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Review

Theoretical predication for transition energies of thermally activated delayed fluorescence molecules

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ABSTRACT

Thermally activated delayed fluorescence (TADF) emitters are primarily comprised of intramolecular charge-transfer (ICT) molecules with small energy difference between the lowest singlet and triplet excited states. They lend extremely favorable electroluminescent performance to organic light-emitting diodes (OLEDs). This paper summarizes relevant issues and research efforts in the theoretical prediction of singlet- and triplet-transition energies of ICT molecules via time-dependent density functional theory (TDDFT). The successful application of the descriptor-based optimal Hartree–Fock percentage method and the optimally tuned range-separated functional to many TADF systems represent an interesting approach to the exact prediction of the complex excited-state molecular dynamics within TDDFT.

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1. Introduction

Metal-free, thermally activated delayed fluorescence (TADF) materials are characterized by luminescent molecules or complexes with small energy gap (ΔE_{ST}) between the lowest singlet (S_1) and triplet (T_1) excited states [1–4]. They can upconvert from the T_1 to S_1 by absorbing environmental thermal energy and then radiatively decay from the S_1. TADF emitters can be employed in OLEDs to convert both singlet and triplet excitons into light with a theoretical yield up to 100% [5–17]. Because OLEDs containing TADF emitters can be up to four times more efficient than OLEDs containing fluorescent molecules, and cheaper than OLEDs containing noble metal-based phosphor, they have garnered considerable research attention in recent years [18–28].

Small ΔE_{ST} value is the key to realizing an efficient TADF. We now know that two conditions must be met to ensure a small ΔE_{ST}: The first is a small exchange integral for the S_1 transition, which is roughly proportional to the degree of overlap between the initial and final state orbitals and is generally realized by an intermolecular or intramolecular charge-transfer (CT) [5–13]; the second is that the locally excited triplet state (^{3}LE) be close to (or even exceed) the ^{3}CT (Fig. 1) [15,18,21]. If theoretical calculations can accurately predict the transition energies of CT molecules, the time and cost of developing new TADF materials can be substantially reduced.

Owing to its ability to balance accuracy and efficiency, the linear response time-dependent density functional theory (LR-TDDFT), which was developed based on density functional theory, has become the most widely used method for theoretical interpretation of excited-state electron structure and dynamics for medium to large molecular systems [29–31]. The resolution of the LR-TDDFT equations performed at optimized ground- and excited-state geometries can reproduce the vertical absorption and emission energies, as well as the adiabatic energy (approximate to the zero-zero transition energy) under the Franck-Condon principle (Fig. 2) [32–34]. However, the TDDFT results for CT states are highly dependent on the selected exchange-correlation (XC) – especially the Hartree–Fock (HF) percentage contained therein – when hybrid-functionals are used [31,35–37]. Consequently, the transition energies of different molecules must be calculated by using different XC-functionals. Moreover, when the singlet-triplet pairs of low-lying excited states are crossed in a TADF molecule, as shown in Fig. 1a, the transitions of S_1 and T_1 involving different orbitals must also be reproduced by different XC-functionals [37]. The challenge for theoretical chemists, to this effect, is to

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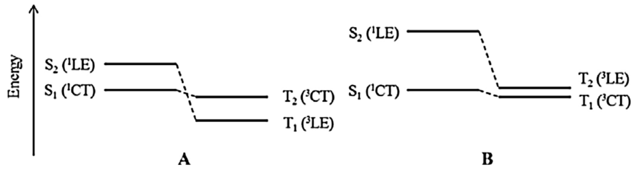

Fig. 1. Singlet and triplet energy levels of ICT molecules. The T_1 of molecule **A** is an LE state, while that of molecule **B** is a CT state. The singlet-triplet splitting of a LE transition is generally larger than that of a CT transition.

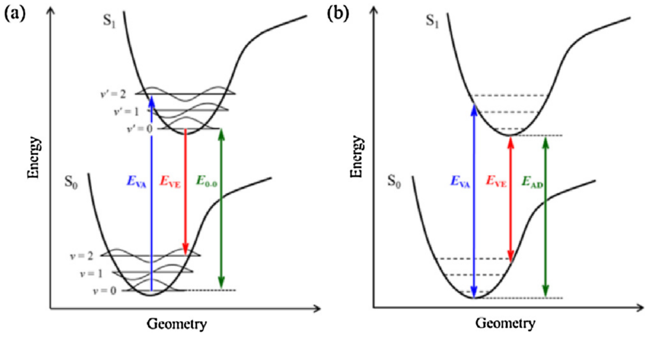

Fig. 2. (a) Illustration of the Franck-Condon principle. Electronic transitions are from level to level. The vertical lines (E_{VA}, E_{VE} and $E_{0\text{-}0}$) represent experimental values. (b) Theoretically computed energies of E_{VA}, E_{VE}, and E_{AD}. The zero-point vibrational energy offsets the energy difference between the potential well and the vibrational level.
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secure a systemic and universal strategy for the selection or correction of XC-functionals to facilitate accurate prediction of the transition energies of various TADF (and even CT) systems.

This brief review begins by introducing the theoretical and experimental error sources in the studies of transition energies of CT-type TADF molecules, then goes on to summarize current efforts to overcome these problems.

2. Error sources in theoretical prediction of TADF molecule transition energy

2.1. Drawbacks to existing theoretical models

The TDDFT scheme derived from linear response formalism is necessary for solving any non-Hermitian eigenvalue equation [31,35,36]:

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}\begin{bmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{bmatrix} \qquad (1)$$

where **A** and **B** are the Hamiltonian matrix elements of the single (de)excitation determinants, **X** and **Y** are the single (de)excitation amplitudes, and ω is the excitation energy. When a hybrid-functional is used, matrices **A** and **B** can be expressed in Mulliken notation as follows:

$$\boldsymbol{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ia|jb) - C_{\mathrm{HF}}(ij|ab) + (1 - C_{\mathrm{HF}})(ia|f_{xc}|jb) \qquad (2)$$

$$\boldsymbol{B}_{ia,jb} = (ia|bj) - C_{\mathrm{HF}}(ib|aj) + (1 - C_{\mathrm{HF}})(ia|f_{xc}|bj) \qquad (3)$$

where i,j are used for ground state occupied orbitals, a,b for vitual orbitals, δ is the Kronecker delta, ε is the orbital energy, f_{xc} is the exchange-correlation kernel, and C_{HF} is the percentage of Hatree-Fock exchange in the hybrid functional.

For a long-range CT transition, the overlap between the original and final orbitals decreases to zero. Thus, **A** and **B** can be simplified to:

$$\boldsymbol{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) - C_{\mathrm{HF}}(ij|ab) \qquad (4)$$

$$\boldsymbol{B}_{ia,jb} = 0 \qquad (5)$$

The neglect of matrix **B** for a CT transition is well known as the Tamm-Dancoff Approximation (TDA) [38,39]. The first term in the expression of matrix **A** is the energy difference between the virtual and occupied orbitals, while the second is a Coulomb-like term that is essential in reproducing the 1/R fall-off condition that results from electrostatic attraction between the separated hole (orbitals that lose electrons) and electron (orbitals that obtain electrons). The absence of a selection rule on C_{HF} generally prevents exact prediction of the transition energies. Additionally, the optimized geometries in excited states are generally more sensitive than those in ground state to C_{HF} due to the relatively flatter potential energy surfaces in the excited states [33], which makes predicting the transition energies (*e.g.*, E_{VA} and E_{AD}) even more difficult on the basis of the excited state geometries.

To theoretically interpret the excitation process in a given environment, the solvation model must be introduced to the TDDFT calculation. Recent studies have indicated that the solvation of some TADF molecules cannot be satisfactorily reproduced by employing a polarizable continuum model (PCM) [16,40–42], while the effects of other solvation models such as CPCM [43,44] SS [45,46] COSMO [47], SCIPCM [48], SMD [49], or SM8 [50] remain unknown. In addition to the solvation model used, the size of the basis set [37,40,51] and weak interaction [40] also affect the TDDFT results (though the influence of either is relatively small).

2.2. Issues in spectrum analysis

Experimental spectroscopic data is the primary evidence utilized to evaluate the reliability of calculated transition energies. Although the $E_{\mathrm{VA}}(\mathrm{S}_1)$, $E_{\mathrm{VE}}(\mathrm{S}_1)$, $E_{0\text{-}0}(\mathrm{S}_1)$, $E_{0\text{-}0}(\mathrm{T}_1)$, and ΔE_{ST} of TADF materials can be determined based on their adsorption, fluorescence, and low-temperature phosphorescence spectra in theory, the complicated experimental spectra do not readily provide reliable data – as discussed above, this makes developing a theoretical approach for the prediction of transition energies quite difficult.

The adsorption and emission spectra of organic molecules in gaseous state are narrow and sharp. Consequently, they allow level-to-level transitions to be easily identified (Fig. 3). In medium polar solvents (*e.g.* toluene) or organic semiconductor films, the spectrum of an LE transition may retain well-defined vibronic structures (*e.g.*, anthracene and carbazole) while that of a CT transition is always broad and featureless (Fig. 3) [52]. According to the Franck-Condon principle, the maxima of CT adsorption and emission correspond to E_{VA} and E_{VE}, respectively, while the average of E_{VA} and E_{VE} or the crossing point between absorption and emission (normalized to the same height) corresponds approximately to the $E_{0\text{-}0}$ of the CT transition [53,54]. A CT transition with slight overlap of the involved orbitals exhibits a weak absorption band which is easily covered by other higher transitions (*e.g.*, S_2), making it difficult to determine $E_{\mathrm{VA}}(\mathrm{S}_1)$. An assumed mirror-image relationship between the first absorption band and the fluorescence spectrum (mirror-image rule) was recently used to determine $E_{\mathrm{VA}}(\mathrm{S}_1)$ from easily identified $E_{\mathrm{VE}}(\mathrm{S}_1)$ [37], however, the premise of this rule is a small structure variation between the ground and excited state geometries, which cannot be guaranteed in CT transitions [55].

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