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Improved description of charge transfer potential energy surfaces via spin-component scaled CC2 and ADC(2) methods

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Abstract

The molecular level understanding of electronic transport properties depends on the reliable theoretical description of charge transfer (CT) type electronic states. In this paper, the performance of spin-component scaled variants of the popular CC2 and ADC(2) methods is evaluated for CT states, following benchmark strategies of earlier studies that revealed a compromised accuracy of the unmodified models. In addition to statistics on the accuracy of vertical excitation energies at equilibrium and infinite separation of bimolecular complexes, potential energy surfaces of the ammonia–fluorine complex are also reported. The results show the capability of spin-component scaled approaches to reduce the large errors of their regular counterparts to a significant extent, outperforming even the CCSD method in many cases. The cost-effective scaled opposite-spin (SOS) variants are found to provide remarkably good agreement with the CCSDT-3 reference data, thereby being recommended methods of choice in the study of charge transfer states.
Introduction

The growing scientific interest in understanding molecular level electronic transport properties, molecular electronics, and related phenomena presents an important demand for a reliable theoretical description. The so-called charge transfer (CT) states play a key role in such processes. These states are special types of electronically excited states formed via an excitation of an electron from one part of the system to another, spatially distant area. Due to the presence of long-range correlation effects and generally, the large size of the systems where these states can appear, describing CT states represents a big challenge for theoretical methods. Mean-field approaches, in particular TDDFT methods are widespread choices in this area,\textsuperscript{1,2} however, their accuracy shows large variation with the functional and the system under inspection.\textsuperscript{3–5} Although many variants of TDDFT show good performance on CT states,\textsuperscript{1,2,6–9} the reliability and consistency offered by correlated wave function methods is highly warranted in this field. The unfortunate scaling of the computational cost of wave function methods with the system size is a serious obstacle though, putting the focus on cheaper, approximate models. Popular techniques of this category are the various second order approximate methods of the Coupled Cluster (CC) family, mostly formulated as more or less systematic approximations to the $\mathcal{O}(N^6)$ scaling Coupled Cluster Singles and Doubles\textsuperscript{10} (CCSD) model at a lower computational cost. From the multitude of such theories\textsuperscript{11} the CC2\textsuperscript{12–14} and the closely related\textsuperscript{11,15} second-order algebraic diagrammatic construction (ADC(2))\textsuperscript{16–18} approaches are dominantly favored in applications thanks to their attractive, fifth-power computational scaling, efficient implementations and the latter being free from issues associated with the non-hermitian nature of CC theory. The reliability and consistency of these models leaves, as showed recently by us\textsuperscript{19–22} as well as by others,\textsuperscript{11,23–30} much to be desired: while vertical excitation energies of valence excitations are predicted with an outstanding accuracy,\textsuperscript{19,20} Rydberg states\textsuperscript{20,21} and potential energy surfaces\textsuperscript{22} can be poorly described.

Moreover, we found recently\textsuperscript{31,32} that the regular CC2 and ADC(2) methods also handle
the CT states with a very compromised accuracy. Our investigations, based on a set of local and CT states of bimolecular complexes,\textsuperscript{31} revealed a significant underestimation of the CT excitation energy at the equilibrium structure of these systems. In ref 32 it was also shown that many issues related to the inappropriate description of CT states are connected to the asymptotic behaviour of the methods, i.e. the description of the charge transfer at infinite separation of the source and destination fragments. At these points the charge transfer corresponds to a simultaneous ionization on the source and an electron attachment on the destination fragment, and the associated excitation energy of the CT state should precisely equal the sum of the ionization potential (IP) and electron affinity (EA) of the respective subsystems. This condition is, however, not fulfilled by methods that are not size extensive in the excited state, e.g. CCSD.\textsuperscript{33,34} (With CC methods, excited states are described either within the Equation-of-Motion (EOM)\textsuperscript{35,36} or the Linear Response\textsuperscript{12,33,37,38} (LR) framework. Since these two provide identical excited state energies – the sole quantity discussed in the present work – we do not distinguish them and omit their notation for brevity.) In addition, the different description of the electron correlation by the various methods influences the accuracy of the IP and EA values considerably, resulting in large errors of the asymptotic CT excitation energy for some models: both CC2 and ADC(2) were found to severely underestimate the reference values.\textsuperscript{32} These flaws seen on CT states are related to the case of Rydberg states in the sense that they both can likely be attributed to the inappropriate description of the electron moved far from its ground state position. A significantly different accuracy of a method in the asymptotic and equilibrium regions has a consequence that the interconnecting potential energy surface (PES) of the CT state, normally characterised by the $1/R$ attraction of the two ions, will also be inaccurate. Such surface scans revealed important problems with the reliability of the CC2 and ADC(2) CT surfaces and the description of their avoided crossings with local excitations.\textsuperscript{32}

The concept of spin-component scaling, originally proposed by Grimme\textsuperscript{39,40} for the MP2 energy and later by Hättig and co-workers for CC2 and ADC(2),\textsuperscript{41,42} introduces different
multiplicative scaling factors $C_{SS}$ and $C_{OS}$ for the same-spin and opposite-spin integrals, respectively, in the energy expression and the terms of the effective Hamiltonian. The variants that are usually labeled as spin-component scaled (SCS) correspond to the parameters $C_{SS} = 1/3$ and $C_{OS} = 6/5$, while the so-called SOS (scaled opposite-spin) methods$^{42}$ only retain the opposite-spin integrals with $C_{OS} = 1.3$. Although the determination of the above factors has been done rather empirically, Szabados$^{43}$ elegantly showed that for the ground state the SCS-MP2 scaling factors are practically the values which satisfy Feenberg’s minimal condition in a two-parameter scaling of the zeroth-order Hamiltonian. The SOS methods are computationally very efficient as implementations with a computational scaling of no more than fourth power of the system size are possible.$^{44-47}$ Nowadays spin-component scaled methods are available in many program packages$^{48-51}$ and can be used for calculations on relatively large systems even on standard computational architectures.

The first experiences on the performance of spin-component scaled methods on excited states were rather mixed,$^{45,52-54}$ which limited their popularity in applications. Recently, however, we pursued a quest to identify the terms responsible for the sometimes seriously bad performance of CC2 on Rydberg states$^{21}$ and excited state gradients,$^{22}$ also evaluating spin-component scaled methods in this context.$^{55}$ It was found that errors of the regular CC2 model - as compared to either CCSD or a higher level reference - can be mitigated to a large extent by these approaches.$^{55}$ Later the analysis was extended to ADC(2) and its spin-component scaled variants with a similar outcome,$^{56}$ which did not come as surprise knowing the very close relationship of the CC2 and ADC(2) theories.$^{11,15}$

In the present work, we investigate the performance of spin-component scaled variants of CC2 and ADC(2) on CT states, encouraged by these promising results on Rydberg states and PESs.$^{55,56}$ Since in our earlier studies no other pair of the $C_{SS}$ and $C_{OS}$ parameters was found to clearly outperform the common SCS and SOS methods,$^{55}$ we only check these two approaches and refrain from the ambiguous, hardly justifiable tweaking of these parameters. In our examination we follow the benchmarking procedures established in refs 31 and 32.
by evaluating CT states of a set of two-component non-covalent molecular complexes in the energetically significant, low-lying area.

**Methods**

We investigate the test systems from refs 31 and 32, i.e. the ammonia–fluorine, acetone–fluorine, pyrazine–fluorine, ammonia–oxygendifluoride, acetone–nitromethane, ammonia–pyrazine, pyrazine–pyrrole (in both stacked and H-bonded alignments), and the ethylene–tetrafluoroethylene bimolecular complexes. On the various considerations about the selection of these systems and their excited states under inspection, the reader is referred to ref 31. In that work, a benchmark set of 14 CT states was compiled from the low-lying states of the complexes via numerical definition of the CT characters (see below), while 41 other states were identified as local excitations. As spin-component scaled approaches have already extensively been benchmarked on local excitations in refs 55 and 56, here we only consider the CT states. The structures of the complexes were taken from that study and, with the exception of the ethylene–tetrafluoroethylene system discussed in detail, correspond to the equilibrium distance between the two fragments.

As reference, the high-level CCSDT-3 data from ref 31 was used, where the excellent accuracy of this method was also confirmed via comparisons to CCSDT results on selected systems.

In all calculations we used the cc-pVDZ basis set of Dunning and co-workers which, despite its limited size and the lack of diffuse functions, was confirmed to provide reliable results for such comparisons. Core electrons were excluded from the correlation treatment, except for the calculation of $\omega$ descriptors and PESs (see below). All CC2, ADC(2) and spin-component scaled calculations were performed with the TURBOMOLE package, while CCSD and CCSDT-3 reference data were taken from ref 31.

To rely on a clear definition of the charge transfer nature of the states, as well as to
free the analysis from ambiguities connected to the sometimes rather intricate mixing of dominant characters of different type in the wave functions (and their variation with the methods), the states are characterized using the $\omega$ descriptors of Plasser and co-workers.\textsuperscript{60–64} In this framework, the CT character $\omega_{CT}$ (ranging from 0.0 of completely local states to 1.0 for pure CT ones) is defined as the weight of configurations in the wave function with charges separated on different fragments. The average exciton position $\omega_{POS}$ ranges from 1 to 2 in a two-component system, with the limits corresponding to local excitations on the first and the second fragment, respectively, while $\omega_{POS} \approx 1.5$ to CT and completely delocalized (one-to-one mixed) Frenkel resonance excitations. The participation ratio $\omega_{PR}$ is close to 1 for both clear CT and local excitations, and in bimolecular complexes $\omega_{PR} \approx 2$ is typical in completely delocalized Frenkel-type and charge resonance states. The detailed introduction and demonstration of these quantities can be read in refs 31, 32, 60–63. The $\omega$ descriptors were evaluated with the TheoDORE program,\textsuperscript{63} using results from calculations performed with TURBOMOLE. We should note that, unlike in the analysis of ref 31 where the full transition density matrix was used even at the CC2 level to calculate these numbers, this workflow approximates the respective transition matrix elements by the corresponding components of the one-particle solution vector of the excited state. Thus, in the present work, even CC2 descriptors can slightly differ from the ones obtained in the rigorous approach of ref 31. The effects of this approximation are, however, minor (no more than 0.01, 0.05 and 0.04 in the CC2 $\omega_{POS}$, $\omega_{PR}$, and $\omega_{CT}$ values, respectively) and thus do not influence the analysis significantly.

To check the problems associated with the asymptotic behaviour, we calculate the CT excitation energies, as well as the associated ionization potential (IP) and electron affinity (EA) values with the spin-component scaled methods, and compare them to the respective CCSDT-3 data and the results of the unscaled variants. The IP and EA calculations were done using the continuum orbital strategy described in ref 65, allowing for the evaluation of these quantities with any method able to predict excitation energies. This approach
makes it possible to treat all ionized states on an equal footing in a closed-shell framework, potentially providing more accurate associated transition moments.\textsuperscript{66} It was successfully employed previously by us\textsuperscript{32,66} even at the TDDFT level, and does not formally require a computer code to specifically support it: by including a separate, molecule-centered function in the basis set with a negligibly low exponent, ionized states are obtained in the excitation energy calculation as excitations to or from this orbital. The asymptotic excitation energies ($E_{\infty}^{\text{exc}}$) were obtained at 10,000 bohrs of intermolecular separation, where the interaction energy of the two charges is already negligible (below 0.003 eV).

The effects on the CT potential energy surface are examined on a system where the various issues were presented and explained previously,\textsuperscript{32} the lowest totally symmetric CT state of the ammonia–fluorine complex and its interaction with a totally symmetric local excited state.

\section*{Results and discussion}

\subsection*{Identification of the CT states}

To evaluate a performance of a theoretical method by comparison to results obtained with higher level reference data, it is vital to ensure that the correct samples are compared in a statistical manner. While establishing a benchmark set for CT states in our previous work,\textsuperscript{31} it was revealed that forming a set of states that can be considered of CT type in all situations is not at all trivial and, due to the frequent mixing of CT and other (usually local valence) contributions in the wave function, requires one to follow a clear numerical definition in the classification of the states. To this end, threshold criteria for the $\omega$ descriptors (see above) prove to be an effective strategy.\textsuperscript{31} In that work, states with $\omega_{\text{CT}} > 0.5$ (with $\omega_{\text{CT}}$ evaluated at the CCSD level) were considered as charge transfer, while all others as local. (To also reflect a 'mixed' nature of some states, the $\omega_{\text{CT}} \leq 0.1$, $0.1 < \omega_{\text{CT}} \leq 0.9$, and $0.9 < \omega_{\text{CT}}$ categories were used for analysis as well.) Nevertheless, if different methods treat the various
contributions in the wave function differently (as it is usually the case), the values of the $\omega$ descriptors can also be considerably different, potentially causing a state classified as CT by the CCSD measures to be a local excitation with that particular method. As including such states in a side-by-side comparison might provide misleading results, we first have to verify that an identical set of states is being used in the statistical analysis. Note that we do not aim to exclude ‘mixed’ states in general, but rather to avoid ones with a significantly different constitution. (For a detailed description of the classification problems that arise with CT states, the reader is referred to sections 4.1 and 4.2 of ref 31)

On Figure 1 the $\omega_{CT}$ and $\omega_{PR}$ characters are shown for all methods. The plots indicate a considerable variation of the character with the methods for many states, although the majority of states (especially the ‘clear’ local and CT ones) remain of the same nature in all models. On Figure 1 a $\omega_{CT} = 0.5$ line is also shown, separating the CT and local states according to our definition. One can see that, fortunately, no states with the CCSD character (green dots) above this threshold fall below this line with any other method, so our definition provides the same set of CT states for all methods. However, for certain states the spin-component scaled variants (especially SOS-CC2 and SOS-ADC(2)) produce $\omega_{CT}$ values very close to the decision threshold, while their unmodified counterparts show them to be much more of a clear CT or local type. This large shift in the wave function constitution caused by the spin-component scaling happens for states of ‘mixed’ character, where the descriptors are very sensitive to the methods’ ability to accurately provide the ratio of dominant contributions. A large difference between the CCSD and the unscaled CC2 and ADC(2) values is observed in these situations, and the spin-component adjusted methods provide measures much closer to CCSD than their regular counterparts. This shows that they somewhat recover the ‘mixed’ nature of these states which are incorrectly predicted as ‘clean’ by CC2 and ADC(2). Regardless of these phenomena, however, we can conclude that the benchmark set of 14 CT states established in ref 31 can also be used to evaluate the SCS and SOS methods without modification.
Figure 1: The charge transfer character ($\omega_{CT}$, top panel) and the participation ratio ($\omega_{PR}$, lower panel) as functions of the CCSDT-3 vertical excitation energy ($E_{\text{CCSDT-3}}$) at equilibrium distance of the complexes, as obtained with different methods. See text for explanation.

Equilibrium excitation energies

The errors of vertical excitation energies relative to the reference CCSDT-3 values for the CT states investigated in ref 31 are presented in Table 1 and Figure 2. The values were obtained at the equilibrium intermolecular distances discussed in detail in ref 31. It is apparent that the SCS type variants SCS-CC2 and SCS-ADC(2) are equally very effective in reducing the underestimation of the CT excitation energies by their unscaled counterparts: the mean errors are no larger than 0.09 eV, and even the maximum errors (0.34 eV and 0.40 eV) are lower than the respective CCSD value. The SOS type approaches, however, show a less appealing statistics: they turn the general underestimation of the equilibrium CT energies into a mean overestimation of similar magnitude which, although does not exceed considerably the CCSD result, comes with a much larger standard deviation with individual errors up to +0.78 eV. Thus, as it is also apparent from the yellow (and orange) bars on the first- and third-row panels of Figure 2, the SOS methods do not seem to outperform the regular CC2 and ADC(2) methods in this regard. The effect we see here is most likely a systematic up-shift of CT excitation energies by spin-component scaling, similar to what
was observed previously on Rydberg states.\textsuperscript{55,56} In this sense, the SOS set of parameters corresponds to a larger modification of the original formulae than the SCS one, thereby shifting the values further in the same direction. However, unlike to the case of Rydberg states where this results in about the same relatively low mean absolute error for both the SCS and SOS models, for CT states only the SCS parametrization predicts the excitation energies with a good accuracy and the SOS one overestimates them considerably.

Table 1: Relative error of the calculated excitation energies ($\Delta_{\text{CCSDT-3}}(E_{eq}^{\text{exc}})$, in eV) at equilibrium separation with respect to CCSDT-3 results for the investigated CT states

| System                     | State   | CC2  | SCS-CC2 | SOS-CC2 | $\Delta_{\text{CCSDT-3}}(E_{eq}^{\text{exc}})$ | ADC(2) | SCS-ADC(2) | SOS-ADC(2) | CCSD |
|---------------------------|---------|------|---------|---------|-----------------------------------------------|--------|------------|------------|------|
| ammonia–fluorine          | $2^1A_1$| -0.65| 0.30    | 0.12    | 0.64                                          | -0.27  | 0.10       | 0.28       |      |
| acetone–fluorine          | $3^1A'$ | -0.72| 0.15    | 0.60    | -0.77                                         | 0.07   | 0.51       |
| pyrazine–fluorine         | $2^1B_2$| -0.70| 0.21    | 0.69    | -0.58                                         | 0.32   | 0.78       |
| ammonia–oxygendifluoride  | $2^1A_2$| -0.18| 0.34    | 0.60    | -0.09                                         | 0.40   | 0.64       |
| acetone–nitromethane      | $5^1A_1$| -0.36| 0.25    | 0.60    | -0.67                                         | -0.03  | 0.27       |
| ammonia–pyrazine          | $5^1A'$ | -0.22| 0.03    | 0.14    | -0.25                                         | 0.00   | 0.10       |
| pyrazine–pyrrole (H-bonded)| $2^1B_1$| -0.21| 0.13    | 0.31    | -0.15                                         | 0.17   | 0.33       |
| pyrazine–pyrrole (stacked)| $3^1A_1$| -0.24| 0.10    | 0.27    | -0.22                                         | 0.10   | 0.26       |
| pyrazine–pyrrole (stacked)| $2^1A''$| -0.15| 0.08    | 0.20    | -0.15                                         | 0.08   | 0.19       |
| ethylene-tetrafluoroethylene| $5^1A'$| -0.14| 0.06    | 0.14    | -0.15                                         | 0.05   | 0.13       |
|                           | $5^1B_1$| -0.40| 0.16    | 0.45    | -0.28                                         | 0.27   | 0.56       |

\begin{itemize}
    \item \textbf{Mean}: \(-0.36\) \(0.09\) \(0.33\) \(-0.36\) \(0.08\) \(0.31\) \(0.30\)
    \item \textbf{SD}: \(0.24\) \(0.15\) \(0.23\) \(0.26\) \(0.17\) \(0.24\) \(0.08\)
    \item \textbf{Max.}: \(-0.10\) \(0.34\) \(0.69\) \(-0.09\) \(0.40\) \(0.78\) \(0.44\)
    \item \textbf{Min.}: \(-0.76\) \(-0.30\) \(-0.12\) \(-0.80\) \(-0.27\) \(-0.10\) \(0.16\)
\end{itemize}

\textbf{Asymptotic limits}

Statistics on the IPs of the source fragments, the EAs of the destination fragments and the asymptotic CT excitation energies are given in Table 2, as a comparison to the respective CCSDT-3 results. (The full set of values is presented in the Supporting Information). As it was shown in ref 31, CCSDT-3 provides these values with very little deviation from the full CCSDT ones, thereby being a reliable choice as a reference in the current investigation.

Table 2 shows the significant underestimation of both the IP and EA values by the unscaled CC2 and ADC(2) models (with a striking similarity between these two), already discussed in ref 32 on a few selected states. As a consequence of this underestimation, the CT excitation energy at infinite separation is underestimated even more severely, almost by 1 eV. The large associated standard deviations (0.30 eV and 0.34 eV for CC2 and ADC(2), respectively,
compared to the 0.06 eV of CCSD) reflect a substantial inconsistency of this behaviour.

The application of spin-component scaling to CC2(ADC(2)) reduces the IP underestimations considerably, by 40(48) percent with the SCS and by 60(62) percent with the SOS parameters, respectively. The EA values are improved to an even larger extent, reducing the mean error by at least 76 percent (SCS-CC2), up to a nearly perfect agreement with CCSDT-3 in the case of SOS-ADC(2). Similar improvements are seen on the infinite separation CT energies, where the SOS variants show absolute mean errors of less than 0.1 eV, considerably outperforming even CCSD in this regard, although they still underestimate the reference value compared to the overestimation seen for CCSD. The standard deviations of all three quantities are also reduced considerably (by up to 59 percent in the case of SOS-CC2) with the scaled models, but clearly do not approach the remarkable consistency of CCSD where no SD value exceeds 0.07 eV. Nevertheless, the spin-component scaling turns out quite effective in eliminating the severe errors of CC2 and ADC(2) at the infinite separation limit.

However, the perhaps most important property of the asymptotic behaviour of a theoretical method is how accurately the CT excitation energy agrees with the sum of the IP and EA values of the source and destination fragments, respectively. Statistics on the difference between these quantities are presented in Table 3. As it was already shown in ref 32, CCSDT-3 reproduces the theoretical asymptotic energy with a very low (< 0.03 eV) error, while CCSD, due to the lack of size extensivity, shows a remarkable overestimation with the mean error being as large as 0.33 eV. Unscaled CC2 and ADC(2) also have a positive, yet significantly lower mean error of 0.19 eV. Compared to them, the spin-component scaled methods behave noticeably better: the mean error is reduced to 0.14 eV and 0.11–0.12 eV with the SCS and SOS variants, respectively. The fact that this is accompanied with low standard deviations (in fact, lower than those of the unscaled models) emphasizes the consistency of this improvement throughout the benchmark set.
Table 2: The mean errors (relative to CCSDT-3 reference values, standard deviations in parentheses) of the ionization potentials of the source fragments (IP), the electron affinities of the destination fragments (EA), and the vertical excitation energies of the investigated CT states at 10,000 bohr separation ($E_{\text{exc}}^\infty$). All values are given in eV units.

|          | CC2   | SCS-CC2 | SOS-CC2 | ADC(2) | SCS-ADC(2) | SOS-ADC(2) | CCSD   |
|----------|-------|---------|---------|--------|------------|------------|--------|
| $\Delta_{\text{CCSDT-3}}$ (IP) | -0.58 (0.31) | -0.35 (0.18) | -0.23 (0.13) | -0.55 (0.34) | -0.33 (0.22) | -0.21 (0.19) | -0.01 (0.07) |
| $\Delta_{\text{CCSDT-3}}$ (EA) | -0.49 (0.18) | -0.12 (0.11) | 0.07 (0.15) | -0.03 (0.17) | -0.17 (0.11) | 0.01 (0.15) | -0.04 (0.03) |
| $\Delta_{\text{CCSDT-3}}$ ($E_{\text{exc}}^\infty$) | -0.90 (0.30) | -0.35 (0.13) | -0.07 (0.15) | -0.91 (0.34) | -0.38 (0.19) | -0.10 (0.20) | 0.27 (0.06) |

Table 3: Statistics on the deviation ($E_{\text{exc}}^\infty - (IP + EA)$, in eV) of the vertical excitation energies of the investigated CT states at 10,000 bohr separation from the sum of the IP (source fragment) and EA (destination fragment) values.

|          | CC2   | SCS-CC2 | SOS-CC2 | ADC(2) | SCS-ADC(2) | SOS-ADC(2) | CCSD   |
|----------|-------|---------|---------|--------|------------|------------|--------|
| Mean     | 0.19  | 0.14    | 0.11    | 0.19   | 0.14       | 0.12       | 0.33   |
| SD       | 0.07  | 0.05    | 0.04    | 0.08   | 0.06       | 0.05       | 0.07   |
| Max.     | 0.30  | 0.20    | 0.17    | 0.31   | 0.23       | 0.19       | 0.44   |
| Min.     | 0.10  | 0.06    | 0.04    | 0.10   | 0.06       | 0.04       | 0.23   |

Potential energy surfaces

While spin-component scaling seems thus to bring a spectacular improvement in the asymptotic behaviour, at equilibrium intermolecular distances the picture is more ambivalent. This can be an indication that investigating the potential energy surfaces and state characters along the separation of the components is, as seen already in ref 32, an important step in evaluating a method’s performance in the description of CT states. To this end, we analyse these curves for the ammonia–fluorine bimolecular complex, one of the systems already studied in ref 32. Figure 3 shows the potential energy curves of the low-lying excited states in the 0-100 bohr range of the intermolecular separation. Beside the $2^1A_1$ and $3^1A_1$ states (blue and magenta curves) which are a local excited state on ammonia and a CT state, two local excitations on fluorine ($1^1E$ state, black curve and $2^1E$ state, red curve) and one on ammonia ($3^1E$, green curve) are shown.

As the energy of the CT state has a very pronounced distance dependence, generally characterized by the $1/R$ decay of two interacting ions, one observes crossings between the CT and several other curves, but, for symmetry reasons, interaction is only possible with the blue curve. As it was already discussed in ref 32, the CCSD curves reproduce the features of higher-level ones very well, with the exception of the slightly overestimated asymptotic limit of the CT state. The unscaled CC2 and ADC(2), due to the sizeable underestimation
of this limit, show a wrong order of states at large distances, and the crossing of the $2^1A_1$ and $3^1A_1$ states happening at a much longer intermolecular distance. It is quite apparent how these erroneous properties of the CT curve are remedied if spin-component scaling is applied, while the locally excited states remain more or less unaffected. While the SCS-CC2 and SCS-ADC(2) results visually act like averages of those of CCSDT-3 and their unscaled counterparts, the SOS variants show curves remarkably similar to the reference method, providing, for example, a more accurate location of the crossing with the $3^1E$ state than CCSD.

On Figures 4 and 5 the interaction region of the CT state and the nearby totally symmetric local state is magnified. In this area, an avoided crossing between the two $^1A_1$ states takes place, accompanied with the interchange of the state characters. The exact location of the avoided crossing, as well as the shape of the surfaces in its vicinity are of special importance in applications that involve multiple interacting excited states, at least one of which having a significant CT character. In this regard, as it was shown first in ref 32, CCSD performs acceptably for this system, giving the location of the minimum separation of the states with a good accuracy, however, the gap of the avoided crossing is somewhat larger than what is provided by the triples methods. Both the regular CC2 and ADC(2) methods show a strikingly different picture here: the interaction of the states is essentially missing, resulting in a rapid swap of the CT character (see Figure 5) and a quasi-degenerate point, which is located at a more than 40 percent larger intermolecular distance than with CCSDT-3 or CCSD. In ref 32 it was shown that the missing interaction in the CC2 (and, due to the close relationship of the two theories, ADC(2)) description is not caused by the larger distance per se, but rather by the underestimated charge separation in these models. The introduction of spin-component scaling, again, turns out to be effective for correcting this qualitatively wrong behaviour. SCS-CC2 and SCS-ADC(2) show a gap between the states, although much smaller than the reference method does, the minimum separation point also being at about 0.5 bohr larger distance. Nevertheless, the $\omega_{CT}$ character curves on Figure 5 (the respective
plots of the $\omega_{PR}$ and $\omega_{POS}$ quantities can be found in the Supporting Information) reflect a correctly described interaction of the states, with the decays and elevations of the curves around the swapping point shaped similarly to CCSD. With the SOS models, an even larger improvement is seen: both the size of the minimum energy gap and its position are very well reproduced, in fact, both SOS-CC2 and SOS-ADC(2) outperform even CCSD in this regard.

It is thus hard to argue against the clear superiority of all spin-component scaled models over their regular counterparts in the description of the CT surface, especially at the vicinity of the avoided crossing. Although we only discussed one CT state of a particular system here, due to the fact that the subpar performance of the unscaled methods stems from the improper description of the charge separation,\textsuperscript{32} it is reasonable to assume the generality of this finding.

**Conclusions**

In this work, we analysed how spin-component scaling approaches impact the normally quite inaccurate description of charge transfer states by the CC2 and ADC(2) models. To this end, we followed the same benchmarking strategy established in earlier works,\textsuperscript{31,32} where this poor performance was shown the first time with calculations performed on a set of bimolecular complexes comparing the results to high-level *ab initio* reference data. In this investigation, we once again confirmed the very close similarity of the CC2 and ADC(2) theories and the performance of their identically parametrised variants, a finding first established and explained in ref 56. Here, specifically looking at the CT states, we discovered practically no difference between any CC2 variant and its ADC(2) counterpart, thus favouring one model over the other would not be founded by our results.

From the spin-component scaling parameters, we checked the SCS and SOS variants and both turned out to reduce the large errors of the regular (unscaled) methods to a considerable extent, although their effectiveness depends somewhat on the situation under inspection. At
the equilibrium separation of the complexes, the vertical excitation energies of CT states, underestimated severely by the standard approximate models, are very accurately predicted by SCS-CC2 and SCS-ADC(2). The SOS methods turn this into a noticeable overestimation which is, however, very close to the unapproximated CCSD result. The investigation of the asymptotic behaviour, i.e. the results at the practically infinite separation of the fragments where the methods’ performance in describing the ionization potentials and electron affinities is critical, revealed that spin-component scaled techniques outperform not only the regular ones but even CCSD. This is most likely due to the better description of charge separation and a lower weight of size-inextensive terms in the wave functions. In this limit, the SOS variants show some degree of superiority compared to the SCS ones.

The region that interpolates between the equilibrium and asymptotic separations, i.e. the potential energy surface of the CT state and its interaction with other states was inspected on a previously studied benchmark system, the ammonia-fluorine complex. Although one would normally warn against drawing general conclusions about a method’s reliability by only looking at a particular example, the findings of this analysis are quite general as they stem from the inconsistent performance of CC2 and ADC(2) at large and short separations. In this test, as compared to CCSD or a higher level reference, both these methods turn out so bad that one should advise against their black-box application in studies where the right shape of CT potential energy surfaces and their interaction with other states can be of importance. Spin-component scaling, on the other hand, remedies the flaws very effectively: both the SCS and SOS parameters bring a noticeable improvement, the latter approaching the quality of the reference CCSDT-3 surfaces.

Our results, although showing a conclusive superiority of the spin-component scaled approaches compared to their parent methods in the handling of CT states, do not generally favor either the SCS or SOS variants over the other. The \( \omega \) characters obtained with the SCS parameters are, probably due to the more modest reshaping of the wave function, somewhat closer to the CCSD ones. In this sense, they act as more accurate in catching the correct
character of the states. In the statistics of the vertical excitation energies, however, CCSD is better approached by the SOS variants. Whether the ability of approximate methods to reproduce the very systematic, albeit imprecise results of CCSD, or their absolute accuracy – sometimes benefiting from error cancellation effects – is considered more important, is, to some extent, a matter of personal preference. Considering both the SCS and SOS parameter sets as empirical modifications, we do not see either as the one that should be clearly preferred for accuracy or consistency. The results where modified CC2 and ADC(2) methods act as superior to CCSD should also be regarded with awareness to the generally less systematic behaviour of these models.

Nevertheless, from the perspective of applicability to large systems, the effectiveness of the SOS-CC2 and SOS-ADC(2) methods should not be ignored. These methods, as it was shown in refs 55 and 56, not only offer a more consistent description of Rydberg states compared to regular CC2 and ADC(2), but also that of CT type ones, while possessing an attractive $O(N^4)$ computational scaling with the system size. The results of this work should be an encouragement for considering spin-component scaled approximate methods, in particular SOS type ones on large systems, in excited state \textit{ab initio} applications in place of the regular variants or lower level, mean field models.

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**Supporting Information Available**

Values of the $\omega_{CT}$, $\omega_{POS}$ and $\omega_{PR}$ descriptors for all considered states; list of vertical excitation energies for CT and local states at equilibrium and infinite separations; individual ionization potentials and electron affinities, and plots of the state characters around the
studied avoided crossing.

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Graphical TOC Entry
Figure 2: Error of the calculated excitation energy (\(\Delta E\)) with respect to CCSDT-3 as the function of the CCSDT-3 excitation energy (\(E_{\text{CCSDT-3}}\)). The color of the bar shows the character of the respective excited state: blue for local states (\(\omega_{CT} < 0.1\)), yellow for CT states (\(\omega_{CT} \geq 0.9\)), and orange for states of mixed character (0.1 \(\leq \omega_{CT} < 0.9\)).
Figure 3: Potential energy of the five lowest ($1^1E$, black; $2^1E$, red; $2^1A_1$, blue; $3^1A_1$, magenta; $3^1E$, green) excited states of the ammonia-fluorine (NH$_3$-F$_2$) complex as functions of the intermolecular separation.
Figure 4: The crossing region of the energy curves for the $2^1A_1$ (blue) and $3^1A_1$ (magenta) states of the ammonia-fluorine complex.
Figure 5: The $\omega_{CT}$ character (see Methods section) of the $2^1A_1$ (blue) and $3^1A_1$ (magenta) states of the ammonia-fluorine complex.
SUPPORTING INFORMATION: Improved description of charge transfer potential energy surfaces via spin-component scaled CC2 and ADC(2) methods

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# Excited state characters

Table 1: The charge transfer character $\omega_{CT}$ (see main text for definition and references) for all investigated states with different methods.

| System                  | Assignment | State | CC2      | SCS-CC2  | SOS-CC2  | ADC(2)   | $\omega_{CT}$ | SCS-ADC(2) | SOS-ADC(2) | CCSD |
|-------------------------|------------|-------|----------|----------|----------|----------|---------------|------------|------------|------|
| ammonia-fluorine        | 2→2        | $1^1E$ | 0.02     | 0.02     | 0.02     | 0.02     | 0.02          | 0.02       | 0.02       | 0.76 |
|                         | 1→2(1)     | $2^1A_1$ | 0.90    | 0.88     | 0.87     | 0.90     | 0.88          | 0.87       | 0.99       | 0.76 |
|                         | 1→1(2)     | $3^1A_1$ | 0.07    | 0.08     | 0.09     | 0.07     | 0.08          | 0.09       | 0.17       |      |
| acetone-fluorine        | 2→2        | $2^1A'$ | 0.00     | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→1        | $1^1A''$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→2        | $3^1A'$ | 0.97     | 0.96     | 0.97     | 0.97     | 0.97          | 0.96       | 0.96       |      |
| pyrazine-fluorine       | 2→2        | $2^1A_1$ | 0.01    | 0.01     | 0.01     | 0.01     | 0.01          | 0.01       | 0.01       |      |
|                         | 1→1        | $1^1A_2$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→2        | $1^1B_2$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→2        | $2^1B_2$ | 1.00    | 1.00     | 0.99     | 1.00     | 1.00          | 0.99       | 0.98       |      |
| ammonia-oxygendifluoride| 2→2        | $2^1A'$ | 0.00     | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 2→2        | $2^1A''$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→1        | $2^1A_1$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→2        | $2^1B_2$ | 1.00    | 1.00     | 0.97     | 0.97     | 0.97          | 0.97       | 0.86       |      |
| acetone-nitromethane    | 2→2        | $2^1A'$ | 0.01    | 0.01     | 0.01     | 0.01     | 0.01          | 0.01       | 0.01       |      |
|                         | 1→1        | $3^1A$ | 0.02    | 0.01     | 0.02     | 0.02     | 0.02          | 0.02       | 0.02       |      |
|                         | 1→2        | $4^1A'$ | 0.97    | 0.87     | 0.68     | 0.97     | 0.81          | 0.79       | 0.86       |      |
| ammonia-pyrazine        | 2→2        | $2^1A'$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 2→2        | $3^1A$ | 0.02    | 0.09     | 0.26     | 0.02     | 0.15          | 0.15       | 0.08       |      |
|                         | 1→1        | $1^1A''$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→2        | $2^1B_2$ | 1.00    | 1.00     | 0.99     | 1.00     | 0.99          | 0.96       | 0.97       |      |
| pyrrole-pyrazine (H-bonded) | 2→2       | $1^1B_2$ | 0.01    | 0.01     | 0.01     | 0.01     | 0.01          | 0.01       | 0.02       |      |
|                         | 1→2        | $2^1B_2$ | 0.99    | 1.00     | 0.98     | 1.00     | 1.00          | 1.00       | 0.00       |      |
|                         | 1→2        | $2^1A_1$ | 1.00    | 0.99     | 0.96     | 0.99     | 0.98          | 0.96       | 0.97       |      |
|                         | 1→2        | $3^1A$ | 1.00    | 1.00     | 0.98     | 1.00     | 1.00          | 0.98       | 0.99       |      |
|                         | 1→1        | $4^1A_1$ | 0.01    | 0.02     | 0.06     | 0.01     | 0.02          | 0.05       | 0.04       |      |
| pyrrole-pyrazine (stacked) | 2→2       | $2^1A'$ | 0.01    | 0.01     | 0.01     | 0.01     | 0.01          | 0.01       | 0.01       |      |
|                         | 2→2        | $3^1A'$ | 0.13    | 0.13     | 0.15     | 0.15     | 0.07          | 0.07       | 0.08       |      |
|                         | 1→2        | $2^1A'$ | 0.01    | 0.01     | 0.01     | 0.01     | 0.01          | 0.01       | 0.01       |      |
|                         | 1→2        | $2^1A''$ | 0.90    | 0.88     | 0.86     | 0.90     | 0.88          | 0.86       | 0.84       |      |
|                         | 2→2        | $3^1A'$ | 0.03    | 0.03     | 0.03     | 0.03     | 0.03          | 0.03       | 0.05       |      |
|                         | 1→2        | $4^1A'$ | 0.82    | 0.68     | 0.56     | 0.83     | 0.70          | 0.58       | 0.66       |      |
|                         | 1→1        | $5^1A'$ | 0.66    | 0.66     | 0.69     | 0.64     | 0.64          | 0.68       | 0.61       |      |
| tetrafluoroethylene (5Å) | 1→1       | $1^1B_2$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→2        | $2^1B_2$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
|                         | 1→1        | $2^1B_2$ | 0.98    | 0.99     | 0.98     | 0.99     | 0.99          | 0.99       | 0.99       |      |
|                         | 1→2        | $5^1B_1$ | 0.00    | 0.00     | 0.00     | 0.00     | 0.00          | 0.00       | 0.00       |      |
Table 2: The average exciton position $\omega_{\text{POS}}$ (see main text for definition and references) for all investigated states with different methods.

| System                  | Assignment | State       | CC2  | SCS-CC2 | SOS-CC2 | ADC(2) | $\omega_{\text{POS}}$ | SCS-ADC(2) | SOS-ADC(2) | CCSD |
|-------------------------|------------|-------------|------|---------|---------|--------|------------------------|-------------|-------------|------|
| ammonia-fluorine        | 1→2(1)    | $^{1}A_{1}$ | 1.48 | 1.47    | 1.46    | 1.48   | 1.47                   | 1.46        | 1.46        | 1.41 |
|                         | 1→1(2)    | $^{3}A_{1}$ | 1.04 | 1.04    | 1.05    | 1.03   | 1.04                   | 1.05        | 1.05        | 1.09 |
| acetone-fluorine        | 2→2       | $^{2}A_{1}$ | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→1       | $^{1}A_{1}$ | 1.00 | 1.00    | 1.00    | 1.00   | 1.00                   | 1.00        | 1.00        | 1.00 |
|                         | 1→1       | $^{3}A_{1}$ | 1.49 | 1.48    | 1.45    | 1.48   | 1.48                   | 1.48        | 1.48        | 1.48 |
| pyrazine-fluorine       | 2→2       | $^{2}A_{1}$ | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→1       | $^{1}A_{2}$ | 1.00 | 1.00    | 1.00    | 1.00   | 1.00                   | 1.00        | 1.00        | 1.00 |
|                         | 1→1       | $^{3}A_{2}$ | 1.00 | 1.00    | 1.00    | 1.00   | 1.00                   | 1.00        | 1.00        | 1.00 |
|                         | 1→1       | $^{1}B_{2}$ | 1.50 | 1.50    | 1.50    | 1.50   | 1.50                   | 1.50        | 1.50        | 1.50 |
|                         | 1→1       | $^{2}B_{2}$ | 1.50 | 1.50    | 1.50    | 1.50   | 1.50                   | 1.50        | 1.50        | 1.50 |
| ammonia-oxygendifluoride| 2→2       | $^{1}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→1       | $^{3}A'$   | 1.01 | 1.01    | 1.01    | 1.01   | 1.01                   | 1.01        | 1.01        | 1.01 |
| acetone-nitromethane    | 2→2       | $^{4}A_{1}$ | 1.99 | 1.99    | 1.83    | 1.99   | 1.99                   | 1.99        | 1.99        | 1.99 |
|                         | 1→2       | $^{5}A_{1}$ | 1.48 | 1.52    | 1.48    | 1.53   | 1.48                   | 1.53        | 1.53        | 1.55 |
| ammonia-pyrazine        | 2→2       | $^{2}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 2→2       | $^{1}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 2→2       | $^{3}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 2→2       | $^{4}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→2       | $^{5}A_{1}$ | 1.46 | 1.38    | 1.32    | 1.46   | 1.34                   | 1.40        | 1.35        | 1.39 |
|                         | 1→2       | $^{6}A_{1}$ | 1.09 | 1.18    | 1.25    | 1.08   | 1.15                   | 1.15        | 1.15        | 1.15 |
| pyrrole-pyrazine (H-bonded) | 2→2   | $^{1}B_{1}$ | 1.99 | 1.99    | 1.99    | 1.99   | 1.99                   | 1.99        | 1.99        | 1.99 |
|                         | 2→2       | $^{2}B_{1}$ | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→2       | $^{2}A_{2}$ | 1.99 | 1.99    | 1.99    | 1.99   | 1.99                   | 1.99        | 1.99        | 1.99 |
|                         | 1→2       | $^{3}A_{2}$ | 1.95 | 1.95    | 1.94    | 1.95   | 1.95                   | 1.95        | 1.95        | 1.95 |
|                         | 1→2       | $^{4}A_{2}$ | 1.47 | 1.40    | 1.33    | 1.48   | 1.41                   | 1.41        | 1.35        | 1.39 |
|                         | 1→2       | $^{5}A_{2}$ | 1.46 | 1.41    | 1.42    | 1.47   | 1.41                   | 1.41        | 1.41        | 1.38 |
| pyrrole-pyrazine (stacked) | 2→2   | $^{2}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 2→2       | $^{3}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→2       | $^{2}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→2       | $^{3}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→2       | $^{4}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
|                         | 1→2       | $^{5}A'$   | 2.00 | 2.00    | 2.00    | 2.00   | 2.00                   | 2.00        | 2.00        | 2.00 |
| tetrafluoroethylene (5Å) | 1→1     | $^{1}B_{1}$ | 1.00 | 1.00    | 1.00    | 1.00   | 1.00                   | 1.00        | 1.00        | 1.00 |
|                         | 2→2       | $^{1}B_{1}$ | 1.89 | 1.95    | 1.72    | 1.92   | 1.95                   | 1.95        | 1.95        | 1.96 |
|                         | 1→2       | $^{2}B_{1}$ | 1.49 | 1.50    | 1.49    | 1.50   | 1.50                   | 1.50        | 1.50        | 1.50 |
|                         | 1→2       | $^{3}B_{1}$ | 1.11 | 1.05    | 1.30    | 1.08   | 1.05                   | 1.03        | 1.03        | 1.03 |
Table 3: The excitation participation ratio $\omega_{PR}$ (see main text for definition and references) for all investigated states with different methods.

| System                  | Assignment | State   | CC2   | SCS-CC2 | SOS-CC2 | ADC(2)$^{PR}$ | SC-ADC(2) | SOS-ADC(2) | CCSD |
|-------------------------|------------|---------|-------|---------|---------|---------------|------------|------------|-------|
| ammonia-fluorine        | 2→2        | $1^1A'$ | 0.02  | 1.02    | 1.02    | 1.02          | 1.02       | 1.02       | 1.02  |
|                         | 1→2(1)     | $2^1A_1$ | 1.11  | 1.13    | 1.15    | 1.11          | 1.14       | 1.15       | 1.29  |
|                         | 1→1(2)     | $3^1A_1$ | 1.07  | 0.99    | 1.10    | 1.07          | 1.09       | 1.10       | 1.20  |
| acetone-fluorine        | 2→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→1        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
| pyrazine-fluorine       | 2→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→1        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
| ammonia-oxygendifluoride| 2→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→1        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
| acetone-nitromethane    | 2→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→1        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
| ammonia-pyrazine        | 2→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→1        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
| pyrrole-pyrazine (H-bonded) | 2→2    | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→1        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
| pyrrole-pyrazine (stacked) | 2→2    | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→1        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
| tetrafluoroethylene (5Å) | 2→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→1        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
|                         | 1→2        | $2^1A'$ | 1.00  | 1.00    | 1.00    | 1.00          | 1.00       | 1.00       | 1.00  |
Figure 1: The average exciton position $\omega_{\text{POS}}$ (see main text for definition and references) as a function of the CCSDT-3 vertical excitation energy ($E_{\text{CCSDT}}$) at equilibrium distance of the complexes, as obtained with different methods.

## 2 Equilibrium excitation energies

Table 4: Vertical excitation energies at the equilibrium intermolecular separation ($E_{\text{eq}}$) for all investigated CT states, as predicted by different methods.

| System                  | State   | CC2   | SCS-CC2 | SOS-CC2 | ADC(2) | $E_{\text{eq}}$ / eV | SCS-ADC(2) | SOS-ADC(2) | CCSD    | CCSDT-3 |
|-------------------------|---------|-------|---------|---------|--------|----------------------|-------------|-------------|---------|---------|
| ammonia–fluorine        | $2^1\text{A}_1$ | 5.96  | 6.32    | 6.50    | 5.99   | 6.34                 | 6.52        | 6.90        | 6.62    |         |
| acetone–fluorine        | $3^1\text{A}''$ | 5.18  | 6.05    | 6.50    | 5.13   | 5.97                 | 6.41        | 6.28        | 5.90    |         |
| pyrazine–fluorine       | $2^1\text{B}_3$ | 5.62  | 6.54    | 7.01    | 5.75   | 6.65                 | 7.11        | 6.77        | 6.33    |         |
| ammonia–oxygendifluoride| $2^1\text{A}_2$ | 6.28  | 6.80    | 7.06    | 6.37   | 6.86                 | 7.10        | 6.73        | 6.46    |         |
| acetone–nitromethane    | $4^1\text{A}'$ | 6.33  | 7.06    | 7.52    | 6.30   | 6.99                 | 7.42        | 7.33        | 7.09    |         |
| ammonia–pyrazine        | $5^1\text{A}'$ | 6.06  | 6.67    | 7.01    | 5.75   | 6.38                 | 6.69        | 6.75        | 6.42    |         |
| pyrazine–pyrrole (H-bonded)| $2^1\text{B}_3$ | 5.96  | 5.41    | 5.58    | 5.12   | 5.44                 | 5.60        | 5.60        | 5.27    |         |
| pyrazine–pyrrole (stacked)| $4^1\text{A}'$ | 5.75  | 6.08    | 6.25    | 5.75   | 6.08                 | 6.24        | 6.32        | 6.00    |         |
| ethylene–tetrafluoroethylene| $3^1\text{A}_1$ | 5.93  | 6.27    | 6.44    | 5.95   | 6.27                 | 6.44        | 6.47        | 6.17    |         |
|                          | $2^1\text{A}''$ | 5.33  | 5.56    | 5.68    | 5.33   | 5.55                 | 5.66        | 5.68        | 5.48    |         |
|                          | $4^1\text{A}'$ | 5.93  | 6.13    | 6.21    | 5.91   | 6.11                 | 6.19        | 6.22        | 6.07    |         |
|                          | $5^1\text{A}'$ | 6.23  | 6.37    | 6.45    | 6.21   | 6.35                 | 6.43        | 6.52        | 6.34    |         |
|                          | $2^1\text{B}_3$ | 10.16 | 10.72   | 11.01   | 10.28  | 10.84                | 11.12       | 10.87       | 10.56   |         |
Table 5: Vertical excitation energies at the equilibrium intermolecular separation ($E_{\text{exc}}^{\text{eq}}$) for the investigated local states, as predicted by different methods.

| System                        | State | CC2   | SCS-CC2 | SOS-CC2 | ADC(2) | $E_{\text{exc}}^{\text{eq}}$ / eV | SCS-ADC(2) | SOS-ADC(2) | CCSD  | CCSDT-3 |
|-------------------------------|-------|-------|---------|---------|--------|-------------------------------|-------------|-------------|--------|---------|
| ammonia–fluorine              | $1^1E$| 4.27  | 4.41    | 4.48    | 4.27   | 4.40                          | 4.40        | 4.40        | 4.08   | 4.00    |
|                               | $3^1A_1$| 7.95  | 8.07    | 8.13    | 7.95   | 8.06                          | 8.12        | 8.04        | 7.99   |         |
| acetone–fluorine              | $2^1A'$| 4.42  | 4.57    | 4.64    | 4.45   | 4.59                          | 4.66        | 4.27        | 4.20   |         |
|                               | $2^1A''$| 4.43  | 4.58    | 4.65    | 4.45   | 4.59                          | 4.66        | 4.27        | 4.21   |         |
| pyrazine–fluorine             | $2^1A_1$| 4.40  | 4.55    | 4.63    | 4.43   | 4.57                          | 4.64        | 4.25        | 4.19   |         |
|                               | $1^1B_1$| 4.43  | 4.58    | 4.65    | 4.46   | 4.60                          | 4.67        | 4.28        | 4.21   |         |
|                               | $3^1A_1$| 4.30  | 4.48    | 4.57    | 4.32   | 4.50                          | 4.59        | 4.44        | 4.33   |         |
|                               | $2^1B_1$| 5.14  | 4.99    | 4.90    | 5.18   | 5.01                          | 4.93        | 5.14        | 5.04   |         |
|                               | $1^1A_2$| 4.93  | 5.19    | 5.32    | 4.95   | 5.21                          | 5.35        | 5.25        | 5.12   |         |
|                               | $1^1B_2$| 6.02  | 6.17    | 6.24    | 6.03   | 6.17                          | 6.24        | 6.10        | 5.90   |         |
| ammonia–oxygendifluoride      | $2^1A'$| 4.26  | 4.51    | 4.63    | 4.29   | 4.54                          | 4.65        | 4.33        | 4.23   |         |
|                               | $1^1A''$| 4.98  | 5.22    | 5.32    | 4.99   | 5.22                          | 5.32        | 5.04        | 4.95   |         |
|                               | $2^1A''$| 6.84  | 7.00    | 7.06    | 6.67   | 6.84                          | 6.90        | 6.78        | 6.70   |         |
|                               | $3^1A'$| 7.22  | 7.37    | 7.33    | 7.10   | 7.23                          | 7.19        | 7.01        | 6.90   |         |
|                               | $3^1A''$| 7.18  | 7.66    | 7.86    | 7.11   | 7.57                          | 7.76        | 7.51        | 7.21   |         |
|                               | $5^1A$ | 7.97  | 8.09    | 8.15    | 7.99   | 8.10                          | 8.15        | 7.98        | 7.98   |         |
| acetone–nitromethane          | $2^1A$ | 4.10  | 4.18    | 4.22    | 3.79   | 3.90                          | 3.95        | 4.08        | 4.04   |         |
|                               | $3^1A$ | 4.51  | 4.58    | 4.61    | 4.28   | 4.37                          | 4.41        | 4.44        | 4.42   |         |
|                               | $4^1A$ | 4.57  | 4.61    | 4.62    | 4.28   | 4.34                          | 4.38        | 4.50        | 4.43   |         |
|                               | $6^1A$ | 6.87  | 6.83    | 6.78    | 6.29   | 6.23                          | 6.21        | 6.62        | 6.58   |         |
| ammonia–pyrazine              | $2^1A'$| 4.37  | 4.55    | 4.64    | 4.40   | 4.58                          | 4.67        | 4.51        | 4.40   |         |
|                               | $3^1A''$| 5.14  | 4.98    | 4.90    | 5.18   | 5.01                          | 4.93        | 5.14        | 5.03   |         |
|                               | $2^1A''$| 4.97  | 5.23    | 5.36    | 4.99   | 5.26                          | 5.39        | 5.30        | 5.16   |         |
|                               | $5^1A$ | 7.73  | 7.89    | 7.98    | 7.72   | 7.87                          | 7.95        | 7.59        | 7.83   |         |
| pyrazine–pyrrole (H-bonded)   | $1^1B_2$| 4.34  | 4.52    | 4.61    | 4.37   | 4.55                          | 4.64        | 4.49        | 4.38   |         |
|                               | $2^1B_1$| 5.12  | 4.96    | 4.88    | 5.16   | 4.99                          | 4.91        | 5.11        | 5.01   |         |
|                               | $3^1A_1$| 5.03  | 5.30    | 5.43    | 5.05   | 5.32                          | 5.45        | 5.36        | 5.22   |         |
|                               | $2^1B_2$| 6.10  | 6.26    | 6.33    | 6.10   | 6.26                          | 6.34        | 6.20        | 6.01   |         |
| pyrazine–pyrrole (stacked)    | $4^1A_1$| 6.66  | 6.58    | 6.54    | 6.65   | 6.57                          | 6.54        | 6.65        | 6.50   |         |
|                               | $3^1A_1$| 5.05  | 4.93    | 4.86    | 5.07   | 4.95                          | 4.89        | 5.08        | 4.98   |         |
|                               | $1^1A_2$| 4.89  | 5.15    | 5.29    | 4.91   | 5.18                          | 5.31        | 5.22        | 5.09   |         |
|                               | $3^1A_2$| 6.00  | 6.15    | 6.22    | 6.00   | 6.16                          | 6.23        | 6.10        | 5.90   |         |
| ethylene-tetrafluoroethylene  | $1^1B_2$| 7.37  | 7.56    | 7.65    | 7.40   | 7.59                          | 7.68        | 7.52        | 7.44   |         |
|                               | $2^1B_1$| 8.61  | 8.67    | 8.69    | 8.54   | 8.60                          | 8.62        | 8.73        | 8.61   |         |
|                               | $2^1B_2$| 8.92  | 9.04    | 9.10    | 8.92   | 9.04                          | 9.10        | 8.83        | 8.80   |         |
|                               | $2^1B_1$| 8.85  | 9.03    | 9.12    | 8.71   | 8.88                          | 8.98        | 9.14        | 8.99   |         |
3 Asymptotic limits

Table 6: Vertical excitation energies at 10,000 bohr separation ($E_{\infty}^{exc}$, in eV units) for all investigated CT states, as predicted by different methods.

| System                  | State       | CC2        | SCS-CC2    | SOS-CC2    | ADC(2)     | $E_{\infty}^{exc}$ / eV | SCS-ADC(2) | SOS-ADC(2) | CCSD  | CCSDT-3 |
|-------------------------|-------------|------------|------------|------------|------------|-------------------------|------------|------------|-------|---------|
| ammonia–fluorine        | $2^1A_1$   | 9.68       | 10.43      | 10.82      | 9.69       | 10.41                   | 10.78      | 11.02      | 10.82 |
| acetone–fluorine        | $3^1A'$    | 9.03       | 9.96       | 10.45      | 8.97       | 9.88                    | 10.34      | 10.79      | 10.44 |
| pyrazine–fluorine       | $2^1B_2$   | 9.12       | 10.08      | 10.57      | 9.20       | 10.14                   | 10.63      | 10.86      | 10.46 |
| ammonia–oxygendifluoride| $2^1A_2$   | 10.14      | 10.72      | 11.01      | 10.19      | 10.74                   | 11.02      | 11.18      | 10.93 |
| acetone–nitromethane    | $4^1A'$    | 10.60      | 11.37      | 11.77      | 10.54      | 11.29                   | 11.66      | 12.14      | 11.95 |
| ammonia–pyrazine        | $5^1A'$    | 10.80      | 11.23      | 11.44      | 10.79      | 11.21                   | 11.41      | 11.88      | 11.67 |
| pyrazine–pyrrole (H-bonded) | $2^1B_1$  | 8.46       | 8.78       | 8.94       | 8.48       | 8.79                    | 8.94       | 9.35       | 9.09  |
| pyrazine–pyrrole (stacked) | $4^1A'$    | 9.30       | 9.62       | 9.79       | 9.29       | 9.61                    | 9.77       | 10.14      | 9.92  |
| pyrazine–pyrrole (H-bonded) | $5^1A'$    | 9.34       | 9.66       | 9.82       | 9.32       | 9.64                    | 9.81       | 10.32      | 10.05 |
| ethylene-tetrafluoroethylene| $5^1B_1$  | 12.85      | 13.47      | 13.78      | 12.98      | 13.59                   | 13.90      | 13.85      | 13.51 |

Table 7: Ionization potential of the source fragment (IP, in eV units) for all investigated CT states, as predicted by different methods.

| System                  | State       | CC2        | SCS-CC2    | SOS-CC2    | ADC(2)     | $I_{\infty}$ / eV | SCS-ADC(2) | SOS-ADC(2) | CCSD  | CCSDT-3 |
|-------------------------|-------------|------------|------------|------------|------------|-------------------|------------|------------|-------|---------|
| ammonia–fluorine        | $2^1A_1$   | 9.72       | 9.96       | 10.08      | 9.74       | 10.23             | 10.08      | 10.32      | 10.40 |
| acetone–fluorine        | $3^1A'$    | 8.28       | 8.75       | 8.99       | 8.22       | 8.68              | 8.91       | 9.32       | 9.38  |
| pyrazine–fluorine       | $2^1B_2$   | 8.40       | 8.89       | 9.14       | 8.48       | 8.97              | 9.22       | 9.42       | 9.42  |
| acetone–nitromethane    | $4^1A'$    | 9.63       | 9.67       | 9.69       | 9.67       | 9.71              | 9.72       | 9.91       | 9.89  |
| ammonia–pyrazine        | $5^1A'$    | 8.25       | 8.72       | 8.97       | 8.19       | 8.65              | 8.88       | 9.31       | 9.36  |
| pyrazine–pyrrole (H-bonded) | $2^1B_1$  | 7.65       | 8.14       | 8.43       | 8.22       | 8.65              | 8.88       | 9.31       | 9.36  |
| pyrazine–pyrrole (stacked) | $4^1A'$    | 7.65       | 7.76       | 7.82       | 7.69       | 7.81              | 7.98       | 8.00       | 8.00  |
| pyrazine–pyrrole (H-bonded) | $5^1B_1$  | 9.64       | 9.99       | 10.16      | 9.82       | 10.16             | 10.33      | 10.26      | 10.08 |
Table 8: Electron affinity of the destination fragment (EA, in eV units) for all investigated CT states, as predicted by different methods.

| System                  | State   | CC2    | SCS-CC2 | SOS-CC2 | ADC(2) | EA / eV | SCS-ADC(2) | SOS-ADC(2) | CCSD   | CCSDT-3 |
|-------------------------|---------|--------|---------|---------|---------|---------|-------------|-------------|--------|---------|
| ammonia–fluorine        | 2 \(^1\)A\(_{1}\) | -0.22  | 0.36    | 0.66    | -0.23   | 0.33    | 0.61        | 0.39        | 0.41   |         |
| acetone–fluorine        | 3 \(^1\)A\(_{2}\) | 0.44   | 1.02    | 1.31    | 0.44    | 1.00    | 1.28        | 1.03        | 1.05   |         |
| pyrazine–fluorine       | 2 \(^1\)B\(_2\) | 0.42   | 0.99    | 1.28    | 0.42    | 0.97    | 1.25        | 1.01        | 1.02   |         |
| ammonia–oxygene (H-bond) | 2 \(^1\)A\(_{2}\) | 0.42   | 0.99    | 1.28    | 0.42    | 0.97    | 1.27        | 1.32        | 1.42   |         |
| acetone–nitromethane    | 5 \(^1\)A | 1.33   | 1.64    | 1.81    | 1.06    | 1.38    | 1.54        | 1.47        | 1.55   |         |
| ammonia–pyrazine        | 5 \(^1\)A\(_{1}\) | 0.74   | 0.97    | 1.09    | 0.71    | 0.94    | 1.06        | 1.12        | 1.15   |         |
| pyrazine–pyrrole (H-bonded) | 2 \(^1\)B\(_1\) | 0.75   | 0.99    | 1.10    | 0.73    | 0.96    | 1.07        | 1.14        | 1.17   |         |
| pyrazine–pyrrole (stacked) | 2 \(^1\)A\(_{1}\) | 1.45   | 1.70    | 1.82    | 1.40    | 1.64    | 1.76        | 1.83        | 1.88   |         |
| ethylene-tetrafluoroethylene | 3 \(^1\)A\(_{1}\) | 1.52   | 1.77    | 1.89    | 1.48    | 1.72    | 1.84        | 1.90        | 1.95   |         |

4 State characters at the avoided crossing
Figure 2: The average exciton positions $\omega_{\text{POS}}$ (see main text for definition and references) of the $2^1A_1$ (blue) and $3^1A_1$ (magenta) states of the ammonia-fluorine complex, as functions of the intermolecular distance.
Figure 3: The excitation participation ratios $\omega_{PR}$ (see main text for definition and references) of the $2^1A_1$ (blue) and $3^1A_1$ (magenta) states of the ammonia-fluorine complex, as functions of the intermolecular distance.
