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Effect of self-consistency and electron correlation on the spatial extension of bipolaronic defects

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Abstract

Electronic structure calculations on oxidized thiophene and phenylene vinylene oligomers have been carried out using a density-functional based tight-binding method. Analysis of the geometrical structure as well as charge and wavefunction distribution shows no indication that localized defects like bipolarons are intrinsically stable in these materials. Opposite results obtained in the Su–Schrieffer–Heeger and Hartree–Fock framework are rationalized in terms of a different treatment of electron–electron interaction in these methods. We find that within a one-particle approach to the many-electron problem, both self-consistency and electron correlation are necessary for a proper description of charge storage in conjugated polymers.

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1. Introduction

The concept of polarons, originally introduced by Landau [1], is widely believed to be of central importance in the conduction mechanism of polymers and π-conjugated oligomers. These quasiparticles form if an excess charge in a polymer chain localizes thereby creating a lattice distorsion in its vicinity. Upon application of an electric field this defect may then move down the chain as a whole and eventually hop to neighbouring chains, leading to a current across the sample. Due to its success in rationalizing the high conductivities observed for doped polymers, the polaron model was used in a variety of studies to interpret experimental data [2–5]. On the theoretical side, calculations using the celebrated Su–Schrieffer–Heeger (SSH) or other Hueckel-type Hamiltonians gave evidence that polarons are indeed stable excitations for such a wide class of systems as *trans*-polyacetylene (*t*-PA), polyparaphenylene (PPP) and polythiophene (PT) [6–8]. Although the electron–electron (e–e) interaction is not fully accounted for in these models, later self-consistent studies at the Hartree–Fock (HF) or semi-empirical levels of theory essentially confirmed these

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results [9–11]. Estimates for the extension of the defects range from 10 to 40 Å depending on the material and charge state.

Despite of this large body of evidence for a localized charge storage, recent experimental (see [12] and references therein) as well as several theoretical [13–15] studies call this finding into question. The mentioned calculations are all based on density functional theory (DFT) [16] which in contrast to HF theory includes the effect of electron correlation. The latter reduces the amount of energy required to distort the geometrical structure so that the excess charge may spread out over the complete chain driven by Coulomb repulsion. In this situation the concept of a polaron as a defect in an otherwise unperturbed chain is no longer appropriate.

In light of this, the purpose of this work is to contribute to the understanding of the conflicting theoretical data. A computational approach well suited for this kind of analysis is the so-called density functional based tight-binding (DFTB) scheme [17,18]. This method may be viewed as an approximation to DFT and was found to give results of comparable accuracy for a wide range of systems. At the same time DFTB is formally equivalent to tight-binding methods and allows for a comparison with results obtained in the SSH framework.

The systems we studied are isolated doubly charged cations of thiophene and phenylene vinylene oligomers. We consider bipolaronic rather than polaronic species because our method is more reliable for closed-shell molecules. Moreover bipolarons are believed to be the more stable excitations in general, although this is still a controversial issue [19–22]. Also we do not include the effect of counterions since we are interested in the intrinsic stability of the defects. Charges solely localized through the interaction with a counterion would be pinned and could not participate as carrier in conduction. Besides the counterions also chain–chain interactions are not considered in our study. As mentioned above the predictions of different theoretical approaches differ considerably already for isolated oligomers and are worth to be analyzed in more detail before turning to the more involved situation in a three-dimensional crystal.

2. Method

In this section we describe the DFTB method only to the extent necessary to work out the similarities and differences with the SSH-model. A detailed discussion of the computational scheme may be found in recent reviews [23,24], which also contain information on its performance and accuracy.

In DFT the total energy of a many-electron system is given as a functional of the electron density $\rho(\mathbf{r})$. The idea of the DFTB method is to expand this functional around a reference density ρ_0, which is taken to be a superposition of neutral atomic densities $\rho_0 = \sum_{\mathrm{A}} \rho^{\mathrm{A}}$. In zeroth order in the difference $\Delta\rho$ between the true and the reference density the total energy may be written

$$E[\rho] = \sum_i \sum_{\mu\nu} c_{\mu i} H^0_{\mu\nu}[\rho_0] c_{\nu i} + U_{\mathrm{rep}}[\rho_0] + \mathrm{O}[\Delta\rho^2], \tag{1}$$

i.e. it takes the standard tight-binding form. In Eq. (1) the term U_{rep} contains the double counting terms at the reference density and the nucleus–nucleus Coulomb repulsion. It can be shown [25] that it may be approximated quite reasonable by a sum of simple two-body potentials,

$$U_{\mathrm{rep}} = \sum_{\mathrm{AB}} U_{\mathrm{AB}}(|\mathbf{R}_{\mathrm{A}} - \mathbf{R}_{\mathrm{B}}|), \tag{2}$$

which can be obtained for every pair of elements from DFT calculations at varying distance between two atoms located at $\mathbf{R}_{\mathrm{A}}$ and $\mathbf{R}_{\mathrm{B}}$.

Further, the matrix elements $H^0_{\mu\nu}$ in Eq. (1) are calculated in a two-center approximation according to

$$\begin{aligned} H^0_{\mu\nu} = \langle \phi_\mu(\mathbf{r} - \mathbf{R}_{\mathrm{A}}) | H_{\mathrm{DFT}}[\rho^{\mathrm{A}} + (1 - \delta_{\mathrm{AB}})\rho^{\mathrm{B}}] | \\ \times \phi_\nu(\mathbf{r} - \mathbf{R}_{\mathrm{B}}) \rangle. \end{aligned} \tag{3}$$

Here, the ϕ_μ are atom-centered basis functions (usually s- and p-type orbitals only) which like the atomic densities ρ^{A} are generated in preceeding self-consistent DFT calculations of neutral atoms. The DFT Hamiltonian in Eq. (3) contains as usual the kinetic energy, the electron–nuclei attraction and the Hartree as well as exchange-correlation potentials, the latter two describing the e–e interaction.

In the SSH-formalism only π-electrons are considered explicitely and the hopping integrals between sites are made into parameters including the dependence on the atomic positions (i.e. the electron–phonon interaction) through a Taylor expansion. It is sometimes stated that the SSH-approach does not account for e–e interaction. This is not completely true since the mentioned parameters can be thought of as beeing obtained in a similar way as in the DFTB scheme given above, where most of the e–e interaction including also exchange and correlation effects are captured in a one-particle Hamiltonian. See also [26] for a discussion of this point.

For charged systems, however, a superposition of neutral atomic densities is no longer a good approximation to the true density and terms of second-order in $\Delta\rho$ have to be considered in Eq. (1). As described in more detail in [18] these terms can be recast in the following form:

$$E_{2\mathrm{nd}} = \sum_{\mathrm{AB}} \gamma_{\mathrm{AB}}(U_{\mathrm{A}}, U_{\mathrm{B}}, |\mathbf{R}_{\mathrm{A}} - \mathbf{R}_{\mathrm{B}}|)\Delta q_{\mathrm{A}}\Delta q_{\mathrm{B}}. \tag{4}$$

In Eq. (4) Δq_{A} stands for the net charge on atom A and is determined from a Mulliken population analysis. The function γ_{AB} interpolates between pure Coulomb repulsion of the charges on atoms A and B for large distances and the on-site e–e interaction for short distances. The latter is given by the parameters $U_{\mathrm{A}}/U_{\mathrm{B}}$ which are again obtained from atomic DFT calculations. Adding the second-order term (4) to Eq. (1) and applying the variational principle for the total energy leads to the following secular equation:

$$\sum_{\nu} c_{\nu i}(H_{\mu\nu} - \epsilon_i S_{\mu\nu}) = 0, \tag{5}$$

which determines the wavefunction coefficients $c_{\mu i}$. The Hamilton matrix elements $H_{\mu\nu}$ in Eq. (5) are given by the zero-order terms from Eq. (3) plus a correction which involves the net charges Δq_{A}:

$$H_{\mu\nu} = H^0_{\mu\nu} + \frac{1}{2}S_{\mu\nu}\sum_{C}(\gamma_{AC} + \gamma_{BC})\Delta q_C, \tag{6}$$

$$S_{\mu\nu} = \langle\phi_\mu|\phi_\nu\rangle. \tag{7}$$

Since these charges depend on the coefficients $c_{\mu i}$, Eq. (5) has to be iterated until self-consistency is achieved. Consequently this scheme is labeled self-consistent charge (SCC)-DFTB, in contrast to the standard DFTB approach where the residual e–e interaction equation (4) is missing and a single diagonalization is sufficient. Although no one-to-one mapping between the SSH-formalism and the standard DFTB method is possible, one might argue that these two are closely related, while the SCC-DFTB scheme can be viewed as an approximate version of the full self-consistent field DFT.

3. Results

3.1. Comparison of DFT and SCC-DFTB

In order to show that DFT and SCC-DFTB give indeed comparable results we first compare the geometrical structure of the seven ring α-oligothiophene dication $7T^{2+}$ as given by the two methods. We chose the all-anti conformation of $7T^{2+}$ and fully optimized it without any symmetry constraints. The DFT calculations were performed with the *Gaussian98* suite of programs using a 6-31G* basis set and the B3LYP exchange-correlation potential. The latter is a gradient-corrected hybrid functional which includes a part of exact HF exchange and is widely used in quantum-chemistry because of its balanced performance. Fig. 1 shows the resulting C–C bond lengths along the path connecting the carbon atoms in the molecule.

Apart from the chain ends a high similarity between the SCC-DFTB and DFT derived geometries is found, which is reflected in the root-mean-square difference between the bond lengths given by the respective methods of 0.014 Å.

Quite generally one would expect that a localized defect leads to a quinoid domain (see Fig. 2) in the alternation pattern for the innermost rings which gradually evolves into the aromatic form of the neutral species towards the end of the chain. Such a defect structure was obtained at the HF and HF-based levels of theory. Ehrendorfer and Karpfen [11] report a defect extension of 9–11

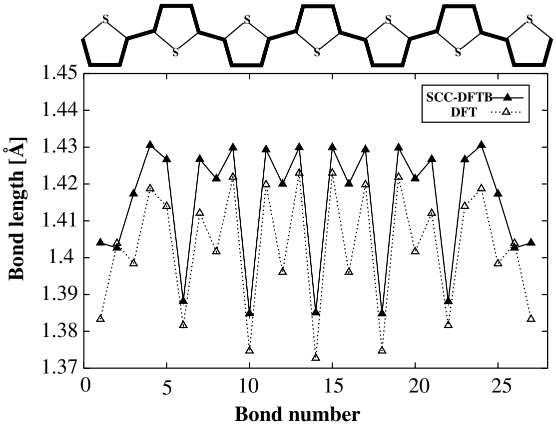

Fig. 1. Optimized C–C bond lengths along the carbon backbone of $7T^{2+}$ as given by the SCC-DFTB and DFT-B3LYP/6-31G* methods.

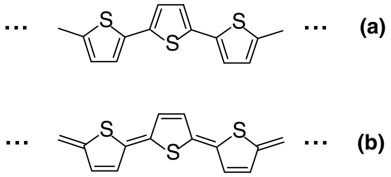

Fig. 2. Aromatic (a) and quinoid (b) bond alternation pattern in oligothiophenes.

rings with a clear enclosing aromatic phase and a bond alternation as large as 0.12 Å. This kind of transition is not observable in both the DFT and SCC-DFTB results. Here the quinoid phase extends over the whole chain and the difference between α–β and interring bond lengths is rather small with about 0.01 Å. Moreover, the maximum bond length alternation does not exceed 0.05 Å. These findings are in line with the DFT calculations of Moro et al. [13] on oligothiophenes with an even number of rings. Since the pure BLYP functional was used in that investigation, the DFT results do not seem to be strongly dependent on the actual exchange-correlation functional used. It should however be mentioned, that by increasing the fraction of HF exchange in a hybrid functional results close to the above mentioned HF predictions are obtained. This has been shown very recently in a BH and HLYP study [27].

3.2. Comparison of SCC-DFTB and DFTB

Next, we analyze the optimized geometries of the $13T^{2+}$ oligomer obtained from the SCC-DFTB and the more approximate DFTB method. Comparison of Figs. 1 and 3(a) shows that within the SCC-DFTB scheme the most prominent effect of increasing the chain length is a lengthening of the interring bond so that both the α–β and β–β bonds are shorter than the latter. Thus, the quinoid alternation pattern present in the $7T^{2+}$ disappears and a very homogenous bond length distribution over the whole chain emerges. These observations are in good agreement with a recent investigation of Brocks [15].

In stark contrast to the SCC-DFTB results, the DFTB calculations show a much richer structure (Fig. 3(b)). Here, the two outermost rings on both sides are aromatic while the three inner rings are quinoid. Like in the SSH-formalism a localized

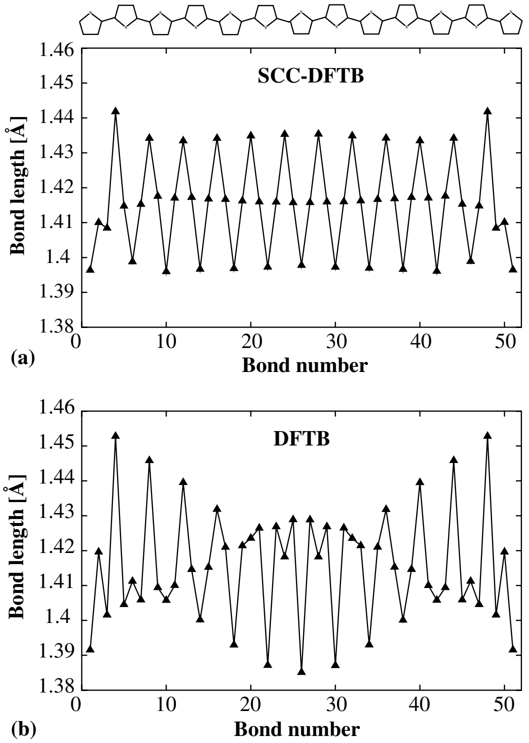

Fig. 3. Optimized C–C bond lengths along the carbon backbone of $13T^{2+}$ as given by the SCC-DFTB (a) and DFTB (b) methods.

defect is therefore predicted. This is also apparent in the charge distribution along the chain, which is shown in the next section. It follows, that the neglected residual e–e interaction given by Eq. (4) leads to a localization which is not present at a higher level of theory.

3.3. Charge distribution for different chain lengths

Up to now, we focused on short chain systems mimicking the situation in real disordered polymer samples and oligomer crystals where the conjugation lengths is rather small and found no clear evidence for bipolaron formation. It is however perfectly possible that as the chain length increases, the energy cost for distorting the whole lattice surmounts the one for charge confinement. In other words the intrinsic defect extension could be larger than the size of the models studied so far. Because of this we also performed SCC-DFTB calculations on the much longer $23T^{2+}$ oligomer. [1] Fig. 4 depicts the charge per thiophene ring as given by a Mulliken population analysis for different lengths of the π-conjugated system.

Examining first the DFTB results (Fig. 4(b)), we find a clear polaron signature which extends over roughly seven thiophene units in line with the HF results of Ehrendorfer and Karpfen [11]. In contrast to this, at the SCC-DFTB level of theory (Fig. 4(a)) the highest values for the charge are found at the terminal rings rather than in the middle of the chain as expected for bipolarons. Thus electron correlation as included in the SCC-DFTB method seems to alter ther relative importance of electron–phonon and e–e interaction. Furthermore we find a very homogeneous and similar distribution of the excess charge over the whole chain for all the systems studied. Taking also the observed bond length homogenity into account we therefore believe that a defect formation at even longer chain lengths is not very likely.

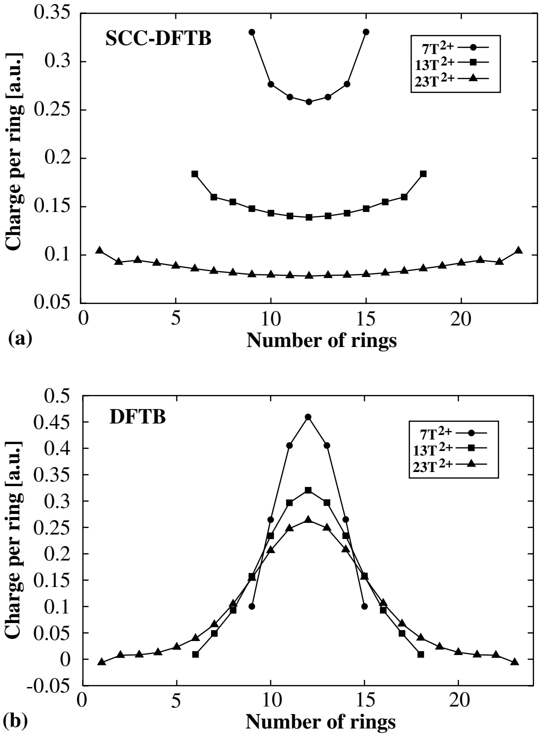

Fig. 4. Net charge per thiophene ring for oligothiophenes of different lengths within the SCC-DFTB (a) and DFTB (b) method.

Here it should be mentioned that our results do not depend on the starting geometry used for the optimization. Even if for example polaron-like structures are used as input, e.g. as obtained from a DFTB calculation, these are not stable conformers on the SCC-DFTB potential energy surface and relax towards the above documented minima.

3.4. Calculations on phenylene vinylene oligomers

In this last section we like to test if the observations made so far are dependent on the actual material under study. To this end we performed calculations on phenylene vinylene (PV) oligomers which are frequently used in practical applications like LED and polymer lasers. To be more specific, the seven ring PV oligomer 7PV in its neutral and doubly ionized form has been optimized with the SCC-DFTB and DFTB methods. After analyzing

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[1] Please note that we are only dealing with closed shell systems here. It has been shown that an increase of the conjugation length may lead to a stabilization of biradical states which correspond to two polarons on a single chain [28,29].

the bond length pattern and the charge distribution in the oligothiophenes, we focus here on the wavefunction characteristics. It is expected that upon formation of a bipolaron two localized levels appear in the gap which are unoccupied in the case of a positive defect. Consequently, subgap absorption should be possible and has indeed been observed in a number of experiments [2,3,22]. The results we obtained with the non-self-consistent DFTB method are in qualitative agreement with this picture. For the neutral 7PV the highest-occupied (HOMO) and lowest-unoccupied (LUMO) orbital energies are $\epsilon_{\mathrm{HOMO}} = -5.7$ eV and $\epsilon_{\mathrm{LUMO}} = -3.9$ eV, respectively, while for the oxidized species the levels associated with the bipolaron defect are located at $\epsilon_{\mathrm{LUMO}} = -5.6$ eV and $\epsilon_{\mathrm{LUMO+1}} = -4.0$ eV, i.e. in the gap of the neutral form. These findings are in strong contrast to the results of the more accurate SCC-DFTB method. Here the LUMO and LUMO+1 levels of the charged system are placed well below the HOMO level of the neutral chain. We have $\epsilon_{\mathrm{HOMO}} = -5.3$ eV for the 7PV and $\epsilon_{\mathrm{LUMO}} = -9.0$ eV, $\epsilon_{\mathrm{LUMO+1}} = -7.5$ eV for the $7\mathrm{PV}^{2+}$. This large difference in the level positioning of the SCC-DFTB and DFTB schemes is reflected in the spatial distribution of the molecular orbitals. Fig. 5 shows a representation of the LUMO π-orbital of the $7\mathrm{PV}^{2+}$ oligomer for the respective methods. Consistent with the results for the oligothiophenes, the missing of the residual e–e interaction in DFTB leads to a localization of the wavefunction, which is connected with the appearance of gap states. The SCC-DFTB scheme, on the contrary, yields a π-orbital which is completely delocalized over the whole chain. In a crystal, this deep level should merge with the valence band and contribute to band-like hole conduction.

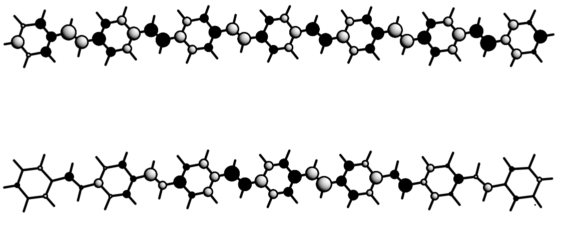

Fig. 5. LUMO of $7\mathrm{PV}^{2+}$ for the SCC-DFTB (upper panel) and DFTB (lower panel) methods. The size of the circles is proportional to the p_z wavefunction coefficient of the respective atom, the shading indicates the sign.

4. Conclusion

The results of the preceeding sections on the geometrical and electronic structure as well as the charge distribution of typical polymers clearly show that the DFTB scheme predicts the existence of localized defects much like the SSH formalism. This is reasonable since both are tight-binding methods, which recast the electron–phonon and most of the e–e interaction including correlation in terms of matrix elements of an effective one-particle hamiltonian. The remaining portion of the e–e interaction was originally thought to be of lower importance for a correct description of conducting polymers. One of the main results of our study is however that at least for charged systems this is not the case. As discussed in Section 2 inclusion of the missing interaction leads to the necessity of a self-consistent solution of the secular equation. The results obtained in this way differ considerably from the DFTB ones in that they show a complete delocalization. This might be surprising since within HF theory the electron density is also determined self-consistently and at the same time charges are well localized. The reason for this discrepancy is the lack of electron correlation in HF and it turns out that both self-consistency and electron correlation are essential for a correct description of doped polymers.

This conclusion is based on the assumption that DFT provides the correct point of view, which might be questioned. In principle, DFT is an exact many-body theory provided that the true exchange-correlation functional is known. In practice the latter is not available and has to be approximated. The common functionals show a realistic description of electron correlation in general, although for the extended conjugated chains considered here, failures in the calculation of polarizabilities [30] and excitation energies [31] have been reported. Moreover, in some systems a tendency of DFT to delocalize electrons is observed [32]. In this context, the instability of bipolarons ascertained in our and other DFT studies could be rooted in an "overshooting" in the treatment of correlation effects compared to the HF case. Because of this the question remains whether wavefunction-based methods like configuration interaction or Møller–Plesset (MP) perturbation theory, which approach the correlation problem in a more systematic way than DFT, yield identical results. Work in this direction has been done by Moro et al. [14], who show that the DFT energy difference between the quinoid and aromatic forms of bithiophene is much closer to the MP2 than the HF value.

There is therefore growing evidence that bipolaronic defects in isolated chains are nor intrisically stable. In this case the conduction mechanism is best described as a conventional band transport rather than a defect migration. In agreement with this, the studies of Karl (see e.g. [12] for a review) on a variety of organic crystals show indeed band-like transport within the molecular planes. Perpendicular to the planes however, the observed mobility at higher temperatures is more in line with an activated hopping of polaronic charge carriers. This, together with the mentioned optical absorption data [2,3,22] clearly point towards the existence of polarons, which raises the question if 3D effects like inter-chain interaction may induce localization. The model calculations of Emin [33] as well as the DFT calculations of Vogl and Campbell [34] on perfect *t*-PA crystals do not support this idea. Nevertheless, the disorder present in real samples might lead to localized defects as shown by Mizes and Conwell [35], although this study was performed within the SSH formalism which predicts polarons to be stable already for isolated chains.

Moreover we mention that our calculations correspond to a temperature of 0 K. This is important since Schelling and Halley [36] recently reported that polaron formation can occur at finite temperature even if there is complete delocalization at vanishing temperature. Unfortunately, these molecular dynamics simulations were carried out on rutile titanium dioxide. It will be interesting to see if this mechanism is also important for conjugated polymers and work is under way to study this question.

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