

## THE ROLE OF MOBILE ORGANIC RADICALS AND IONS (SOLITONS, POLARONS AND BIPOLARONS) IN THE TRANSPORT PROPERTIES OF DOPED CONJUGATED POLYMERS

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### Abstract

We discuss the formation of charged defects such as solitons, polarons and bipolarons, in doped conjugated polymers. We present the results of *ab initio* quality calculations on the modifications of geometric and electronic structures occurring upon doping. A transport model for spinless conduction through bipolarons applicable to doped polymers with or without degenerate ground state is described.

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### 1. Introduction

During the last few years, the discovery of doped conjugated polymers with high conductivities has generated substantial research interest among chemists and physicists alike, as exemplified in these Proceedings. Besides the potential technological applications of conducting polymers, a very interesting aspect of this field is that a new physics is developing which is significantly different from the physics of doped inorganic semiconductors such as Si, Ge or GaAs. In these introductory remarks, we will point out some of these differences.

In inorganic semiconductors, the atoms are connected by covalent bonds in all three dimensions. Carrier mobilities are quite high, so that reasonable conductivities are achieved at fairly low doping levels, of the order of ppm. Doping is usually substitutional and generally does not lead to

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major disruption of the lattice. Doping of inorganic semiconductors results in the appearance in the gap of electronic levels that can be thermally populated at room temperature. Rigid-band models give a good description of the physics of these systems.

In organic polymers, the interactions are highly anisotropic since atoms are linked by strong covalent bonds along the polymer chains, whereas interactions between chains are much weaker, usually of the Van der Waals type; this anisotropy opens the door to possible collective instabilities, typical of quasi-one-dimensional materials, such as Peierls distortions. Doping levels are around a few per cent, so that some authors use the term loading rather than doping; dopant atoms or molecules intercalate between the polymer chains and undergo charge transfer with the chains. Since these polymers are organic compounds, it is expected that charge-transfer (or electron-excitation) processes result in significant local modifications (relaxations) of the chain geometry. Indeed, in organic systems, the equilibrium geometry in the ionized state is usually quite different from that in the ground state. In solid-state physics terminology, this means the electron-phonon coupling is strong. Furthermore, the local geometric modification of the chain markedly affects the electronic structure by inducing localized electronic states in the gap. These levels are all attributable to charge-transfer induced modifications of the  $\pi$  system of the polymer and in that sense are intrinsic to the parent material (the organic polymer); this contrasts to the situation in doped inorganic semiconductors where the states in the gap are dopant levels. The fact that upon ionization or electron excitation, a local relaxation of the lattice geometric and electronic structures is energetically favorable, or in other words that charged defects are formed, constitutes the basis of the fascinating physics occurring in doped organic polymers.

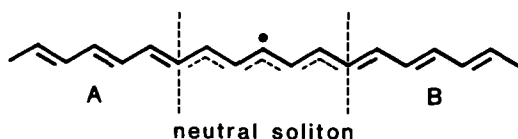
We first discuss here the qualitative concepts involved in the formation of charged defects upon doping of conjugated polymers and compare the situation in *trans*-polyacetylene, a system with a degenerate ground state, and in polymers without a degenerate ground state. We then present a summary of our *ab initio* quality calculations on the band structure evolution upon doping of polyparaphenylene, polypyrrole and polythiophene. We show that: (1) the charged defects that are formed during the doping process in these systems are polarons and bipolarons; (2) these defects play a major role in the conduction mechanisms. Finally, we discuss carrier transport and present a model for spinless conduction in doped polymers, with polyacetylene and polypyrrole taken as examples.

## 2. Band structure evolution upon doping of conjugated polymers

So far, polyacetylene (PA) has been the focus of most experimental and theoretical work [1]. *Trans*-PA is unique among studied systems in possessing a degenerate ground state, *i.e.*, two geometric structures having exactly the same total energy.



These two structures (A and B) differ from one another by the exchange of the alternating single and double carbon-carbon bonds along the chain. This degeneracy leads to the possibility of formation of so-called soliton excitations on the chains; in *trans*-PA, the soliton denotes a one-dimensional domain wall marking the separation and the gradual passage between the two ground-state structures along one chain [2, 3].



In principle, this domain wall can propagate freely with a very small kinetic mass, of the order of a few times the free-electron mass. A very important feature is that the presence of a soliton provokes the appearance of a localized electronic level at midgap, *i.e.*,  $\approx 0.7$  eV above the valence band (VB) edge (Fig. 1). The energy of creation of a soliton is calculated to be about 0.45 eV [2]. Solitons have peculiar charge-spin relationships since neutral solitons have spin 1/2 whereas charged solitons (although carrying a single charge) have no spin. In *trans*-PA, a neutral soliton (radical) is expected to be present on each chain having an odd number of carbon atoms; this accounts for the concentration of about one spin per 3000 carbon atoms observed in ESR experiments [4].

At low doping levels, charges transferred on the chains can be accommodated in two ways: (1) as a charged soliton when an existing neutral soliton is ionized; charged solitons are to be viewed simply as polymeric anions (n-doping) or cations (p-doping) associated with a local relaxation of the chain geometry and a localized electronic state at midgap; (2) otherwise as a radical-ion which also causes a local geometry relaxation, *i.e.*, as a

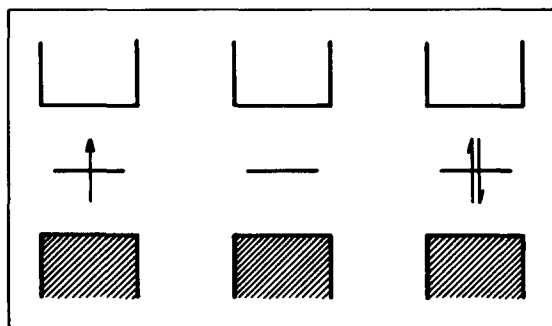


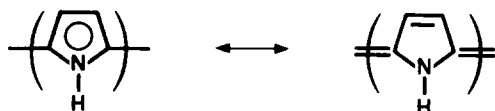
Fig. 1. Band structure for a polyacetylene chain containing a soliton: left, neutral soliton; middle, positively charged soliton; right, negatively charged soliton.

polaron [5 - 8]. Polarons have spin 1/2 and can also be described as an interacting charged soliton-neutral antisoliton pair. It has been shown [8] that two adjacent polarons recombine (pair their spins) and leave two charged solitons on the chain. As a result, for doping levels of the order of a few per cent, only charged solitons are present on the chains. The corresponding picture for the electronic structure is: (1) a full valence band; (2) soliton states around midgap which are fully occupied (n-doping) or empty (p-doping); when these states start overlapping, they broaden to form a soliton band; (3) an empty conduction band. Note that there are no levels incompletely filled.

At doping levels between a few tenths of a per cent and about 7%, high conductivity is observed, though the Pauli susceptibility is measured to be very small [1, 9, 10]. This has been considered as evidence, *e.g.*, in AsF<sub>5</sub>- [9] and sodium-doped [10] polyacetylene, that highly mobile spinless charged solitons are the charge carriers in that regime. Note that this mechanism is very unusual in the sense that high conductivity is obtained, whereas in the electronic structure all states are fully occupied or empty. It must be stressed, however, that in iodine-doped PA, which is a more disordered system, another mechanism has been proposed [11]; this mechanism is based on the Mele and Rice [12] theory and implies a small but finite density of states at the Fermi level and a variable-range-hopping model for electrons jumping among soliton sites [11].

At very high doping levels, above 7%, Pauli susceptibility sets in. This can be explained by the merging of the soliton band with the valence band (VB) and the conduction band (CB). A normal conduction process, with electrons as charge carriers, can then take place.

In other polymers, such as polyparaphenylene (PPP), polypyrrole (PPy) or polythiophene (PT), the ground state is non-degenerate. The ground-state geometry in PPP, PPy and PT corresponds to an aromatic structure within rings and a single-like bond between rings. The resonance structure that can be envisioned is quinoid-like, the bonds between rings acquiring a strong double-bond character.



The quinoid form has a higher total energy than the aromatic form; the difference per ring is of the order of 0.4 eV [13, 14]. Therefore, it is not possible to have soliton excitations in these systems.

The quinoid structure has a lower ionization potential and a larger electron affinity than the aromatic structure (and, as a result, a smaller band-gap). This explains why upon doping the presence of a charge on the chain can provoke a local geometry relaxation from the aromatic structure towards the quinoid structure. The formation of such a charged defect actually occurs when the lowering in ionization energy due to the presence of a

quinoid segment more than compensates for the increase in  $\pi + \sigma$  energy required to form that quinoid segment.

We have performed calculations on PPP [8] and PPy [15], using Huckel theory with sigma compressibility, *i.e.*, the quantum-chemical equivalent of the Su–Schrieffer–Heeger Hamiltonian as applied to PA [2]. We find that, at low doping levels, radical-ions (polarons) are formed, associated with a quinoid segment extending over 4 to 5 rings. The presence of a polaron introduces two states in the gap, a ‘bonding’ state slightly above the VB edge and an ‘antibonding’ state slightly below the CB edge. The calculations indicate that two adjacent polarons are unstable with respect to the pairing of their spins and the formation of a bipolaron, *i.e.*, a doubly-charged defect *having no spin* [8, 15]. Note that in contrast to *trans*-PA, since solitons are not possible in these systems, the charges cannot move separately but are correlated in pairs. The geometrical defect associated with a bipolaron has a width similar to that of the polaron. However, the bond-length modifications are larger so that the two states in the gap are pushed further away from the band edges. The absence of Pauli susceptibility in the highly conducting regime of PPP [16] and PPy [17] is consistent with our suggestion [8, 15] that the *bipolarons are the corresponding spinless charge carriers*.

We have calculated at the *ab initio* level the bond-length modifications appearing in PPP [18], PPy [19] and PT [14] when a bipolaron is formed and the band-structure evolution at high doping levels. Using Hartree–Fock *ab initio* techniques, we optimize fully the geometry of a large oligomer (quaterphenyl, quaterpyrrole or quaterthiophene); the geometric optimization is carried out first in the undoped state, then in the doped state by adding two Li or Na atoms in order to simulate the formation of a bipolaron on the chain. Typical bond-length modifications are given in Table 1.

Taking the geometries obtained in that way for the charged defects and using the *ab initio* quality Valence Effective Hamiltonian (VEH) technique [20, 21], we calculate the electronic structure of polymer chains: (1) in the undoped state; (2) containing one bipolaron; (3) doped at the maximum level experimentally achieved, *i.e.*, 50% (on a per monomer basis) for PPP and 33% for PPy and PT; (4) for a hypothetical 100% doping level. The band structure evolution for PPP is presented in Fig. 2.

In the undoped state (Fig. 2(a)), the bandgap is calculated to be 3.5 eV, in good agreement with experiment [22]. The presence of a bipolaron provokes the appearance of two localized electronic states in the gap, 0.7 eV away from the band edges (Fig. 2(b)). In case of n-(p)-type doping, these two states are fully occupied (empty). At high doping levels, the bipolaron states overlap and broaden to form bipolaron bands. At 50% doping level, usually achieved with alkali metal ions, the two bipolaron bands are about 0.5 eV wide (Fig. 2(c)). This picture is in agreement with recent electron energy loss data [23]. For a hypothetical 100% doping level, the lower bipolaron band merges with the VB and the upper one with the CB (Fig. 2(d)). A traditional conduction mechanism would then occur due to the unfilled character of either the VB (p-doping) or the CB (n-doping), in much

TABLE 1

Results of Hartree-Fock *ab initio* geometry optimizations on tetramers of polyparaphenylene, polypyrrole and polythiophene, undoped and doped with two sodium atoms. Bond lengths are given in Å

	Undoped	Doped
Polyparaphenylene		
r(C-C)	1.384 - 1.393	
r(C=C)		1.352
r(C-C)		1.462
r(inter-ring)	1.507	1.371
Polypyrrole		
r(C-N)	1.385	1.428
r(C-C)	1.424	1.380
r(C=C)	1.363	1.437
r(inter-ring)	1.474	1.357
Polythiophene		
r(C-S)	1.721	1.776
r(C-C)	1.444	1.370
r(C=C)	1.346	1.432
r(inter-ring)	1.480	1.362

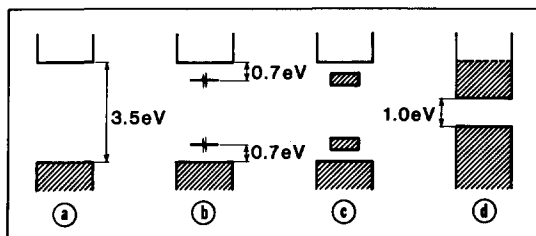


Fig. 2. Band-structure evolution upon (n)-doping of polyparaphenylene: (a) undoped; (b) intermediate doping level: non-interacting bipolarons present on the chain; (c) per monomer 50% doping level; (d) per monomer 100% doping level.

the same way as what happens in PA above 7% doping. Here, however, note that the original bandgap would not close (but rather decreases to the band-gap value in the purely quinoid form).

The band structure evolution calculated for PPy is very similar to that presented for PPP, except that the locations of the bipolaron states in the gap are asymmetric with respect to the gap centre [19]. The bonding state is located about 0.45 eV above the VB edge and the antibonding state, 0.9 eV below the CB edge. This asymmetric location seems to be confirmed experimentally [15]. It is due to the fact that in PPy the atoms contributing to the highest occupied molecular orbital (HOMO) are quite different from those contributing to the lowest unoccupied MO (LUMO); *e.g.*, the HOMO has no contributions from the nitrogen  $\pi$  orbitals whereas the LUMO does.

In PT the bandgap is calculated to be significantly smaller, 2.2 eV, in agreement with experiment [24]. The bipolaron states appear 0.6 and 0.7 eV away from the band edges (the asymmetry is thus smaller than in PPy, although the HOMO and LUMO characteristics are the same as in PPy). The bipolaron bands formed at 33% doping level have widths of the order of 0.3 eV.

So far, PPy is the highly conducting polymer where experimental and theoretical evidence for the presence and role of spinless bipolarons in the transport process is most conclusive. Now that a clean chemical synthesis has been developed for PT [24], it will be very interesting to look for similar evidence in this compound.

### 3. Carrier transport in polyacetylene and polypyrrole

A question of fundamental importance in the conducting polymers area is how the charged species (solitons, bipolarons) we have described in the previous section can migrate through the polymer/dopant array. As pointed out above, the question is made very interesting by the observation of spinless transport, *i.e.*, a spin concentration that is far too low to account for the observed conductivities [9, 10, 16, 17]. In this section, we discuss a model based on bipolarons which could account for truly spinless transport at intermediate and high doping levels in *trans*-PA and non-degenerate ground state systems. A detailed presentation of this model is given elsewhere [25].

In *trans*-PA, a number of authors [2, 9] have suggested that charged solitons are the charge carriers in the spinless conductivity regime (up to about 7% doping level). However, they fail to consider how these species can get from one chain to another, it being well-established that interchain transport must be easy for efficient carrier migration. Actually, interchain conduction is likely to be the rate-limiting step in all conducting polymer systems. In Fig. 3, we consider an infinite PA chain containing one charged soliton and a neighbouring chain without defect. The soliton cannot easily hop to the next chain since an infinitely large activation barrier is required in the reorganization of bond lengths that would ensue from such a jump. The soliton mechanism is also unattractive for finite chains, since the soliton cannot hop isoenergetically in that case. The model developed by Kivelson [26] gets around those problems by requiring a neutral soliton on the next chain. However, this model is only applicable at low doping levels [26].

The above problems are eliminated by a model in which there are two charged solitons on an infinite chain. The soliton pair, that can be referred to as a bipolaron, can hop to the next chain isoenergetically and with a reasonable activation barrier (Fig. 3). The hopping probability for two charged solitons separated by  $x$  carbon atoms,  $P(x)$ , is constructed as follows:

$$P(x) = F(x)Qa(x)Qb(x)$$

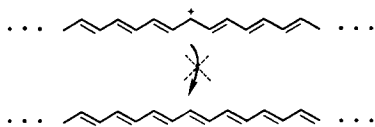
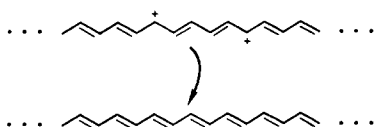
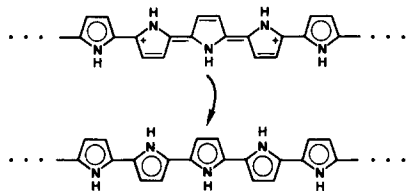
**Polyacetylene****Soliton hopping****Bipolaron hopping****Polypyrrole****Bipolaron hopping**

Fig. 3. Interchain transport for solitons and bipolarons in *trans*-polyacetylene and bipolarons in polypyrrole.

where  $F(x)$  is the Franck–Condon factor (or square of the vibrational overlap) for the jump;  $Qa(x)$  is the probability of finding a second charged soliton  $x$  carbon atoms from the first on a single chain;  $Qb(x)$  is the probability of finding an unoccupied site on the next chain to receive the  $x$ -length soliton pair.  $F(x)$  is expected to decrease rapidly as  $x$  increases.  $Qa(x)$  is expected to be peaked at roughly  $1/C$  ( $C$  is the concentration in solitons, taken to be the dopant concentration) due to the coulombic repulsion between solitons of like charge.  $Qb(x)$  is obtained from  $Qa(x)$  and leads to saturation of the spinless contribution to the conductivity at high  $C$ .

We have modelled this process and calculated conductivity *versus*  $C$  curves that are very similar to those obtained experimentally. We now discuss the qualitative aspects of the results of the model. At low  $C$ , there are few soliton pairs, 'bipolarons', of small enough  $x$  for transport to take place due to the  $F(x)$  term. Indeed,  $F(x)$  at the peak in the  $Qa(x)$  distribution is small. As  $C$  increases, the spinless contribution to the conductivity increases superlinearly since the peak in  $Qa(x)$  shifts to lower  $x$  values where  $F(x)$  gets very large. At still larger  $C$  values, the spinless contribution levels off and eventually decreases due to the small value of the  $Qb(x)$  term. The reason is



that few sites remain available on the next chain to accept the bipolaron. The net result of the model is an S-shaped curve for the spinless contribution to the conductivity.

For PPP, PPy or PT, the situation is different since the two charged defects which make up the bipolaron are bound. The bipolaron is thus a well-defined entity of limited spatial extent, so that the  $F(x)$  and  $Qa(x)$  terms become constant. Therefore, the spinless contribution to the conductivity rises in proportion to  $C$ , eventually saturating and decreasing when the  $Qb(x)$  term becomes small. This qualitative behaviour is consistent with the experimental data in PPy [27], although no detailed conductivity *versus* doping level curve has been reported so far for any of these systems.

Bipolaron transport offers a reasonable explanation for spinless transport in PA, PPP, PPy and PT. It should be emphasized, however, that we have made no explicit consideration of the effect of the dopant ion array on the transport process.

#### 4. Conclusions

In summary, we offer the following qualitative picture of the doping and transport process of general applicability to conducting polymers. The dopant (which we take to be an acceptor) first ionizes the chain to produce a polaron (radical-cation). The polaron is pinned to the counter-ion and does not contribute significantly to conductivity. As more dopant is added, the chain is ionized further and a higher concentration of polarons is formed. Also, the polarons can be further ionized to produce bipolarons (dications) since the polaron can be more easily ionized than the polymer chain. As the polaron concentration gets higher, adjacent polarons interact to produce bipolarons, which are uncorrelated charged solitons in the PA case and correlated dications in the other cases. The bipolarons transport charge via inter-chain hopping and are responsible for the observed spinless conductivity. The corresponding picture for the electronic structure reveals the presence of a full valence band, an empty conduction band and wide bands within the gap due to solitons in the PA case and bipolarons in the other cases. In cases where still higher doping levels can be achieved, the bands in the gap merge with the VB and CB; at this point, conventional conductivity involving carriers with spin sets in, as for PA above 7% doping. It should be stressed that this description applies equally well for systems with or without a degenerate ground state.

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