Structural Relaxations in Electronically Excited Poly(*para*-phenylene)

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Structural relaxations in electronically excited poly(*para*-phenylene) are studied using many-body perturbation theory and density-functional-theory methods. A sophisticated description of the electron-hole interaction is required to describe the excitonic energies, but the associated structural relaxations can be obtained quite accurately within a constrained density-functional-theory approach. We find that the structural relaxations in the low-energy excitonic states extend over about eight monomers, leading to an energy reduction of 0.22 eV and a Stokes shift of 0.40 eV.

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The sustained growth of interest in conjugated polymers arises from their potential as the active material in low-cost field-effect transistors, photovoltaic devices, and light emitting diodes (LEDs) [1,2]. Investigating electronically excited states is an important part of this effort, which has proved a great challenge for theoretical techniques. An accurate description of the excited electronic states of conjugated polymers requires the inclusion of the strong electron-hole interaction and the structural relaxations which occur in the excited state.

In its simplest form, a polymer LED consists of a layer of conjugated polymer sandwiched between two electrodes. Electrons and holes are injected into the polymer where they are attracted to one another and form bound excitons. Light is then emitted by exciton recombination. In an excited state the polymer may lower its energy by structural relaxations so that the peak optical emission frequency is lower than the peak absorption frequency. Although this "Stokes shift" can, at least in principle, be measured, the actual relaxations have not been determined experimentally. These relaxations localize excitons and are relevant for the technologically important processes of exciton migration and recombination.

We have investigated structural relaxations in the low-energy excited states of poly(*para*-phenylene) (PPP). A PPP LED has been demonstrated which emits blue light in a band around 2.7 eV [3,4]. PPP is, however, insoluble and therefore difficult to process and, instead, soluble derivatives of PPP with various side groups are preferred for manufacturing LEDs. The low-energy optical properties of PPP and its derivatives are similar, although the structural relaxations in the excited states depend on the nature of the side groups. We have chosen to study PPP because it has a simpler structure than its derivatives.

As we show below, systems containing more than 100 atoms are required for studying the excited-state relaxations of PPP, which pose significant problems to theory. Such systems can be treated by density-functional theory (DFT) [5], but DFT alone has difficulties in describing excited states. Excited states can be described by many-body perturbation theory (MBPT) [6], but this is numerically demanding and cannot currently be applied to such large systems. However, we find that the forces in the excited states of PPP obtained within DFT are very similar to those within MBPT, which indicates that the relaxed structures and Stokes shift obtained within DFT are reliable.

A PPP chain (Fig. 1) consists of phenyl rings joined by single C-C bonds, with adjacent rings being rotated with respect to one another by a torsional angle θ. Our DFT structures for the ground states of the single chain and crystal are in excellent agreement with a previous DFT calculation and in accord with experiment [7]. Our DFT band gaps for the single chain (2.44 eV) and crystal (1.70 eV) are in good agreement with a previous calculation [7].

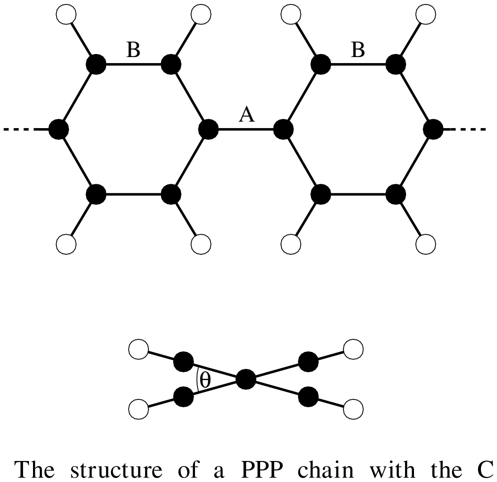

FIG. 1. The structure of a PPP chain with the C atoms represented by filled circles and the H atoms by open circles. (a) Side view showing the *A* and *B* bonds. (b) End view showing the torsional angle θ.

We began by using a simple model of how an optical excitation affects the bonding in PPP: we performed DFT calculations of the changes in the electronic charge distribution due to a single excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In both the isolated chain and crystalline forms we found an increase in the electronic charge in the *A* bonds and to a lesser extent in the *B* bonds (see Fig. 1). These changes indicate the development of double-bonding character which is expected to favor both a more planar arrangement of rings (reduction in θ) and compression of the *A* and *B* bonds.

In a perfect chain or crystal an exciton would, in principle, be delocalized because localization within some region of space costs kinetic energy. However, a larger energy may be gained by structural relaxations so that an exciton may localize itself. The low-energy excitonic states of PPP may therefore be self-localized by structural relaxations, i.e., local reductions in θ and the lengths of the *A* and *B* bonds.

We investigated the structural relaxations in the lowest excited states of a single PPP chain using a constrained-DFT method. We modeled the excited state by promoting an electron from the HOMO to the LUMO at wave vector $k = 0$ and performing full structural relaxations. A unit cell containing 28 monomers was found to be sufficient to converge the excited-state structure. The important parameters of the minimum energy structure are shown in Fig. 2. The relaxations are largely confined to a region of approximately eight monomers over which the torsional angle and the lengths of the *A* bonds are significantly reduced, and the lengths of the *B* bonds are somewhat reduced. The gain in energy from the relaxation is 0.22 eV, and the Stokes shift, calculated as the difference between the band gaps of the ground and excited-state structures, is 0.40 eV [8].

We analyzed the localization of the exciton in terms of the compression of the *A* and *B* bonds and the reduction in θ. We performed two constrained-DFT calculations for the excited state in which only relaxations (1) along the axis of the chain and (2) in the plane perpendicular to the chain were allowed. The relaxation energies of 0.14 eV and 0.17 eV, respectively, add up to significantly more than the full relaxation energy of 0.22 eV, indicating that the modes are strongly coupled. The relaxations along the chain led to a Stokes shift of only 0.06 eV and to very weak localization of the exciton, whereas the relaxations perpendicular to the chain gave a Stokes shift of 0.16 eV and much stronger localization. The torsional relaxation is therefore very important in determining the Stokes shift, although the coupling to the bond compression is strong and both types of relaxation are important in determining the full relaxation energy and Stokes shift.

Stokes shifts in PPP derivatives have been measured in dilute solutions and solid films. "Laddered" PPP derivatives are commonly used in which some or all of the phenyl rings are joined to their neighbors by chemical "bridges," which hinder rotation about the *A* bonds and reduce the Stokes shift. Hertel *et al.* [9] report absorption and emission measurements on a series of laddered and nonladdered polymers, which clearly show that laddering reduces the Stokes shift. As shown in Fig. 3b of Hertel *et al.* [9], in dilute solution, the nonladdered polymer dodecyloxy-poly(*para*-phenylene) (DDO-PPP) exhibits a Stokes shift of 0.6 ± 0.2 eV. Considering the presence of the solvent and different side chains in the experimental system, the agreement with our single-chain PPP value of 0.40 eV is reasonable. The measured Stokes shifts for the laddered polymers are smaller, in agreement with our picture that changes in θ couple strongly to the band gap. Our picture also suggests that structural relaxations for excitons in laddered PPP derivatives should only lead to a weak localization effect.

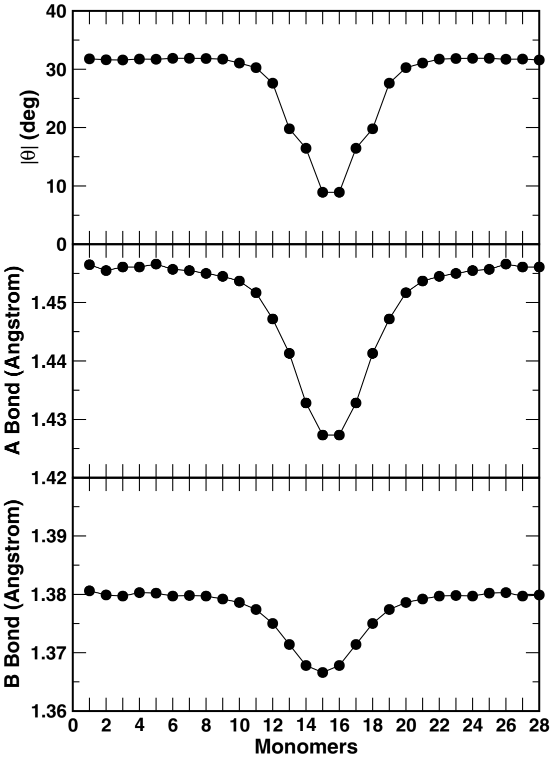

FIG. 2. The torsional angle, θ, and the lengths of the *A* and *B* bonds (see Fig. 1) as a function of monomer number for the excited-state of a single PPP chain.

We now investigate the reliability of the constrained-DFT results for the relaxation and Stokes shift of the exciton. The formation of a completely delocalized exciton leads to a vanishingly small change in the charge density and therefore vanishingly small forces on the atoms. Excitons are, however, attracted to regions where a structural distortion occurs which reduces the band gap. If the lowering of the energy of the exciton is greater than the energy required to form the distortion, then the exciton will stabilize the distortion, leading to a self-localized exciton. Changes in the band gap due to structural distortions are described approximately within our DFT calculations. The excitonic energies themselves, however, are strongly modified by many-body effects arising from the electron-hole interaction. We now investigate the dependence of these many-body effects on the structural distortion.

MBPT provides a rigorous approach to electronic many-body effects for excited electronic states [6]. We have used the *GW* approximation to describe the addition or removal of an electron and the Bethe-Salpeter equation (BSE) for the excitation of an electron including the electron-hole interaction [6]. These techniques have recently been used to describe excitons in solids [10], clusters [11], and polymers [12,13].

To investigate the effects of electronic correlation and validate the constrained-DFT approach, we proceeded as follows. We performed DFT and MBPT calculations for a series of structures involving torsional angles and compressions of the A and B bonds which are similar to those found in the self-localized exciton of Fig. 2. We considered the relaxation of the two central monomers of Fig. 2 as indicating the maximum relaxations which occur in the exciton. We then periodically repeated this structure, obtaining a reference system which can be investigated within both constrained-DFT and MBPT. We defined a structural parameter x which takes the value $x = 0$ for the ground state structure ($\theta = 33.7\,°$, $A = 1.456$ Å, and $B = 1.380$ Å), and $x = 1$ for the geometry corresponding to the central monomers of the self-localized exciton ($\theta = 9.1\,°$, $A = 1.427$ Å, and $B = 1.366$ Å). Intermediate values of x correspond to linearly interpolating θ, A, and B between the extremal values. Figure 3 shows the corresponding excitation energies as a function of x. The four curves denote the DFT energy gap, the quasiparticle (QP) energy gap, and the transition energies of the lowest spin-singlet and spin-triplet excitons obtained from solving the BSE [14]. The QP gaps are 2.3–3.0 eV larger than the DFT gaps due to the significant QP corrections typical of semiconducting systems. The exciton energies, on the other hand, are 1.5–2.9 eV smaller than the QP gaps due to the attractive electron-hole interaction. The singlet (triplet) excitation energy ranges from 3.41 eV (2.62 eV) at $x = 0$ to 2.18 eV (1.61 eV) at $x = 1$.

The change in the excitation energy when going from $x = 0$ to $x = 1$ constitutes the excited-state contribution to the force on the structure projected onto the relaxations studied. The most important feature of Fig. 3 is that this change (-1.22 eV or -1.01 eV, respectively, for the singlet and triplet state) is very similar to the change in the DFT gap energy (-0.95 eV). Changes in the DFT gap energy, in turn, correspond to the excited-state forces given by constrained-DFT. Our results therefore imply that the forces are indeed given reliably by the constrained-DFT theory, even though the exciton binding energies are large and the absolute values of the DFT band gaps are in poor agreement with the excitonic energies [15].

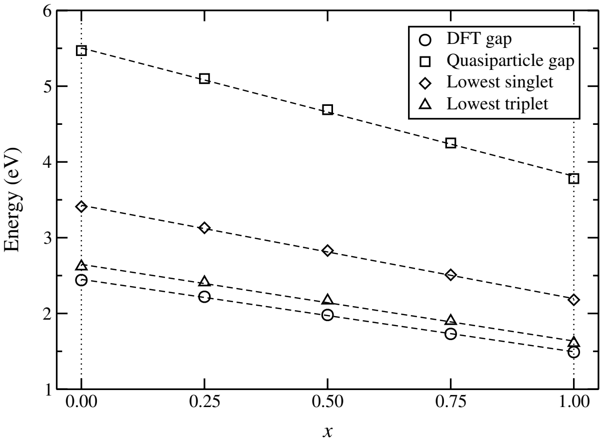

FIG. 3. Excitation energies calculated within the DFT and *GW* approaches and the *GW*-BSE singlet and triplet energies as a function of the structural parameter x for a single PPP chain.

The singlet excitation energy for the ground state structure of the single chain (3.41 eV) is in good agreement with experimental absorption spectra which show maximum absorption around 3.5 eV [3,4]. We find that the singlet-triplet splitting depends rather weakly on the relaxations, changing from 0.79 eV at $x = 0$ to 0.57 eV at $x = 1$. We therefore expect the splitting for the relaxed excited-state structure to be in the region of 0.5 eV, which is consistent with the splitting of 0.7–0.8 eV obtained from emission spectra of PPP derivatives [9].

Another important characteristic of the excitons is the average electron-hole separation along the chain, which we find to be about five rings for the singlet state and about four for the triplet. These average separations were found to be essentially independent of the relaxations, which is further evidence that the relaxations and electron-hole interaction are weakly coupled.

We have analyzed the reasons for the success of the constrained-DFT approach for calculating excited-state geometries. The details of this analysis will be published elsewhere, but we conclude that the various approximations should work well when the excitons are delocalized over many atoms and when the relaxations are small and do not include large changes such as bond breaking. The constrained-DFT approach would be inaccurate if the excitonic wave function contained contributions from more than one electron or hole band, but this mixing could be calculated from BSE calculations on high symmetry structures and then used in DFT studies of large structures. Our study suggests that the constrained-DFT approach is likely to work for other conjugated polymers.

Our main calculations are for single chains, in which the electron-hole interaction is larger than in solids.

Therefore, our calculations are an even stronger test of the idea of neglecting the electron-hole interaction when calculating the excited-state relaxations than would be encountered in the more technologically relevant solid state. In the solid, many chains are packed together at van der Waals distances, which gives rise to three main additional features: (i) electronic overlap between chains, (ii) van der Waals interactions, and, in particular, (iii) the effect of interchain dielectric screening on the electron-hole interaction. The first of these is well described within DFT while MBPT includes the second and third.

To study the effects of interchain dielectric screening, we considered a 3D crystalline array of PPP chains in which the electronic overlap between chains is small and consequently the DFT results are only weakly perturbed. The calculated QP correction to the DFT gap and the electron-hole interaction are, however, both reduced by more than 1 eV as a consequence of the more effective dielectric screening in a 3D solid. The QP state, which describes an additional electron or hole, shows significant interaction with the polarizable neighboring chains, and the QP gap closes. The QP corrections also depend on x, indicating that the intrachain screening changes when the geometry relaxes. The exciton energies are, however, only weakly affected by the changes in the inter- or intrachain screening. In the solid, the singlet (triplet) energy ranges from 3.66 eV (3.14 eV) at $x = 0$ to 2.55 eV (2.23 eV) at $x = 1$, which is only a little higher than the single-chain results. This insensitivity derives from the charge-neutral character of the exciton, which is much less influenced by electrostatic screening than the single-particle excitations. Similar effects have been observed for other polymers by van der Horst *et al.* [13]. Our singlet exciton binding energy for $x = 0$ of 0.64 eV is in reasonable agreement with available experimental estimates for PPP derivatives of 0.5–0.85 eV [16,17]. The changes in the excitation energies as x varies from 0 to 1 ($-$ 1.11 eV for the singlet, -0.91 eV for the triplet) are very similar to the change in the DFT gap ($-$ 0.95 eV), confirming the reliability of the constrained-DFT forces. The weak interactions between chains have to be handled with care, however, and the self-trapping of the exciton in the solid state will be the subject of a further study.

In summary, we have shown that while the electron-hole interaction is very important in determining the excitonic energies in PPP, it is less important for the excited-state geometries. We have demonstrated that a simple constrained-DFT approach is sufficient for calculating relaxations in the low-energy excited states of PPP. In this case, we find that the structural relaxations extend over about eight monomers, leading to an energy reduction of 0.22 eV and a Stokes shift of 0.40 eV. The DFT method is tractable for studying the influence of structural disorder on the optical properties of polymers.

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