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Excitons and the band gap in poly(phenylene vinylene)

P. Gomes da Costa and E. M. Conwell
Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York 14627
and Xerox Webster Research Center, Webster, New York 14580

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The large extent of the singlet exciton in poly(phenylene vinylene) (PPV) and the small Stokes shift suggest an effective-mass calculation for determining the exciton binding energy E_b. We have carried out such a calculation using the electron and hole masses determined by a local-density-functional band-structure calculation. The resulting E_b is 0.4 eV, which leads to a gap of ~2.8 eV rather than the usually accepted 2.4 eV.

It has been well documented that photon absorption in poly(phenylene vinylene) (PPV), which was found to rise rapidly for photon energies ~2.4 eV,[1] results in creation of a singlet exciton.[2] Radiative decay of the exciton produces photoluminescence with the highest energy within 0.1 eV of the absorption edge.[3] Because photoconductivity has also been observed to occur for photons of energy ~2.4 eV,[4] it has generally been assumed that the band gap of PPV is 2.4 eV.[1] This implies that the binding energy of the exciton is negligible. We show below that this is not the case, and the value of the gap must be corrected for this binding energy. Increase of the size of the gap has implications for the size of the polaron binding energy, as will be discussed below.

Comparison of emission and absorption of PPV oligomers of different lengths with that of the polymer led to the conclusion that the singlet exciton extends over at least six unit cells, i.e., 39 Å.[5] More recent studies, with PPV of greater conjugation length, and oligomers up to seven phenyl rings, suggest that the exciton length is even greater.[6] The small difference observed between emission and absorption edges, specifically a Stokes shift of less than 0.08 eV,[7] suggests that little lattice distortion is involved in the creation of this exciton. On the basis of the great length and apparent unimportance of lattice distortion we have carried out an effective-mass treatment for this exciton of the kind that has been done for Wannier excitons in many inorganic semiconductors.[8,9]

PPV is monoclinic. Ideally it can occur in two structural modifications, corresponding to the space groups $P2_1/a$ and $P2_1/n$, which differ by a displacement of neighboring chains. We have carried out a local-density-functional calculation of the band structure for both $P2_1/a$ and $P2_1/n$ structures.[10] The total energies for the two structures are quite close. In both cases the constant energy surfaces close to the conduction- and valence-band edges are ellipsoidal with one principal axis directed essentially along the chain axis. The masses $m_\parallel$ parallel to the chain axis of electrons at the conduction-band edge and holes at the valence-band edge are almost the same for $P2_1/n$ and $p2_1/a$. However, the principal axes in the plane perpendicular to the chain axis are different for the conduction and valence band in both structures. The significance of the latter result for actual PPV samples must be assessed in light of the facts that the experiments are usually done on unoriented spin-coated samples and the interchain ordering is poor, electron microscope analysis of one group showing ordered or coherent regions 5–10 nm in size alternating with disordered regions.[11] For our calculations we therefore took the cross sections of the ellipsoids perpendicular to the chain direction to be circular, with mass $m_\perp$ given by the average mass for the two principal axes perpendicular to the chain direction. Although the band edges are not at the center of the Brilloun zone, they are, within the error of our calculations, at the same **k** value for the conduction and valence bands.[10] With that, and the cylindrical symmetry we have assumed, the effective-mass equation for the envelope function $F(x,y,z)$ for the exciton takes the form[8,9]

$$\left[-\frac{\hbar^2}{2\mu_\perp}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]-\frac{\hbar^2}{2\mu_\parallel}\frac{\partial^2}{\partial z^2} + V(x,y,z)+E\right]F(x,y,z)=0\ , \quad (1)$$

where x, y, and z are the relative coordinates of electron and hole. The exciton mass transverse to the chains, $\mu_\perp$, is the product of electron and hole masses perpendicular to the chain axis divided by their sum. A similar relation holds for the mass $\mu_\parallel$ parallel to the chains. The potential energy is given by[12]

$$V(x,y,z)=-e^2[\varepsilon_\perp\varepsilon_\parallel(x^2+y^2)+\varepsilon_\perp^2 z^2]^{-1/2}\ , \quad (2)$$

where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are the components of the static dielectric tensor parallel and perpendicular to the chain, respectively. In Eq. (1) it has been assumed that the center of mass of the exciton is stationary. E is the negative of the exciton binding energy because the zero of energy is taken at the edge of the conduction band. We now make the substitutions in Eqs. (1) and (2),

$$z'=(\mu_\parallel/\mu_\perp)^{1/2}z,\ \ x'=x,\ \ y'=y\ , \quad (3)$$

and introduce as units of energy and length the effective Rydberg R_B and the effective Bohr radius a_B, given by

$$R_B=\mu_\perp e^4/2\hbar^2\varepsilon_\parallel\varepsilon_\perp\ , \tag{4}$$

$$a_B=\hbar^2(\varepsilon_\parallel\varepsilon_\perp)^{1/2}/\mu_\perp e^2\ . \tag{5}$$

With these changes we obtain from Eqs. (1) and (2):

$$[-\nabla^2(x',y',z')-2(x'^2+y'^2+\gamma z'^2)^{-1/2}+E]F(x',y',z')=0\ , \tag{6}$$

where $\gamma=\varepsilon_\perp\mu_\perp/\varepsilon_\parallel\mu_\parallel$.

We have solved Eq. (6) both by a variational method and exactly with a numerical solution. The variational solution was taken to be of the form

$$F(x',y',z')=(\pi a^2 b)^{-1/2}\exp[-(r'^2/a^2+z'^2/b^2)^{1/2}]\ . \tag{7}$$

The standard procedure was followed to obtain the values of a and b that minimize the energy. To obtain an exact solution we made use of the fact that the solution of

$$H\Psi=-\partial\Psi/\partial t\ , \tag{8}$$

where H is the Hamiltonian of Eq. (6), may be written as a sum of solutions of Eq. (6), i.e.,

$$\Psi=\sum_n c_n F_n(x',y',z')\exp(-E_n t)\ , \tag{9}$$

E_n being the eigenvalue corresponding to the solution F_n. When Eq. (8) is solved iteratively, and the eigenfunction normalized at each iteration, only the lowest-energy solution survives for large t. This provides a quick method for finding the lowest-energy solution, avoiding diagonalization of large matrices.[13]

It is clear from Eq. (6) that in units of R_B the binding energy E_b decreases monotonically with γ. In fact, we found from the exact solution that E_b in units of R_B decreases linearly as γ increases from unity, for which it has its maximum value of 1.3, to a value of 16, the largest for which we calculated. At $\gamma=1$ the anisotropy of the dielectric tensor just compensates that of the exciton mass. As will be seen, the mass anisotropy is much larger than that of ε, and $\gamma>1$. Note, however, that an increase in $\mu_\perp/\mu_\parallel$ does not necessarily decrease E_b in units of eV because R_B increases with $\mu_\perp$.

To evaluate E_b we took the static values of $\varepsilon_\parallel=8$,[14] $\varepsilon_\perp=3$. The latter has been measured as 2.25±0.4 for frequencies in the range 1000–4000 wave numbers.[15] Effective masses of the electron and hole were obtained from our band-structure calculations,[10] specifically from the curvature of E versus k at the band edge. For $P2_1/a$ where the band edge is at (or very close to) point B in the Brillouin zone, we obtain the effective masses parallel to the chain $m_\parallel=0.117m_0$ for electrons, $0.0658m_0$ for holes, where m_0 is the free electron mass. Combining these gives $\mu_\parallel=0.0421m_0$ for $P2_1/a$. The same value was obtained for $P2_1/n$. The electron masses perpendicular to the chain direction for $P2_1/a$ were $7.63m_0$ and $2.07m_0$, giving an average of $4.86m_0$. For holes the perpendicular masses were $1.52m_0$ and $3.80m_0$, giving an average of $2.66m_0$. These values combined to give $\mu_\perp=1.72m_0$ for $P2_1/a$. The value for $P2_1/n$ is sufficiently close that separate calculations were not done for that case. For the values of the various parameters given, $\gamma=15.3$ and $R_B=0.974$ eV. The variational calculation resulted in $E=-0.317R_B$, and thus a binding energy of 0.31 eV. The exact calculation gave $-0.42R_B$, corresponding to a binding energy of 0.41 eV. As noted earlier, because the absorption edge corresponds to exciton absorption, this result indicates that the band gap in PPV is 0.4 eV larger than was previously considered to be the case.

Before we discuss further the significance of this result, we should point out that it is somewhat uncertain because of the uncertainty of the parameters. The uncertainty of $\varepsilon_\perp$ is clear from the above discussion. The masses are also somewhat in doubt because they were obtained from a local-density-functional (LDF) calculation[10] in which, as is usually the case for such calculations, the gap was considerably underestimated (by about a factor 2). As pointed out by Zhu, Hybertsen, and Louie,[16] for a carrier effective mass $m<m_0$ the underestimate of the gap leads to the LDF mass value being too small. This can be understood from the perturbation theory expansion of $(1/m-1/m_0)$ obtained by the $\mathbf{k}\cdot\mathbf{p}$ method.[17] For the conduction-band edge, for example, with energy E_c, each term in the expansion contains the absolute squared of the momentum matrix element connecting the conduction band with the nth band, divided by $(E_c-E_n)>0$, making $1/m>1/m_0$. If (E_c-E_n), i.e., the LDF calculated gap, is too small, $(1/m-1/m_0)$ is too large and m is too small. Thus $m_\parallel$ obtained from the LDF calculation is too small, perhaps by as much as a factor 2. For $m_\perp$, which is greater than m_0, the bands above the conduction band, i.e., $E_n>E_c$, must dominate the expansion. This will result in $m_\perp$ being underestimated also.[18] The terms due to the higher bands are not expected to be much affected in the error leading to the smaller gap, but the larger value of the term involving the gap will result in $(1/m_\perp-1/m_0)$ being less negative, thus $m_\perp$ smaller. The likely result is that the correct ratio $\mu_\perp/\mu_\parallel$ is somewhat larger than that obtained from the uncorrected LDF masses.[18] This would increase γ, decreasing the binding energy in R_B units. That would be counteracted, however, as discussed earlier, by the increase in R_B due to the increase in $\mu_\perp$. It is likely that correcting the underestimates in the exciton mass would not affect the binding energy much.

The values of the parameters in Eq. (7) obtained by the variational solution are $a=2.1$, $b=1.5$. The latter, with the other parameters we are using, gives the dependence of F on z along the chain direction as $\exp(-z/14.5)$ for z in Å. The exact solution, two quadrants of which are shown in Fig. 1, decays much more slowly, dropping to $1/e$ of its value at the origin at $z=37$ Å, a distance of almost six unit cells. Even at 50 Å F is 16% of its value at the origin. Thus the exciton length is ~100 Å according to the calculation. Unlike the case of the binding energy, however, the underestimate of the masses should result in the length being overestimated due to the dependence of a_B on $1/m_\perp$. For example, if both $m_\perp$ and $m_\parallel$ were actually twice as large as the LDF result, leaving γ and the

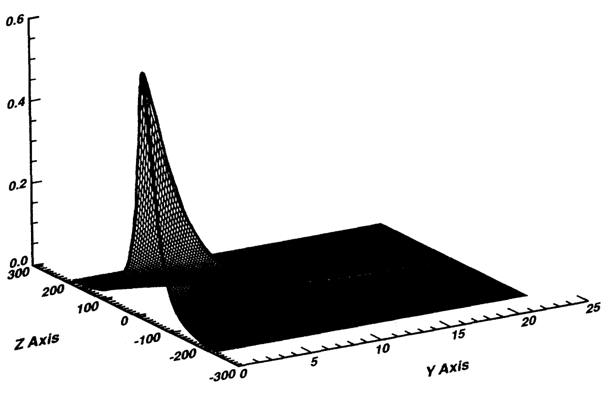

FIG. 1. Calculated wave function vs distance for singlet exciton in PPV. Note that the scales are different along the z (chain) and y axes.

solution of Eq. (6) unchanged, a_B and thus the extent of the exciton on the chain would be exactly $\frac{1}{2}$ as large as shown. This would still be consistent with the oligomer results of Ref. 5. Perpendicular to the chain the variational solution gives $F \propto \exp(-r/3.17)$. Again, the exact solution extends further, with the $1/e$ point at 5 Å. With the average interchain distance ~4 Å, this indicates, if we allow for an error in $m_\perp$, that the amplitude on the next chain is ~10% or less. In regions of poor interchain registry the amplitude on the next chain could be very much less. Thus it is not unreasonable that the properties of the excitons in the polymer should be similar to those on the oligomers.

It is instructive to note the similarities and differences between the singlet excitons in PPV and PDATS (polydiacetylene with toluene sulfonate side groups). Due to the relatively large side groups, PDATS is more one dimensional than PPV, with an interchain distance of 7.5 Å compared to the average interchain distance of ~4 Å in PPV. The energy gaps are about the same, however. Reflectance and electroflectance studies of PDATS and other polydiacetylenes have led to the picture of a singlet exciton extended over a number of unit cells with a binding energy of 0.5 eV.[19] Also similar to PPV, the effective mass of this exciton parallel to the chains, deduced from comparison of the observed Franz-Keldysh effect to theory, is $0.05m_0$,[19] quite close to the $0.04m_0$ value obtained for PPV. The considerably larger interchain distance suggests that $m_\perp$ for PDATS is larger than that for PPV. As discussed earlier, how the larger $m_\perp$ affects the value of E_b depends both on the values of γ and $m_\perp$. The larger E_b in this case suggests a γ value comparable to that of PPV or lower.

For PDATS and other polydiacetylenes photoconductivity is observed to start at a photon energy a few tenths of an eV above the absorption edge.[20] This, in fact, was taken as evidence that the conduction-band edge lies some tenths of an eV above the absorption edge, the difference being the binding energy of the exciton.[20] As noted earlier, the situation in PPV is different, photoconductivity being observed to start at the absorption edge.[4] This suggests that photoconductivity is due to exciton dissociation in PPV.[21] A mechanism for the dissociation was suggested by Frankevich *et al.* on the basis of the magnetic-field dependence of photoconductivity observed by them.[21] The first step in the dissociation would be a hop of the electron or hole to a nearby chain. The electron and the hole would then evolve into polarons, still bound to each other by Coulomb attraction. Subsequent thermal motion would result either in dissociation of the geminate polaron pair, creating free carriers, or reassociation into excitons. In the model of Frankevich *et al.* the exciton was considered to be a tightly bound (Frenkel) exciton confined to a single chain. This was inconsistent with the assumption of the model that the interchain hop of the electron and hole requires no activation energy. In our model of the exciton, however, the separation could occur with reasonable probability and no activation energy because the wave function of the exciton is still sizable on the next chain. (The larger interchain separation for PDATS, with the resulting much smaller amplitude of the exciton wave function on the next chain, could explain why exciton dissociation, and the resulting photocarrier generation, do not occur in that case.) One may envision the dissociation as occurring when the exciton in its thermal motion drifts from a coherent region (adjacent chains in registry), in which the electron and hole are momentarily on different chains, to an incoherent region. The binding energy of the resulting polaron pair should be quite similar in magnitude to that of the exciton. The combination of thermal motion and proximity of other coherent and incoherent regions would determine whether the geminate polaron pair dissociated, creating free carriers, or reassociated into an exciton.

Having a value for the binding energy of the exciton we know the correction to the threshold for photon absorption required to give the energy gap. Unfortunately this threshold is difficult to determine because optical absorption measurements show a long tail to low energy, due to disorder, scattering, and the effects of uncorrected reflection contributions.[22] From site-selective single-photon fluorescence excitation in long conjugation length samples Baker, Gelsen, and Bradley estimate the energy of the zero phonon transition as 2.36 eV. Adding 0.4 eV for the exciton binding energy, we obtain a gap of 2.76 eV. Although our results for the exciton binding energy are somewhat uncertain because of the uncertainty in the parameters there are indications that our value for the gap is correct to within ~0.1 eV. For PDATS and other polydiacetylenes the oscillations representing the vibronic progression are reduced to very small amplitude in ε_2, the imaginary part of the dielectric tensor, at the energy where the conduction band starts. In PPV at 78 K the oscillations in the absorption are reduced to small amplitude at ~2.7 eV. An upper limit for the gap is set by the optical absorption due to the transition between the flat band just below the top pair of valence bands and its (approximate) mirror image (about midgap) above the lowest pair of conduction bands. These bands correspond to wave functions concentrated on the phenyls.[10] Because of the small dispersion of these bands transitions between them produce a narrow high-intensity absorption band above 5.5 eV, reaching a peak at about 6 eV.[23] On the basis of our band-structure calculations fitting this absorption sets an upper limit of ~2.7 eV on the gap.

We noted earlier that our LDF band structure for PPV, although giving quite good results for the valence-band density of states,[24] considerably underestimated the gap. As is frequently done, we corrected the calculations by incorporating a rigid upward shift of the conduction-band states calculated to match what we took to be the experimental gap, 2.4 eV.[10] In light of the above discussion our band structure must be further corrected by shifting the conduction band upward by another 0.4±0.1 eV.

The observation that the emission in electroluminescent diodes is the same as the photoluminescence has led to the suggestion that the polaron levels are at or very close to the valence- and conduction-band edges.[25] Polarons with levels within, say, 0.1 eV of the band edge would, however, be unstable versus thermal decomposition at room temperature. The current carriers in electroluminescent diodes at room temperature would then be free electrons and holes. A binding energy for the exciton of 0.4 eV, however, allows the polaron levels to be separated from the band edges by up to 0.4 eV, and thus to be stable. Optically detected magnetic resonance experiments have documented the existence of polarons in PPV.[26]

In conclusion, using effective-mass theory and the electron and hole masses obtained from our calculation of the three-dimensional band structure of PPV, we find the singlet exciton binding energy to be 0.4 eV, within ~0.1 eV. The calculation includes no arbitrary parameters. Justifying the use of the effective-mass formalism, we find along the chain the amplitude of the exciton wave function drops by a factor $1/e$ only after an electron-hole separation of ~5 unit cells. Perpendicular to the chain the extent of the exciton wave function on the next chain is sufficient to lend support to the mechanism for photocarrier generation by Frankevich *et al.*[21] Our best estimate of the band gap of PPV is 2.8 eV, within ~0.1 eV.

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