

Electronic and optical excitations in crystalline conjugated polymers

J.-W. van der Horst, P.A. Bobbert, M.A.J. Michels

*Polymer Physics group, Faculty of Applied Physics and Dutch Polymer Institute, Technische Universiteit Eindhoven,
P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands*

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Abstract

We calculate the electronic and optical excitations of crystalline polythiophene and poly(phenylene vinylene), using the *GW* approximation for the electron self-energy and including excitonic effects by solving the electron-hole Bethe-Salpeter equation. Surprisingly, we find optical gaps and exciton binding energies that are much smaller than experimental values and our earlier calculations on chains embedded in a dielectric medium. We attribute the disagreement to the absence of quantum mechanical coherence in most experimental situations and discuss possible reasons for this absence. An aggregate-forming ladder-type PPP appears to be an interesting exception.

Keywords: Many-body and quasiparticle theories, Greens function method, Polythiophene and derivatives, Poly(phenylene vinylene) and derivatives

1. Introduction

Recently, *ab-initio* Greens function methods were applied to calculate the one-particle (electron or hole) and two-particle (electron-hole pair = exciton) excitations of conjugated polymers [1,2]. The calculated optical gaps of isolated poly(phenylene vinylene) (PPV) [1] and polythiophene (PT) [2] chains were found to agree well with experiment. Large exciton binding energies of 0.9 and 1.85 eV were found for these two polymers, respectively. It was shown by us [2] that screening by neighboring chains drastically reduces the exciton binding energy in PT to 0.76 eV, leaving the optical gap virtually unaffected. A similar drastic reduction of the exciton binding energy by interchain screening effects was predicted earlier by Moore and Yaron [3] in polyacetylene, within the semiempirical Pariser-Parr-Pople theory. Simplified exciton calculations with an empirical dielectric constant $\epsilon=3$ for the embedding medium gave us an exciton binding energy of 0.61 eV for PT and 0.54 eV for PPV [4]. These simplified calculations were also performed for a number of other conjugated polymers and exciton binding energies were systematically found in the range 0.4–0.6 eV [4]. The reason for the reduction of the exciton binding energy, compared to the isolated chain, is that the polarization of neighboring chains leads to an additional, long-range, screening of the Coulomb interaction between the electron and the hole. This screening also reduces the one-particle gap, and apparently by about the same amount. It is

important to note that these calculations are still quasi-one-dimensional, in the sense that the wave-function overlap between adjacent chains, and hence their quantum-mechanical coherence, is neglected.

In a very recent study [5], the one-particle spectrum of crystalline polyacetylene was calculated. Wave-function overlap leads to level splittings of the order of 0.5 eV at several points in the Brillouin zone. The one-particle gap, however, was found to be almost the same as for the isolated chain (2.1 eV). No results were given for the two-particle spectrum of crystalline polyacetylene. Here, we present the results of a study of the one-particle and two-particle excitations of PT and PPV in a crystalline geometry, replacing the effective dielectric environment in our previous calculations by the actual environment in the crystal. Furthermore, the crucial difference between the present calculations and our earlier work on PT [2] is that in the present calculations we allow for wave-function overlap between adjacent chains. An extensive discussion can be found elsewhere [6].

2. Methods

We use three complementary *ab-initio* methods: (a) density-functional theory in the local-density approximation (DFT-LDA) to calculate ground state atomic configurations, (b) the *GW* approximation for the one-particle self-energy, using the DFT-LDA Kohn-Sham

wave-functions and energies as input, to calculate one-particle excitations (quasiparticles), and (c) a solution of the Bethe-Salpeter equation (BSE) for an electron-hole pair, using the Kohn-Sham wave-functions and the *GW* quasiparticle energies as input, to calculate two-particle optical excitations (excitons). It has been established that this chain of methods yields reliable results for a range of materials and molecules [7]. The necessary cut-offs in our computations were determined such that the *GW* quasiparticle gaps were converged to within 0.05 eV and exciton energies to within 0.1 eV (the DFT-LDA results were much more accurate). We restrict our exciton calculations to excitons with zero total momentum. Below, we will only give the results for the singlet excitons. The results for triplet excitons are as easily obtained [6]. The crystal structures of PT and PPV (two chains in an orthorhombic and monoclinic unit cell, respectively) were obtained from literature [8,9], with the atomic configurations optimized by DFT-LDA.

3. Results

In Table 1, we give the main results of our calculations for the crystalline situation. We compare with previous calculations for isolated single chains [1,2], single chains with intrachain and interchain screening [2], simplified exciton calculations for single chains with a dielectric constant $\epsilon=3$ [4], and experiment. We note that for PT the crystalline calculation actually predicts an *indirect* quasiparticle gap of 1.48 eV between Γ and Z. The minimal direct gap of 1.64 eV occurs at Z. The exciton binding energy should be defined with respect to the latter gap. The calculations predict crystalline PPV to be a direct semiconductor with a gap of 2.10 eV at the point B of the corresponding Brillouin zone.

Table 1

Minimal quasiparticle (QP) direct gaps, optical gaps, and exciton binding energies in eV for three different situations, I: isolated single chains, II: single chains with intrachain and interchain screening, II': single chains with interaction between electron and hole equal to (Coulomb interaction)/ ϵ with $\epsilon=3$, and III: the crystalline situation. Some experimental results are also given. References are indicated.

		I	II	II'	III	expt.
PT	QP gap	3.59 [2]	2.49 [2]		1.64	
	opt. gap	1.74 [2]	1.73 [2]		1.49	1.8 [10]
	bind. en.	1.85 [2]	0.76 [2]	0.61 [4]	0.15	0.6 [11]
PPV	QP gap	3.3 [1]			2.10	
	opt. gap	2.4 [1]			1.75	2.4 [12]
	bind. en.	0.9 [1]		0.54 [4]	0.35	0.5 [13]

In crystalline PT, the excitons occur in pairs with very small Davydov splittings ≤ 0.01 eV. The lowest-lying pair is clearly identified as on-chain excitons. It is interesting to note that only about 0.04 eV higher a pair of off-chain (charge-transfer) excitons is found. In crystalline PPV, the hybridization between the excitons is much larger than in PT and a simple characterization of the excitons cannot be given. The lowest-lying exciton appears to have a rather

small optical matrix element compared to the next exciton lying 0.09 eV higher in energy.

4. Conclusion and discussion

It is clear from Table 1 that the results of the calculations for situations II and II', in which screening by neighboring chains is included, but in which quantum mechanical coherence and therefore hybridization between chains is neglected, agree best with experiment. The optical gaps and the exciton binding energies of the crystalline calculation are too small compared to experiment. We carefully checked that this is not caused by technical flaws of our methods and approximations [6]. Hence, the inevitable conclusion from this observation is that hybridization between chains is apparently absent in most experiments on conjugated polymers. We can think of three explanations for this, 1: the presence of side chains in most experimental situations (and absent in our calculations), 2: static disorder, and 3: dynamic, thermal disorder. All three effects will tend to decrease the hybridization between the main chains.

It is an intriguing question whether the effects of hybridization predicted here can be observed in very pure polymer crystals at low temperatures. A clue in this direction may be the recent STM experiments on a ladder-type polyparaphenylene [14], a polymer that, due to its stiffness, is very prone to crystal formation. Regions with different band gaps and exciton binding energies appear to exist in this polymer: disordered regions with a relatively large (0.45–0.85 eV) and aggregate regions with a relatively small (~ 0.1 eV) exciton binding energy. This finding is qualitatively in line with the present work.

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