

## Optical Excitations in Conjugated Polymers

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(Received 2 November 1998)*

We investigate optical absorption spectra and excitons in conjugated polymers from first principles. This is done by calculating the one-particle and the two-particle Green's function, including relevant many-body effects, and evaluating quasiparticle and optical excitations. Trans-polyacetylene and poly-phenylene-vinylene are studied as prototype long chain polymers. The electron-hole interaction gives rise to large exciton binding energies ( $\sim 1$  eV) and dramatically alters the optical spectra. The calculated exciton wave functions are very extended in real space. [S0031-9007(99)08570-1]

PACS numbers: 78.40.Me, 36.20.Kd, 42.70.Jk, 71.20.Rv

Conjugated polymers constitute a fast-growing field of fundamental research and technological applications due to their fascinating electronic and optical properties [1–10]. As a part of the systematic progress in this field, theoretical investigations of the electronic structure and excitations of conjugated polymers are very important. To obtain most reliable results, it would be highly desirable to employ *ab initio* techniques that overcome the need for adjusted parameters in empirical methods. Unfortunately, such *ab initio* studies are very demanding for complex polymers with large unit cells. Therefore, only limited information about the electronic ground state and excited states of these systems is available so far. In particular, the effect of excitons on the optical properties is not fully resolved. This is the focus of our present work.

A systematic *ab initio* approach to optical excitations of an electronic system is to calculate its one-particle and two-particle Green's functions, including all relevant aspects of electronic interaction and correlation [11–14]. The key quantity in this context is the electron self-energy operator which can be evaluated very accurately for many materials in the *GW* approximation [11]. The one-particle Green's function describes quasiparticle (QP) excitations (i.e., the individual excitation of electrons and holes) [11,15,16] while the two-particle Green's function describes coupled electron-hole excitations and allows for the evaluation of the optical spectrum [12–14,17–20]. This approach has yielded highly reliable results for the full absorption spectrum of small semiconductor clusters [19] and of extended bulk crystals from first principles [20]. In the present paper we employ these techniques to investigate two conjugated polymers, trans-polyacetylene and poly-phenylene-vinylene (PPV).

To obtain their basic intrinsic optical properties, we consider infinitely long chain polymers. This is distinctly different from previous quantum-chemical calculations that focused on molecules of limited length [3,8]. For the systems studied here, infinitely long chains are more appropriate to describe the properties of long polymers since the intrinsic correlation length of electrons and holes in the

exciton states is very large. We concentrate on polymers in their ground-state geometry and focus on the interaction of electrons, holes, and light in the optical *absorption* process. Coupling of the excited states to phonons, lattice relaxation, polaronic effects, as well as the decay of excitons into other excitations (such as solitons) are not considered.

The simplest conjugated polymer is trans-polyacetylene [4–7], serving as a natural candidate for studying fundamental properties of conjugated polymers. Figure 1a shows the corresponding QP band structure. It has a direct fundamental band gap of 2.1 eV at the X point of the one-dimensional Brillouin zone. The highest occupied and the lowest unoccupied bands (labeled  $\pi$  and  $\pi^*$ ) are formed from delocalized  $\pi$  states.

The QP band-structure energies (i.e., the spectrum of the one-particle Green's function), however, do not yield reliable information on optical properties. The one-particle Green's function corresponds to processes in which isolated electrons are added to the system (creation of quasielectrons) or are removed from the system

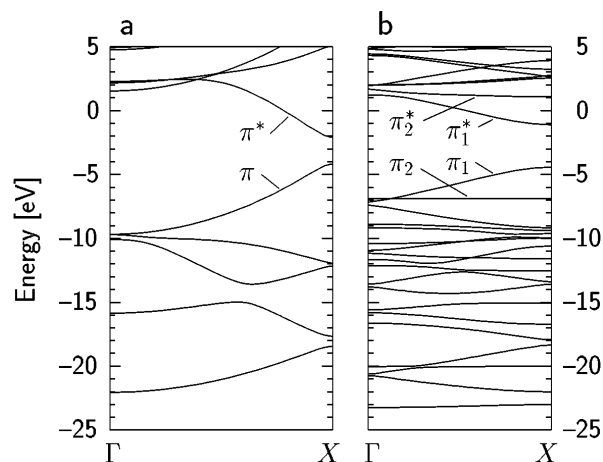


FIG. 1. Quasiparticle band structures of trans-polyacetylene (a) and of PPV (b), as calculated within the *GW* approximation. The vacuum level is at 0 eV.

(creation of quasiholes). In optical absorption processes, on the other hand, electrons and holes are created simultaneously, interact with each other, and can form bound electron-hole pairs. The description of electron-hole pair excitations goes beyond the quasiparticle band-structure concept. It requires solving the Bethe-Salpeter equation (BSE) for the two-particle Green's function, including the electron-hole interaction [14].

Figure 2a shows our calculated optical absorption spectrum for trans-polyacetylene. The dashed line denotes the spectrum neglecting the electron-hole interaction (thus corresponding to vertical  $\pi \rightarrow \pi^*$  transitions of free electron-hole pair states within the QP band-structure picture). This spectrum exhibits the typical behavior of a one-dimensional joint density-of-states (JDOS), i.e., it diverges as  $(\hbar\omega - E_g)^{-1/2}$  at  $E_g = 2.1$  eV. When the electron-hole interaction is included, the spectrum (now given by the solid line in Fig. 2a) is drastically changed. The absorption at and above the energy gap is reduced by 2 orders of magnitude and the material is nearly transparent above 2.0 eV. This does not result from an absence of states in this energy range; in fact, we find virtually the same JDOS above the gap as in the noninteracting case.

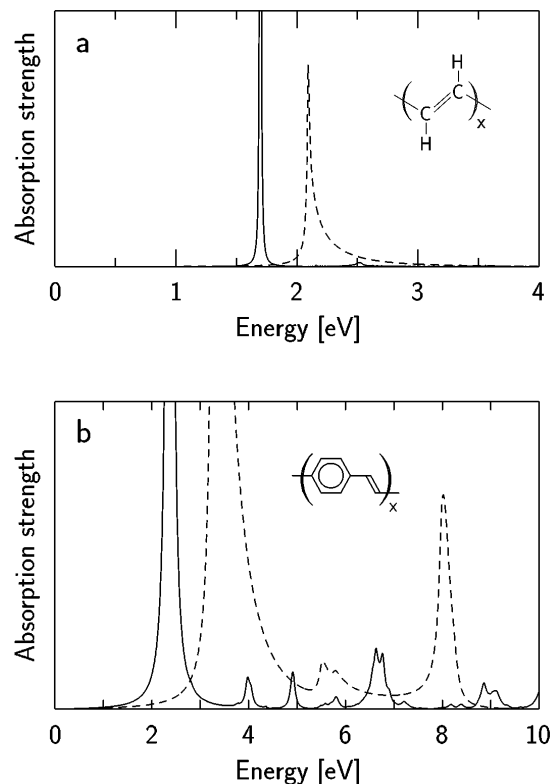


FIG. 2. Calculated optical absorption spectrum of trans-polyacetylene (a) and PPV (b) in arbitrary units. The solid (dashed) lines denote spectra including (neglecting) electron-hole interaction. The polarization vector of the electric field is along the polymer chain. The figure includes an artificial broadening of 0.005 eV (0.05 eV) for trans-polyacetylene (PPV).

The changes in the absorption strength are caused by a destructively coherent coupling of the optical matrix elements of the electron-hole pair configurations in the formation of the excitations.

Below the gap, two bound exciton states are formed (mainly from  $\pi \rightarrow \pi^*$  transitions), at excitation energies of 1.7 and 1.8 eV [21]. The first one shows a constructive, coherent superposition of oscillator strength, resulting in a pronounced signal in the optical spectrum. The optical transition matrix element of the second exciton, on the other hand, is zero. The absorption spectrum thus consists of one single line at 1.7 eV, in good agreement with the measured spectrum which shows maximum absorption at 1.7 eV [5]. It should be noted, however, that the measured spectrum is much broader than our single-line spectrum, with an asymmetric tail structure above 1.7 eV. This could result from static lattice distortions, leading to finite conjugation lengths, or from simultaneous excitation of excitons and phonons.

The absorption spectrum presented in Fig. 2a has been calculated for light with the electric field polarization vector parallel to the chain, in which direction the  $\pi$  electrons are highly polarizable. For the polarization perpendicular to the chain but still within the plane of the polymer, we observe nearly the same shape of the spectra as in Fig. 2a, but the absorption strength is smaller by 3 orders of magnitude, which is also observed experimentally [5]. For polarization perpendicular to the plane, the absorption is zero due to the mirror symmetry of the  $\pi$  states. For the latter two polarizations, significant absorption strength is observed only above 8 eV, resulting from transitions other than  $\pi \rightarrow \pi^*$ .

Our approach allows us to evaluate the two-particle wave function of each exciton state and to visualize the electron-hole correlation in real space [20]. Figure 3a shows the distribution of the electron relative to the hole along the chain, for the two bound excitons in trans-polyacetylene. The hole is fixed at an arbitrary position on the polymer chain (placed in the center of the panel). The first exciton state (at 1.7 eV) has an even envelope function, giving rise to the strong optical peak since the  $\pi \rightarrow \pi^*$  interband transition is dipole allowed. The second exciton state, on the other hand, has an odd envelope function that vanishes at zero distance between electron and hole, leading to optical inactivity because of the dipole selection rule. Already the first exciton is very extended in real space, covering a range of about 50 Å. The second exciton is even larger. These large sizes are related to the strong dispersion of the  $\pi$  and  $\pi^*$  bands close to the fundamental gap at the X point of the band structure. Only electron-hole configurations close to X contribute to the formation of the excitons. They are thus strongly localized in reciprocal (or momentum) space and hence very extended in real space.

The results discussed above are for spin-singlet transitions in trans-polyacetylene. When we look at spin-triplet

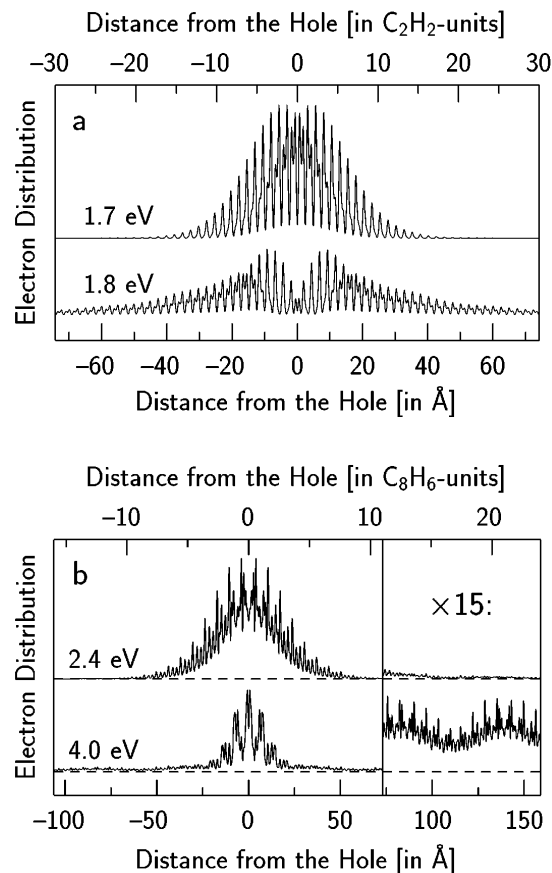


FIG. 3. Real-space electron-hole wave function of the exciton states, showing the distribution of the electron relative to the hole which is fixed at some arbitrary position on the chain (at 0 Å, in the center of each panel). The electron distribution is averaged over a plane perpendicular to the chain, resulting in its one-dimensional density along the polymer. Panel a is for the optically active (at 1.7 eV) and the inactive (at 1.8 eV) bound exciton states in trans-polyacetylene. Panel b shows two optically active exciton states in PPV, at 2.4 and 4.0 eV.

transitions (that cannot be excited by light), we again find two bound excitons, at 0.9 and 1.7 eV. These two states correspond to the equivalent spin-singlet excitons at 1.7 and 1.8 eV, respectively. The triplet energies are smaller since the repulsive exchange interaction between the electron and the hole is absent for spin-triplet configurations. As a consequence of the spatial confinement of the electron and the hole in the polymer, the present singlet-triplet splittings of 0.8 and 0.1 eV for the first and second exciton levels, respectively, are much larger than those for excitons in bulk semiconductors.

Now we focus on a technologically more relevant polymer, PPV [3,8–10], which is much more difficult to treat than trans-polyacetylene due to the larger unit cell of 14 atoms. Figure 1b gives the calculated QP band structure of the material. Again, the fundamental band gap (3.3 eV) is at the  $X$  point. The highest valence and the lowest conduction states ( $\pi_1$  and  $\pi_1^*$ ) are given

by  $\pi$  states distributed over all C atoms, forming an uninterrupted  $\pi$  electron system over the entire chain. The second-highest valence and second-lowest conduction bands ( $\pi_2$  and  $\pi_2^*$ ) are also formed from  $\pi$  states, but are mainly localized on the benzene rings [8].

Figure 2b depicts the calculated optical absorption spectrum for PPV, with the electric field of the light polarized along the chain direction. Neglecting the electron-hole interaction (dashed line), the spectrum is mainly given by an asymmetric peak structure due to  $\pi_1 \rightarrow \pi_1^*$  transitions, which diverges at  $E_g = 3.3$  eV. Additional structures due to  $\pi_1 \rightarrow \pi_2^*$ ,  $\pi_2 \rightarrow \pi_1^*$ , and  $\pi_2 \rightarrow \pi_2^*$  transitions occur at 5.5, 5.8, and 8.0 eV, respectively. This spectrum is in distinct disagreement with experiment: the measured absorption spectrum shows transitions at 2.5, 3.7, 4.8, and 6.0 eV [3,9].

When we include the electron-hole interaction, the spectrum is completely changed (see the solid curve in Fig. 2b) and now consists of a number of sharp peaks (see Table I). The lowest transition is to a bound exciton at 2.4 eV (0.9 eV below  $E_g$ ), in excellent agreement with the measured value of 2.5 eV [9]. This exciton consists of coherently coupled transitions between the bands  $\pi_1$  and  $\pi_1^*$ . In Fig. 3b we show the electron-hole wave function of this exciton in real space. The wave function is similar to the optically active exciton in polyacetylene (cf. Fig. 3a), confirming the similarity in the excitation process in the two materials. Again, the exciton is very extended in real space. We also find another bound exciton at 2.8 eV with a vanishing transition matrix element, thus not observable in the optical spectrum. Corresponding to these spin-singlet excitons, two spin-triplet excitons occur at 1.5 and 2.7 eV excitation energy.

Besides the bound excitons below the gap, we find absorption at 4.0 and at 4.9 eV, compared with the experimental results of 3.7 and 4.8 eV, respectively. These excitations are mainly given by coupled  $\pi_1 \rightarrow \pi_2^*$  and  $\pi_2 \rightarrow \pi_1^*$  transitions. The nature of these excitations is, however, distinctly different from the bound exciton below  $E_g$ . Being above the gap, the excitations interact with the free  $\pi_1 \rightarrow \pi_1^*$  electron-hole continuum. Therefore they have to be understood as resonances rather than sharp, long-lived eigenstates. The resonant character of these excitations is directly visible in their electron-hole wave function (see Fig. 3b for the excitation at 4.0 eV).

TABLE I. Calculated optical excitation energies in PPV (in eV), compared with measured absorption energies [9] and with calculated transition energies by Mukamel *et al.* [3].

This work	Expt. [9]	Ref. [3]
2.4	2.5	2.8
4.0	3.7	3.3
4.9	4.8	4.5
5.8, 6.5–6.9	6.0	5.6, 7.0

Similar to the exciton at 2.4 eV, the distribution of the electron is strongly enhanced near the hole (which corresponds to the strong optical transition matrix element of the state). Far from the hole, however, the electron distribution does not decay, but remains at a finite value. The slight long-range oscillations at large distances (where the distribution should be constant) arise from the boundary conditions in our numerical approach.

At higher energies, we observe a small absorption peak at 5.8 eV and a broad structure between 6.5 and 6.9 eV. In experiment, absorption is found at 6.0 eV. Our calculated absorption peak at 5.8 eV is too small in amplitude to be assigned to that measured transition. Instead, the excitations at 6.7 eV in our spectrum may correspond to the experimental data. The absorption spectrum of PPV has also been calculated by Mukamel *et al.*, using a model Hamiltonian [3]. Their results are included in Table I. Our findings and assignments are in general agreement with those results.

We have also evaluated the absorption spectrum for polarization of the electric field in the polymer plane, but perpendicular to the chain. In this case, no absorption takes place below 5 eV, and the absorption strength above 5 eV is more than 1 order of magnitude smaller than that in Fig. 2b. Finally, for the electric field perpendicular to the polymer plane, the absorption is one more order of magnitude smaller, and is zero below 6 eV.

For both polymers studied here, the influence of the electron-hole interaction is enormous. It completely rearranges the optical spectrum and lowers the absorption threshold by 0.4 and 0.9 eV, respectively [22]. Moreover, the absorption is concentrated in a small number of frequencies associated with the bound and resonant exciton states. These effects are much more pronounced than in bulk semiconductors, where the interaction gives rise to effects on an energy scale of about 0.01 eV. The reason for this strong increase of the interaction is the lower-dimensional character of the polymers, leading to spatial confinement of the electron and hole wave functions in two dimensions and enhanced overlap between them. This is consistent with the observation that in small semiconductor clusters of subnanometer dimensions, the excitonic binding energy is again increased by another order of magnitude and can be as large as 5 eV [19].

In summary, we have calculated the optical absorption spectrum of two conjugated polymers from first principles, fully including the effects of electronic interaction and correlation. The electron-hole interaction gives rise to very large exciton binding energies and plays a crucial role in the optical spectrum. Both for trans-polyacetylene and for poly-phenylene-vinylene, we obtain optical spectra in very good agreement with available experimental data. The calculated real-space wave functions for the electron-hole amplitudes yield detailed pictures of the nature and character of the exciton states, and suggest that the absorption edge of the conjugated polymers could be

sensitive to conjugation lengths below about 50 Å, which is the size of the intrinsic excitons.

We thank G. Martinez for valuable discussions. This work was supported by the Deutsche Forschungsgemeinschaft (Bonn, Germany) under Grant No. Ro-1318/1-1, by National Science Foundation Grant No. DMR-9520554, and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Computational resources have been provided by the National Energy Research Scientific Computing Center (NERSC).

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- [21] We observe only two bound excitons. Thus the situation is distinctly different from a three-dimensional semiconductor where a Rydberg series of excitons occurs.
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