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Bound excitons and optical properties of bulk *trans*-polyacetylene

Murilo L. Tiago,[1,*] Michael Rohlfing,[2] and Steven G. Louie[1]
[1]*Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA*
and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
[2]*School of Engineering and Science, International University Bremen, P.O. Box 750561, 28725 Bremen, Germany*

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Using the GW approximation and solving the Bethe-Salpeter equation, we performed a first-principles study of the electronic configuration and linear optical response of crystalline polyacetylene $(-C_2H_2-)$, one of the simplest conjugated polymers. The optical spectrum is dominated by a low-energy bound exciton, denoted 1^1B_u. A "dark" interchain bound exciton is found to be almost degenerate with state 1^1B_u. Interchain interactions are found to be responsible for a reduction of both the electronic energy gap and the binding energy of bound excitons, compared to previous single-chain calculation. The optical absorption spectrum is compared to measurements performed on thin films of oriented polyacetylene.

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Since their discovery, conjugated polymers have been the subject of intense investigation due to their promising applications in light-emitting diodes and other optoelectronic devices.[1] On the other hand, the nature of elementary excitations in such materials is a complex and often controversial issue. In particular, there are theoretical predictions for the binding energy of excitons ranging from an upper bound of 1.0 eV to less than 0.1 eV.[2–9] On the experimental side, the debate is equally unsettled.[2,10]

Different empirical or semi-empirical theories have been proposed in order to describe excitation energies and the dynamics of the lowest excitations of conjugated polymers.[1–4] In addition, in spite of their complexity, *ab initio* methods, which are more reliable and general than empirical or semi-empirical models, have been successfully applied to a variety of different systems.[11–14] Some of the ground state properties of polyacetylene have been predicted successfully by first-principles calculations.[5,15,16] Both descriptions, either as a single isolated polymeric chain or in a crystalline environment, have been explored. Optical properties have been addressed both by fully *ab initio* methods[5] and by *ab initio* methods with model electronic screening[6–8] or self-energy corrections.[9] Our purpose is to investigate more deeply the role of interchain interactions in the electronic properties, linear optical response, and properties of excitons without any assumption on the electronic properties of the system. To this end, we employ the GW method[11] to calculate the quasiparticle band structure, with electronic screening obtained from the random-phase approximation (RPA). Having the quasiparticle band structure, we solve the Bethe-Salpeter equation (BSE)[12–14] for the two-particle Green's function and obtain a detailed description of the linear optical response of the system, including exciton effects. Interchain interactions are included by considering a clean periodic crystal.

The ground state properties of the system are described within density functional theory in the generalized gradient approximation (DFT-GGA).[17] A basis of plane waves is used to expand the electronic states. Photoexcitations are taken to be in the form of correlated electron-hole pairs, as

$$|S\rangle = \sum_{cv\mathbf{k}} A^S_{cv\mathbf{k}} |c\mathbf{k};v\mathbf{k}\rangle, \tag{1}$$

where $|c\mathbf{k};v\mathbf{k}\rangle$ represents a configuration in which a quasielectron is promoted from valence band v to conduction band c. The coefficients $A^S_{cv\mathbf{k}}$ satisfy the BSE

$$(E_{c\mathbf{k}} - E_{v\mathbf{k}})A^S_{cv\mathbf{k}} + \sum_{cv\mathbf{k},c'v'\mathbf{k}'} \mathcal{K}^{c'v'\mathbf{k}'}_{cv\mathbf{k}} A^S_{c'v'\mathbf{k}'} = \Omega^S A^S_{cv\mathbf{k}}, \tag{2}$$

where $\mathcal{K}^{c'v'\mathbf{k}'}_{cv\mathbf{k}}$ describes the interaction between the excited electron and hole and Ω^S is the energy of state $|S\rangle$.[13,14] If this is a bound state, its binding energy will be given by the difference between Ω^S and the electronic quasiparticle energy gap.[25] The quasiparticle energies of the electronic states, $E_{c\mathbf{k}}$ or $E_{v\mathbf{k}}$, are taken from the GW calculation. The linear optical response is obtained by solving Eq. (2). This is the essence of the GW/BSE method.[5,11–14]

X-ray measurements on polyacetylene have indicated a monoclinic lattice with two monomers per unit cell. There are two possible arrangements of chains within the unit cell: the double bonds in neighboring chains can be either in phase ($P2_1/a$ stacking), or out of phase ($P2_1/n$ stacking). The actual geometry is not well understood, with different measurements supporting both arrangements.[18,19] Considering the experimental technique and a better analysis of data, it seems that evidence for the out-of-phase arrangement, $P2_1/n$ is stronger. Vogl and Campbell[15] have shown that the $P2_1/a$ stacking is theoretically more stable than the $P2_1/n$, having slightly lower total energy. Taking into account the elaborate method of preparation, that requires stretching and heating at temperatures well above room temperature, it seems reasonable to expect that *trans*-polyacetylene crystallizes in the $P2_1/n$ configuration, as indicated by the latest experiment. We followed the structural conformation determined by Zhu *et al.*[19] One additional assumption in our work is that the polymer chains are taken to be rigid in optical absorption.

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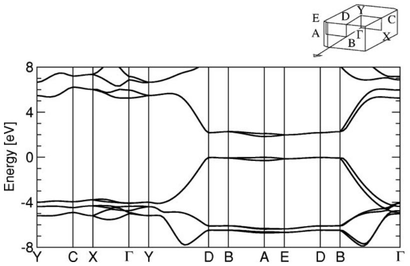

FIG. 1. Band structure of polyacetylene calculated within DFT/GGA, with GW corrections. The four lowest valence bands are not shown. The minimum gap is at the *A* point. The first Brillouin zone is shown in the upper right corner.

The quasiparticle band structure is shown in Fig. 1. The special arrangement of the two monomers inside a unit cell is responsible for the series of degeneracies and band splittings shown. Moreover, we found a direct electronic gap of 1.8 eV at the *A* point. As expected, the DFT gap is substantially smaller, with a value of only 0.47 eV. The small overlap of atomic orbitals positioned at different chains is reflected in somewhat "flat" bands along the paths *DBAED* and *YCX*Γ*Y*, both perpendicular to the chain direction.

It is worth mentioning that we kept control of all precision parameters involved in the calculation. In addition, we kept control of the effect of anisotropy in the calculation of the static dielectric matrix for the construction of the screened Coulomb interaction and of the self-energy operator in the GW calculation. Since the crystalline arrangement is highly anisotropic, the long-wavelength, static limit of the dielectric function, $\epsilon(\omega=0, q\rightarrow 0)$, is nonanalytic, changing by up to one order of magnitude between polarization along the chain direction and perpendicular to it (see Ref. 20 and discussion below). We estimate a precision of 0.1 eV in the calculation of the minimum electronic gap.

Linear optical response is obtained by solving the Bethe-Salpeter equation.[13,14] The BSE approach goes beyond the random-phase approximation (RPA) in that electron-hole correlation effects are included in the dielectric function and in the excitation energy of optical transitions. We follow closely the procedure outlined in Ref. 14. Since the bands closer to the electronic energy gap are the most important ones for optical response, we restrict our analysis to these ones. The Brillouin zone was sampled in a grid containing approximately 23 000 *k*-points, distributed so that we could get a well converged spectrum in the optical range, up to 5 eV, with resolution 0.02 eV.

The complex dielectric function is shown in Fig. 2, with polarization direction along the orientation of the chains. Uncorrelated interband transitions give rise to an onset of absorption at the electronic energy gap, as shown by the dashed curve in Fig. 2. By including electron-hole correlations, the absorption spectrum changes significantly and it becomes dominated by a high, narrow peak located at 1.65 eV, at the energy of the lowest energy singlet exciton. In the range 1.7–1.8 eV, we see contributions from higher energy bound states, resulting in an asymmetric peak, with a smooth high-energy tail.

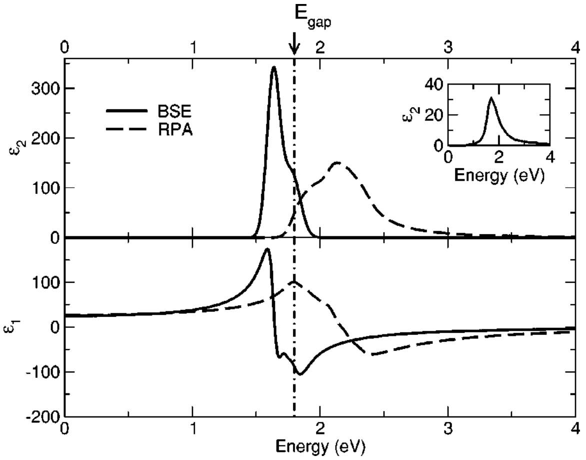

FIG. 2. Real and imaginary parts of the dielectric function, $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$, calculated within BSE (solid line) and RPA (dashed line). The polarization vector is chosen along the chain direction. The GW electronic energy gap is indicated. Curves are broadened by 0.05 eV. The inset shows the measured imaginary part of the dielectric function (Ref. 20).

The calculated spectrum is in agreement with a measurement performed in thin films of highly oriented polyacetylene.[20] It is not clear whether the observed peak asymmetry is due solely to bound excitons or if chain relaxation effects are also present. Such effects play an important role in conjugated polymers and they are responsible for a "broadening" of the absorption peak. In addition, the presence of defects and misalignment of chains in the experimental sample reduce the observed electric polarizability along the chain direction, while increasing the polarizability along perpendicular directions. This should account for the discrepancy in peak height.

The strong anisotropy in electronic screening is present in the calculated (static) dielectric tensor. The components with polarization direction along the chain direction ($\epsilon_\parallel$) and perpendicular to it ($\epsilon_\perp$) are 24 and 2.2, respectively, which should be compared to measured values of $\epsilon_\parallel=10.5$, $\epsilon_\perp=3.0$.[20] As expected, the measured parallel component is much lower than the calculated quantity, whereas the perpendicular component is underestimated in our calculations. This is a result of imperfect alignment of chains. Excitonic effects in the dielectric tensor are found to be around 10%.

In the solution of the BSE, we found a pair of deeply bound spin singlet excitons, with binding energies 0.16 and 0.15 eV, which will be referred to as S_d and S_b, respectively. Since this energy difference is smaller than the level of accuracy attainable, we are unable to resolve the quasidegeneracy of this pair. Despite having almost the same binding energy, these states have quite different properties: state S_b is optically active ("bright" exciton) and it is responsible for most of the calculated optical absorption of the crystal, whereas state S_d has very low optical activity ("dark" exciton). State S_b is well known in the literature, where it is referred to by the group theory nomenclature 1^1B_u in previous studies.[6,7,21] State S_d may be related to the many-body optically inactive state 2^1A_g,[7] but this association is not clear because there is indication that the state 2^1A_g is a superposi-

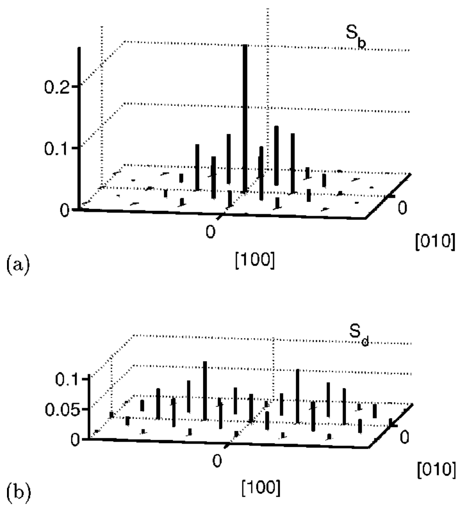

FIG. 3. Electron-hole probability distribution integrated along each chain, for states S_b (a) and S_d (b). The horizontal plane shows schematically the position of the chains on a plane perpendicular to chain axis. The amplitude shows the probability of finding an electron on a chain given that the hole is located on a chain that is at the center of the plane at site (0,0).

tion of singly and doubly excited states.[3,21,22] Doubly excited states are beyond the scope of the GW/BSE method.

Figure 3 shows the electron-hole distribution function (integrated along chains) on the different chains for states S_b and S_d. For a hole fixed on a particular chain, this function indicates the probability of finding the electron in the vicinity of a nearby chain. A striking feature of state S_d is that its electron-hole distribution function is suppressed when electron and hole are on the same chain, and it is maximized when these particles are on separate chains. The interchain character of this state reduces drastically the repulsive exchange electron-hole interaction leading to an increase in binding energy. This explains why it has binding energy comparable to S_b despite having a larger electron-hole correlation length. The state S_b, on the other hand, has a maximum in the electron-hole distribution function when both particles are on the same chain (probability 23%), as shown in Fig. 3.

Using the same theoretical machinery, we have studied the spin triplet excitations, which are inaccessible to linear optics experiments. The two lowest spin triplet states are bound, on-chain excitons with binding energy of 0.44 and 0.37 eV, respectively, and they come from the split pairs of conduction and valence bands closer to the energy gap. The formation of a pair of triplet states follow the same mechanism responsible for the Davydov splitting in molecular solids.[23] In a molecular solid with two sites per cell, two Frenkel excitons are formed with energy splitting dictated by the strength of intersite interactions. In solid polyacetylene, the same picture applies, but the "sites" are now one-dimensional, linear chains.[26] The third state is a bound exciton with binding energy 0.16 eV, and it has strong interchain character. This state, as well as singlets S_b and S_d, are composed almost exclusively of states from the topmost valence band and bottom most conduction band alone. Other energy bands contribute less than 2%.

TABLE I. Binding energy of the lowest energy bound states of crystalline and single-chain polyacetylene. The calculated optical gap in crystalline polyacetylene is 1.65 eV.

		Crystal	Single chain	Single chain, Ref. 5
Singlet	S_b	0.15	0.50	0.4
	S_d	0.16	0.38	0.3
Triplet	T_1	0.44	0.99	1.2
	T_2	0.37	0.43	0.4
	T_3	0.16	$\cdots$	$\cdots$

In order to investigate more deeply the interchain interaction effects, we have used our same computer code to compute the properties of an isolated polyacetylene chain using a supercell geometry with truncated Coulomb interaction.[24] These results are also presented in Table I and compared to a similar calculation from Ref. 5. Binding energies of the first two spin singlet and the second spin triplet states from the two calculations differ by less than 0.1 eV, except for the first spin triplet exciton, where we found a discrepancy of 0.2 eV between the present approach and Ref. 5. The underlying quasiparticle band structure for the isolated chain system is also consistent with Ref. 5.

Comparing our crystalline system results to those on a single-chain system,[5] we observe a reduction in the binding energy of both singlet and triplet states. This phenomenon was also pointed out in previous work[6,7,9] and it is due to strong dispersion of the q-dependent dielectric function at directions perpendicular to chain, and ultimately to interchain screening. The optical gap, defined as the excitation energy of the lowest energy optically active exciton, remains almost unchanged, decreasing from 1.7 to 1.65 eV as one goes from a single chain to a crystal. We attribute discrepancies in the actual *value* of the binding energies among the present work and Refs. 6,7 and 9 to different methodologies in dealing with electronic screening: first-principles quasiparticle energies and RPA screening in this work as opposed to *ad hoc* models for interchain screening in Refs. 6 and 7 or model self-energy corrections in Ref. 9. We stress that electronic screening, self-energy corrections, and the optical spectrum are calculated here from first principles, without any input parameter besides the crystalline structure. Finally, the fact that Table I presents results obtained using different basis sets (Gaussian functions in Ref. 5, and plane wave functions in the present work) is gratifying because we were able to reproduce with good accuracy the early results on an isolated polymer chain using a very different basis set and computer code.

In summary, we have investigated the electronic and optical properties of *trans*-polyacetylene in crystalline environment employing fully *ab initio* methods. We observe a significant reduction in both the energy gap and exciton binding energy when compared to single-chain calculations. This is the result of interchain interactions, in qualitative agreement with previous studies on this system. Quantitative disagreement exists in the exciton binding energy among previous work,[6,7,9] and this calculation is attributed mainly to different ways of including interchain effects in the electronic screening: first-principles RPA here, and *ad hoc* models in previous work. The linear optical response is almost completely dominated by the state 1^1B_u (S_b in our nomenclature). The theory predicts the existence of a quasidegeneracy between state S_b and a dark, interchain spin singlet state (S_d), although direct experimental evidence of such a state is still lacking. The calculated anisotropy of the optical response is stronger than what was observed in thin films of oriented polyacetylene.[20] We believe that the presence of defects and misalignment of chains in the real material play an important role in this effect.

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*Present address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455.

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[25] In principle, the binding energy could be defined as the difference between an excitation energy calculated without electron-hole interactions and the corresponding one obtained with those interactions included, but the kernel $\mathcal{K}_{cv\mathbf{k}}^{c'v'\mathbf{k}'}$ destroys the one-to-one correspondence between those solutions. As a result, the only meaningful definition of binding energy involves the lowest RPA excitation energy between bands c and v included in Eq. (2) which, for the present system, is the electronic gap.

[26] We did not observe a similar pair of singlet state because the splitting of energy bands, 0.2 eV, is comparable to the binding energy of that state.