Charge transfer excitations from excited state Hartree-Fock subsequent minimization scheme

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Photoinduced charge transfer processes play a key role for novel photovoltaic phenomena and devices. Thus, the development of ab initio methods that allow for accurate and computationally inexpensive treatment of charge transfer excitations is a topic that attracts nowadays a lot of scientific attention. In this paper we extend an approach recently introduced for the description of single and double excitations (M. Tassi, I. Theophilou and S. Thanos, Int. J. Quantum Chem., 113, 690 (2013), M. Tassi, I. Theophilou and S. Thanos, J. Chem. Phys. 138, 124107 (2013)) to allow for the description of intermolecular charge transfer excitations. For the description of an excitation where an electron is transferred from a donor system to an acceptor one, it is necessary to keep the excited state orthogonal to the ground state in order to avoid variational collapse. These conditions are achieved by decomposing the space spanned by the Hartree-Fock (HF) ground state orbitals into four subspaces: The subspace spanned by the occupied orbitals that are localized in the region of the donor molecule, the corresponding for the acceptor ones and two more subspaces containing the virtual orbitals that are localized in the neighborhood of the donor and the acceptor respectively. Next, we create a Slater determinant with a hole in the subspace of occupied orbitals of the donor and a particle in the virtual subspace of the acceptor. Subsequently we optimize both the hole and the particle by minimizing the HF energy functional in the corresponding subspaces. Finally, we test our approach by calculating the lowest charge transfer excitation energies for a set of tetracyanoethylene-hydrocarbon complexes, that have been used earlier as a test set for such kind of excitations.

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I. INTRODUCTION

Organic photovoltaics have received recently a great deal of attention, as they have the potential of harvesting solar light cheaply and easily\textsuperscript{1}. For this purpose a lot of scientific effort has been devoted to simulating some of the fundamental steps occurring in natural photosynthesis, one of the most important being the photoinduced charge separation\textsuperscript{2}. Thus, it is a major task of the scientific community to develop methods that can reliably and inexpensively describe charge transfer (CT) excitations, where light absorption causes a charge transfer from a donor to an acceptor. The donor-acceptor system, consists of either two or more different molecules that interact weakly or two sites of the same big molecule. In this work we shall deal with the first mentioned class of donor acceptor complexes.

Although TDDFT\textsuperscript{3–5} is currently successfully applied for the description of excitations of large molecular systems, charge transfer excitations in the linear response regime with standard time-independent exchange-correlation kernels exhibit significant failures, giving underestimations of several eV\textsuperscript{6,7}. This failure is attributed to the wrong asyymtotic shape of ground-state xc potentials, which leads to errors in orbital energies.\textsuperscript{8} Moreover, the Kohn-Sham orbital overlaps of the donor—acceptor system that enters the exchange-correlation part of the Dyson equation vanish using non-hybrid xc kernels, having as a consequence the charge transfer energy to be given as the orbital energy difference\textsuperscript{9}. Currently, there is a lot of effort on the development of exchange correlation kernels that mitigate this deficiency\textsuperscript{10–14}. Using the range-separated hybrid functionals\textsuperscript{10,14}, where the exchange functional is split in two terms, one of short-range that is represented by a LDA or GGA potential and one of long-range that is treated via an exact exchange term, improve the results obtained with TDDFT for charge transfer excitations. In this case one has to determine the range-splitting parameter. This is done either empirically by fitting to a set of data\textsuperscript{12} or by introducing a system dependent parameter by tuning the homo orbital close to minus the ionization potential\textsuperscript{14}. A time-independent variational approach of DFT, that is not based on response theory, termed relaxed constrained-variational DFT, gives promising results on charge transfer excitations\textsuperscript{15}. In this case, the charge constraint is imposed on a region of the orbital space. There is also a constrained-variational DFT scheme where the charge is constrained in real space\textsuperscript{16}. Recently, a perturbative-\textDelta SCP\textsuperscript{20} approach has been developed, where a non-Aufbau occupation of the density during a normal self consistent field optimization is
enforced as in traditional $\Delta$SCF\textsuperscript{21}, in combination with perturbation theory, giving for the systems tested a good description of excitations in donor-acceptor complexes.

Recently, a variational approach was introduced, based on solving the Unrestricted Hartree-Fock\textsuperscript{25} eigenvalue equations in different subspaces spanned by the occupied and virtual ground state orbitals\textsuperscript{22}. In this approach, an excited state was considered with a hole in the subspace of the occupied orbitals and a particle in the subspace of virtual orbitals, where both were determined variationally. Conceptually, this scheme is close to the $\Delta$SCF one, however within this scheme there is no possibility of a variational collapse to the ground state, as it may happen in $\Delta$SCF, since the state defined in this way, is always orthogonal to the ground state. In a recent paper an extension of this approach was given which includes double excitations\textsuperscript{23}. In the current work in order to study an excitation where an electron is transferred from a donor system to an acceptor one, it is necessary to take into account not only orthogonality, but also the localization of orbitals in the donor and acceptor regions, with some overlap in the intermediate region. For this purpose we create four subspaces: one that belongs to the occupied orbitals that are localized mostly in the donor region and a similar one of the virtual ones. A third set consists of the occupied orbitals localized in the neighborhood of the acceptor and a fourth set is spanned by the virtual ones. See Fig.\textit{(1)} for an example where the donor side contains three occupied orbitals and four unoccupied ones in the respective subspaces and the acceptor side provides two occupied and five unoccupied orbitals. Next, we describe the electron transfer excited state by a Slater determinant with a hole in the donor occupied subspace and a particle at the acceptor virtual subspace and both, the particle and the hole, are determined variationally by minimizing the Hartree Fock functional. In this way we are able to calculate intermolecular charge transfer excitations. More details will appear in the next section. We applied our scheme on a series of TCNE-various donors systems that have been used before\textsuperscript{14,15,20,21} and found that our results compare well with the experimental ones. This paper is organized as follows: In section II we explain the main idea of this approach and give the equations used for its realization. In section III we examine the performance of this scheme in obtaining charge transfer excitation energies and we show that at least for the system tested, it can provide a good description. Finally, in section IV we give our concluding remarks.
II. RESTRICTIONS TO THE CHARGE TRANSFER EXCITED STATE ORBITALS

Let us consider an excitation of one electron from the donor to the acceptor. We assume that the excited electron is a spin up one and for simplifying our notation we shall omit the spin index when we refer to spin up. All the orbitals derived from the Hartree-Fock ground state calculation, which will be denoted by \( \varphi_j \), are used to build two orthogonal subspaces, \( S^D \), consisting of the orbitals \( \varphi^D \) that are localized mostly in the donor and \( S^A \) of orbitals similarly localized mostly in the acceptor system \( \varphi^A \). This classification is performed by summing for each orbital \( \varphi_j \), its projections on the gaussians centered in the donor or correspondingly in the acceptor. Thus, in order to check whether the orbital \( \varphi_i \) is more localized in the area of the donor or the acceptor, we calculate the sum of the overlaps \( \sum_k |\langle g_k | \varphi_i \rangle|^2 \) with \( k \) running over all gaussians \( |g_k\rangle \) centered in the donor or the acceptor system. Then, depending on which sum is bigger, we attribute the orbital \( \varphi_j \) to the donor or acceptor subspace. When donor and acceptor are not molecules of the same type an orbital cannot have exactly equal projections on both the donor and the
acceptor. Next, we further separate $S^D$ to a subspace $S^{D\text{occ}}$ spanned by the occupied orbitals $\{\varphi^D_1, .., \varphi^D_{N^D\text{occ}}\}$ and $S^{D\text{vir}}$ of the virtual ones $\{\varphi^D_{N^D\text{occ}+1}, .., \varphi^D_{N^D}\}$. Similarly $S^A$ consists of $S^{A\text{occ}}$ spanned by $\{\varphi^A_1, .., \varphi^A_{N^A\text{occ}}\}$ and $S^{A\text{vir}}$ of virtuals of the acceptor $\{\varphi^A_{N^A\text{occ}+1}, .., \varphi^A_{N^A}\}$. The subspace dimensions are denoted by $N^D$ for $S^D$, $N^A$ for $S^A$, and correspondingly by $N^A$, $N^{A\text{occ}}$. The charge transfer excited state orbitals that are localized in the donor system are denoted by $\chi^D_i$ and the ones that are localized in the acceptor by $\chi^A_i$. Then, we demand that the excited state $|\Phi_{CT}\rangle = |\chi^D_1, .., \chi^D_{N^D\text{occ}-1}, \chi^A_1, .., \chi^A_{N^A\text{occ}+1}\rangle$ has one more electron in $S^{A\text{vir}}$, than the ground HF and one hole in $S^{D\text{occ}}$. Thus, in addition to the normalization of the orbitals the following conditions should be satisfied:

i) $\langle \chi^D_i | \varphi^A_j \rangle = 0$ for $i \leq N^D_{\text{occ}} - 1$ and $j = 1, .., N^A$

ii) $\langle \chi^D_i | \varphi^D_j \rangle = 0$, for $i \leq N^D_{\text{occ}} - 1$ and $j \geq N^D + 1$

The two relations above imply that the excited orbitals $\chi^D_1, .., \chi^D_{N^D_{\text{occ}}-1}$ belong to the subspace $S^{D\text{occ}}$.

iii) $\langle \chi^A_{N^A_{\text{occ}}+1} | \varphi^A_j \rangle = 0$, for $j \leq N^A_{\text{occ}}$

iv) $\langle \chi^A_{N^A_{\text{occ}}+1} | \varphi^D_j \rangle = 0$, for $j = 1, .., N^D$

Relations (iii) and (iv) imply that $|\Phi_{CT}\rangle$ comprises one orbital named $\chi^A_{N^A_{\text{occ}}+1}$ that belongs to $S^{A\text{vir}}$.

v) $\langle \chi^A_i | \varphi^A_j \rangle = 0$, for $i \leq N^A_{\text{occ}}$ and for $j > N^A_{\text{occ}}$ and

vi) $\langle \chi^A_i | \varphi^D_j \rangle = 0$, for $i \leq N^A_{\text{occ}}$ and for $j=1, .., N^D$

Relations (v) and (vi) imply that the excited orbitals $\chi^A_1, .., \chi^A_{N^A_{\text{occ}}}$ belong to $S^{A\text{occ}}$.

Minimizing the energy functional $\langle \Phi_{CT} | \dot{\hat{H}} | \Phi_{CT} \rangle$, under the above conditions, taking also into account the orbital normalization, one gets the following set of one particle equations:

\begin{equation}
\hat{F}|\chi^D_i\rangle - \sum_{j \leq N^A} |\varphi^A_j\rangle \langle \varphi^A_j | \hat{F} |\chi^D_i\rangle - \sum_{j > N^D_{\text{occ}}} |\varphi^D_j\rangle \langle \varphi^D_j | \hat{F} |\chi^D_i\rangle = \epsilon^D_i |\chi^D_i\rangle , \quad \text{for } i < N^D_{\text{occ}}
\end{equation}

As usually, the Fock operator $\hat{F}$ corresponding to $\Phi_{CT}$ is defined by the following equation

\begin{equation}
(\hat{F}^s \chi^s_i)(\mathbf{r}) = \hat{h}\chi^s_i(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho_s(\mathbf{r}', \Phi_{CT})}{|\mathbf{r} - \mathbf{r}'|} \chi^s_i(\mathbf{r}') - \int d\mathbf{r}' \frac{\rho_s(\mathbf{r}, \mathbf{r}'; \Phi_{CT})}{|\mathbf{r} - \mathbf{r}'|} \chi^s_i(\mathbf{r}')
\end{equation}

where $\hat{h}(\mathbf{r}) = \frac{1}{2}\nabla^2 + \hat{V}(\mathbf{r})$ is the kinetic plus external potential operator, which is the same as the one of the UHF ground state and $\rho_s(\mathbf{r}, \mathbf{r}'; \Phi_{CT})$ is the spin density matrix of $|\Phi_{CT}\rangle$:

\begin{equation}
\rho_s(\mathbf{r}, \mathbf{r}'; \Phi_{CT}) = \sum_{i=1}^{N^s} \chi^s_i(\mathbf{r}) \chi^s_i(\mathbf{r}')
\end{equation}
where $N_s$ stands for the number of orbitals with $s \uparrow$ or $\downarrow$. Finally, $\rho(r; \Phi_{CT}) = \rho_\uparrow(r, r; \Phi_{CT}) + \rho_\downarrow(r, r; \Phi_{CT})$. We used the notation $(\hat{F}s_i^s)(m)$ to show that $\hat{F}s$ maps a function and not its value to another function in order to account for the nonlocal operator. The
\[
\sum_{j>N_{occ}^D} |\varphi_j^D\rangle\langle\varphi_j^D| \text{ and the } \sum_{j\leq N_A} |\varphi_j^A\rangle\langle\varphi_j^A| \text{ are projection operators in the subspaces } S_{vir}^D \text{ and } S_{A}^A \text{ respectively, which act as identity operators in the corresponding subspaces.}
\]

The second sum that appears in Eqs. 4, 5 correspond to the projection operator in $S^D$ and the first sums to projections in $S_{occ}^A$ and $S_{vir}^A$ respectively. Then the left hand side of Eq.1 can be identified as the projection of the Fock operator in the subspace of the occupied orbitals of the donor, Eq.4 as the projection of the Fock operator in the virtual orbitals of the acceptor and Eq.5 as the projection of the Fock operator in the occupied orbitals of the acceptor.

The equation for the spin down orbitals has the usual UHF form \(^{25}\) i.e.
\[
\hat{F}^\downarrow|\chi_i^\downarrow\rangle = \epsilon_i^\downarrow|\chi_i^\downarrow\rangle
\]
since no constraints are imposed beyond that of normalization. Note however that these orbitals are not identical to those of the UHF ground state since the Hartree term changes because it includes the density of the spin up particles. Since we assumed that the electron which gives the charge transfer excited state is an up electron, the Fock matrices in Eqs.1,4,5 are Fock matrices of spin up, with the spin up index dropped throughout the text in order to simplify our notation.

As mentioned earlier, the left hand side of Eqs.1, 4, 5 is nothing more than the projection of the Fock matrices in the subspaces $S_{occ}^D$, $S_{vir}^A$ and $S_{occ}^A$ respectively, forcing our one electron eigenvalue equations to have solutions that belong to these subspaces, making it possible to avoid using Lagrange multipliers. This is achieved by constructing the Fock matrices using as basis set the ground state HF orbitals that span the corresponding subspaces. For more
Once we manage to restrict the Fock operator in the subspaces $S_{\text{occ}}^D$, $S_{\text{vir}}^A$ and $S_{\text{occ}}^A$ the Eqs.1,4,5 assume the following simple form:

\[
\hat{F}_{\text{occ}}^D |\chi_i^D\rangle = \epsilon_i^D |\chi_i^D\rangle \quad (7)
\]

\[
\hat{F}_{\text{vir}}^A |\chi_i^A\rangle = \epsilon_i^A |\chi_i^A\rangle \quad (8)
\]

\[
\hat{F}_{\text{occ}}^A |\chi_i^A\rangle = \epsilon_i^A |\chi_i^A\rangle \quad (9)
\]

Thus, from the $N^D - 1$ lowest energy solutions of Eq.7, the lowest energy solutions of Eq.8 and all the solutions of Eq.9 we can find the the $N^D - 1 \chi_i^D$, the $\chi_{N_{\text{occ}}^A + 1}^A$ and the $\chi_1^A, ..., \chi_{N_{\text{occ}}^A}^A$ orbitals of $|\Phi_{\text{CT}}\rangle$. Thus, one has to self consistently solve the system of Eqs.7, 8, 9 together with the equation for the down orbitals 6. The determinant $|\Phi_{\text{CT}}\rangle$ that corresponds to the approximate eigenstate of the excited charge transfer state will be orthogonal to the ground state one, i.e. $\langle \Phi_0|\Phi_{\text{CT}}\rangle = 0$. This is true since the highest occupied orbital of the acceptor in $|\Phi_{\text{CT}}\rangle$ belongs to $S_{\text{vir}}^A$, thus this orbital by construction has zero overlap with all the ground state occupied orbitals.

The next step is to express the Fock operators that appear in the eigenvalue equations above in some matrix form in order to do the appropriate numerical calculations. Since any basis set we use to do this expansion will lead to an eigenvalue problem giving the same results (as long as the basis is complete), we can use the ground state orbitals that span the subspaces $S_{\text{occ}}^D$, $S_{\text{vir}}^A$ and $S_{\text{occ}}^A$ and express the Fock matrices of equations 7, 8, 9. In this way the matrix elements of the new Fock matrix $F_{\text{occ}}^D$, $F_{\text{vir}}^A$, $F_{\text{occ}}^A$ with respect to the ground state orbitals are:

\[
F_{\text{occ},i,j}^D = \langle \varphi_i | \hat{F} | \varphi_j \rangle \text{ where } \varphi_i, \varphi_j \in S_{\text{occ}}^D \quad (10)
\]

\[
F_{\text{vir},i,j}^A = \langle \varphi_i | \hat{F} | \varphi_j \rangle \text{ where } \varphi_i, \varphi_j \in S_{\text{vir}}^A \quad (11)
\]

\[
F_{\text{occ},i,j}^A = \langle \varphi_i | \hat{F} | \varphi_j \rangle \text{ where } \varphi_i, \varphi_j \in S_{\text{occ}}^A \quad (12)
\]

It is worth to note that one could also treat charge transfer excitations where more than one electrons are transferred from the donor to the acceptor system. The only difference in the treatment is to introduce two or more excited state orbitals from $S_{\text{vir}}^A$ and to create two or more holes respectively in the subspace of $S_{\text{occ}}^D$. 

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Table I. Charge transfer excitation energies (eV) for \( \pi \) donor to \( \pi^* \) (TCNE) transitions in donor-TCNE complexes in gas phase

| Donor       | TDDFT-B3LYP \(^a\) | TDDFT-BNL\(\gamma^b\) | \(\Delta\text{SCF}^c\) | This work | Exp\(^d\) |
|-------------|---------------------|------------------------|--------------------------|------------|----------|
| Benzene     | 2.1                 | 3.80                   | 3.30                      | 3.46       | 3.59     |
| Toluene     | 1.8                 | 3.40                   | 3.60                      | 3.16       | 3.36     |
| O-xylene    | 1.5                 | 3.00                   | 2.62                      | 2.89       | 3.15     |
| Naphtalene  | 0.9                 | 2.70                   | 2.26                      | 2.61       | 2.60     |

\(^a\) Taken from Ref.\(^{14}\)  
\(^b\) Range-split BNL functional from Ref.\(^{14}\)  
\(^c\) Taken from Ref.\(^{15}\)  
\(^d\) Experimental gas-phase data from Ref. \(^{18}\)

We stress the fact that all orbitals that contribute to \( \Phi_{CT} \) are obtained by one electron eigenvalue equations where they are "repelled" correctly by an electrostatic charge of \( N - 1 \) electrons. This is in contrast to HF virtual orbitals which are artificially diffused as they are repelled by \( N \) electrons. Occupying the HF virtual orbitals without further minimization, as it is well known, would lead to large excitation energies.

III. RESULTS AND DISCUSSION

The approach developed in section II was applied in order to calculate the charge transfer excitation energies of a test set of various aromatic donor - TCNE complexes and Anthracene substituted derivatives - TCNE, for which experimental results are available. This test set was introduced by Stein et al.\(^{14}\) to examine the performance of their dual-range functional in charge transfer excitations. Thereafter, it has been used as a standard set by other authors to validate their approaches in this kind of excitations\(^{15,20,24}\). For all the donor-TCNE results obtained by using the approach presented in this work, the 6-31G* basis set was adopted. The geometries used were the B3LYP-optimized and were taken from Stein et al.
Table II. Charge transfer excitation energies (eV) for $\pi$ donor to $\pi^*$ transitions in Substituted Anthracene - TCNE complexes in solution

| Substituent      | TDDFT-PBE a | TDDFT-B3LYP b | TDDFT-BNL $\gamma^*$ c | This work Exp d |
|------------------|-------------|---------------|-------------------------|-----------------|
| None             | 0.9         | 1.00          | 1.82                    | 1.60            |
| 9-cyano          | fail        | 0.5           | 2.03                    | 2.00            |
| 9-chloro         | 0.9         | 1.0           | 1.82                    | 1.72            |
| 9-carbo-methoxy  | 0.8         | 0.9           | 1.74                    | 1.80            |
| 9-methyl         | 1.0         | 1.1           | 1.71                    | 1.40            |
| 9,10-dimethyl    | 1.3         | 1.4           | 1.77                    | 1.36            |
| 9-formyl         | 0.8         | 1.0           | 1.95                    | 1.90            |
| 9-formyl 10-chloro | 0.8       | 0.9           | 1.96                    | 2.03            |

- a Taken from Ref. (14)
- b Taken from Ref. (14)
- c Range-split BNL functional from Ref. (14)
- d Experimental solution data from Ref. (19) with CH3Cl as solvent

In Table I, we present the gas phase excitation energies from various aromatic donors to TCNE. For comparison, we also give the experimental values of these excitations and the results obtained by applying TDDFT-B3LYP, TDDFT dual-range BNL $\gamma^*$ taken from reference (14) and $\Delta$SCF from (15). As one can see all the TDDFT-B3LYP results for these systems underestimate by about 1.5 eV the experimentally measured excitation energies, whereas those of the present approach are in good agreement with experiment and those obtained by TDDFT-BNL $\gamma^*$. The charge transfer excited state for benzene and naphthalene involves an excited state of the same symmetry as the ground state, making possible a partial variational collapse to the ground state for the $\Delta$SCF scheme, as pointed out by Ziegler et al. The $\Delta$SCF underestimation of the excitation energy in these two cases is probably due to variational collapse, which cannot occur within our scheme, since the excited states by construction are always orthogonal to the ground state.

In Table II we give the results obtained from Anthracene substituted derivatives-TCNE in methylene chloride solution. As no solvation model was used, 0.32 eV were subtracted from every calculated gas phase value, following the suggestion by Stein et al. Thus all the calculated results that appear in Table II are the calculated values minus 0.32 eV to account...
for the solvent effect. We give for comparison the TDDFT-PBE, TDDFT-B3LYP, TDDFT dual-range BNL $\gamma^*$ and the experimental results for these excitations. The TDDFT-PBE and TDDFT-B3LYP results are not only too low, but also the descending order relation of the various donor-acceptor excitations is violated. Our results are close to TDDFT-BNL$\gamma^*$ and compare well to experiment.

The charge transfer excitations at large intermolecular distances follow the Mulliken’s rule\textsuperscript{17} which states that the lower photon energy $E_{CT}$ required to induce an electron transfer between a donor - acceptor system in asymptotically large intermolecular distances $R$ is:

$$E_{CT} = IP^D - EA^A - 1/R$$

where $IP^D$ is the ionization potential of the donor and $EA^A$ is the electron affinity of the acceptor. To check whether the energy grows asymptotically with $1/R$, we studied the lowest charge transfer energy of the systems C2H4-C2F4, C2H4-Ne in different large intermolecular distances $R$ (see Fig. 2) and we present the results in Figs. 3, 4. We plot in both cases for comparison the curve we get from Mulliken’s law, the fitted curve to our points where energy grows with $1/R$, the curve derived from TDDFT-B3LYP with its $1/R$ curve. For both complexes the aug-cc-pVDZ basis set was used for all the energy calculations. Although in both cases, our results are below the ones from Mulliken’s rule, they seem to satisfy the $1/R$ behavior contrary to TDDFT-B3LYP results that apart from being too low they give energies that are almost constant with $R$. 

Figure 2. Structures of C2H4-Ne and C2H4-C2F4
It must be taken into account that we used the ground state HF orbitals that correspond to the $S_{occ}^A$ subspace instead of solving the eigenvalue equation 9. This is due to the fact that optimizing this set of orbitals gave only a minor change to the total energy, much smaller than the accuracy of our results. Nevertheless, we cannot claim that one can always omit this equation, although it is expected that in this subspace we will have less change with respect to the ground state orbitals than in the other two, $S_{vir}^A$ and $S_{occ}^D$, where we had the particle and the hole.

For all of our calculations we used basis sets with diffuse functions. In particular in the cases where the donor-acceptor subsystems are not close to each other they will not interact using no diffuse functions and one then calculates two isolated systems instead of two weakly interacting ones. All the ground state and the TDDFT-B3LYP calculations for the C2H4-Ne C2H4-C2F4 systems were carried out using Gamess US26 and a code developed for our approach. For the visualization of the structures the xcrysden program was used27.
Figure 4. The C2H4-Ne charge transfer energy in different intermolecular separations $R$. Apart from the energies calculated from the approach presented here, we give for comparison the fit of these values to a 1/R curve, the curve that one gets from Mulliken’s rule as well as the TDDFT-B3LYP curve with its own 1/R fitted curve.

IV. CONCLUDING REMARKS

In this work we extend our Hartree-Fock (HF) excited state subsequent minimization scheme developed recently to describe charge transfer excitations. This is achieved by creating a particle-hole pair excited state, which is always orthogonal to the ground state and both the particle and the hole are determined variationally. This is done by separating the ground state HF orbitals to two sets, the one mostly localized in the donor and the other in the acceptor. Each such set is further separated in subspaces of occupied and virtual orbitals. Thus, we have four subspaces and the HF energy functional is minimized in each subspace separately. In this way variational collapse and self-interaction are avoided. We tested the above approach on a standard set of pairs of molecules and found that our theoretical results are in good agreement with the experimental ones and show the correct asymptotic behavior. It is worth mentioning that the computational cost of this scheme is the same as the one of a HF ground state calculation. Finally, one could easily calculate
double or multiple excitations within this approach as the only difference is that one would need to create more than one particle-hole pair in the appropriate subspaces.

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REFERENCES

1 S. Günes, H. Neugebauer, and N. S. Sariciftci, Chem. Rev. 107, 1324 (2007)
2 G. Bottari, G. de la Torre, D. M. Guldi, and T. Torres, Chem. Rev., 110, 6768 (2010)
3 E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).
4 Time-Dependent Density Functional Theory, edited by M. A. L. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross (Springer-Verlag, Berlin Heidelberg 2012)
5 M.E. Casida, J. Mol. Struct. (Theochem) 914, 3 (2009).
6 A. Dreuw, J. L. Weisman, and M. Head-Gordon, JCP 119, 6 (2003)
7 D. J. Tozer, J. Chem. Phys. 119, 12697 (2003)
8 Dmitrij Rapport and Jürg Hutter, Fundamentals of Time Dependent Density Functional Theory, edited by M. A. L Marques, N. T. Maitra, F. M. S. Nogueira, E. K. U Gross, (Springer-Verlag, Berlin Heidelberg, 2012), p. 330.
9 M. J. G. Peach, P. Benfield, T. Helgaker, and D. J. Tozer, J. Chem. Phys. 128, 044118 (2008)
10 Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and K. Hirao, J. Chem. Phys. 120, 8425 (2004)
11 O. Gritsenko and E. J. Baerends, J. Chem. Phys. 121, 655 (2004)
12 W. Lange, M. A. Rohrdanz, and J. M. Herbert, J. Phys. Chem. B 112, 6304 (2008)
13 A. Hesselmann, A. Ipatov, and A. Gorling, Phys. Rev. A 80, 012507 (2009).
14 T. Stein, L. Kronik, R. Baer, J. AM. CHEM. SOC. 131, 2818 (2009). 7345 (2008).
15 T. Ziegler and M. Krykunov, JCP 133, 074104 (2010)
16 Q. Wu and T. Van Voorhis, PRA 72, 024502 (2005)
17 Mulliken, R. S. J. Am. Chem. 72, 600 (1950)
18 I. Hanazaki, J. Phys. Chem. 76, 1982 (1972)
19 Masnovi, J. M.; Seddon, E. A.; Kochi, J. K. Can. J. Chem. 62, 2552 (1984)
20 T. Baruah, M. Olguin and R. Zope, JCP 137, 084316 (2012)
21 T. Ziegler, A. Rauk, and E. J. Baerends, Theor. Chim. Acta 43, 261 (1977).
22 M. Tassi, I. Theophilou and S. Thanos, Int. J. Quantum Chem., 113, 690 (2013).
23 M. Tassi, I. Theophilou and S. Thanos, J. Chem. Phys. 138, 124107 (2013)
24 X. Blase and C. Attaccalite, Appl. Phys. Lett. 99, 171909 (2011)
25 A. Szabo and N. S. Ostlund, Modern Quantum Chemistry, (Mac-Milan Publishing, New York, 1996), p.205.
26 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S.T. Elbert, M.S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su., T. L. Windus, M. Dupuis, J. A. Montgomery, J. Comput. Chem. 14, 1347 (1993).
27 A. Kokalj, Comp. Mater. Sci., 28, 155 (2003)