Charge Transfer Excitations in TDDFT: A Ghost-Hunter Index

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This work presents a new index, M_{AC}, enabling the on-the-fly detection of ghost charge transfer (CT) states, a major problem in time-dependent density-functional theory calculations. This computationally inexpensive index, derived as a modification of the Mulliken estimation of transition energy for CT excitations, relies on two basic ingredients: an effective CT distance, computed using our density-based index (D_{CT}), and an orbital weighted estimation of the Ionization Potential and Electron Affinity. Some model systems, representative of both intermolecular and intramolecular CT excitations, were chosen as test cases.

The robustness of our approach was verified by analyzing the behavior of functionals belonging to different classes (GGA, global hybrids and range separated hybrids). The results obtained show that ghost states are correctly spotted, also in the delicate case of intramolecular excitations displaying substantial donor-bridge-acceptor delocalization, in a regime for which the standard Mulliken formulation attends its limits. © 2017 Wiley Periodicals, Inc.

Introduction

Time-dependent density-functional theory (TDDFT)[1] extends the fundamental ideas of the ground state density-functional theory (DFT)[2] to excited electronic states. As for DFT, TD-DFT equations are simple to tackle numerically, and they can be routinely solved for systems with a large number of electrons. Indeed, this method represents a sophisticated, yet moderately expensive tool to calculate excited states properties for a large variety of molecules in the gas-phase, in solution or even in more anisotropic environments (see for instance Refs. [3 and 4]).

Nevertheless, TD-DFT has a number of drawbacks, as deeply discussed in literature (see for instance Refs. [5–7]). In particular, TD-DFT is quite ineffective in describing (long-range) charge transfer (CT) excitations,[8] a class of electronic transitions of particular importance in chemistry. Indeed, these transitions play a key role in many systems of relevance for biological and/or technological application, such as, for instance, light-harvesting complexes in plants and bacteria or as semi-conductor polymers.[9,10]

As matter of fact, short-range CT transitions, such as those occurring in some transition metal complexes (see for instance Ref. [11]) can be reproduced with an acceptable error ($<$ 0.2 eV in the UV-vis range) at TDDFT level. However, at larger CT distances deviations w.r.t. experimental data could be significantly higher ($>$ 0.2 eV). Not surprisingly, the accuracy of TD-DFT calculations depends on the hole-electron distance at the excited state and, more generally, on the "trough space" character of the electronic transitions involved.

In particular, it has been shown how the error associated to CT is related to the incorrect $1/r$ asymptotic behavior,[12,13] r being the nucleus-electron distance, and to the missing derivative discontinuity[14] of the approximate exchange-correlation functional used. This error can be particularly relevant for functionals resting on the generalized gradient approximation (GGA).[15] These drawbacks are mitigated using global and range-separated hybrid (GH and RSH) functionals, which introduce, in a different way, a fraction of Hartree–Fock (HF)-like exchange.[16] Even better results can be obtained by less-standard and more computationally demanding methods, such as for instance by tuning the RSH functional on the system under investigation.[17] Unfortunately, the excitation energies provided are often overestimated by RSH and not always of sufficient quality to allow for a quantitative agreement with the experimental spectra,[18] so that most calculations still resort on the use of GH which are those still potentially affected by error in the estimation of CT transitions.

Beside an erroneous evaluation of electronic energies, which can be monitored by dedicated diagnostic indexes,[19–22] the above mentioned approximation leads TD-DFT to be affected by another major drawback: the appearance of low-lying CT ghost states energetically well below the bright (real) state of a given system for both intermolecular and intramolecular excitations.[23] This spurious effect can be very important for the interpretation and prediction of the spectroscopic properties of a given molecular system as it would suggest, for instance, that an energetically higher bright state could decay non-radiatively into the lower CT states, leading to an electron-transfer quenching of the excited-state fluorescence. In other words, the limitations of the TD-DFT model used have an impact that is much larger than its numerical performances (i.e., the error in computed transition energies w.r.t. a given reference) leading to a wrong

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interpretation of the photophysical behavior of the system under investigation. The undesirable consequences for chemical applications of these computational models are evident.

The existence of these low-lying CT states, referred to as "ghost" states, was discussed in the seminal works of Dreuw and Head-Gordon.[23,24] In the case of a donor (D)–acceptor (A) system, these authors shown that TD-DFT transitions do not satisfy the relation for the (long-range) CT excitation energy, that is:

$$\omega_{CT} = IP_D - EA_A - \frac{1}{R} \tag{1}$$

In this formula, originally proposed by Mulliken,[25] ω_{CT} represents the excitation energy for a net one electron transfer from the donor (D) to the acceptor (A) placed at a distance R. In eq. (1), IP is the ionization potential of D, EA the electron affinity of A, and $1/R$ the Coulomb interaction, expressed in atomic units. This simple and intuitive relation can be considered as a lower energetic bond for a true CT transition and it has been used to verify the nature of the TD-DFT excitations in model systems.[16,23,24,26]

Up to now, this equation has been applied in the case of CT systems considering as R the geometrical distance between the donor and acceptor units and evaluating IP and EA from the Koopmans' theorem (i.e., from HOMO and LUMO orbital energies), mainly in model systems.[16,23]

In this context, with the aim of providing a simple and robust reliable tool for the detection of ghost CT states in TDDFT, we present here a new descriptor, relying on the Mulliken's relationship [eq. (1)] and using our CT index[27] (D_{CT}) to evaluate the CT distance R. The validity and robustness of this descriptor, which has been called M_{AC}, acronym of *Mulliken averaged configuration* (see infra), have been tested on selected model systems, already used in literature as peculiar cases to analyzed TD-DFT performances in evaluating CT transitions.[23,24,28]

Theory and Computational Details

The M_{AC} index is derived from the original Mulliken formula [eq. (1)]. To have a realistic estimate of the hole-electron distance, R, the D_{CT} index has been used. This last index is computed as the distance between the two barycenters of the spatial regions corresponding to an increase and to a decrease of the electron density on excitation as detailed in Ref. [27]. It represents, in a very realistic and intuitive fashion, the effective (average) charge/hole distance associated to an electronic excitation. Furthermore, as a given electronic transition could be the combination of different one-electron excitations, IP_D and EA_A of eq. (1) will be approximated as a weighted average of the starting (ε_i) and final (ε_a) Kohn–Sham orbital energies, in analogy with the Koopmans' theorem. Taking all this into account, and casting the D_{CT} into eq. (1), the following expression is obtained:

$$M_{AC} = \sum_{ia} \frac{C_{ia}(-\epsilon_i - \varepsilon_a)}{\sum_{ia} C_{ia}} - \frac{1}{D_{CT}} \tag{2}$$

where the used weights for IP_D and EA_A (C_{ia}) are the CI coefficients obtained as solution of TD-DFT equations,[29] and R is substituted

by the effective D_{CT} distance computed for each electronic transition. A given TD-DFT transition will be, therefore, identified as ghost (and discharged) if its energy is lower than the corresponding *Mulliken averaged configuration* (M_{AC}) index while proper CT excitations will have an energy greater than M_{AC}, that is for each electronic transition

$$\text{if } E_{TDDFT} < M_{AC} => \text{ghost CT state}$$

$$\text{if } E_{TDDFT} > M_{AC} => \text{real CT state} \tag{3}$$

Only transitions with sufficient CT character will be discussed, due to relevance of the Mulliken formula for this specific case.

All structures were optimized using the PBE0 functional[30] and the 6-31G(d,p) basis set. They were characterized as energy minima by computing harmonic vibrational frequencies. Single point calculations were subsequently carried out at the TD-DFT level to compute vertical excitation energies, as well as D_{CT} and M_{AC} descriptors using the ground state structures. When not differently specified TDDFT calculations were performed using the PBE0, PBE,[31] and LC-PBE[32] functionals and the 6-31G(d,p) basis set. Reference calculations were performed at CIS level, on the same ground state structures, using the 6-31G(d,p) basis.

Details concerning the calculations of the D_{CT} index are reported in the original work.[27] All calculations were performed with a development version of the Gaussian program,[33] while the evaluation of the M_{AC} parameter is performed using the freely distributed software WurStEl (see www.quanthic.fr). The D_{CT} index can be directly computed using the commercial release of the Gaussian software.[34]

Results and Discussion

To test the reliability of M_{AC} index, first the zinc bacteriochlorin-bacteriochlorin (ZnBC-BC), a model system used for study intermolecular long range CT,[24] will be discussed. Here, the donor (ZnBC) and the acceptor (BC) are coplanar and placed at a distance of 5.8 Å (see Fig. 1). These two moieties are electronically not coupled, and the orbitals involved in the lowest electronic transitions are clearly localized on only one of the two (D or A) parts.[24] The calculations were carried out using the PBE0 functional[30] as the behavior of different DF approximations, ranging from GGA to RSH, has been already well described in literature.[35] All results are reported in Table 1.

The general picture emerging from the PBE0 results is coherent with previous theoretical analysis, with alternating CT and valence excitations ($\pi \rightarrow \pi^*$), localized on only one of the two moieties. In the present case, however, just one CT state appears at lower energy, while GGA functionals predict at least four ghost states at low energies.[24] Comparison of the M_{AC} index (4.56 eV) and transition energy (1.96 eV) computed for the first excited state allows to class it as ghost CT state [following eq. (3)]. Notwithstanding, RSH,[35] the symmetry adapted cluster configuration interaction method[36] and experiments[37] all agree in pointing out this TDDFT predicted CT state is indeed a ghost, in agreement with the M_{AC} based diagnostic.
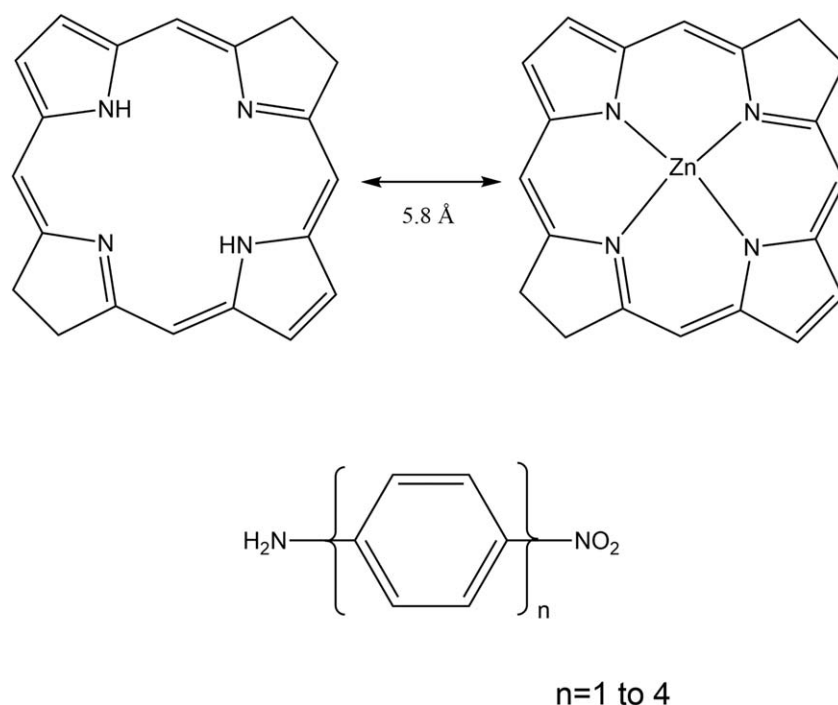
5.8 Å

n=1 to 4

Figure 1. Sketches of the molecules analyzed: upper panel) zinc bacteriochlorin-bacteriochlorin; lower panel) the push-pull family of molecules considered.

The second and third transitions are valence excitations π-π*, localized either on the ZnBC or on BC moieties, corresponding to the so-called Qx band. Consequently, for these states a very small D_{CT} index is computed. The Qy band appears at slight high energy, but is preceded by another ghost state. Analogously, the sixth and seventh excited states are classed as ghosts, the first real CT state occurring higher in energy, at 3.32 eV.

In short, these calculations on a model system show that the M_{AC} index can easily identify ghost states at D–A distance for which the Mulliken's relation [eq. (1)] is valid. This is the far-nucleus asymptotic regime defined by Hirao and cow-orkers,[16] which in our cases corresponds to $D_{CT} > 5$ Å. At the same time, it should be pointed out that the hole-electron distance in this specific model can be roughly estimated as the

geometrical distance between the D and A moieties as previously done in literature. Indeed, the edge-to-edge distance (5.8 Å) is not too far from the D_{CT} values computed for the CT transitions (6.5–6.6 Å).

Real chemical systems are, however, a more difficult playground, as holes and electrons are often not clearly localized, due to electronic conjugation/delocalization effects. The

Table 1. Excitation energies (E, in eV), Mulliken averaged configurations index (M_{AC} in eV), charge transfer index (D_{CT} in Å), and assignment, for the first 10 electronic transitions of the zinc bacteriochlorin-bacteriochlorin complex.

State	E (eV)	M_{AC} (eV)	D_{CT} (Å)	Assignment
1	1.97 (1.94)	4.56 (5.03)	6.62 (6.64)	Ghost
2	2.06 (2.00)	–	0.37 (0.29)	$\pi \rightarrow \pi$*
3	2.11 (2.06)	–	0.17 (0.56)	$\pi \rightarrow \pi$*
4	2.13 (2.10)	4.69 (5.16)	6.64 (6.67)	Ghost
5	2.54	–	0.69	$\pi \rightarrow \pi$*
6	2.58	–	1.28	$\pi \rightarrow \pi$*
7	2.72	5.24	6.52	Ghost
8	2.81	5.37	6.53	Ghost
9	3.32	3.17	6.52	CT
10	3.42	–	1.34	$\pi \rightarrow \pi$*

The values have been computed at the PBE0/6–31G(d) level of theory, while the values in parentheses have been obtained with the -larger- 6-31++G(d,p) basis set, to check for basis set dependence.
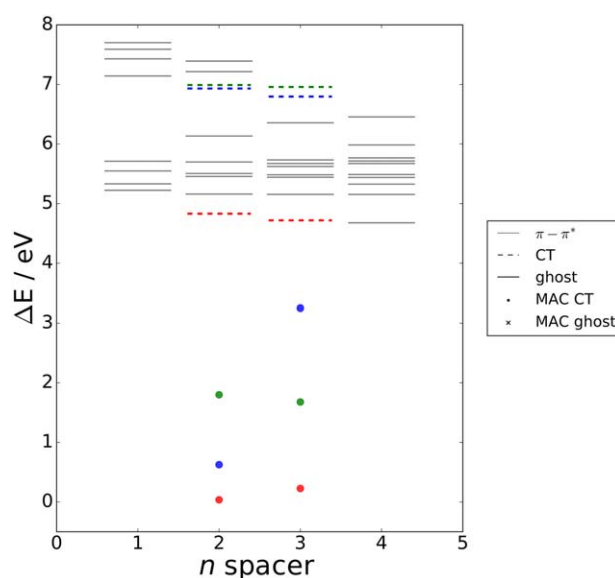

Figure 2. Excitation energies (straight lines) and M_{AC} parameters (dots and stars) computed for CT transitions and evaluated at the CIS level for the model push-pull family of molecules. M_{AC} values and TD-DFT energies associated to the same electronic transition are depicted with the same color. The values are reported as a function of spacers' number (n). [Color figure can be viewed at wileyonlinelibrary.com]
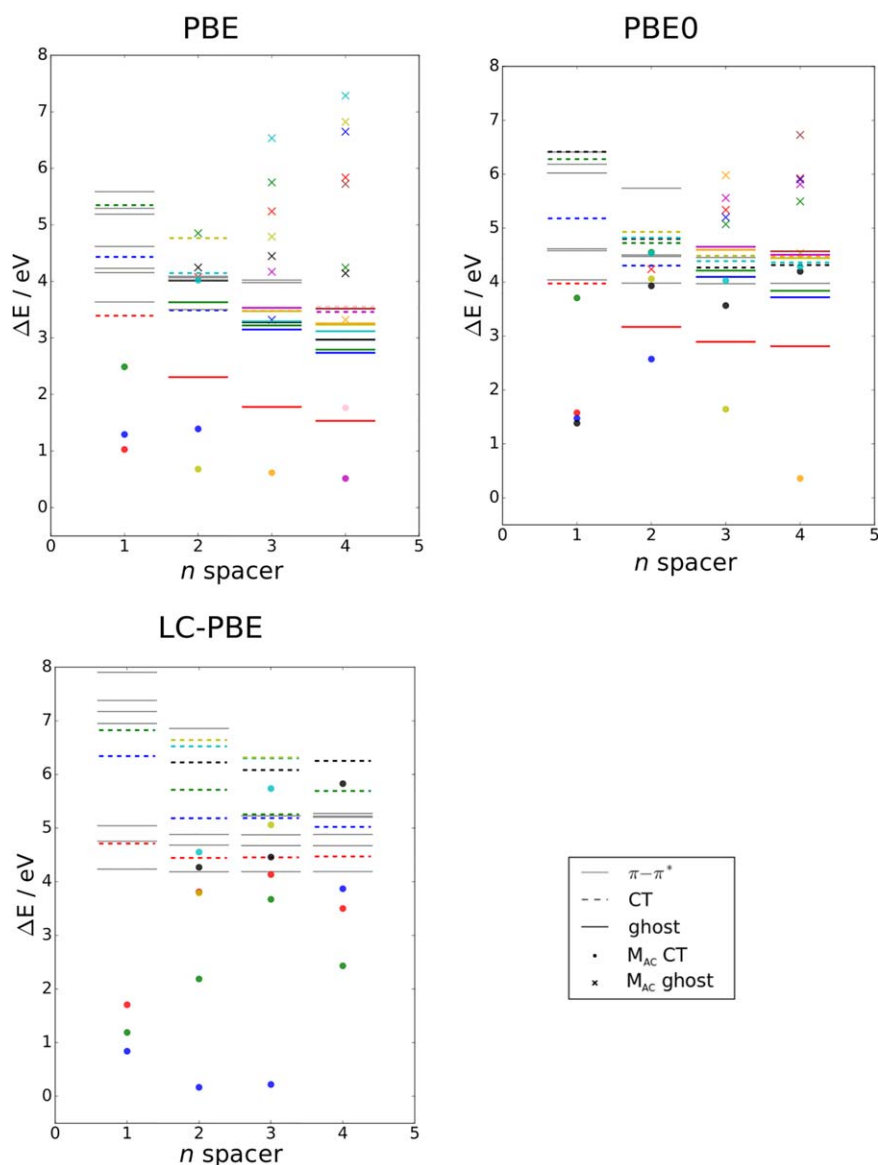
Figure 3. Excitation energies (straight lines) and M_{AC} parameters (dots and stars) computed for CT transitions and evaluated at TDDFT level using different functionals for the model push-pull family of molecules considered (see Fig. 1). M_{AC} values and TD-DFT energies associated to the same electronic transition are depicted with the same color. The values are reported as a function of spacers' number (n). [Color figure can be viewed at wileyonlinelibrary.com]

effective CT distance is therefore more difficult to be evaluated in terms of geometrical parameters only. Push-pull systems, such as the one reported in Figure 1, can be considered as prototypes of donor–acceptor molecular dyads where D and A moieties are partially coupled via a –phenyl- bridge, allowing π electron delocalization. In this case, the CT character associated to the lowest excitation is modulated by the number of spacer present in the molecule. Indeed, up to two phenyl spacers the first transition has a CT character while for a greater number of spacers the bright transition shows a more localized π-π* character.[28] For this class of molecules, TD-DFT calculations were carried out using the PBE GGA functional and its GH (PBE0) and RSH (LC-PBE) counterparts.[30–32] CIS calculations have been also carried out on the same systems to get both M_{AC} and transition energy reference values. It is worth to mention that the CIS method is known to yield a

systematic bias in evaluating the energies of CT excitations.[38] Nonetheless, this method shows the correct $1/r$ limiting behavior[16] and respects the Mulliken's rule [eq. (1)]. No ghost states are, therefore, expected using such an approach. The relevant parameters that will be discussed in the following to evaluate if the M_{AC} index is suitable or not to detect ghost state will be only the relative order and nature of the electronic transitions as well as the M_{AC} and TDDDT energy values, rather than the absolute transition energies.

The CIS results are plotted in Figure 2, while the corresponding values are reported in Supporting Information (Table S1). The smallest push-pull molecule ($n = 1$) show no low lying CT excitations, all transitions having a $\pi \rightarrow \pi$* character and a low D_{CT} value, due to the strong electronic coupling between D, A, and the π aromatic system of the phenyl spacer. CT states appear instead for molecules containing two and three

phenyls ($n = 2$ and 3, see Fig. 1). All these CT states respect the condition given in eq. (3), that is their CIS computed energy is higher than the corresponding M_{AC} value. For the largest system ($n = 4$), the nature of the excitations drastically change, all having a clear $\pi \rightarrow \pi^*$ character as demonstrated by the computed D_{CT} value, and as already discussed in literature for similar push-pull conjugate molecules.[27]

The excitation energies and corresponding M_{AC} values computed using the PBE, PBE0 and LC-PBE functionals for the same push-pull family of molecules are reported in Figure 3. The corresponding raw values are collected in Supporting Information (Table S1). The three functionals provide a similar picture of the absorption spectrum of the smallest system ($n = 1$), with an alternation of $\pi \rightarrow \pi^*$ and CT transitions (see Supporting Information Table S1). More importantly, no ghost transitions are present in this case and the overall picture is in agreement with CIS results. When two phenyl spacers are present ($n = 2$) ghost states start to appear at low energies for PBE (3 states). Their number increases for $n = 3$ (7 states) and $n = 4$ (8 states), in parallel with the corresponding D_{CT} values. These states, whose energy is always lower than the corresponding M_{AC} [cf., eq. (3)], are often grouped within few tenths of eV (see Supporting Information Table S1). When using PBE0, the presence of a fraction of HF exchange mitigates this effect, partially reducing the number of ghost states: 1 for $n = 2$, to 5 for $n = 3$, and 6 to for $n = 4$ (see Fig. 3). Finally, the LC-PBE approach, which recovers the correct $1/r$ behavior, presents, as expected, no ghost states in the case of all push-pull molecules considered.

These results confirm the robustness of the M_{AC} index for intermolecular CT excitations, even for D_{CT} values lower than the far-nucleus asymptotic regime threshold. Nonetheless, it should be pointed out that, while R, the distance between the donor and acceptor (here represented by the geometrical distance between the amino and nitro nitrogen atoms), ranges from 5.6 Å (for $n = 1$) to 18.5 Å ($n = 4$), the corresponding CT distances (D_{CT}) used to compute the M_{AC} are significantly shorter, due to the significant electronic coupling between donor, acceptor, and spacer(s). Indeed, in the smallest push-pull system ($n = 1$) the largest D_{CT} value computed is 2.0 Å (first CT transition), while the highest value is computed for the tenth transition for the largest molecules ($n = 4$, $D_{CT} = 6.6$ Å), still far from the geometrical distance between donor and acceptor in such systems.

These data clearly show the importance of the evaluation of an effective CT distance (using the D_{CT}) over the use of a simple geometrical distance especially in the case of systems possessing intramolecular CT excitations, when electron delocalization/conjugation can play a relevant role. Finally, it is worth stressing that especially higher energy excitations can possess a non-negligible multi-determinant character so that the weighted average, performed when computing the M_{AC} index, is relevant for a correct estimation of IP and EA.

Conclusions

In this work, we have presented a new index (M_{AC}) that is able to detect ghost CT states, a major problem in TDDFT calculations. This index was tested in the case of model systems

representative of both intermolecular and intramolecular CT excitations also for cases out of the Hirao's regime and therefore of the validity of the original Mulliken's formulation. In all the considered cases, our descriptor was able to spot the ghost states, also in the case where the electronic features of the molecules (i.e., electronic delocalization) do not allow for *a priori* geometrical evaluation of the donor–acceptor distance. The widespread use of GGA and GH functionals, many of them providing accurate electronic absorption energies for valence excitations, can be made "safer" by the use of this descriptor. Of note, the evaluation of this index is rather computationally inexpensive and, even if in the present analysis relaxed ground and excited state densities have been used to evaluate the D_{CT} distance, work is in progress to compute the M_{AC} index directly from unrelaxed excited state density.

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