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Accurate Treatment of Charge-Transfer Excitations and Thermally Activated Delayed Fluorescence Using the Particle–Particle Random Phase Approximation

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Abstract

Thermally activated delayed fluorescence (TADF) is a mechanism that increases the electroluminescence efficiency in organic light-emitting diodes by harnessing both singlet and triplet excitons. TADF is facilitated by a small energy difference between the first singlet (S_1) and triplet (T_1) excited states ($E(ST)$), which is minimized by spatial separation of the donor and acceptor moieties. The resultant charge-transfer (CT) excited states are difficult to model using time-dependent density functional theory (TDDFT) because of the delocalization error present in standard density functional approximations to the exchange–correlation energy. In this work we explore the application of the particle–particle random phase approximation (pp-RPA) for the determination of both S_1 and T_1 excitation energies. We demonstrate that the accuracy of the pp-RPA is functional dependent and that, when combined with the hybrid functional B3LYP, the pp-RPA computed $E(ST)$ have a mean absolute deviation (MAD) of 0.12 eV for the set of examined molecules. A key advantage of the pp-RPA approach is that the S_1 and T_1 states are characterized as CT states for all of experimentally reported TADF molecules examined here, which allows for an estimate of the singlet–triplet CT excited state energy gap ($E(ST) = {}^1CT - {}^3CT$). For experimentally known TADF molecules with a small (<0.2 eV) $E(ST)$ in this data set, a high accuracy is demonstrated for the prediction of both the S_1 (MAD = 0.18 eV) and T_1 (MAD = 0.20 eV) excitation energies as well as $E(ST)$ (MAD = 0.05 eV). This result is attributed to the consideration of correct antisymmetry in the particle–particle interaction leading to the use of full exchange kernel in addition to the Coulomb contribution, as well as a consistent treatment of both singlet and triplet excited states. The computational efficiency of this approach is similar to that of TDDFT, and the cost can be reduced significantly by using the active-space approach.

Graphical Abstract

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Supporting Information

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xyz coordinates for B3LYP/ cc-pVDZ optimized geometries (PDF)

Complete listing of convergence tests, all computed and experimental energies, and orbital plots (PDF)

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1. INTRODUCTION

Organic light-emitting diodes (OLEDs) are a viable technology for next-generation display and solid-state lighting applications because of low cost and power consumption with high brightness and contrast.^{1–4} Since the development of phosphorescent OLEDs (PhOLEDs),^{5–7} the field has continued to make notable breakthroughs in device efficiency through higher internal quantum efficiency (IQE) made possible from harnessing both singlet and triplet excitons that requires circumventing the limitation of spin-statistics for charge recombination. Phosphorescence can be emphasized by incorporating heavy metals,⁸ which incites intersystem crossing from the first singlet (S_1) to the first triplet (T_1) excited state through strong spin–orbit coupling. Alternatively, higher IQE can be achieved through the population of S_1 from T_1 through thermally activated delayed fluorescence (TADF).^{9,10} TADF is an efficient up-conversion mechanism of excitons from T_1 to S_1 , bypassing the theoretically spin-forbidden T_1 relaxation through reverse intersystem crossing, leading to enhanced fluorescence from S_1 . TADF, which historically has been known by multiple names, including both α -phosphorescence and delayed thermal fluorescence,^{11–13} has been observed as early as 1941 in fluorescein by Lewis and co-workers.¹⁴ TADF is a promising mechanism for applications of organic electronics because it pushes the theoretical maximum IQE from 25 to 100% without need for heavy metals. Adachi and co-workers have demonstrated that OLEDs built with TADF emitters can reach external quantum efficiency higher than non-TADF fluorescence OLEDs and comparable to PhOLEDs.^{15,16}

Because reverse intersystem crossing is an endothermal process, efficient TADF requires the energy splitting of the lowest singlet and triplet excited states to be minimized.¹⁷ The difference in energy between S_1 and T_1 , $E(ST)$, can be approximated by $2K$,^{11,18} where K is the exchange integral between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), and therefore can be minimized by spatial separation of the HOMO and LUMO. As a result, TADF can be realized in π -conjugated, donor–acceptor molecules, which leads to charge-transfer (CT) excited states that correspond to a transfer of electron density from the electron-rich (donor) to the electron-deficient (acceptor) portion of the molecule.

Molecular modeling can aid in characterization and prediction of properties of TADF molecules by making it possible to evaluate the impact of the specific donor and acceptor components on the electronic properties.¹⁵ Recent computational advances have led to prediction of novel, highly efficient TADF emitters through virtual screening.¹⁹ Excited-state properties of large molecules can be computed using various approaches, including both wave function methods and time-dependent density functional theory (TDDFT).^{20–22}

However, accurately modeling TADF molecules is particularly difficult when the standard density functional approximations to the exchange-correlation (xc) functional are used because of the delocalization error present in these approximations.²³ This error manifests as significant underestimation of CT excited states for TADF molecules. Indeed, TDDFT tends to underestimate CT states due to the local character of xc functionals describing a nonlocal charge-separated state.^{24,25} Furthermore, the delocalization error is known to be more significant for extended systems with delocalized electron distributions,^{23,26} which is particularly relevant for large molecules with conjugated moieties such as those that are typically used in TADF applications. TADF molecules possess small $E(\text{ST})$ and require high accuracy methods (e.g., $E(\text{ST})$ as small as 60 meV have been reported²⁷).

To mitigate the errors associated with standard xc correlation functionals for reproducing CT states, range-separated functionals are often used.^{28–31} These functionals contain a range separation parameter (μ) to spatially separate the treatment of the exchange, with exact exchange in the long-range to recover the correct asymptotic decay of the xc potential, which has been shown to result in higher accuracies for modeling CT states.^{32–35} Further, μ is system-dependent, so parameter tuning has been carried out in a system-dependent fashion^{32,36–38} to reduce the delocalization error^{39,40} compared to standard DFT methods.^{35,41–44} Range-separated approaches with tuning perform well for small systems but are problematic for large systems, because of the size-dependent manifestation of the delocalization error.^{23,45} Tuned, long-range corrected functionals combined with the Tamm-Dancoff approximation to TDDFT (TDDFT/TDA)⁴⁶ have shown promise in the description of TADF emitters.^{47,48} For example, Sun and coworkers applied the tuned LC- ω PBE to TADF molecules and reported a mean absolute deviation (MAD) of 0.09 eV for $E(\text{ST})$,⁴⁷ and Penfold reported a MAD of 0.05 eV for $E(\text{ST})$ using tuned LC-BLYP.⁴⁸ Sun et al.⁴⁷ report μ ranging from 0.14 to 0.20 Bohr⁻¹, and Penfold⁴⁸ reports μ ranging from 0.15 to 0.19 Bohr⁻¹, whereas the standard μ for LC- ω PBE and LC-BLYP are 0.400 and 0.33 Bohr⁻¹, respectively, indicating that the amount of exchange found in standard range-separated functionals is too large to accurately describe TADF molecules.

Although tuned range-separated functionals are one route for reducing the errors in the computed S_1 and T_1 energies, it has been shown that the percentage of Hartree–Fock exchange in a given functional has a larger effect on the T_1 energy compared to the S_1 energy for a set of known TADF molecules,²⁷ and this can lead to large errors for the TDDFT-computed T_1 energies for moderately sized TADF emitters due to triplet instabilities.^{49,50} This result has motivated the use of the TDDFT/TDA formalism instead.^{51,52} Another strategy for modeling TADF molecules combining restricted open-shell Kohn–Sham with spin DFT has been shown to accurately reproduce CT states using hybrid functionals.⁵³ An advantage of this time-independent procedure is that ground-state contamination of excited states is avoided.

In this work, we apply the particle–particle random phase approximation (pp-RPA)⁵⁴ to compute excitation energies for a set of CT and TADF molecules.²⁷ The pp-RPA approach for computing excitation energies can be understood as a Fock space embedding method—describing the ground and excited states of an N-electron system by embedding a many-electron description of two electrons in a density functional description of an (N-2)-electron

system.⁵⁵ It has been shown to yield high accuracy for single, double, CT, and Rydberg excitations,⁵⁴ as well as for the singlet–triplet energy gaps for diradicals⁵⁶ and polyacenes.⁵⁷ In a different context, the pp-RPA method has been shown to give ground-state correlation energy with the correct energy derivative discontinuity at integer particle number.⁵⁸ Given the success of the pp-RPA at reproducing excitation energies, we apply the pp-RPA to a set of TADF molecules with small excited-state singlet–triplet energy gaps (Figure 1), which were reported and analyzed by Adachi and co-workers.²⁷ We compute vertical absorption energies, E_{VA} , for both S_1 and T_1 , as well as the zero-to-zero transition energy for T_1 , $E_{0-0}(T_1)$, to compare to experimental data for $E_{VA}(S_1)$, $E_{0-0}(T_1)$, and adiabatic $E(ST)$. These molecules range in size from 32 to 118 atoms and are the largest systems studied with the pp-RPA to our knowledge. A $E(ST)$ of ~0.1 eV is ideal for TADF,¹⁵ and accordingly, molecules with $E(ST) < 0.2$ eV, including PIC-TRZ (**5**), 4CzPN (**12**), PXZ-TRZ (**13**), Spiro-CN (**14**), 4CzIPN (**15**), 4CzTPN (**16**), and 4CzTPN-Me (**17**), will be grouped as efficient TADF molecules; results for these molecules will be emphasized in the discussion.

2. COMPUTATIONAL DETAILS

Molecular geometries were optimized at B3LYP/cc-pVDZ level of theory (see the Supporting Information for the Cartesian coordinates).^{59–62} The pp-RPA energies reported here are calculated using both B3LYP and CAM-B3LYP⁶³ (N-2)-electron references using the cc-pVDZ basis set. Single-point calculations on the (N-2)-electron state are carried out in Gaussian09⁶⁴ (with the same functionals and basis set), and the resultant density matrix is then read into QM4D⁶⁵ to perform the pp-RPA calculation. Singlet and triplet excitation energies were computed using the active-space pp-RPA approach⁵⁵ with 8 active occupied and 8 active virtual orbitals. To ensure that the active-space size is suitable, the convergence of the energies with respect to the truncation size was tested for molecule **2**; $E_{VA}(S_1)$ ($E_{VA}(T_1)$) changed by 0.05 (0.009) eV between active space sizes of (8, 8) and (50, 50) (Supporting Information, Table S1), indicating that this choice of active space is sufficient. We carried out calculations in cc-pVTZ^{61,62} for molecules **2** and **11** to assess the impact of basis set size and found that the computed excitation energies change by at most 0.11 eV when the basis set is increased from double- to triple- ζ level (Table S2). The pp-RPA with the (N-2)-electron reference orbitals computed with B3LYP/cc-pVDZ is used throughout this analysis and will be referred to as pp-RPA in the text below unless otherwise stated.

The eigenvalues of the pp-RPA matrix equations correspond to two-electron addition and removal energies. Focusing on two-electron addition energies, one can begin from the (N-2) electronic state and add back two electrons to recover the ground state and all singlet and triplet excited state configurations of the N-particle system. The vertical excitation energies are obtained by taking the difference between the eigenvalues for two-electron addition to the (N-2)-particle system. The vertical excitation energies, $E_{VA}(S_1)$ and $E_{VA}(T_1)$, are calculated according to eqs 1 and 2,

$$E_{VA}(S_1) = E_{S_1}^N - E_{S_0}^N = (E_{\text{ref}}^{N-2} + \omega_{S_1}) - (E_{\text{ref}}^{N-2} + \omega_{S_0}) = \omega_{S_1} - \omega_{S_0} \quad (1)$$

$$E_{\text{VA}}(T_1) = E_{T_1}^N - E_{S_0}^N = (E_{\text{ref}}^{N-2} + \omega_{T_1}) - (E_{\text{ref}}^{N-2} + \omega_{S_0}) = \omega_{T_1} - \omega_{S_0} \quad (2)$$

where $E_{S_0}^N$, $E_{S_1}^N$ and $E_{T_1}^N$ are the total energy of the N-electron ground state (S_0), S_1 , and T_1 , respectively. E_{ref}^{N-2} represents the energy of the two-electron deficient reference system. ω_{S_0} , ω_{S_1} and ω_{T_1} are the pair addition energies that lead to S_0 , S_1 , and T_1 , respectively. The corresponding vertical $E(\text{ST})$ energies are computed as the difference between the E_{VA} values.

$$\Delta E(\text{ST}) = E_{\text{VA}}(S_1) - E_{\text{VA}}(T_1) = \omega_{S_1} - \omega_{T_1} \quad (3)$$

For direct comparison to phosphorescence data, we compute the zero-to-zero transition energy, E_{0-0} , for T_1 , which corresponds to emission from the lowest-energy vibronic level of T_1 to the lowest vibronic level of the ground state, by correcting $E_{\text{VA}}(T_1)$ with the relaxation energy, λ . This correction is computed as the difference between the T_1 energy at both the S_0 and T_1 geometries and including zero-point energy correction according to the following equation:

$$E_{0-0}(T_1) = E_{\text{VA}}(T_1) - \lambda(T_1) + \Delta \text{ZPE} \quad (4)$$

The relaxation term $\lambda(T_1) = E_{\text{Sgeo}}(T_1) - E_{\text{Tgeo}}(T_1)$, and the zero-point energy correction $\text{ZPE} = E_{\text{ZPE}}(T_1) - E_{\text{ZPE}}(S_0)$. The pp-RPA values are also compared to previously reported energies using TDDFT and TDDFT/TDA (all are consistently computed using the B3LYP functional and are listed in Table S3).

The performance of the pp-RPA is compared with TDDFT energies computed using B3LYP/6-31G(d),²⁷ whereas the TDDFT/TDA results were carried out at the B3LYP/6-31+G(d) level of theory and account for solvent effects using the polarizable continuum model.⁴⁷ To assess the impact of the difference in basis sets and geometries on the excitation energies, we computed TDDFT and TDDFT/TDA excitation energies using cc-pVDZ for molecules **3**, **4**, **6**, **7**, and **10**. The results differ by 60 meV (average 26 meV) for TDDFT and 180 meV (average 69 meV) for TDDFT/TDA (Table S4). Noting the small differences with different basis sets, we carry out a comparison of the results from pp-RPA with those from TDDFT and TDDFT/TDA.

The experimental data²⁷ used in this study were measured in nonpolar solvents (cyclohexane and toluene), which should have minimal effects on the energies, as solute-solvent interactions are weak with low polarity solvent⁶⁶ and are therefore excluded in this work.

3. RESULTS AND DISCUSSION

To assess the performance of the pp-RPA in the determination of the S_1 and T_1 energies, we compare the computed excitation energies to the available experimental data for $E_{VA}(S_1)$, $E_{0-0}(T_1)$, and $E(ST)$ for 17 molecules whose chemical structures are shown in Figure 1. All computed and experimental S_1 and T_1 energies are provided in Table S5.

3.1. Singlet Energies.

The pp-RPA computed $E_{VA}(S_1)$ values have a MAD of 0.24 eV (mean signed deviation (MSD) of 0.05 eV) compared to the experimental $E_{VA}(S_1)$ energies. In comparison, the TDDFT (MAD = 0.36 eV, MSD = -0.29 eV)²⁷ and TDDFT/TDA (MAD = 0.39 eV, MSD = -0.35 eV)⁴⁷ tend to underestimate $E_{VA}(S_1)$ energies, which can be seen in Figure 2; a complete summary of the error analysis appears in Table 1. The improved performance of the pp-RPA for $E_{VA}(S_1)$ is attributed to the better description of CT states, which are typically underestimated by TDDFT. In donor-acceptor TADF molecules, S_1 has significant CT character, which can be evaluated qualitatively through analysis of the molecular orbitals that correspond to the pair-addition eigenvectors for the excited-state configuration. The S_1 state is dominated by HOMO $\rightarrow$ LUMO transition (>90%) for all molecules except **4**, which also has HOMO $\rightarrow$ LUMO + 2 character (which is degenerate with HOMO $\rightarrow$ LUMO). For these 17 molecules, the HOMO (LUMO) is mainly localized on the donor (acceptor) moieties (see Figures S1–17 for HOMO and LUMO pictures). From orbital analysis based on pp-RPA derived eigenvectors, S_1 is determined to have significant CT character for all molecules, while molecule **4** possesses a mixture of both CT and locally excited (LE) character. A summary of the transitions can be found in Table S6.

Focusing on the molecules for which the pp-RPA computed $E_{VA}(S_1)$ gives the largest error, the energies for molecules **1** (+0.48 eV), **6** (+0.51 eV), and **7** (+0.45 eV) are overestimated, while it is underestimated for molecule **14** (-0.46 eV). In comparison, $E_{VA}(S_1)$ for molecule **1** is also overestimated by TDDFT (+0.38 eV)²⁷ and TDDFT/TDA (+0.31 eV), which is surprising considering that TDDFT methods combined with a functional that contains a large delocalization error tend to underestimate CT states (Figure 2). Although the pp-RPA, TDDFT, and TDDFT/TDA all overestimate the experimental energy (3.66 eV), these methods agree with the result $E_{VA}(S_1)$ of 3.98 eV from coupled cluster (CC2) theory.⁴⁷ A possible source of error comes from the fact that the current implementation of pp-RPA does not include contributions of transitions involving orbitals below the HOMO. However, an analysis of the configuration interaction (CI) data from ref 27 (comparison of CI and pp-RPA data appears in Table S7) for molecules **1**, **6**, and **7** reveals small contribution to S_1 from HOMO-1 transition (<5%), indicating that the contribution to these excited states will be minimal and should have a minor effect on the energy. Molecules grouped as representative TADF (**5** and **12–17**) are described well with the pp-RPA, yielding a MAD of 0.18 eV, whereas these CT states are underestimated by TDDFT (TDDFT/TDA) with a MAD of 0.45 eV (0.48 eV), indicating the importance of capturing CT states for accurate estimations of excitation energies in TADF molecules.

3.2. Triplet Energies.

With an understanding of the performance of the pp-RPA for $E_{\text{VA}}(S_1)$, the T_1 energies can now be discussed. The experimental T_1 energies are obtained from phosphorescence measurements and correspond to the zero-to-zero transition between the lowest vibronic levels of T_1 and the ground state, $E_{0-0}(T_1)$. For molecules **13**, **16**, and **17**, $E_{0-0}(T_1)$ was not directly measured from phosphorescence because of the broad emission band indicative of a CT state; instead, the experimental values for these systems were derived indirectly from the rate of the delayed fluorescence. To compare to experiment, the computed $E_{\text{VA}}(T_1)$ results are corrected with a relaxation term, λ , and ZPE according to eq 4. The $E_{\text{VA}}(T_1)$ results from TDDFT and TDDFT/TDA are adjusted with the same λ and ZPE for each molecule (Table S3). In comparison to the experimental $E_{0-0}(T_1)$, the pp-RPA has a MAD of 0.26 eV (MSD = -0.11 eV). The results for T_1 computed with TDDFT (MAD = 0.46 eV) and TDDFT/TDA (MAD = 0.43 eV) are consistently underestimated compared to experiment (see Figure 3), which is similar to what was found for the S_1 CT state. In fact, the MSD = -MAD for TDDFT and TDDFT/TDA (Table 1). Molecules grouped as prototypical TADF emitters (**5** and **12–17**) are characterized better than others in the entire set with the pp-RPA approach, yielding a MAD of 0.20 eV for $E_{0-0}(T_1)$. For this subset of molecules, the errors are larger with TDDFT (MAD = 0.53 eV) and TDDFT/TDA (MAD = 0.56 eV) using B3LYP, which showcases the effect of delocalization error in standard density functional approximations on predicting energies of CT states.

Next we make comparison of the nature of the T_1 state computed with the pp-RPA to the experimental characterization. With the pp-RPA, T_1 is dominated by HOMO $\rightarrow$ LUMO transitions (Table S6), which we assign qualitatively as CT states based on an analysis of the orbitals (Figures S1–S17). T_1 for molecule **2** is described by a HOMO $\rightarrow$ LUMO + 2 CT transition (there is degeneracy in lowest unoccupied orbitals). Similar to the discussion of S_1 , molecule **4** is characterized by both HOMO $\rightarrow$ LUMO (49%) and HOMO $\rightarrow$ LUMO + 2 (41%), which are CT and LE states, respectively. The results computed with the pp-RPA are in contrast to experimental characterization of T_1 as LE for all molecules, except for molecules **13**, **16**, and **17**, which are experimentally assigned as CT states.²⁷ The discrepancy on the nature of the T_1 state may be due to either a limitation of the method or variance in the assignment of the spectra. The pp-RPA approach does not capture contributions from orbitals below the HOMO; however, for CT states dominated by a HOMO $\rightarrow$ LUMO transition, this limitation should not be an issue. Excitations with small contribution from lower orbitals can still be described within the pp-RPA as long as the contribution from the HOMO is relatively large.⁶⁷

Phosphorescence measurements are carried out in toluene at low temperature (77 K) in order to avoid the low barrier reverse intersystem crossing transition. CT bands are usually broad and devoid of vibronic information, whereas LE peaks are sharper. However, spectra measurements carried out at low temperature (e.g., frozen toluene) will reduce half bandwidth and number of peaks and lead to sharper peaks, as the effect of temperature broadening is minimized. Therefore, we do not expect that a broad CT band will be observed in phosphorescence measurements carried out at 77 K, making assignment of the

nature of this state difficult. We note that performing the measurements in increasingly polar solvents should red-shift a CT band and could resolve the assignment.

3.3. Singlet–Triplet Energy Gap.

The energy splitting between S_1 and T_1 is arguably the most important parameter when characterizing and designing molecules with delayed fluorescence. Because $E(\text{ST})$ is small, reverse intersystem crossing occurs at ambient temperature and phosphorescence is not observed. Ideally $E(\text{ST})$ can be approximated by the difference in vertical absorption energies, which is a simpler computational task. Comparing vertical $E(\text{ST})$ to adiabatic $E(\text{ST})$ is a fair approximation when S_1 and T_1 surfaces are locally parallel.⁶⁸

The vertical $E(\text{ST})$ gaps computed with pp-RPA, TDDFT, and TDDFT/TDA are plotted along with experimental adiabatic $E(\text{ST})$ gaps in Figure 4 (all data appear in Tables S3 and S5). The vertical $E(\text{ST})$ computed with pp-RPA have an MAD of 0.12 eV (MSD = −0.01 eV) compared to experimental adiabatic $E(\text{ST})$ values. Similarly, a MAD of 0.10 eV is computed for both TDDFT (MSD = 0.00 eV) and TDDFT/TDA (MSD = −0.08 eV).

A key advantage of the pp-RPA method over TDDFT and TDDFT/TDA (using B3LYP) is realized for the TADF systems with a small $E(\text{ST})$. Efficient TADF design aims at achieving $E(\text{ST}) \approx 0.1$ eV.¹⁵ For molecules **5** and **12–17**, which all have a $E(\text{ST}) < 0.2$ eV, the pp-RPA estimate for $E(\text{ST})$ has a MAD of 0.05 eV, which is similar to the MAD of 0.03 eV obtained for both TDDFT and TDDFT/TDA. Further for $E_{\text{VA}}(S_1)$ [$E_{0-0}(T_1)$], the MAD is 0.18 eV [0.20 eV], 0.45 eV [0.53 eV], and 0.48 eV [0.56 eV], for pp-RPA, TDDFT, and TDDFT/TDA (all using B3LYP), respectively. This result indicates that all methods yield good approximations of singlet–triplet energy differences; however, TDDFT and TDDFT/TDA combined with B3LYP systematically underestimate the individual energies of the most relevant systems. Therefore, information about the fluorescent properties (the energy of S_1) requires higher accuracy, which can be achieved with the pp-RPA.

3.4. Effect of Relaxation.

We now discuss a structural relationship between the excited states. If S_1 and T_1 are locally parallel, then the vertical $E(\text{ST})$, computed from the difference $E_{\text{VA}}(S_1)$ and $E_{\text{VA}}(T_1)$, should give the adiabatic $E(\text{ST})$, the variable of interest. It follows that, if S_1 and T_1 are parallel, then the relaxation energies on the S_1 and T_1 surface are equal, $\lambda(S_1) = \lambda(T_1)$. Therefore, if $\lambda(S_1)$ and $\lambda(T_1)$ are similar, then the vertical approximation should recover the adiabatic singlet–triplet energy gap, that is, if $\lambda(S_1) = \lambda(T_1)$ then vertical $E(\text{ST}) =$ adiabatic $E(\text{ST})$ (Figure 5). To test this, we compare the relaxation energy $\lambda(S_1)$ determined from experiment²⁷ and computed $\lambda(T_1)$ values along with the difference between the computed vertical and experimental adiabatic $E(\text{ST})$. The results are shown in Table 2 (all energies appear in Table S9). When the difference between the relaxation energies is small, the approximation of the singlet–triplet gap by vertical estimates reproduces the experimental adiabatic gap (when both λ and $E(\text{ST})$ are small). This is particularly true for molecules **5** and **12–17**, which have $E(\text{ST}) < 0.2$ eV and are the most characteristic of molecules that exhibit TADF. Sun and co-workers⁴⁷ have previously discussed the relaxation energy in both S_1 and T_1 but have found a different result:

molecules with small $E(\text{ST})$ have larger $\lambda(\text{S}_1)$ compared to $\lambda(\text{T}_1)$. Our result indicates that vertical estimates of $E(\text{ST})$ are appropriate for modeling TADF molecules, for which $E(\text{ST})$ is small and S_1 and T_1 surfaces are locally parallel. This indicates that the computational cost of computing $E(\text{ST})$ for TADF molecules can be reduced from three optimizations (ground state, S_1 , and T_1) to one (the ground state) without sacrificing accuracy.

3.5. Comments on Functionals.

To examine how the underlying density functional impacts the pp-RPA computed excitation energies, the results obtained using B3LYP are also compared with energies obtained using a CAM-B3LYP reference (Table S10). Interestingly the B3LYP reference yields values closer to experiment for $E_{\text{VA}}(\text{S}_1)$ (MAD = 0.24 eV) than those with the CAM-B3LYP reference for $E_{\text{VA}}(\text{S}_1)$ (MAD = 0.92 eV). Although the pp-RPA shows a functional dependence for $E_{\text{VA}}(\text{S}_1)$ and $E_{\text{VA}}(\text{T}_1)$, a consistent shift in the individual energies leads to similar error for $E(\text{ST})$ with CAM-B3LYP reference (MAD = 0.14 eV) and B3LYP (MAD = 0.12 eV). In contrast, using TDDFT/TDA, a larger error was seen for both $E_{\text{VA}}(\text{S}_1)$ and $E(\text{ST})$ with CAM-B3LYP (MAD = 0.49 and 0.26 eV, respectively) compared to B3LYP (MAD = 0.39 eV for $E_{\text{VA}}(\text{S}_1)$ and 0.10 eV for $E(\text{ST})$).⁴⁷ A MAD of 0.15 eV was achieved for $E_{\text{VA}}(\text{S}_1)$ using a tuned LC- ω PBE functional with TDDFT/TDA for this set of TADF systems.⁴⁷ The tuned μ parameters used for each system range from 0.142 to 0.204 Bohr⁻¹, whereas the energies computed with LC- ω PBE (in which $\mu = 0.4$ Bohr⁻¹) lead to values that are much larger, resulting in MAD of 1.03 eV for $E_{\text{VA}}(\text{S}_1)$. In comparison, the μ value for the CAM-B3LYP functional is 0.33 Bohr⁻¹. The intricacies of the μ -tuning procedure reveal that the origin of the error for CAM-B3LYP is the larger incorporation of Hartree–Fock exchange in the short-range.⁴⁷ Therefore, an accurate calculation of the excited states of TADF molecules using TDDFT or TDDFT/TDA necessitates a smaller amount of exact exchange than what is used in standard range-separated functionals. In contrast, the $E(\text{ST})$ gaps with the pp-RPA display a much smaller shift with a change in the functional.

4. CONCLUSIONS

We have applied the pp-RPA to a set of 17 molecules with CT excited states and small singlet–triplet energy splitting. Accurately reproducing small energy differences is a challenge for excited-state methods. Our study demonstrates that the pp-RPA approach combined with B3LYP yields low error for $E_{\text{VA}}(\text{S}_1)$ (MAD = 0.24 eV), $E_{0-0}(\text{T}_1)$ (MAD = 0.26 eV), and $E(\text{ST})$ (MAD = 0.12 eV) for all 17 molecules. For prototypical TADF emitters (with $E(\text{ST}) < 0.2$ eV) the results are especially accurate, with MAD of 0.18 eV [0.20 eV] for $E_{\text{VA}}(\text{S}_1)$ [$E_{0-0}(\text{T}_1)$]. Therefore, the pp-RPA combined with B3LYP is able to accurately describe CT states, which is an important property of TADF molecules. The results from the pp-RPA indicate that both S_1 and T_1 are CT states, whereas T_1 was assigned as LE from experimental spectra for phosphorescence measurements for all molecules except **13**, **16**, and **17**, which were assigned as CT.

Whereas all methods produce accurate results for $E(\text{ST})$, the TDDFT and TDDFT/TDA approaches combined with B3LYP systematically underestimate the individual energies of

S_1 and T_1 CT states. The singlet–triplet energy splitting is accurately reproduced by approximating the adiabatic transition energy by vertical absorption energies using the pp-RPA. Using the pp-RPA to approximate the adiabatic $E(\text{ST})$ with the vertical $E(\text{ST})$, a MAD of 0.12 eV is achieved, further demonstrating the ability to analyze TADF molecules by approximating adiabatic $E(\text{ST})$ with the difference between vertical absorption energies. This is especially true for molecules with the smallest $E(\text{ST})$, for which T_1 and S_1 are locally parallel. This simplifies the computational protocol for describing TADF emitters without loss of accuracy.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Chemical structures of the 17 TADF molecules examined here with pp-RPA that were previously reported.²⁷

Figure 2.

Comparison of experimental $E_{VA}(S_1)$ to results computed with the pp-RPA, TDDFT, and TDDFT/TDA using ground-state orbitals from B3LYP. TDDFT²⁷ and TDDFT/TDA⁴⁷ data are listed in Table S3, and experimental and pp-RPA results are in Table S5.

Figure 3.

Comparison of experimental $E_{0-0}(T_1)$ to results computed with the pp-RPA, TDDFT, and TDDFT/TDA using ground-state orbitals from B3LYP. TDDFT²⁷ and TDDFT/TDA⁴⁷ data are listed in Table S3, and experimental and pp-RPA results are in Table S5.

Figure 4.

Comparison of experimental, adiabatic $E(\text{ST})$ to vertical $E(\text{ST})$ results computed with the pp-RPA, TDDFT, and TDDFT/TDA using B3LYP ground-state orbitals. TDDFT²⁷ and TDDFT/TDA⁴⁷ data are listed in Table S3, and experimental and pp-RPA results are in Table S5.

Figure 5.

Pictorial representation of the potential energy surfaces for the ground state, S_0 , and S_1 and T_1 , to show the relationship between the excited-state surfaces. When S_1 and T_1 are locally parallel, the difference between vertical absorption energies, $E(ST)$, is equal to the adiabatic $E(ST)$ difference. In this scenario, the relaxation energies, $\lambda(S_1)$ and $\lambda(T_1)$, are equal.

Table 1.

Mean Absolute Deviation (MAD) and Mean Signed Deviation (MSD) for the pp-RPA, TDDFT,²⁷ and TDDFT/TDA⁴⁷ Are Compared to Experimental Data;²⁷ All Values Reported in Units of eV^a

	MAD (MSD)		
	$E_{\text{VA}}(\text{S}_1)$	$E_{0-0}(\text{T}_1)$	$E(\text{ST})$
pp-RPA	0.24 (0.05)	0.26 (-0.11)	0.12 (-0.01)
TDDFT	0.36 (-0.29)	0.46 (-0.46)	0.10 (0.00)
TDDFT/TDA	0.39 (-0.35)	0.43 (-0.43)	0.10 (-0.08)

$$^a\text{MAD} = (1/n) \sum_{i=1}^n |x_{\text{calc}} - x_{\text{exp}}|. \text{MSD} = (1/n) \sum_{i=1}^n (x_{\text{calc}} - x_{\text{exp}}).$$

Table 2.Comparison of Experimental, Adiabatic $E(\text{ST})$, and Computed Vertical $E(\text{ST})^a$

	molecule	$E(\text{ST})$ calculated	$E(\text{ST})$ experimental	$ E(\text{ST}) $	$ \lambda $
1	PhCz	0.90	0.55	0.35	0.25
2	NPh ₃	0.51	0.57	0.06	0.25
3	CBP	0.42	0.71	0.29	0.35
4	α -NPD	0.37	0.73	0.36	0.25
5	PIC-TRZ	0.19	0.18	0.01	0.02
6	DPA-DPS	0.57	0.52	0.05	0.04
7	DTPA-DPS	0.52	0.46	0.06	0.01
8	ACRFLCN	0.49	0.24	0.25	0.12
9	CC2TA	0.05	0.20	0.15	0.18
10	DTC-DPS	0.23	0.36	0.13	0.02
11	2CzPN	0.34	0.31	0.03	0.01
12	4CzPN	0.10	0.15	0.05	0.02
13	PXZ-TRZ	0.12	0.06	0.06	0.13
14	Spiro-CN	0.00	0.06	0.06	0.01
15	4CzIPN	0.16	0.10	0.06	0.02
16	4CzTPN	0.16	0.09	0.07	0.04
17	4CzTPN-Me	0.15	0.09	0.06	0.05

^aThe difference is reported as $|E(\text{ST})|$. When the relaxation energies of T₁ (computed) and S₁ (from experiment²⁷) are equal (when $|\lambda| = 0$), the vertical approximation reproduces the experimental adiabatic gap. All energies are listed in units of eV.