# Multiconfiguration Pair-Density Functional Theory Outperforms Kohn–Sham Density Functional Theory and Multireference Perturbation Theory for Ground-State and Excited-State Charge Transfer

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Ⓢ *Supporting Information*

ABSTRACT: The correct description of charge transfer in ground and excited states is very important for molecular interactions, photochemistry, electrochemistry, and charge transport, but it is very challenging for Kohn–Sham (KS) density functional theory (DFT). KS-DFT exchange-correlation functionals without nonlocal exchange fail to describe both ground- and excited-state charge transfer properly. We have recently proposed a theory called multiconfiguration pair-density functional theory (MC-PDFT), which is based on a combination of multiconfiguration wave function theory with a new type of density functional called an on-top density functional. Here we have used MC-PDFT to study challenging ground- and excited-state charge-transfer processes by using on-top density functionals obtained by translating KS exchange-correlation functionals. For ground-state charge transfer, MC-PDFT performs better than either the PBE exchange-correlation functional or CASPT2 wave function theory. For excited-state charge transfer, MC-PDFT (unlike KS-DFT) shows qualitatively correct behavior at long-range with great improvement in predicted excitation energies.
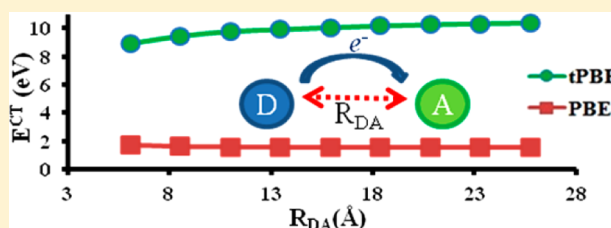
1. INTRODUCTION

Charge-transfer complexes have become the focus of extensive research, because of their importance in a multitude of applications, including molecular interactions,[1] photochemistry,[2] biological systems,[3] organic electronics,[4,5] and photocatalysis.[6]

Mulliken[7] described ground-state charge-transfer complexes as a resonance superposition of a nonbonded donor–acceptor (D–A) configuration and a configuration involving transfer of an electron from D to A. Modern research also identifies the importance of dispersion,[8,9] electrostatic,[10] and polarization[11] contributions. Quantitative modeling of charge transfer complexes is difficult for both wave function theory (WFT)[12] and Kohn–Sham (KS) density functional theory (DFT).[13–15] But it is particularly so for KS-DFT, which has a tendency to overestimate the amount of charge transfer, because of underestimation of the HOMO–LUMO gap. As first pointed out in a classic study by Salahub and co-workers,[13] the problem is ameliorated by hybrid exchange-correlation functionals, which contain a portion of Hartree–Fock exchange.

To illustrate the progress that has been made on ground-state charge transfer, we consider a database called CT7, which contains the interaction energies of seven ground-state charge-transfer complexes.[16] The mean unsigned error (MUE) on this database has been calculated for many density functionals.[17] The hybrid B3LYP functional shown to have improved performance for charge transfer by Salahub and co-workers

has an MUE of 0.71 kcal/mol for this database. BPW91, a functional older than B3LYP, has a MUE of 1.39 kcal/mol; BPW91 is a gradient approximation (a functional that depends only on spin densities and their gradients). Improvement by modern gradient approximations is slight; in particular, the lowest MUEs for gradient approximations are 1.31 kcal/mol (by HCTH407) and 1.35 kcal/mol (by SOGGA11). However, the best performances by meta approximations (which also depend on kinetic energy density) are 0.70 kcal/mol (by MN12-L) and 0.94 kcal/mol (for M11-L), and the lowest MUEs by the best performing hybrid functionals are very small: 0.21 kcal/mol (by SOGGA11-X) and 0.23 kcal/mol (by MPWB1K).

Even for exchange-correlation functionals specifically designed to reduce the error in treating charge transfer, the problem of excited-state charge transfer is more recalcitrant,[18–23] especially for long-range charge transfer from one molecule to another,[18,23,24] where errors in excess of 1 eV are not uncommon (we follow the common convention of expressing ground-state interaction energies in units of kcal/mol and excitation energies in units of eV; recall that 1 eV = 23.06 kcal/mol). KS linear response (LR) time-dependent density functional theory (TDDFT)[25] with the adiabatic approximation for the exchange-correlation functional (i.e.,

Table 1. Dissociation Energy of Charge-Transfer Dimers[a]

	Dissociation Energy (kcal/mol)						
	CASSCF	CASPT2	tPBE	PBE	PBE0	ωB97X	CAM-B3LYP	ref[b]
ClF $\cdots$NH$_3$[c]	1.85	12.51	12.42	16.89	13.29	10.88	11.57	10.62
Cl$_2$ $\cdots$NH$_3$[c]	1.15	6.67	4.55	8.11	5.76	5.18	4.83	4.88
F$_2$ $\cdots$NH$_3$[c]	0.05	2.96	1.11	5.35	2.31	1.85	2.10	1.81
HCN $\cdots$FCl[d]	1.30	6.33	3.67	6.07	4.79	5.34	4.87	4.86
H$_2$O $\cdots$FCl[e]	1.72	6.78	4.38	7.24	5.66	6.06	5.65	5.36
C$_2$H$_2$ $\cdots$FCl[f]	−0.86	5.29	4.01	6.29	4.51	4.47	3.53	3.81
C$_2$H$_4$ $\cdots$F$_2$[g]	−0.28	3.49	0.33	3.12	1.22	1.02	0.97	1.06
MUE[h]	3.92	1.66	0.85	2.95	0.75	0.35	0.28	

[a]All geometries are obtained from ref 16. All calculations in this table are done with the jul-cc-pVTZ[55] basis set. In addition, we report results with another comparable basis set, ANO-L-VTZP,[56] in Supporting Information. [b]Reference values are obtained from ref 16. These values are calculated using the W1 model.[57] [c]Active spaces for the dimers are (10, 10), and active space for NH$_3$ is (8,8). Active spaces for ClF, Cl$_2$, and F$_2$ are (2,2). [d]Active space for the dimer is (8,8), and active spaces for HCN and FCl are (6,6) and (2,2), respectively. [e]Active space for the dimer is (10,10), and active spaces for H$_2$O and FCl are (8,8) and (2,2), respectively. [f]Active space for the dimer is (10, 10), and active spaces for C$_2$H$_2$ and FCl are (10,10) and (2,2), respectively. [g]Active space for the dimer is (14,14), and active spaces for C$_2$H$_4$ and F$_2$ are (12,12) and (2,2), respectively. [h]MUE ≡ mean unsigned error (mean absolute deviation from the reference value given in the last column).

using the ground-state functional even for excited states without adding frequency dependence) is the most widely used theory for the calculation of excitation energies of molecules; LR-TDDFT underestimates long-range charge-transfer excitation energies. This failure is usually attributed to the wrong long-range behavior of the exchange−correlation functional,[18,26−28] although a higher-order analysis shows that it can be traced back to the assumption of linear response.[29] One way to correct the long-range behavior is to mix high or full HF exchange at long range with DFT correlation. Although functionals with full HF exchange improve the long-range charge-transfer problem, this approach does not lead to a completely satisfactory solution, as we shall see below.

We have recently proposed[30,31] and tested a new formulation of density functional theory called multiconfiguration pair-density functional theory (MC-PDFT), which is based on a combination of multiconfiguration WFT with a new type of density functional called an on-top density functional. In the present paper, we report that MC-PDFT with an on-top density functional obtained by translation of a gradient approximation to the exchange-correlation functional of KS-DFT gives remarkably good results for long-range intermolecular charge-transfer excitations, even though the energy is computed without Hartree−Fock exchange.

MC-PDFT calculations have two steps. First, one carries out a correlated wave function calculation such as a multiconfiguration self-consistent field (MCSCF)[32] calculation, for example, a complete active space self-consistent field (CASSCF)[33] calculation. Then, one computes the total energy in the following way: first, the kinetic energy is the one determined in the MCSCF calculation; then, the total density and on-top pair density arising from the MCSCF wave function are used to calculate the remaining contributions to the energy in a post-SCF step. We obtain first approximations to the on-top density functional by a translation prescription starting with the local-spin-density approximation or a gradient approximation (GA) to the exchange-correlation functionals. For example, we obtain the translated PBE functional called tPBE by translating the PBE[34] exchange-correlation functional.

Because the final step of an MCSCF calculation is a configuration interaction diagonalization, one automatically obtains excited states orthogonal to the lower-energy states, and the method (unlike standard KS-DFT) can be applied even to

excited states of the same symmetry as the ground state. The advantage of MC-PDFT over MCSCF calculations is that the on-top density functional includes dynamic correlation energy that is missing in MCSCF. The most widely used examples of other post-SCF methods built on an MCSCF reference wave function are complete active space second-order perturbation theory (CASPT2)[35] and multireference configuration inter-action (MRCI).[36] The advantage of MC-PDFT over these methods is that the cost of MC-PDFT is essentially the same as the cost of the first step (i.e., the MCSCF calculation), whereas CASPT2 and MRCI (with the usual inclusion of single and double excitations) are orders of magnitude more expensive and have a worse cost scaling with system size. The advantage of MC-PDFT over LR-TDDFT is that MC-PDFT is based on representing the density and kinetic energy by a multi-configuration wave function that provides a good first-order description and has the correct spatial and spin symmetry, whereas LR-TDDFT represents the excited-state density and kinetic energy by adiabatic linear response of a single Slater determinant, which has limited flexibility, does not necessarily provide a good first-order description of the wave function, and often has the wrong symmetry. Therefore, MC-PDFT is very promising for excited states, which are usually multiconfigura-tional in character.

Here, we report the performance of MC-PDFT for the complexation energy of the seven ground-state charge-transfer complexes in the CT7[16] database and for the electronic excitation energy of three intermolecular charge-transfer complexes, H$_2$N−H$\cdots$H−NO$_2$, C$_2$H$_4$$\cdots$C$_2F_4$, and NH$_3$$\cdots$F$_2$. To test the accuracy of the results, we use reference data derived from high-level calculations. Results are also compared with KS-DFT and LR-TDDFT calculations by employing four standard exchange-correlation functionals, namely, the PBE gradient approximation,[34] the global-hybrid PBE0[37] functional, and two long-range-corrected functionals (CAM-B3LYP[38] and ωB97X[39]). We will also make comparisons to CASSCF and CASPT2 calculations; for the latter, we compare to single-state CASPT2 for the ground-state charge-transfer complexes and multistate (MS) CASPT2 for excited electronic states. (The MS-CASPT2 method[40,41] is also called multiconfiguration quasidegenerate perturbation theory.[42])

2. COMPUTATIONAL DETAILS

MC-PDFT is designed to represent the state of any single-reference or multireference system with a well-defined wave function and then compute the energy, including a good description of dynamic correlation, by an inexpensive method. In previous work, we used single-state CASSCF wave functions for the first step; for the present work, we have extended this for some of the excited-state calculations to the state-average[40,43] (SA) version, which we have incorporated into the Molcas 7.9 electronic structure package.[44] CASSCF variationally optimized for the energy averaged over N states will be called SA(N)-CASSCF.

All CASSCF, CASPT2, and MC-PDFT calculations in this article are done nonrelativistically in a locally modified version of Molcas. Reasonable active spaces are chosen for the calculations, and they are specified in footnotes to the tables, in which the active space for a particular calculation is labeled as (m,n), where m is the number of electrons in the active space and n is the number of active orbitals. In all cases, the same active space is used for CASSCF, CASPT2, and MC-PDFT calculations on a given system. All CASPT2 calculations were performed with the standard imaginary shift[45] of 5.44 eV and the default IPEA shift[46] of 6.80 eV.

All KS-DFT calculations are done using the Gaussian 09[47] software, and the EOM-CCSD[48−50] and δ-CR-EOMCC-(2,3),A[51−53] calculations are done using the GAMESS[54] software package with the 2013 patch.

3. RESULTS AND DISCUSSION

Section 3.1 discusses interaction energies (i.e., dissociation energies) of ground-state charge-transfer complexes. Section 3.2 discusses some challenging charge-transfer excitation energies.

3.1. Dissociation Energy of Ground-State Charge-Transfer Complexes. In Table 1, the dissociation energies of seven ground-state charge-transfer complexes are reported. The CASSCF method has a mean unsigned error (MUE) of 3.92 kcal/mol, which is highest among all the methods tested here. This is understandable since it is the only method shown that does not attempt to approximate the full dynamic correlation energy. The two long-range-corrected density functionals that use range separation to increase the fraction of Hartree−Fock exchange at large interelectronic distances (to 100% in ωB97X and to 65% in CAM-B3LYP) perform well and are the two most accurate methods (both have an MUE of <0.4 kcal/mol).

The column headed "tPBE" contains the results with the new method, MC-PDFT. One notices that tPBE performs better than CASPT2 and than PBE, which contains no Hartree−Fock exchange, and it performs almost as well as PBE0, which contains 25% Hartree−Fock exchange and which has an MUE value that is only 0.10 kcal/mol smaller. This good performance of MC-PDFT is especially notable, because the tPBE on-top density functional is a gradient approximation, and the energies are calculated without Hartree−Fock exchange (or any other type of nonlocal exchange or nonlocal correlation).

3.2. Charge-Transfer Excitations. Excitation energies obtained in this section are compared with both KS-DFT and high-level wave function calculations (EOM-CCSD,[48−50] SAC−CI,[58,59] δ-CR-EOMCC(2,3),A,[51,52,54] or MS-CASPT2[40]).

At long range, the lowest-energy intermolecular charge-transfer excitation energy should follow the asymptotic equation

$$\omega_{CT}(R) \underset{R \to \infty}{\sim} IP_D + EA_A - \frac{1}{R} \quad (1)$$

where IP_D is the ionization potential of the donor, EA_A is the electron affinity of the acceptor, and R is the distance between the donor and acceptor centers. Equation 1 is equally applicable to singlet and triplet charge-transfer excitation energies.

3.2.1. Intermolecular Charge-Transfer Excitation for the $H_2NH\cdots HNO_2$ System. First, we consider charge-transfer excitation energies and their behavior with increasing distance R between the donor N atom and acceptor N atom for the $H_2NH\cdots HNO_2$ system that was suggested[23] as a prototype singlet intermolecular charge-transfer system by Song and Hirao. For comparison, we calculated the excitation energy by a very accurate method, δ-CR-EOMCC(2,3)A, at the three smallest distances and by EOM-CCSD and MS-CASPT2 at all distances. Table 2 shows that, at the three distances where δ-

Table 2. Excitation Energies of the $^1A_1$ Charge-Transfer Excited State of $NH_3\cdots HNO_2$[a]

distance (Å)	Excitation Energy (eV)		
	EOM-CCSD	MS-CASPT2	δ-CR-EOMCC(2,3),A
3.6772	7.51	7.10	6.84
6.1133	8.58	8.22	8.04
8.5632	9.15	8.75	8.52
MUE[b]	0.61	0.22	

[a]All calculations are done with the jul-cc-pVTZ[55] basis set. All geometries are obtained from ref 23. The active space for MS-CASPT2 is (2,2). For MS-CASPT2, the ground and excited-state energies are obtained by averaging over two states. [b]The mean unsigned error (MUE) is computed with respect to δ-CR-EOMCC(2,3),A.

CR-EOMCC(2,3)A is available, it agrees better with the latter. Therefore, we use δ-CR-EOMCC(2,3),A as the reference at the distances where it is available and MS-CASPT2 as the reference at the other distances. The results are in Table 3 and Figure 1.

Other than PBE, all the methods in Table 3 predict an increase of excitation energy with the intermolecular distance, as expected from eq 1. Although PBE0 with 25% Hartree−Fock exchange predicts an excitation energy that increases with R, it severely underestimates excitation energies and the rate of increase of the excitation energy. We also note the large MUEs of the long-range-corrected exchange-correlation functionals. First, consider CAM-B3LYP; this exchange-correlation functional has 65% Hartree−Fock nonlocal exchange in the large-R limit. Although it does not have 100% Hartree−Fock nonlocal exchange at long range, it was developed specifically[38] to improve performance for charge-transfer excitations, and it performs reasonably well for some charge-transfer transitions with intermediate spatial overlap[60] (sometimes even out-performing functionals with 100% Hartree−Fock exchange at large interelectronic separation[61]) but it is not very accurate for this case of charge-transfer between systems whose electron density does not significantly overlap. Next, consider ωB97X; this exchange-correlation functional has 100% Hartree−Fock nonlocal exchange in the large-R limit. The unsatisfactory performance of this method illustrates the comment made in the Introduction that even exchange-correlation functionals

Table 3. Excitation Energies of the $^1A_1$ Charge-Transfer Excited State of $NH_3\cdots HNO_2$[a]

distance (Å)	SA- CASSCF	PBE[b]	PBE0[b]	ωB97X[b]	CAM-B3LYP[b]	EOM-CCSD	tPBE	MS- CASPT2
				Excitation Energy (eV)				
3.6772	6.05	2.21	3.94	6.24	5.23	7.51	7.49	7.10
6.1133	7.16	1.85	3.90	7.18	5.70	8.58	8.59	8.22
8.5632	7.69	1.78	3.97	7.71	6.01	9.15	9.16	8.75
11.0156	8.01	1.75	4.03	8.03	6.21	9.47	9.49	9.13
13.4708	8.22	1.74	4.07	8.24	6.34	9.68	9.71	9.35
15.9272	8.37	1.73	4.10	8.39	6.44	9.83	9.86	9.51
18.3868	8.48	1.73	4.13	8.51	6.51	9.95	9.97	9.62
23.3034	8.64	1.72	4.16	8.66	6.61	10.10	10.06	9.77
25.7630	8.70	1.72	4.18	8.72	6.65	10.16	10.11	9.83
MUE[c]	1.06	7.47	5.15	1.04	2.91	0.39	0.40	NA[d]

[a]All calculations are done with the jul-cc-pVTZ[55] basis set. All geometries are obtained from ref 23. The active space for SA-CASSCF, MS-CASPT2, and tPBE is (2,2). For SA-CASSCF, MS-CASPT2 and tPBE, the calculations of ground and excited-state energies are obtained by averaging over two states. [b]LR-TDDFT is used to calculate excitation energies for PBE, PBE0, ωB97X, and CAM-B3LYP. [c]The MUE is computed with respect to δ-CR-EOMCC(2,3),A at the three smallest distances (see Table 2) and with respect to MS-CASPT2 at other distances. [d]Not applicable (see text).
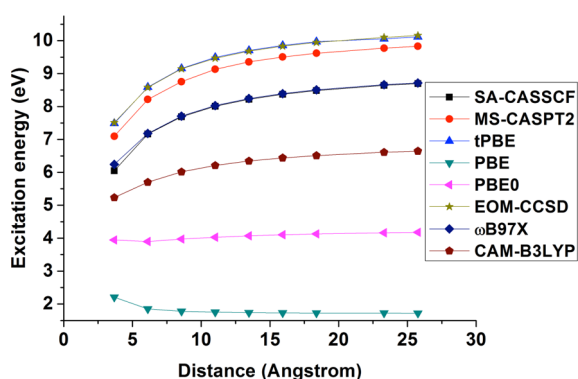

Figure 1. Distance dependence of $^1A_1$ charge-transfer excitation energies for the $NH_3\cdots HNO_2$. Note that the tPBE curve is visually indistinguishable from EOM-CCSD.

designed to have improved long-range behavior do not solve the long-range intermolecular charge-transfer excitation energy problem. Therefore, as already noted in the previous studies just referenced, simply adding full Hartree−Fock exchange at long range is not a satisfactory solution of the problem (although M06-HF,[20] which has 100% Hartree−Fock exchange at all interelectronic separations, combined with an optimized functional of the density and kinetic energy density, does perform well for this problem[62]). In this light, the outstanding performance of the MC-PDFT method with the gradient approximation tPBE for the on-top density functional is very encouraging, because this energy is computed with no nonlocal exchange or nonlocal correlation in the energy expression and has an MUE that is as good as EOM-CCSD. Furthermore, unlike MS-CASPT2, MC-PDFT does not require an empirical IPEA shift, and the cost, memory requirements, and computational scaling are all much more affordable.

The EOM-CCSD calculation is generally even more expensive than MS-CASPT2. One interesting and somewhat

Table 4. Excitation Energies for the $C_2F_4\cdots C_2H_4$ $^3B_2$ State[a]

distance (Å)	SA-CASSCF	MS-CASPT2	tPBE	PBE[b]	PBE0[b]	ωB97X[b]	CAM-B3LYP[b]
			Excitation Energy (eV)				
5	12.68	9.85	10.71	5.04	6.72	9.05	7.20
6	13.23	10.35	11.25	5.10	6.91	9.90	8.45
7	13.59	10.68	11.61	5.13	7.15	10.18	8.63
8	13.93	10.91	11.88	5.15	7.20	10.42	9.05
9	14.13	11.10	12.08	5.16	7.26	10.61	9.19
10	14.29	11.26	12.24	5.16	7.30	10.76	9.28
11	14.43	11.39	12.38	5.17	7.34	10.89	9.34
12	14.54	11.50	12.49	5.17	7.37	11.00	9.42
13	14.63	11.59	12.58	5.17	7.39	11.09	9.48
14	14.72	11.67	12.66	5.17	7.42	11.17	9.53
15	14.78	11.74	12.73	5.17	7.42	11.24	9.57
Δ[c]	0.65	0.64	0.65	0.01	0.26	0.63	0.38

[a]All calculations are done using the aug-cc-pVDZ[63] basis set. The geometry for $C_2F_4-C_2H_4$ at 8 Å is taken from ref 20. The rest of the geometries are obtained by changing the intermolecular distance between two molecules without changing their internal structure. The SA-CASSCF, MS-CASPT2, and tPBE calculations are done with a (4,4) active space. For SA-CASSCF, MS-CASPT2, and tPBE, the ground-state energies are calculated from single-state calculations, and the excited state is calculated by averaging over four triplet states. The active space includes the π and π^* orbitals of C_2H_4 and C_2F_4. [b]LR-TDDFT is used to calculate excitation energies for PBE, PBE0, ωB97X, and CAM-B3LYP. [c]Δ is the difference in excitation energies at $R = 9$ and 15 Å; the reference value of Δ is 0.64 eV (see text).

unexpected result in Table 3 is the way that tPBE and EOM-CCSD track each other. In fact, they have a mean unsigned deviation from each other of only 0.04 eV over the entire range of R.

3.2.2. Triplet Charge-Transfer Excitation Energy of Ethylene−Tetrafluoroethylene Dimer. Next, we consider the lowest triplet charge-transfer excitation energy ($^3B_2$) for the $C_2H_4\cdots C_2F_4$ system, again as a function of increasing intermolecular distance. The absolute excitation energies at large R differ because the different methods predict different ionization energies for C_2F_4 and different electron affinities for C_2H_4, so we draw conclusions on the basis of the R dependence. According to eq 1, the excitation energy should increase as $1/R$ in the long-range region, where the subsystem charge clouds do not overlap. We define Δ as the increase in excitation energy over the region from $R = 9$ Å to $R = 15$ Å. Assuming that both of these distances are in the nonoverlapping region, eq 1 leads to the expectation that $\Delta = 0.64$ eV. Table 4 gives our computed excitations in this case, and the last row of the table gives the Δ values.

In Table 4, CASSCF, CASPT2, and tPBE all have the correct long-range behavior, with Δ close to 0.64 eV. On the other hand, both PBE and PBE0 seriously underestimate the excitation energies and show the wrong long-range dependence as functions of R. Although tPBE overestimates the excitation energy at $R \to \infty$, it is a huge improvement over PBE, PBE0, and CASSCF. The table shows that it is even better than CAM-B3LYP for the excitation energy in the large-R limit, although, in this triplet case, the ωB97X functional, with 100% Hartree−Fock nonlocal exchange at large R, is in much better agreement with the MS-CASPT2 value of the excitation energy in the large-R limit.

3.2.3. Triplet Charge-Transfer Excitation Energy for $NH_3\cdots F_2$ at 6 Å. Table 5 shows excitation energies for the lowest

Table 5. Excitation Energy for Lowest Charge-Transfer Excited State ($^3A_1$) of $NH_3\cdots F_2$ at a Separation Distance of 6 Å[a]

	Excitation Energy, ΔE (eV)
CASSCF	7.58
CASPT2	7.66
tPBE	8.32
PBE[b]	0.12
PBE0[b]	2.83
ωB97X[b]	6.20
CAM-B3LYP[b]	4.65
SAC−CI[20]	9.46

[a]All calculations are done using the 6-31+G**[64] basis set. The geometry of the $NH_3\cdots F_2$ system is taken from ref 20. CASSCF, CASPT2, and MCPDFT calculations are done with a (2,5) active space. For CASSCF, CASPT2, and tPBE, the excited-state and ground-state energies are obtained from single-state calculations. [b]LR-TDDFT is used for calculating ΔE.

charge-transfer excited state, the $^3A_1$ state, in the $NH_3\cdots F_2$ system at an intermolecular distance of 6 Å. The trends present in Table 5 are similar to those already discussed with regard to Table 3. Our conclusions are qualitatively the same, whether we use CASPT2 or SAC−CI as the reference value. In particular, all the density functionals except tPBE underestimate the excitation energy by more than 1 eV; tPBE is too low when compared to SAC−CI, and too high when compared to

CASPT2. In fact, tPBE, even outperforms the long-range-corrected functionals (ωB97X and CAM-B3LYP).

4. CONCLUDING REMARKS

MC-PDFT involves the on-top density, which equals the diagonal element of the two-particle density matrix in the coordinate representation. The on-top density offers a way to treat inherently multiconfigurational systems with the correct symmetry, and MC-PDFT uses on-top density functionals to create a systematic new density functional method. The first step in this theory is a correlated WFT calculation, for which we have so far used a CASSCF calculation. We take only the kinetic energy, the density, and the on-top density from the CASSCF wave function; the final energy is calculated without using the CASSCF total energy in order to avoid double counting of the correlation energy. An appealing aspect of MC-PDFT is that its computational cost scales with system size in the same way as CASSCF (the cost depends on the choice of active space), but we produce results similar to (and even better than) CASPT2 quality.

We have previously tested MC-PDFT on a variety of problems with encouraging results.[30,31] The main goal of the present article was to test the performance of MC-PDFT for problems involving charge transfer, which has been a major stumbling block for KS-DFT. We find that MC-PDFT performs very well for ground-state charge-transfer complexes, much better than PBE, even better than CASPT2, and about as well as PBE0. For intermolecular charge-transfer excitations, tPBE is a great improvement over CASSCF, PBE, PBE0, and CAM-B3LYP, and is comparable to, if not better than, ωB97X, EOM-CCSD, and SAC−CI. It reduces the error for the excitation energy, compared to other forms of DFT, and it also shows correct long-range behavior, which has been difficult for functionals not having 100% Hartree−Fock exchange in the energy expression. The mean unsigned error for long-range charge transfer in the singlet excitation of $NH_3\cdots HNO_2$ (which was suggested as a prototype test case by Song and Hirao[23]), is smaller than any other method tested (except for EOM-CCSD, whose error equals that of MC-PDFT within the precison of our tables), and it eliminates the poor long-range behavior that KS-DFT shows, even for long-range-corrected exchange-correlation functionals. This is especially notable when we consider that the energy functional is calculated without any component of nonlocal exchange (e.g., Hartree−Fock exchange), and the current on-top density functional used in MC-PDFT is a first-generation gradient approximation.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Dissocation energies of charge tranfer dimers calculated with the ANO-L-VTZP basis set. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00456.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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