

# Quantum Modelling of Photo-Excited Processes

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## Abstract

In the framework of quantum field theory and the dipole approximation, a self-consistent quantum molecular dynamics method is used to investigate the effect of chain length on the probability of formation or decay of both singlet and triplet excitons due to photon absorption or emission in isolated poly(p-phenylene vinylene) (PPV) chains. We found that the probability of the photo-induced intra-molecular singlet exciton formation and decay increases linearly with chain length and the probability for triplet exciton formation and decay do not depend on the chain length. Polymers with long chains have thus an advantage over small molecules in solar cell and light emitting diode (LED) applications because their efficiency depends on the number of intra-molecular singlet excitons formed or emitted in the device, which is expected to increase with the conjugation length.

**Keywords:** quantum modelling, photo-excited processes, solar cell, LED, conducting polymer.

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## 1. Introduction

During the past decade a great progress has been made in the understanding of electronic and optical properties of conjugated polymers [1]. Among these polymers, poly(p-phenylene vinylene) (PPV) has attracted a great deal of attention as an active material for photovoltaic

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cells, photo-detectors, electrically pumped lasers and light-emitting diodes (LEDs) [2]. For all these optical devices the efficiency depends on the excitation and emission processes.

The literature concerning the spectroscopic and photophysical behaviour of conjugated polymer systems clearly indicates that photo-excited processes in these materials are both an intra-chain and inter-chain processes. A number of experimental results suggest that many optical properties of conjugated polymers are directly influenced by an effective conjugation length [3]. Therefore, the effect of conjugation length on the formation of both singlet and triplet intra-molecular excitons by photo-induced absorption can be described on the basis of quantum mechanical calculations performed on isolated polymer chains of different size.

Since conjugated polymers such as PPV have strong electron-lattice interactions [4], there are doubts about the validity of the usual rigid lattice assumption of conventional exciton theories [5] for understanding the chain-length dependence of photo-induced spin-dependent exciton formation probabilities at molecular scale.

In this work we concentrate on the formation probability of the lowest singlet and triplet excited states of isolated PPV chains as a result of photon absorption and discuss the influence of two factors, namely the effect of structural relaxation and the effect of chain length on the formation of excitons.

## **2. Computational methods and models**

Conjugated polymers are quite different from inorganic materials, since they are flexible and have strong electron-lattice interactions. Thus, exciton formation is expected to induce lattice distortions at molecular level which should affect the intra-molecular photo-excited processes. Since the electronic and lattice motions influence each other, they must be treated self-consistently. To address these basic issues the theoretical approach we adopt combines a self-consistent quantum chemistry method with a molecular dynamics method [6]. After selecting

a starting geometry for the polymer molecule, the electronic structure calculations were performed using an approximate self-consistent-field molecular orbital method called CNDO (Complete Neglect of Differential Overlap) [7], which is a semi-empirical application of Hartree-Fock theory, until self-consistency in energy is achieved. Once the electronic problem has been solved, the gradients of the total self-consistent energy, evaluated at each atomic position, yield the atomic force and a molecular dynamical method is used to move the atoms during 1fs according to Newtonian equations of motion. Both electronic structure calculations and atomic relaxation are repeated in parallel until a minimum energy is achieved for the polymer molecule.

The above approach has been used to study the behaviour of neutral PPV molecules with chain length ranging from 6 to 16 monomers units, in their ground state and the lowest singlet and triplet states, and to obtain their intra-molecular properties, namely the fully relaxed molecular geometry, the electronic structure, the wave function and the Mulliken atomic charges (the net charge at each atom).

In order to study the distortion induced by exciton formation in a PPV chain we define a dimerisation parameter, which represents the degree of dimerisation along the chain, by:

$$d_n = (-1)^n (b_{n,n+1} - b_{n-1,n}) \quad (1)$$

where  $b_{n,n+1}$  is the bond length between carbon atoms  $n$  and  $n+1$ .

In the calculations reported here, we use the CNDO parameters selected by Pople and Beveridge [7]. Besides, we treat spin polarisation by recourse to the unrestricted Hartree-Fock (UHF) method [7,8], where the self-consistent-field (SCF) wave function is written as a single Slater determinant in which alpha and beta spin electrons are assigned to two independent sets of spatial orbitals. Moreover, each molecular orbital is expressed as a linear combination of atomic orbitals (LCAO) and a minimal basis set is used. The unrestricted Hartree-Fock wave function is not an eigenfunction of the total spin operator  $\hat{S}^2$ . Thus, the

UHF wave function of singlet (or triplet) exciton does not describe a pure singlet (or triplet) state, but has a mixture of other multiplicities [7, 8].

When the PPV molecule is exposed to light, such molecule is under the influence of a radiation field. In the framework of quantum field theory and the dipole approximation [9, 10], we can calculate the probability per unit time for the absorption or emission of a photon in the transition of a single electron from a discrete occupied level to a discrete unoccupied level of the molecule. For an incident beam of one photon crossing unit area per unit time per unit frequency range, the probability per unit time for photon absorption or emission is given by

$$W_{if} = \frac{4\pi^2}{\hbar^2 c} I(\omega_{fi}) |\langle f | \hat{d} | i \rangle|^2 = \frac{4\pi^2 \alpha}{e^2 \hbar} E |\langle f | \hat{d} | i \rangle|^2 \quad (2)$$

where  $i$  and  $f$  refer to initial and final electronic states,  $I(\omega_{fi})$  is the intensity of radiation per unit frequency range,  $E = |E_f - E_i| = \hbar \omega_{fi}$  is the transition energy between the electronic states  $i$  and  $f$ ,  $\langle f | \hat{d} | i \rangle$  is the transition dipole moment,  $\alpha$  is the fine structure constant,  $e$  is the electron charge,  $c$  is the velocity of light and  $\hbar = h/(2\pi)$  where  $h$  is the Planck's constant.

In the theoretical approach followed here, the lowest singlet and triplet excited states are obtained by promoting a single electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the ground state isolated PPV chain. We consider also that the probability of exciton formation or exciton decay is dominated by the molecular levels and molecular orbitals involved in the single excitation. The photo-induced absorption or emission transition probabilities are then calculated by equation (2) where  $i$  and  $f$  are the HOMO and the LUMO of the fully relaxed exciton.

Our approach goes beyond standard quantum chemistry analyses since it recognizes that photon absorption can induce lattice distortion and charge rearrangement among the polymer

atoms, and it allows them to be included systematically and self-consistently in the electronic structure calculation of both singlet and triplet excitons.

### 3. Results and discussion

In order to study the effect of photo-induced singlet and triplet exciton formation on the geometry of isolated PPV chains, we calculated the change in the dimerisation pattern, given by equation (1), of both singlet and triplet excitons relative to the ground-state chain. The results obtained for a PPV chain with 16 monomer units are shown in Figure 1. The exciton formation induces distortion in the central region of the polymer backbone as a result of changes in adjacent carbon-carbon bond lengths of the same region where distortion occurs.

The distortion is accompanied by a charge rearrangement among the PPV atoms at the distortion site. The changes in the Mulliken atomic charge of carbon and hydrogen atoms of PPV chain with 16 monomer units due to both singlet and triplet exciton formation are given in Figure 2. We notice that charge rearrangement is greatest for the carbon atoms since the states on either side of the HOMO-LUMO gap are predominantly carbon  $\pi$ -states. For triplet excitons we find a charge alternation on both carbon and hydrogen atoms, whereas the formation of singlet exciton leads to charge storage of opposite sign on hydrogen and carbon atoms of the same monomer unit.

The width and amplitude of the distortion in the dimerisation of the singlet exciton is greater than that of the triplet exciton. This is probably due to storage of charges of opposite signs across the defect on the carbon and hydrogen atoms of the singlet exciton shown in Figure 2. A similar behavior was found by Cornil *et al.* [11] polyene chains containing 20 carbon atoms; in this case they calculated atomic transition densities for carbon atoms associated with the optical excitation between the ground state and the lowest excited singlet state using

Intermediate Neglect of Differential Overlap coupled to a Single Configuration Interaction scheme (INDO/SCI).

Photo-induced absorption measurements by Wohlgenannt *et al.* [12] show that the ratio of the formation cross-section of singlet and triplet excitons that are generated in conjugated materials increases with the chain length. In order to study the effect of chain length on photo-induced spin-dependent exciton formation and decay, we used equation (2) to calculate the transition probability between the ground state and lowest lying excited singlet and triplet states in an isolated PPV chain with varying length. One of the reasons for using the exciton wave functions generated by the self-consistent quantum chemistry molecular dynamics method in the transition probability calculations was the desire to account for the strong lattice distortion and charge rearrangement induced in the polymer molecule by the exciton formation. The chain-length dependence results obtained are shown in Figure 3. These results show that singlet states are formed with higher probability than triplets for chain lengths varying from 6 to 16 monomer units. Our results also suggest that the probability of singlet exciton formation or decay increases linearly with chain length whereas the probability for triplet exciton formation or decay remains roughly constant. These results are in agreement with Wohlgenannt *et al.* experiments [12], which showed that the larger the conjugation length, the higher the singlet exciton population generated in conjugated materials.

We should note that the calculated energy levels and molecular orbitals are strongly dependent on the CNDO parameters used and on the basis set of atomic orbitals used to construct the exciton wave function; also, the CNDO approximations are too extreme to give a proper account of the spin polarisation contribution to the unpaired electron distribution in the molecule. Therefore, the absolute value of calculated transition probabilities for photo-induced exciton formation or decay may not be correct, but we expect the predicted trends for the effect of chain length to be reliable and to show important features.

Nevertheless, results of these investigations are expected to increase our knowledge of intra-molecular exciton formation and exciton decay in PPV as a consequence of photon absorption and photon emission, respectively, as well as to provide information on the effect of both charge-induced defect and conjugation length on intra-molecular excitation and emission processes in fluorescent and phosphorescent LEDs and solar cells which is hard to obtain directly from the experiments.

#### **4. Conclusion**

The optical excitation between the ground state and the lowest excited singlet and triplet states induces local geometric relaxation in the central region of PPV chains and charge rearrangement among the polymer atoms within the distorted region. Although the distortion patterns of singlet and triplet excitons are similar, the distortion within the triplet exciton is sharper which corresponds to a more localized wave function. The charge rearrangements are greater for the carbon atoms and have opposite sign across the distortion region in the case of singlet exciton. A charge alternation within the distortion region is predicted for triplet exciton.

Our probability calculation for the spin-dependent photo-induced exciton formation in PPV suggests that singlet excitons are formed with higher probability than triplet excitons. Besides, the chain length seems to increase the probability of singlet exciton formation or decay but does not seem to affect the triplet exciton formation or decay. Since the efficiency of PPV-based solar cells and light emitting diodes is mainly determined by spin-singlet exciton formation and decay, the effect of chain length on the increasing number of these events indicates that polymers with long polymer chains are better materials for both applications.

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**List of figure captions:**

Figure 1 – Variation of the dimerisation pattern of a singlet exciton (left-hand side) and a triplet exciton (right-hand side) relative the ground state values of a PPV chain with 16 repeat units.

Figure 2 – Changes in Mulliken atomic charges for carbon (closed mark) and hydrogen (open mark) atoms relative the ground state values of a PPV chain with 16 repeat units induced by: singlet exciton formation (left-hand side); triplet exciton formation (right-hand side).

Figure 3 – Calculated probabilities of photo-induced transition between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the lowest lying singlet (circles) and triplet (triangles) excitons of isolated PPV chains as a function of the chain length (measured in monomer units). The lines through the calculated points are a linear fit.

Figure 1

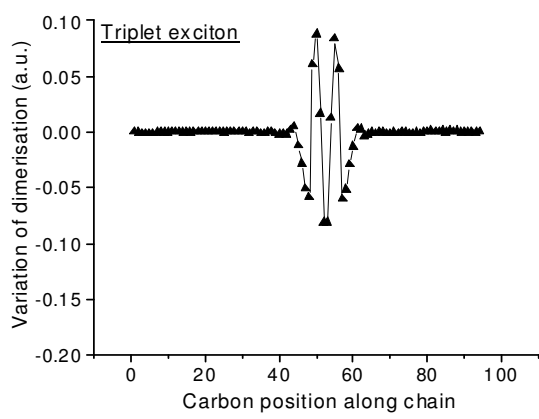
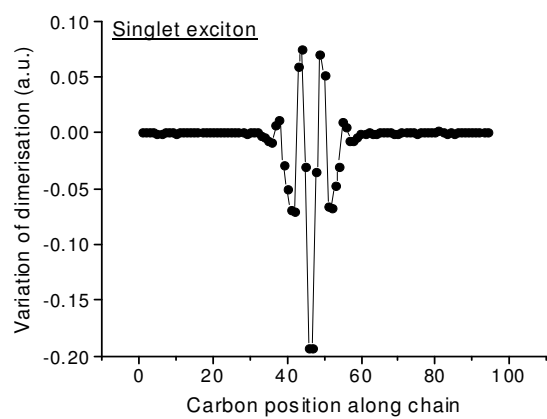


Figure 2

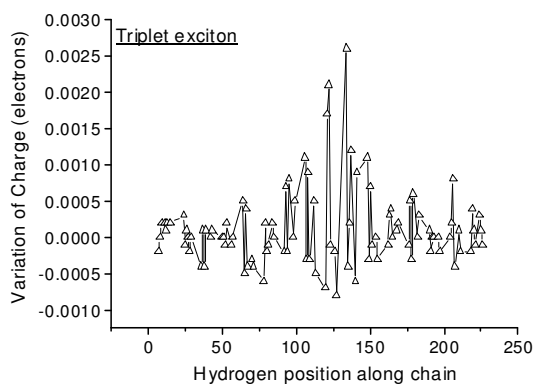
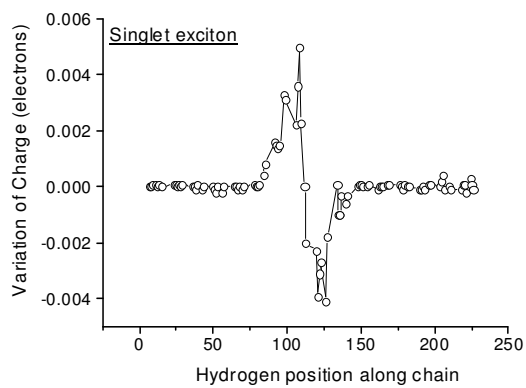
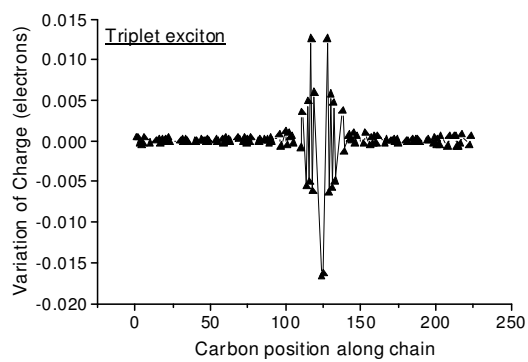
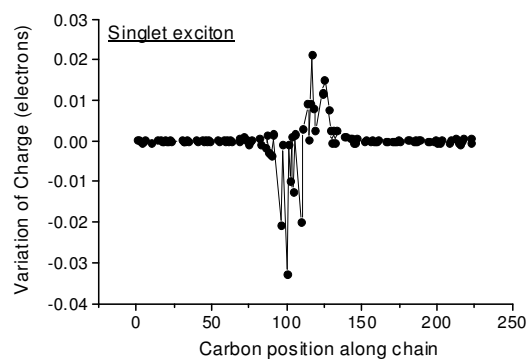


Figure 3

