Charge Transfer Excitation Energies From Ground State Density Functional Theory Calculations

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Calculating charge transfer (CT) excitation energies with high accuracy and low computational cost is a challenging task. Kohn-Sham density functional theory (KS-DFT), due to its efficiency and accuracy, has achieved great success in describing ground state problems. To extend to excited state problems, our group recently demonstrated an approach with good numerical results to calculate low-lying and Rydberg excitation energies of an $N$-electron system from a ground state KS or generalized KS calculations of an $(N - 1)$-electron system via its orbital energies. In present work, we explore further the same methodology to describe CT excitations. Numerical results from this work show that performance of conventional density functional approximations (DFAs) is not as good for CT excitations as for other excitations, due to the delocalization error. Applying localized orbital scaling correction (LOSC) to conventional DFAs, a recently developed method in our group to effectively reduce the delocalization error, can improve the results. Overall, the performance of this methodology is better than time dependant DFT (TDDFT) with conventional DFAs. In addition, it shows that results from LOSC-DFAs in this method reach similar accuracy to other methods, such as $\Delta$SCF, $G_0W_0$ with Bethe-Salpeter equations, particle-particle random phase approximation, and even high-level wavefunction method like CC2. Our analysis show that the correct $1/R$ trend for CT excitation can be captured from LOSC-DFA calculations, stressing that the application of DFAs with minimal delocalization error is essential within this methodology. This work provides an efficient way to calculate CT excitation energies from ground state DFT.

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I. INTRODUCTION

Charge transfer (CT) excitation energy calculation has gained much attention in materials and biological sciences\textsuperscript{1–3}. In a spatially separated donor-acceptor (D-A) system with intermolecular distance $R$, the CT excitation process involves electron transition from donor molecule (D) to acceptor molecule (A), and the CT excitation energy at asymptotically large $R$ is given by

$$E_{\text{CT}} = \text{IP}(D) - \text{EA}(A) - 1/R,$$

where IP(D) and EA(A) are the ionization potential (IP) of donor and electron affinity (EA) of acceptor, and the $1/R$ term comes from the Coulomb attraction. In practice, calculating CT excitation energy with high accuracy and low computational cost is interesting and challenging. Among the theoretical developments, Kohn-Sham density functional theory (KS-DFT)\textsuperscript{4,5}, as a useful method to ground state problems with great success during the past decades, has not been well justified for direct application to excited states. However, many methods developed in the framework of DFT have been reported. The time-dependant DFT (TDDFT) has been widely used for single low-lying excitation energy calculation\textsuperscript{6–9}. However, TDDFT faces the challenge in describing CT excitation problems with commonly used density functional approximations (DFAs)\textsuperscript{8,10,11}. It is known that TDDFT with application of conventional functionals, such as local density approximation (LDA), generalized gradient approximation (GGA) and hybrid functionals, normally underestimates the CT excitation energies, and cannot capture the correct asymptotically $1/R$ dependence at a long distance. Such failure of TDDFT is attributed to two factors. One is related to the energy bandgap between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) that is used to approximate the fundamental gap (IP – EA), the leading term in Eq. 1 at large separation distance.\textsuperscript{12–18} The other reason is that exchange-correlation kernel, $f_{xc}$, from conventional functionals vanishes exponentially at long distance, leading to the absence of the $1/R$ behavior\textsuperscript{12,19}.

On the physical meaning of HOMO and LUMO energies, it has been proved that for conventional DFAs, when the approximate exchange-correlation energy $E_{xc}[\rho(r)]$ is an explicit and continuous functional of electron density, either local or nonlocal, the Kohn-Sham HOMO energy $\varepsilon_{\text{HOMO}}^{\text{KS}}$ is equal to the chemical potential for electron removal (as a prediction of the corresponding DFA); namely $\varepsilon_{\text{HOMO}}^{\text{KS}} = (\frac{\partial E}{\partial N})_{V}^{-} = \mu^{-}$. Similarly, the Kohn-
Sham LUMO energy $\varepsilon_{\text{LUMO}}^{\text{KS}}$ is equal to the chemical potential for electron addition; namely $\varepsilon_{\text{LUMO}}^{\text{KS}} = \left( \frac{\partial E}{\partial N} \right)_{V}^{+} = \mu_{+}$. When the approximate exchange-correlation energy $E_{\text{xc}}[\rho(r, r')]$ is an explicit and continuous functional of the non-interacting one-electron density matrix $\rho_{s}(r, r')$, the generalized Kohn-Sham HOMO energy $\varepsilon_{\text{HOMO}}^{\text{GKS}}$ is equal to the chemical potential for electron removal; namely $\varepsilon_{\text{HOMO}}^{\text{GKS}} = \left( \frac{\partial E}{\partial N} \right)_{V}^{-} = \mu_{-}$, and the generalized Kohn-Sham LUMO energy $\varepsilon_{\text{LUMO}}^{\text{GKS}}$ is equal to the chemical potential for electron addition; namely $\varepsilon_{\text{LUMO}}^{\text{GKS}} = \left( \frac{\partial E}{\partial N} \right)_{V}^{+} = \mu_{+}$. Note that in the case of $E_{\text{xc}}[\rho_{s}(r, r')]$, the Kohn-Sham (or the optimized effective potential) HOMO and LUMO eigenvalues are different from the chemical potentials. When a DFA satisfies the linearity condition for fractional numbers of electrons, the chemical potential are related to the predicted ionization $I$ and electron affinity $A$; namely $\mu_{-} = -I$ and $\mu_{+} = -A$. For finite and small systems, the deviation of the DFA from the linearity conditions is the delocalization error of a DFA. Therefore accurate prediction of $I$ and $A$ can be obtained from the (G)KS HOMO and LUMO energy, when the DFA has minimal delocalization error. However, because commonly used DFAs have significant delocalization error, the (G)KS HOMO underestimates $I$ and the (G)KS LUMO overestimates $A$, leading to the underestimation of energy bandgaps and also the CT excitation energies.

One attempt to cure the problem is to reduce the delocalization error by introducing hybrid functionals with a fraction of Hartree-Fock (HF) exchange, which is known to produce localization error. In addition, it has been discussed that the full HF exchange can recover the $1/R$ trend in principle at long distance. With this aspect, applying range-separated functional with system-dependent tuned parameters becomes a good solution for TDDFT to describe CT excitations, and the accuracy can reach to 0.1 eV in the best case. Other methods developed from DFT framework, including constrained DFT (CDFT), $\Delta$ self-consistent field approach ($\Delta$SCF), and the perturbative $\Delta$SCF have been reported to provide accurate CT excitations energy as well, and the computational cost can be maintained at DFT calculation level.

Similarly to TDDFT, particle-particle random phase approximation (pp-RPA) can be viewed as a linear response theory for the time-dependent perturbation of a pairing field on the ground states described with DFT. It has been shown to produce good CT results, as well as excellent description of the asymptotically correct $1/R$ trend. Building beyond the framework of DFT, there are other methods successfully developed
to describe CT excitations. The many-body perturbation theory at GW level and Bethe-Salpeter approach (BSE)\textsuperscript{43,44} can yield results of similar accuracy as TDDFT from the best range-separated functional. However, in terms of computational cost, these methods in general have computational scaling higher or similar to TDDFT.

We would like to explore if it is possible to describe CT excitation well directly from the ground state DFT calculation. The (G)KS HOMO and LUMO energies from density functional approximation (DFA) with minimum delocalization error are good approximations to $-I$ and $-A$, based on the rigorously proven results on connection to the chemical potentials.\textsuperscript{20} We observed from our recent work\textsuperscript{45} that the remaining (G)KS orbital energies from the localized orbital scaling correction (LOSC), a DFA with minimal delocalization error,\textsuperscript{46} approximate the corresponding quasiparticle energies well. Thus the entire set of (G)KS orbital energies from a DFA with minimal delocalization error can be used to obtain the photoemission spectrum with good agreement to the experimental reference, suggesting these orbital energies are good approximations to the quasiparticle energies. Based on this observation, we have demonstrated that the excitation energy of an $N$-electron system can be approximated by the orbital energy difference from an $(N-1)$-electron system. Bartlett\textsuperscript{47} and our group\textsuperscript{45,48} demonstrated this is an efficient way to calculate the excitation energy by orbital energies from (G)KS-DFT. Results from our previous work have showed good performance for the low-lying and Rydberg excitation energies within this methodology.\textsuperscript{45} Therefore, in this paper, we further explore this approach for application to CT excitation problems.

II. METHOD AND CALCULATIONS

Here, we briefly review the calculation method. Note here, we refer orbital energies to the ones either from KS calculations for approximated exchange-correlation energy $E_{xc}$ as an explicit and continuous functional of electron density or from GKS calculations for approximate $E_{xc}$ as an explicit and continuous functional of the non-interesting one-particle density matrix. As we demonstrated in our recent work, orbital energies $\varepsilon_m(N)/\varepsilon_n(N)$ from a DFA with minimal delocalization error are good approximation to the quasiparticle/quasihole
energies $\omega^{+/-}(N)$\textsuperscript{45}; namely,

$$\varepsilon_m(N) \approx \omega_m^+(N) = E_m(N + 1) - E_0(N)$$

and

$$\varepsilon_n(N) \approx \omega_n^-(N) = E_0(N) - E_n(N - 1).$$

In Eq. 2, the virtual orbital energy, $\varepsilon_m(N)$, is connected to a one-electron addition process and approximates the electron affinity of the $N$-electron system. In Eq. 3, the occupied orbital energy, $\varepsilon_n(N)$, is connected to a one-electron removal process and approximates the ionization potential of the $N$-electron system. Utilizing these properties, the $m$th excitation energy $\Delta E_m(N)$, defined as the energy difference between the $m$th excited states and ground state of $N$-electron system, can be calculated from a ground-state $(N - 1)$-electron system via its virtual orbital energy difference, namely,

$$\Delta E_m(N) = E_m(N) - E_0(N)$$

$$= [E_m(N) - E_0(N - 1)] - [E_0(N) - E_0(N - 1)]$$

$$= \omega_m^+(N - 1) - \omega_{mn}^+(N - 1)$$

$$\approx \varepsilon_m(N - 1) - \varepsilon_{LUMO}(N - 1).$$

An alternative way to $(N - 1)$-electron system calculation, one can switch to $(N + 1)$-electron system calculation and use occupied orbital energies instead. However, the anionic $(N + 1)$-electron system normally are difficult to calculate and yields unreliable results\textsuperscript{45}. Therefore we only focus on the $(N - 1)$-electron system calculation in this paper. In details, starting with a doublet ground state $(N - 1)$-electron system (assuming one more alpha electron than beta electron), adding one electron to alpha orbital yields a triplet state, $E_{\uparrow\uparrow}(N)$, which can be directly used for triplet excitation, and adding one electron to beta orbital gives a spin-mixed state, $E_{\uparrow\downarrow}(N)$. In order to obtain singlet excited state, commonly used spin purification process\textsuperscript{31} are applied, i.e.

$$E^{\text{singlet}}(N) = 2E_{\uparrow\downarrow}(N) - E_{\uparrow\uparrow}(N),$$
which leads singlet excitation energy to be expressed as

\[
\Delta E_{m}^{\text{singlet}}(N) \approx [2\varepsilon_{m}^{\beta}(N-1) - \varepsilon_{m}^{\alpha}(N-1)] - \varepsilon_{\text{LUMO}}^{\beta}(N-1).
\]

To test the performance of this methodology for CT excitations, we chose the standard CT set from Stein et al\textsuperscript{26}, in which each system is composed of one strong electron withdrawing molecule, tetracyanoethylene (TCNE), and one electron donating molecule ranging from benzene to derivatives of anthracene, and their first excitation possesses clear CT characteristics from HOMO to LUMO. In this work, we mainly focused on the calculation of the singlet excitation energy and the description of $1/R$ trend for the test set via Eq. 6. We tested the performance of several conventional DFAs, including LDA,\textsuperscript{49,50} BLYP,\textsuperscript{51} B3LYP,\textsuperscript{52,53} and CAMB3LYP,\textsuperscript{54} which are in a decreasing order of delocalization error. In addition, we tested the performance of these DFAs with localized orbital scaling correction (LOSC)\textsuperscript{46}. This correction method was recently developed in our group and has been demonstrated to be capable of largely and systematically eliminating delocalization error for conventional DFAs. Through this work, the LOSC calculation was applied to the results from DFAs in a post-SCF approach. In particular, the SCF calculation from conventional DFAs was performed first to get the canonical orbitals and orbital energies, then a restrained Boys localization was applied to get a set of special localized orbitals called orbitalets, and only one-step correction, based on the orbitalets, was added to the orbital energies at the end. The correction process in LOSC can also be performed with an SCF manner, however, applying post-SCF calculation in LOSC is more efficient and the results have been demonstrated to be only slightly different from the ones obtained by SCF process\textsuperscript{46}. Therefore, we only applied LOSC with the post-SCF calculations in this work. For all the DFT calculation in this work, we used our in-house developed package, QM4D\textsuperscript{55}. An unrestricted calculation was applied to all the test molecules. The basis set used for DFT calculation is cc-pVTZ, and an auxiliary basis set, used for density fitting in LOSC calculation\textsuperscript{46}, is aug-cc-pVTZ.

III. RESULTS AND DISCUSSION

To evaluate the performance of our methodology (Eq. 6), we first test the dependence of results on basis set. Table I shows the singlet HOMO-LUMO excitation energy of Xylene-
TABLE I: Basis set dependence for the singlet HOMO-LUMO excitation energy (in eV) of Xylene-TCNE complex, calculating from DFT with BLYP and LOSC-BLYP functionals.

| Basis                   | BLYP | LOSC-BLYP |
|-------------------------|------|-----------|
| cc-pVTZ                 | 2.65 | 2.43      |
| cc-pVQZ                 | 2.64 | 2.33      |
| 6-31G*                  | 2.74 | 2.55      |
| 6-31G**                 | 2.73 | 2.54      |
| 6-31++G**               | 2.66 | 2.38      |
| 6-311++G**              | 2.65 | 2.36      |
| 6-311++G(3df, 3pd)      | 2.63 | 2.28      |

TCNE complex from several common basis sets, and the results were calculated from BLYP and LOSC-BLYP functional. According to this table, it suggests that excitation energy from conventional DFA does not have much dependence on basis set choice. For BLYP, the maximum excitation energy difference is only 0.1 eV. For results from LOSC-DFA, the excitation energy keeps dropping, and the maximum difference was 0.27 eV for LOSC-BLYP. Considering the cost and accuracy, we finally selected cc-pVTZ as the basis set for the remaining calculations.

A. Excitation energies

To show the results, we start with the performance of CT excitation energy calculation. Table II shows the results from tested DFAs and LOSC-DFAs via Eq. 6. In addition, we summarize results from other methods, including TD-DFT, pp-RPA, CC2, GW-BSE, and ∆SCF in Table III. Gas phase experimental data were used as reference. Among all the test cases, there are some molecules, of which only the liquid phase experimental data were applicable. As suggested in Ref. 26, a universal correction (0.32 eV) was added to liquid phase data for the compensation of solvation energy, hence, a complete set of gas phase reference was able to obtained. According to Table II, we observed that the results from conventional DFAs show mean absolute error (MAE) over 0.5 eV. Meanwhile, we noticed that MAE generally shows a decreasing trend from 0.76 eV (LDA) to 0.56 eV (CAMB3LYP). This decreasing order matches with the decreasing amount of delocalization error in the approximate functionals from LDA to CAMB3LYP, demonstrating the role of delocalization error in CT excitations within this method. This idea was further supported by the results
from LOSC-DFAs. As applying LOSC can largely eliminate the delocalization error, the MAE of results from LOSC-DFAs drops down as expected, especially for LOSC-LDA and LOSC-BLYP. In particularly, the MAE from LOSC-LDA, the best case, can reach to 0.41 eV. Comparing the results from our method with other calculation approaches shown in Table III, we noticed that our method cannot yield results with similar accuracy to TDDFT with system-dependent tuned functional, however, our method still performs better than TDDFT with conventional functionals. Especially compared with TD-B3LYP (MAE of 1.06 eV), the MAE from our method LOSC-B3LYP drops to 0.67 eV. We further noticed that the performance of our method with LOSC-DFAs was similar to $\Delta$SCF method. In the case of $\Delta$-BLYP and LOSC-BLYP from our method, the MAE and mean signed error (MSE) are very similar. Compared our results with $GW$-$BSE$ results, we observed that our best results are slightly better than $G_0W_0$-$BSE$, but still worse than $GW$-$BSE$ with partial self-consistent calculations. At the end, we noticed that most of the results from Table II and III show strong bias of underestimation to the experimental reference. This could be related to the systematic error caused by the universal correction from the liquid phase experimental data. Concerning this issue, we performed CC2 calculation, which is a high-level wavefunction method and computationally affordable for this test set. Results from CC2 also shows 0.37 eV underestimation to the experimental reference. Comparing our results directly with CC2, we found that our best results, 0.41 eV from LOSC-LDA, are similar.

B. $1/R$ dependence analysis

Followed by showing the CT excitation energies, we now verify the description of $1/R$ dependence from this method. The excitation energy curve of benzene-TCNE complex with respect to the variation of intermolecular distance was plotted in Fig. 1. By observing Fig. 1, we noticed that applying B3LYP fails to describe the $1/R$ behavior. Especially at long distance, the curve from B3LYP in Fig. 1 shows a critical drop starting around 5 Å. The reason for the poor performance of B3LYP can be mainly attributed to the delocalized orbital density at long distance. To clarify this point, figure (a) and (b) of Fig. 1 show the LUMO electron distribution of $(N-1)$-electron system with different separation distances at 4.65 and 6.65 Å. According to these figures, the LUMO of the $(N-1)$-electron system starts to
TABLE II: Charge transfer excitation energies (in eV) obtained from DFT calculation with DFAs, LOSC-DFAs, comparing with experimental reference.

| System (TCNE)       | Exp $^a$ | LOSC-LDA | LOSC-BLYP | LOSC-B3LYP | LOSC-CAMB3LYP | LDA   | BLYP  | B3LYP | CAMB3LYP |
|---------------------|----------|----------|-----------|------------|---------------|-------|-------|-------|----------|
| Benzene             | 3.59     | NA       | NA        | 3.06       | 3.06          | NA    | NA    | 3.47  | 3.30     |
| Toluene             | 3.36     | 2.79     | NA        | 2.64       | 2.65          | 2.79  | NA    | 2.96  | 2.85     |
| Xylene              | 3.15     | 2.39     | 2.43      | 2.35       | 2.32          | 2.63  | 2.65  | 2.61  | 2.50     |
| Naphtalene          | 2.60     | 2.20     | 2.08      | 2.02       | 2.24          | 2.12  | 2.06  | 2.05  | 2.14     |
| Anthracene $^b$     |          |          |           |            |               |       |       |       |          |
| None                | 2.05*    | 1.74     | 1.78      | 1.44       | 1.64          | 1.27  | 1.21  | 1.30  | 1.50     |
| cyano               | 2.33*    | 2.10     | 1.57      | 1.48       | 1.81          | 1.36  | 1.32  | 1.43  | 1.66     |
| chloro              | 2.06*    | 1.65     | 1.63      | 1.37       | 1.58          | 1.19  | 1.14  | 1.24  | 1.44     |
| carbomethoxy        | 2.16*    | 1.77     | 1.79      | 1.53       | 1.62          | 1.19  | 1.14  | 1.25  | 1.47     |
| methyl              | 1.87*    | 1.52     | 1.46      | 1.26       | 1.41          | 1.10  | 1.05  | 1.13  | 1.30     |
| dimethyl            | 1.76*    | 1.57     | 1.54      | 1.33       | 1.46          | 1.15  | 1.11  | 1.22  | 1.38     |
| formyl              | 2.22*    | 1.91     | 1.71      | 1.43       | 1.71          | 1.35  | 1.29  | 1.39  | 1.60     |
| formychloro         | 2.28*    | 1.74     | 1.67      | 1.40       | 1.70          | 1.34  | 1.28  | 1.40  | 1.62     |
| MAE                 | 0.41     | 0.48     | 0.68      | 0.52       | 0.76          | 0.82  | 0.67  | 0.56  |          |
| MSE                 | -0.41    | -0.48    | -0.68     | -0.52      | -0.76         | -0.82 | -0.67 | -0.56 |          |

$^a$Experimental data refer to gas phase. Data was taken from Ref. 56,57. If an asterisk was labeled to the experimental data, it refers to that the data was corrected from the liquid phase experimental data by 0.32 eV as suggested by Ref. 26. $^b$Systems shown below are substitutes of anthracene.
TABLE III: Charge transfer excitation energies (in eV) from TDDFT, pp-RPA, \(GW-BSE\), CC2 and \(\Delta\text{SCF}\), comparing with experimental reference.

| System (TCNE) | Exp\(^a\) | TD-tuned-BNL\(^b\) | TD-B3LYP\(^b\) | pp-RPA\(^c\) | CC2\(^d\) | \(G_0W_0BSE\)\(^e\) | \(GW_{psc-BSE}\)\(^e\) | BLYP-MOM\(^f\) |
|---------------|-----------|---------------------|-----------------|-------------|---------|-----------------|-----------------|----------------|
| Benzene       | 3.59      | 3.80                | 2.10            | NA          | 3.40    | 3.03            | 3.58            | NA             |
| Toluene       | 3.36      | 3.40                | 1.80            | NA          | 3.03    | 2.52            | 3.27            | 2.67           |
| Xylene        | 3.15      | 3.00                | 1.50            | NA          | 2.75    | 2.23            | 2.89            | 3.23           |
| Naphtalene    | 2.60      | 2.70                | 0.90            | 2.27        | 2.29    | 1.96            | 2.55            | 3.22           |

| Anthracene    |           |                     |                 |             |         |                 |                 |                |
| None          | 2.05\(^*\) | 2.14                | 1.32            | 1.62        | 1.65    | 1.66            | 2.17            | NA             |
| cyano         | 2.33\(^*\) | 2.35                | 0.82            | 1.74        | 1.87    | 1.89            | 2.32            | 1.85           |
| chloro        | 2.06\(^*\) | 2.14                | 1.32            | 1.58        | 1.65    | NA              | NA              | 1.57           |
| carbomethoxy  | 2.16\(^*\) | 2.16                | 1.22            | 1.58        | 1.69    | 1.64            | 2.05            | 1.61           |
| methyl        | 1.87\(^*\) | 2.03                | 1.42            | 1.39        | 1.49    | 1.21            | 1.99            | 1.46           |
| dimethyl      | 1.76\(^*\) | 2.09                | 1.72            | 1.41        | 1.53    | 2.00            | 2.21            | 1.43           |
| formyl        | 2.22\(^*\) | 2.27                | 1.32            | 1.78        | 1.81    | 1.89            | 2.32            | 1.76           |
| formychloro   | 2.28\(^*\) | 2.28                | 1.22            | 1.79        | 1.85    | NA              | NA              | 1.78           |
| MAE           | 0.10      |                     | 0.46            | 0.37        | 0.55    | 0.13            | 0.46            |                |
| MSE           | 0.08      | -1.06               | -0.46           | -0.37       | -0.51   | 0.03            | -0.32           |                |

\(^a\)Experimental data refer to gas phase. Data was taken from Ref. 56,57. If an asterisk was labeled to the experimental data, it refers to that the data was corrected from the liquid phase experimental data by 0.32 eV as suggested by Ref. 26. \(^b\)Data taken from Ref. 26. \(^c\)Results from pp-RPA with CAMB3LYP reference. Data were taken from Ref 42. \(^d\)CC2 calculation was performed by package Turbomole\(^58\). Aug-cc-pVTZ was used as basis set, which was tested to reach the basis set convergence. \(^e\)Data were taken from Ref 44. \(GW_{psc}\) stands for partial self-consistent \(GW\). \(^f\)\(\Delta\text{SCF-BLYP}\) with maximum overlap method\(^33\). \(^g\)Systems shown below are substitutes of anthracene.
delocalize from the donor (benzene) to the acceptor (TCNE), when the separation increases to large distance. Since the LUMO of the \((N - 1)\)-electron system is used to retrieve the ground state of \(N\)-electron system, such orbital delocalization to acceptor molecule leads only partial, rather than one-net, electron transition within this method, and brings the calculated CT excitation energies lower than expected. When LOSC is applied to B3LYP to reduce the delocalization error, it shows that \(1/R\) behavior can be correctly captured.

To understand the reason that the \(1/R\) trend can only be captured from DFA with minimal delocalization error within this methodology, we start analysis on a model donor-acceptor system. First, the CT excitation of the donor-acceptor complex is concerning the transition of one electron from the donor molecule to the acceptor molecule. When we start

![Diagram](image)

FIG. 1: Variation of the benzene-TCNE complex first singlet charge transfer excitation energies (in eV) with intermolecular distance \(R\). Subfigure (a) and (b) show the electron distribution of LUMO orbital of the \((N - 1)\)-electron benzene-TCNE complex system with increasing intermolecular distance at 4.65 and 6.65 Å, respectively.
the calculation from the ground state \((N - 1)\)-electron system, it would be reasonable to assume one electron was completely removed from the donor molecule only. This assumption of \((N - 1)\)-electron system will make the donor molecular become one positively charged, and leave the acceptor molecule to stay neutral. Under this condition, the virtual orbital from such \((N - 1)\)-electron system, in particular, the LUMO orbital should be localized on the donor molecular, since adding one electron to LUMO gives the ground state \(N\)-electron system. In contrast, the orbitals above LUMO from \((N - 1)\)-electron system should be localized on acceptor molecular, since adding one electron to these orbitals gives the CT excited state of \(N\)-electron system. This consideration of the localization for virtual orbitals from \((N - 1)\)-electron system was confirmed to be reasonable by plotting the electron distribution of orbitals from one test case, benzene-TCNE complex. As shown in Fig. 2, LUMO of the complex at short separation distance (3.65 Å) is localized on benzene molecule (donor), while LUMO+1 is localized on the TCNE molecule (acceptor).

![Fig. 2](image_url)

**FIG. 2:** Electron distribution of (a) LUMO and (b) LUMO+1 orbital of the \((N - 1)\)-electron benzene-TCNE complex system from B3LYP calculation at short intermolecular distance, 3.65 Å.

Based on the above assumption that the concerning orbitals from \((N - 1)\)-electron system are localized in corresponding subspace, the positive charge on the donor molecule acts as an external +1 point charge field to the neutral acceptor molecule. Therefore, the orbitals above LUMO, which are localized on the acceptor molecule, should be lowered by \(1/R\).
In contrast, the LUMO, which is localized on the donor molecule, should have negligible effect from the neutral acceptor molecule, if we ignore the higher-order polarization effect. According to this analysis, the CT excitation energy from this method, (Eq. 6), should have the dependence of

$$\Delta E^\text{singlet}_m \propto [-2/R - (-1/R)] - 0 = -1/R,$$

(7)

if the orbital localization condition holds.

As conventional DFAs suffer from delocalization error seriously and the orbitals start to delocalize at long distance, 1/R trend as described in Eq. 7 will not be expected from conventional DFAs. In the case of LOSC calculation, if the correction was performed with an SCF manner, the orbitals will be expected to be localized from conventional DFAs (see Ref. 46), hence, the 1/R trend would be expected in principle. If the LOSC calculation was only performed with a post-SCF manner, which is the case in this work, we still observed the qualitatively 1/R trend. Although the post-SCF LOSC calculation does not update the orbital density information from parent DFAs, it may still be delocalized at long distance. It turns out that orbital energies are corrected accurately by LOSC to the quasiparticle energies. Therefore, the CT excitation energy, Eq. 1, is well approximated by Eq. 6 numerically, and the 1/R dependence is observed.

IV. CONCLUSION

In conclusion, we demonstrated a simple and efficient way to calculate the CT excitation energy of an N-electron system from the Kohn-Sham orbital energies of a ground state (N −1)-electron system. With numerical results, we show that our method performs better in CT excitation energy calculation to the TDDFT with conventional functionals. To obtain reliable results within this method, applying density functional approximation with minimal delocalization error, such LOSC-DFAs, are important. The computational cost from this method is only at the level of a DFT ground state calculation. However, the accuracy can reach to a degree similar to the $\Delta$SCF, $G_0W_0$-BSE, pp-RPA and even close to high-level wavefunction method, like CC2. In addition to the CT excitation energy calculations, we verified that this method is capable of capturing the 1/R trend of CT excitation, in which applying LOSC-DFAs is essential. Analysis shows that the 1/R trend is always expected from this method, as long as the orbital localization condition holds. Considering the good
results and inexpensive computational cost from the ground state DFT calculations, we believe this method provides an efficient path to describe CT excitation problems.

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REFERENCES

1. A. V. Akimov, A. J. Neukirch, and O. V. Prezhdo, Chem. Rev. 113, 4496 (2013).
2. J.-L. Brédas, D. Beljonne, V. Coropceanu, and J. Cornil, Chem. Rev. 104, 4971 (2004).
3. R. Mason, Discuss. Faraday Soc. 27, 129 (1959).
4. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
5. R. Parr and Y. Weitao, Density-Functional Theory of Atoms and Molecules, International Series of Monographs on Chemistry (Oxford University Press, 1994).
6. E. Runge and E. K. Gross, Phys. Rev. Lett. 52, 997 (1984).
7. A. D. Laurent and D. Jacquemin, Int. J. Quantum Chem. 113, 2019 (2013).
8. A. Dreuw and M. Head-Gordon, Chem. Rev. 105, 4009 (2005).
9. M. A. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. Gross, Time-dependent density functional theory, Vol. 706 (Springer Science & Business Media, 2006).
10. O. Gritsenko and E. J. Baerends, J. Chem. Phys. 121, 655 (2004).
11. N. T. Maitra, J. Phys.: Condens. Matter 29, 423001 (2017).
12. J. Autschbach, ChemPhysChem 10, 1757 (2009).
13. O. Gritsenko and E. J. Baerends, J. Chem. Phys. 121, 655 (2004).
14. N. T. Maitra, J. Chem. Phys. 122, 234104 (2005).
15. S. Kümmel, Adv. Energy Mater. 7, 1700440 (2017).
16. D. J. Tozer, J. Chem. Phys. 119, 12697 (2003).
17. B. Moore, H. Sun, N. Govind, K. Kowalski, and J. Autschbach, J. Chem. Theory Comput. 11, 3305 (2015).
18. M. Srebro and J. Autschbach, J. Phys. Chem. Lett. 3, 576 (2012).
19. A. Dreuw, J. L. Weisman, and M. Head-Gordon, J. Chem. Phys. 119, 2943 (2003).
20. A. J. Cohen, P. Mori-Sánchez, and W. Yang, Phys. Rev. B 77, 115123 (2008).
21. J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982).
22. W. Yang, Y. Zhang, and P. W. Ayers, Phys. Rev. Lett. 84, 5172 (2000).
23. P. Mori-Sánchez, A. J. Cohen, and W. Yang, Phys. Rev. Lett. 100, 146401 (2008).
24. A. J. Cohen, P. Mori-Sánchez, and W. Yang, Chem. Rev. 112, 289 (2011).
25. A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science 321, 792 (2008).
26. T. Stein, L. Kronik, and R. Baer, J. Am. Chem. Soc. 131, 2818 (2009).
27. Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and K. Hirao, J. Chem. Phys. 120, 8425 (2004).
28. A. W. Lange, M. A. Rohrdanz, and J. M. Herbert, J. Phys. Chem. B 112, 6304 (2008).
29. T. Minami, M. Nakano, and F. Castet, J. Phys. Chem. Lett. 2, 1725 (2011).
30. Q. Wu and T. Van Voorhis, Phys. Rev. A 72, 024502 (2005).
31. T. Ziegler, A. Rauk, and E. J. Baerends, Theor. Chim. Acta 43, 261 (1977).
32. R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989).
33. A. T. Gilbert, N. A. Besley, and P. M. Gill, J. Phys. Chem. A 112, 13164 (2008).
34. G. M. Barca, A. T. Gilbert, and P. M. Gill, J. Chem. Theory Comput. 14, 1501 (2018).
35. T. Baruah, M. Olguin, and R. R. Zope, J. Chem. Phys. 137, 084316 (2012).
36. T. Baruah and M. R. Pederson, J. Chem. Theory Comput. 5, 834 (2009).
37. F. Amerikheirabadi, C. Diaz, N. Mohan, R. R. Zope, and T. Baruah, Phys. Chem. Chem. Phys. 20, 25841 (2018).
38. H. van Aggelen, Y. Yang, and W. Yang, Phys. Rev. A 88, 030501 (2013).
39. H. van Aggelen, Y. Yang, and W. Yang, J. Chem. Phys. 140, 18A511 (2014).
40. Y. Yang, H. van Aggelen, and W. Yang, J. Chem. Phys. 139, 224105 (2013).
41. D. Peng, H. van Aggelen, Y. Yang, and W. Yang, J. Chem. Phys. 140, 18A522 (2014).
42. Y. Yang, A. Dominguez, D. Zhang, V. Lutsker, T. A. Niehaus, T. Frauenheim, and W. Yang, J. Chem. Phys. 146, 124104 (2017).
43. X. Leng, F. Jin, M. Wei, and Y. Ma, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 6, 532 (2016).
44. X. Blase and C. Attaccalite, Appl. Phys. Lett. 99, 171909 (2011).
45. Y. Mei, C. Li, N. Q. Su, and W. Yang, J. Phys. Chem. A 123, 666 (2019).
46. C. Li, X. Zheng, N. Q. Su, and W. Yang, Natl. Sci. Rev. 5, 203 (2017).
47. R. L. A. Haiduke and R. J. Bartlett, J. Chem. Phys. 149, 131101 (2018).
48. Y. Mei, C. Li, N. Q. Su, and W. Yang, ArXiv181009906 Phys. (2018), arXiv:1810.09906 [physics].
49. J. C. Slater, *Quantum theory of molecular and solids. Vol. 4: the self-consistent field for molecular and solids* (McGraw-Hill: New York, 1974).
50. S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980).
51. A. D. Becke, Phys. Rev. A 38, 3098 (1988).
52. A. D. Becke, J. Chem. Phys 98, 5648 (1993).
53. C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).
54. T. Yanai, D. P. Tew, and N. C. Handy, Chem. Phys. Lett. 393, 51 (2004).
55. An in-house developed program for qm/mm simulations; available from http://www.qm4d.info.”.
56. J. Masnovi, E. Seddon, and J. Kochi, Can. J. Chem. 62, 2552 (1984).
57. I. Hanazaki, J. Phys. Chem. 76, 1982 (1972).
58. TURBOMOLE V7.2 2017, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.”.