

# Coulomb interactions and linear, nonlinear, and triplet absorption in poly(para-phenylenevinylene)

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Within a model Hamiltonian with variable on-site and long-range Coulomb interactions between the  $\pi$  electrons for poly(para-phenylenevinylene), we conduct a thorough search in the parameter space to determine the magnitudes of the effective Coulomb interaction parameters necessary to fit all four absorption bands that are seen in the experimental absorption spectra of this material. We find best agreement between the calculated and experimental absorption spectra with Coulomb interactions that are slightly smaller than the standard Pariser-Parr-Pople parameters. For these values of the Coulomb parameters, the primary photoexcitation in poly(para-phenylenevinylene) is to an exciton with binding energy close to  $0.9 \pm 0.2$  eV. This result, obtained from fitting the linear absorption, is in agreement with nonlinear absorption studies, viz. electroabsorption, two-photon absorption, and picosecond photoinduced absorption, within our model. We have also calculated the energies of the lowest triplet state, and the final state to which triplet absorption occurs. The excited triplet state is an exciton. We show that the latter result, taken together with the known experimental triplet absorption energy, indicates that estimates of 0.2 eV or less for the binding energy are incorrect. We briefly discuss the possibility that the binding energy has an intermediate magnitude. [S0163-1829(97)10204-1]

## I. INTRODUCTION

In the previous paper (hereafter I) (Ref. 1) we demonstrated that the four absorption bands in poly(para-phenylenevinylene) (PPV) are characteristics of the  $\pi$ -conjugation network, and that (3,5) chemical substitution plays an insignificant role in optical processes. Here we focus on determining the Coulomb interaction parameters necessary to describe these polymers semiquantitatively. We conduct a thorough search through a wide parameter space in order to fit all four absorption bands seen in the experimental spectrum of PPV (see Fig. 2 in I). The importance of such a search has been stressed by several different recent theoretical investigations.<sup>2-7</sup> The validity of the interaction parameters reached from our search is then tested against experimental *nonlinear* optical absorption and triplet absorption. We show that the *same* interaction parameters that are required to fit the linear absorption give highly satisfactory self-consistent descriptions of nonlinear and triplet absorptions within our model.

The lowest optical state within Coulomb-correlated theoretical models in one dimension is an exciton. A variety of recent experiments<sup>8-14</sup> have demonstrated the exciton character of the primary photoexcitation in PPV. The magnitude of the exciton binding energy, however, is currently highly controversial. While the most widely held view currently is that the binding energy is close to 0.4 eV,<sup>6,10,14-18</sup> estimates of this quantity range from as low as 0.1–0.2 eV (Refs. 5, 13, and 18) to as high as 0.9 eV.<sup>2,3,11</sup> In the following, we shall refer to estimates of exciton binding energy up to 0.2 eV as “small,” 0.4–0.5 eV as “intermediate,” and any value greater than 0.7 eV as “large.” Within our calculations, which give satisfactory descriptions of singlet, nonlinear, and

triplet absorption energies, the exciton binding energy is  $0.9 \pm 0.2$  eV. Although considered extreme by proponents of weaker binding energy, we point out that several recent optical experiments<sup>19-21</sup> support this large value, which has also received support from very recent theoretical work.<sup>7,22</sup>

The results of our search through the parameter space within the Pariser-Parr-Pople (PPP)-type model introduced in I are reported in Sec. II, where we present the calculated excited-state energies corresponding to the four absorption bands in PPV. We demonstrate that within our model there exists only one parameter set that can quantitatively fit all four absorption bands in the experimental absorption spectrum. In Sec. III we discuss nonlinear absorption and picosecond photoinduced absorption (ps PA) within the theory, and point out that these experiments give independent lower limits for the binding energy of the optical exciton. In Sec. IV we give a brief discussion of triplet states in PPV. The excited state to which triplet PA occurs is an exciton. Finally, in Sec. V we compare theoretical predictions with existing experimental nonlinear absorption and PA measurements in freshly prepared thin films as well as solutions. These results give strong support to our estimate of large binding energy. We point out that the triplet absorption energy<sup>11,16</sup> rules out the small exciton binding energy. We present a brief discussion of theoretical and experimental work that predict the intermediate binding energy. At least in some of these cases, the data as well as the calculations are conceivably consistent with the large exciton binding energy (see also the discussions in Ref. 23).

## II. COULOMB PARAMETERS AND LINEAR ABSORPTION

The theoretical model we use is the PPP-type model introduced in I [see Eqs. (1)–(3) in I]. Unless otherwise men-

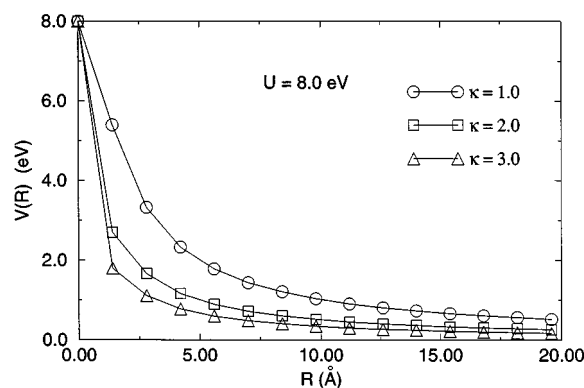


FIG. 1. The decay of  $V_{ij}$  as a function of distance for three different values of  $\kappa$ .

tioned, we choose the same values of  $t_0$  (2.4 eV),  $t_1$  (2.2 eV), and  $t_2$  (2.6 eV), corresponding to the hopping integrals among the phenyl carbon atoms and the single and double bonds of the vinylene linkage, respectively, as in I. The constant  $\kappa$  introduced there to scale the long-range Coulomb interaction  $V_{ij}$  models the dielectric constant of the medium. Figure 1 shows the decay of  $V_{ij}$  as a function of  $R_{ij}$  for the specific case of  $U = 8.0$  eV and  $\kappa = 1, 2$ , and  $3$ . We note that  $\kappa$  does not change the rate of decay of  $V_{ij}$ , but rather changes the effective charge seen at a given distance. We conduct a thorough search through the parameter space by taking many different combinations of  $U$  and  $\kappa$ , in order to arrive at the best set of effective parameters to fit the experimental optical absorption within the singles configuration interaction (SCI) approximation. The screening of the long-range part of the Coulomb potential is similar in spirit to the approach of Tavan and Schulten,<sup>24</sup> where interatomic distances in linear chain polyenes were scaled by a factor of 2 in order to model the presence of electrons in the  $\sigma$  core. Different functional forms of  $V_{ij}$  such as screened Mataga-Nishimoto or exponential decay with different decay constants<sup>25</sup> can also be used to model the screening in the solid-state material. The results of such calculations are similar to the results of the present work,<sup>26</sup> and will not be discussed.

We have not included electron-phonon interactions explicitly. Partial justification of this comes from the small Stokes shift of the photoluminescence spectrum,<sup>8,27</sup> implying that electron-phonon interactions play a relatively weak role in the optical absorption of PPV. Additional justification comes from previous calculations of relaxation energies of the optical  $1B_u$  state and of the singly charged polaron.<sup>7,15,18</sup> These relaxation energies, upon inclusion of realistic electron-phonon interactions, are about 0.3 and 0.15 eV, respectively, thereby suggesting a near cancellation between the relaxation energies of the exciton and the two free polarons. Electron-phonon interactions therefore contribute minimally to the exciton binding energy in PPV.<sup>7,15,18</sup>

Our nomenclature for the four general classes of eigenstates are the same as in I, viz., we label  $\Psi_I = \chi_{d \rightarrow d^*}$ ,  $\Psi_{II} = (\chi_{d \rightarrow l^*} - \chi_{l \rightarrow d^*})$ ,  $\Psi_{III} = (\chi_{d \rightarrow l^*} + \chi_{l \rightarrow d^*})$ , and  $\Psi_{IV} = \chi_{l \rightarrow l^*}$ , where  $d$  and  $d^*$  refer to the innermost delocalized valence and conduction bands (see I), respectively. We recall that the experimental absorption bands at 2.4, 4.7, and 6.0 eV correspond to the transitions to states  $\Psi_I$ ,  $\Psi_{III}$ , and  $\Psi_{IV}$ ,

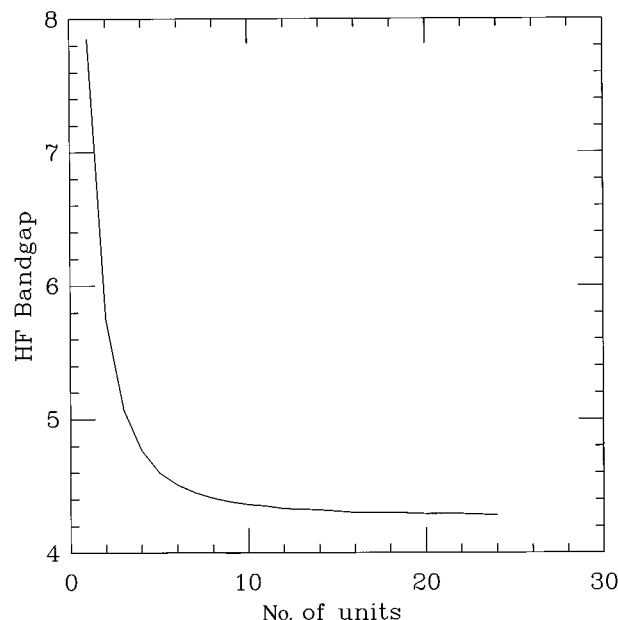


FIG. 2. The Hartree-Fock band gap as a function of the number of units. Note that the band gap is nearly identical to its infinite-chain value by 8–10 units.

respectively. Transitions to  $\Psi_{II}$  are forbidden. The absorption band at 3.7 eV is due to the higher energy  $\chi_{d \rightarrow d^*}$  that split from  $\Psi_I$  due to correlation effects, and that remain visible in the absorption spectra of finite chains (see I). As in I we refer to these states as  $\Psi_{Ib}$ .

The search through the parameter space is conducted as follows. For each set of Coulomb interaction parameters we calculate all SCI eigenvalues and eigenfunctions. Although correlated wave functions are more difficult to interpret than single-particle wave functions, it is still possible to perform a complete wave-function analysis and classify all eigenstates by their dominant Hartree-Fock (HF) contributions (see I). For each set of Coulomb parameters we compare the calculated and experimental energies of  $\Psi_I$ ,  $\Psi_{Ib}$ ,  $\Psi_{III}$ , and  $\Psi_{IV}$ .

We define the  $n$ -unit oligomer to be the system consisting of  $n$  phenyl rings and  $n-1$  vinylene units. The results we report are for calculations performed on eight-unit oligomers. At 8–10 units, the chain is long enough that the energies of the different excitons and the HF band gap have effectively converged to their infinite-chain values, yet short enough to still have a visible finite-size absorption band to account for the absorption feature at 3.7 eV. This convergence is shown in Fig. 2, where we plot the energy of the HF band gap as a function of chain length. At 8–10 units, the energy of the HF band gap is only  $\leq 5\%$  higher than at 24 units.

In Table I, we show the calculated energies of the four classes of states corresponding to the four bands in the experimental absorption spectrum in I for many different values of  $U$  and  $\kappa$ . We begin our discussion with  $\kappa=1$ , which corresponds to an unscreened Ohno potential. For the weakest correlations shown,  $U = 4.8$  eV, the energies of  $\Psi_I$ ,  $\Psi_{Ib}$ , and  $\Psi_{III}$  are all reasonably close to the experimental transition energies (see I), but the energy of  $\Psi_{IV}$  is considerably lower than the observed experimental transition energy of

TABLE I. Calculated energies of absorption bands *I*, *Ib* (the “finite-size” band; see text), *III*, and *IV* for the eight-unit oligomer of PPV for different values  $U$  and  $\kappa$  with  $t_0 = 2.4$  eV. Multiple entries for the energies of bands *Ib* and *III* indicate the energies of multiple eigenstates corresponding to the absorption bands in the calculated spectrum in that energy region. Note that  $U = 8.0$  eV and  $\kappa = 2$  give a nearly quantitative fit to the experimental absorption spectra of Fig. 2 in Ref. 1.

$\kappa$	$U$ (eV)	$I$ (eV)	$Ib$ (eV)	$III$ (eV)	$IV$ (eV)
1.0	4.8	2.49	3.51	4.67	5.24
			3.88		
			3.68		
			3.92		
	6.0	2.61	4.99	5.68 <sup>a</sup>	5.32
			3.92		
			5.68 <sup>a</sup>		
			5.53 <sup>a</sup>		
	8.0	2.77	4.12	5.89 <sup>a</sup>	5.53 <sup>a</sup>
			4.12		
			4.12		
			4.12		
2.0	4.8	2.34	3.28	4.13	5.66
			3.47		
			3.83		
			3.71		
	6.0	2.47	4.35	4.37	5.87
			3.71		
			4.37		
			4.37		
	8.0	2.72	4.68	4.68	6.23
			3.75		
			3.75		
			3.75		
3.0	4.8	2.22	3.67	3.90	5.77
			3.74		
			3.91		
			3.93		
	6.0	2.34	4.06	4.06	5.99
			4.07		
			4.10		
			4.10		
	8.0	2.49	4.31	4.31	6.32
			3.61		
			4.34		
			4.34		
	10.0	2.66	4.56	4.56	6.63
			3.69		
			4.56		
			3.88		

<sup>a</sup>Note the energy crossing between  $\Psi_{III}$  and  $\Psi_{IV}$ . See text for discussion.

6.0 eV. As is clear from Table I, for  $\kappa = 1$ , the energy of band *IV* is underestimated for all values of  $U$  shown. Since the energy of band *IV* increases with  $U$ , a much larger  $U$  should bring this band closer to the experimentally observed energy. However, we note that at  $U = 8.0$  eV, the energy of  $\Psi_{III}$  is already too high for a reasonable fit to experiment, and the energies of  $\Psi_{III}$  and  $\Psi_{IV}$  have actually crossed. A similar crossing of the energies of  $\Psi_{III}$  and  $\Psi_{IV}$  within the bare PPP model was previously also found within calculations pertaining to trans-stilbene.<sup>28</sup> Such a crossing of energy levels in the real material would contradict the results of the polarization study of the absorption bands (see I), and we therefore conclude that  $\kappa = 1$  is not suitable for PPV.

It is therefore for the quantitative fitting of the absorption bands that we need the parameter  $\kappa$ . The strongest effect of varying  $\kappa$  is to modify the strength of the long-range interaction between electrons in localized MO's centered on different phenyl groups. As seen in Table I, the energies of both bands *I* and *Ib*, which do not involve the localized molecular orbitals, are only weakly affected by the value of  $\kappa$ . In contrast, the energies of the states in band *III* (*IV*) are seen to be strongly suppressed (enhanced) by increasing  $\kappa$  (see Table I).

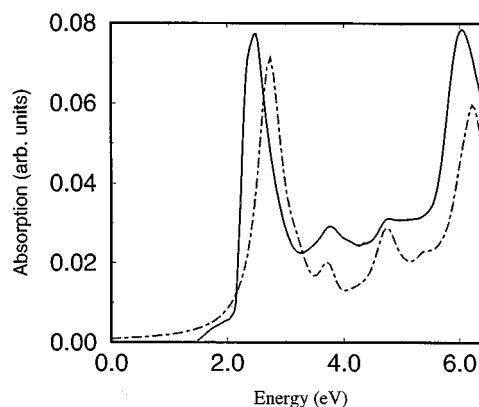


FIG. 3. Experimental absorption spectrum of MEH-PPV (solid line) and the calculated absorption spectrum (dashed line) for an eight-unit oligomer with  $U = 8$  eV and  $\kappa = 2$ . The calculation includes all excited states up to 6.2 eV, and used the standard Lorentzian expression for the absorption. The line width parameters are 0.15 eV within the energy range 3.5–4.0 eV, and 0.25 eV elsewhere.

Thus we expect that with  $\kappa > 1$ , we can increase the Hubbard  $U$  to a value large enough to raise the energy of band *IV* to the experimental range while still retaining the proper band assignments (see I). This conjecture is borne out by our calculations, as shown below.

With  $\kappa = 2$ , a small  $U$  of 4.8 eV fits absorption band *I* well, but fails to fit bands *III* and *IV* accurately. A larger  $U$  of 6.0 eV still underestimates the energy of band *III*. Only at even stronger interactions, with  $U = 8.0$  eV, do we obtain a reasonable fit to all the absorption band energies. It is clear from Table I that at even larger  $U$  the short-range part of the interaction will strongly overestimate the energy of band *I*. As  $\kappa$  increases to 3,  $U$  cannot be raised enough to accurately fit the energy of band *III* without making the energy of band *IV* unacceptably high. We feel that  $U = 8.0$  eV and  $\kappa = 2$  best reproduce the experimental energies. Obviously, further fine tuning of  $U$  and  $\kappa$  is possible for an even better fitting of the absorption spectrum (in particular, of band *I*), but the resultant modification in the difference between excited states (and therefore the exciton binding energy) is minimal. The procedure therefore ceases to be cost effective. In Fig. 3, we show our calculated absorption spectrum for an eight-unit PPV oligomer with  $U = 8$  eV and  $\kappa = 2$ , and the experimental absorption spectrum of poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4 phenylenevinylene] (MEH-PPV). We find nearly quantitative agreement between the calculated and experimental spectra. We reemphasize that our purpose here is to identify the best set of effective parameters for the solid-state material only, and not to deduce a parametrization for either the gas-phase materials or the PPP model in general.

The parameter search in the above is based on one assumption, viz.,  $t_0 = 2.4$  eV. We have conducted a parameter search similar to the above with larger  $t_0$ , notably  $t_0 = 3.0$  eV, in order to compare with the results of Rice and co-workers,<sup>5,6</sup> who used this value of the atomic hopping integral to arrive at much smaller Coulomb interactions. Within our procedure, the best results for  $t_0 = 3.0$  eV are obtained with  $\kappa = 1$  and  $U = 1.2$ –2.4 eV. The results for  $\kappa = 2$  and 3 yield unrealistically large energy for  $\Psi_{IV}$  even for

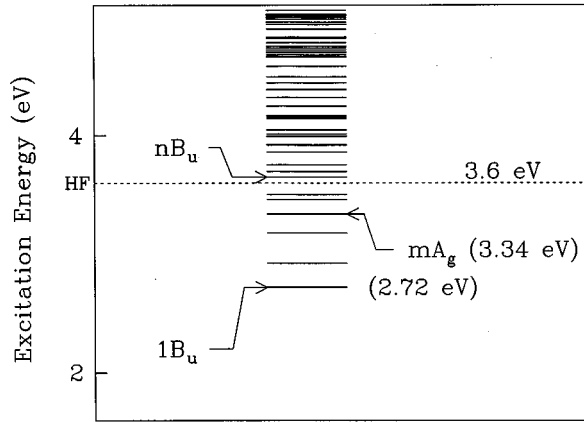


FIG. 4. The energy spectrum of an eight-unit oligomer of PPV with  $U=8.0$  eV and  $\kappa=2$ .

these small  $U$ . We do not show these results here, as the triplet absorption energies calculated with such small  $U$  are completely inconsistent with experiment (see Sec. IV).

### III. EXCITON BINDING ENERGY AND TWO-PHOTON STATES

In estimating the exciton binding energy from the calculation of the absorption spectrum, we make the following hypothesis. Previous work<sup>29</sup> showed that the conduction-band threshold state has odd-parity  $B_u$  symmetry (this is trivially true in the limit of zero intersite Coulomb interactions and arbitrary Hubbard  $U$ , where an exciton does not exist). We assume that the effective SCI Coulomb parameters that reproduce the energies of all four observed absorption features also reproduce the energies of other low-lying  $B_u$  states, including the electron-hole continuum threshold to which absorption may be weak. The chief objection to this procedure is that higher-order CI is ignored in our calculations. We do not believe this to be a serious problem, as long as we recognize that the effective Coulomb parameters obtained within SCI are not necessarily absolute and fundamental quantities, and that incorporation of higher-order CI might require modified effective Coulomb parameters, which, however, leave the separations between the low-energy  $B_u$  levels nearly intact.

In Fig. 4 we show the calculated energy spectrum of an eight-unit PPV chain for  $U=8$  eV and  $\kappa=2$ .  $1B_u$  is the lowest optical exciton. In SCI theory the continuum band threshold is at the HF band gap, which is also indicated in the figure. An alternate way to determine the conduction-band threshold is from calculations of dipole moments and nonlinear third-order optical susceptibilities.<sup>29</sup> Within both SCI theory<sup>30</sup> and exact finite-chain calculations (as interpreted by Guo *et al.*<sup>29</sup>) of the third-order optical nonlinearities of linear chains within PPP-type models, it has been demonstrated that the optical nonlinearity is primarily determined by  $1B_u$  optical exciton, the continuum band threshold state (hereafter  $nB_u$ ), and an even-parity exciton (hereafter the  $mA_g$ ) that lies energetically between  $1B_u$  and  $nB_u$ . The  $mA_g$  can be considered a charge-transfer exciton with greater electron-hole separation than the  $1B_u$ ,<sup>31</sup> and can be found from its very large transition dipole coupling with the  $1B_u$ .

The  $nB_u$  is then an even higher  $B_u$  state that also has a very large transition dipole coupling with  $mA_g$ .<sup>29</sup> Calculations of dipole moments then allow us to determine the  $nB_u$  state here in a two-step procedure. The  $nB_u$  state is also shown in Fig. 4, where it is seen to occur very close to the HF band threshold. We expect the calculated energy of  $nB_u$  (3.65 eV) to be somewhat on the high side, as is the calculated energy of  $1B_u$  (2.7 eV). Our interest, however, lies in the difference between these levels, and even with the uncertainties intrinsic to the SCI approach, we estimate the exciton binding energy to be  $0.9 \pm 0.2$  eV.

We now discuss nonlinear absorption. The  $mA_g$  state in Fig. 4 is an even-parity state that should become visible in nonlinear absorption studies like electroabsorption and two-photon absorption.<sup>29,30</sup> It should also be detectable in ps PA measurements, because of its large dipole coupling with  $1B_u$ . As in linear polyenes,<sup>24,25,32</sup> we expect all even-parity states to be described poorly within SCI, but this is not of concern here. Rather, we point out that, within the theory, the *experimental* location of the  $mA_g$  gives a lower limit of the exciton binding energy.

Within SCI there are no other interesting even-parity states. With the large exciton binding energies calculated here, one expects stable biexcitons, especially with the one-dimensional confinement in these systems. Calculations of biexcitons necessarily require multiple electron excitations (i.e., higher-order CI), and currently exist only for linear chains.<sup>31,33</sup> However, a lower limit for the energy of the lowest biexciton is easily estimated for one-dimensional systems. This lower limit is simply given by the inequality  $E_{BX} > 2 \times E_{1B_u} - \text{B.E.}$ , where  $E_{1B_u}$  and  $E_{BX}$  are the energies of the exciton and the biexciton, respectively, and B.E. is the binding energy of the exciton. In obtaining the above inequality, we ignore the repulsive interactions between the like charges in the biexciton, and therefore the true biexciton energy can only be higher than the right-hand side of the inequality. Note that, as with  $mA_g$ , the biexciton should also be visible in nonlinear absorption and ps PA studies. Furthermore, the experimentally determined energy locations of these two even-parity states give *two independent* estimates of the exciton binding energy, and establish stringent consistency requirements.

The above description of nonlinear absorptions are within the SCI, and following the interpretation of exact finite-chain calculations by Guo *et al.*,<sup>29</sup> who claimed that within the limited energy region between the optical exciton and the conduction-band thresholds, there is no fundamental difference between the results obtained within SCI and exact finite-chain calculations.<sup>31</sup> The interpretation of finite-chain calculations given by Soos and co-workers is different.<sup>34,35</sup> According to the latter authors, the  $mA_g$  actually occurs at a relatively high-energy state in weakly correlated (or strongly bond-alternated) chains. This state gradually shifts to lower energies as the effective Coulomb interaction increases (or as the effective bond alternation decreases), and for large Hubbard  $U$ , as slightly above the optical  $1B_u$  state. The energy of  $2A_g$ , the lowest even-parity states, is simultaneously lowered, and it occurs below  $1B_u$  for moderate to strong Coulomb interaction.<sup>24,25,32</sup> For intermediate Coulomb interactions then,  $mA_g$  can occur above the conduction-band threshold within the picture of Soos and co-workers. Al-

though the interpretations of nonlinear absorptions in systems with weak effective bond alternation (identified by the occurrence of  $2A_g$  below  $1B_u$ ) differ within the two interpretations of finite-chain calculations, we believe that the interpretations are similar for the opposite case of strong effective bond alternation (as would be appropriate for PPV). Now both  $2A_g$  and  $mA_g$  occur above  $1B_u$ , and within the theory of Soos and co-workers, the lowest experimentally observed two-photon state is  $2A_g$ , while  $mA_g$  is the higher-energy state.<sup>35</sup> Since the  $2A_g$  in all cases occurs below all  $B_u$  states except  $1B_u$ , and since the conduction-band threshold is  $B_u$ , we believe that even within this scenario the experimentally observed low-energy two-photon state gives a lower bound for the conduction-band threshold. Such an interpretation would agree with the case of poly(di-*n*-hexylsilane) (PDHS), where the experimental energy of the low-energy two-photon state is known precisely,<sup>35</sup> and the location of the conduction band threshold is agreed upon to be higher.<sup>36</sup>

#### IV. TRIPLET ABSORPTION

SCI is known to give too low an energy for the lowest triplet state  $T$ , relative to that of the lowest singlet excited state.<sup>37</sup> In the present case, the calculated lowest triplet for  $t_0=2.4$  eV,  $U=8$  eV, and  $\kappa=2$ , is at 1.4 eV, in agreement with the estimate by Leng *et al.*<sup>11</sup> However, this agreement is somewhat fortuitous, as the quantity more relevant than the absolute energy of  $T$  is its energy difference from the  $1B_u$ , and this is certainly overestimated in our calculation. Nevertheless, our calculation suggests that alternate theoretical estimates<sup>6,15</sup> for the energy of  $T$  are too high.

In the present context, what is more important than the absolute energy of  $T$  is the nature and location of  $T^*$ , the excited triplet to which optical absorption from  $T$  occurs. Within the SCI approximation,  $T^*$  is degenerate with the  $mA_g$ , and is therefore also an exciton.<sup>38</sup> Recent exact finite-chain calculations for the linear polyene structure have shown that higher-order CI lowers the energy of  $T^*$  relative to that of the  $mA_g$  for arbitrary Coulomb interactions.<sup>39</sup> Thus  $T^*$  occurs below the  $nB_u$ , and is also an exciton. Indeed, in the case of the linear chain and the extended Hubbard model with only nearest-neighbor intersite Coulomb interaction, extrapolations against  $1/N$  (where  $N$  is the number of carbon atoms in the chain) of the energies of  $T^*$  and the optical  $1B_u$  singlet states indicate that these energies converge in the long-chain limit.<sup>39</sup> This is not surprising, as, within correlated models,  $T$  is a covalent triplet state, and therefore  $T^*$  is the lowest ionic triplet of appropriate symmetry. With long-range intersite Coulomb interactions, it is difficult to precisely determine the energy of  $T^*$ , but in all cases it occurs below the  $mA_g$ . Nonlinear absorption measurements, which give the energy of  $mA_g$ , therefore, provide an upper limit for the energy of  $T^*$ . From the experimental triplet PA data<sup>11,16</sup> then, it becomes possible to determine an upper limit for the energy of  $T$ , which can be compared to the calculated energies of  $T$  and  $T^*$  that we and others have obtained. As discussed in Sec. V, such a comparison with experiment clearly indicates that the upper limit for the experimental energy of  $T$  is 1.4–1.5 eV. We will show from completely general arguments that the identification of  $T^*$  as an exciton rules out the possibility that the exciton binding energy is small ( $<0.2$  eV).

In Sec. II, we indicated that it is possible to explain the optical absorption of PPV with the choice of a large  $t_0=3$  eV, and relatively weak Coulomb interactions, viz.,  $U=1.2$ – $2.4$  eV within Eqs. (3) and (4). We have calculated the energies of  $T$  and  $T^*$  within the SCI for the eight-unit PPV oligomer. The calculated energies for  $T$  are 2.43 and 2.45 eV, while for  $T^*$  they are 2.83 and 3.24 eV, for  $U=1.2$  and 2.4 eV, respectively. The corresponding energy differences between  $T^*$  and  $T$  are considerably smaller than the experimental triplet absorption energy (see below). This particular result is in agreement with the work in Ref. 6, where the binding energy of  $T$  was calculated to be only 0.8 eV, and allows us to discard the large- $t_0$  weak Coulomb interaction parametrization.

#### V. COMPARISON TO EXPERIMENTS

In this section we list different spectroscopic measurements that seem to support our estimate of the exciton binding energy,  $0.9\pm0.2$  eV. We also point out that these experiments rule out the small estimate of the exciton binding energy.<sup>5,13,18</sup> Following this, we discuss theoretical and experimental work that claimed to obtain the intermediate value for the binding energy.<sup>6,10,14,15,17</sup> Clearly, the situation here is more complicated, and further work is warranted to resolve some of the issues.

The low-energy two-photon exciton state, predicted within our theory, has been seen in two-photon fluorescence spectroscopy<sup>19</sup> and electroabsorption,<sup>11,40</sup> and, more recently, in direct two-photon absorption<sup>20</sup> and ps PA.<sup>21,41</sup> The experimentally determined energy of this state is nearly the same from the four different kinds of experiments. Two-photon fluorescence spectroscopy places this important even-parity state at 2.95 eV in unsubstituted PPV,<sup>18</sup> about 0.55 eV above the exciton in the unsubstituted material, in which the excitons is thought to occur at 2.4 eV. Note that in the substituted PPV derivatives there is general agreement that the  $1B_u$  exciton occurs at still lower energy,  $\sim 2.1$ – $2.2$  eV, and the occurrence of the  $A_g$  state at the same energy as in the unsubstituted material would be in strong agreement with our theoretical result. Vardeny and co-workers carried out electroabsorption studies on a number of PPV derivatives<sup>11,40</sup> as well as in polyphenyleneacetylene,<sup>42</sup> which is structurally related to PPV, and in which the vinylene linkage replaced by an acetylenic bond. In all cases, the lowest two-photon state is determined to be located considerably above  $1B_u$ , at nearly the same energy as obtained in the earlier two-photon study.<sup>19</sup> Based on their fittings of the electroabsorption spectra, these authors place  $1B_u$  in PPV derivatives at 2.15 eV and the observed two-photon state at greater than 2.8 eV, which would indicate that the exciton binding energy is greater than 0.65 eV.

Two different PA bands are seen in ps PA measurements: a low-energy band in the infrared<sup>21,41</sup> and a second high-energy band in the visible.<sup>11,41</sup> The interpretation of the PA in thin films has been controversial, and ps PA has been claimed to originate both from the optically created exciton<sup>11</sup> as well as a “spatially indirect exciton” or “bound polaron pair,”<sup>41,43</sup> in which the electron and hole reside on different

chains or different conjugated segments of an interrupted strand.<sup>41,43</sup> The origin of this controversy lies in the seemingly uncorrelated dynamics of photoluminescence (PL) and PA in some thin-film samples at long times ( $>400$  ps), when PL is nearly quenched but PA is still existent.<sup>41</sup> Interestingly, PA and PL dynamics are correlated in solutions and blends, while at the same time the PA energies are the same in all cases, thus suggesting a common origin of PA and PL, viz., the optical exciton. Very recent experimental work by Frolov *et al.*<sup>21</sup> on samples of (2,5)-dioctyloxy PPV in the form of freshly prepared films and solutions has very clearly demonstrated that PL and PA dynamics are correlated, and has also suggested that the lack of correlation between these two processes is extrinsic in origin and is sample dependent. Identical conclusions were reached by Samuel *et al.*,<sup>44</sup> who also found that the lack of correlation is strongly sample dependent. High-energy PA has also been observed in poly(pyridilvinylene) by Blatchford *et al.*,<sup>45</sup> who examined thin films, solutions, and powder samples, and concluded that PA in all cases is from the optical exciton. According to these authors, the origin of the difference in emission efficiencies between solutions and thin films arises from the tendency to aggregate formation in the latter.<sup>46</sup> The details of the aggregate formation process as well as the reason behind the smaller emission efficiency from the exciton within the aggregate structure are currently not well understood.

Note that PA from the optical exciton would be in agreement with our theory. The low-energy PA in the infrared has a sharp threshold behavior at about 0.7 eV,<sup>21</sup> which would correspond to the energy difference between the dominant  $A_g$  exciton below the conduction band and the  $1B_u$  exciton. This interpretation of the low-energy PA is consistent with the direct two-photon absorption measurement,<sup>20</sup> which finds a sharp threshold behavior in the two-photon absorption, due to an even-parity state that occurs at 3–3.1 eV. It is also to be noted that a very recent third-harmonic-generation measurement of unsubstituted PPV places the conduction band threshold at  $3.2 \pm 0.1$  eV.<sup>47</sup> All of these results would agree with the large exciton binding energy calculated here.

In the above we have focused on the low-energy PA. The high-energy PA occurs at 1.7 eV in the unsubstituted PPV, and at 1.5 eV in the derivatives.<sup>11,41</sup> Within our model this PA is from the exciton to the biexciton, whose energy we have already estimated to be greater than  $2 \times E(1B_u) - B.E.$  Substituting for the experimental  $1B_u$  energy and the experimental biexciton energy (as obtained from the PA energy) in this expression, we once again arrive at the result that the binding energy of the exciton is greater than 0.7 eV. We believe that as far as the location of the conduction-band threshold is concerned, these interpretations of ps PA do not change fundamentally even within the scenario of Soos and co-workers,<sup>34,35</sup> as discussed above. The situation in PPV is analogous to that in PDHS, a strongly dimerized linear chain. Two strong two-photon features have been detected also in PDHS, and the conduction-band threshold is above the lower two-photon state.<sup>36</sup>

In addition to the singlet PA, the triplet PA is also of interest. Experimentally, the triplet PA occurs at 1.4 eV.<sup>11,16</sup> Within the SCI,  $T^*$  is degenerate with the  $mA_g$  exciton. If the latter is placed at 2.9–3.0 eV (see above), then state  $T$  would be at about 1.5 eV, considerably below other theoretic

cal estimates.<sup>6,15</sup> Our identification of  $T^*$  as an exciton, even within complete CI investigation of finite chains,<sup>39</sup> precludes the small exciton binding energy. This conclusion is reached in the following manner. Based on the luminescent characteristic of PPV, it is known that the true correlated  $2A_g$  state in PPV is above the  $1B_u$ .<sup>48</sup> It is further known that  $E(2A_g) \leq 2 \times E(T)$ , where  $E(2A_g)$  and  $E(T)$  are the energies of the correlated  $2A_g$  and the lowest triplet state. This inequality simply reflects the fact that, in the weakly correlated limit,  $2A_g$  and  $T$  have nearly equal energies in the long-chain limit, whereas in the strongly correlated limit  $2A_g$  is the bound state of two antiferromagnetic magnons. Even assuming that  $2A_g$  is considerably below the experimentally observed low-energy two-photon state at 2.9–3.0 eV, the lowest possible energy of  $2A_g$  is then 2.4 eV, which would place state  $T$  at 1.2 eV or above. Consequently, from the triplet PA energy of 1.4 eV, the lowest energy possible for the  $T^*$  exciton is 2.6 eV or more, and the exciton binding energy is greater than 0.2 eV. It is easily ascertained that the same arguments lead to a binding energy of greater than 0.3 eV if  $1B_u$  is assumed to be at 2.2 eV instead of 2.4 eV, and that the estimate for this lower limit for the binding energy increases the higher the energy of the  $2A_g$  is assumed to be.

The intermediate binding energy has been estimated from the experimental works by the Marburg group (Ref. 10) and the Cambridge group (Ref. 14), and has also been claimed in different theoretical calculations.<sup>6,15,17</sup> Although it is not possible to rule out this estimate from simple considerations (as would be the case for the small binding energy, see above), we point out that the experimental estimates are not based on direct measurements, and at least in some cases, the experimental results can equally well be interpreted within the large binding-energy scenario. For example, Bässler and co-workers, in a systematic fashion, showed that photogeneration of carriers in unsubstituted PPV and PPV derivatives is a secondary process that involves electric-field-induced exciton dissociation and formation of geminate pairs (note that this is in agreement with the result obtained by us and others that the real materials have short conjugated segments).<sup>9,10,23</sup> The occurrence of photoconductivity at the absorption threshold is therefore not a signature of weak exciton binding. Bässler and co-workers therefore focused on the field-induced quenching of luminescence in a poly(phenylphenylenevinylene) blend, and within a phenomenological model were able to fit the dynamics of field-induced quenching, obtained by femtosecond luminescence spectroscopy, with a binding energy of 0.4 eV.<sup>10</sup> The number of parameters that enter into their description of luminescence quenching is large, and very recent work by the same research group indicates that the data can also be fit by a binding energy as large as 1 eV.<sup>23</sup> In Ref. 14, it was found that within the single-layer light-emitting diode structure the photocurrent is strongly dependent on the bias voltage, thus indicating an internal field within the device. At each bias voltage the photocurrent is temperature dependent, with nearly Arrhenius-type behavior. Extrapolating to a high bias voltage where the internal field was supposedly zero, the activation energy could be determined, and it is this energy that is 0.4 eV. Whether or not this is the true binding energy of the material

is, we believe, debatable. We point out, for instance, that from very similar measurements it was found in Ref. 2 that at high bias voltages the slope of the photoconductivity changes dramatically at about 3.1–3.2 eV, in a region where there is little absorption, suggesting this to be the continuum threshold.

As far as the existing theoretical literature supporting the intermediate binding energy is concerned, we have already shown that result obtained in Ref. 6 is primarily a consequence of choosing a large  $t_0$ , which leads to small Coulomb interactions and consequently, small exciton binding energy. We are unable to compare our results against those obtained in Ref. 15. Although it is claimed there that the results are in agreement with the intermediate binding energy, we have been unable to see how this conclusion is reached. Only the singlet and triplet absorptions were calculated by these authors. Neither the continuum threshold was evaluated, nor the nature of  $T^*$  determined. Finally, within the theoretical work of Gomes da Costa and Conwell<sup>17</sup> that uses a formalism valid for Wannier excitons in conventional semiconductors, the exciton binding energy is inversely proportional to the transverse static dielectric constant  $\epsilon_{\perp}$  [see Eq. (4) of Ref. 17]. The authors quote an  $\epsilon_{\perp}$  of  $2.25 \pm 0.4$  (measured at 1000–4000  $\text{cm}^{-1}$ ), but choose to evaluate their binding energy for  $\epsilon_{\perp}=3$  to obtain the value of 0.4 eV. If the lower limit for the transverse dielectric constant is chosen instead, one obtains a value for the binding energy that is close to our lower limit for this quantity.

## VI. CONCLUSION

Within a model involving long-range Coulomb interactions, the multiple absorption bands in the absorption spectra of PPV derivatives can be fit with a unique set of interaction parameters. This reflects the balancing of the short- and long-range part of the intersite Coulomb interactions that is required for fitting both the low- and high-energy bands in the absorption spectra, and very similar results have been obtained by us with other functional forms for the Coulomb interactions. From the calculated electronic structure for the best parameter set the exciton binding energy is large,  $0.9 \pm 0.2$  eV, a result supported by electroabsorption, two-photon absorption, ps and cw PA. The triplet absorption energy rules out a binding energy of 0.2 eV or less. At least some of the theoretical and experimental results suggesting an intermediate binding energy can also be explained within the large binding-energy scenario. Further theoretical and experimental work would be necessary to settle the issue of the exciton binding energy in PPV completely.

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