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_Citation for published version (APA):_

_DOI:_
10.1103/PhysRevB.71.205206

_Document status and date:_
Published: 01/01/2005

_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:_

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
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Polarons in semiconducting polymers: Study within an extended Holstein model

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(Received 11 October 2004; revised manuscript received 28 January 2005; published 19 May 2005)

We present a study of electron- (hole-) phonon interaction and polaron formation in semiconducting polymers within an extended Holstein model. A minimization of the lowest electronic state of this Hamiltonian with respect to lattice degrees of freedom yields the polaronic ground state. Input parameters of this Hamiltonian are obtained from ab initio calculations based on the density-functional theory. We calculate optical phonon modes and the coupling constants of these modes to the highest occupied and lowest unoccupied molecular orbital bands, respectively. For the studied polymers [polythiophene, poly(phenylenevinylene), poly(para-phenylene)] the polaron binding energy, its size, and the lattice deformation as a function of conjugation length have been determined. Self-trapped polarons are found for long conjugation lengths. Energies of prominent PPV modes involved in polaron formation agree with infrared spectra. The polaron binding energies we find are much smaller than the width of the energy disorder in polymeric systems of practical importance, thus self-trapping effects can be ignored in practice.

DOI: 10.1103/PhysRevB.71.205206

PACS number(s): 71.38.Ht, 63.20.Kr, 78.30.Jw

I. INTRODUCTION

The concept of a self-trapped carrier or polaron in conjugated polymers has played an important role in theories about the electronic structure of these materials, starting with the groundbreaking work of Su, Schrieffer, and Heeger.1

Within the framework of ab initio electronic structure theory, studies of self-trapped carriers have been performed by taking a finite polymer segment (oligomer) of N units and analyzing the change of the atomic equilibrium configuration upon charging the system, for large N.2–7

The general conclusion drawn from such calculations based on the density-functional theory (DFT) is that no clear self-trapping, which should always occur in a one-dimensional system,8 is observed for the studied oligomers of computationally feasible sizes.3–5,7 In Ref. 3 oligothiophenes were studied up to 16 thiophene units. The author found a lower bound for the localization length of 60 Å and an upper bound for the relaxation energy of 0.04 eV. In these calculations the extra charge was observed to be almost equally distributed across the whole length of the oligomer. The same conclusion was drawn by Moro et al. for oligothiophenes up to ten units.4 Similar observations were made for oligo(phenylenevinylene) (OPVs).5,7 In stark contrast to this, calculations for oligomers based on (parametrizations of) Hartree-Fock (HF) show a clear localization of the charge in the middle of the oligomer.2,4,7

All DFT calculations for charged oligomers mentioned earlier were based on the local density approximation (LDA), some including the generalized gradient approximation (GGA). However, it has been shown that in order to describe the static polarizabilities of oligomers of increasing size correctly9 it is necessary to take into account the ultranonlocality of the exact exchange-correlation potential in DFT.10 Within LDA/GGA the calculated polarizabilities are overestimated by a substantial amount. This fact casts doubts on the use of LDA/GGA for calculating the properties of charged oligomers, because the screening of the extra charge will be too large. This in turn will counteract localization effects and may explain the fact that no localization effects have been observed in calculations based on DFT.

In the present paper we adopt a different strategy, avoiding calculations for charged oligomers. The key idea is based on the statement that the ionization energy of a large system is correctly described by the Kohn-Sham energy of the highest occupied state given by DFT.11 This means that the hole-polaron energy should be correctly obtained by minimization of $E_{\text{el}} + E_{\text{el}}$. Here, $E_{\text{lat}}$ is the total lattice energy and $E_{\text{el}}$ is minus the Kohn-Sham energy of the highest occupied state. By definition, $E_{\text{el}}$ contains all the effects of coupling with the vibrational degrees of freedom of the lattice. We stress that both these energies refer to the neutral system. An analogous statement for the lowest unoccupied state does not strictly hold true, because of the gap problem in DFT,11,12 but since we are interested in energy differences instead of absolute values the error made when applying a similar minimization should be small. Since in the DFT calculations later we only determine properties of uncharged systems the problems related to overestimation of polarizabilities mentioned earlier will not occur.

The strategy described in the previous paragraph could in principle be applied to oligomers of different size. However, we want to make our method as flexible as possible and applicable to large systems. Therefore, we now make the following further assumptions: (1) We assume that not only the coupling of the vibrations to the energies of band extrema are correctly described within DFT, but also the coupling to the dispersions around the band extrema (the band masses). This assumption is justified by the fact that, although band gaps are not predicted reliably by DFT, DFT band masses turn out to be quite comparable to those of more sophisticated many-body approaches.12 (2) We assume that the electron-phonon coupling has a local character, meaning that the vibrations located at a certain unit of the polymer (which we will specify in the next section) only influence the electronic structure parameters of that unit and the coupling to...
neighborsing units. This locality assumption also means that we can limit ourselves to optical phonons at the \( \Gamma \) point, which describe local vibrations. Although the locality assumption will have its limitations, we expect this assumption to hold if the chosen unit cell is large enough. (3) On the other hand, in our method we assume that the chosen unit cell is small compared to the size of the polaron. The reason why we make this assumption is that the size of the Brillouin zone of the model Hamiltonian to be discussed later should be larger than the region in the vicinity of the band extrema needed to describe the polaron state. We will demonstrate that both conditions (2) and (3) can be satisfied simultaneously.

II. METHOD DESCRIPTION

Within DFT-LDA we perform calculations with the \textit{ab initio} program \textsc{vasp},\textsuperscript{13,14} which enables both the electronic and geometric structure optimization of the studied polymer systems [polythiophene (PT), poly(phenylenevinylene) (PPV), and poly(\textit{para}-phenylene) (PPP)]. The calculations are performed with a supercell geometry, and the lattice parameters are such that our results reflect those of a single infinite polymer chain. In case of PT, there are two thiophene rings in the unit cell (see Fig. 1). In the case of PPV the unit cell contains one phenyl ring and one vinyl group. PPP is represented by a repeated unit cell with two phenyl rings with a torsional angle which was found to be 32°. For all three polymers the unit cell is also chosen to be the unit in the model Hamiltonian later. We calculate the normal vibrational modes at the \( \Gamma \) point by the direct method.\textsuperscript{15} For the polymer chain distorted by a small amount \( x^\nu \) (in the harmonic regime) according to every normal mode \( \nu \) the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) bands are obtained.

We introduce an extended Holstein model Hamiltonian to describe the interaction between electrons (holes) and phonons. The electrons (holes) are treated quantum mechanically, and phonons classically. The full Hamiltonian has the form

\[
H_{\text{tot}}(\{x\}) = H_{\text{el}}(\{x\}) + E_{\text{lat}}(\{x\})
\]

\[
= \sum_i \left( \epsilon + \sqrt{\sum_{\nu} g^\nu x^\nu_i} a_i^\dagger a_i \right) + \sum_{(i,j)} \left( J + \frac{1}{\sqrt{2}} \sum_{\nu} \phi^\nu (x^\nu_i + x^\nu_j) \right) a_i^\dagger a_j + \frac{1}{2} \sum_{\nu,i} E^\nu (x^\nu_i)^2,
\]

where \( \epsilon \) is the on-site energy of an electron (hole) and \( J \) is the transfer integral from one unit to the neighboring unit, both within a nondistorted polymer chain. \( x^\nu_i \) is the amplitude of phonon mode \( \nu \) at unit cell \( i \). \( g^\nu \) and \( \phi^\nu \) are the local and nonlocal coupling constants for phonon mode \( \nu \) with energy \( E^\nu \). We have assumed that the lattice distortions are small enough for the harmonic approximation to hold.

We obtain the parameters of this Hamiltonian in the following way. We fit the parabolic vicinity of the DFT LUMO and HOMO band extrema to that of a tight-binding model to obtain \( \epsilon \) and \( J \) for the undistorted configuration, and \( g^\nu \) and \( \phi^\nu \) for the configuration distorted according to each phonon mode separately. From this we find

\[
g^\nu = \frac{\epsilon^\nu - \epsilon}{\sqrt{2} \epsilon^\nu} \quad \phi^\nu = \frac{J^\nu - J}{\sqrt{2} \epsilon^\nu}.
\]

The index \( i \) of the variable \( x^\nu_i \) has been dropped because at this stage we consider a periodic infinite chain, in which the amplitude of each phonon mode \( \nu \) is the same for all unit cells. In the later stage of our calculations the phonon amplitude will be free to vary along the polymer chain. Nevertheless, we will use the same coupling constants, on-site energies, and transfer integrals. This is where we use the locality approximation (2), assuming that the phonon amplitude at a certain site affects the on-site energy of this site and the transfer integrals to the neighboring sites only.

In fact, the Hamiltonian Eq. (1) can be considered as a convenient discretization of space. The actual HOMO and LUMO bands in the whole Brillouin zone cannot be accurately described by this Hamiltonian. However, the lowest polaron state is built up from states close to the band extrema. The purpose of the Hamiltonian Eq. (1) is to describe these states correctly.

Having calculated all parameters of our model Hamiltonian, which describes the combined system of electrons (holes) and phonons, we can now proceed to calculate the polaronic ground state. The total energy of the system is a sum of the ground state electronic energy and the lattice energy

\[
E_{\text{tot}}(\{x\}) = E_{\text{el}}(\{x\}) + E_{\text{lat}}(\{x\}).
\]

We need to find the minimum of \( E_{\text{tot}} \), hence

\[
\frac{\partial}{\partial x_i} E_{\text{tot}}(\{x\}) = 0
\]

has to be satisfied. For the lattice part of the total energy we can write
invoke the Hellmann-Feynman theorem to obtain the lattice configuration $x$, changing the problem for $J$.

To find the lowest-energy configuration of the system we make our method much more flexible than straightforward calculations for oligomers.

The atomic displacements lower the potential energy $E_{\text{lat}}$ for the undistorted and distorted lattice configuration. For this part of the energy we invoke the Hellmann-Feynman theorem to obtain

$$\frac{\partial}{\partial x_i} E_{\text{lat}}(\{x\}) = E^x_{x_i}. \quad (5)$$

The electronic ground state energy is obtained from the Schrödinger equation

$$H_{\text{el}}(\{x\})|\phi(\{x\})\rangle = E_{\text{el}}(\{x\})|\phi(\{x\})\rangle,$$ \quad (6)

where $|\phi(\{x\})\rangle$ is the electron (hole) wave function for a certain lattice configuration $x$. For this part of the energy we invoke the Hellmann-Feynman theorem to obtain

$$\frac{\partial}{\partial x_i} E_{\text{el}}(\{x\}) = \langle \phi(\{x\}) | \frac{\partial H_{\text{el}}}{\partial x_i} | \phi(\{x\}) \rangle. \quad (7)$$

Combining Eqs. (3)–(5) and (7), we obtain a set of equations

$$E^x_{x_i} = -\langle \phi(\{x\}) | \frac{\partial H_{\text{el}}}{\partial x_i} | \phi(\{x\}) \rangle. \quad (8)$$

To find the lowest-energy configuration of the system we employ an iterative procedure, by which we obtain a self-consistent solution to the set of Eqs. (6) and (8). As an initial configuration we take a wave function localized on the site $i=0$, and displacements $x_i^0 = \sqrt{2} \alpha \delta_{i0}$, which is the solution of the problem for $J=0$ and $\phi^0=0$. Then we proceed by slowly changing $J$ and $\phi^0$ until they reach the calculated values, calculating the self-consistent solution along the way.

In the model Hamiltonian calculation we take a finite chain and use open boundary conditions at both ends. System sizes of several hundreds of units can easily be handled, making our method much more flexible than straightforward ab initio calculations for oligomers.

III. RESULTS

In Fig. 2 we have displayed the binding energy of an electron (hole) polaron, which is defined as the difference between $E_{\text{lat}}$ for the undistorted and distorted lattice configuration. The atomic displacements lower the potential energy of the charge carrier and eventually produce a potential well in which it is trapped, forming the polaron. We also display in Fig. 2 the contributions of the electronic energy and the lattice energy to the binding energy. The above energies are given as a function of system size. A finite system size can be interpreted as a finite "conjugation length." The limit of a self-trapped carrier is unambiguously observed.

In Figs. 3 and 4 the probability distributions of the self-trapped electron (hole) along very long chains of PPV, PT, and PPP chains are depicted. In the case of PPP we have also displayed the change of the torsion angle, which is due to the mode coupling by far most strongly to the electron (hole). In Fig. 5 we plot the change of the bond lengths at the center of the polarons. Clearly, the single bonds become shorter and the double bonds become longer in the presence of the polaron. The sizes of the unit cells (PT, 7.70 Å; PPV, 6.60 Å; PPP, 8.54 Å) are small compared to the polaron sizes. Hence, assumption (3) mentioned in the Introduction is satisfied.

We show in Fig. 6 the contribution of each phonon mode involved in polaron formation to the total lattice energy $E_{\text{lat}}$. A general conclusion that we can draw from Fig. 6 is that the coupling to electrons and holes is quite dissimilar. In the case of PT the most important phonon modes involved in the polaron formation are the modes at 154.5 and 183.4 meV, both related to C—C bond vibrations. The high-energy mode couples strongly both to the electron and hole, whereas

![FIG. 2. Lattice distortion energy $E_{\text{lat}}$ (up-pointing triangles), change of electronic energy $\Delta E_{\text{el}}$ (down-pointing triangles), and the resulting polaron binding energy $E_{\text{bind}}$ (diamonds) for PT, PPV, and PPP. Filled symbols correspond to electron polarons, empty to hole polarons. The lines are drawn to guide the eye.](image1)

![FIG. 3. Electron and hole probability distribution along PT and PPV chains in the polaronic ground state. The lines are drawn to guide the eye. The number of sites is 149. The full width at half maximum (FWHM) is indicated.](image2)

![FIG. 4. Electron and hole probability distribution along a PPP chain in the polaronic ground state (top) and the corresponding torsion angle (bottom). The FWHM is indicated. The number of sites is 25. The lines are drawn to guide the eye.](image3)
the low energy mode couples strongly only to the hole. For PPV we observe several modes that couple more strongly to the electron than to the hole. For PPP the ring torsion mode clearly stands out and the coupling to the electron is stronger than to the hole.

As a check of the fulfillment of the locality condition (2) mentioned in the Introduction, we performed a calculation for PPV using a unit cell with two phenylenevinylene (PV) units instead of one in our model Hamiltonian. Using this doubled unit cell we obtain about 10% larger polaron binding energies. This is an estimate of the error involved in making assumption (2). Of course, in contrast to full electronic structure calculations our method has an inherently approximative character, but it has the advantage that substantially larger system sizes can be treated, so that the limit of a self-trapped carrier can unambiguously be obtained.

IV. DISCUSSION AND CONCLUSIONS

The most important result of our calculations is the clear demonstration of the presence of self-trapped carriers within an approach based on DFT. All earlier DFT-based full electronic structure approaches for charged oligomers did not show localization. The reason for this might either be the fact that the studied system sizes were not large enough, or that the localization effects are reduced due to the problem of ultranonlocality for charged systems, discussed in the Introduction. On the other hand, the hole-polaron binding energy 0.022 eV calculated by Grozema et al. for 12PV is comparable to the value we find: 0.017 eV for conjugation length of 79.2 Å.

We do not reproduce the very high relaxation energies of about 300 meV obtained within the AM1 model, based on a parametrization of HF results, for electron and hole polarons for nPVs with n ≳ 6. The discrepancy between HF-based and DFT-based results was attributed by Moro et al. to the different predictions for the energy difference between the aromatic and quinoid configurations of the oligomers. The HF prediction for this energy difference is about three times larger than the DFT prediction, leading to a much stronger electron-phonon coupling and stronger localization. The post-HF MP2 calculation of this energy difference agrees with the DFT result, casting doubt on the application of HF and supporting the DFT approach. On the other hand, it was shown by Geskin et al. that MP2 and HF predictions for the charge distribution in 8 T oligomer are very similar, although the lattice deformations in MP2 are much larger than in HF. However, it is questionable whether MP2, being a post-HF perturbative approach, can qualitatively change the HF results. The AM1 calculations of Zuppiroli et al. show that there is a qualitative difference between the results for nPVs with n ≤ 4, where the relaxation energies are rather close to the DFT results, and n ≳ 6, where an apparently qualitatively different situation arises. The HF tendency towards localization is also demonstrated by the hybrid BHandHLYP approach (one-half of the HF exchange and one-half of the DFT-LDA/GGA exchange), which leads to some localization effects in the 8 T oligomer.

In real polymer systems, charge carriers will be localized on sites consisting of polymer segments of a finite conjugation length. The site energies have a disorder with a width of

FIG. 5. Bond length alteration in the middle site of the polaron for long PT, PPV, and PPP chains. We take 99 units for PT and PPV and 25 units for PPP. Bonds are numbered as in Fig. 1. The lines are drawn to guide the eye.

FIG. 6. Lattice energy due to phonon modes involved in electron- and hole-polaron formation in PT (top), PPV (middle), and PPP (bottom) in the limit of long polymer chains.
typically $0.1 - 0.2 \text{ eV}$. \cite{17,18} Hence, in the interplay between disorder and self-trapping \cite{19-21} the effect of the polaron binding energy can be neglected. On the other hand, the information obtained by us about the phonon modes involved in the lattice relaxation and their coupling strength will be relevant in a microscopic description of the charge transport by hopping from one conjugated segment to another.

It has been argued that interchain coupling prevents self-localization in crystalline polymers. \cite{22,23} Interchain transfer integrals in crystalline polymer systems (without side chains) have been calculated to be of the order of $0.1 \text{ eV}$. \cite{24,25} However, it was found that the exciton spectra of these crystalline systems are not in agreement with most of the experimental data. \cite{24} This was attributed to disorder and/or the presence of side chains in most polymeric systems, which quenches interchain coupling. Hence, our consideration of single polymer chains should be realistic.

Self-localization effects for (uncharged) singlet excitations in PPP within a restricted DFT approach have recently been found by Artacho et al. \cite{26} The size of the resulting exciton polaron is comparable to ours. The change of the torsion angle at the center of the polaron is about twice our value, which can be understood from the fact that the effects of hole and electron add up. The total energy reduction of the system by the formation of the exciton polaron is $0.22 \text{ eV}$. The sum of the electron-polaron and hole-polaron binding energies in our case is $0.09 \text{ eV}$ (see Fig. 2). The difference of about $0.13 \text{ eV}$ could be attributed to increased electron-hole correlation effects.

An interesting aspect of our method is that we can immediately determine which phonon modes are involved in the polaron formation. The phonon modes coupling most strongly to the electron (hole) are centroymmetric in the electronic ground state, hence they are not optically active. When a polaron is present this symmetry is broken and these modes become optically active. Infrared active vibrational modes (IRAV) with energies $134$ and $185 \text{ meV}$, which are close to our calculated values ($142.6, 191.4, \text{ and } 195.6 \text{ meV}$), have been observed in a photoexcited MEH-PPV/C60 blend due to the presence of hole polarons on the MEH-PPV. \cite{27} This is a further confirmation of the reliability and usefulness of our method. It would be interesting to measure IRAV spectra for other polymers and in particular to measure the difference in IRAV spectra between electron and hole polarons, verifying the dissimilarity predicted in this work.

V. SUMMARY

We have devised a versatile \textit{ab initio} computational scheme for calculating the properties of charged polarons in conjugated polymers. The scheme is based on the DFT, but it avoids calculations for charged systems by looking at changes of the HOMO and LUMO bands of the neutral system upon lattice deformations. Thereby possible errors related to incorrect screening properties of DFT, using standard approximations, for large systems are avoided. By mapping the problem onto an extended Holstein model, for which the parameters are obtained from DFT calculations, we can treat very long polymer chains and unambiguously observe self-trapping effects and polaron formation. Our calculations establish a clear demonstration of self-trapping in a DFT-based approach for charged polarons. The involved polaron binding energies are much smaller than the typical width of the energy disorder in polymer systems of practical interest. Hence, self-trapping effects are not relevant in practice. Our method also allows the calculation of polarons in finite polymer chains and, hence, the study of the effects of finite conjugation length. An advantage of our approach is that we can immediately determine the phonon modes involved in the polaron formation. This information is very helpful in the detection of polarons by optical techniques and will be important in a microscopic description of charge transport.

We have applied the method to three polymers: PT, PPV, and PPP. The polaron sizes (the full widths at half maximum) are in the range $60 - 110 \text{ Å}$ for PT and PPV, with binding energies in the range $3 - 7 \text{ meV}$, and about $20 - 25 \text{ Å}$ for PPP, with binding energies in the range $30 - 60 \text{ meV}$. The qualitative differences between PT and PPV on the one hand, and PPP on the other hand, are related to the importance of bond torsions in the latter polymer. For hole polarons in PPV the most important phonon modes for polaron formation agree with available IRAV data.

ACKNOWLEDGMENTS

This work is supported by the Dutch foundation FOM (Fondamenteel Onderzoek der Materie). We would like to thank Stefan C. J. Meskers for fruitful discussions, in particular concerning IRAV spectra.

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