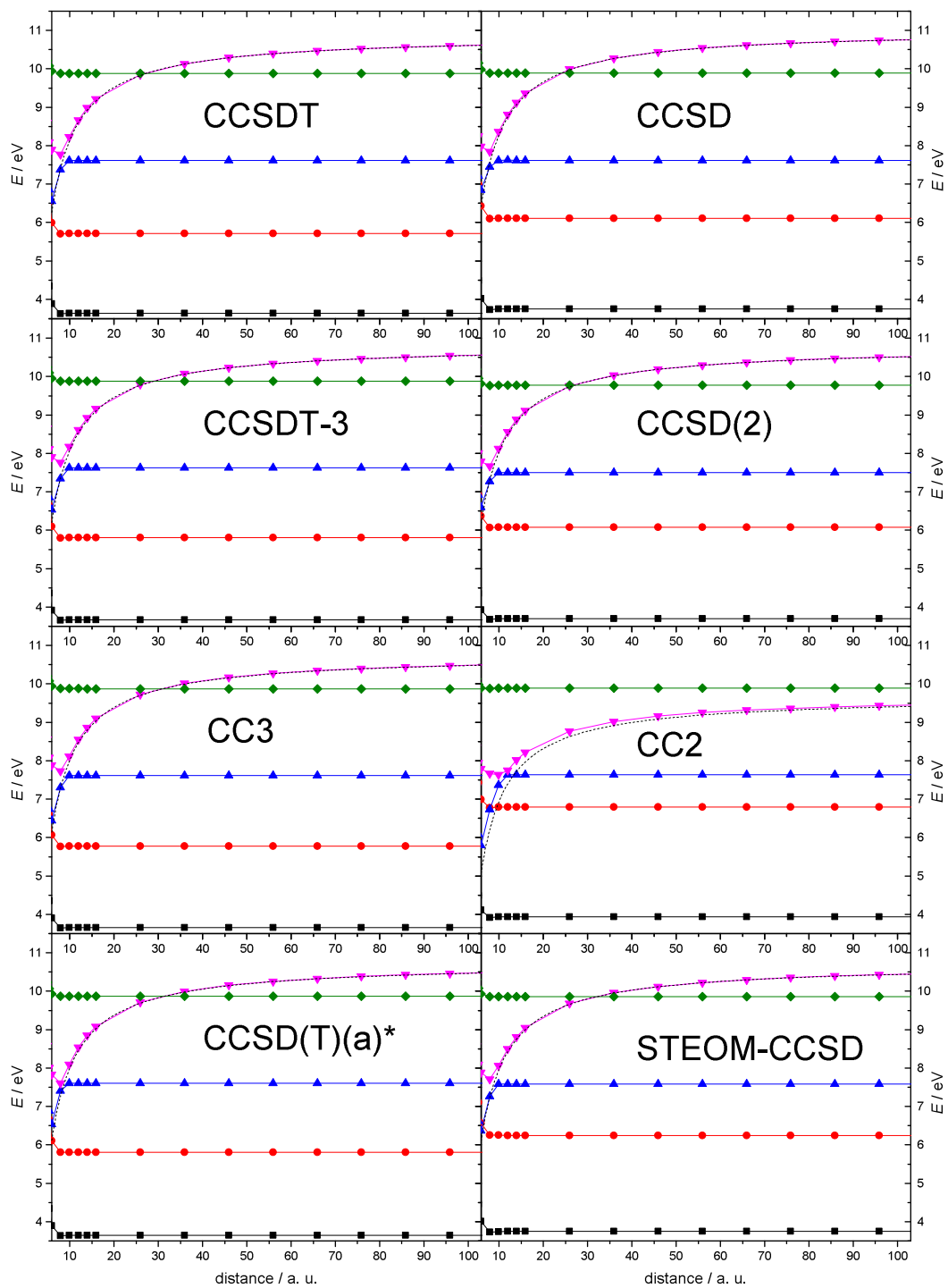
Figure 2. Potential energy curves of the lowest five excited (1^1E, black; 2^1E, red; 2^1A_1, blue; 3^1A_1, magenta; 3^1E, green) states of the ammonia-fluorine complex. Dashed lines: charge attraction curve of the ionic states
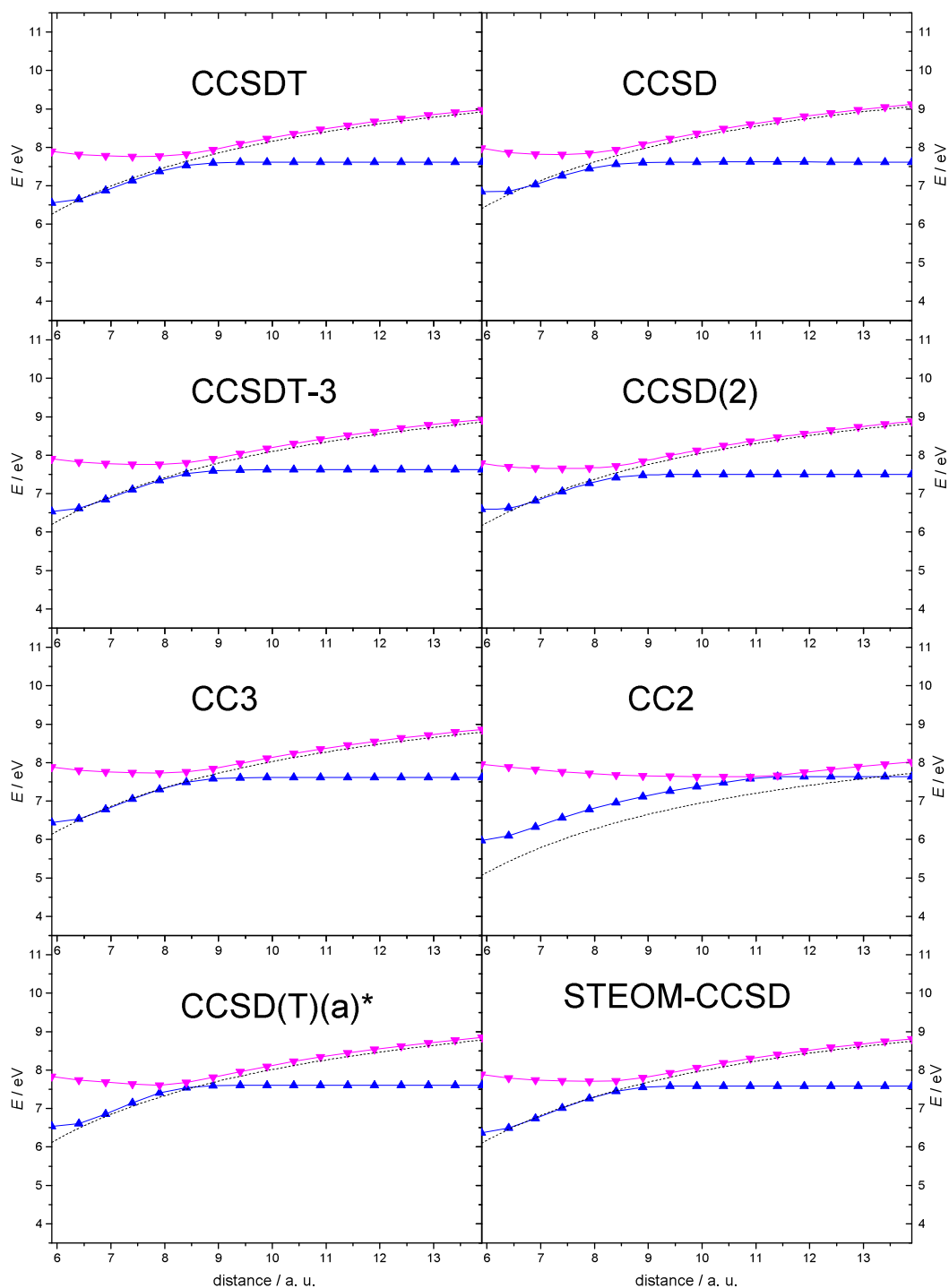
Figure 3. The crossing region of the energy curves for the 2^1A_1 (blue) and 3^1A_1 (magenta) states of the ammonia-fluorine complex. Dashed lines: charge attraction curve of the ionic states

and also CCSD resembles these curves with a slightly larger gap at the location of the crossing. On the other hand, CCSD(T)(a)* shows a smaller gap at this point, a typical behavior for a perturbative method. Still, CCSD(T)(a)* correctly predicts the distance where the two curves have the smallest separation. This is a clear improvement over CCSD where this closest point is at a shorter distance.

The curves obtained with the CC2 method are, on the other hand, very different from the others: the avoided crossing shows up at a considerably larger distance, and the gap is very small showing a much smaller interaction between the two curves. The figure shows clearly that the CT curve substantially deviates also from the charge attraction curves, a pronounced difference to all other methods investigated here.

On Figure 4 the ω_{CT}, ω_{POS}, and ω_{PR} characters are shown as calculated at the CCSD and CC2 levels. The CCSD figures nicely show the properties of a typical crossing: the CT character is "exchanged" between the 3^1A_1 and 2^1A_1 states at about 7.75 bohr; the participation ratio (ω_{PR}) curves show a maximum of 1.5 at the same distance, indicating that both states are extended to both molecules. A similar conclusion can be drawn from the ω_{POS} curves, as well. It is interesting to note that at shorter distances some mixing of the local and CT state persists: this can be explained by the fact that in the repulsive region the two states are again close in energy. On the other hand, as expected, by separating the two molecules, the interaction of the local and CT states decreases rapidly.

In case of CC2, the character curves are much sharper showing that the swap of characters happens much faster compared to CCSD. This is a typical behavior in the case of a very small interaction between the two states. It is tempting to say that the smaller interaction is due to the larger distance: over 10 bohrs the two fragments interact only slightly. Indeed, the curve of the local state is practically constant here, and it is the decrease of the CT curve that causes the crossing (see Figure 3). However, as discussed above, and seen on the figure, as well, the CT curve shows an early deviation from the theoretical charge attraction curve. This means that CC2 at this distance predicts much less charge separation than higher level methods do. While this happens to correct the too low asymptotic limit to a certain extent, is clearly an indication of an improper description of this phenomenon in the CC2 model.

The above discussion underlines the importance of the accurate description of the asymptotic region of potential energy curves for the CT states. In principle, the CT curves should converge to the sum of the corresponding ionization potential (IP) and electron affinity (EA) values, a trivial requirement for size extensivity. Therefore, in Table 1 we summarize the relevant data.

The asymptotic values of excitation energies (E_∞^{exc}) were obtained by each methods at 10000 bohrs, where the interaction energy of the two charges is already negligible (below 0.003 eV). The benchmark CCSDT result is 10.88 eV. Approximate triples methods underestimate this value by 0.06, 0.13 and 0.14 eV in the cases of CCSDT-3, CC3 and CCSD(T)(a)*, respectively. Note that these results are larger in magnitude than the error of the CT excitation energies (-0.03, -0.12, and -0.01 eV, respectively) at the equilibrium distance[1]. Doubles methods, unsurprisingly, show a larger variance of this value: while STEOM-CCSD also underestimates the CCSDT asymptotic limit (by 0.17 eV), CCSD overestimates it by about the same amount. The underestimation by CCSD(2) comes as a surprise, since this method usually gives results much closer to CCSD. The worst result is produced again by CC2 which underestimates the limit by more than 1.2 eV. For comparison, at the equilibrium geometry the difference between the CCSDT and CC2 excitation energies is about the half of this value (-0.68 eV), yet still by far the largest among the methods considered here. This finding is an indica-
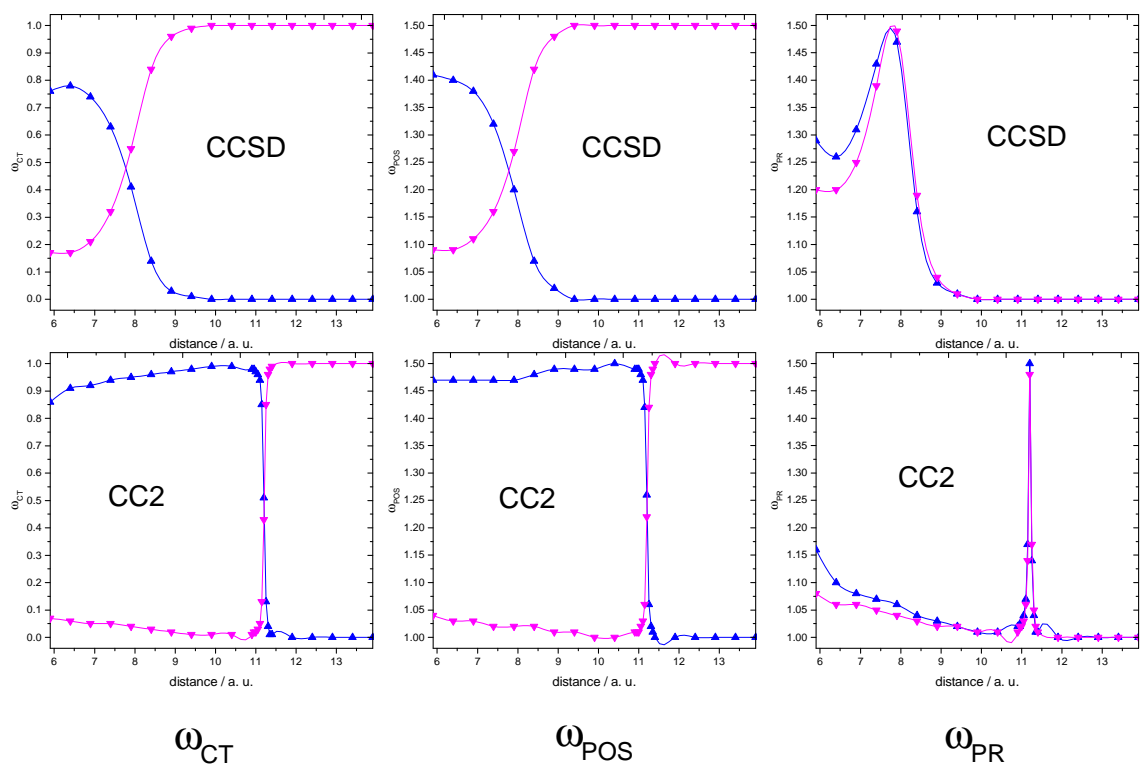
Figure 4. Change of the characters (see the text for definition) at the crossing region for the $2^1 A_1$ (blue) and $3^1 A_1$ (magenta) states of the ammonia-fluorine complex.

tion that CC2 does better with describing the bonding situation than the complete separation of charges. The improvement for smaller distances is equivalent with the CC2 curve deviating from the theoretical e^2/R function; an observation clearly seen and discussed above.

For the sum of the IP of ammonia and the EA of fluorine similar errors with respect to CCSDT can be observed as for the asymptotic CT excitation energy, except for CCSD where the errors have opposite signs: the IP+EA value is underestimated by -0.16 eV. The errors of the individual IP and EA values are less than 0.1 eV, the well-known inaccuracy of CCSD. Note that, by definition, the STEOM-CCSD IP and EA values are the same as the CCSD ones, [7] therefore their sum has the same error. The essential difference is, however, that in case of STEOM-CCSD this value matches the asymptotic excitation energy, while for CCSD it does not (see below). We note in passing that in case of CC2 the sum of the IP and EA values is even more underestimated than E_∞^{exc}. This large discrepancy is due to the underestimation of both the IP and the EA by CC2, the latter value is even negative. This suggests that the problem of CC2 is related to its considerable underestimation of the energy of ionic species.

The triples methods provide very accurate IPs, while a somewhat larger error (up to 0.13 eV underestimation) can be seen for the electron affinity. The deviation of the IP+EA sum and E_∞^{exc} remains small, but we note that the values reported in Table 1 are real, i. e. the numerical inaccuracy is one order of magnitude smaller. Thus, even CCSDT shows some size extensivity error, but no more than just 0.01 eV. The zero value seen for CCSD(T)(a)* is most probably the result of error cancellation. On the other hand, as discussed in detail by Bartlett and Nooijen [7], STEOM-CCSD is size extensive, the present calculations confirm this numerically for a high precision. In the case of CC3 the error is still very small but significantly larger in magnitude than for other triples methods; this finding correlates with the inaccuracy found for the CT excitations, in fact it is an underestimation in both cases. CCSD, CCSD(2) and CC2 all give positive errors, i.e. the limiting value is larger than the sum of the IP and the EA by 0.31 eV for CCSD as well as CCSD(2), and 0.18 eV for CC2. In this respect, CC2 seems to perform better, however, the very low values for both quantities certainly have a significant role in the underestimation of the CT excitation energies. The size extensivity error of CCSD is quite large (0.31 eV) compared to e. g. the substantially smaller finding of Nooijen and Bartlett [7] for the Be-C_2 system (0.06 eV).

Table 1. Comparison of the limiting values of the CT potential energy curves calculated at different levels of theory for ammonia–fluorine. All values in eV units. The values referring to infinity have been calculated at 10000 bohrs, where the interaction energy of the two charges is below 0.003 eV.

Method	IP (NH_3)	EA (F_2)	IP+EA	$E_\infty^{exc,a}$	Error[b]	Δ to CCSDT (IP+EA)	Δ to CCSDT (E_∞^{exc})
CCSD	10.32	0.39	10.71	11.02	0.31	-0.16	0.14
CCSD(2)	10.25	0.22	10.47	10.78	0.31	-0.40	-0.10
CC2	9.72	-0.22	9.50	9.68	0.18	-1.37	-1.20
STEOM-CCSD	10.32	0.39	10.71	10.71	0.00	-0.16	-0.17
CCSD(T)(a)*	10.38	0.35	10.73	10.74	0.00	-0.13	-0.14
CC3	10.40	0.39	10.79	10.75	-0.04	-0.08	-0.13
CCSDT-3	10.40	0.41	10.81	10.82	0.01	-0.06	-0.06
CCSDT	10.39	0.48	10.87	10.88	0.01	0.00	0.00

[a] The asymptotic excitation energy of the CT state.
[b] The deviation of E_∞^{exc} and (IP+EA), i. e. the asymptotic size extensivity error.

Table 2. Comparison of the limiting values of the CT potential energy curves calculated at different levels of theory for ammonia–oxygen-difluoride. All values in eV units. The values referring to infinity have been calculated at 10000 bohrs, where the interaction energy of the two charges is below 0.003 eV.

Method	IP (NH$_3$)	EA (OF$_2$)	IP+EA	$E_\infty^{exc,a}$	Error^b	Δ to CCSDT (IP+EA)	Δ to CCSDT (E_∞^{exc})
CCSD	10.46	1.32	11.78	12.14	0.35	-0.16	0.19
CCSD(2)	10.39	1.16	11.55	11.90	0.35	-0.39	-0.05
CC2	9.86	0.47	10.32	10.60	0.28	-1.62	-1.34
STEOM-CCSD	10.46	1.32	11.78	11.78	0.00	-0.16	-0.17
CCSD(T)(a)*	10.53	1.35	11.87	11.86	-0.01	-0.07	-0.09
CC3	10.54	1.40	11.93	11.84	-0.09	-0.01	-0.10
CCSDT-3	10.54	1.42	11.97	11.95	-0.01	0.02	0.00
CCSDT	10.53	1.41	11.94	11.95	0.01	0.00	0.00

^{a} The asymptotic excitation energy of the CT state.
^{b} The deviation of E_∞^{exc} and (IP+EA), i. e. the asymptotic size extensivity error.

3.2. Ammonia–oxygen-difluoride

In the study of Ref. [1], it was the ammonia–oxygen-difluoride system where the assignment problem due to the crossing of local and CT states turned up at the first time. Since this crossing region involves three states, we include this example in the present discussion to gain more insight into the performance of certain methods in such a complicated situation.

In Table 2 the limiting values for ammonia–oxygen-difluoride are shown. The same pattern is seen here as in case of the ammonia-fluorine system, the errors and deviations are even numerically very similar. Thus we see substantial size extensivity errors for CCSD, CCSD(2), and CC2, while almost negligible ones for the triples methods, except CC3 where it is now almost -0.1 eV. While CCSD overestimates the limiting value, CC2 underestimates it by large, in line with the finding on the CT excitation energies at equilibrium distances [1]. The larger size extensivity error of CC3 is due to the underestimation of the limiting values, since the IP and EA values are nearly perfect. Note that in Ref. [1] CC3 showed the largest error for this molecule, a finding which is partly explained now.

On Figure 5 the potential energy curves in the crossing region, along with the respective curves of the CCSD and CC2 level CT characters (ω_{CT}) are presented for three electronic states, $3\,^1A'$, $4\,^1A'$ and $5\,^1A'$. These states of the complex correspond to two local (one on the OF$_2$ and one on the NH$_3$ fragment) and one CT type excitation. As start one should note that the coordinate range here is much smaller than it was for the ammonia–fluorine system, and in fact the coordinate values themselves are also much shorter, meaning that these crossings are very close to the equilibrium structure. This is an explanation of the trouble we were facing while trying to assign the proper states in Ref. [1].

At large distance it is the red curve which represents the CT state and it decreases more rapidly as the molecules approach each other, resulting in an avoided crossing with one of the local states. This avoided crossing of the red and black curves are well shown on the curves obtained at the CCSDT, CCSDT-3, CCSD(T)(a)* STEOM-CCSD and CCSD levels. Indeed, the ω_{CT} curve at the CCSD level reflects a swap of

characters between the two affected states around this point. Compared to CCSDT, both CCSDT-3 and STEOM-CCSD predict the location of the crossing accurately, while CCSD and CCSD(T)(a)* show it at somewhat too small intermolecular separations, which is not surprising knowing the overestimated asymptotic excitation energy E_∞^{exc} of CCSD. Nevertheless, the smallest gap between the two curves is similar in magnitude at the CCSD and CCSDT levels. The triples corrected CCSD(T)(a)* method shows again a much smaller gap, similarly to the previous observation for ammonia-fluorine. However, now the triples contribution is only partially able to correct the location of the "crossing", a non-surprising behaviour for a perturbative method.

The purple curve, which corresponds to an excitation on ammonia at large separations, approaches the black one (excitation on oxygen-difluoride) with decreasing separation and an avoided crossing can be observed even before the above discussed crossing with the CT state happens. This interaction is very weak and appears for CCSDT, CCSDT-3, CCSD(T)(a)*, STEOM-CCSD, as well as CCSD at about 3.22 bohrs. In the cases of CCSDT, CCSDT-3, and STEOM-CCSD the two avoided crossings are very close, while with CCSDT(T)(a)* and CCSD they are well separated due to the underestimation of the distance where the CT crossing takes place.

CC2, again, shows a very contrasting picture. On the corresponding panels of Figure 5 we had to use a larger distance range in order to make the relevant CT crossing visible, since this one, as in the ammonia-fluorine case, appears at a larger separation. Therefore, the CC2 picture is qualitatively different from the other cases: besides the crossing of the red and black curves, the CT state forms an avoided crossing also with the other local state. Even this second crossing is located at a larger separation than the single one seen with the other methods. The crossing of the two local states appears at an even smaller distance. The consequence is very severe: at the reference geometry (which is the equilibrium distance of the complex at about 3.14 bohrs of separation) the order of the states is different, the CT state being the lowest energy state followed by the two local states. In contrast, the other methods predict the CT state to be middle one. This is clearly a consequence of the general underestimation of the CT state by CC2, in line with the findings discussed above.

We note in passing that the ω_{CT} curve at the CC2 level indicates an additional crossing at large distance. The corresponding fourth state is not visible on the figure and will not be discussed any further.

4. Discussions and Conclusions

The main objective of this study was to extend the benchmark on vertical excitation energies presented in our previous paper [1] with the investigation of the potential energy curves of some selected CT states and their interaction with local ones. Besides the global view of the potential energy curves, we focused on two particular regions: the region of the crossing and the asymptotic (infinite separation) limit.

In agreement with previous findings on the excitation energies of CT states, CCSD potential curves resemble those of CCSDT with two key differences: the crossing happens at a shorter distance and the asymptotic excitation energy is somewhat overestimated. The two discrepancies are of course related, since the higher E_∞^{exc} results in a crossing with the local state at a shorter distance. This also explains why in Ref. [1] a larger overestimation of excitation energies for CT states than for local (valence) ones was found. The biggest problem of CCSD is the lack of size extensivity: the asymptotic excitation energy overestimates the sum of the ionization potential and the electron
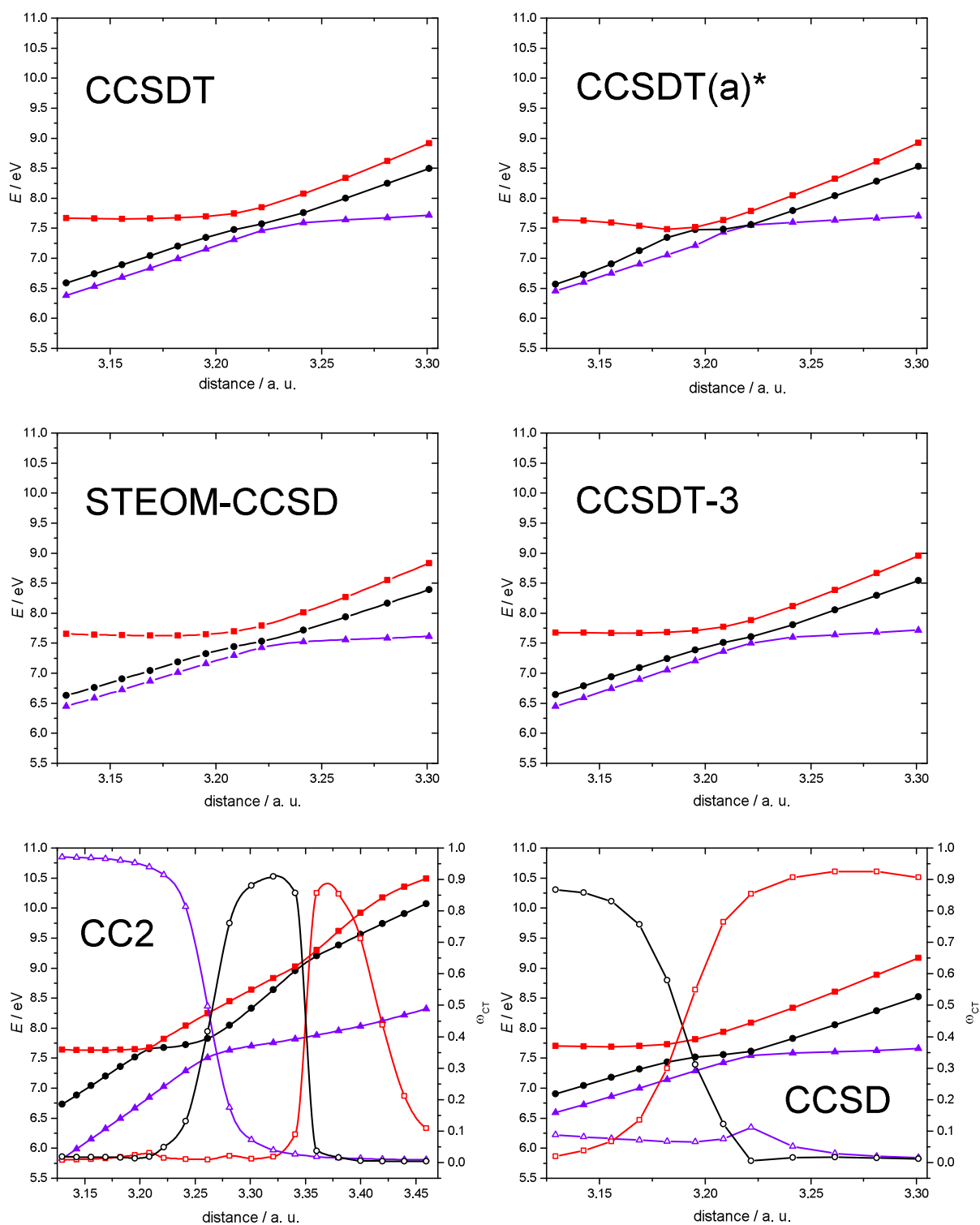
Figure 5. Potential energy surfaces (filled symbols, in eV) and the charge transfer characters (ω_{CT}, empty symbols) along the intermolecular separation for the $3^1A'$ (purple curves), $4^1A'$ (black curves), and $5^1A'$ (red curves) states of the ammonia–oxygen-difluoride bimolecular complex. Note that a slightly larger coordinate interval is used for CC2, see text for explanation.

affinity by up to 0.35 eV.

As discussed already by Meissner, Nooijen and Bartlett, [7, 36, 37] the inclusion of triple excitation effects is needed to restore the charge transfer separability. In accordance, we have found here that both the non-iterative triples correction in CCSD(T)(a)* and the implicit inclusion of triples in STEOM-CCSD [7] restores size extensivity. This also explains why these methods have been found quite accurate for CT excitation energies [1]. STEOM-CCSD describes also the crossing excellently. In general, STEOM-CCSD shows more resemblance to triples methods in the description of CT states, a conclusion already drawn in our previous paper based on excitation energies. CCSD(T)(a)* describes the overall shape and the asymptotic behaviour of the potential curves very well, but, due to the perturbative nature of the energy, the details around the avoided crossing are not perfect: while the position of the crossing is preditced accurately for of ammonia-fluorine, only a slight improvement with respect to CCSD was observed in the case of ammonia–oxygen-difluoride. In both cases, the somewhat smaller splitting at the avoided crossing can be explained by the missing proper diagonalization.

Both analyses showed that iterative triples methods give similar results which is a pleasing indication that CCSDT provides converged results. Still we have seen a small size extensivity error of 0.01 eV with CCSDT and CCSDT-3. The same error for CC3 is -0.09 eV, in accordance with the observation[1] that CC3 slightly underestimates CT excitation energies.

All the details investigated in this paper show significant problems with CC2. With respect to CCSDT, the asymptotic excitation energy is too low by up to 1.34 eV. Although this method is not size extensive, this underestimation is clearly related to the seriously too low IP and the EA values. As a consequence, when the two monomers approach each other, the CT state interacts very early with the local states, at a much larger distance than the one observed for other methods. In case of NH_3–OF_2 this results in a qualitatively different picture of the three curves: even a second local-CT crossing shows up. As a consequence, the order of the three states at the equilibrium structure of the complex will differ from that obtained by any other method. The interaction between the CT and local states can be very small, resulting in an artificially small gap at the crossing point. It has to be noted, that this small interaction is not explained by the larger intermolecular separation, as it is shown by the significant deviation of the NH_3–F_2 CT potential energy curve from the theoretical attraction function already at this point.

The hierarchy of CCSD-CCSD(2)-CC2 investigated in Ref. [38] can be used to discuss the effect of different second-order approximations. In this series, all IP, EA, and E_∞^{exc} values decrease, i.e. neglecting more and more terms in the transformed Hamiltonian results in smaller and smaller values. Since both IP and EA are already underestimated at the CCSD level, the additional approximations lead to even larger errors. On the contrary, the overestimated asymptotic E_∞^{exc} excitation energy can be improved by the second order approximation, as it is shown by the CCSD(2) results. Further approximation, in particular, the diagonal approximation of the double-double block by CC2 leads then to very low values. This means that the cancellation of errors present for the valence states [39] does not work here, most probably due to the very large effect of these matrix elements on the charge separated system.

In summary, the present investigation shows that triple excitations are needed to accurately describe potential energy surfaces of CT states. Both STEOM-CCSD and CCSD(T)(a)* are promising in this respect. While STEOM-CCSD is cheaper and e.g. with the PNO approximation can be used also for larger molecules [5, 40],

CCSD(T)(a)* is also accurate for valence excited states [41]. On the other hand, the perturbative treatment of triple excitations in CCSD(T)(a)* might become significant at the crossings and influence diabatization. The somewhat larger error of CCSD for CT states can be explained by its size extensivity error and the overestimation of the asymptotic E_∞^{exc} excitation energy. Second order approximations do not seem to be advantageous for the error cancellation, in fact CC2 is much worse for CT states than any other method investigated here. The presented results also show that the topology of the potential energy curves, the location of the (avoided) crossings of local and CT states depend very much on this accuracy. In the particular case of CC2 this resulted in different order of excited states at the equilibrium geometry, but a mismatch in the order of states can be potentially observed for any method if the geometry of interest is close to a crossing. We note that this topological difference might affect dynamics studies, and a warning, in particular in the case of CC2, should be issued if CT states play a role in the physics of the problem.

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