Can time-dependent density functional theory predict the excitation energies of conjugated polymers?

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Excitation energies of light-emitting organic conjugated polymers have been investigated with time-dependent density functional theory (TDDFT) within the adiabatic approximation for the dynamical exchange-correlation potential. Our calculations show that the accuracy of the calculated TDDFT excitation energies largely depends upon the accuracy of the dihedral angle obtained by the geometry optimization on ground-state DFT methods. We find that, when the DFT torsional dihedral angles between two adjacent phenyl rings are close to the experimental dihedral angles, the TDDFT excitation energies agree fairly well with experimental values. Further study shows that, while hybrid density functionals can correctly respect the thumb rule between singlet-singlet and singlet-triplet excitation energies, semilocal functionals do not, suggesting inadequacy of the semilocal functionals in predicting triplet excitation energies of conjugated polymers.

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The most important progress made in the development of molecular electronics is the discovery of electroluminescent conjugated polymers [1] — that is, fluorescent polymers that emit light when these polymers in the excited states are stimulated by, say, electric current. Conjugated polymers are organic semiconductors with delocalized \( \pi \)-molecular orbitals along the polymeric chain. These materials are a major challenge to inorganic materials which have been dominating the commercial market in light-emitting diodes for display and other purposes [2].

The attraction of conjugated polymers lies at their versatility, because their physical properties such as color purity and emission efficiency can be fine-tuned by manipulation of their chemical structures. The systematic modification of the properties of emissive polymers by synthetic design has become a vital component in the optimization of light-emitting devices.

Theoretical investigation of their optical absorption plays a significant role in computer-aided design and optimization of the electroluminescent polymers. The method of choice for the simulation of the optical absorption of electronic materials is time-dependent density functional theory (TDDFT) [3], owing to its high computational efficiency and comparable accuracy. TDDFT is the most important extension of Kohn-Sham ground-state DFT, the standard method in electronic structure calculations. The only approximation made in TDDFT is the dynamical exchange-correlation (XC) potential, which includes all unknown many-body effects. The simplest construction is called adiabatic (ad) approximation [4], which takes the same form of the static XC potential but replaces the ground-state density \( n_0(r) \) with the instantaneous time-dependent density \( n(r,t) \): 

\[
\nu_{xc}^{ad}[\eta_0; \mathbf{r}, t] = \frac{\partial E_{xc}[\eta_0]}{\partial \eta_0} |_{\eta_0(r) = n(r,t)}.
\]

The advantage of this approach is its simplicity in both theoretical construction and numerical implementation. Although the adiabatic TDDFT cannot properly describe multiple excitations, it has become the most popular approach in the study of low-lying single-particle excitations (i.e., only one electron in the excited states).

Our previous studies of small molecules [5] and molecular materials [6] show that the excitation energies obtained with the adiabatic TDDFT agree fairly well with experiments. In the present work, we calculate the lowest singlet-singlet (\( S_0 - S_1 \)) and singlet-triplet (\( S_0 - T_1 \)) excitation energies of a series of light-emitting organic conjugated polymers (see Fig. 1 for their chemical structures). The singlet-singlet excitation is responsible for...

FIG. 1: Chemical structures of the computationally studied light-emitting conjugated polymers.
the strong ultraviolet (UV) or near-UV optical absorption, while the singlet-triplet excitation is responsible for weak fluorescence. Our calculations show that, when the dihedral angles $\phi$ between two adjacent phenyl rings obtained by the geometry optimization on ground-state DFT methods are close to experimental dihedral angles, the calculated TDDFT excitation energies agree well with experiments, regardless of whether the excitations arise from singlet-singlet excitations or singlet-triplet excitations. This suggests that in TDDFT calculations, there are two sources of error. One is from the adiabatic approximation itself $\delta$, and the other, much larger than the first one, arises from inaccuracy of the ground-state DFT geometries. In order to identify these errors, here we employ five commonly-used density functionals. Two of them, the local spin density approximation (LSDA) and the meta-generalized gradient approximation (meta-GGA) of Tao, Perdew, Staroverov, and Scuseria (TPSS) $\delta$, are pure density functionals, while the other three, TPSSh $\delta$ (a hybrid of the TPSS meta-GGA with 10% exact exchange), B3LYP $\delta$ (a hybrid with 20% exact exchange), and PBE0 $\delta$ (a hybrid of the Perdew-Burke-Ernzerhof (PBE) $\delta$ GGA with 25% exact exchange) are hybrid functionals with increasing amount of exact exchange from TPSSh, B3LYP to PBE0.

Moreover, in the simulation of electronic excitations of small molecules and molecular materials, the most effort has been devoted to the study of the absorption arising from singlet-singlet excitation, leaving the singlet-triplet excitation less investigated $\delta$.$\delta$. An important reason for this omission is that triplet-state energies are not easy to measure through direct optical absorption due to very low singlet-triplet ($S_0 - T_1$) absorption coefficient $\delta$.$\delta$ and low phosphorescence quantum yield $\delta$ ($< 10^{-6}$). The major approaches to probe triplet states in conjugated polymers are the charge recombination or energy transfer, and singlet-triplet ($T_1 - S_0$ or $S_1 - T_1$) intersystem crossing $\delta$.$\delta$.$\delta$. The observation of $T_1 - S_0$ phosphorescence from molecules initially excited into $S_1$ is clear evidence for a radiationless transition from $S_1$ to an isoenergetic level of the triplet manifold, corresponding to singlet-triplet intersystem crossing. Singlet-triplet intersystem crossing can occur either from the zero-point vibrational level of $S_1$ or from thermally-populated vibrational level of $S_1$ into an excited vibrational level of $T_1$, or more probably into a higher excited triplet state $T_3$ which is closer in energy to $S_1$. It has been found $\delta$.$\delta$.$\delta$. that the properties of the triplet states directly impact device performance. For example, the formation of triplet states may cause the loss of the device efficiency in these materials and thus can limit device performance and operational life span. Therefore, investigation of triplet excitations is crucial for a full understanding of electroluminescence behavior of conjugated organic polymers and for the improvement of new materials.

Monkman and collaborators $\delta$.$\delta$.$\delta$ investigated the photophysics of triplet states in a series of conjugated polymers and measured the excitation energies of the lowest singlet- and triplet-excited states. Their measurements show that the excitation energies in general respect the well-known rule of thumb found for small molecules:

$$E_T \approx 2E_S / 3,$$

(1)

where $E_T$ is the triplet excitation energy and $E_S$ is the singlet-singlet excitation energy. As a second part of our work, we calculate the singlet-triplet excitation energies of the polymers with the adiabatic TDDFT. We find that, without exact exchange mixing, a pure semilocal density functional cannot satisfy the thumb rule of Eq. (1), suggesting inadequacy of the adiabatic semilocal functionals in predicting the triplet excitation energies for polymers.

**Computational method:** All our calculations were performed on the molecular-structure code Gaussian 03 $\delta$. The initial geometries are prepared with GaussView 4,
while the dihedral angles are manually adjusted to be \( \sim 30^\circ \). Then we optimize the geometries on respective ground-state DFT methods. Finally we calculate the excitation energies from the optimized ground-state geometries with the adiabatic TDDFT density functionals. For consistency, basis set 6-31G was used in both ground-state and time-dependent DFT calculations. In order to check whether our conclusion is affected by the choice of basis set, we repeat our calculations for polymer P3OT using a larger basis set 6-31G(d) that has diffusion functions. Our calculations show that the excitation energy obtained with 6-31G(d) is larger only by \( < 0.2 \) eV than that obtained with 6-31G basis set. The excitation energies of the polymers in benzene solvent are calculated with 6-31G basis set. The excitation energies tend to be overestimated. Further- more, we find that, a semilocal functional without exact exchange increases as the amount of exact exchange increases. However, some studies suggest [25, 26] that for semilocal density functionals (LSDA, GGA, and meta-GGA), this difference may vanish in the limit of infinite chain length, a result similar to the performance of semilocal functionals for solids. Mixing exact exchange into a semilocal functional will partly correct the errors from self interaction, improve the asymptotic behavior of the XC potential, and build in other many-body properties such as excitonic effects [25, 26] which have not been taken into account properly in pure density functional approxima-
tions and thus will lead to a finite difference in this limit. Interestingly, we find that when the theoretical dihedral angle is close to the experimental one, the TDDFT excitation energies are in good agreement with experiments. Our calculations show that in rare cases, theoretical dihedral angles can be greater that experimental estimates. In this case, the excitation energies are overestimated by the TDDFT methods. A comparison of the dihedral angles between theoretical and experimental estimates is displayed in Table 2. The origin of torsional angles (or generally torsional disorder) of polymers is complicated. It may arise from interchain interaction in amorphous polymeric materials [27, 28] or from van der Waals interaction [29, 31] between phenyl rings. These effects have not been properly taken into account in current DFT methods.

The excitation energies of the polymers in benzene solvent are summarized in Table 3. From Table 3, we can see that the lowest singlet-singlet excitation energies in solution have a red shift of \( \sim 0.01 - 0.05 \) eV, compared to those in gas phase (Table 1). This is consistent with what we have observed for oligomers [3, 4, 8]. However, this trend does not apply to the triplet excitation. Triplet excitation energies are nearly the same whether the polymer is in gas phase or in solution.

In conclusion, we have investigated the lowest excitation energies of several light-emitting conjugated polymers from the adiabatic TDDFT methods. Our calculations show that the calculated excitation energies are in good agreement with experiments only when the theoretical torsions agree with experimental estimates. If the theoretical dihedral angles are smaller than the experimental dihedral angles, the TDDFT methods tend to underestimate the excitation energies regardless of whether the excitation is singlet or triplet. When the theoretical dihedral angle is close to the experimental one, the TDDFT excitation energies are in good agreement with experiments. Our calculations show that in rare cases, theoretical dihedral angles can be greater that experimental estimates. In this case, the excitation energies are overestimated by the TDDFT methods. A comparison of the dihedral angles between theoretical and experimental estimates is displayed in Table 2. The origin of torsional angles (or generally torsional disorder) of polymers is complicated. It may arise from interchain interaction in amorphous polymeric materials [27, 28] or from van der Waals interaction [29, 31] between phenyl rings. These effects have not been properly taken into account in current DFT methods.

### Table 2: Torsions of the conjugated polymers

| Polymer | Expt | PBE0 | Energy |
|---------|------|------|--------|
| P3OT    | \( \sim 24^\circ \) | \( \sim 0^\circ \) | red shift |
| PBOPT   | \( \sim 35^\circ \) | \( \sim 40^\circ \) | On experiment |
| MEHPPV  | \( \sim 20^\circ \) | \( \sim 1^\circ \) | red shift |
| PFO     | \( \sim 40^\circ \) | \( \sim 38^\circ \) | On experiment |
| DHOPPV  | \( \sim 20^\circ \) | \( \sim 0^\circ \) | red shift |
| PPY     | \( \geq 0^\circ \) | \( \sim 0 - 1^\circ \) | slightly red shift |
| CN-MEHPPV | \( \sim 20^\circ \) | \( \sim 0^\circ \) | red shift |
| PANi    | \( \sim 0^\circ \) | \( \sim 18 - 26^\circ \) | too blue shift |
exchange mixing does not satisfy the well-known “two-third” thumb rule relation between the singlet-singlet and singlet-triplet excitation energies. For semilocal functionals, the difference in energy between singlet state and triplet state is less than 0.1 eV for polymers with finite chain length as well as with infinite chain length. Compared to semilocal functionals, hybrid functionals yield much larger difference between singlet-singlet and singlet-triplet excitation energies for polymers with finite chain length as well as with infinite chain length. This difference increases with more exact exchange mixed in semilocal functionals, and is nonzero even in the limit of infinite chain length.

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| Polymer       | Expt\(^{a}\) | LSD | TPSS | TPSSh | B3LYP | PBE0 | Expt\(^{b}\) | LSD | TPSS | TPSSh | B3LYP | PBE0 |
|---------------|-------------|-----|------|-------|-------|------|-------------|-----|------|-------|-------|------|
| P3OT(28)      | 2.8-3.8     | 0.97| 0.97 | 1.32  | 1.56  | 1.73 | 1.7-2.2     | 0.89| 0.80 | 0.87  | 0.95  | 0.94 |
| PBOPT(32)     | 2.52        |     |      |       |       |     | 1.60        |     |      |       |       |      |
| MEHPPV(16)    | 2.48        | 1.12| 1.25 | 1.64  | 1.91  | 2.04 | 1.30        | 1.03| 1.07 | 1.18  | 1.32  | 1.25 |
| PFO(36)       | 3.22        | 2.30| 2.45 | 2.88  | 3.12  | 3.29 | 2.30        | 2.22| 2.24 | 2.35  | 2.46  | 2.43 |
| DHOPPV(16)    | 2.58        | 1.12| 1.25 | 1.64  | 1.92  | 2.04 | 1.50        | 1.03| 1.07 | 1.18  | 1.32  | 1.25 |
| PPY(24)       | 3.4-3.9     | 2.08| 2.16 | 2.61  | 2.85  | 3.01 | 2.4-2.5     | 2.02| 1.99 | 2.11  | 2.23  | 2.20 |
| CN-MEHPVV(16) | 2.72        | 1.10| 1.32 | 1.80  | 2.10  | 2.21 | N/A         | 1.05| 1.21 | 1.34  | 1.48  | 1.43 |
| PANi(20)      | 2.00        | 2.33| 2.53 | 3.03  | 3.27  | 3.41 | < 0.9       | 2.30| 2.42 | 2.62  | 2.75  | 2.73 |

\(^{a}\)From Ref. [22]. \(^{b}\)Notation of Ref. [19] is used. Note that all the groups of -(CH\(_2\))\(_n\)-CH\(_3\) in polymers have been replaced with the hydrogen (-H).

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