

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 an accurate and computationally inexpensive treatment of charge-transfer excitations is a topic that nowadays attracts 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. We describe an excitation where an electron is transferred from a donor system to an acceptor one, keeping the excited state orthogonal to the ground state and avoiding 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

Recently, organic photovoltaics have attracted a great deal of attention, as they have the potential of harvesting solar light cheaply and easily¹. 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 separation². Thus, the scientific community adopted as one of its major tasks 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 of two sites of the same big molecule. In this work we shall deal only with the first class of donor-acceptor complexes.

Although time-dependent density-functional theory (TDDFT)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 frequency-independent exchange-correlation kernels exhibit significant failures, giving underestimations of several eV^{6,7}. This failure is attributed to the wrong asymptotic shape of the ground-state exchange correlation (xc) potential, which leads to errors in the orbital energies⁸. Moreover, the Kohn-Sham orbital overlaps of the donor-acceptor system that enter the exchange-correlation part of the Dyson equation vanish when non-hybrid xc kernels are used. Consequently, the charge-transfer energy is given as the orbital energy difference⁹. Currently, there is a lot of effort on the development of exchange correlation kernels that mitigate this deficiency¹⁰⁻¹⁴. Using range-separated hybrid functionals^{10,14}, where the exchange functional is split in two terms, a short-range term that is represented by a local density approximation (LDA) or generalized gradient approximation (GGA) potential and a long-range term that is treated via exact exchange, improve the results obtained by 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 data¹² or by introducing a system dependent parameter by tuning the highest occupied molecular orbital (HOMO) close to minus the ionization potential¹⁴. A time-independent variational approach of density functional theory (DFT), that is not based on response theory, termed as relaxed constrained-variational DFT, gives promising results on charge-transfer excitations¹⁵. 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 space¹⁶. Recently, a perturbative-delta self consistent field (Δ SCF)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 Δ SCF²¹, which in combination with perturbation theory, gives 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 (UHF)²⁵ eigenvalue equations in different subspaces spanned by the occupied and virtual ground state orbitals²². 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 Δ SCF one, however within this scheme there is no possibility of a variational collapse to the ground state, as it may happen in Δ SCF, since the state defined in this way, is always orthogonal to the ground state. The orthogonality of approximate excited states to the ground state is desirable since the exact eigenstates of the Hamiltonian also have this property. In a recent paper an extension of this approach was given which includes double excitations²³. 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 the 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 consisting 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 orbitals of the acceptor. See Fig.(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 CT excited state by a Slater determinant with a hole in the donor occupied subspace and a particle in the acceptor virtual subspace. 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 are given in the next section. We applied our scheme to a series of Tetracyanoethylene (TCNE)-various donors systems that have been used before^{14,15,20,24} 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 our approach

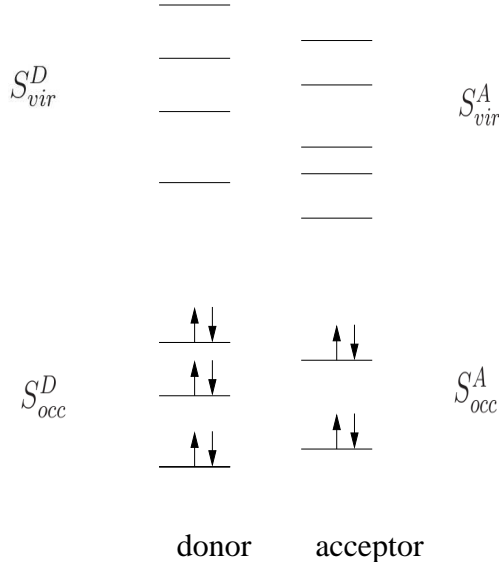


Figure 1: Sketch of the subspaces S^D_{occ} (occupied orbitals of the donor), S^A_{occ} (occupied orbitals of the acceptor), S^D_{vir} (virtual orbitals of the donor) and S^A_{vir} (virtual orbitals of the acceptor). Note that in practice we perform the subspace decomposition only for the up orbitals and the down electrons are just given here to complete the picture.

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 φ_j , are used to build two orthogonal subspaces, S^D , consisting of the orbitals φ_j^D that are localized mostly in the donor and S^A of orbitals similarly localized mostly in the acceptor system φ_j^A . This classification is performed by summing for each orbital φ_j , its projections on the gaussians centered at the donor or correspondingly at the acceptor. Thus, in order to check whether the orbital

φ_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 larger, we attribute the orbital φ_i to the donor or the 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 into a subspace S_{occ}^D spanned by the occupied orbitals $\{\varphi_1^D, \dots, \varphi_{N_{occ}^D}^D\}$ and S_{vir}^D of the virtual ones $\{\varphi_{N_{occ}^D+1}^D, \dots, \varphi_{N^D}^D\}$. Similarly S^A consists of S_{occ}^A spanned $\{\varphi_1^A, \dots, \varphi_{N_{occ}^A}^A\}$ and S_{vir}^A of the virtuals of the acceptor $\{\varphi_{N_{occ}^A+1}^A, \dots, \varphi_{N^A}^A\}$. The subspace dimensions are denoted by N^D for S^D , N_{occ}^D for S_{occ}^D and correspondingly by N^A , N_{occ}^A for the acceptor. The charge-transfer excited state orbitals that are localized in the donor system are denoted by χ_i^D and the ones that are localized in the acceptor by χ_i^A . Then, we demand that the excited state $|\Phi_{CT}\rangle = |\chi_1^D, \dots, \chi_{N_{occ}^D-1}^D, \chi_1^A \dots \chi_{N_{occ}^A+1}^A, \chi_1^\downarrow, \dots, \chi_{N^\downarrow}^\downarrow\rangle$ has one more electron in S_{vir}^A than the ground state HF and one hole in S_{occ}^D . Thus, in addition to the normalization of the orbitals the following conditions should be satisfied:

- i) $\langle \chi_i^D | \varphi_j^A \rangle = 0$ for $i \leq N_{occ}^D - 1$ and $j = 1, \dots, N^A$
- ii) $\langle \chi_i^D | \varphi_j^D \rangle = 0$, for $i \leq N_{occ}^D - 1$ and $j \geq N_{occ}^D + 1$

The two relations above imply that the excited orbitals $\chi_1^D, \dots, \chi_{N_{occ}^D-1}^D$ belong to the subspace S_{occ}^D .

- iii) $\langle \chi_{N_{occ}^A+1}^A | \varphi_j^A \rangle = 0$, for $j \leq N_{occ}^A$
- iv) $\langle \chi_{N_{occ}^A+1}^A | \varphi_j^D \rangle = 0$, for $j = 1, \dots, N^D$

Relations (iii) and (iv) imply that $|\Phi_{CT}\rangle$ comprises one orbital named $\chi_{N_{occ}^A+1}^A$ that belongs to S_{vir}^A .

- v) $\langle \chi_i^A | \varphi_j^A \rangle = 0$, for $i \leq N_{occ}^A$ and for $j > N_{occ}^A$ and
- vi) $\langle \chi_i^A | \varphi_j^D \rangle = 0$, for $i \leq N_{occ}^A$ and for $j=1, \dots, N^D$

Relations (v) and (vi) imply that the excited orbitals $\chi_1^A, \dots, \chi_{N_{occ}^A}^A$ belong to S_{occ}^A .

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

$$\hat{F}|\chi_i^D\rangle - \sum_{j \leq N^A} |\varphi_j^A\rangle \langle \varphi_j^A | \hat{F} | \chi_i^D \rangle - \sum_{j > N_{occ}^D} |\varphi_j^D\rangle \langle \varphi_j^D | \hat{F} | \chi_i^D \rangle = \epsilon_i^D |\chi_i^D\rangle, \quad \text{for } i < N_{occ}^D \quad (1)$$

As usual, the Fock operator \hat{F} corresponding to Φ_{CT} is defined by the following equation

$$(\hat{F}^s \chi_i^s)(\mathbf{r}) = \hat{h} \chi_i^s(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}', \Phi_{CT})}{|\mathbf{r} - \mathbf{r}'|} \chi_i^s(\mathbf{r}) - \int d\mathbf{r}' \frac{\rho_s(\mathbf{r}, \mathbf{r}'; \Phi_{CT})}{|\mathbf{r} - \mathbf{r}'|} \chi_i^s(\mathbf{r}'), \quad (2)$$

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 $|\Phi_{CT}\rangle$:

$$\rho_s(\mathbf{r}, \mathbf{r}'; \Phi_{CT}) = \sum_{i=1}^{N_s} \chi_i^s(\mathbf{r}) \chi_i^s(\mathbf{r}'), \quad (3)$$

where N_s stands for the number of occupied orbitals with $s \uparrow$ or \downarrow . Finally, $\rho(\mathbf{r}; \Phi_{CT}) = \rho_{\uparrow}(\mathbf{r}, \mathbf{r}; \Phi_{CT}) + \rho_{\downarrow}(\mathbf{r}, \mathbf{r}; \Phi_{CT})$. We use the notation $(\hat{F}^s \chi_i^s)(\mathbf{r})$ 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 sums $\sum_{j > N_{occ}^D} |\varphi_j^D\rangle \langle \varphi_j^D|$ and $\sum_{j \leq N^A} |\varphi_j^A\rangle \langle \varphi_j^A|$ are projection operators onto the subspaces S_{vir}^D and S^A respectively, which act as identity operators in the corresponding subspaces. For the excited orbitals of the acceptor we obtain:

$$\hat{F}|\chi_i^A\rangle - \sum_{j \leq N^D} |\varphi_j^D\rangle \langle \varphi_j^D| \hat{F}|\chi_i^A\rangle - \sum_{j \leq N_{occ}^A} |\varphi_j^A\rangle \langle \varphi_j^A| \hat{F}|\chi_i^A\rangle = \epsilon_i^A |\chi_i^A\rangle, \quad \text{for } i > N_{occ}^A \quad (4)$$

and

$$\hat{F}|\chi_i^A\rangle - \sum_{j \leq N^D} |\varphi_j^D\rangle \langle \varphi_j^D| \hat{F}|\chi_i^A\rangle - \sum_{j > N_{occ}^A} |\varphi_j^A\rangle \langle \varphi_j^A| \hat{F}|\chi_i^A\rangle = \epsilon_i^A |\chi_i^A\rangle, \quad \text{for } i \leq N_{occ}^A \quad (5)$$

The first sum that appears in Eqs.(4), (5) corresponds to the projection operator in S^D and the second sum 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 onto 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. Note that we need no equation for obtaining orbitals that belong to S_{vir}^D since these orbitals do not enter our $|\Phi_{CT}\rangle$ state.

The equation for the spin down orbitals has the usual UHF form²⁵ i.e.

$$\hat{F}^{\downarrow} |\chi_i^{\downarrow}\rangle = \epsilon_i^{\downarrow} |\chi_i^{\downarrow}\rangle \quad (6)$$

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 electrons.

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 the use of Lagrange multipliers. This is achieved by constructing the Fock matrices in the basis of the ground state HF orbitals that span the corresponding subspaces. For more details see Appendix B of²³. Once we manage to restrict the Fock operator in the subspaces S_{occ}^D , S_{vir}^A and S_{occ}^A , Eqs.(1),(4),(5) assume the following simple form:

$$\hat{F}_{occ}^D|\chi_i^D\rangle = \epsilon_i^D|\chi_i^D\rangle, \quad (7)$$

$$\hat{F}_{vir}^A|\chi_i^A\rangle = \epsilon_i^A|\chi_i^A\rangle, \quad (8)$$

$$\hat{F}_{occ}^A|\chi_i^A\rangle = \epsilon_i^A|\chi_i^A\rangle. \quad (9)$$

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 $N^D - 1$ χ_i^D , the $\chi_{N_{occ}^A+1}^A$ and the $\chi_1^A, \dots, \chi_{N_{occ}^A}^A$ orbitals of $|\Phi_{CT}\rangle$. Thus, one has to self consistently solve the system of Eqs.(7),(8),(9) together with the equation for the down orbitals, Eq.(6). The determinant $|\Phi_{CT}\rangle$ that corresponds to the approximate eigenstate of the excited charge-transfer state will be orthogonal to the ground state one, i.e. $\langle\Phi_0|\Phi_{CT}\rangle = 0$. This is true since the highest occupied orbital of the acceptor in $|\Phi_{CT}\rangle$ belongs to S_{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 as matrices in some basis set 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_{occ}^D , S_{vir}^A and S_{occ}^A to express the Fock matrices of equations (7), (8), (9).

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

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

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

The equations above are the ones that we solve in order to obtain $|\Phi_{CT}\rangle$. 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 in S_{vir}^A and to create two or more holes respectively in the subspace of S_{occ}^D .

We stress the fact that all orbitals that contribute to Φ_{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 diffuse as they are repelled by N electrons. Consequently, occupying the HF virtual orbitals without further minimization, as it is well known, leads to large excitation energies.

III. RESULTS AND DISCUSSION

The approach developed in section II was used 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 ones and were taken from Stein et al¹⁴.

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

Donor	TDDFT-B3LYP ^a	TDDFT-BNL γ^* ^b	Δ SCF-HF	This work	Exp ^c
Benzene	2.1	3.80	3.06	3.46	3.59
Toluene	1.8	3.40	2.75	3.16	3.36
O-xylene	1.5	3.00	2.56	2.89	3.15
Naphtalene	0.9	2.70	2.21	2.61	2.60

^a Taken from Ref.(¹⁴)

^b Range-split BNL functional from Ref.(¹⁴)

^c Experimental gas-phase data from Ref. (¹⁸)

Table II: Charge transfer excitation energies (eV) for π donor to π^* transitions in Substituted Anthracene - TCNE complexes in solution

Substituent	TDDFT-PBE ^a	TDDFT-B3LYP ^b	TDDFT-BNL γ^* ^c	Δ SCF-HF	This work	Exp ^d
None	0.9	1.00	1.82	1.63	1.60	1.73
9-cyano	fail	0.5	2.03	1.36	2.00	2.01
9-chloro	0.9	1.0	1.82	1.57	1.72	1.74
9-carbo-methoxy	0.8	0.9	1.74	1.38	1.80	1.84
9-methyl	1.0	1.1	1.71	1.37	1.40	1.55
9,10-dimethyl	1.3	1.4	1.77	1.57	1.36	1.44
9-formyl	0.8	1.0	1.95	1.64	1.90	1.90
9-formyl 10-chloro	0.8	0.9	1.96	1.70	2.03	1.96

^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 γ^* taken from reference¹⁴ and Δ SCF-HF. Δ SCF-HF results are obtained by starting with the UHF orbitals of the ground-state as initial guess and then solving the UHF equations using a SCF procedure in which the lowest $N^\uparrow-1$ orbitals and the $(N^\uparrow + 1)^{th}$ are occupied in each update of the density. As one can see, all the TDDFT-B3LYP results for these systems underestimate the experimentally measured excitation energies by about 1.5 eV, Δ SCF-HF results are better but still underestimate the energy by 0.4-0.6 eV, whereas those of the present approach are in good agreement with experiment and those obtained by TDDFT-BNL γ^* .

In Table II we give the results obtained for 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 al¹⁴. Thus all the calculated results that appear in Table II are the calculated values minus 0.32 eV to account for the solvent effect. For comparison we give the TDDFT-PBE, TDDFT-B3LYP, TDDFT

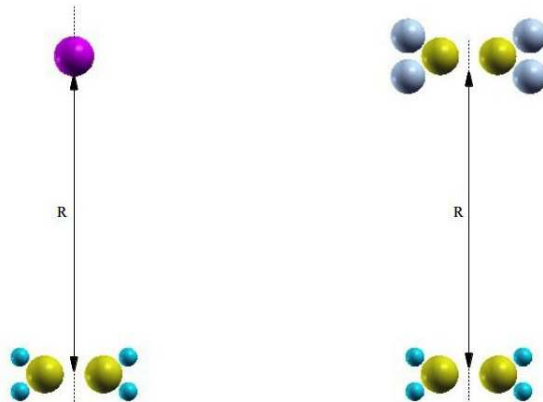


Figure 2: Structures of C_2H_4-Ne and $C_2H_4-C_2F_4$

dual-range BNL γ^* 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. The descending order relation is also violated by Δ SCF-HF results. Our results keep the descending order, are close to TDDFT-BNL γ^* and compare well to experiment.

As expected from the self-interaction problem of virtual HF orbitals, replacing in the ground state Slater determinant the HOMO of the donor with the lowest unoccupied molecular orbital (LUMO) of the acceptor and calculating the energy difference from the ground state HF energies gave more than 1eV overestimation of the CT energies for all the systems tested.

The charge-transfer excitations at large intermolecular distances follow the Mulliken's rule¹⁷ 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 two systems $C_2H_4-C_2F_4$ and C_2H_4-Ne at different large intermolecular distances R (see Fig.2) and we present the results in Fig.3. For comparison, we plot the curve we get from Mulliken's law, the fitted curve to our points where energy grows with $1/R$ and the curve derived from TDDFT-B3LYP with its $1/R$ fit. For both

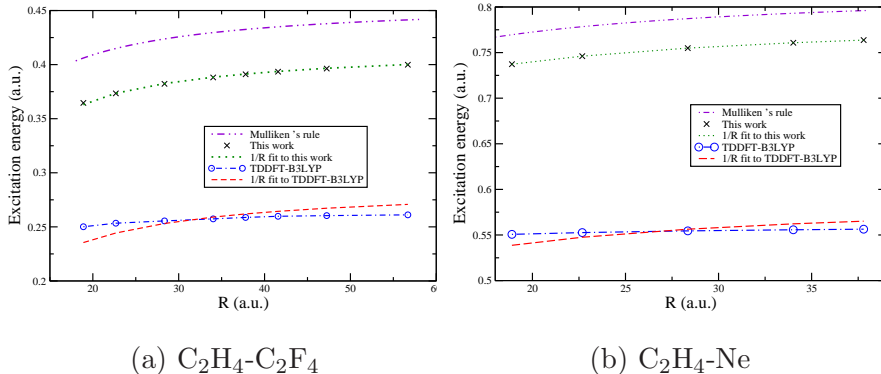


Figure 3: Charge-transfer energy at different intermolecular separations R . Apart from the energies calculated from the approach presented here, we give for comparison the fit of these values to a $1/R$ curve, the curve that one gets from Mulliken's rule as well as the TDDFT-B3LYP curve with its own $1/R$ fitted curve.

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 satisfy the $1/R$ behavior contrary to the TDDFT-B3LYP results that apart from being too low in energy are almost constant with R .

For all the calculations with our minimization scheme 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 solving this equation, although it is expected that in this subspace the changes with respect to the ground state orbitals are smaller than in the other two, S_{vir}^A and S_{occ}^D , where the particle and the hole are located.

For all of our calculations we used basis sets with diffuse functions. Those functions are particularly important when the donor and acceptor subsystems are not close to each other to ensure that one treats two weakly interacting systems and not two isolated ones. All the ground state and the TDDFT-B3LYP calculations for the C_2H_4-Ne $C_2H_4-C_2F_4$ systems were carried out using Gamess US²⁶ and a code was developed for our approach. For the visualization of the structures the xcrysden program was used²⁷.

IV. CONCLUDING REMARKS

In this work we extend our 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 into two sets: one mostly localized at the donor and the other at 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 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.

V. ACKNOWLEDGMENTS

The authors would like to thank Dr. N. Helbig, Dr. N.N. Lathiotakis and Prof. A.K. Theophilou for usefull discussions. I.T. acknowledges financial support from the DFG through the Emmy-Noether program.

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