Research paper

A fragmentation-based approach for evaluating the intra-chain excitonic couplings in conjugated polymers

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ABSTRACT

For computing the intra-chain excitonic couplings in polymeric systems, here we propose a new fragmentation approach. A comparison for the energetic and spatial properties of the low-lying excited states in PPV between our scheme and full quantum chemical calculations, reveals that our scheme can nicely reproduce full quantum chemical results in weakly coupled systems. Further wavefunction analysis indicate that improved description for strongly coupled system can be achieved by the inclusion of the higher excited states within each fragments. Our proposed scheme is helpful for building the bridge linking the phenomenological descriptions of excitons and microscopic modeling for realistic polymers.

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1. Introduction

Polymer solar cells (PSCs) have attracted great research interests due to their advantages of low cost, flexibility, lightweight, transparency and less adverse environment impact [1], and their power conversion efficiency (PCE) has recently been increased to be over 11% [2]. In PSCs, large exciton diffusion lengths are highly desired so that excitons can migrate efficiently to regions where charge separation can occur. Depending on the magnitude of the excitonic couplings between neighboring chromophores, the mechanisms of exciton diffusion in polymers or biological macromolecules may be quite different, either coherent with an ultrafast timescale around 1–100 femtoseconds (fs) [3–8] or incoherent with typical exciton transfer rates no more than $10^{11}\,s^{-1}$ [9,10]. Therefore, the accurate evaluation of the excitonic couplings in polymeric materials is fundamental and of crucial importance for a thorough rationalization of the microscopic working mechanism in PSCs and a successful design of new efficient PSCs.

Nevertheless, the accurate calculation of excitonic couplings in PSCs is non-trivial. Although one polymer chain might be infinitely long, its electronic excitation is usually localized at one chromophore with the conjugation length of only several monomer units. It results from the strong electron-phonon interactions in organic systems and the structural and energetic disorder induced by thermal fluctuations [11–16]. Therefore, one polymer chain contains a large number of chromophores and the excitons can migrate between chromophores located at the same chain or different chains. Accordingly for PSCs it is necessary to investigate not only the inter-chain excitonic couplings but also intra-chain ones. The widely used Förster dipole-dipole interaction model between small molecules [17] and its improved version with the use of atomic transition charge [18,19] can be generalized for the study of inter-chain excitonic couplings in polymers [16,20], but recent investigations demonstrated that this theory breaks down for long molecules with inter-molecular separation similar to or smaller than the length of the interacting chromophores, a limit is typically found in conjugated polymer thin films [21,22].

The quantitative evaluation of the intra-chain excitonic couplings in polymers is even more challenging because of the following two reasons. The usual quantum chemical calculation of the polymer chain can only produce the adiabatic states of the whole chain (eigenstates of the full system), and cannot provide specific diabatic states (with excitations confined on the different chromophores within the same chain), which are the basis for the evaluation of the intra-chain couplings. The second reason is that theory beyond dipole-dipole interaction model is necessary to include the exchange contributions for the evaluation of the

excitonic couplings between neighboring chromophores with short separations within the same chain. Although the direct computation of intra-chain parameters is difficult, one can use the higher-level quantum chemical calculations of the whole polymeric system to fit these parameters in a simplified model. For example, Tozer and Barford determined the parameters in a Frenkel-Holstein model for poly(p phenylenevinylene) (PPV) by comparing the low-energy spectrum to configuration interaction-singles (CIS) calculations on the Pariser−Parr−Pople model of PPV polymers, and simulated the exciton dynamics of ultrafast interconversion, dynamical localization and diffusion in PPV with this Frenkel-Holstein model [9,23]. However, to the best of our knowledge, no general bottom-up approaches, which don't rely on experimental data or a full calculation of the whole system, have been reported for quantitative evaluation of the intra-chain excitonic couplings in polymers.

In this paper, we propose a fragmentation-based scheme for evaluating the intra-chain excitonic couplings in conjugated polymers, which can generate diabatic excitonic states within the same chain and include non-Coulombic contributions. Test calculations were implemented on one of the most studied prototypical conjugated polymers, PPV (see Fig. 1). Our main goal in this paper is to present such an approach and show its validity under different structural configurations.

2. Theoretical methodology and computational details

2.1. Construction of intra-chain diabatic excited states in a PPV model chain

Here, we take a PPV model chain with 32 units (see Fig. 1) as an example to illustrate how we construct intra-chain diabatic excited states in polymers. As the structural conformation of the polymer chain can significantly affect the features of the electronic structure and dynamics of its excited state, in this paper we consider polymer chains with different conjugation lengths and different dihedral angle values between adjacent fragments. (Here we call a conjugation moiety as a fragment.) For convenience, the PPV model chain will be denoted by PPV-$M_iF_jD_k$, where i, j and k represent the number of units (M) in one fragment, the number of fragments (F) in a chain and the dihedral angle (D) between two adjacent fragments, respectively. As a result, the model chain in Fig. 1 is therefore denoted by PPV-$M_8F_4D_{90}$.

In order to confine the exciton at a specific moiety of a polymer chain, we employ a fragmentation approach for electronic structure calculation, the fragment molecular orbital (FMO) method developed by Kitaura, Fedorov and their coworkers [24,25]. In FMO, the whole system is considered to be composed of many

sub-fragments, and the energy of the whole system is approximated by the linear combinations of the energies of the monomers, dimers, etc. of the fragments. By the two-body fragment molecular orbital method (FMO2) combined with Time-dependent density functional theory (TDDFT), the excited state with energy E^* is assumed to be mostly local to fragment M with two-body corrections from other fragments,

$$E^* = E_M^* + \sum_{I \neq M} E_I^0 + \sum_{I \neq M} (E_{MI}^* - E_M^* - E_I^0) + \sum_{\substack{I > J \\ I,J \neq M}} (E_{IJ}^0 - E_I^0 - E_J^0) \quad (1)$$

where the superscript ^{0} and * denote the ground state and excited states, respectively. Then, the excitation energy ω is given in FMO2-TDDFT by

$$\omega \equiv E^* - E^0 = \omega_M + \sum_{I \neq M} (\omega_{MI} - \omega_M) \quad (2)$$

where the single fragment excitation energy $\omega_M \equiv E_M^* - E_M^0$ is corrected by pair contributions from dimer terms $\omega_{MI} \equiv E_{MI}^* - E_{MI}^0$. Therefore, the main task for FMO2-TDDFT is to perform ground and excited state calculations of a number of fragment monomers and fragment dimers. As only electronic structure calculations of small fragment oligomers are required, the scaling of FMO2-TDDFT's computational cost is low. Consequently, it is feasible for the investigations of large molecules or polymers.

If we take PPV-$M_8F_4D_{90}$ in Fig. 1 as an example, (1)∗234 (1 represents the first fragment as F_1) denotes an electronic excited state on F_1 with self-consistency with the electrostatic environment of the rest fragments F_2-F_4 in their electronic ground states by FMO2-TDDFT calculation. Similarly, 1(2)∗34, 12(3)∗4 and 123(4)∗ represent the local excitations on F_2, F_3 and F_4 respectively. Therefore, we get the corresponding excitation energies and transition dipole moments for the four diabatic states ((1)∗234, 1(2)∗34, 12(3)∗4 and 123(4)∗, abbreviated to $|1\rangle, |2\rangle, |3\rangle, |4\rangle$ respectively), which are used to construct the diabatic Hamiltonian $\mathbf{H^D}$ and transition dipole matrix $\mathbf{U^D}$. Using the similar procedures as above, one may perform FMO2-TDDFT calculations for (12)∗34, 1(23)∗4 and 12(34)∗ and then get the adiabatic states for given fragment dimers. Correspondingly, the adiabatic Hamiltonian $\mathbf{H^A}$ and transition dipole matrix $\mathbf{U^A}$ for each fragment dimer can be obtained. With the physical quantities obtained above, the excitonic couplings between adjacent fragments are derived with the methodology described in the following subsection.

2.2. Evaluation of the excitonic coupling and construction of a model Hamiltonian for the polymer chain

In order to derive the off-diagonal elements of $\mathbf{H^D}$ (the intra-chain excitonic coupling J) with the consideration of not only the
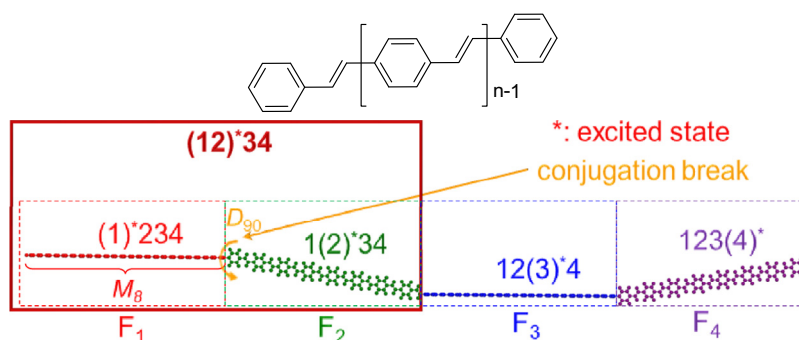

Fig. 1. Schematic illustration of PPV polymer and its fragmentation. Top panel shows the structure of (PV)$_n$P. The PPV model chain here contains eight phenyl rings in each of the four fragments and the dihedral angle between the two adjacent fragments is 90°, i.e. PPV-$M_8F_4D_{90}$. (1)∗234 as the diabatic state represents that the first fragment F_1 is at the electronic excited state and the rest fragments F_2–F_4 are at the ground state. (12)∗34 as the adiabatic state represents the fragment dimer F_1–F_2 is at the electronic excited state as a whole.