

Reliable prediction of the singlet-triplet gap in TADF molecules with GW/BSE approach

Debapriya Chaudhuri*, and Charles H. Patterson*

*School of Physics, Trinity College Dublin, Dublin 2, Ireland

Email: chaudhud@tcd.ie; Charles.Patterson@tcd.ie

Abstract—Organic light emitting diode (OLED) molecules that exhibit thermally activated delayed fluorescence (TADF) have emerged as a promising technology for various lighting and display applications. Such systems depend on low singlet-triplet gaps of the order of kT to allow reverse inter-system crossing. Here, we demonstrate the capability of a GW/BSE method to predict excitation energies and singlet-triplet gaps. We compare the results with time-dependent density functional theory of two organic molecules. The BSE results (in comparison to TDDFT-TDA) show absolute minimum deviations of 0.04 eV in the first absorption peak and 0.04 eV in the singlet-triplet splitting for the PhCz molecule and serve as a reliable tool to explore the design concepts in TADF molecules with small singlet-triplet splittings.

Index Terms—OLEDs, TADF, singlet-triplet splitting

I. INTRODUCTION

Organic π -conjugated molecules with donor-acceptor (D-A) type structural arrangement display interesting charge-transfer (CT) properties upon photo-excitation [1]. Such systems possess a small singlet-triplet splitting (ΔE_{ST}) between the lowest emitting singlet and triplet excited states which stems from the spatial separation between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [1]. Time-dependent density functional theory (TDDFT) [2] is an inexpensive method that provides a reasonable description of the excited states in organic molecules, but when dealing with D-A type systems with strong CT character, excitation energies are significantly underestimated due to the absence of long-range, screened electron-hole attraction in local functionals [3]. In this respect, optimally tuned range-separated TDDFT methods and G_0W_0 /BSE provide reliable optical spectra and ΔE_{ST} [4]. Note, the latter method relies on screening of the electron-hole interaction to determine electron, hole and optical excitation energies and has been used to predict electron affinities (EA), ionization potentials (IP) and excited states in organic molecules that are relevant to TADF emitter molecules [4].

Here, we demonstrate the ability of G_0W_0 /BSE method to accurately predict (i) excitation energies, (ii) absorption spectra and (iii) singlet-triplet splittings for two organic molecules in the gas phase, namely PhCz and NPh₃, that are generally used as hole/electron transport layers. Furthermore, we compare the results with standard density functional M06-2X and optimally tuned density functional LC- ω PBE. Ground state optimized geometries for both molecules are shown in Fig. 1.

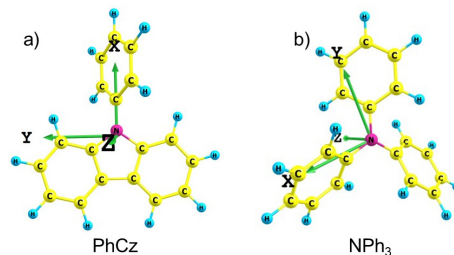


Fig. 1. (Color online) Ground state equilibrium geometry for a) PhCz and b) NPh₃ optimized at B3LYP/6-31g(d) level.

II. THEORETICAL FRAMEWORK

Perturbative G_0W_0 calculations are commonly performed using Kohn-Sham states as a starting point for calculation of G_0 and W_0 . Here, Hartree-Fock (HF) states are used as the starting point, which includes the unscreened Fock exchange. Linear response many-body approximations such as BSE and TDDFT can be expressed as,

$$\begin{pmatrix} \mathbf{A} - \Omega & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* - \Omega \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \mathbf{0}, \quad (1)$$

where the matrices \mathbf{A} and \mathbf{B} contain the HF or DFT energy eigenvalues and electron repulsion integrals (ERIs). Omission of the coupling \mathbf{B} matrices in Eq. 1 results in the Tamm-Dancoff approximation (TDA) and is used here. For the BSE results discussed in this article we use the G_0W_0 /BSE module implemented in the Exciton code [5] and TDDFT-TDA calculations were performed using the GAMESS code [6]. A recent application of the Exciton code to an emitter molecule (DPTZ-DBTO2) showed good agreement of the optical spectra and ΔE_{ST} when compared to TDDFT results [7]. Thus, the adopted framework is a good starting point to explore the electronic structure in TADF molecules.

III. RESULTS

The ground state geometries for both molecules were optimized at the B3LYP/6-31G(d) level and optimal ω values were adopted from Bredas *et al.* [8]. Vertical singlet (triplet) excitation energies were calculated using three distinct methods, namely a) M1: M06-2X@TDDFT, b) M2: LC- ω PBE@TDDFT and c) M3: G_0W_0 @HF/BSE. For the first two methods we used the cc-PVDZ basis, ω is optimally

TABLE I

METHOD TYPE, NAME OF THE MOLECULE, CT SINGLET EXCITED STATE ($E_{CT}^{S_1}$), CT TRIPLET EXCITED STATE ($E_{CT}^{T_1}$), CORRESPONDING ΔE_{ST} , AND HOMO-LUMO (H-L) GAP FOR THE GAS PHASE GROUND STATE GEOMETRY.

| Method | Molecule | $E_{CT}^{S_1}$ (eV) | $E_{CT}^{T_1}$ (eV) | ΔE_{ST} (eV) | H-L Gap (eV) |
|------------------------|------------------|------------------------|------------------------|-------------------------|-----------------|
| MO6-2X@TDDFT | PhCz | 4.46 | 3.74 | 0.72 | 6.65 |
| LC- ω PBE@TDDFT | PhCz | 4.23 | 3.46 | 0.77 | 7.76 |
| G_0W_0 @HF/BSE | PhCz | 4.42 | 3.66 | 0.76 | 8.63 |
| MO6-2X@TDDFT | NPh ₃ | 4.42 | 3.70 | 0.72 | 6.65 |
| LC- ω PBE@TDDFT | NPh ₃ | 4.15 | 3.40 | 0.75 | 7.67 |
| G_0W_0 @HF/BSE | NPh ₃ | 4.52 | 3.75 | 0.77 | 8.89 |

tuned to 0.206 for PhCz and 0.198 for NPh₃ whereas for G_0W_0 @HF/BSE calculations we used the def2-TZVP basis set along with corresponding def2-TZVP-RI auxiliary basis sets for density fitting Coulomb matrix elements. In Table I we present a comparison of the first CT singlet state (S_1), triplet CT state (T_n), corresponding ΔE_{ST} and HOMO-LUMO (H-L) gaps. Note, we present the results for the $H \rightarrow L$ transition and thus we can identify the individual states easily from the corresponding eigenvectors. For PhCz, the MO6-2X@TDDFT calculation exhibits a singlet CT state at 4.46 eV (see Fig. 2a) and the corresponding ΔE_{ST} is 0.72 eV. With LC- ω PBE@TDDFT the corresponding singlet absorption peak is at 4.23 eV (see Fig. 2b) and ΔE_{ST} is 0.77 eV. Lastly, the G_0W_0 @HF/BSE calculation exhibits an absorption at 4.42 eV for the CT transition (see Fig. 2c) and deviates from M1 (M2) by only 0.04 eV (0.19 eV). The corresponding ΔE_{ST} is 0.76 eV. This matches previous theoretical studies that reported splitting of around 0.73 eV [8], whereas the experimentally measured singlet-triplet gap is 0.55 eV for PhCz [9]. We furthermore benchmark the G_0W_0 @HF/BSE results for the NPh₃ molecule (see Table I). With M1 the S_1 state and ΔE_{ST} are 4.42 eV and 0.72 eV, respectively. Using M2, the corresponding S_1 state is reduced to 4.15 eV whereas the overall ΔE_{ST} is 0.75 eV. Lastly, with G_0W_0 @HF/BSE the S_1 state is at 4.52 eV and the resulting singlet-triplet splitting is 0.77 eV. Previous theoretical (experimental) studies reported a ΔE_{ST} of 0.74 eV (0.57 eV) and deviates from M3 results by only 0.03 eV (0.20 eV) [9] for the NPh₃ molecule. Overall, the BSE results predict the required singlet-triplet splitting in both molecules accurately and sets the launchpad for future investigations of CT excited state geometry relaxations.

IV. SUMMARY

Summarizing our findings : (a) The singlet excited energy states obtained by a G_0W_0 @HF/BSE method are in good agreement with two TDDFT-TDA methods and deviate by a maximum value of 0.19 eV (0.35 eV) for the PhCz (NPh₃) molecule. (b) ΔE_{ST} values obtained via G_0W_0 @HF/BSE change by a maximum value of 0.04 eV (0.05 eV) for PhCz (NPh₃) molecule. (c) Oscillator strengths for optical transitions in all the methods agree reasonably well and the corresponding transitions for each state in each method can be easily identified by monitoring the $H \rightarrow L$ transitions.

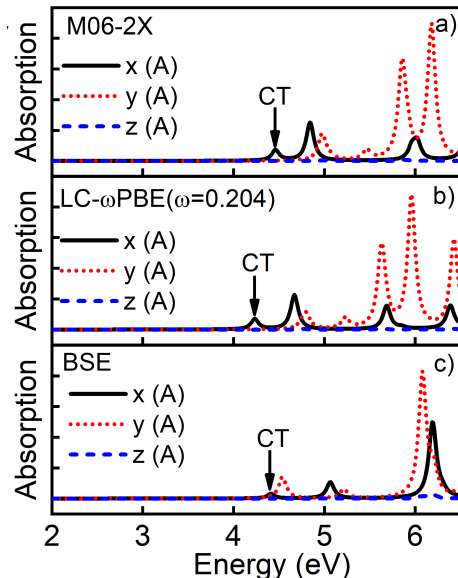


Fig. 2. (Color online) Vertical singlet absorption spectrum of PhCz molecule in the ground state equilibrium geometry for three distinct methods namely a) MO6-2X@TDDFT b) LC- ω PBE@TDDFT and c) G_0W_0 @HF. Positions of the first DA CT absorption are indicated by arrows. The solid black line, dotted red line and the dashed blue line are for optical fields along x, y and z directions.

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