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Triplet-Tuning: A Novel Non-Empirical Construction Scheme of Exchange Functionals

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Abstract

In the framework of density functional theory (DFT), the lowest triplet excitation energies, E_T , can be evaluated using multiple formulations, the most straightforward of which are unrestricted ground state DFT (UDFT) and time-dependent DFT (TDDFT). Assuming the exact exchange–correlation (XC) functional is applied, both formulations should provide identical values for E_T , which is a constraint that approximate XC functionals should obey. However, this condition is not satisfied by most commonly used XC functionals, resulting in inaccurate predictions of low-lying, photochemically important excited states, such as the lowest triplet (T_1) and singlet (S_1) excited states. In the present study, we propose a novel and *non-empirical* prescription to approximate the exact XC functional, referred to as “triplet tuning”, by enforcing the aforementioned agreement of E_T between UDFT and TDDFT. This scheme allows us to construct the XC functional on a case-by-case basis using the molecular structure as the exclusive input, without fitting to any experimental data. The first triplet-tuned XC functional, TT- ω PBEh, is formulated as a long-range-corrected (LRC) hybrid and tested on four test sets of large organic molecules. TT- ω PBEh manages to provide more accurate predictions for key observables in photochemical measurements, including but not limited to E_T , optical band gaps (E_S), singlet–triplet gaps (ΔE_{ST}), and ionization potentials (I). This promising triplet

tuning scheme can be applied to a wide range of systems, as it adjusts the effective electron-hole interactions to arrive at the correct excitation energies.

1 Introduction

Due to its affordable computational cost, density functional theory (DFT) has become the workhorse for the theoretical investigation of large molecules, especially functional materials where most wave function based approaches become infeasible.¹⁻⁴ DFT was originally established as a ground-state approach, while various excited-state extensions have also been formulated to predict more interesting experimental observables. These excited-state methods include Δ self-consistent field (Δ SCF),⁵ restricted open-shell Kohn–Sham (ROKS),⁶ time-dependent DFT (TDDFT),⁷ and spin-flip DFT (SFDFT).⁸ Despite being formally exact, a few intrinsic issues with DFT have hindered its predictive power for excited-state properties of molecules, especially organic molecules with large π -conjugated structures. For example, the accuracy of widely used empirical density functionals heavily relies on the selection of parameters in the approximate exchange–correlation (XC) functional, which is sensitive to the collection of data including in the empirical fitting process. Also, the self-interaction error (SIE) and the locality problem can lead to unphysical density distributions and the catastrophic failure for asymptotic, one-particle properties such as ionization potentials (I) and charge-transfer (CT) excitation energies.⁹⁻¹⁶

Many methodological efforts to resolve these issues have been reported in the literature within the recent decade. New DFT variants have been invented, such as constrained variational DFT (CV(∞)-DFT),¹⁷ constrained DFT (CDFT),¹⁸ self-interaction corrected DFT (SIC-DFT)¹⁹ and average density self-interaction correction (ADSIC).²⁰ As a more broad applicable solution, new density functionals have also been developed to better approximate the exact XC functional. Some of these XC functionals include *meta*-generalized gradient approximation (*meta*-GGA) that involves the second gradient of the density (TPSS,²¹ SCAN,²² M06-L,²³ M06-2X,²⁴ *etc.*) and range-separation treatment that reproduces partial or full asymptotic density decay by implementing the Hartree–Fock (HF) exchange in the long range (CAM-B3LYP,²⁵ CAM-QTP,²⁶ ω B97X-V,²⁷ ω B97M-V²⁸ LRC- ω PBE,^{29,30} LRC- ω PBEh,^{31,32} *etc.*). In the latter situation, the range-separation parameter, ω , is still empirically determined.

More recently, several optimally-tuned variants of range-separated XC functionals have been

proposed and applied, including OT-BNL,³³ OT- ω B97XD,³⁴ OT- ω PBEh,³⁵ *etc.*. These functionals optimize ω in a non-empirical, system-dependent manner, and the algorithm can be considered as a “black box” in which the molecular structure serves as the exclusive input. For instance, Kronik, Baer, and co-workers developed the most frequently used optimal tuning scheme^{33,36,37} based on Iikura’s idea of range separation³⁸ and Koopmans’ theorem,³⁹ which enforces an agreement between the ionization potential (I) and the negative eigenvalue for the highest occupied molecular orbital ($-\varepsilon_{\text{HOMO}}^{(N)}$). This condition is supposed to be satisfied by the exact XC functional. These conventional optimally tuned functionals have successfully improved the prediction of one-electron properties such as fundamental band gaps, photoelectron spectra, and charge-transfer excitation energies, but have so far presented weaker predictive powers for photophysically/photochemically important properties like optical band gaps and fluorescence/phosphorescence spectra.^{40–44} This can lead to serious problems for large photoactive organic molecules.

Motivated by reaching more accurate predictions of photophysically/photochemically important excited states, we propose the very first triplet tuning scheme based on the lowest triplet excited states (T_1) and develop the first triplet tuned functional in this series, TT- ω PBEh. We imitated the formula of LRC- ω PBEh,^{29,30} leaving one or both of the following two parameters to be determined: ω and the percentage of the Hartree–Fock exchange in the short range, C_{HF} . Both parameters were tuned in a *non-empirical* manner by matching the lowest triplet excitation energies ($E_{\text{T}} = E_{T_1} - E_{S_0}$) evaluated using two excited-state variants of DFT, namely Δ SCF and TDDFT. The details of these methods are provided in the Theory section.

In the Result and Discussion section, the accuracy and reliability of TT- ω PBEh were evaluated using four groups of large organic molecules with rich photophysics/photochemistry and that are notoriously difficult to investigate theoretically, even for low-lying excited states. Compared to most existing XC functionals, TT- ω PBEh provides excellent agreement with experimentally observed energies, including E_{T} , the optical gaps ($E_{\text{S}} = E_{S_1} - E_{S_0}$), the singlet–triplet gaps ($\Delta E_{\text{ST}} = E_{S_1} - E_{T_1}$), and vertical ionization potentials ($I_{\perp} = -\varepsilon_{\text{HOMO}}^{(N)}$). Our triplet tuning prescription essentially reproduces the screening of the electron-hole interaction in the excited states

and serves as the basis for more accurate prediction of absorption/fluorescence/phosphorescence spectra and photophysical/photochemical dynamics.

2 Theory

2.1 Triplet Excitation Energy

The most popular version of DFT was constructed by Kohn and Sham to evaluate the ground state based on molecular orbitals.^{2,3} In this framework, the lowest excited state with a non-singlet spin configuration can be evaluated using unrestricted DFT (UDFT) that relaxes α and β orbitals individually, rather than the original restricted version (RDFT).⁴⁵ Most organic molecules possess a closed-shell, spin-restricted ground state (S_0) and can achieve the lowest triplet excited state (T_1) by promoting one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and flipping its spin accordingly. The triplet excitation energy in question, $E_T = E_{T_1} - E_{S_0}$, corresponds to an experimental measure of E_{T_1} and can be evaluated using the following Δ SCF scheme,

$$E_T^{\Delta\text{SCF}} = E_{T_1}^{\text{UDFT}} - E_{S_0}^{\text{RDFT}}. \quad (1)$$

In an alternative scheme, T_1 can be treated as an excited state using linear-response time-dependent DFT (TDDFT).^{7,46} As such

$$E_T^{\text{TD}} = E_{T_1}^{\text{TDDFT}} - E_{S_0}^{\text{RDFT}}. \quad (2)$$

2.2 Triplet Tuning Protocols

Since Δ SCF and TDDFT are both formally exact approaches under the valid adiabatic local-density approximation (ALDA),^{7,11,47-49} Eqs. (1) and (2) would provide identical values of E_T using the exact XC functional,

$$E_T^{\Delta\text{SCF}} \equiv E_T^{\text{TD}}. \quad (3)$$

In order to optimize our constructed XC functional, we enforced Eq. (3) as a constraint by adjusting the intrinsic parameters associated with the functional *without introducing any empiricism*. In other words, the following objective function,

$$J_{\text{TT}}^2 = (E_{\text{T}}^{\Delta\text{SCF}} - E_{\text{T}}^{\text{TD}})^2, \quad (4)$$

is minimized when an optimal set of parameters is reached. Similar to Kronik and Baer’s protocol of optimal tuning,^{33,36,37} we minimized the value of J_{TT}^2 so as to approximate the exact XC functional.

The first triplet-tuned functional in the series, referred to as TT- ω PBEh, was designed to predict accurate density in both short and long ranges and to reproduce the correct electron-hole interactions in molecules. TT- ω PBEh utilizes a range-separated hybrid formula^{29–32,50} which separates the exchange functional into the short-range (SR) and long-range (LR) contributions.³⁸ We focus on the tuning of the exchange functional as it has a greater contribution to the energetic corrections than the correlation functional. As such

$$E_{\text{XC}} = E_{\text{X}}^{\text{SR}} + E_{\text{X}}^{\text{LR}} + E_{\text{C}}. \quad (5)$$

Such a range separation is achieved by re-expressing the Coulomb operator, $1/r_{12}$, as³⁸

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - \text{erf}(\omega r_{12})}{r_{12}}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\omega r_{12})}{r_{12}}}_{\text{LR}}, \quad (6)$$

in which $r_{12} = |\vec{r}_1 - \vec{r}_2|$ is the inter-electron distance and “erf” represents the Gauss error function.⁵¹ Eq. (6) introduces a tunable range-separation parameter (ω), which is the reciprocal of distance at which E_{X}^{SR} transitions to E_{X}^{LR} .³⁸ As the non-local Hartree–Fock (HF) exchange exhibits correct asymptotic behavior,⁵² we selected

$$E_{\text{X}}^{\text{LR}} \equiv E_{\text{X}}^{\text{HF}}. \quad (7)$$

On the other hand, E_X^{SR} takes a hybrid form with HF and a selected DFT exchange functional in order to balance the localization error from HF and delocalization error from most local exchange functionals.⁵³ As such

$$E_X^{\text{SR}} = C_{\text{HF}} E_{X,\text{HF}}^{\text{SR}} + C_{\text{DFT}} E_{X,\text{DFT}}^{\text{SR}}. \quad (8)$$

C_{HF} and C_{DFT} represent the fractions of the HF and DFT components in E_X^{SR} , and they are related to each other through the uniform electron gas constraint,

$$C_{\text{HF}} + C_{\text{DFT}} = 1. \quad (9)$$

Eqs. (8) and (9) suggest the second tunable parameter, C_{HF} . In various range-separated hybrid formulations, the expressions of E_C in Eq. (5) and $E_{X,\text{DFT}}^{\text{SR}}$ in Eq. (8) can be selected among LDA,² GGA,⁵⁴⁻⁵⁶ or *meta*-GGA²¹⁻²⁴ based on the demands of the systems. In TT- ω PBEh we utilized the Perdew–Burke–Ernzerhof formulas for both of them⁵⁷ and optimized both ω and C_{HF}

It is also possible to tune only one parameter at a time, and we employed that approach to tune ω (TT- ω PBEh ω , similar to LRC- ω PBEh³²) and C_{HF} (TT- ω PBEhC). This enables us to compare the performance of TT- ω PBEh against one parameter tuned TT- ω PBEh ω and TT- ω PBEhC functionals for selected molecules. Throughout the present study, we applied TT- ω PBEh to all molecules in question and compared its results with TT- ω PBEh ω and TT- ω PBEhC for selected molecules.

2.3 Consideration of One-Electron Properties

As was discussed in the Introduction section, the triplet tuning scheme focuses on the correct electron-hole interactions while the prescriptions of Kronik and Baer provide excellent one-electron properties. Therefore a performance comparison between two approaches has become necessary. To achieve that we also constructed the OT- ω PBEh functional using the same range-separated hybrid formulations described in Eqs. (5)-(9). The objective function was established based on the

Koopmans’ theorem³⁹ following the literature,^{33,36,37}

$$J_{\text{OT}}^2 = \left[I_{\perp} + \varepsilon_{\text{HOMO}}^{(N)} \right]^2 + \left[A_{\perp} + \varepsilon_{\text{HOMO}}^{(N+1)} \right]^2, \quad (10)$$

where I_{\perp} and A_{\perp} represent the vertical ionization potential and electron affinity, and $\varepsilon_{\text{HOMO}}^{(N)}$ and $\varepsilon_{\text{HOMO}}^{(N+1)}$ stand for the HOMO energy of the neutral and anionic species. $\varepsilon_{\text{HOMO}}^{(N+1)}$ is a substitute of $\varepsilon_{\text{LUMO}}^{(N)}$ due to the incorrect physical interpretation of virtual orbitals in the Kohn–Sham picture.^{3,58}

I_{\perp} and A_{\perp} in Eq. (10) are evaluated using ΔSCF ,

$$I_{\perp} = E_{\text{C}^+}^{\text{UDFT}} - E_{\text{S}_0}^{\text{RDFT}}, \quad (11)$$

$$A_{\perp} = E_{\text{S}_0}^{\text{RDFT}} - E_{\text{A}^-}^{\text{UDFT}}, \quad (12)$$

where C^+ and A^- represent cationic and anionic species with the molecular structure of the neutral species.

In addition, we combined the OT and TT tuning recipes to formulate another functional called mix- ωPBEh , in order to take into account both one-electron properties and electron-hole interactions using the same set of parameters. Its objective function is consequently the average of J_{TT}^2 and J_{OT}^2 ,

$$J_{\text{mix}}^2 = \frac{J_{\text{TT}}^2 + J_{\text{OT}}^2}{2}. \quad (13)$$

2.4 Test Sets of Organic Molecules

In order to evaluate the performance and applicability of TT- ωPBEh and compare its behavior to OT- ωPBEh and mix- ωPBEh , we selected a total of 110 organic molecules with various molecular structures and reliable experimental measurements of E_{T} , E_{S} , ΔE_{TS} , and I_{\perp} . Most of these molecules possess π -conjugated semiconducting structures and, in spite of being closed-shell, are notorious for being difficult cases for theoretical investigations. These molecules were divided into four test sets based on their molecular configurations, excited-state properties, and applica-

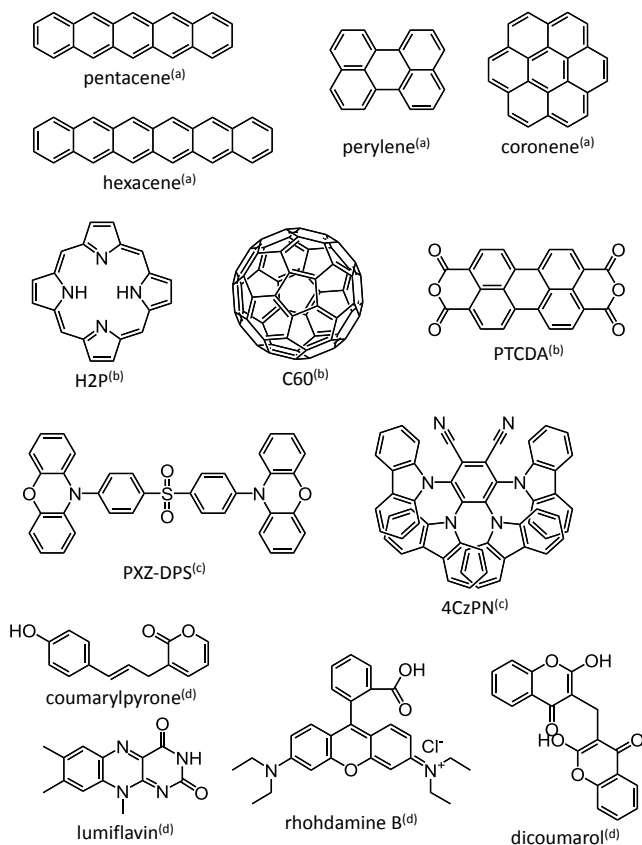


Figure 1: Structures of representative organic molecules included in four test sets: (a) polycyclic aromatic hydrocarbon molecules (PAH), (b) organic photovoltaic materials (OPV), (c) thermally activated delayed fluorescence emitters (TADF) and (d) π -conjugated bioorganic molecules (BIO).

tions. These four test sets includes polycyclic aromatic hydrocarbons (PAH),^{59–92} organic photovoltaics materials (OPV),^{42,59,65,67,70,78,93–168} thermally activated delayed fluorescence emitters (TADF),^{169–173} and π -conjugated bioorganic molecules (BIO).^{67,110,174–207} The molecules in the PAH, OPV and BIO sets possess locally excited states with different sizes of delocalized π -bonds, while TADF molecules have charge-transfer excited states. The structures of all molecules are listed in Figs. S1–S9 in the Supporting Information, and representative species are provided in Fig. 1.

2.5 Computational Details

With nuclear relaxation effect in consideration, we evaluated E_T , E_S and ΔE_{ST} in three different geometric variants, “absorption” (abs), “emission” (em) and “adiabatic” (adi), as illustrated

in Fig. 2. One particle properties, I_{\perp} , A_{\perp} , $-\varepsilon_{\text{HOMO}}^{(N)}$ and $-\varepsilon_{\text{HOMO}}^{(N+1)}$, were evaluated at the S_0 geometry. In all cases, the optimized molecular configurations associated with the states of S_0 and T_1 were determined using ground state RDFT and UDFT respectively,²⁰⁸ while those of the first singlet excited states (S_1) were evaluated using the restricted open-shell Kohn–Sham (ROKS) approach.⁶ All these optimizations utilized the B3LYP functional²⁰⁹ and the CC-PVDZ basis set. The system-dependent ω and/or C_{HF} -tuning calculations were performed at the optimized S_0 geometries by minimizing Eqs. (4), (10), or (13). For one-parameter versions of TT- ω PBEh, we optimized C_{HF} at $\omega = 0.200a_0^{-1}$ (TT- ω PBEh ω , $a_0 \equiv \text{bohr}$), or optimized ω at $C_{\text{HF}} = 0.20$ (TT- ω PBEhC), and performed the one-dimensional minimization using a gold-section search.^{210,211} For TT- ω PBEh, OT- ω PBEh and mix- ω PBEh with two tunable parameters, the two-dimensional minimizations were carried out using the simplex algorithm.²¹¹

Following the tuning of the parameters, E_{T} , E_{S} , ΔE_{ST} , I_{\perp} and A_{\perp} were evaluated using the tuned parameters and single point calculations of ΔSCF , TDDFT, and/or ROKS. For molecules with large-scale π -conjugations that suffer from singlet–triplet instability or failed diagonalization of the linear response matrix, the Tamm–Dancoff approximation (TDA)²¹² was included in the TDDFT calculations in the tuning process. $\varepsilon_{\text{HOMO}}^{(N)}$ and $\varepsilon_{\text{HOMO}}^{(N+1)}$ were extracted as eigenvalues of the Kohn–Sham (KS) orbitals produced in the ground state calculations of neutral and anionic species. All these calculated values were compared with the experimental measurements performed at the appropriate geometry variants shown in Fig. 2. If two or three geometric variants are experimentally available, we averaged the absolute errors (AE) over these variants. The accuracy of a XC functional was calibrated using the mean absolute error (MAE) between calculated and experimental energies over all molecules within each test set.

The results obtained from OT- ω PBEh, TT- ω PBEh and mix- ω PBEh were also compared with ten existing functionals, including HF,⁵² B3LYP,²¹³ CAM-B3LYP,²⁵ PBE,⁵⁷ PBE0,²¹⁴ LRC- ω PBE ($\omega = 0.300a_0^{-1}$, $C_{\text{HF}} = 0.00$),³⁰ LRC- ω PBEh ($\omega = 0.200a_0^{-1}$, $C_{\text{HF}} = 0.20$),³² TPSS,²¹ M06-2X²⁴ and M06-L.²³ All calculations reported in the present study used the CC-PVDZ basis set²¹⁵ and the Q-Chem 4.4 package.²¹⁶

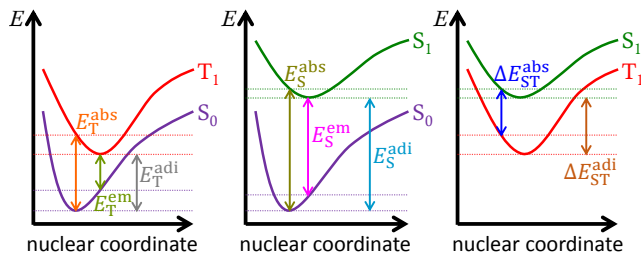


Figure 2: Different geometric variants of E_T , E_S , and ΔE_{ST} that are evaluated in the present study. Here “abs”, “em” and “adi” represent the absorption, emission and adiabatic energy gaps.

3 Results and Discussions

3.1 Problems with One-Parameter Functionals

In the present section, we show the necessity to tune both the range-separation parameter (ω) and the percentage of Hartree–Fock (HF) exchange in the short range (C_{HF}) in TT- ω PBEh by showing the problem with its one-parameter versions, TT- ω PBEh ω (fixing $C_{\text{HF}} = 0.20$, and tuning ω) and TT- ω PBEhC (fixing $\omega = 0.200a_0^{-1}$ and tuning C_{HF}). The discussion is based on two series of organic oligomers from our test sets: oligoacenes ($n = 1-6$, included in PAH) and oligothiophenes ($n = 1-7$, included in OPV).

The reciprocal of ω (ω^{-1}) provides the distance where the Perdew–Burke–Ernzerhof (PBE) exchange transitions to the HF exchange. A large ω^{-1} represents a small overall fraction of HF exchange, and *vice versa*. Fig. 3(a) illustrates a comparison in optimal ω^{-1} between TT- ω PBEh ω and TT- ω PBEh. Although the trend of the overall HF fraction is not obvious, the large values of ω^{-1} ($\omega^{-1} > 20a_0$) in optimized TT- ω PBEh ω indicate a negligible contribution from HF exchange and/or a difficulty to locate a minimum on the one-dimensional surface of ω . Similarly, TT- ω PBEhC presents a constant of $C_{\text{HF}} = 0.00$ (Fig. 3(b)), also showing a tiny contribution from HF and the difficulty of finding the optimal C_{HF} .

To evaluate how well the exact constraint in Eq. (3) is satisfied for TT- ω PBEh ω and TT- ω PBEhC, we also compared the following difference in triplet excitation energies,

$$J_{\text{TT}} = E_{\text{T}}^{\Delta\text{SCF}} - E_{\text{T}}^{\text{TD}}, \quad (14)$$

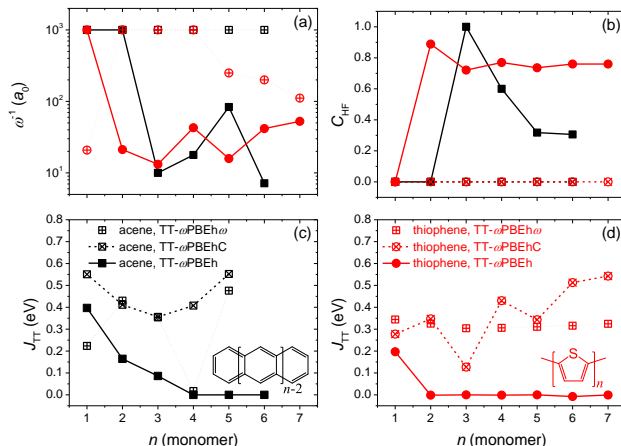


Figure 3: (a) Optimized ω^{-1} in TT- ω PBEh ω ($C_{\text{HF}} = 0.20$, hollow with plus) and TT- ω PBEh (solid) for oligoacenes (black square) and oligothiophenes (red circle). (b) Optimized C_{HF} for TT- ω PBEhC ($\omega = 0.200a_0^{-1}$, hollow with cross) and TT- ω PBEh (solid) for oligoacenes (black square) and oligothiophenes (red circle). (c) Optimized J_{TT} for oligoacenes based on TT- ω PBEh ω (hollow with plus), TT- ω PBEhC (hollow with cross), and TT- ω PBEh (solid). (d) Optimized J_{TT} for oligothiophenes based on TT- ω PBEh ω (hollow with plus), TT- ω PBEhC (hollow with cross), and TT- ω PBEh (solid). (ω^{-1} can never exceed $1000a_0$ as limited by Q-Chem.)

which is the signed square root of the minimized objective function in Eq. (4), in Fig. 3(c) and (d). Among the three functionals in question, TT- ω PBEh ω and TT- ω PBEhC both exhibit huge differences between $E_{\text{T}}^{\Delta\text{SCF}}$ and E_{T}^{TD} (as large as 0.6 eV), validating the conclusion that the one-dimensional triplet tuning process over ω or C_{HF} *does not necessarily* find the effective minimum and therefore the two-parameter triplet tuning is needed.

3.2 Triplet Excitation Energies

As was mentioned in the Introduction and Theory sections, the TT- ω PBEh functional proposed in the present study focuses on the *non-empirical* matching of the triplet excitation energies, $E_{\text{T}} = E_{\text{T}_1} - E_{\text{S}_0}$ (Eq. 3). Therefore the accuracy of E_{T} has become the a natural physical quantity to calibrate TT- ω PBEh. Given the well-minimized J_{TT}^2 , we expected TT- ω PBEh to provide more accurate E_{T} than most existing XC functionals, especially for notorious molecules with large-scale π -conjugations or charge-transfer excitations. Note that ω and C_{HF} in TT- ω PBEh are evaluated *independently* from any experimental data, and therefore the theoretical value of E_{T} presents no

fitting artifacts.

In the present subsection and those that follow, the error of each functional under investigation is characterized using the mean absolute errors (MAEs) that represent the absolute difference between theoretical calculations and experimental measurements, averaged over each of the four test sets described in the Theory section. We report the results for TT- ω PBEh, OT- ω PBEh and mix- ω PBEh obtained from single-point Δ SCF, TDDFT (TD) and TDDFT/TDA (TD/TDA) calculations based on optimized ω and C_{HF} , and compare them with ten frequently used XC functionals described in the Theory section. In order to characterize the lower and upper limits of the accuracy as well as the tightness of the exact constraint (Eq. (3)) in the present formulation, we also selected the smallest (or largest) absolute error (AE) among Δ SCF, TDDFT and TDDFT/TDA for every molecule, and averaged them into the “best” (or “worst”) MAEs. We summarize all such MAEs in Tables S1, S5, S9 and S11 in the Supporting Information and present selected MAEs in Table 1. For selected molecules in the PAH and OPV sets, we also illustrate in Fig. 4 the “best” AEs.

Table 1: Mean absolute errors (MAEs) of the triplet excitation energies, E_{T} , are compared across various functionals for the test sets of PAH, OPV, TADF and BIO.

energy XC functional	TD				worst			
	PAH	OPV	TADF	BIO	PAH	OPV	TADF	BIO
TT- ω PBEh	0.158	0.263	0.258	0.239	0.226	0.393	0.298	0.310
OT- ω PBEh	0.315	0.429	0.212	0.365	0.397	0.529	0.374	0.527
mix- ω PBEh	0.306	0.468	0.341	0.404	0.428	0.582	0.474	0.547
HF	0.235	0.284	0.288	0.272	0.771	1.037	1.077	0.869
B3LYP	0.255	0.307	0.272	0.313	0.331	0.352	0.324	0.356
CAM-B3LYP	0.244	0.352	0.298	0.350	0.330	0.476	0.545	0.445
PBE	0.174	0.323	0.753	0.416	0.199	0.339	1.074	0.439
PBE0	0.331	0.287	0.236	0.340	0.392	0.847	0.316	0.406
LRC- ω PBE	0.367	0.371	0.299	0.428	0.455	0.499	0.700	0.514
LRC- ω PBEh	0.352	0.462	0.282	0.403	0.431	0.570	0.610	0.475
TPSS	0.251	0.335	0.683	0.419	0.281	0.350	0.688	0.436
M06-2X	0.206	0.267	0.352	0.192	0.405	0.442	0.557	0.322
M06-L	0.210	0.275	0.555	0.424	0.259	0.311	0.564	0.461

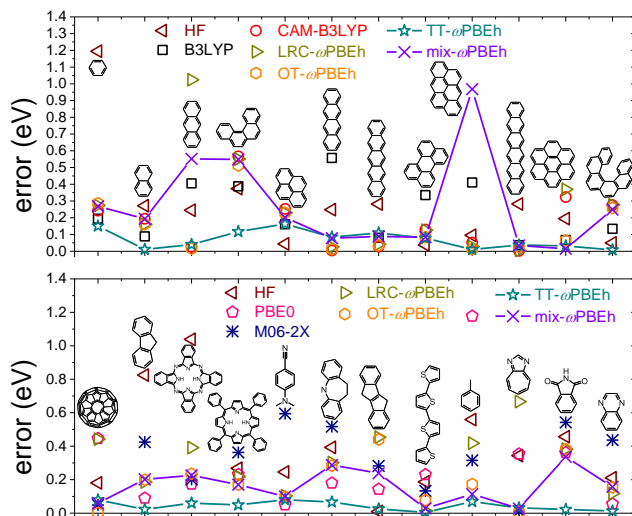


Figure 4: The absolute error in triplet energy, $E_T = E_{T_1} - E_{S_0}$, is illustrated for selected molecules in the test set of (a) PAH and (b) OPV. The results are compared among TT- ω PBEh (dark cyan star), OT- ω PBEh (orange hexagon), mix- ω PBEh (violet cross), HF (wine left triangle), B3LYP (black square), CAM-B3LYP (red circle), PBE0 (pink pentagon), M06-2X (navy double cross) and LRC- ω PBEh (dark yellow right triangle). TT- ω PBEh exhibits a consistently excellent performance.

3.2.1 Locally Excited Triplet States

In the present subsection, we will show the excellent performance of TT- ω PBEh for locally excited triplet states, for the test sets of PAH, OPV and BIO.

PAH and OPV molecules are expected to possess moderate- or large-scale π -conjugation. Based on results presented in Table 1, TT- ω PBEh has proved to achieve most accurate predictions (smallest MAEs) among all XC functionals in question, including OT- ω PBEh and mix- ω PBEh. For example, TT- ω PBEh provides an MAE of 0.158 eV for PAHs using TDDFT while all commonly-used functionals are more than 0.174 eV, most over 0.206 eV. Especially, OT- ω PBEh and mix- ω PBEh provide 0.315 eV and 0.306 eV respectively, which are almost doubled from TT- ω PBEh. On the other hand, for the BIO molecules that are anticipated to retain smaller π -conjugations, TT- ω PBEh outperforms every other functional except for M06-2X. This is probably due to the similarity between the small bioorganic molecules and those belonging to the database that was used for the construction of M06-2X (nucleobase *et al.*).²⁴ For all three test sets TT- ω PBEh is superior to OT- ω PBEh and mix- ω PBEh, which agrees with our expectation that TT- ω PBEh should

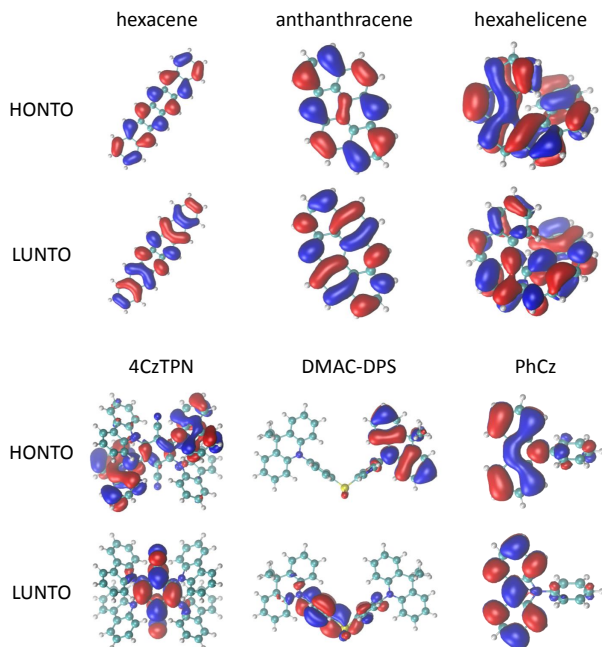


Figure 5: Highest occupied and lowest unoccupied natural transition orbitals (HONTO and LUNTO) of the T_1 state for six representative molecules: hexacene, anthanthracene and hexahelicene from PAH (upper panel) and 4CzTPN, DMAC-DPS and PhCz from TADF (lower panel). TT- ω PBEh exhibits a consistently excellent performance.

reproduce the accurate electron-hole interactions relevant to locally-excited states while the consideration of Koopmans' theorem will dilute this advantage. Overall, TT- ω PBEh has reached the overall best approximation to the exact functional in terms of locally excited T_1 state.

In addition, to validate the locality of these triplet excited states, we illustrate the natural transition orbitals (NTO) for the T_1 states of three selected molecules, hexacene, anthanthracene, and hexahelicene from the PAH set, in the upper panel of Fig. 5. The perfect spatial overlap between the highest occupied NTO (HONTO) and the lowest unoccupied NTO (LUNTO) confirm our hypothesis of locally-excited T_1 states. In general, for similar molecules the accuracy of TT- ω PBEh on the essential electron-hole interactions can be guaranteed.

3.2.2 Charge-Transfer Triplet Excited States

Based on the results obtained for TADF emitters, we will show that TT- ω PBEh exhibits an equally strong predictive power as OT- ω PBEh for charge-transfer excitation energies, which are approxi-

mately one-particle properties.

As was shown in Table 1, TT- ω PBEh is slightly less accurate than OT- ω PBEh and PBE0 when determining E_T using TDDFT (0.258 eV vs. 0.212 eV and 0.236 eV in MAE), but its “worst” MAE is smaller than those of the latter (0.298 eV vs. 0.374 eV and 0.316 eV). This illustrates the gains of complying with Eq. (3) at the small costs of accuracy, but the difference in MAE is significantly smaller than uncertainty of the hybrid functional approach itself.^{217–219} At the same time, TT- ω PBEh still outperforms the other functionals. Since the self-interaction error has the greatest contribution to the overall error associated with charge-transfer excited states, the *unexpectedly* excellent performance of TT- ω PBEh is probably due to its arrival at exact HF exchange in the asymptotic region, like OT- ω PBEh, and the one-quarter fraction of HF exchange ($C_{\text{HF}} = 0.25$) in PBE0²¹⁴ can play a similar role here.

To deepen our discussion, we will explore the relationship between the spatial separation of charges in the T_1 state and the performance of TT- ω PBEh. In the lower panel of Fig. 5, we illustrate the HONTO and LUNTO for the T_1 state of three representative TADF emitters, 4CzTPN, DMAC-DPS, and PhCz. For molecules like 4CzTPN and DMAC-DPS, the HONTO and LUNTO are located on the donor and the acceptor respectively, partially or fully separated in space. Construction of XC functionals for molecules like these have always been challenging in DFT as their accuracies are very sensitive to the choice of parameters. In general, the more separated the HONTO and LUNTO are in space, the worse performance is observed for TT- ω PBEh. As an extreme charge-transfer example, HONTO and LUNTO of 4CzTPN are well separated in space, and the single-point Δ SCF calculations reach AEs of 0.647 eV (TT- ω PBEh) and 0.188 eV (OT- ω PBEh), making a huge difference. In contrast, HONTO and LUNTO in PhCz almost fully overlap with each other in space, and TT- ω PBEh predicts a more accurate E_T than OT- ω PBEh (0.169 eV vs. 0.350 eV). From this we can conclude that TT- ω PBEh preserves a strong predictive power for charge-transfer excited states, except for a few extremely strong charge-transfer cases. The invalidity of ALDA in TDDFT can contribute to the large errors for these extreme charge-transfer molecules, for which the incorporation of the frequency dependence in the XC functional can be a

solution.^{47–49}

3.2.3 Spin Contamination

Although we have shown the excellent performance of TT- ω PBEh, the large AEs for some extreme charge-transfer excited states still raise a red flag. We noticed in some unrestricted DFT (UDFT) calculations the T_1 state is contaminated by higher spin configurations (quintet, sextet, *etc.*), which usually occurs at a large fraction of HF exchange. Such a spin contamination could be the origin of these large errors. For instance, the optimized parameters for 4CzTCN are $\omega = 0.147a_0^{-1}$ and $C_{\text{HF}} = 0.85$, and the expectation value of the spin, $\langle S^2 \rangle = 2.3358$, which is equivalent to a state with approximately 92% triplet ($\langle S^2 \rangle = 2$) and 8% quintet ($\langle S^2 \rangle = 6$).

In an attempt to resolve this issue, we re-evaluated $E_{\text{T}}^{\Delta\text{SCF}}$ in the single-point restricted DFT (RDFT) calculations based on UDFT-tuned parameters. However, this treatment turned out to overestimate E_{T} by more than 1 eV. Based on the current observation, we suggest two future strategies to improve the triplet tuning protocol, depending on whether the T_1 state is truly spin-contaminated. If it is not, $E_{\text{T}_1}^{\text{UDFT}}$ in Eq. (1) can be replaced with $E_{\text{T}_1}^{\text{RDFT}}$; but if it is, $E_{\text{T}_1}^{\text{SPDFT}}$ (spin-flip DFT) will be a potential replacement for $E_{\text{T}_1}^{\text{TDDFT}}$ in Eq. (2).

3.2.4 Constraints of Exact Functionals

To end the present subsection on E_{T} , we will comment on the tightness of the exact condition (Eq. 3) for TT- ω PBEh. The difference between “worst” and “best” MAEs, illustrated in the last column of Tables S3, S7, S11 and S13 in the Supporting Information, is positively correlated to J_{TT}^2 and is a measure of the tightness. Since TT- ω PBEh was constructed based on Eq. (3), we expected a very small difference between “best” and “worst” MAEs. This expectation has been validated by smallest difference obtained by TT- ω PBEh among all functionals for the TADF (0.119 eV vs. > 0.170 eV) and BIO (0.155 eV vs. > 0.200 eV) sets. For PAH and OPV sets, on the other hand, B3LYP, PBE and TPSS can arrive at comparable or even smaller differences due to the error cancellation, but their predictive power for E_{T} are not as strong as TT- ω PBEh due to the lack of

long-range HF correction, as shown earlier in the present subsection.

3.3 Optical Band Gaps

Although it is not the direct tuning object, the optical band gap, $E_S = E_{S_1} - E_{S_0}$, is a more interesting observable as it can be directly measured via absorption or emission spectroscopy. Given the abundant data available in the literature, E_S has become the most important independent benchmark of the accuracy of our triplet tuning scheme. For a normal closed-shell molecule, E_S is the energy difference between the singlet ground state and the lowest bright singlet excited state (S_1), which possesses an identical orbital configuration to T_1 . Therefore the optimized values of ω and C_{HF} for E_T are expected to provide almost equally accurate prediction for E_S .

We summarize all MAEs for E_S in Tables S2, S6, S10 and S12 in the Supporting Information and list the results obtained from TDDFT (TD) and the average of the “worst” AE for each molecule among ROKS (in the place of ΔSCF), TD and TD/TDA in Table 2. In addition, the average “best” AEs are illustrated for the TADF and BIO sets in Fig. 6.

Table 2: Mean absolute errors (MAEs) of the optical band gaps, E_S , are compared across various functionals for the test sets of PAH, OPV, TADF and BIO.

energy XC functional	TD				worst			
	PAH	OPV	TADF	BIO	PAH	OPV	TADF	BIO
TT- ω PBEh	0.381	0.326	0.266	0.370	0.581	0.664	0.337	0.571
OT- ω PBEh	0.343	0.512	0.338	0.506	0.563	0.825	0.440	0.720
mix- ω PBEh	0.331	0.418	0.352	0.584	0.518	0.675	0.482	0.889
HF	0.774	0.802	1.792	1.292	0.774	0.802	1.651	1.358
B3LYP	0.276	0.402	0.390	0.309	0.525	0.594	0.399	0.432
CAM-B3LYP	0.336	0.410	0.565	0.507	0.449	0.528	0.539	0.658
PBE	0.416	0.509	1.017	0.456	0.741	0.788	0.970	0.614
PBE0	0.257	0.409	0.312	0.597	0.581	0.603	0.330	0.679
LRC- ω PBE	0.494	0.526	0.768	0.545	0.854	0.717	0.841	0.773
LRC- ω PBEh	0.348	0.436	0.627	0.499	0.463	0.546	0.602	0.635
TPSS	0.371	0.471	0.920	0.351	0.399	0.537	0.876	0.375
M06-2X	0.312	0.442	0.477	0.466	0.484	0.574	0.457	0.605
M06-L	0.330	0.421	0.773	0.306	0.369	0.481	0.743	0.353

In the OPV, TADF and BIO sets, TT- ω PBEh exhibits the strongest (OPV and TADF) predic-

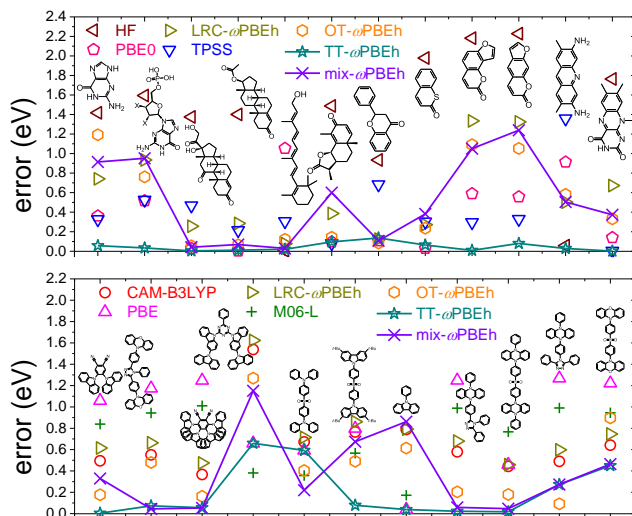


Figure 6: The absolute error of the optical band gap, $E_S = E_{S_1} - E_{S_0}$, is illustrated for selected molecules in the test set of (a) BIO and (b) TADF. The results are compared among TT- ω PBEh (dark cyan star), OT- ω PBEh (orange hexagon), mix- ω PBEh (violet cross), HF (wine left triangle), CAM-B3LYP (red circle), PBE (magenta up triangle), PBE0 (pink pentagon), M06-L (green plus sign), TPSS (blue down triangle) and LRC- ω PBEh (dark yellow right triangle).

tive power or among the strongest (BIO) for E_S . This result confirms the suggested similarity in the orbital configurations between S_1 and T_1 , as well as the transferability of TT- ω PBEh from a difficult observable, E_T , to an easy one, E_S . Both conclusions facilitate the usage of triplet-tuned XC functionals in large-scale screening and design of photochemically active materials. Similar to the assessment in Sec. 3.2, within the BIO set TT- ω PBEh is outperformed by three existing functionals, B3LYP, M06-L and TPSS, due to the error cancellations and/or the availability of test molecules in their fitting database.

Interestingly, TT- ω PBEh has overestimated E_S of PAH molecules more seriously than seven out of the ten existing functionals, probably because of the singlet–triplet instability problem that significantly overestimates the gap between S_1 and T_1 in the linear-response version of TDDFT.²²⁰ As a result, parameters evaluated by matching E_T^{TD} with $E_T^{\Delta\text{SCF}}$ can lead to an overestimated E_S . Inclusion of Tamm–Dancoff approximation (TDA)²¹² solves the instability problem, but implementing it in single-point calculations does not reduce the error (0.381 eV vs. 0.394 eV) if it is not applied in the tuning process. This issue indicates another strategy to modify the present triplet tuning prescription.

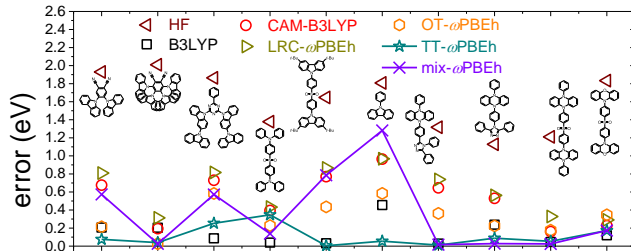


Figure 7: The absolute error of the singlet–triplet gap, $\Delta E_{ST} = E_S - E_T$, is illustrated for selected molecules in the test set of TADF. The results are presented for TT- ω PBEh (dark cyan star), OT- ω PBEh (orange hexagon), mix- ω PBEh (violet cross), HF (wine left triangle), B3LYP (black square), CAM-B3LYP (red circle), and LRC- ω PBEh (dark yellow right triangle).

3.4 Singlet–Triplet Gaps

In TADF systems, the singlet–triplet gap ($\Delta E_{ST} = E_S - E_T$) serves as a direct predictor for the (reversed) intersystem crossing process and the efficiency of the emitter. Due to its small absolute value in charge-transfer excited states, ΔE_{ST} in TADF emitters is very sensitive to the level of theory and is therefore an additional measure to the accuracy of our TT- ω PBEh functional.

3.4.1 Accuracy of Various Functionals

In the present study we illustrated the MAEs of ΔE_{ST} over the TADF test set in Table 3, as well as AEs for selected TADF emitters in Fig. 7. As we have discussed in an earlier subsection, although TT- ω PBEh does not treat charge transfer excited states in an explicit manner, its long-range component allows its accuracy to approach OT- ω PBEh.²¹⁷ The difference between the MAEs of TT- ω PBEh and OT- ω PBEh in ΔE_{ST} are within 0.09 eV in all variants of single-point calculations. On the other hand, the non-long-range-corrected (non-LRC) functionals like B3LYP, PBE0 and M06-2X also show good performance on average due to the cancellation of errors from E_S and E_T that are both underestimated as charge-transfer excited states.

3.4.2 Solvation Effect

Due to the high polarizability of donor–acceptor systems, the extent of charge transfers in TADF emitters can be modulated by the electric properties of the environment, *i.e.* the dielectric constants

Table 3: Mean absolute errors (MAEs) of the singlet–triplet gap, ΔE_{ST} , are compared across various functionals for the test set of TADF.

XC functional	Δ SCF/ROKS	TD	TD/TDA	best	worst
TT- ω PBEh	0.298	0.298	0.297	0.227	0.362
TT- ω PBEh (PCM)	0.309	0.268	0.278	0.118	0.447
OT- ω PBEh	0.298	0.310	0.208	0.156	0.381
OT- ω PBEh (PCM)	0.456	0.314	0.292	0.220	0.551
mix- ω PBEh	0.355	0.463	0.345	0.233	0.526
mix- ω PBEh (PCM)	0.392	0.361	0.237	0.156	0.525
HF	-	1.487	1.487	1.487	1.487
B3LYP	0.226	0.279	0.305	0.186	0.358
CAM-B3LYP	-	0.487	0.258	0.232	0.513
PBE	0.219	0.394	0.393	0.205	0.418
PBE0	0.212	0.264	0.267	0.166	0.338
LRC- ω PBE	0.360	0.672	0.349	0.242	0.727
LRC- ω PBEh	-	0.567	0.285	0.271	0.581
TPSS	-	0.375	0.381	0.372	0.384
M06-2X	-	0.225	0.214	0.190	0.249
M06-L	-	0.365	0.376	0.360	0.382

of the solvents. Energetically, the charge-transfer S_1 and T_1 states can both be stabilized by the polarized solvents, leading to unpredictable ΔE_{ST} .^{221–224} In recent studies, Sun *et al.* and Huang *et al.* modeled the solvation effect using the polarizable continuum model (PCM) and found that the dielectric constant is correlated to the energetics of the system. However, in order to minimize the computational costs, all triplet tuning and single point calculations reported in the present study were performed in the gas phase, while the experimental data were collected by Adachi and coworkers from TADF emitters dissolved in toluene or dispersed in the mCP thin films.^{170–172}

Large errors of TT- ω PBEh in extreme charge-transfer excited states motivated us to explore the solvation effect for TADF emitters. Based on the optimized set of parameters, we re-performed single-point calculations of ΔE_{ST} in toluene ($\epsilon = 2.38$) using PCM, and presented these results in Table 3 (labeled with PCM). When we compared PCM and gas-phase results, we discovered that the PCM treatment improves, or at least does not hurt, the accuracy of TT- ω PBEh and mix- ω PBEh, as the polarized environment increases the extent of charge transfer that was underestimated by the triplet tuning process in the gas phase. On the other hand, OT- ω PBEh has already overestimated

the charge transfer extent, even tuned in the gas phase, so the implementation of the solvation effect plays an adverse role and results in raised MAEs. For example, the “best” MAEs for these TADF emitters were reduced from 0.227 eV and 0.233 eV to 0.118 eV and 0.156 eV for TT- ω PBEh and mix- ω PBEh, respectively, while that for OT- ω PBEh was raised from 0.156 eV to 0.220 eV. Our findings here further validate the strong charge-transfer character of TADF emitters and indicate a future direction that implements the solvation effect in the construction of TT- ω PBEh, such as replacing r_{12} with ϵr_{12} .^{225–228}

3.5 One-Particle Properties

Experimentally important one-particle properties, such as ionization potential (I), electron affinity (A), and fundamental band gap ($I - A$), provide additional calibrations for any constructed functional including TT- ω PBEh. Like all optimally-tuned functionals proposed by Kronik, Baer and coworkers, OT- ω PBEh focuses on these one-particle properties and exhibits excellent performance,^{36,40,41,229–231} and we will discuss the improvement illustrated by TT- ω PBEh compared to other frequently used functionals. As was mentioned in the Theory section, the vertical properties, I_{\perp} and A_{\perp} , can be evaluated using the Δ SCF approach (Eqs. (11) and (12)), and they are also supposed to be equivalent to $-\epsilon_{\text{HOMO}}^{(N)}$ and $-\epsilon_{\text{HOMO}}^{(N+1)}$ in an exact XC functional, based on Koopmans’ theorem.³⁹

To evaluate the accuracy of TT- ω PBEh, we compared calculated $-\epsilon_{\text{HOMO}}^{(N)}$ and $-\epsilon_{\text{HOMO}}^{(N+1)}$ versus experimental I_{\perp} and A_{\perp} and provided all relevant MAEs in Tables S3, S4, S7, S8 and S13 in the Supporting Information. In addition, we list MAEs of $-\epsilon_{\text{HOMO}}^{(N)}$ in Table 4 and showed $-\epsilon_{\text{HOMO}}^{(N)}$ vs. I_{expt} relations for selected OPV molecules in Fig. 8. Again, the accuracy of TT- ω PBEh was compared against OT- ω PBEh, mix- ω PBEh and ten existing XC functionals.

As we expected because of the incorrect long-range nature of various XC functionals, Δ SCF approach is much more predictive than $-\epsilon_{\text{HOMO}}^{(N)}$ and $-\epsilon_{\text{HOMO}}^{(N+1)}$ for I_{\perp} and A_{\perp} for all non-LRC functionals. Also, A_{\perp} is less accurately predicted due to the difficulty in experimental measurements as well as calculations without diffuse functions in the basis set. Here we will skip the

Table 4: Mean absolute errors (MAEs) of the eigenvalue of the highest occupied molecular orbital, $-\varepsilon_{\text{HOMO}}^{(N)}$, are compared for the test set of TADF.

XC functional	PAH	OPV	BIO
TT- ω PBEh	1.182	1.737	2.037
OT- ω PBEh	0.174	0.213	0.352
mix- ω PBEh	0.191	0.173	0.327
HF	0.394	0.298	0.429
B3LYP	1.901	2.055	2.472
CAM-B3LYP	0.728	0.708	1.999
PBE	2.446	2.868	3.355
PBE0	1.678	1.791	2.104
LRC- ω PBE	0.170	0.231	0.177
LRC- ω PBEh	0.139	0.219	0.396
TPSS	2.500	2.857	3.323
M06-2X	1.491	1.311	1.571
M06-L	2.354	2.661	2.980

detailed discussions that were thoroughly made by Kronik and coworkers.^{36,40,41,229–231} Instead, we will focus on the performance of TT- ω PBEh only.

In agreement with our prediction, TT- ω PBEh is better-behaving than most of the non-LRC functionals except for M06-2X, but is surpassed by HF and LRC functionals. This has confirmed an inevitable trade-off between one-particle properties and electron-hole interactions in DFT. However, interestingly, mix- ω PBEh has constantly good performance as indicated in Fig. 8, which is comparable to OT- ω PBEh for PAH and even better than OT- ω PBEh for OPV and BIO. This indicates that the inclusion of triplet tuning can account for electron-hole interactions that play an auxiliary role in the one-particle properties. As a result, we can safely assert the importance of the fully and partially triplet tuned XC functionals in the accuracy of photophysically/photochemically important excited states.

4 Conclusion and Future Directions

In the present study, we proposed triplet tuning, a novel scheme that allows us to construct the XC functional, based on the energy of the lowest triplet excited state (T_1), in a *non-empirical*

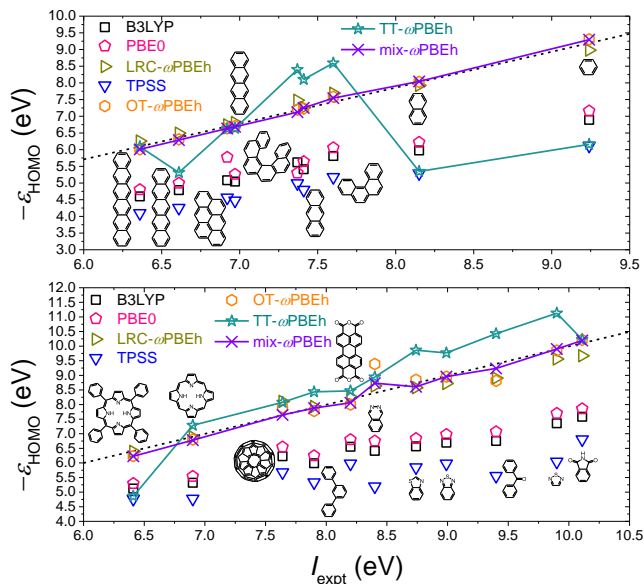


Figure 8: The inverse energy of the highest occupied molecular orbital, $-\varepsilon_{\text{HOMO}}$, is compared against the experimental ionization potential, I_{expt} , for selected molecules in the test set of (a) PAH and (b) OPV. The results are presented for TT- ω PBEh (dark cyan star), OT- ω PBEh (orange hexagon), mix- ω PBEh (violet cross), B3LYP (black square), PBE0 (pink pentagon), TPSS (blue down triangle), and LRC- ω PBEh (dark yellow right triangle). The exact agreement stated by Koopmans' theorem,³⁹ $I_{\text{expt}} = -\varepsilon_{\text{HOMO}}$, is presented as the black dashed line.

fashion. The first triplet tuned functional, TT- ω PBEh, was constructed by internal matching of triplet excitation energies (E_{T}) from two variants of DFT approaches, Δ SCF and linear-response TDDFT. To evaluate the behavior of TT- ω PBEh, we compared its errors for various calculated energetics against existing XC functionals, including conventional optimal tuning scheme, OT- ω PBEh. Without fitting the experimental data, the TT- ω PBEh functional provides an accurate prediction of electron-hole interactions in organic molecules and is in general significantly more predictive in triplet excitation energies, optical band gaps, and singlet-triplet gaps, than all existing functionals. On the other hand, it also improves the one-electron properties like $-\varepsilon_{\text{HOMO}}^{(N)}$ relative to semi-local, non-LRC XC functionals. In the end, given the difficulty of balancing local electron-hole interactions and non-local one-electron properties, the mix- ω PBEh functional that attempts to consider both aspects has achieved reasonable improvements.

Similar to conventional optimally tuned functionals,²³²⁻²⁴¹ we expected a wide application of our approach for π -conjugated organic molecules that were considered challenging before. In

particular, the method can set stage for future rational design of photoactive materials. In parallel projects, the present version TT- ω PBEh has been applied to molecules and clusters that are involved in singlet fission, fluorescence and phosphorescence.

As indicated in the Results and Discussions section, there is room for future modification of the triplet tuning approach based on the nature of the molecules being investigated, including the usage of alternative algorithms and the implementation of environment factors and frequency dependence.^{47,48,242,243} For two obvious examples, adjustable ω and C_{HF} do not seem to span a large enough two-dimensional space to approach the exact exchange functional, and the PBE correlation functional⁵⁷ can be inaccurate in many molecules. These issues can be resolved by reformulating triplet tuned functionals. In addition, the application of machine learning in DFT has inspired a new way of optimizing the tunable parameters.

5 Associated Content

In the Supporting Information, we provide the names and structures for all organic molecules that are included in the four test sets being calculated in the present study, as well as the tables that present all mean absolute errors for energetics in question.

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