

## Suppression of Electron-Hole Correlations in 3D Polymer Materials

Peter Puschnig\* and Claudia Ambrosch-Draxl

*Institute for Theoretical Physics, Karl-Franzens-Universität Graz, Universitätsplatz 5, A-8010 Graz, Austria*

(Received 14 March 2002; published 16 July 2002)

We present an *ab initio* study of the optical absorption spectra of isolated as well as crystalline trans-polyacetylene. We include excitonic effects by solving the Bethe-Salpeter equation for the electron-hole two-particle correlation function. We observe that the strength of the electron-hole interactions drastically reduces when going from an isolated polymer chain to a crystalline arrangement. This is not only a result of enhanced screening in the 3D material, but also of the increased spatial extent of the exciton perpendicular to the polymer chains. We point out that these findings apply to crystalline phases of conjugated polymers and molecular crystals in general.

DOI: 10.1103/PhysRevLett.89.056405

PACS numbers: 71.15.Qe, 71.15.Ap, 71.20.Rv, 71.35.-y

It is now almost 25 years since polyacetylene was shown to reach electrical conductivities comparable to conventional metals [1]. These findings marked the birth of a whole new field of research focusing on the electronic and optical properties of conjugated polymers. Since then, a number of different technological applications, such as light emitting diodes [2–6], photovoltaic cells [7,8], or field effect transistors [9–11] based on organic polymers or molecular crystals have been proposed. Progress in applied scientific research depends on the existence of accurate theoretical models. In particular, highly reliable *ab initio* methods that do not depend on adjustable parameters are indispensable for designing novel materials as well as for a detailed understanding of their properties. While density functional theory (DFT) provides a profound framework for the description of *ground state* properties, it does not account for *excited state* quantities. However, these are the properties that are probed in spectroscopic methods and that are utilized for technological applications. The focus of the present work is therefore on the optical properties of conjugated polymers and, in particular, on the effect of electron-hole (*e-h*) correlations going beyond DFT.

The solution of the Bethe-Salpeter equation (BSE) for the *e-h* two-particle Green's function represents a systematic first-principles approach for the calculation of optical absorption spectra including excitonic effects [12–14]. In the past few years solutions of the BSE within an *ab initio* framework have appeared in the literature and have demonstrated that *e-h* interactions are indeed important in order to correctly describe quantitative (oscillator strengths) as well as qualitative (bound excitons) features of optical spectra of semiconductors and insulators [15–21]. While most authors so far focused on inorganic materials, the above scheme has also been applied to conjugated polymers, namely, to *isolated* chains of trans-polyacetylene (PA) and poly(phenylene vinylene) (PPV) [15], as well as to poly-thiophene (PT) [16]. For all three polymers the authors emphasize the importance of *e-h* correlations and calculate exciton binding energies in ex-

cess of 0.5 eV for the isolated polymer chains. van der Horst and co-workers [16,22] have already pointed out that enhanced screening in a three-dimensional (3D) arrangement of PT chains considerably reduces the size of the exciton binding energy. However, they used a model for the screening of the crystalline polymer and did not take into account crystalline effects in the one-particle band structure, such as band splittings due to interchain coupling. In a more recent investigation the exciton binding energies of a series of polymers including PA have been calculated using the bulk dielectric constant for the screening [23]. However, also in this work the electron and the hole forming an exciton are assumed to be located at the same chain. In this Letter we present—for the first time—the solution of the BSE for a crystalline arrangement of polymer chains and thereby discuss the effects of *interchain interactions* on the exciton binding. This problem appears particularly interesting since technological applications are restricted to the solid state in which interactions between neighboring polymer chains or molecules are inherently present. For instance, Bussi *et al.* have pointed out very recently the implications of interchain interactions in polythiophene for the luminescence efficiency [24].

Because of its simple structure, PA serves as an ideal candidate for studying the role of *e-h* correlations since *ab initio* solutions of the BSE are computationally very demanding. Before we show our main results for the crystalline PA material we discuss the optical absorption spectrum of an *isolated* PA chain, which we also compare to previous findings of Rohlffing and Louie [15]. All computations presented in this Letter are based on the linearized augmented plane wave (LAPW) basis set, to which we have adopted the BSE formalism, and we are utilizing the WIEN97 code [25]. The calculation of the optical absorption spectrum including *e-h* correlations consists of three steps: (i) a standard DFT calculation using the LAPW method, (ii) expansion of the dielectric matrix in a plane wave basis for the dielectric matrix using the LAPW wave functions, and (iii) computation of the exchange and direct *e-h* interaction and diagonalization of the BSE. We use a

rigid shift of the conduction bands in order to obtain the quasiparticle from the Kohn-Sham energies. Details about our approach will be given in a forthcoming paper [26].

We have taken experimental values for the structural parameters of a PA chain as listed in Ref. [27]. We particularly want to emphasize that we have used a dimerization of  $u_C = 0.052 \text{ \AA}$  since structural optimizations using a local density approximation (LDA) or generalized gradient approximation (GGA) potential underestimate this dimerization considerably. We have found that a geometry optimization using the Perdew-Burke-Ernzerhof-GGA exchange correlation potential [28] leads to a dimerization of less than  $u_C = 0.01 \text{ \AA}$ . The LDA-DFT calculations give a direct band gap of 0.85 eV at the Z point in accordance with previous studies [27]. Rohlfiing and Louie have found the quasiparticle band gap of an isolated PA chain in the GW approximation to be 2.1 eV [15]. We have therefore shifted the conduction bands rigidly upward by a value of  $\Delta_c = 1.25 \text{ eV}$ . The inclusion of  $e$ - $h$  correlations produces a single *bound* exciton state at 1.55 eV inside the quasiparticle gap. This state exhibits a strong oscillator strength (OS) for optical transitions polarized parallel to the polymer chain. Rohlfiing and Louie have calculated this exciton to lie at 1.7 eV [15]. Thus, our exciton binding energy of 0.55 is 30% larger than the previously reported value. The next higher exciton state  $S_2$ , on the other hand, has virtually no OS in accordance with previous results [15]. Summing up the results for the *isolated* polymer chain, we confirm the strong effect of the  $e$ - $h$  correlations leading to a bound exciton state in 1D polyacetylene with a large binding energy of roughly half an eV in accordance with earlier calculations [15].

Polyacetylene, as many other conjugated polymers or oligomers, crystallizes in the so-called herring-bone arrangement with two polymer chains per unit cell. There are two different crystal structures belonging to the space groups  $P2_1/a$  and  $P2_1/n$ , respectively, differing by a modified arrangement of the second polymer chain with respect to the first one. In the following, we abbreviate the  $P2_1/a$  and  $P2_1/n$  structures with  $a$ -PA and  $n$ -PA, respectively. It has been found that the total energy for  $a$ -PA is slightly smaller than for  $n$ -PA [27]. Thus, the former is expected to be more stable. In Fig. 1, we depict the LDA-DFT band structures of  $a$ -PA (left panel) and  $n$ -PA (right panel). These band structures have already been discussed by Vogl and Campbell [27,29]. We have used the same geometry of the polymer chain as for the one-dimensional case. The lattice constants and the other structural parameters have been taken from Table II of Ref. [27].

There are several interesting features that can be recognized from Fig. 1. First, we notice that the band dispersions along the polymer chain—compare the  $\Gamma Z$  and  $YD$  directions—are much higher than perpendicular to it, where the valence and conduction bands close to the Fermi level (dashed line) are comprised by states having  $\pi$  symmetry. Second, the fact that there are two polymer chains per unit

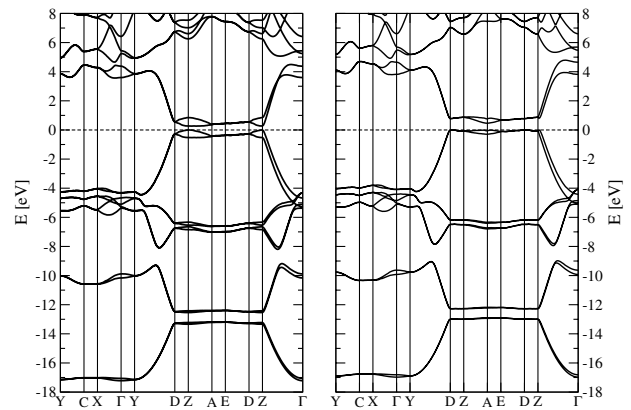


FIG. 1. Electronic band structure of crystalline polyacetylene along high symmetry directions in the Brillouin zone. Panels (left) and (right) correspond to the  $P2_1/a$  and  $P2_1/n$  crystal structures, respectively.

cell doubles the number of bands when compared to the results for an isolated chain. The splitting of these bands is a measure for the interchain interaction. It is of course quite weak; therefore, the splittings are of the order of only 0.2 eV. The features mentioned above are common to both  $a$ -PA and  $n$ -PA. There are, however, also subtle differences which are in fact the reason why we want to compare these two structures. The distinct arrangement of the two chains in  $a$ -PA and  $n$ -PA leads to different interchain interactions. For instance, these result in the band splitting of the top valence band at the Z A point of 0.50 (0.0) and 0.01 (0.25) eV for  $a$ -PA and  $n$ -PA, respectively. As a consequence,  $a$ -PA is a direct band-gap semiconductor with an LDA-DFT gap of 0.27 eV at the Z point, while  $n$ -PA has an indirect band gap with a valence band maximum at D and a conduction band minimum at A, and an LDA-DFT gap of 0.49 eV.

We can now turn to the discussion of excitonic effects in the two crystalline polyacetylene structures  $a$ -PA and  $n$ -PA, respectively. The spectra are displayed in Fig. 2, where the left and right panels, respectively, correspond to  $a$ -PA and  $n$ -PA. For both structures we compare the RPA result (dashed line) with the spin singlet (solid line) solutions. We have plotted the energies with respect to the quasiparticle band gap denoted by  $E_0$  which is indicated by the vertical dotted line. We focus on absorption spectra calculated for light polarized parallel to the polymer chain since the perpendicular polarizations contribute only at higher energies. The results for both crystalline structures  $a$ -PA and  $n$ -PA are quite different to those obtained for the isolated PA chain. For the isolated chain we found a strong bound exciton peak with an exciton binding energy of 0.55 eV. In the crystalline environment, however, the electron-hole interaction is greatly reduced due to two effects. First, the screening is more effective for the crystalline material as compared to the isolated chain. This effect has already been observed by van der Horst and

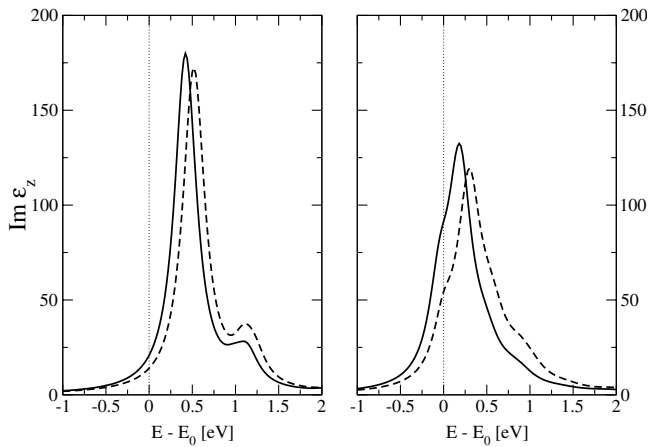


FIG. 2. The imaginary part of the DF for *a*-PA (left panel) and *n*-PA (right panel) for light polarized parallel to the polymer chain. The dashed lines are the RPA spectra; the solid lines correspond to the spin singlet excitations. The energy scale has been shifted with respect to the quasiparticle gap  $E_0$  indicated by the vertical dotted line.

co-workers [16,22] who have found the interchain screening to drastically reduce the exciton binding energies.

The second effect, which is equally important, concerns the spatial extent of the exciton. While the exciton is obviously confined to one polymer chain for the isolated polymer, it appears to be extended over the neighboring chains in the crystalline case. We have illustrated this effect in Fig. 3, where we have plotted the exciton wave function for the lowest optically active state of *a*-PA in a plane perpendicular to the polymer axis. We notice that if we fix the position of the hole on one chain, there is a finite probability for the electron to be located on neighboring

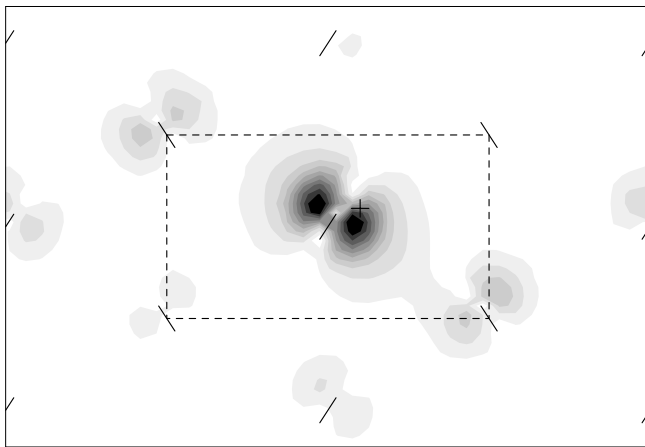


FIG. 3. The electron distribution with respect to the hole (cross) of the  $S_4$  state of *a*-PA in a plane perpendicular to the polymer chains and through a C atom. The unit cell axis  $a$  (vertical) and  $b$  (horizontal) are shown by dashed lines, and the projections of the C polymer backbone are indicated by the short lines.

chains. Consequently, the average distance between the electron and the hole is increased. Thus, the interaction between the electron and the hole is reduced, and the exciton binding energy is much smaller than for the isolated polymer chain. Note that this effect can be accounted for only by taking the band structure and wave functions of the three-dimensional material as the starting point for the computation of the direct and exchange Coulomb matrix elements.

Quantitatively, the excitonic spectra are also strongly influenced by the details of the interchain interaction, which can be seen from a comparison of the results for *a*-PA and *n*-PA. For both systems, the lowest singlet exciton  $S_1$  has a binding energy of 0.05 eV. While it has almost no OS for optical transitions in *a*-PA, it is optically active for the *n*-PA phase. The lowest triplet state  $T_1$  lies at an energy of 0.10 and 0.20 eV in *a*-PA and *n*-PA, respectively. We notice that the singlet-triplet splitting of lowest lying states  $S_1 - T_1$  is only 0.05 eV for the *a*-PA phase, while it is considerably larger in *n*-PA (0.15 eV).

In summary, we have seen that interchain interactions crucially alter the excitonic states in trans-polyacetylene. We find strongly bound exciton states for the isolated chain with exciton binding energies in the order of 0.5 eV. On the other hand, a crystalline arrangement of the polymer chains as in the two considered phases *a*-PA and *n*-PA, respectively, drastically reduces the strength of the electron-hole interaction. This is because (i) the screening of the electron-hole interaction is more efficient in the crystalline case than it is for the isolated chain and (ii) the electron and the hole are allowed to be spread over several neighboring polymer chains in the crystalline phase. Both effects increase the average distance between the electron and the hole and thereby reduce the exciton binding energy. We calculate this binding energy to be only 0.05 eV for both *a*-PA and *n*-PA. We conclude that the qualitative arguments given above do not only apply for trans-polyacetylene, but quite generally for the whole class of conducting polymers and oligomers. Moreover, the details of the interchain (or intermolecular) interaction determine the actual values of the exciton binding energies as we have also seen from the comparison of the two phases *a*-PA and *n*-PA. Consequently, we propose that it is not sufficient to treat the interchain interactions in the screening only as has been suggested by van der Horst and co-workers [16,22,23]. One should also take into account the correct band structure (band splittings) and wave functions allowing the exciton to be spread over neighboring chains. For the future, it will be highly desirable to obtain the quasiparticle spectrum in an *ab initio* manner, for instance, by performing a GW calculation, instead of simply shifting the conduction bands rigidly upward. Thereby it will be possible to obtain the absolute energetic positions of the excited states.

Peter Puschnig acknowledges the financial support from the *Österreichische Akademie der Wissenschaften* in the

form of their *Doktorandenstipendium*. The work was also partially supported from Project No. P14237 of the Austrian Science Fund.

---

\*Electronic address: peter.puschnig@uni-graz.at

- [1] C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, and A.G. MacDiarmid, *Phys. Rev. Lett.* **39**, 1098 (1977).
- [2] C.W. Tang and S.A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- [3] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, and A.B. Holmes, *Nature (London)* **347**, 539 (1990).
- [4] D. Braun and A.J. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991).
- [5] G. Grem, G. Leditzky, B. Ullrich, and G. Leising, *Adv. Mater.* **4**, 36 (1992).
- [6] R.H. Friend *et al.*, *Nature (London)* **397**, 121 (1999).
- [7] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, and F. Wudl, *Science* **258**, 1474 (1992).
- [8] J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, and A.B. Holmes, *Nature (London)* **376**, 498 (1995).
- [9] F. Garnier, G. Horowitz, X. Peng, and D. Fichou, *Adv. Mater.* **2**, 592 (1990).
- [10] F. Garnier, R. Hajlaoui, A. Yassar, and P. Srivastava, *Science* **265**, 1684 (1994).
- [11] A. Dodabalapur, L. Torsi, and H.E. Katz, *Science* **268**, 270 (1995).
- [12] L.J. Sham and T.M. Rice, *Phys. Rev.* **144**, 708 (1966).
- [13] W. Hanke and L.J. Sham, *Phys. Rev. Lett.* **43**, 387 (1979).
- [14] G. Strinati, *Phys. Rev. B* **29**, 5718 (1984).
- [15] M. Rohlfig and S.G. Louie, *Phys. Rev. Lett.* **82**, 1959 (1999).
- [16] J.-W. van der Horst, P.A. Bobbert, M.A.J. Michels, G. Brocks, and P.J. Kelly, *Phys. Rev. Lett.* **83**, 4413 (1999).
- [17] S. Albrecht, G. Onida, and L. Reining, *Phys. Rev. B* **55**, 10 278 (1997).
- [18] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, *Phys. Rev. Lett.* **80**, 4510 (1998).
- [19] L.X. Benedict, E.L. Shirley, and R.B. Bohn, *Phys. Rev. Lett.* **80**, 4514 (1998).
- [20] M. Rohlfig and S.G. Louie, *Phys. Rev. Lett.* **81**, 2312 (1998).
- [21] B. Arnaud and M. Alouani, *Phys. Rev. B* **63**, 085208 (2001).
- [22] J.-W. van der Horst, P.A. Bobbert, P.H.L. de Jong, M.A.J. Michels, G. Brocks, and P.J. Kelly, *Phys. Rev. B* **61**, 15 817 (2000).
- [23] J.-W. van der Horst, P.A. Bobbert, M.A.J. Michels, and H. Bässler, *J. Chem. Phys.* **114**, 6950 (2001).
- [24] G. Bussi, A. Ruini, E. Molinari, M.J. Caldas, P. Puschnig, and C. Ambrosch-Draxl *Appl. Phys. Lett.* **80**, 4118 (2002).
- [25] P. Blaha, K. Schwarz, and J. Luitz, *WIEN97, A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* (Karlheinz Schwarz, Technische Universität Wien, Vienna, 1999), ISBN .
- [26] P. Puschnig and C. Ambrosch-Draxl (to be published).
- [27] P. Vogl and D.K. Campbell, *Phys. Rev. B* **41**, 12 797 (1990).
- [28] J.P. Perdew, K. Burke, and M. Enzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [29] P. Vogl and D.K. Campbell, *Phys. Rev. Lett.* **62**, 2012 (1989).