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Citation for published version (APA):

DOI:
10.1063/1.1356015

Document status and date:
Published: 01/01/2001

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Calculation of excitonic properties of conjugated polymers using the Bethe–Salpeter equation

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(Received 14 November 2000; accepted 24 January 2001)

The excitonic spectra of a number of conjugated polymers, polythiophene (PT), polyphenylenevinylene (PPV), ladder-type poly-para-phenylene (LPPP), trans-polyacetylene (PA), and polydiacetylene (PDA), are calculated by solving the Bethe–Salpeter equation for the two-body Green function of the electron–hole pair. The only input to the calculation is the bulk dielectric constant. We find intermediate binding energies of 0.4–0.6 eV for the lowest optical $1^1B_u$ exciton, obtaining good agreement with recent experiments for each polymer individually. The agreement for the singlet–triplet splittings and the $1^1B_u$ polarizabilities is satisfactory. This also holds for the $1^1B_u-2^1A_g$ splittings in PT, LPPP, and PPV. For PA and PDA we find the $2^1A_g$ exciton above the $1^1B_u$ exciton, in contrast with experiment; a possible explanation for this discrepancy is the absence of lattice relaxation effects and double excitations in our calculations. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356015]

I. INTRODUCTION

Conjugated polymers and oligomers are attracting interest as candidates for the active material in electronic and optical devices, such as transistors, light-emitting diodes and photovoltaic devices. Crucial for the optimization of these devices is knowledge of the electronic and optical properties, and the exciton binding energy. A small exciton binding energy means that a molecular exciton picture can be described starting from a solid-state band picture; a large binding energy means that electron-hole recombination mechanisms, and the excitation spectra. We will focus on the latter in this paper. One of the important aspects of the exciton binding energy is the magnitude of the binding energy of an important material like polyphenylenevinylene (PPV) has been reached. The discussions at recent conferences about the interpretation of the available experimental data reflect the prolonged discussion between the advocates of small (~0.1 eV or less), intermediate (~0.5 eV) and large (~1.0 eV) exciton binding energies.

On the theoretical side, a similarly large spread of values for the exciton binding energy has been found. Since most theoretical models are semiempirical, it is usually hard to separate the real physical effects in these models from effects arising from different or inconsistent parameterizations. Fully first-principles calculations, containing no adjustable parameters, of excitonic properties of extended systems have only recently become computationally feasible. A recent study yielded a binding energy of 0.9 eV for PPV. However, this value was calculated for a chain in vacuum, and therefore, no interactions between the chain and neighboring chains were taken into account. In a similar calculation, we showed that by including interchain contributions into the screened Coulomb interaction in polythiophene (PT), the exciton binding energy is drastically reduced, from 1.86 eV for a chain in vacuum to 0.76 eV for a chain in the bulk. We argued that a similar reduction for PPV would result in a binding energy of ~0.4 eV.

In the present study we perform many-body calculations for the excitonic spectrum of a number of polymers, including the important interchain screening of the Coulomb interaction by using the bulk dielectric constant in the screened interaction. The paper is outlined as follows: in the next section we give a summary of the theoretical and computational methods, in Sec. III we present the results for a variety of conjugated polymers: Polythiophene, polyphenylenevinylene, ladder-type poly-para-phenylene (LPPP), trans-polyacetylene (PA), and polydiacetylene (PDA). The molecular structures are given in Fig. 1. Section IV is devoted to an extensive discussion of the results and Sec. V contains our conclusions.

II. METHODOLOGY

Our computational method can be sketched as follows: First the geometry of the isolated polymer chain is obtained, either from a density functional theory (DFT) calculation (PT, PPV, and LPPP) or from diffraction experiments (PA and PDA). Next, for a given geometry the one-(quasi-)particle excitations are calculated, i.e., the energy required to add (remove) a single electron to (from) the system. In the final step, the interactions between two one-particle excita-

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tions (electron and hole) are taken into account to compute the two-particle excitations and exciton binding energies. This can be accomplished by solving the electron–hole Bethe–Salpeter equation \(^{15,16}\) (BSE).

**A. Geometry**

DFT calculations (in this case within the local density approximation, referred to as DFT-LDA) generally yield reliable results for covalent bonds (errors in length and angle <1%). Such calculations have been shown to fail for PA,\(^{17}\) yielding a too small dimerization of the \(sp^2\) carbon–carbon bonds in the backbone. While inclusion of many-body correlations in the calculation of the geometry can resolve this error,\(^{18}\) we take the geometry of PA and PDA (for which we found the same problem to occur) from experiment. Since the physics relevant to excitonic properties occurs on the backbone, and the side-chains and substituents used in experiments serve mainly to increase the polymer’s processibility, we replace them by hydrogen atoms, and assume a planar geometry. In substituted PDAs, the exciton binding energy, which is known very accurately experimentally, varies somewhat (from 0.45 to 0.55 eV) with the different substituents.\(^{19}\) Changes of the exciton binding energy as a function of substituents of a somewhat larger magnitude have been observed in PPV.\(^{7}\)

We perform the calculations on isolated chains in a periodically repeated supercell, for which we take the size perpendicular to the chain direction large enough to prevent interaction between the periodically repeated images of the chain. This means that we ignore wave function overlap between adjacent chains. The interchain screening effects on the Coulomb interaction are introduced in a later stage of the calculation; the geometries of isolated chains and chains in the bulk are not much different.

**B. One-particle excitations: Quasi-particles**

The one-particle excitation energies \(E_{nk}\) can be evaluated by solving the quasi-particle equation for the quasi-particle wave functions \(\phi_{nk}\) (we use atomic units, \(\hbar = 1, m_e = 1, e^2/(4\,\pi\,\varepsilon_0) = 1\), throughout this paper, unless mentioned otherwise)

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

where \(V_H\) is the Hartree potential, \(V_{\text{ion}}\) the potential of the atoms (which we replace by a pseudo-potential,\(^{20}\)) and \(\Sigma\) the electronic self-energy. The periodicity in the chain direction leads to a one-dimensional wave-vector \((k)\) dependence of the quasi-particle energies and wave functions. Within the GW approximation\(^{21}\) for the self-energy \(\Sigma(\mathbf{r},\mathbf{r}',\mathbf{t}) = iG(\mathbf{r},\mathbf{r}',\mathbf{t})W(\mathbf{r},\mathbf{r}',\mathbf{t}),\) where \(G\) is the one-particle Green function or propagator and \(W\) the dynamically screened Coulomb interaction] very reliable quasi-particle energies have been obtained. In DFT-LDA, \(\Sigma\) is approximated by \(\Sigma(\mathbf{r},\mathbf{r}',\omega) = V_{xc}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')\), where \(V_{xc}\) is the exchange-correlation potential. The locality and energy-independence of this approach makes it computationally much faster in comparison with the GW approximation. Since DFT is a ground-state theory only, the excitation energies calculated with it have strictly speaking no meaning. Comparison of DFT and GW calculations for a wide variety of semiconductors, has proven that while the gap (also called one-particle or quasi-particle gap) separating the occupied and unoccupied states is too small in DFT compared to the GW values, the shape of the energy bands is more or less correct in DFT. More specifically, we recently showed this to be the case for PT.\(^{12,13}\) Since in the BSE the energy of the exciton is defined relative to the quasi-particle gap \(E_g\), the DFT quasi-particle values give us a reliable exciton spectrum relative to the quasi-particle gap. See also Fig. 2.

**C. Two-particle excitations: Excitons**

The exciton wave function \(\Phi(\mathbf{r},\mathbf{r}_h)\) is expanded in terms of electron (conduction) and hole (valence) wave functions\(^{15,16}\)
\[ \Phi(r_e, r_h) = \sum_{k,c} A_{k,c} \phi_{ek}(r_e) \phi_{ch}^*(r_h). \]  

In principle this expansion runs over all valence and all conduction bands, but most couplings are zero due to symmetry, and bands contribute less with increasing energy distance from the gap. In fact, typically 90% or more of the total amplitude \( \sum_{k,c} |A_{k,c}|^2 \) for the lowest few excitons results from coupling between the \( \pi \) - and \( \pi^* \) - bands. A few valence and a conduction bands are required for a convergence of 0.05 eV or better. In this expansion we have restricted our- selves to the optically relevant zero-momentum excitons. The exciton binding energies \( E_b \) then follow from a Schrödinger-type equation,\(^{10-13} \)

\[ [E_{ek} - E_{ck} - E_g + E_b] A_{k,c} + \sum_{k', c'} [2V_{k, k'} c', v'] \delta_{k, 0} - W_{k, k', c', v'} A_{k', c'} \delta_{k, 0} = 0, \]  

where \( E_g \) is the quasi-particle gap, \( E_b \) the exciton binding energy and \( W_{k, k', c', v'} \) and \( V_{k, k', c', v'} \) are the matrix elements of the static (\( \omega = 0 \)) screened Coulomb interaction and the exchange matrix elements (present for singlet excitons only) of the bare Coulomb interaction, respectively. For more details on the treatment of the Coulomb divergencies in direct and reciprocal space, see Ref. 13.

From the exciton wave function Eq. (2) we can obtain the exciton–hole distance probability distribution in the chain (i) direction \( P(x_e - x_h) \):

\[ P(x_e - x_h) = \int \int d^3r_e d^3r_h \delta(x_e - x_h)|\Phi(r_e, r_h)|^2, \]

and the root-mean-square electron–hole distances \( \rho_{rms} \)

\[ \rho_{rms} = \int \int d^3r_e d^3r_h (x_e - x_h)^2 |\Phi(r_e, r_h)|^2. \]

D. Screened interaction

If we base our exciton description on one-particle energies calculated with the GW approximation, we have access to the full details of the static screened Coulomb interaction, \( W(r, r', \omega) = 0 \). Here we will base the BSE calculations directly on DFT calculations. We approximate \( W \) by

\[ W(r, r', \omega = 0) = W_e (|r - r'|) = \frac{1}{\epsilon |r - r'|}. \]

where \( \epsilon \) is the dielectric constant of the bulk polymer. This immediately takes care of screening effects due to the surroundings of the chain, which we showed to be crucial for a correct description of the exciton properties.\(^{12} \) In an ordered situation, where the polymer chains are aligned, the dielectric constant will be anisotropic, and the question arises whether the dielectric constant perpendicular to the chains or the dielectric constant parallel to the chains should be used. While it may appear that the latter should be used this is not the case!\(^{22} \) (This mistake is made in Ref. 23.) For completeness, we give the derivation in the Appendix. We take \( \epsilon = \epsilon_r = 3.0 \), a typical value for the polymers at hand, and also supported by our calculations for ordered PT.\(^{12,13} \)

E. Off-chain excitons

In Eqs. (2)–(6) we have assumed that the electron and the hole forming an exciton are located on the same chain, i.e., we look at on-chain, or direct, excitons only. Experimental evidence\(^{24} \) suggests that in some processes in LPPP excitons are formed that have the hole and the electron on a separate chain, i.e., off-chain, or indirect, excitons.\(^{25} \) Moreover, an unknown fraction of these off-chain excitons should be stable with respect to on-chain excitons, i.e., have a higher binding energy. The mean off-chain energy should of course be higher than the mean on-chain energy, otherwise the off-chain excitons, with no direct radiative pathway to the ground state, would quench the luminescence, which is not observed. Since two counteracting effects are at work (the decreasing exchange interaction due to reduced wave function overlap will increase the binding energy while the increased distance between the electron and the hole will decrease the binding energy) it is not a priori clear what the resulting energy for the off-chain exciton will be.

The off-chain excitons can be described within the method outlined above if we assume that no hybridization between the wave functions on adjacent chains takes place. If we look at the form of the matrix elements of the \( W \)

\[ W_{k, k', c', v'} (d) = \int \int d^3r d^3r' \phi_{k,c}(r') \phi_{k',c'}(r) \times \frac{1}{\epsilon |r - r' - d|} \phi_{k',v'}^*(r' + d) \phi_{k,c'}(r). \]

Under the assumption that the wave functions on both chains are the same, we have \( \phi_{k, c}(r + d) = \phi_{k, c}(r) \). By a similar argument the matrix elements \( V_{k, k', c', v'}^x (d) \) take the form

\[ V_{k, k', c', v'}^x (d) = \int \int d^3r d^3r' \phi_{k,c}(r') \phi_{k',c'}(r + d) \times \frac{1}{|r - r' - d|} \phi_{k',v'}^*(r' + d) \phi_{k,c'}(r). \]

F. Additional considerations

The major advantage of using the DFT-LDA quasi-particle energies and a screened interaction of the form of Eq. (6) instead of the DFT/GW/BSE procedure as outlined in Refs. 12 and 13, is that the most time-consuming computational step in the latter procedure, the calculation of the screened interaction \( W(r, r', \omega) \), is skipped. We will show in Sec. III that there is good agreement between the results of calculations using the present scheme and those of...
DFT/GW/BSE calculations. We have also shown that calculations using Eq. (6) for the screened interaction yielded good results for the radiative lifetimes and polarizabilities of excitons on polymer chain dissolved in benzene, with the benzene dielectric constant, \( \epsilon = 2.28 \).

In the scheme as outlined in the previous paragraphs, no lattice relaxation effects are included. The magnitude of the relaxation energy involved for the optically active \( 1^1B_u \) exciton may be 0.1–0.3 eV, which follows from the relation \( E_{\text{rel}} = \hbar \omega_{\text{ph}} \), where \( \hbar \omega_{\text{ph}} \) is the phonon energy involved in the relaxation, typically \( \approx 0.15–0.20 \) eV and \( S \) the Huang–Rhys factor, which differs from sample to sample \( \approx 0.8–2.0 \). Note that, since the exciton binding energy is the difference between two energy levels (one-particle gap and two-particle gap), for both of which the relaxation is ignored, the effect of lattice relaxation on the binding energy is smaller than that on the absolute exciton energy, i.e., smaller than 0.1 eV for systems with a small \( S \), e.g., for well-ordered LPPP, where \( S \) is typically 1.0 or smaller.

All integrals for the matrix elements, Eqs. (7)–(9), appearing in the BSE, Eq. (3), are performed on a three-dimensional real space grid with \( \Delta r \approx 1.0 \) a.u. (small differences occur for different polymers due to small differences in the size of the unit cells). For all polymers 16 \( k \)-points in the one-dimensional Brillouin zone were used, with the exception of PA and PDA, for which 48 and 32 \( k \)-points were used, respectively. With these parameters, the resulting spectra are converged to within 0.05 eV. The accuracy for the polarizabilities is \( \sim 10\% \).

### III. RESULTS

We have listed the exciton binding energies, reduced effective masses (defined as \( 1/\mu = 1/m_{\pi} + 1/m_{\pi^*} \), with \( m_{\pi} \) and the \( m_{\pi^*} \) the effective masses of the hole and electron, respectively), exciton polarizabilities (calculated from perturbation theory in the same way as in Ref. 26), and root-mean-square electron–hole distances \( r_{\text{rms}} \) of the optically active \( 1^1B_u \) excitons in Table I. The energies of the \( 1^3B_u \) and \( 2^1A_g \) excitons relative to the \( 1^1B_u \) exciton are given in Table II, as well as the singlet–triplets \( (1^3B_u - 1^1B_u) \) splitting. The \( 2^1A_g \) and the \( 2^1A_g \) are almost degenerate; due to symmetry the probability of finding an electron and hole with zero relative distance, is zero, and hence the exchange interaction is small. In Fig. 2, the relevant levels are shown schematically. For PT, we can compare the present results with our previous \textit{ab initio} calculations. The results obtained with Eqs. (2)–(6) are in good agreement with these earlier

### Table I. Properties of the \( 1^1B_u \) exciton: Binding energy \( E_b \), reduced mass \( \mu \), polarizability \( \alpha \) and the root-mean-square electron–hole distance \( r_{\text{rms}} = \sqrt{\left(\langle x_{\pi}^2 - x_{\pi^*}^2\rangle\right)} \).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Source</th>
<th>( E_b ) (eV)</th>
<th>( \mu ) ((m_e))</th>
<th>( \alpha )(10(^2)(\text{Å}^2))</th>
<th>( r_{\text{rms}} )(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT</td>
<td>This work</td>
<td>(-0.61)</td>
<td>0.076</td>
<td>1.6</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>Experiment(^a)</td>
<td>(-0.6)</td>
<td>1–11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>\textit{Ab initio}(^b)</td>
<td>(-0.76)</td>
<td>0.065</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>PPV</td>
<td>This work</td>
<td>(-0.54)</td>
<td>0.048</td>
<td>2.9</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>Experiment(^c)</td>
<td>(-0.48)</td>
<td>3–11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>\textit{Ab initio}(^d)</td>
<td>(-0.4)</td>
<td>0.044</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPPP</td>
<td>This work</td>
<td>(-0.64)</td>
<td>0.058</td>
<td>1.6</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>Experiment(^e)</td>
<td>(-0.6)</td>
<td>2.0</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>PA</td>
<td>This work</td>
<td>(-0.43)</td>
<td>0.029</td>
<td>6.4</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>Experiment(^f)</td>
<td>(-0.5)</td>
<td>0.1–1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>\textit{Ab initio}(^g)</td>
<td>(-0.4)</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDA</td>
<td>This work</td>
<td>(-0.47)</td>
<td>0.035</td>
<td>5.6</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>Experiment(^h)</td>
<td>(-0.53)</td>
<td>0.04–0.06</td>
<td>6.6</td>
<td>11.0</td>
</tr>
</tbody>
</table>

\(^a\)Reference 32.
\(^b\)Reference 12.
\(^c\)Reference 11, calculation for an isolated chain.
\(^d\)Reference 31, \( \alpha \) and \( r_{\text{rms}} \) from Ref. 28.
\(^e\)Reference 32.
\(^f\)Reference 19.

### Table II. Energies of the \( 1^3B_u \) and \( 2^1A_g \) excitons relative to the \( 1^1B_u \) exciton. \textit{Ab initio} refers to DFT/GW/BSE-type calculations.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Source</th>
<th>( E_b(1^3B_u) - E_b(1^1B_u) ) (eV)</th>
<th>( E_b(2^1A_g) - E_b(1^1B_u) ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT</td>
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<td>(-0.43)</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Experiment(^a)</td>
<td>(-0.45)</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>\textit{Ab initio}(^b)</td>
<td>(-0.39)</td>
<td>0.53</td>
</tr>
<tr>
<td>PPV</td>
<td>This work</td>
<td>(-0.57)</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>Experiment(^c)</td>
<td>(-1.0)</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>\textit{Ab initio}(^d)</td>
<td>(-0.9)</td>
<td>0.4</td>
</tr>
<tr>
<td>LPPP</td>
<td>This work</td>
<td>(-0.41)</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>Experiment(^e)</td>
<td>(-0.62)</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>\textit{Ab initio}(^f)</td>
<td>(-0.50)</td>
<td>0.37</td>
</tr>
<tr>
<td>PA</td>
<td>This work</td>
<td>(-0.61)</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Experiment(^g)</td>
<td>(-0.6)</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>\textit{Ab initio}(^h)</td>
<td>(-0.8)</td>
<td>0.1</td>
</tr>
<tr>
<td>PDA</td>
<td>This work</td>
<td>(-0.56)</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>Experiment(^i)</td>
<td>(-0.9)</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\(^a\)Reference 37.
\(^b\)Reference 12.
\(^c\)Reference 31, \( E_b(1^3B_u) - E_b(1^1B_u) \) from Ref. 8, \( E_b(2^1A_g) - E_b(1^1B_u) \) from Ref. 38.
\(^d\)Reference 11, calculation for an isolated chain.
\(^e\)Reference 28.
\(^f\)Reference 39.
\(^g\)Reference 40.
\(^h\)Reference 41.
results, although the exciton binding energy is reduced somewhat. This gives use confidence that the results for other polymers will also be reliable. To show the dependence of the 1\(^1\)B\(_u\) binding energy on the dielectric constant, we have plotted in Fig. 3 the binding energy in PPV as a function of the dielectric constant. In Fig. 4, we have plotted the exciton binding energy in the different polymers as a function of their reduced mass.

We also have good agreement between our calculated and the experimental exciton polarizabilities. We note that the polarizabilities for PPV and PT are increased by almost a factor of two to three compared to the values for the same polymers dissolved in benzene,\(^{26}\) which has only a slightly smaller dielectric constant (2.28 instead of the 3.0 used here). The trend of increasing polarizability is accompanied by a decreasing binding energy and an increasing mean electron–hole distance, as can be seen from the values of \(r_{\text{rms}}\) in Table I and the electron–hole distance probability distribution in Fig. 5.

In Fig. 6 we have plotted the binding energies of off-chain excitons in LPPP as a function of the distance \(d\) between the two chains, using Eqs. (8) and (9) for the matrix elements of the screened Coulomb interaction and the exchange interaction, respectively. Because the integral in Eq. (8) is performed on a grid, only shifts commensurate with this grid have been considered. We shift the second chain in the direction perpendicular to the polymer plane. The binding energy of the relevant 1\(^1\)B\(_u\) off-chain exciton is 0.1–0.2 eV higher in energy than its on-chain counterpart. Note that the singlet–triplet splitting is close to zero for off-chain excitons, due to the fact that there is no longer overlap between the electron and hole wave functions.

**IV. DISCUSSION**

**A. The binding energies and splittings**

We find good agreement between our calculations and specific experiments for the exciton binding energy of the lowest optically active exciton in PT, PPV, LPPP, PA, and PDA. Earlier, the onset of photoconductivity in LPPP at 1.1 eV above the 1\(^1\)B\(_u\) absorption was interpreted as being the result of a 1.1 eV binding energy of this exciton.\(^{29}\) Nowadays, the binding energy in LPPP is generally agreed to be approximately equal to the 1\(^1\)B\(_u\)–2 \(^1\)A\(_g\) splitting, i.e., 0.6–0.7 eV.\(^{28,30}\) The scanning tunneling microscope (STM) measurements on LPPP\(^{31}\) have confirmed this. The same technique has been used to measure the binding energy in PPV.\(^{7}\) In PDA, \(E_b\) was determined directly from a Franz–Keldysh electric field effect,\(^{19}\) the \(E_b\) data for PA and PT were derived from an in principle less reliable electro-absorption measurement.\(^{32}\) Note that our value for PPV deviates considerably from an earlier DFT/GW/BSE result.\(^{11}\) However, this calculation was performed for an isolated chain and, therefore, did not include the important interchain contributions in the screened interaction, which results in an exciton binding energy which is a factor of 2 too large compared to the experimental value and the present result.

The exciton binding energy in inorganic semiconductors is well described by \(E_b = \mu / e^2 E_H\), where \(E_H\) is the binding energy of the electron in the hydrogen atom. Here the general trend is indeed that \(E_b\) increases with increasing reduced mass \(\mu\), but the relation does not follow the form \(E_b \approx \mu\), as can be clearly seen in Fig. 4. If we exclude PT, we can obtain a reasonable fit to this form. As can be seen from Fig. 3, where we have plotted the binding energy in PPV as

**FIG. 4.** The exciton binding energy of the 1\(^1\)B\(_u\) excitons (+) as a function of the reduced mass \(\mu / e^2 = 3.0\) for all polymers. The linear fit (dashed line) does not include the result for PT. See Sec. IV A for details.

**FIG. 5.** The probability distribution for the electron–hole distance \(P(x_e, -x_h)\) of the lowest optically active 1\(^1\)B\(_u\) excitons.

**FIG. 6.** The binding energy of the 1\(^1\)B\(_u\) singlet exciton (+) and the 1\(^3\)B\(_u\) triplet exciton (×) as a function of the interchain distance \(d\). The lines are a guide to the eye. The second chain is shifted with respect to the first chain perpendicular to the first chain and perpendicular to the plane of the polymer. \(d = 0.0\) a.u. corresponds to an on-chain exciton. Note that the result for \(d = 3.5\) a.u. is not physically realistic in the sense that the chains can not be close together in a real system. It is given only to shown the behavior of the binding energies as a function of \(d\).
a function of the dielectric constant, the relation $E_b \propto 1/e^2$ is well obeyed. However, the proportionality constant (not taking PT into account) is not $E_H = 13.6$ eV, but larger, viz. 106 eV. This is due to the confinement of the exciton to the chain, a quasi-one-dimensional system. The exceptionally large $\mu$ in PT is not caused by the presence of sulfur; $m_{\perp}$ is 20% larger than $m_e$, but only the former contains a substantial sulfur contribution. This alone cannot explain why the exciton in PT is ~50% heavier than expected from this model. Obviously, this simple model has a limited validity for the prediction of properties of such complex systems.

A tendency to underestimate (by 0.1–0.3 eV) the singlet–triplet splitting can be seen in PPV, LPPP, and PDA. A reason may be the fact that no excitonic lattice relaxation is included in our calculations. While the Huang–Rhys factor, and hence the amount of lattice relaxation energy, for the $B_u$ singlets is well known, data for the corresponding triplets is available for LPPP only where it is almost the same as for the singlet. This is not necessarily the case for all conjugated polymers: since states lower in energy are typically more localized, the relaxation energy for this state may be larger. Therefore, in a calculation with lattice relaxation included, the singlet–triplet splitting may well increase by a few tenths of an eV. In fact, in a density matrix renormalization group (DMRG) calculation for the Pariser–Parr–Pople–Peierls Hamiltonian for PA, the lattice relaxation of triplet was found to be 0.2 eV larger than that of the singlet.

For all polymers we find a binding energy in the intermediate range, 0.4–0.6 eV, with an average deviation of the experimental values of less than 10%. As mentioned before, there is a wealth of experimental evidence for both intermediate and small binding energies, and continuing discussions about the validity of the methods used to obtain these values. Only for PDAs there seems to be no discussion at all; the consensus is that the binding energy is 0.45–0.55 eV. The fact that we recover this binding energy and, with the same method and without changing the dielectric constant, find binding energies in the same range for other polymers is strong evidence for an intermediate binding energy in conjugated polymers in general. While it is possible to obtain smaller binding energies with this method, as was shown explicitly for PPV, these smaller binding energies are obtained with unrealistically large values of the dielectric constant $\varepsilon$, i.e., $\varepsilon \sim 8.0$ to obtain $E_b \sim 0.1$ eV, as can be seen in Fig. 3.

### B. Off-chain excitons in LPPP

Thermally stimulated photoluminescence experiments recently performed on LPPP suggest that at least a fraction of the off-chain excitons is stable with respect to on-chain excitons, i.e., they are expected to be lower in energy—or have a higher binding energy—than their on-chain counterparts. In these experiments a LPPP sample is illuminated by a mercury lamp for 30 s at 4.2 K. After the lamp is switched off and after the afterglow has disappeared, the temperature is increased with a constant heating rate and the luminescence as a function of time/temperature is observed. A peak in luminescence is observed at 40 K. If all off-chain excitons were higher in energy than their on-chain counterparts, they would decay into on-chain excitons and decay radiatively immediately after the mercury lamp is switched off.

As mentioned earlier, the mean energy of off-chain excitons should be higher than that of on-chain excitons, since no luminescence quenching is observed. Moreover, these off-chain excitons have a charge-transfer character only and are therefore not excimers, which are superpositions of charge-transfer and on-chain excitons. The later component gives the excimers a radiative pathway to the groundstate resulting in a radiative lifetime which is only one order of magnitude larger than that of on-chain excitons. The pure off-chain excitons in LPPP are stable (with respect to on-chain excitons and the following radiative decay) for several minutes or longer.

Indeed we find the off-chain excitons to be higher in energy than the on-chain excitons in LPPP. Since in realistic materials, the on- and off-chain exciton energies have a certain distribution, which for LPPP has a typical width of 0.035–0.05 eV, overlap in the high-energy tail of the on-chain excitons and the low-energy tail of the off-chain excitons will result in configurations where the off-chain exciton indeed has a lower energy. The experimental data are inconclusive with respect to the question which fraction of the off-chain excitons has a lower energy.

### C. The $A_g - B_u$ exciton order in PA and PDA

If no luminescence, which according to Kasha’s rule should come from the lowest excited singlet state, is observed in a material, this means that there is a singlet exciton below the lowest optically active exciton. Optical excitations in such materials become trapped in this ‘‘dark’’ singlet state, which does not couple to the ground state radiatively. This is the case in PA and PDA, where the $1^1A_g$ state is known to be below the optically active $1^1B_u$ state, in PA by $\sim 0.5$ eV, in PDA by $\sim 0.4$ eV, depending somewhat on the nature of the substituents. While we do find a correct value for the exciton binding energy in PDA, we find in both PA and PDA the $2^1A_g$ above the $1^1B_u$ state, which is qualitatively wrong. This is not a result of our approximations for the screened interaction and the one-particle excitation energies as outlined in Sec. II; a DFT/GW/BSE calculation for a single chain of PA also finds the $2^1A_g$ above the $1^1B_u$ state, albeit by a smaller value.

It has been suggested that the $A_g$ state is actually a bound state of two $B_u$ triplets, i.e., a four-particle excitation, or at least a superposition of two- and four-particle excitations. This would explain why this state is not described correctly within the two-particle excitation formalism used here. The fact that this kind of complication does not occur in PT, LPPP, or PPV, where the lowest $A_g$ state is above the lowest $B_u$ state with correct energy difference, is then a result of the fact that in these polymers much less mixing between two- and four-particle excitations occurs, due to smaller electron–electron correlation.

Another explanation, as yet for PA only, was given by Bursill and Barford who found the $A_g$ exciton above the $B_u$ exciton in the DMRG study mentioned before if no lattice
relaxation was included, but below it when lattice relaxation was included. Lattice relaxation resulted in a weak downward shift of the $B_u$ state ($\approx 0.2$ eV for the infinite chain), but in a strong downward shift of the $A_g$ state ($\approx 1.0$ eV). A similar calculation for PDA, without lattice relaxation as yet, results in an $A_g$ state above the $B_u$ state. It is expected that including lattice relaxation in this calculation will also bring the $A_g$ state below the $B_u$ state.\[36\] The latter is not the case for PT, PPV, and LPPP, since with our approach (i.e., without lattice relaxation) we do have good agreement for the $A_g$ state for these polymers relaxation effects for these polymers are probably not markedly different for the $B_u$ and $A_g$ singlet states in these polymers.

The exceptional character of PA and PDA with respect to both the large differences in relaxation energy for the $B_u$ and $A_g$ excitons and the role of four-particle excitations seems to be in line with the fact that the description of their ground state geometries is also extremely complicated,\[37,38\] which is also an exception, as discussed earlier in Sec. II A. In fact, to reproduce the correct order of the $B_u$ and $A_g$ excitons in PA and PDA, it might be necessary to include both four-particle excitations and lattice relaxation effects in our formalism.

Note that the incorrect position, related to its possible four-particle character, of the $A_g$ state in PA and PDA does not influence the reliability of the prediction of the $1B_u$ polarizabilities in these materials. While the perturbation expression for the $1B_u$ polarizability couples the $1B_u$ exciton to the $2A_g$ exciton, the $1B_u$ exciton is correctly described with a two-particle formalism, and hence also its polarizability, irrespective of the nature of the other excitations.

V. CONCLUSIONS

We have shown that ab initio methods (in this case containing one parameter, the dielectric constant) can be used to give reliable predictions for a number of excitonic properties of conjugated polymers, most notably about the heavily disputed value of exciton binding energy, for which we find 0.4–0.6 eV for all five polymers studied here, obtaining very good agreement with several experiments for each polymer individually. The important gain in computational speed compared to earlier fully ab initio work for conjugated polymers, is in the approximation of the screened interaction between the electron and hole forming the exciton $W(r,r')$, which is computationally very hard to calculate, by a Coulomb interaction screened by the dielectric constant. This approximation gives results which are in agreement with the earlier calculations for bulk systems.\[3,33,34\]

A few questions remain. First of all, what effect will wave function overlap and hybridization between wave functions on adjacent chains have on the binding energies, of both on-chain and off-chain excitons? It might be argued that this effect is relatively small for substituted polymers, where bulky sidegroups prohibit effective hybridization between the backbone wave functions. In such systems, the only form of interchain interaction would be the polarization and screening effects on the Coulomb interaction, which we have already included in our present calculations. Second, while the effect of lattice relaxation for the $1B_u$ singlet exciton binding energy is small ($\sim 0.1$ eV), a larger relaxation energy may be expected for the $1B_u$ triplet and the $2A_g$ excitons, the latter especially in PA and PDA. Third, for PA and PDA the effect of including also four-particle excitations (biexciton) on the $A_g-B_u$ exciton order has to be investigated. All three questions will be the subject of future investigations.

ACKNOWLEDGMENTS

We thank S. C. J. Meskers, V. I. Arkhipov, and W. Barford for useful discussions, and S. F. Alvarado also for making his data available to us prior to publication. Financial support from the Onderzoekschool Polymeren PTN is gratefully acknowledged.

APPENDIX: THE SCREENED INTERACTION IN AN ANISOTROPIC HOMOGENEOUS MEDIUM

If we look at the screened interaction $W$ of a charge $q$ in an anisotropic but homogeneous dielectric (with dielectric constants $\epsilon_1$, $\epsilon_2$, and $\epsilon_3$ along the principle axes $x_1$, $x_2$, and $x_3$), the Poisson equation reads

$$\frac{\partial^2 W}{\partial x_1^2} + \frac{\partial^2 W}{\partial x_2^2} + \frac{\partial^2 W}{\partial x_3^2} = q \delta(x).$$  (A1)

Substituting $\sqrt{\epsilon_i} y_i = x_i$ and solving for $\tilde{W}(y)$ we find

$$\tilde{W}(y) = \frac{q}{\sqrt{\epsilon_1 \epsilon_2 \epsilon_3}} \frac{1}{\sqrt{y_1^2 + y_2^2 + y_3^2}}.$$  (A2)

Substituting $x_i / \sqrt{\epsilon_i} = y_i$ we find for $W(x)$

$$W(x) = \frac{q}{\sqrt{\epsilon_1 \epsilon_2 \epsilon_3} x_1^2 + \epsilon_2 \epsilon_3 x_2^2 + \epsilon_1 \epsilon_3 x_3^2}.$$  (A3)

If we have a polymer along the $x_1$ axis, we have $\epsilon_1 = \epsilon_3 = \epsilon_l$ and hence we have

$$W(x) = \frac{q}{\sqrt{\epsilon_2 \epsilon_3 x_1^2 + \epsilon_1 \epsilon_3 (x_2^2 + x_3^2)}}.$$  (A4)

Since the exciton is extended along the chain, we typically have $x_1^2 \gg x_2^2 + x_3^2$, and Eq. (6) is a good approximation.

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