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THEORETICAL STUDIES OF THE PHYSICS OF CHARGED DEFECT FORMATION IN DOPED ORGANIC POLYMERS : TOWARDS A COHERENT THEORETICAL PICTURE

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Résumé - A partir de calculs Hartree-Fock en méthode du champ auto-cohérent sur le polyacétylène trans, le polyparaphénylène et le polypyrrole, nous voyons émerger une représentation théorique cohérente des mécanismes de conduction dans les polymères organiques dopés. Nous mettons en évidence l'importance primordiale des modifications géométriques survenant sur les chaînes polymériques suite au transfert de charge. Nous démontrons que ces modifications font apparaître des états électroniques nouveaux dans la bande interdite qui jouent un rôle essentiel dans le mécanisme de conduction. Des calculs MNDO sur des chaînes de polyacétylène trans indiquent que les géométries des défauts de type soliton et polaron dépendent fortement de leur état de charge.

Abstract - From Hartree-Fock self-consistent-field calculations on trans-polyacetylene, polyparaphenylene, and polypyrrole, a coherent theoretical description emerges for the physics of conducting doped organic polymers. The importance of the geometric modifications that occur on the polymer chains upon charge transfer is stressed. These modifications are shown to lead to the appearance of electronic states in the gap that play a major role in the conductivity mechanism. MNDO calculations on trans-polyacetylene chains indicate that the geometries of soliton or polaron defects vary significantly with their charge state.

I - INTRODUCTION

In recent years, a number of conjugated organic polymers have been discovered that can be made electrically conductive through doping with either electron acceptors or donors. Polymers with doped derivatives reported to have conductivities larger than 1 S/cm include polyacetylene /1/, polyparaphenylene /2/, polypyrrole /3/, and various polyphenylene chalcogenides /4/.

Doped organic polymers display phenomena in some ways similar to conventional semiconductors and were therefore described theoretically in early works as usual doped inorganic semiconductors with rigid band models. However, these polymers possess highly anisotropic interactions which can lead to collective instabilities typical of quasi-one-dimensional materials, such as Peierls-Frölich modes. Furthermore, because these polymers are organic compounds, it can be anticipated that electronic excitations or charge-transfer processes will markedly affect the atomic geometry, just as in typical organic molecules ; important effects due to electron-phonon coupling are therefore expected.

These characteristics have led to the development of a rich class of fascinating concepts (where nonlinearity is a fundamental ingredient), in order to properly des-

cribe the physics of doped organic polymers, as exemplified in the paper by Brazovski in these Proceedings /5/. These concepts involve e.g. the formation of defects or excitations such as solitons, polarons, or bipolarons and can be very interestingly connected with relativistic field theory models /6/.

In trans-polyacetylene, Su, Schrieffer, and Heeger /7/ have shown that the peculiarity of the double-well potential with minima of the same energy can lead to soliton formation and related lattice deformation. On the basis of the soliton model, many unusual properties have been predicted for trans-polyacetylene (PA), including a conductivity mechanism through charged solitons carrying no spin /7,8/. Recent studies have indicated that at low (homogeneous) doping level, single charges appearing on the trans-PA chain are accomodated as polarons rather than solitons /9-11,6/. At high doping level, polarons should recombine to lead to charged solitons /6,9/. Brédas, Chance,and Silbey /9/ have treated within the same theoretical model trans-PA and polyparaphenylene (PPP) ; the latter is a system that does not possess a degenerate ground state but nevertheless displays transport properties very similar to doped polyacetylene /2/. In trans-PA, they have predicted that a barrier exists to the recombination of polarons into charged solitons up to $\sim$ 3% (homogeneous) doping level /9/. The existence of that barrier has now been verified experimentally up to $\sim$ 1% /12/. In PPP, they have suggested the appearance of bipolarons (doubly charged defects that carry no spin) at high doping levels. Conductivity through motion of bipolarons in PPP is consistent with the absence of any significant Pauli susceptibility in the metallic regime of SbF_5 doped PPP /13/.

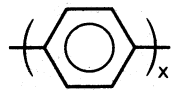
Unfortunately, most of the theoretical work on doped organic polymers has so far been constructed in the framework of very crude methods such as Hückel-type models. Despite its usefulness in attaining physical insight into complex systems, the Hückel Hamiltonian has several drawbacks : (i) it is not self-consistent. No distinction is possible between neutral, positively charged and negatively charged defects. (Via perturbative treatments or using Pariser-Parr-Pople Hamiltonians, distinction can be made between neutral and charged defects but not among charged defects) ; (ii) only π electrons are explicitly taken into account ; the σ framework, very important for the geometry, is usually poorly described ; (iii) a functional dependence has to be assumed for the geometry of the defects (e.g. a tanh function for a soliton defect). Furthermore, the dopant is usually neglected.

It is thus of prime importance to be able to go beyond these models and to study in a reliable way, possibly from first principles, the geometric and electronic modifications that appear upon doping of organic polymers. In this paper, we present : (i) ab initio Hartree-Fock self-consistent-field (SCF) geometry optimization calculations on the electronic structure of undoped and highly Li and/or Na doped polyparaphenylene and polypyrrole chains. (We do not include here our PA calculations that are already relatively old /14/). We demonstrate that charge transfer induces dramatic geometric modifications on the polymer chains. These modifications in turn lead to the appearance of electronic states in the gap that are predicted to play a major role in the conductivity mechanism ; (ii) semi-empirical Hartree-Fock SCF-MNDO (Modified Neglect of Differential Overlap) calculations of the geometry of neutral, positive and negative solitons and positive and negative polarons in trans-PA. It is shown that the geometry of each defect strongly depends on its charge state and that the lattice relaxation around the defect is spatially less extended than the polarization cloud (SDW or CDW) that the defect induces.

II - ELECTRONIC STRUCTURE OF UNDOPED AND HIGHLY DOPED POLYPARAPHENYLENE AND POLYPYRROLE CHAINS

Calculations are performed in the framework of the Restricted Hartree-Fock (RHF) SCF-LCAO-MO ab initio technique, at minimal STO-3G basis set level. Because of computational constraints, we are forced to deal with model polymer chains, that are taken to be p-quaterphenyl (PQP) for PPP and α,α'-quaterpyrrole (QPy) for polypyrrole (PPy). The geometry is optimized for the undoped chain and for the highly Li and/or Na doped chain. Positions of the dopant atoms are fixed in analogy with what is known in graphite intercalation compounds /15/.

A - Polyparaphenylene



In the undoped case, optimized bond lengths and bond angles are in close agreement with experimental data (see ref. 16). The very large 37.8° torsion angle between adjacent rings agrees very well with the 42° value for gaseous biphenyl. The maximum C-C bond length difference is 0.123 Å, slightly larger than in PA (∿ 0.1 Å).

In the Li doped case, we add two dopant atoms to PQP, each Li being located 1.85 Å above the middle of an inner ring /16/. We now allow for different relaxations of bond angles and lengths, between the inner and outer rings. We are then in a position to determine the extent of the influence of the Li atoms. The calculations predict a charge transfer toward the chain of the order of 0.64 e per Li, most of the charge (78%) being transferred to the inner rings. This strongly suggests that in longer chains, the charge transferred to and the influence of the dopant on next-nearest-neighbor rings will be very small. Note that since we take into account charge transfer from two close Li atoms, this mimics the situation where a bipolaron is possibly present on the chain. Charge transfer causes drastic modifications of PQP geometry, the chain becoming nearly coplanar. The inner rings acquire a strong quinoid character. The same is true for the outer rings, however to a lesser extent since the charge transferred to them is smaller. The maximum C-C bond length difference in the inner rings becomes 0.063 Å.

The influence of the geometric modifications on the electronic structure is such that the level corresponding to the highest occupied molecular orbital (HOMO) of the undoped chain is pushed up in energy whereas the level corresponding to the lowest unoccupied MO (LUMO) is pushed down in energy by a similar amount. As indicated by valence effective Hamiltonian (VEH) calculations /17/, the shift is of the order of 0.45 eV. Importantly enough, the other levels remain at almost the same energies as in the undoped case. *We thus observe very naturally the appearance of two states in the gap due to the charge transfer and the geometric modifications implied by the formation of a bipolaron on the chain.* These states in the gap can then be referred to as bipolaron states and are fully occupied (empty) in the case of n(p)-type doping. Two other states (impurity states) corresponding to a mixture of Li 2s and C_π orbitals, are present between the highest bipolaron state and the conduction band (CB) edge.

In the case of Na doping, the charge transfer is almost complete (0.93 e per Na) with 80% of the charge going to the inner rings. The chain becomes coplanar. The inner rings are almost purely quinoid with 1.352 Å and 1.371 Å double bonds and 1.462 Å single bonds ; note that the maximum C-C bond length difference is larger than in the Li doped case. Due to these stronger geometric modifications, the bipolaron states move closer to the center of the gap, being 0.7 eV away from the band edges. The Na 3s impurity states appear within the conduction states and not within the gap.

VEH polymer calculations on polymer chains having Li or Na doped inner rings geometry indicates that the original 3.5 eV PPP band gap does not close as in PA. It decreases to 1.7 eV for the Li doped structure and 1.0 eV for the Na doped one. The VB and CB edges move symmetrically with respect to the gap center.

We can thus draw the following picture for the evolution of the band structure e.g. upon Na doping of PPP, Fig.1. At low doping level, bipolaron states are formed in the gap, 0.7 eV above (below) the VB (CB) edge. As doping level increases, bipolaron states overlap and lead to the formation of bands. Possible motion of bipolarons in these bands leads to a conductivity mechanism without spin. This picture is consistent, as noted earlier, with the absence of any significant Pauli susceptibility in the metallic regime of SbF_5 doped PPP /13/. If higher doping levels could

be achieved, we then conceive bipolaron bands merging with the VB and CB.Conductivity with spin then occurs due to the partially filled character of the CB.

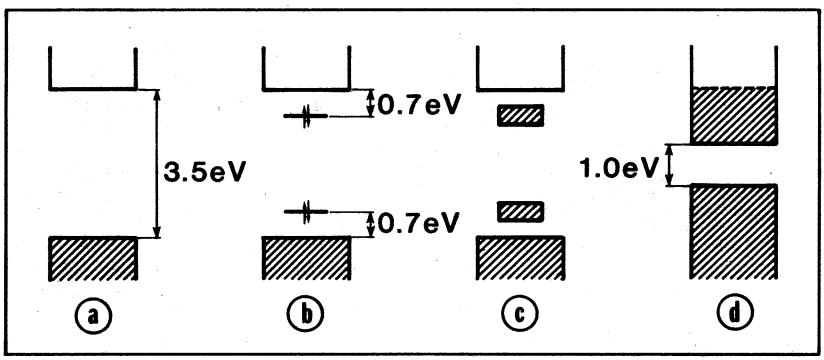
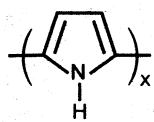


Fig. 1 - Evolution of the band structure upon Na doping of PPP : a) undoped ; b) low doping level (formation of bipolaron states in the gap) ; c) high doping level (formation of bipolaron bands) ; d) very high doping level (merging of bipolaron bands with VB and CB).

B - Polypyrrole



Calculations on quaterpyrrole (QPy) indicate that Li doping does not lead to any charge transfer whereas Na doping does. This reflects the smaller electron affinity of PPy with respect to PPP. Note however that no successful n-type doping of PPy has been reported so far.

The undoped QPy chain is coplanar with a maximum C-C or C-N bond length difference of 0.111 Å : within a ring, $r_{C=C}$ = 1.363 Å, r_{C-C} = 1.424 Å, r_{C-N} = 1.385 Å;between rings : r_{C-C} = 1.474 Å. This geometry leads to a VEH band gap of 4.0 eV, a bit larger than the 3.2 eV estimate for neutral PPy /18/. When doping with Na, one Na atom is located 1.98 Å above each of the inner rings. The charge transfer is 0.94 e per Na and, as previously, charge mainly goes (80%) to the inner rings. Geometric modifications in the inner rings are such that along the carbon path (resembling a cis-polyacetylene backbone), the C-C single and double bonds are interchanged with respect to the undoped case. C-N bonds elongate to 1.428 Å. An analysis of the frontier orbitals indicates that the modifications upon p-type doping would be very similar, at least along the carbon path. Geometric modifications in the outer rings are small, implying a smaller extension for a bipolaron defect than in PPP.

In contrast to PPP, the shifts (with respect to the undoped case) of the HOMO and LUMO levels to form bipolaron states in the gap are not similar. VEH calculations predict the two states appear respectively at 0.45 eV above the VB edge and 0.9 eV below the CB edge. This asymmetry is also illustrated via VEH calculations on a polymer having the geometry of the Na doped inner rings of QPy. The band gap decreases from 4.0 eV to 1.4 eV with the VB moving up by 1.0 eV and the CB down by 1.6 eV. Taking this asymmetry into account, the same overall picture for the band structure evolution upon Na doping can be given for PPy as for PPP in Fig. 1. Thus,

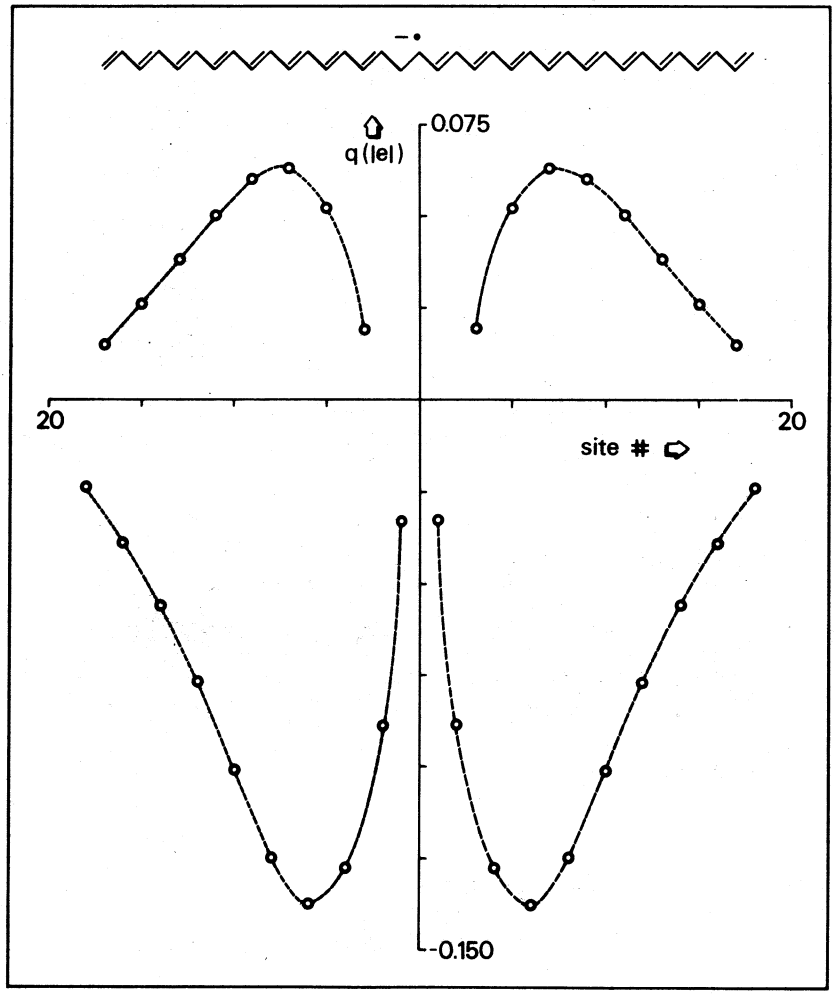


Fig. 2 - Lattice polarization (net charges per CH unit) for a negative polaron.

at high doping, motion of bipolarons in the bipolaron bands can lead to a conductivity mechanism without spin. It is remarkable to note that this is fully consistent with the observation that in electrochemically cycled highly conducting PPy, no ESR signal is obtained /19/.

In summary, we see emerging for all the polymers we have considered up to now the same theoretical description. At low doping levels, states appear in the gap as a result of the presence of charged defects with related lattice deformation, such as polarons, solitons and bipolarons. Impurity states can also be present in the gap, depending on the dopant. At high doping levels, broadening of the states in the gap can lead to the formation of bipolaron bands (PPP, PPy) or soliton bands (trans-PA). Motion of doubly charged bipolarons or charged solitons produces a conductivity mechanism without spin. Conductivity with spin can occur at higher doping levels, when soliton or bipolaron bands merge with the CB and VB.

III - GEOMETRIES OF SOLITONS AND POLARONS IN TRANS-POLYACETYLENE

We have performed Hartree-Fock SCF-MNDO complete geometry optimizations on trans-PA chains containing 40 or 41 carbons. In this case, the dopant is not explicitly taken into account. Our goal is to investigate the dependence on charge, of the geometries of soliton and polaron defects in trans-PA. Note that for a chain without defects, MNDO optimization results in a bond length alternation Δr_0 = 0.105 Å /20/, in close agreement with experimental estimates /21/.

As previously pointed out, no distinction is possible between neutral, positive and negative species in the Hückel framework. However, it must be stressed that, in the CH_3^+ cation or $CH_3\cdot$ radical, the carbon atom tends to be in sp^2 hybridization, the π orbital being empty (half-occupied) in the cation (radical). On the contrary, in the CH_3^- anion, the carbon prefers to adopt an sp^3 hybridization. Therefore, there is no reason to expect that, e.g. the positive and negative solitons should be identical.

The MNDO calculations show that all three solitons are different /20/. For the neutral soliton, the evolution of the bond length alternation can be fitted by a tanh function with halfwidth l = 3 ; i.e. the reversal of the phase of the bond length alternation takes (2l + 1 =) 7 carbons. This is half the value predicted with an Hückel model and in much closer agreement with the Pariser-Parr-Pople calculations of Fukutome and Sasai /22/. With the neutral soliton there is associated a damped spin density wave (SDW) whose width is larger (l = 5) than the kink itself, also in agreement with Fukutome and Sasai /22/.

The positive soliton is more extended (l = 5) than the neutral one. It is interesting to note that the screening of the positive charge is accomplished by polarization of alternate π bonds yielding a marked oscillation of charge from site to site (all + charges on one side of the chain, all - charges on the other side) which decreases in magnitude as one gets further from the defect center (see Fig. 2 in Ref. 20). Note that this can have significant impact on the motion of similar defects on neighboring chains and lead to strong coupling between PA chains. This damped CDW also has a width larger (l = 8) than that of the lattice kink.

The negative soliton is much more compact ($l \sim 2$) and is not very well fitted by a tanh function. This compactness could be explained by the higher intrinsic energy of this defect in which negatively charged carbons are forced into sp^2 hybridization. The associated CDW is however the same (l = 8) as for the positive soliton.

Turning now to polarons, we find that the negative polaron has a larger depression of the bond length alternation in the middle of the defect (Δr middle = 0.32 Δr_0) than the positive polaron (Δr middle = 0.50 Δr_0). As in the case of solitons, the negative polaron is narrower and both positive and negative defects lead to similar lattice polarizations. Due to the center of inversion symmetry of the polaron, the lattice polarization is quite different from the soliton case. The four middle sites carry charges of same sign ; oscillation of charge sign from site to site starts from the third site away from the middle of the defect and, very interestingly, the largest charges are obtained on the sixth and seventh sites away from the middle (see Fig. 2). Strong coupling between PA chains is also expected in the case of polarons.

Although the results presented in this section may be modified if the dopant is explicitly taken into account, they are fully relevant in cases e.g. of charge injection processes.

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