

Ab initio calculation of the electronic and optical excitations in polythiophene: effects of intra- and interchain screening

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***Ab Initio* Calculation of the Electronic and Optical Excitations in Polythiophene: Effects of Intra- and Interchain Screening**

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We present an *ab initio* calculation of the electronic and optical excitations of an isolated polythiophene chain as well as of bulk polythiophene. We use the *GW* approximation for the electronic self-energy and include excitonic effects by solving the electron-hole Bethe-Salpeter equation. The inclusion of interchain screening in the case of bulk polythiophene drastically reduces both the quasiparticle band gap and the exciton binding energies, but the optical gap is hardly affected. This finding is relevant for conjugated polymers in general.

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The interest in the electronic and optical properties of semiconducting conjugated polymers has increased enormously since the discovery of electroluminescence [1] of these materials. The microscopic modeling of charge carriers and excitations in conjugated polymers is a subject of intensive research at present. In particular, knowledge of the single-particle bands and the electron-hole (exciton) binding energies is important. In conventional semiconductors such as GaAs the optical excitations are well described in terms of very weakly bound electron-hole pairs (Wannier excitons). In crystals made of small organic molecules such as anthracene, the electron-hole correlation energy is large, which essentially confines the exciton to a single molecule (Frenkel exciton). Exactly where conjugated polymers fit in between conventional semiconductors on the one hand and molecular crystals on the other is the subject of a heated debate [2]. Most of the experimental results have been obtained from optical experiments on the condensed (thin film or bulk) material. Most of the theoretical modeling has been at the level of a single molecule or a single polymer chain. In this paper we focus on the differences between an isolated polymer chain and a bulk polymer material and show that these have a large effect on basic electronic parameters such as the band gap and the exciton binding energies. We calculate the electronic structure and the optical excitation of conjugated polymers in an *ab initio* manner, i.e., without “tunable” parameters.

Ab initio calculations of several polymers within the local density approximation of density functional theory (DFT-LDA) yield band gaps that are typically 40% smaller than the experimental optical gaps [3]. However, it is well known that DFT-LDA formally cannot be applied to excited states. Moreover, no excitonic effects are taken into account in these calculations. An *ab initio* many-body *GW* approximation (*GWA*) [4] calculation on polyacetylene (PA) was performed by Ethridge *et al.* [5], but ex-

citonic effects were not taken into account in their work either. Very recently, a calculation by Rohlfling and Louie [6] for *isolated* chains of both PA and poly-phenylenevinylene (PPV), including both single- (quasiparticle) and two-particle (exciton) excitations, yielded optical gaps in good agreement with experiment. However, the calculated lowest-lying singlet exciton binding energy for PPV in that work is much larger than in a recent experiment [7].

In this Letter, we calculate single- and two-particle excitations for an isolated polythiophene (PT) chain *as well as* for bulk PT, where we show that the differences between the two cases have very important consequences. We focus on PT, since it is one of the simplest and most studied polymers. Our main conclusions, however, are relevant for conjugated polymers in general.

Computational methods.—Many successful *ab initio* calculations of the quasiparticle (QP) band structure of conventional anorganic semiconductors have been performed with the *GWA* for the electronic self-energy Σ of the one-particle Green function. Very recently [8,9], important progress has been made in the evaluation of the two-particle Green function, from which the optical properties can be obtained. This is done by solving the Bethe-Salpeter equation [10,11] (BSE), which is equivalent to a two-body Schrödinger equation, for an electron and a hole forming an exciton. We adopt these two methods and neglect the differences in geometry between the excited states and the ground state. DFT-LDA calculations on oligothiophenes show that relaxation energies, calculated by relaxing an excited state from the ground state geometry to its optimized geometry, typically are in the range 0.1–0.2 eV [12]. Such values are upper bounds for the corresponding states of the polymer.

We start our calculations with a pseudopotential plane-wave DFT-LDA calculation [3] of a geometry-relaxed PT chain in a tetragonal supercell (14.8 a.u. in the chain

direction; 15 a.u. in the perpendicular directions, the latter value large enough to consider the chains as isolated in this calculation). We use Hartree atomic units unless specified otherwise. The single-particle excitation energies E_{nk} are evaluated by solving the QP equation

$$\left[-\frac{1}{2} \nabla^2 + V_H(\mathbf{r}) \right] \phi_{nk}(\mathbf{r}) + \int [V_{PP}(\mathbf{r}, \mathbf{r}') + \Sigma(\mathbf{r}, \mathbf{r}', E_{nk})] \phi_{nk}(\mathbf{r}') d^3 r' = E_{nk} \phi_{nk}(\mathbf{r}), \quad (1)$$

where V_{PP} is the pseudopotential of the atomic core, V_H is the Hartree potential due to the valence electrons, and Σ is the self-energy. We make the usual approximation that the QP wave functions ϕ_{nk} can be replaced by the DFT-LDA wave functions. In DFT-LDA, $\Sigma(\mathbf{r}, \mathbf{r}', \omega) = V_{xc}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$, with $V_{xc}(\mathbf{r})$ the exchange-correlation potential, while in the GWA the first term in the many-body expansion of Σ in terms of the Green function G and screened interaction W of the system is used, $\Sigma(\mathbf{r}, \mathbf{r}', t) = iG(\mathbf{r}, \mathbf{r}', t)W(\mathbf{r}, \mathbf{r}', t)$, after Fourier transformation from frequency to time. The screened interaction is evaluated in the random-phase approximation (RPA). We calculate these approximations of Σ and W in the mixed-space imaginary-time formalism [13,14], from the DFT-LDA

wave functions and energies. To study a truly isolated chain, we remove the ‘‘crosstalk’’ between periodic images of the chain by taking as a unit cell the spatial region closer to the atomic positions of a specific chain than to those of any other; the Coulomb interaction $v(\mathbf{r} - \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ is then cut off by setting it zero if \mathbf{r} and \mathbf{r}' belong to different cells.

The two-body electron-hole Schrödinger equation related to the BSE is solved by expanding the exciton wave functions $\Phi(\mathbf{r}_e, \mathbf{r}_h)$ of zero-momentum excitons, which are the optically relevant ones, in products of conduction (c) and valence (v) wave functions, $\Phi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{kcv} A_{kcv} \phi_{ck}(\mathbf{r}_e) \phi_{vk}^*(\mathbf{r}_h)$. The expansion coefficients A_{kcv} and the exciton binding energy E_b should obey [8–11]:

$$[E_{ck} - E_{vk} - E_g + E_b] A_{kcv} + \sum_{k'c'v'} [2V_{kcv, k'c'v'}^x - W_{kcv, k'c'v'}] A_{k'c'v'} = 0, \quad (2)$$

where E_g is the QP band gap, E_{ck} and E_{vk} are the QP energies, and $W_{kcv, k'c'v'}$ and $V_{kcv, k'c'v'}^x$ (only present for singlet excitons) are the matrix elements of the static ($\omega = 0$) screened interaction and the exchange matrix elements of the bare Coulomb interaction, respectively. Formally, dynamical screening effects may be ignored in the BSE only if $E_g \gg E_b$. However, it has been shown that dynamical effects in the electron-hole screening and in the one-particle Green function largely cancel each other [15] and hence the static approximation is expected to be accurate, even when the relation $E_g \gg E_b$ does not strictly hold.

As was shown by several authors [16,17], in a quasi-1D system (such as an isolated polymer chain with only intrachain screening) there is no long-range screening. For realistic bulk polymers, however, both intra- and interchain screening are important, the latter giving rise to the screening at long distances. While it is in principle possible to perform a GWA and exciton calculation for a crystalline structure, the amount of computational work is as yet prohibitively large. Instead, we choose to include the interchain screening in the following way, capturing the essential physics. From the imaginary-frequency dependent RPA polarizability tensor of an isolated chain in the long-wavelength limit we obtain a dielectric constant parallel (x) to the chain direction, $\varepsilon_{||}(i\omega)$, and perpendicular (y, z) to the chain direction, $\varepsilon_{\perp}(i\omega)$, by performing a 2D line-dipole lattice sum in the perpendicular directions, for an experimentally determined PT crystal structure [18,19]. Details of this approach will be given in a future paper [20]. We now take for the interchain screening interaction

$W^{\text{scr}} \equiv W - v$ the following form:

$$W_{\text{inter}}^{\text{scr}}(\mathbf{r}, i\omega) = (1 - e^{-r/r_{\text{inter}}}) \times \{[\varepsilon_{\perp}^2(i\omega)x^2 + \varepsilon_{||}(i\omega)\varepsilon_{\perp}(i\omega) \times (y^2 + z^2)]^{-1/2} - v(\mathbf{r})\}, \quad (3)$$

which is correct for distances much larger than the typical interchain distance r_{inter} , for which we take 10 a.u. (typical for the crystal structure of Refs. [18,19]). The prefactor in this equation takes care of a soft cutoff for distances below r_{inter} , for which the interchain screening should vanish. We remark that the details of this interaction cannot be important since PT samples prepared in many different ways show very similar optical behavior; probably, most samples consist of small crystallites separated by disordered regions. We now construct a total screened interaction

$$W_{\text{total}}(\mathbf{r}, \mathbf{r}', i\omega) = W_{\text{intra}}^{\text{scr}}(\mathbf{r}, \mathbf{r}', i\omega) + W_{\text{inter}}^{\text{scr}}(\mathbf{r} - \mathbf{r}', i\omega) + v(\mathbf{r} - \mathbf{r}'), \quad (4)$$

where $W_{\text{intra}}^{\text{scr}}$ is the screening interaction already calculated for the isolated chain. The interaction Eq. (4) is correct at short and long range and is expected to be sufficiently good at intermediate range. We remark that the overlap between wave functions on, and therefore the *electronic* coupling between, neighboring chains is very small; hence, we can again use the isolated chain wave functions to calculate the Green function and self-energy. In our exciton calculations, we take the electron and hole on the same chain (so-called intrachain excitons). Hence, the only, but essential, difference between our calculations

for the isolated PT chain and bulk PT is in the screened interaction used.

We determine the various cutoff parameters in our calculations (number of k points, bands, grid mesh in space and imaginary time) such that the QP band gap is converged to within 0.05 eV. In the construction of the exciton wave functions we use only the π and π^* wave functions, resulting in an accuracy of the lowest-lying exciton binding energies of about 0.1 eV. Below we give all calculated energies in eV with a precision of two decimal places.

Results.—The calculated GWA QP band structure of the isolated chain is shown in Fig. 1. We find a band gap of 3.59 eV (DFT-LDA: 1.22 eV). The binding

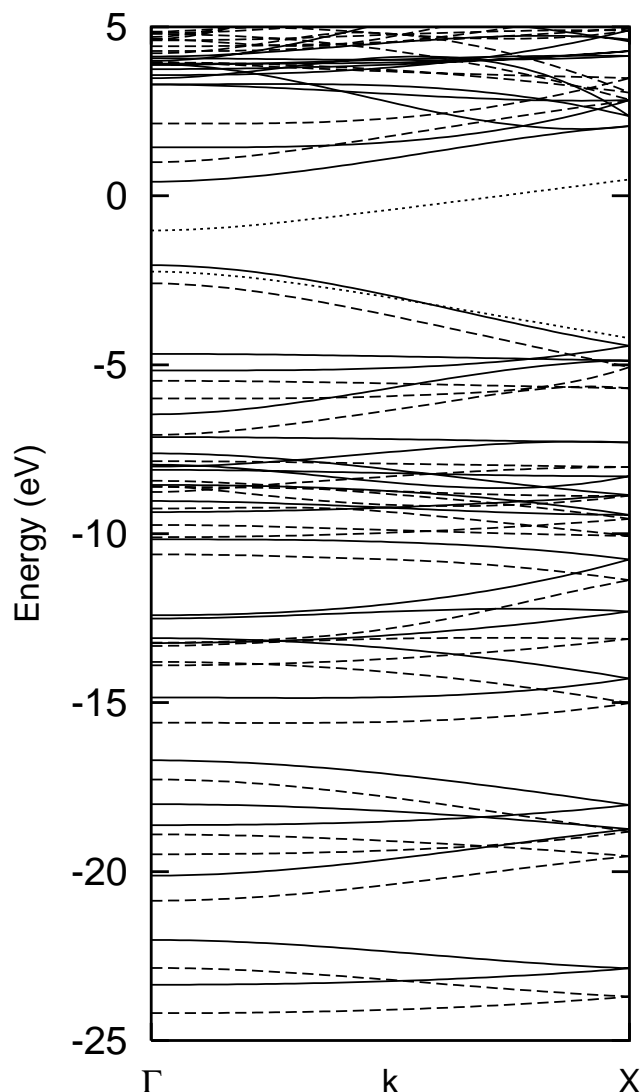


FIG. 1. The single-particle band structure of the valence electrons of polythiophene along the chain direction calculated within the GWA, including intrachain screening only (isolated chain, dashed lines) and including both intra- and interchain screening (bulk, full lines). The DFT-LDA highest valence (π) and lowest conduction (π^*) bands are drawn dotted.

energies of the lowest-lying excitons and the resulting optical band gap are listed in Table I. The lowest-lying singlet exciton (1B_u) for the isolated chain has a binding energy of 1.85 eV, leading to an optical gap of 1.74 eV. To our knowledge, no direct experimental information is available for either the QP band gap or the 1B_u exciton binding energy of PT separately. Only the difference, i.e., the optical gap, corresponding to the onset of the optical absorption in a well-ordered alkyl-substituted polythiophene, is known to be about 1.8 eV [21,22]. This is in good agreement with our calculated optical gap. Similar conclusions regarding the optical gap were reached by Rohlifing and Louie [6] for isolated PA and PPV chains.

However, the *difference* between the 1B_u and 1A_g binding energies of the isolated PT chain is definitely *not* in agreement with a recent experiment [22]; see Table I. Moreover, the 1B_u exciton binding energy of 1.85 eV is very large compared to values currently discussed in the literature. There is a heated debate going on about the magnitudes of exciton binding energies in conjugated polymers [2]. Negligibly small (0.1 eV or less [23]), intermediate (~ 0.5 eV [7]), and large (~ 1.0 eV [24]) energies have been proposed. However, these values concern either films or bulk systems, both of which are essentially 3D.

The QP band structure calculated with our model 3D interaction Eq. (4) for bulk PT is also given in Fig. 1. The band gap has decreased to 2.49 eV. The results for the exciton binding energies are included in Table I. The 1B_u exciton binding energy has decreased to 0.76 eV, resulting in an optical gap of 1.73 eV. So, even though both the exciton binding energy and the band gap have changed considerably, the optical gap has hardly changed compared to the isolated chain. Furthermore, the relative exciton energies are now in good agreement with the experimental data [22]. If we fit our exciton coefficients to the hydrogenlike form $A_k/A_{k=0} = 1/(1 + a_{ex}^2 k^2)^2$, we obtain for the 1B_u exciton sizes $a_{ex} \sim 12$ a.u. and ~ 18 a.u. in the case of the isolated chain and the bulk situation, respectively.

TABLE I. Binding and transition energies of the four lowest-lying excitons in polythiophene, and quasiparticle (E_g) and optical (E_o) band gaps calculated with intrachain screening only (isolated chain) and intra- plus interchain screening (bulk). Experimental data before/after lattice relaxation according to Ref. [22]. All in eV.

	intra	intra + inter	Experiment
1A_g	0.96	0.23	
3A_g	1.11	0.32	
1B_u	1.85	0.76	
3B_u	2.36	1.15	
$^3B_u \rightarrow ^1B_u$	0.51	0.39	0.45/0.45
$^1B_u \rightarrow ^1A_g$	0.89	0.53	0.50/0.55
E_g	3.59	2.49	
E_o	1.74	1.73	2.0/1.8

In order to test the sensitivity of our results to the precise value of the cutoff distance r_{inter} we performed similar calculations for $r_{\text{inter}} = 8$ a.u. and $r_{\text{inter}} = 12$ a.u. The QP band gaps are 2.32 and 2.61 eV, respectively. The 1B_u binding energies are 0.64 and 0.86 eV and hence the optical gaps are 1.68 and 1.73 eV, respectively. This means that the optical gap is quite insensitive to the choice of r_{inter} . The energy differences between the excitons are also hardly influenced.

Discussion and conclusions.—Summing up, we have calculated the single-particle band structure and lowest-lying exciton binding energies of an isolated polythiophene chain and bulk polythiophene. For the isolated chain (only intrachain screening) we find a large band gap and large exciton binding energies, due to the absence of long-range screening. Upon including interchain screening, responsible for the long-range screening present in bulk polythiophene, we find that both the band gap and exciton binding energies are drastically reduced. However, the optical gap hardly changes.

We suggest that these conclusions hold for conjugated polymers in general. In this light, we can understand the fact that the calculations by Rohlfing and Louie [6] on isolated chains of polyacetylene and PPV yield good results for the optical gaps, whereas their lowest-lying singlet exciton binding energy of 0.9 eV for PPV is far in excess of a recent experimental value of 0.35 ± 0.15 eV [7], obtained by a direct STM measurement. The inclusion of interchain screening effects will drastically reduce the calculated binding energy (by more than a factor of 2 in our case of polythiophene) and may well lead to better agreement with this experiment. A similar drastic reduction of the exciton binding energy by interchain screening effects was predicted recently by Moore and Yaron [25] in polyacetylene, within the semiempirical Pariser-Parr-Pople theory. Clearly, it would be very interesting to repeat the experiment in Ref. [7] for polythiophene and polyacetylene.

We conclude that a correct many-body description of the electronic properties of bulk polymer systems should include the effect of interchain screening. An important consequence is that neither Hartree-Fock nor DFT-LDA calculations should be relied upon in this context, since Hartree-Fock does not contain screening effects at all and since the exchange-correlation potential in DFT-LDA depends only on the local density and cannot describe the nonlocal effects due to the long-range screening.

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