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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 anorganic semiconductors has been performed with 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.

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

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*Ab Initio* Calculation of the Electronic and Optical Excitations in Polythiophene: Effects of Intra- and Interchain Screening
\[
\left[ -\frac{1}{2} \nabla^2 + V_H(r) \right] \phi_{nk}(r) + \int \left[ V_{PP}(r, r') + \Sigma(r, r', E_{nk}) \right] \phi_{nk}(r') d^3 r' = E_{nk} \phi_{nk}(r),
\]

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

\[
\begin{align*}
\left[ E_{ck} - E_{vk} - E_g + E_b \right] A_{kcv} + \sum_{k'c'v'} \left[ 2V_{kcv,k'c'v'} - W_{kcv,k'c'v'} \right] A_{k'c'v'} &= 0, \\
W^{\text{scr}} &= W - v \text{ the following form:}
\end{align*}
\]

\[
W^{\text{scr}}_{\text{int}}(r, i\omega) = (1 - e^{-r/r_{\text{int}}}) \times \left[ \frac{1}{\varepsilon(c)(i\omega)^2 + \varepsilon_{||}(i\omega)\varepsilon_{\perp}(i\omega) - \varepsilon(r)} \right] - v(r),
\]

which is correct for distances much larger than the typical interchain distance \( r_{\text{int}} \), 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 \( r_{\text{int}} \), 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

\[
W_{\text{total}}(r, r', i\omega) = W^{\text{scr}}_{\text{int}}(r, r', i\omega) + W^{\text{scr}}_{\text{int}}(r - r', i\omega) + v(r - r'),
\]

where \( W^{\text{scr}}_{\text{int}} \) 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

[51x45]4414
[51x219]sible to perform a screening at long distances. While it is in principle pos-
[51x231]trachain screening) there is no long-range screening. For
[51x279]system (such as an isolated polymer chain with only in-
[51x136]allel (\( \Sigma_{\parallel}(i\omega) \)) screened interaction and the exchange matrix
[51x148]long-wavelength limit we obtain a dielectric constant par-
[51x160]ential effects in the electron-hole screening and in
[51x160]that dynamical effects in the electron-hole screening and in
[51x195]yet prohibitively large. Instead, we choose to include the
[51x195]where \( W_{\text{total}}(r, r', i\omega) = W^{\text{scr}}_{\text{int}}(r, r', i\omega) + W^{\text{scr}}_{\text{int}}(r - r', i\omega) + v(r - r') \).

\[
\begin{align*}
W^{\text{scr}} &= W - v \text{ the following form:}
\end{align*}
\]

\[
W^{\text{scr}}_{\text{int}}(r, i\omega) = (1 - e^{-r/r_{\text{int}}}) \times \left[ \frac{1}{\varepsilon(c)(i\omega)^2 + \varepsilon_{||}(i\omega)\varepsilon_{\perp}(i\omega) - \varepsilon(r)} \right] - v(r),
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which is correct for distances much larger than the typical interchain distance \( r_{\text{int}} \), 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 \( r_{\text{int}} \), 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

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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 $\pi$ and $\pi^*$ 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 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 Rohlfing 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 $\sim 18$ a.u. in the case of the isolated chain and the bulk situation, respectively.

![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 ($\pi$) and lowest conduction ($\pi^*$) bands are drawn dotted.](image)

<table>
<thead>
<tr>
<th>Exciton</th>
<th>intra</th>
<th>intra + inter</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_g$</td>
<td>0.96</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>$^3A_g$</td>
<td>1.11</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>$^1B_u$</td>
<td>1.85</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>$^3B_u \rightarrow ^1B_u$</td>
<td>0.51</td>
<td>0.39</td>
<td>0.45/0.45</td>
</tr>
<tr>
<td>$^1B_u \rightarrow ^1A_g$</td>
<td>0.89</td>
<td>0.53</td>
<td>0.50/0.55</td>
</tr>
<tr>
<td>$E_g$</td>
<td>3.59</td>
<td>2.49</td>
<td></td>
</tr>
<tr>
<td>$E_o$</td>
<td>1.74</td>
<td>1.73</td>
<td>2.0/1.8</td>
</tr>
</tbody>
</table>
In order to test the sensitivity of our results to the precise value of the cutoff distance $r_{\text{inter}}$, 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 $r_{\text{inter}}$. 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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[12] The properties of excited states in finite systems such as oligothiophenes can be calculated within the DFT-LDA formalism, provided they have a symmetry different from that of the ground state. For instance, the relaxation energy associated with the $^3B_u$ state of 12T (an oligothiophene consisting of 12 thiophene rings) is 0.2 eV. Singlet states typically have a smaller relaxation energy.