Prediction of excitation energies for conjugated polymers using time-dependent density functional theory

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Excitation energies of light-emitting conjugated polymers have been investigated with time-dependent density functional theory (TDDFT) within the adiabatic approximation. Our calculations show that the accuracy of the calculated TDDFT excitation energies largely depends on the dihedral angles obtained by the ground-state DFT geometry optimization. We find that, when the DFT torsional dihedral angles are close to experimental estimates, the TDDFT excitation energies agree well with experiments. This trend is observed based on calculations of eight different polymeric systems considered here. We further show that while hybrid density functionals can respect the thumb rule of $E_T \approx 2E_S/3$, where E_S is the singlet-singlet excitation energy and E_T the singlet-triplet excitation energy, nonhybrid functionals do not.

PACS number(s): 71.15.Mb, 31.15.ee, 71.45.Gm

I. INTRODUCTION

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 π-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 purpose.[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 good 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 $n_0(\mathbf{r})$ with the instantaneous time-dependent density $n(\mathbf{r},t)$: $v_{XC}^{ad}([n];\mathbf{r},t) = \delta E_{XC}[n_0]/\delta n_0(\mathbf{r})|_{n_0(\mathbf{r})=n(\mathbf{r},t)}$. 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) of atoms and molecules and is gaining popularity for solids.

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 S_0-S_1 excitation is responsible for the strong UV-visible optical absorption and strong fluorescence in visible region while the singlet-triplet excitation is responsible for weak fluorescence and transport properties. Our calculations show that when the dihedral angles[7] 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 cal-
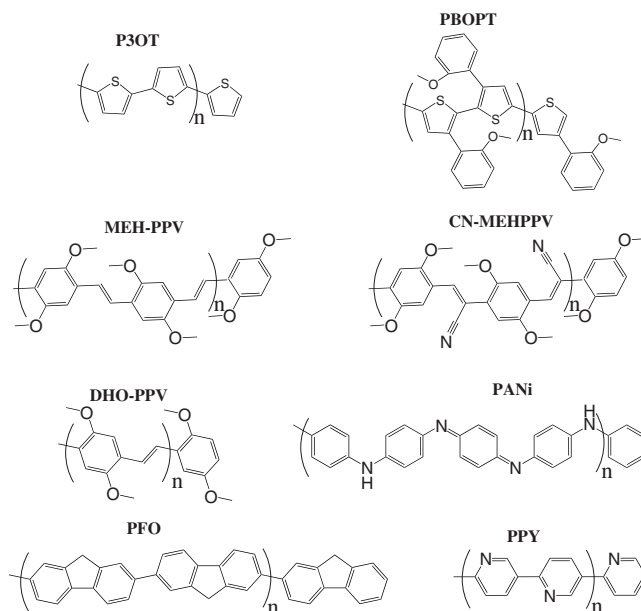

FIG. 1. Chemical structures of the computationally studied light-emitting conjugated polymers.

culations, there are two possible sources of error. One is from the adiabatic approximation itself[8] 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),[9] are pure density functionals while the other three, TPSSh (Ref. 10) (a hybrid of the TPSS meta-GGA with 10% exact exchange), B3LYP (Ref. 11) (a hybrid with 20% exact exchange), and PBE0 (Ref. 12) [a hybrid of the Perdew-Burke-Ernzerhof (PBE) (Ref. 13) 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.[14] 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[15] and low phosphorescence quantum yield[16] ($<10^{-6}$). 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.[17–19] It has been found[20,21] 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 co-workers[21,22] investigated the photophysics of triplet states in a series of conjugated polymers and measured the excitation energies of the lowest singlet-excited and triplet-excited states. Their measurements show that the excitation energies, in general, respect the well-known rule of thumb found for small molecules,

$$E_T \approx 2E_S/3, \tag{1}$$

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.

II. COMPUTATIONAL METHOD

Physical excitation energy can be calculated as a pole of the true linear-response function but not as a pole of the single-particle Kohn-Sham response function. However, while the latter can be obtained from the Kohn-Sham single-particle orbitals, the former must be calculated from the complicated correlated wave function whose exact form remains unknown. In TDDFT, the physical excitation is calculated as the sum of the Kohn-Sham excitation energy and a small energy shift due to the many-body effects, using the linear-response theory through the density-density response function $\chi(\mathbf{r},\mathbf{r}',t,t')$ in which the only unknown part is the XC kernel defined by $f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}',t,t') \equiv \delta v_{\mathrm{XC}}([n];\mathbf{r},t)/\delta n(\mathbf{r}',t')$, which must be approximated as a functional of the instantaneous density. The detailed discussion for the calculation of the excitation energies within the TDDFT linear-response theory have been documented in Refs. 23–26 and briefly discussed in Ref. 5. After computing the excitation energies, the corresponding optical transition strengths are obtained from the transition dipole moments calculated as expectation values of the dipole operator on the respective transition densities. Transition dipole moments and excitation energies constitute the essential ingredients for modeling optical observation spectra. In this work, we employ the adiabatic approximation for the XC potential, which can be easily calculated from commonly used semilocal density functionals and hybrids. Calculations of the excitation energies with the time-dependent XC potentials[27–30] beyond the adiabatic approximation can be found in Refs. 31–33.

All our calculations were performed using the molecular-structure code Gaussian 03.[34] The initial geometries are prepared with GaussView 4 while the dihedral angles are manually adjusted to be ~30°. Then we optimize the geometries using 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 PCM (polarizable continuum model).[35]

At some critical length, optical properties of finite chain segments well represent those of an infinite chain in polymers. Moreover, due to disorder, *infinite chains* of polymers are thought to be finite segments.[36–39] The polymers we study here have chain length of ~10 nm. The segment of this chain length contains at least 16 molecular rings, which mimics the optical properties of polymers with infinite chain quite well.[40,41] The groups of -$(CH_2)_nCH_3$ has little effect on the optical properties of the polymers.[5] These side chains only affect some physical and chemical properties, such as phase-transition temperature, solubilities, etc., and thus have been removed from the backbone of polymers in all calculations.

III. RESULTS AND DISCUSSION

Table I shows the first singlet and triplet excitation energies of the polymers in gas phase calculated with the adia-

TABLE I. Excitation energies of singlet-singlet (S_0-S_1) and singlet-triplet (S_0-T_1) gaps (in units of eV) of polymers of length of $\sim$10 nm in gas phase calculated using the adiabatic TDDFT methods with the ground-state geometries optimized on the respective density functionals. Basis set 6-31G is used in all calculations. The number in parentheses is the number of rings included in our calculations. 1 hartree =27.21 eV.

Polymer	S_0-S_1						S_0-T_1 [b]					
	Expt.[a]	LSDA	TPSS	TPSSh	B3LYP	PBE0	Expt.[a]	LSDA	TPSS	TPSSh	B3LYP	PBE0
P3OT(28)	2.8–3.8	0.99	0.99	1.35	1.59	1.76	1.7–2.2	0.90	0.80	0.88	0.96	0.95
PBOPT(32)	2.52	1.49	1.55	1.96	2.26	2.39	1.60	1.37	1.31	1.42	1.57	1.54
MEHPPV(16)	2.48	1.14	1.27	1.66	1.94	2.07	1.30	1.04	1.08	1.18	1.31	1.24
PFO(36)	3.22	2.30	2.45	2.89	3.13	3.30	2.30	2.22	2.23	2.34	2.45	2.43
DHOPPV(16)	2.58	1.14	1.27	1.67	1.95	2.07	1.50	1.04	1.08	1.18	1.32	1.24
PPY(24)	3.4–3.9	1.82	2.10	2.61	2.87	3.03	2.4–2.5	1.82	1.99	2.11	2.23	2.20
CN-MEHPPV(16)	2.72	1.10	1.34	1.84	2.16	2.27	N/A	1.06	1.22	1.34	1.48	1.43
PANi(20)	2.00	2.34	2.53	3.05	3.30	3.44	<0.9	2.31	2.43	2.63	2.75	2.73

[a]From Ref. 22 in which there is a small redshift in gas phase, compared to those in solvent (see discussion in the context).

[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).

batic TDDFT. The experimental results are also listed for comparison. Usually a polymer has very long chain length. In practical calculations, we only choose several repeating monomeric units. The number of "molecular" rings included in our calculations for each polymer is given in the parentheses in Tables I and III. These numbers are chosen so that the lengths of the polymers are about 10 nm. This size effect will be reduced by increasing the repeating units. However, adding the repeating units will simultaneously increase the computational time. On the other hand, high accuracy usually can be achieved by using large basis set, which will result in significant increase in computational time. In the present calculations, we use a basis set which is relatively smaller than those used in small molecular calculations and prepare the polymers with moderate length of chain. This is a balanced choice between the size effect and the accuracy we can tolerate.

From Table I we observe that, among the five adiabatic TDDFT methods, the adiabatic PBE0 functional yields the most accurate excitation energies. This is consistent with our previous studies.[5,6] We can see from Table I that the difference between the singlet and the triplet excitation energies, $E_S - E_T$, is $\sim$0–0.1 eV for LSDA, $\sim$0.1–0.2 eV for meta-GGA, $\sim$0.5 eV for TPSSh, $\sim$0.6 eV for B3LYP, and $\sim$0.8 eV for PBE0. The difference increases as the amount of exact exchange increases. However, some studies suggest[40,42] 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 will build in other many-body properties such as excitonic effects[40,42] which have not been taken into account properly in pure density functional approximations and thus will lead to a finite difference in this limit.

Interestingly, we find that when the theoretical dihedral angle is smaller than the experimental dihedral angle, 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 II. The origin of torsional angles (or generally tortional disorder) of polymers is complicated. It may arise from interchain interaction in amorphous polymeric materials[43,44] or from van der Waals interaction[45,46] between phenyl rings, which have not been taken into consideration in current DFT methods.

The excitation energies of the polymers in benzene solvent are summarized in Table III. From Table III, we can see that the lowest singlet-singlet excitation energies in solution have a redshift of $\sim$0.01–0.05 eV, compared to those in gas phase (Table I). This solvent stabilization is attributed to a strong S_0-S_1 transition dipole moment and is consistent with what we have observed for oligomers.[5,6] However, this trend does not apply to the triplet excitation which has no dipolar

TABLE II. Torsions of the conjugated polymers.

Polymer	Expt. (deg)	PBE0 (deg)	Energy
P3OT	$\sim$24	$\sim$0	Redshift
PBOPT	$\sim$35	$\sim$40	On experiment
MEHPPV	$\sim$20	$\sim$1	Redshift
PFO	$\sim$40	$\sim$38	On experiment
DHOPPV	$\sim$20	$\sim$0	Redshift
PPY	$\gtrsim$0	$\sim$0–1	Slightly redshift
CN-MEHPPV	$\sim$20	$\sim$0	Redshift
PANi	$\sim$0	$\sim$18–26	Too blueshift

TABLE III. The same as Table I but in benzene solution. The solvent effects are taken into account through PCM method.

Polymer	S_0-S_1						S_0-T_1 [b]					
	Expt.[a]	LSD	TPSS	TPSSh	B3LYP	PBE0	Expt.[a]	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-MEHPPV(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).

strength. Triplet excitation energies are nearly the same whether the polymer is in gas phase or in solution.

IV. CONCLUSION

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 aggrement with experiments only when the theoretical torsions agree with experimental estimates. If the theoretical dihedral angles are smaller than the experiments, the TDDFT excitation energies tend to be underestimated. If the theoretical dihedral angles are greater than the experiments, as in rare case, the TDDFT excitation energies tend to be overestimated. Our calculations suggest this trend for all eight polymers we study. It may not be automatically valid for other polymeric systems. Furthermore, we find that a semilocal functional without exact 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 chain length of 10 nm and may vanish in the limit of 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. 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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