# Improving the Accuracy of the Charge Transfer Integrals Obtained by Coupled Cluster Theory, MBPT(2), and TDDFT

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ABSTRACT: Theoretical modeling of the charge transport in organic materials in the diabatic representation requires an accurate evaluation of the charge transfer integrals. In this paper, we show that the coupled cluster and MBPT(2) approaches are the methods of choice for performing the benchmark calculations of this quantity, in contrast to some recently published results. We demonstrate that a proper treatment of the involved ionized states, achieved by applying the continuum-orbital strategy, reduces the error of the transfer integrals by one order of magnitude, which in the case of the CC2 method corresponds to a lowering of the mean relative unsigned error (MRUE) from 39.9 to 3.8%. Moreover, we extend the application of the continuum-orbital strategy to the TDDFT method, and show that it leads to a dramatic improvement of the description of ionized states compared to the conventional TDDFT approach, characterized by lowering of MRUE from 209.0 to 24.5%.

$$J_{ij} \equiv \langle \Phi_i | H_e | \Phi_j \rangle \approx\ ?$$
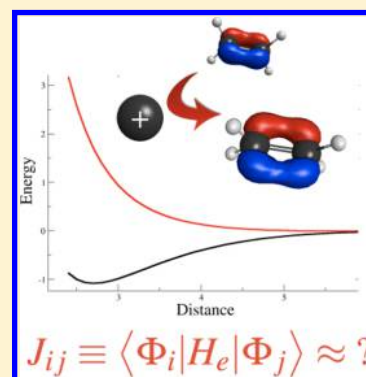
INTRODUCTION

The study of the charge transport in organic materials is a timely issue, which has been the subject of large scientific attention over the past years, primarily due to a wide range of applications these systems offer.[1−3] Among them, great expectations are put on the organic solar cells and organic light-emitting diodes (OLEDs),[4,5] which can replace inorganic materials like silicon which are not available in the sufficient amount to fulfill associated needs, at the same time offering devices with lightweight and low production costs.[6] Moreover, recent technologies in the field profit from the unique properties of organic macromolecules, such as the ability to self-assemble and efficient molecular recognition,[7−9] which allow tailoring the nanostructure and mechanical properties of the traditional materials.[10,11] In addition to these applications, charge transfer is also an important step in photocatalytic processes,[12,13] excess energy quenching in proteins,[14] and oxidative damage of DNA.[15]

From a theoretical point of view, the mechanism of charge transport in organic materials differs significantly from that in inorganic counterparts.[16] Unlike the conduction band in inorganic solids, the states characterizing the charge distribution in organic systems are energetically well-separated and usually localized on small fragments, such as single molecules or several monomeric units in case of conductive polymers. The charge transport process in organic systems is therefore mostly caused by a stepwise transition between those states, promoted by an efficient electron−nuclear coupling. Therefore, nonadiabatic effects are crucial for the description of charge transfer phenomena in organic materials, especially at high temperature. To characterize the dynamical picture of the charge transport in the diabatic representation, one evaluates the transfer integral parameter, which reflects the strength of interactions between the states, and is defined as[17]

$$J_{ij} = \langle \Phi_i | \hat{H}_e | \Phi_j \rangle \tag{1}$$

where Φ_i and Φ_j are diabatic wave functions, and $\hat{H}_e$ is the electronic Hamiltonian. The transfer integral is associated with a transition probability between the states, and clearly, the accurate calculation of the parameter plays a key role in the efficiency of models applied to describe the charge transport processes. To this end, several schemes for computing the transfer integral were proposed, including the energy splitting in dimer method,[18] fragment charge difference method,[19] generalized Mulliken−Hush formalism,[20] Boys localization scheme,[21,22] Taylor expansion scheme,[23] and others; however, their performance in terms of accuracy is still to be realized. Moreover, these approaches often result in a controversial description of the parameter fluctuations upon the change of molecular geometry, which is due to both the different choice of diabatization schemes and the internal approximations of the particular methods. A systematic discussion of these issues taking ethylene dimer as an example can be found in our recent publication.[23]

Apart from the choice of the appropriate scheme to calculate the transfer integral, the question of how the level of electronic structure theory influences the results is also important. Indeed, it is known that the equation-of-motion ionization potential coupled cluster singles and doubles (EOMIP-CCSD) method[24] (for alternative derivations, see also refs 25, 26) enables an accurate description of the ionized states (see, e.g., refs 27, 28). The multireference configuration interaction (MRCI) method[29] is also often used for describing the ionized states.[30] Although the MRCI approach is originally intended to solve the multireference problems and, according to our previous

calculations, is much less computationally efficient than the EOMIP-CC approach,[23] it correctly describes the conical intersections, whereas some artifacts for the CC theory were reported (see, e.g., Köhn and Tajti[31]). However, despite an extensive growth of the computational power together with the development of new efficient algorithms[32] and reliable approximations,[33] these methods are still primarily used for benchmark calculations of the electronic structure, whereas the size limit is reached soon, the present limit being, e.g., a nucleobase pair. For larger systems, density functional theory (DFT) and time-dependent DFT (TDDFT) often become the methods of choice for ground and exited states, respectively, due to a good balance between accuracy and computational cost. However, due to a number of the well-known failures, clear understanding of the performance of TDDFT for computing the charge transfer integral is particularly important. In addition, various perturbation theories, especially, the second-order many-body perturbation theory (MBPT(2)) and the second-order approximate coupled cluster model (CC2),[34] are also applied to treat the systems of moderate size, and seem to give more reliable results than TDDFT.[35,36]

To answer the question, how the level of theory affects the accuracy of the transfer integrals, it is convenient to consider the special case of a symmetric donor–acceptor molecular dimer, and investigate distance dependence between the monomers. This nuclear coordinate is suitable, since the transfer integral decays exponentially with the increase of the intermolecular distance. Note that for this arrangement most of the above-mentioned schemes estimate the parameter as the half of the energy difference between the states involved, therefore allowing a technically simple calculation of the transfer integral involving only state energies of two ionized states. For the development of this idea, a benchmark study of the various DFT methods, including the constrained density functional theory (CDFT),[37] fragment orbital density functional theory (FODFT),[38] and fragment orbital density functional tight-binding (FODFTB),[39] was recently provided by Kubas et al.[35] In this work the authors define the so-called HAB11 database, containing 11 symmetric π-stacked molecular dimers, where the monomers are separated by various distances. To provide the reference data, the MRCI+Q approach was selected, which, however, due to the rapid growth of the singles and doubles space, could only be applied to seven dimers with the smallest number of π-electrons. In the course of providing benchmark data for the larger systems, the authors tested both multireference (n-electron valence state perturbation theory, NEVPT2[40]) and single-reference (spin-component scaled approximate coupled cluster model, SCS-CC2[41]) methods, both based on perturbational truncations. One important characteristic of these calculations was that the two ionized states considered are the two lowest states obtained by the particular method. This does not cause any problem in the MR calculations (MRCI+Q and NEVPT2) since the two lowest ionized states are treated equally in these schemes as the first two roots of a CI problem. In the case of single-reference methods (CC2 and also TDDFT), however, ground and excited states are not treated equally; therefore, the description of the two lowest ionized states are biased (see later in more detail). In addition, to treat an ionized state as a ground state, open-shell formalism needs to be applied which introduces additional problems in the calculations, like potential spin-contamination. For further development in the field, especially before switching to larger systems, it is important to answer the

question of whether these effects influence the accuracy of the calculated transfer integral and whether there is a way to minimize their impact. Before going into detail, we state here that the bad performance of the CC2 method (39.9% relative error with respect to MRCI+Q) for these non-multireference systems was a big surprise and contradicts earlier results (see, e.g., ref 36) stating that CC2 competes in performance with the well-established coupled cluster single- and double-excitation (CCSD) approach for the π-systems; the latter was extensively used for solving similar problems, in particular, for computing the charge transfer integrals,[42,43] and no problem was reported.

In this paper, we analyze the accuracy of the transfer integrals, obtained with single-reference methods by comparison to the HAB11 reference data (MRCI+Q). Of particular interest were three accurate methods for computing the electronic structure, namely, the MBPT(2), CC2, and CCSD approaches, for which we ensured a balanced description of the first and second ionized states. This was achieved by applying a computational strategy different from that used by Kubas et al., where we considered the two ionized states as being the specific electronic excitations from the closed-shell ground state to a fictitious continuum-orbital. The results of the calculations revealed that an application of our scheme enabled a proper description of the involved states, characterized by a decrease of the relative error by one order of magnitude relative to the results of Kubas et al. in the case of the CC2 method. Moreover, we show that the same strategy can be used in the case of the time-dependent density functional theory (TDDFT) approach which also leads to improved results.

■ THEORY

To realize the idea of the balanced description of ionized states involved in the charge transfer process, let us consider how the ionization process can be treated within the linear response treatment which both EOM and TDDFT approaches use. In the EOM-CC methods, the description of excited states includes the conventional CC ground state calculations and subsequent application of configuration interaction (CI)-like excitation operator, $\hat{R}$, acting on the ground state wave function. In a second-quantized form the $\hat{R}$ is given as[44]

$$\hat{R} = r_0 + \sum_{i,a} r_i^a \{\hat{a}^\dagger \hat{i}\} + \sum_{i<j,a<b} r_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\} + \ldots \tag{2}$$

where $\hat{a}^\dagger$ and $\hat{i}$ are the creation and annihilation operators for the appropriate spin orbitals, respectively, and r is the expansion coefficient. The formalism requires the same set of spin orbitals for the ground and excited states, but the number of electrons in the ground and the excited states may be different. This stimulated the development of the so-called ionization potential (IP) EOM-CC method,[24] where the $\hat{R}$ operator includes only those excitations which reduce the number of electrons by one, viz.

$$\hat{R}^{IP} = \sum_i r_i \hat{i} + \sum_{i<j,b} r_{ij}^b \{\hat{i} \hat{b}^\dagger \hat{j}\} + \cdots \tag{3}$$

When applying the new $\hat{R}^{IP}$ operator on the ground state wave function, the resulting states accurately describe the ionized state. This strategy was also used on the MBPT (2) level by Stanton and Gauss[45] which is equivalent to Green's function based method, suggested by Nooijen and Snijders.[46] An alternative treatment of ionized states was introduced by Stanton and Gauss[47] for the EOMIP-CCSD approach and is

Table 1. Deviations of the Transfer Integrals $|H_{ab}|$ for the Seven Representatives of the HAB11 Database Relative to the MRCI+Q Data[35,a]

dimer	property	distance	MBPT(2)	CC2	CCSD	MRCI+Q[35]
ethylene	$|H_{ab}|$	3.5	−10.1	−12.3	−5.4	519.2
		4.0	−3.2	−4.9	−1.0	270.8
		4.5	0.6	−0.5	1.6	137.6
		5.0	1.9	1.2	2.2	68.5
acetylene	$|H_{ab}|$	3.5	−19.9	−4.5	−10.3	460.7
		4.0	−10.8	−16.4	−5.3	231.8
		4.5	−6.0	−7.1	−3.2	114.8
		5.0	−3.9	−4.4	−2.4	56.6
cyclopropene	$|H_{ab}|$	3.5	−1.9	−1.6	3.3	536.6
		4.0	−1.1	−0.6	2.1	254
		4.5	0.3	0.7	1.6	118.4
		5.0	1.4	1.6	2.2	54
cyclobutadiene	$|H_{ab}|$	3.5	−24.1	−24.3	−17.6	462.7
		4.0	−12.7	−12.0	−8.7	239.1
		4.5	−5.4	−4.7	−3.2	121.7
		5.0	−2.7	−2.1	−1.6	62.2
cyclopentadiene	$|H_{ab}|$	3.5	−15.2	−14.1	−5.3	465.8
		4.0	−4.4	−2.6	2.1	234.4
		4.5	2.1	3.6	6.0	114.3
		5.0	5.1	6.1	7.3	53.4
furane	$|H_{ab}|$	3.5	−18.7	−17.2	−7.3	440.3
		4.0	−4.8	−3.4	2.3	214.9
		4.5	1.9	3.9	6.0	101.8
		5.0	4.9	5.4	7.1	46
pyrrole	$|H_{ab}|$	3.5	−18.6	−16.3	−5.3	456.3
		4.0	−6.1	−3.8	2.2	228.6
		4.5	1.1	2.8	6.3	111.3
		5.0	4.4	5.5	7.4	52.2
$|H_{ab}|$	MUE (meV)		6.9	6.6	4.7	
	MRSE (%)		−0.8	−0.4	1.6	
	MRUE (%)		3.6	3.8	3.7	
	MAX		24.1	24.3	17.6	

[a]The values were obtained by the MBPT(2), CC2, and CCSD methods at various intermolecular distances between the monomers involved.

based on the application of the continuum-orbital strategy: the authors suggest inclusion of an additional continuum-orbital into the basis set and describe the ionization as an excitation to this fictitious orbital. In this way the same ionized states can be reached as in the EOMIP-CC formalism without the need of modifying the $\hat{R}$ excitation operator. With this strategy, IP calculations can be performed for such cases, and with such codes when only the excitation energy version is available. This also means that the ionized states can be described at every level of the CC theory (see, e.g., MRCC program[48]). Moreover, among the promising features of the continuum-orbital strategy, one could also mention the simultaneous access of both usual excited and ionized states, which might be helpful when describing the dynamics of the ionization process. Note, however, that when only ionized states are of interest, the conventional IP calculations are faster, since the $\hat{R}^{IP}$ operator includes a lower number of terms than $\hat{R}$.

In the case of the TDDFT, an accurate description of the ionization energies is challenging, primarily due to the simultaneous treatment of open-shell and closed-shell systems. As is often the case in the DFT community, one looks for a proper functional, which enables the most efficient error cancellation and overcomes the problem this way. For instance, in their benchmark calculations, Su et al.[49] suggest to apply a doubly hybrid functional, XYG3, to reduce the associated error

with respect to other tested functionals. Among the more systematic approaches one should mention the spin-flip TDDFT formalism[50] to resolve a similar problem in case of open-shell singlet states. In this approach, a triplet configuration is chosen as the reference state, whereas the target singlet states are obtained from those triplets by flipping the spin of one electron. Although one could think of a similar strategy for the ionized states, the tendency of DFT calculations to show spin-contamination for open-shell systems[51] might be a source of unpredictable errors. Since TDDFT is also a linear response method (similarly to an alternative derivation in case of CC[52]), we suggest to explore also here the efficiency of the continuum-orbital strategy in connection to the TDDFT formalism. Unlike in the spin-flip TDDFT, in the new treatment the reference state is a closed-shell one that therefore is not prone to spin-contamination issues and also requires fewer computational resources. Note that, to the best of our knowledge, the continuum-orbital approach was never previously introduced for treating ionized states with the TDDFT method.

■ COMPUTATIONAL DETAILS

In this work, we explore the continuum-orbital strategy by applying it not only to CCSD but also to the MBPT(2) and CC2 methods, as well as to the TDDFT approach, and calculate the hole transfer integral for the dimers of the HAB11

database. The details of the calculations are as follows. The 44 geometries of the 11 π-stacked symmetric dimers, where each pair of the monomers was studied at separations of 3.5, 4, 4.5, and 5 Å, were taken from the HAB11 database without further modifications.[35] All the calculations were performed with the cc-pVDZ basis[53] for the hydrogen atoms and aug-cc-pVTZ basis set[53,54] for non-hydrogen atoms. For the CCSD and MBPT(2) calculations with restricted Hartree−Fock (RHF) reference wave functions, the CFOUR program package[55] was used, while in the case of the CC2 as well as the TDDFT calculations, we used the TURBOMOLE software.[56] Moreover, for the sake of comparison with the results of Kubas et al.,[35] in the TDDFT calculations the Perdew−Burke−Ernzerhof (PBE) functional[57] was employed. In addition, in those all-electron calculations no symmetry constrains were applied.

The continuum-orbital strategy was implemented in a slightly different way than the original suggestion by Stanton and Gauss.[47] More specifically, when performing the electronic structure calculations on the dimer of interest, we introduced into the system an additional hydrogen atom, which possessed only a single continuum-orbital. This hydrogen atom was placed at a large distance from the dimer to make the interaction negligible. Moreover, the orbital energy of the continuum-orbital was tuned to zero, by using a special atom-centered basis function with nearly zero (10^{-20}) exponent. By this choice, when reducing the number of electrons by one, it was ensured that the electron was removed from the continuum-orbital, i.e., from the hydrogen atom. Note that this procedure makes it possible to introduce the continuum-orbital into the system on the input level, and no change in the source code of quantum chemical software is necessary.

Finally, the evaluation of the quality of the transfer integrals, obtained by the particular electronic structure method, was based on the analysis of the following quantities: the mean unsigned error [$MUE = \sum (y_{calc} - y_{ref})/n$], mean relative signed error [$MRSE = (\sum ((y_{calc} - y_{ref})/y_{ref})/n$], mean relative unsigned error [$MRUE = \sum (|y_{calc} - y_{ref}/y_{ref}|)/n$], and maximum unsigned error ($MAX = \max|y_{calc} - y_{ref}|$), where y_{ref} is the reference value, whereas y_{calc} is the transfer integral calculated with the method of interest.

■ RESULTS AND DISCUSSION

The main results of this work are summarized in Table 1, where we show the transfer integrals for the HAB11 database, obtained with the MRCI+Q method in ref 35 and the deviations of the CCSD, CC2, and MBPT(2) values relative to it. The table also lists the associated statistical quantities, including the MUE, MRSE, MRUE, and MAX.

The distance dependence of the transfer integrals for the HAB11 database was well-described in the original paper of Kubas et al.; therefore, we focus on the performance of the selected methods, starting with the most accurate CCSD results. The computed statistical quantities suggest that the CCSD method provides much more reliable values of the transfer integral than either SCS-CC2 or NEVPT2 approaches which were tested as possible alternatives of MRCI+Q for larger systems by Kubas et al.[35] More specifically, we observe that the MRUE of the CCSD results (3.7%) is significantly lower than that of SCS-CC and NEVPT2 (6.9 and 10.8%, respectively, see Table 5 of ref 35). Among the CCSD results the only considerable deviation of the transfer integral was found in the case of the cyclobutadiene dimer at 3.5 Å (17.6 meV); in all other cases the error did not exceed 10.3 meV. For

SCS-CC2 and NEVPT2 these values are 50.8 and 57.6 meV, respectively. Considering the small deviation between MRCI+Q and CCSD, as well as the major methodological difference between the two methods, one can not even exclude the possibility that CCSD results are more accurate in absolute terms. This hypothesis is supported by the absence of problems which could make CCSD less accurate (closed-shell systems with the absence of multireference effects in the majority of the dimers) but could only be proven by performing higher level calculations, e.g., CC3 or CCSD(T). In the present paper we refrain from these tests due to their high computational costs, in particular, since these methods are hardly applicable to the larger representatives of the HAB11 database. Since, in addition, some (perturbative) truncation of the expansion space was applied in the MRCI+Q calculations of Kubas et al.,[35] we believe that CCSD results represent an alternative reference data set for further use. Note also that the CCSD method possesses higher potential in applications to larger systems due to its lower cost.

Now we focus on the performance of the CC2 and MBPT(2) approaches which can be treated as second-order approximations to CCSD. It follows from Table 1 that the MSU of 6.4 and 6.9 meV for the CC2 and MBPT(2) approaches, respectively, is slightly larger than that of the CCSD results. However, both methods show more systematic fluctuations relative to the MRCI+Q data than in case of CCSD, which is evident by lowering of MRSE to −0.4% and −0.8%. This leads to an excellent agreement between both the CC2 and MBPT(2) data and the MRCI+Q results, characterized by MRUE of 3.8% and 3.6%, respectively. In turn, when taking CCSD results as a reference, the deviations in MRUS are equal to 0.1% for both methods showing that the second-order approximation hardly influences the results. This good performance of the second-order methods is especially impressive when it is compared to the accuracy of the open-shell CC2 approach used by Kubas et al.:[35] there, the MRUE value, mentioned above, is 39.9%! Moreover, as can been seen in Table 5 of ref 35, the relative error for the open-shell CC2 data grows systematically with the increase of intermolecular distance, while the closed-shell description suggested in this paper (see Table 1) results in a uniform deviation with respect to this coordinate. The CC2 and MBPT(2) results in Table 1 are also closer to the MRCI+Q and also to the CCSD results than NEVPT2 and SCS-CC2 results from ref 35. Therefore, we can safely conclude that also the single-reference second-order methods with a proper description of the ionized states considered in this work accurately estimate the hole transfer integral. It is hard to compare the costs of CC2 and MBPT(2) calculations with the multireference NEVPT2, since for the latter approach the computational costs depend on the size of the active space; however, it is known that the method is identical to the MBPT(2) when the active space includes a single function.[58] Therefore, we suggest that the MBPT(2) or CC2 approaches with the continuum-orbital (or their IP versions) for further accurate calculations of transfer integrals are more accurate, less computationally demanding, and, generally, more stable than the earlier suggested NEVPT2 with the reference wave functions taken from unrestricted HF calculations. The present approaches seem also to be a better choice than the open-shell SCS-CC2 method even if the error has been reduced substantially by spin scaling. Still, the method suffers from the unbalanced description of the two ionized states and the open-shell treatment bears the potential of spin-

Table 2. New Set of Benchmark Values of the Transfer Integrals $|H_{ab}|$ for the HAB11 Database Obtained by MBPT(2) and CCSD Methods as Well as the Deviations of NEVPT2 Values[35] Relative to the MBPT(2) Results

dimer	property	distance	CCSD	MBPT(2)	ΔNEVPT2
ethylene	$|H_{ab}|$	3.5	513.8	509.1	−21.7
		4.0	269.8	267.6	−15.3
		4.5	139.2	138.2	−9.0
		5.0	70.7	70.4	−4.3
acetylene	$|H_{ab}|$	3.5	450.4	440.8	−0.7
		4.0	226.5	221.0	−1.4
		4.5	111.6	108.8	−1.5
		5.0	54.2	52.7	−1.1
cyclopropene	$|H_{ab}|$	3.5	539.9	534.7	−48.9
		4.0	256.1	252.9	−29.8
		4.5	120.0	118.7	−17.3
		5.0	56.2	55.4	−9.2
cyclobutadiene	$|H_{ab}|$	3.5	445.1	438.6	−3.7
		4.0	230.4	226.4	−2.2
		4.5	118.5	116.3	0.2
		5.0	60.6	59.5	3.4
cyclopentadiene	$|H_{ab}|$	3.5	460.5	450.6	−10.3
		4.0	236.5	230.0	−6.8
		4.5	120.3	116.4	−4.4
		5.0	60.7	58.5	−1.3
furane	$|H_{ab}|$	3.5	433.0	421.6	−8.9
		4.0	217.2	210.1	−9.3
		4.5	107.8	103.7	−6.3
		5.0	53.1	50.9	−2.0
pyrrole	$|H_{ab}|$	3.5	451.0	437.7	−13.2
		4.0	230.8	222.5	−12.4
		4.5	117.6	112.4	−9.5
		5.0	59.6	56.6	−6.8
thiophene	$|H_{ab}|$	3.5		441.5	7.5
		4.0		220.8	−1.9
		4.5		109.1	−2.6
		5.0		53.6	0.8
imidazole	$|H_{ab}|$	3.5		415.5	3.9
		4.0		207.2	4.4
		4.5		102.6	3.5
		5.0		50.7	−1.0
benzene	$|H_{ab}|$	3.5		444.6	−9.4
		4.0		221.2	−6.9
		4.5		108.6	−4.6
		5.0		52.9	−1.2
phenol	$|H_{ab}|$	3.5		366.1	8.9
		4.0		176.7	−2.9
		4.5		84.5	0.7
		5.0		40.4	0.9
	MUE (meV)				7.3
	MRSE (%)				−3.1
	MRUE (%)				4.0
	MAX				48.9

contamination (UHF treatment) or doublet instability (ROHF treatment).

The performance of the MBPT(2) and CC2 methods for estimation of the transfer integrals is very similar (some deviations were observed only in case of the acetylene dimer), whereas the difference in the computational cost rather depends on the implementation. Since an efficient EOMIP-MBPT(2) code is available,[55] we performed the benchmark calculations for the HAB11 database with this method, to provide a consistent reference data set, obtained on one level of theory, and also to improve the results for larger dimers calculated earlier with NEVPT2.[35] The new data set for the HAB11 database shown in Table 2 and the MRUE of 4.0% for the NEVPT2 was calculated relative to the new reference data. The results from MBPT(2) and NEVPT2 are generally in good agreement, but for some systems (ethylene and cyclopropene) the differences are quite large, which is consistent with the data from ref 35. It might seem surprising to prefer MBPT(2) to the multireference NEVPT2, but the discussion above and the computational efficiency of the single-reference method explain

this choice. Note that eventually the NEVPT2 results can also be improved by performing closed-shell calculations and obtaining the ionized states by excitations to the continuum-orbital. The results of Table 2 can be used to improve the quality of scaling factors, obtained by Kubas et al. for the DFT methods, and in this way give access to more accurate data. The latter is especially important since the numbers were already used as reference values in other studies.[59]

In the last part of the discussion, we deliberate the performance of the TDDFT methods using different strategies to describe the ionized states. The results of two types of TDDFT calculations are shown in Table 3. The one labeled as "open-shell" corresponds to the treatment when the two ionized states are described as the open-shell ground and first excited state in the TDDFT calculations. The column denoted as "continuum" uses the strategy suggested in this paper, i.e., from closed-shell calculation the ionized states are obtained by

Table 3. Deviations of the Transfer Integrals $|H_{ab}|$ for the Seven Representatives of the HAB11 Database Relative to the MRCI+Q Data[a]

dimer	property	distance	TDDFT (continuum)	TDDFT (open-shell)
ethylene	$|H_{ab}|$	3.5	−129.1	414.7
		4.0	−77.5	385.1
		4.5	−36.9	325.8
		5.0	−14.7	259.7
acetylene	$|H_{ab}|$	3.5	−113.8	457
		4.0	−82.7	404.1
		4.5	−32.6	326.7
		5.0	−16.3	249.3
cyclopropene	$|H_{ab}|$	3.5	−98.5	161.0
		4.0	−52.4	341.1
		4.5	−25.4	304.6
		5.0	−10.3	235.7
cyclobutadiene	$|H_{ab}|$	3.5	−116.0	127.0
		4.0	−66.4	304.0
		4.5	−35.4	263.6
		5.0	−18.0	214.2
cyclopentadiene	$|H_{ab}|$	3.5	−106.8	277.6
		4.0	−58.4	283.1
		4.5	−28.8	250.2
		5.0	−10.9	208.2
furane	$|H_{ab}|$	3.5	−106	264.4
		4.0	−54.3	295.7
		4.5	−25.0	254.5
		5.0	−8.3	205.5
pyrrole	$|H_{ab}|$	3.5	−107.2	286.6
		4.0	−57.8	200.5
		4.5	−27.9	252.5
		5.0	−10.2	208.2
$|H_{ab}|$	MUE (meV)		54.6	277.2
	MRSE (%)		−24.5	209.6
	MRUE (%)		24.5	209.6
	MAX		129.1	414.7

[a]The values were obtained by the TDDFT method at various intermolecular distances between monomers involved with the two different treatment of the states: (i) balanced description achieved by using the continuum-orbital strategy (designated as TDDFT (continuum)), and (ii) unbalanced, where the transfer integral is calculated as a half of the energy splitting between the open-shell ground and the appropriate excited states (TDDFT (open-shell)).

excitations to the continuum-orbital. In both cases the PBE functional was used. Kubas et al.,[35] on the basis of the open-shell results, discourage the reader from using the TDDFT based approach for computing the transfer integrals due to the large inaccuracy of the results. They explain this by the strong electron delocalization error of the commonly used functionals. The results in Table 3 support this statement, showing that the relative error in the case of open-shell TDDFT is strongly distance dependent; therefore, the results are characterized by the MRUE of 209.0% and MAX of 414.7 meV. Application of the continuum-orbital strategy drastically improves the statistics. Here, the MAX of 129.1 meV is in our opinion still too high, but the variations of the transfer integral values exhibit a much more systematic character, which can be realized through the decrease of MRUE to 24.5%. We also point out that, considering results with the PBE functional, the continuum-orbital TDDFT shows a considerably better performance than CDFT, FODFT, and FODFTB methods applied by Kubas et al., for which MRUEs of 38.7%, 37.6%, and 42.4%, respectively, were obtained. Moreover, our results show that the failure of the open-shell TDDFT is due to the cooperative effect of imbalanced state description and spin-contamination. However, the latter effect is not supposed to be large in these calculations, since it was shown that the functionals without HF exchange like the PBE functional are not affected much by spin-contamination.[51]

■ CONCLUSIONS

To sum up, in this work we showed that the accuracy of the transfer integrals obtained with the single-reference methods drastically depends on how balanced the description of the involved ionized states is. We demonstrated that when treating all the (ionized) states of interest as excitations from the neutral ground state of the system, one reduces the relative error of the parameters by more than one order of magnitude. To this end, we extended the applicability of the continuum-orbital strategy, originally suggested for the CCSD calculations,[47] to other, more approximate methods, including CC2, MBPT(2), as well as TDDFT approaches. More specifically, we observed a decrease of MRUE from 39.9% to 3.2% and from 209.0% to 24.5%, for the CC2 and TDDFT, respectively, relative to the MRCI+Q results. We also showed that both the CC2 and MBPT(2) outperform previously suggested NEVPT2 and SCS-CC2 schemes, and provide more accurate data for the larger representatives of HAB11 database. To simplify the calculations we suggest an easy way to introduce continuum-orbitals into the calculations by specifying them on the input level without the need of modifying codes. This enabled us to use this strategy also in the case of TDDFT where we also obtained a considerable improvement of the results. Finally, recent calculations of Kubas et al. indicated some difficulties with extending their methodology based on the SCS-CC2 method to the electron transfer problem in the highly symmetric dimers.[60] We expect that the EOM methods can also be useful in computing the electron transfer integrals in these cases, as long as the calculations are performed for the balanced electron-attached states [see, e.g., ref 61 and references therein].

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Notes

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■ REFERENCES

(1) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297−302.

(2) McCulloch, I. *Adv. Mater.* **2013**, *25*, 1811−1812.

(3) Malliaras, G. G. *Biochim. Biophys. Acta, Gen. Subj.* **2013**, *1830*, 4286−4287.

(4) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365−377.

(5) Yersin, H. *Transition Metal and Rare Earth Compounds*; Springer: New York, 2004; pp 1−26.

(6) Kaltenbrunner, M.; White, M. S.; Głowacki, E. D.; Sekitani, T.; Someya, T.; Sariciftci, N. S.; Bauer, S. i. *Nat. Commun.* **2012**, *3*, 770.

(7) Wei, Q.; Nishizawa, T.; Tajima, K.; Hashimoto, K. *Adv. Mater.* **2008**, *20*, 2211−2216.

(8) Donets, S.; Pershin, A.; Christlmaier, M. J.; Baeurle, S. A. *J. Chem. Phys.* **2013**, *138*, 094901.

(9) Yao, K.; Chen, L.; Chen, X.; Chen, Y. *Chem. Mater.* **2013**, *25*, 897−904.

(10) Weickert, J.; Dunbar, R. B.; Hesse, H. C.; Wiedemann, W.; Schmidt-Mende, L. *Adv. Mater.* **2011**, *23*, 1810−1828.

(11) Malinkiewicz, O.; Yella, A.; Lee, Y. H.; Espallargas, G. M.; Graetzel, M.; Nazeeruddin, M. K.; Bolink, H. J. *Nat. Photonics* **2014**, *8*, 128−132.

(12) Kamat, P. V. *J. Phys. Chem. Lett.* **2012**, *3*, 663−672.

(13) Zhang, J.; Yu, J.; Zhang, Y.; Li, Q.; Gong, J. R. *Nano Lett.* **2011**, *11*, 4774−4779.

(14) Ahn, T. K.; Avenson, T. J.; Ballottari, M.; Cheng, Y.-C.; Niyogi, K. K.; Bassi, R.; Fleming, G. R. *Science* **2008**, *320*, 794−797.

(15) Núñez, M. E.; Hall, D. B.; Barton, J. K. *Chem. Biol.* **1999**, *6*, 85−97.

(16) Bässler, H.; Köhler, A. *Unimolecular and Supramolecular Electronics I*; Springer: New York, 2012; pp 1−65.

(17) Coropceanu, V.; Cornil, J.; da Silva Filho, D. e. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926−952.

(18) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767−792.

(19) Voityuk, A. A.; Rosch, N. *J. Chem. Phys.* **2002**, *117*, 5607−5616.

(20) Cave, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1996**, *249*, 15−19.

(21) Subotnik, J. E.; Yeganeh, S.; Cave, R. J.; Ratner, M. A. *J. Chem. Phys.* **2008**, *129*, 244101.

(22) Subotnik, J. E.; Cave, R. J.; Steele, R. P.; Shenvi, N. *J. Chem. Phys.* **2009**, *130*, 234102.

(23) Pershin, A.; Szalay, P. G. *J. Chem. Phys.* **2015**, *143*, 074109.

(24) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1994**, *101*, 8938.

(25) Sinha, D.; Mukhopadhyay, S. K.; Chaudhuri, R.; Mukherjee, D. *Chem. Phys. Lett.* **1989**, *154*, 544−549.

(26) Nooijen, M.; Snijders, J. G. *Int. J. Quantum Chem.* **1993**, *48*, 15−48.

(27) Stanton, J. F. *Chem. Phys. Lett.* **1995**, *237*, 20−26.

(28) Crawford, T. D.; Stanton, J. F. *J. Chem. Phys.* **2000**, *112*, 7873−7879.

(29) Szalay, P. G.; Müller, T.; Gidofalvi, G.; Lischka, H.; Shepard, R. *Chem. Rev.* **2012**, *112*, 108−181.

(30) Plasser, F.; Lischka, H. *J. Chem. Phys.* **2011**, *134*, 034309.

(31) Köhn, A.; Tajti, A. *J. Chem. Phys.* **2007**, *127*, 044105.

(32) Pillió, Z.; Tajti, A.; Szalay, P. G. *J. Chem. Theory Comput.* **2012**, *8*, 3108−3118.

(33) Vahtras, O.; Almlöf, J.; Feyereisen, M. *Chem. Phys. Lett.* **1993**, *213*, 514−518.

(34) Christiansen, O.; Koch, H.; Jørgensen, P. *Chem. Phys. Lett.* **1995**, *243*, 409−418.

(35) Kubas, A.; Hoffmann, F.; Heck, A.; Oberhofer, H.; Elstner, M.; Blumberger, J. *J. Chem. Phys.* **2014**, *140*, 104105.

(36) Kánnár, D.; Szalay, P. G. *J. Chem. Theory Comput.* **2014**, *10*, 3757−3765.

(37) Wu, Q.; Van Voorhis, T. *J. Chem. Phys.* **2006**, *125*, 164105.

(38) Oberhofer, H.; Blumberger, J. *J. Chem. Phys.* **2010**, *133*, 244105.

(39) Kubař, T.; Elstner, M. *J. Phys. Chem. B* **2010**, *114*, 11221−11240.

(40) Angeli, C.; Cimiraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J.-P. *J. Chem. Phys.* **2001**, *114*, 10252−10264.

(41) Hellweg, A.; Grün, S. A.; Hättig, C. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4119−4127.

(42) Cukier, E.; Daniels, S.; Vinson, E.; Cave, R. J. *J. Phys. Chem. A* **2002**, *106*, 11240−11247.

(43) Cave, R. J.; Stanton, J. F. *J. Chem. Phys.* **2014**, *140*, 214112.

(44) Shavitt, I.; Bartlett, R. J. *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory*; Cambridge University Press: Cambridge, U.K., 2009.

(45) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1995**, *103*, 1064−1076.

(46) Nooijen, M.; Snijders, J. G. *J. Chem. Phys.* **1995**, *102*, 1681−1688.

(47) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1999**, *111*, 8785−8788.

(48) Rolik, Z.; Szegedy, L.; Ladjánszki, I.; Ladóczki, B.; Kállay, M. *J. Chem. Phys.* **2013**, *139*, 094105.

(49) Su, N. Q.; Zhang, I. Y.; Wu, J.; Xu, X. *Frontiers of Chemistry in China* **2011**, *6*, 269−279.

(50) Shao, Y.; Head-Gordon, M.; Krylov, A. I. *J. Chem. Phys.* **2003**, *118*, 4807−4818.

(51) Menon, A. S.; Radom, L. *J. Phys. Chem. A* **2008**, *112*, 13225−13230.

(52) Koch, H.; Jørgensen, P. *J. Chem. Phys.* **1990**, *93*, 3333.

(53) Dunning, T. H., Jr *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(54) Woon, D. E.; Dunning, T. H., Jr *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(55) Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. *CFOUR, a Quantum Chemical Program Package*; for the current version, see http://www.cfour.de. In addition, integral packages MOLECULE (Almlöf and Taylor), PROPS (Taylor), ABACUS (Helgaker, Jensen. Jørgensen, and Olsen), and ECP routines by Mitin and van Wüllen were used.

(56) *TURBOMOLE V6.2 2010*, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989−2007; TURBOMOLE GmbH; available from http://www.turbomole.com.

(57) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(58) Angeli, C.; Pastore, M.; Cimiraglia, R. *Theor. Chem. Acc.* **2007**, *117*, 743−754.

(59) Kitoh-Nishioka, H.; Ando, K. *Chem. Phys. Lett.* **2015**, *621*, 96−101.

(60) Kubas, A.; Gajdos, F.; Heck, A.; Oberhofer, H. a.; Elstner, M.; Blumberger, J. *Phys. Chem. Chem. Phys.* **2015**, *17*, 14342−14354.

(61) Dutta, A. K.; Gupta, J.; Pathak, H.; Vaval, N.; Pal, S. *J. Chem. Theory Comput.* **2014**, *10*, 1923−1933.