

Moffitt's Theorem as a Bridge between the Delocalized Picture of Band Theory and the Local Picture of Resonance Structures in a Solid: Peierls Distortions and Conductivity of Polyacetylene

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By extending to solid state chemistry a methodology developed in molecular chemistry, we show how one can calculate the contribution of a resonance structure in a solid by using the Bloch orbitals or, in general, the delocalized crystal orbitals. The method is applied to polyacetylene: the Peierls distortions and the conductivity of this system are explained by examining the contributions of some ionic resonance structures. © 1992 Academic Press, Inc.

1. Introduction

The use of methods and concepts developed initially in molecular chemistry has been very useful in solid state chemistry (1–3). On the other hand, the band theory and concepts such as Fermi surfaces or charge density waves (CDWs), originated from solid state physics, are widely used in solid state chemistry (4). For example, the nesting of Fermi surfaces and the associated CDWs in low-dimensional solids (5) is actually the principal tool to explain and rationalize the (anti-) conducting properties of these systems.

In molecular chemistry, resonance structures within the “resonance or mesomeric theory” are a very useful tool, especially for an experimental chemist. Recently, we have developed a methodology allowing the calculation of resonance structures of a bond or a functional group inside a given molecule

by analyzing the traditional molecular orbital (MO) wavefunction: the delocalized MO-wavefunction is decomposed in a totally local (6) one by means of Moffitt's theorem (7) and then the contributions of resonance structures are calculated as the expectation values of multielectron density operators (8) in the frame of the multielectron population analysis (9).

Resonance structures are useful not only in molecular chemistry, but also in solid state chemistry. Since the early years of quantum chemistry, a theory of resonance of valence-bond structures of metals was established, and applications were given in actual problems of solid state (10–12).

The band theory gives a delocalized picture of a solid, exactly as the usual MO theory gives the (most) delocalized picture of a molecule. Contrarily, in resonance theory, an electron pair is not delocalized over the whole system, and therefore the local

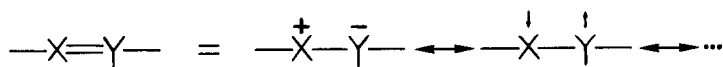


FIG. 1. Ionic and covalent resonance structures of a double bond, ---X=Y--- .

pictures of this theory are closer to the experimental chemist's thinking and reasoning. Both approaches seem to be mutually exclusive, even though it is well known that both can converge to the same result, especially when they are refined (13). The success of the projection of Hückel MOs into a Heisenberg-type space (composed of neutral spin alternant and nonalternant situations) (14) is also a consequence of the equivalence of these two approaches. The purpose of this work is to give a *simple bridge between the delocalized picture of band theory and the local one of resonance structures* by extending our methodology, which is established in molecular chemistry. Moffitt's theorem is, therefore, formulated for solid state, and an application is given for polyacetylene (PA). In the present work, we wish to show also how a simple inspection of the Bloch orbitals of PA can lead to useful conclusions for the contributions of some resonance structures which are crucial for Peierls distortions and conductivity of PA.

2. Method and Results

2.a. Resonance Structures in Polyacetylene

In molecular chemistry, a double bond, ---X=Y--- , can be considered as the "resonance" of the ionic and covalent structures with various contributions, depending on the molecular system (see Fig. 1).

In analogy with this traditional chemical point of view, one can consider the ground state of PA as the "resonance" of similar structures, as shown in Fig. 2.

The ionic structure I_1 is representative of the CDWs in PA; since from band theory it is well known that CDWs are directly related to the conductivity (5), one can suppose that if a structure like I_1 has an important contribution, one can expect insulating properties, and if it has very small contribution, a nonnegligible conductivity.

The ionic structure I_x can be considered to be responsible for the Peierls distortions by both the (+, -) attractions and the (+, +), or (-, -), repulsions; contrarily, struc-

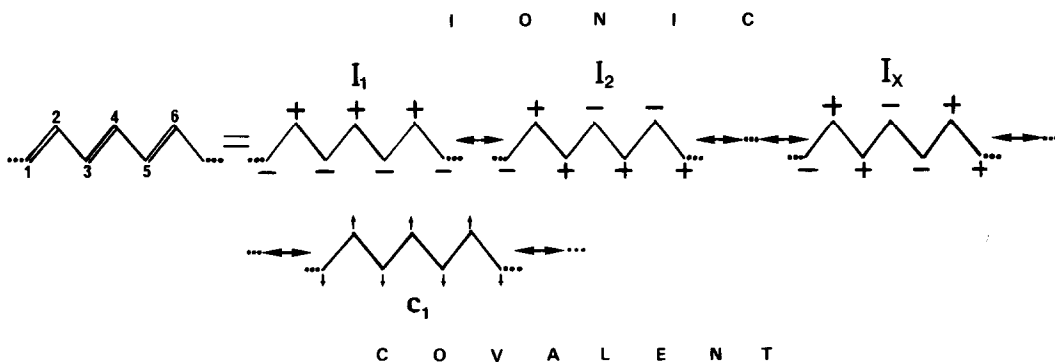


FIG. 2. Various ionic and covalent resonance structures of polyacetylene.

ture I_1 does not contribute to Peierls distortions, since the (+, -) attractions are equally distributed for all the C-C bonds. Consequently, the contributions of these two structures, I_1 and I_x , must also be crucial for the Peierls distortions in PA.

All structures illustrated in Fig. 2 are accompanied, of course, by symmetric ones having obviously the same contributions. For example, structure I_1 (. . . , -, +, -, +, -, +, -, . . .) is accompanied by its symmetric one (. . . , +, -, +, -, +, -, +, . . .), structure I_x (. . . , -, +, +, -, -, +, +, . . .) by (. . . , +, -, -, +, +, -, -, . . .), etc. Since the symmetric structures have exactly the same role for the conductivity and Peierls distortions, in what follows we deal only with the structures illustrated in Fig. 2.

In analogy with molecular chemistry, the contributions of the various structures of Fig. 2 can be calculated as the expectation values of some multielectron density operators (8). For example, the contribution of the CDW structure, I_1 , is the expectation value of the density operator

$$\phi_1^+ \phi_1^+ \phi_2 \phi_2 \phi_3^+ \phi_3^+ \cdots \phi_6 \phi_6 \phi_6^+ \phi_6^+ \cdots \phi_3 \phi_3 \phi_2^+ \phi_2^+ \phi_1 \phi_1$$

(where ϕ are the P_z -AOs of PA); it gives the *probability* to find an electron pair in the AO ϕ_1 when *simultaneously* the AO ϕ_2 is empty, *simultaneously* an electron pair is located in ϕ_3 , etc.

The calculation of such expectation values needs the knowledge of the expansion coefficients T_{I_1} , T_{I_2} etc., in the following wave function, Φ :

$$|\Phi\rangle = T_{I_1}|\Phi_{I_1}\rangle + T_{I_2}|\Phi_{I_2}\rangle + \cdots + T_{I_x}|\Phi_{I_x}\rangle + \cdots + T_{C_1}|\Phi_{C_1}\rangle + \cdots, \quad (1a)$$

or shortly

$$|\Phi\rangle = \sum_{\Phi} T_{\Phi}|\Phi\rangle. \quad (1b)$$

The basis set $\{\Phi\}$, that is, $\Phi_{I_1} \dots \Phi_{I_x}$, etc., is composed from totally local Slater deter-

minants, which correspond to the chemical graphs $I_1 \dots I_x$ etc. of Figure 2:

$$\begin{aligned} \Phi_{I_1} &= \|\cdots \phi_1 \phi_1 \phi_3 \phi_3 \phi_5 \phi_5 \cdots\| \\ &\vdots \\ \Phi_{I_x} &= \|\cdots \phi_1 \phi_1 \phi_4 \phi_4 \phi_5 \phi_5 \cdots\| \end{aligned} \quad (2)$$

As in molecular chemistry, a totally local wavefunction, as the above Φ , could be calculated, in principle, from valence-bond calculations; an alternative way is to start from the usual delocalized MO wavefunction and then decompose it to a local one (6, 8, 9) using Moffitt's theorem (7).

By assuming that the electron population analysis of the delocalized wavefunction is made in a model orthogonal AO-basis set (as for instance the P_z -AOs of polyenes used in solid state physics, within the Hubbard method (15)), the expectation values of an above-mentioned density operator are given very simply as the square of the expansion coefficients, T^2 .

2.b. Formulation of Moffitt's Theorem in Solid State Chemistry

The Bloch equations, within the LCAO (linear combination of atomic orbitals) approximation, are the basic equations in solid state chemistry:

$$\psi_k = \sum_n e^{ikna} \phi_n, \quad (3)$$

where ϕ_n are AOs, k is the wavenumber, and a is the lattice spacing.

Starting from delocalized crystal orbitals, as the above Bloch orbitals, ψ_k , one can calculate the expansion coefficients, T_{Φ} , in the wavefunction Φ given in relation (1) by means of Moffitt's theorem (7), which is known from molecular chemistry. In solid state chemistry, this theorem can be formulated as follows:

The expansion coefficient, T_{Φ} , of a given local structure $\Phi = \|\cdots \phi_n \cdots \phi_m \cdots\|$ is the product of two determinants containing

the LCAO coefficients of the occupied crystal orbitals, ψ_k , with α -spin electrons (one determinant) and β -spin electrons (second determinant). These determinants are built in such a way that column indices are the wave numbers, k , of the occupied crystal orbitals, and line indices are those of the AOs, which are occupied in Φ .

2.c. Application of Moffitt's Theorem in Polyacetylene (Half-Filled Bands)

Let us consider first that the lattice spacing, a , is equal for all the C-C bonds of PA. Since the band is half-filled, the highest (singly) occupied crystal orbitals ψ_A and ψ_B , of a $4n$ fragment (16) are given in Fig. 3 (after

performing a $\pi/4$ rotation in these degenerate orbitals): in the AO-positions 1, 3, 5, . . . , where ψ_B has zero LCAO coefficients, ψ_A has nonzero coefficients; the opposite occurs for the AO-positions 2, 4, 6,

Moffitt's theorem is now applied for the various possibilities of electron spin occupation of the degenerate orbitals ψ_A and ψ_B :

(i) ψ_A and ψ_B have antiparallel spins. Let us consider that there is an electron with α -spin in crystal orbital ψ_A and an electron with β -spin in ψ_B : $\psi_1\psi_{\bar{1}} \dots \psi_A\psi_{\bar{B}}$. According to Moffitt's theorem, the expansion coefficients, T_{I_1} and T_{I_x} , of structures I_1 and I_x (see Fig. 2 and expressions (2)) are calculated as follows:

$$T_{I_1} = \begin{array}{c} n \\ \parallel \\ \cdot \\ \cdot \\ \cdot \\ 1 \\ 3 \\ 5 \\ \cdot \\ \cdot \\ \cdot \end{array} \begin{array}{c} k = 1 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad A \\ \cdot \\ \cdot \\ \cdot \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad + \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad - \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad + \\ \cdot \\ \cdot \\ \cdot \end{array} \times \begin{array}{c} n \\ \parallel \\ \cdot \\ \cdot \\ \cdot \\ \bar{1} \\ \bar{3} \\ \bar{5} \\ \cdot \\ \cdot \\ \cdot \end{array} \begin{array}{c} k = \bar{1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \bar{B} \\ \cdot \\ \cdot \\ \cdot \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 0 \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 0 \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 0 \\ \cdot \\ \cdot \\ \cdot \end{array} = 0,$$

where + or - means positive or negative LCAO coefficients,

$$T_{I_x} = \begin{array}{c} n \\ \parallel \\ \cdot \\ \cdot \\ \cdot \\ 1 \\ 4 \\ 5 \\ \cdot \\ \cdot \\ \cdot \end{array} \begin{array}{c} k = 1 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad A \\ \cdot \\ \cdot \\ \cdot \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad + \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 0 \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad + \\ \cdot \\ \cdot \\ \cdot \end{array} \times \begin{array}{c} n \\ \parallel \\ \cdot \\ \cdot \\ \cdot \\ \bar{1} \\ \bar{4} \\ \bar{5} \\ \cdot \\ \cdot \\ \cdot \end{array} \begin{array}{c} k = \bar{1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \bar{B} \\ \cdot \\ \cdot \\ \cdot \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 0 \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad - \\ + \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 0 \\ \cdot \\ \cdot \\ \cdot \end{array} \neq 0.$$

The T_{I_1} is zero since there is one column in the determinant of β -spins which involves only zeros; the contribution, therefore, of the CDW structure I_1 , $T_{I_1}^2$, is zero, while that of I_x is different from zero.

The same result is also true by considering an inverse spin occupation of ψ_A and ψ_B : $\psi_1 \psi_{\bar{1}} \dots \psi_A \psi_B$ (the $T_{I_1}^2$ is zero since the determinant of α -spins is, in this case, zero).

(ii) ψ_A and ψ_B have parallel spins. Let us consider that both ψ_A and ψ_B have α -spin electrons:

$$\psi_1 \psi_{\bar{1}} \dots \psi_w \psi_A \psi_B.$$

The application of Moffitt's theorem gives

$$T_{I_1} = \begin{vmatrix} n \\ \parallel \\ k = 1 & \dots & A & B \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ 1 & + & \cdot & + & 0 \\ 3 & + & \cdot & - & 0 \\ 5 & + & \cdot & + & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} \times \begin{vmatrix} n \\ \parallel \\ k = \bar{1} & \dots & \bar{W} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \bar{1} & + & \cdot & \cdot & \cdot & * \\ \bar{3} & + & \cdot & \cdot & \cdot & * \\ \bar{5} & + & \cdot & \cdot & \cdot & * \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0,$$

$$T_{I_x} = \begin{vmatrix} n \\ \parallel \\ k = 1 & \dots & A & B \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ 1 & + & \cdot & + & 0 \\ 4 & + & \cdot & 0 & - \\ 5 & + & \cdot & + & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} \times \begin{vmatrix} n \\ \parallel \\ k = \bar{1} & \dots & \bar{W} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \bar{1} & + & \cdot & \cdot & \cdot & * \\ \bar{4} & + & \cdot & \cdot & \cdot & * \\ \bar{5} & + & \cdot & \cdot & \cdot & * \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} \neq 0.$$

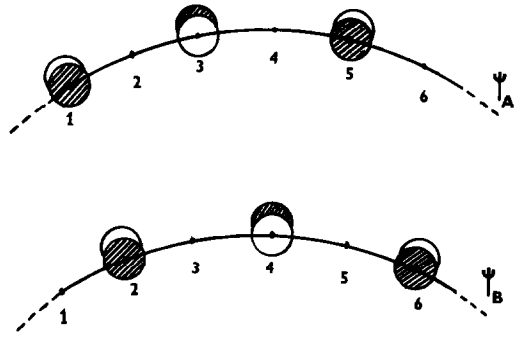


FIG. 3. The highest occupied (and degenerate) crystal orbitals ψ_A and ψ_B in the half-filled band of polyacetylene.

In the present case, the contribution of the CDW structure, I_1 , is also zero, while that of I_x is different from zero.

The same result is also true for the spin occupation $\psi_1 \psi_{\bar{1}} \dots \psi_{\bar{A}} \psi_{\bar{B}}$ (the T_{I_1} is zero since the determinant of β -spins is zero).

In all the above examples we have supposed that all the C–C bonds are equal, and therefore there are (at least) two singly occupied crystal orbitals having (after a $\pi/4$ rotation) the shapes of Fig. 3. If we suppose that the C–C bonds have alternate short and long lengths, the alternance of zero in crystal orbitals, as ψ_A and ψ_B , is destroyed, and therefore both structures I_1 and I_x have *nonzero contributions*.

All these qualitative predictions have been verified by numerical calculations in polyenes with a small number of atoms. For the case of equal C–C bond lengths, we have considered the systems of cyclobutadiene and cyclooctatetraene. The MO-wavefunctions are obtained by PPP calculations with standard parametrization (17); the Hartree–Fock MO-wavefunction is improved by configuration interaction (CI) calculations in order to take into account important correlation effects, such as spin polarization (18). In the case of cyclobutadiene we have performed full-CI calculations and then the ground singlet state of a multideterminantal MO-wavefunction is used in order to calculate the contributions of the resonance structures as usual (8, 9). In the case of cyclooctatetraene, the CI calculations are performed by means of the CIPSI method (19), which selects iteratively the CI space; since the criterion in the second-order correction in energy is chosen very small (5×10^{-5} au), our CI can be considered as quasi-total. The final space of the Slater determinants which are selected by the CIPSI method is then diagonalized, and the contributions of the resonance structures are calculated from the ground singlet MO-multiplet eigenvalue. In other cases, when the cyclic symmetry with equal the C–C bonds is destroyed, as in a linear polyene with a limited number of carbon atoms, numerous previous calculations (20), in accordance with fundamental chemical intuition, show that the CDW structure I_1 has nonzero contribution (more precisely, the

most important contribution between the ionic structures).

2.d. Peierls Distortions and Conductivity of Polyacetylene

We have shown that the CDW structure, I_1 , has zero contribution if all the C–C bond lengths are equal, and nonzero if these bonds have alternating short and long lengths. Ionic structures with nonalternant charges, such as I_x , have nonzero contributions in both cases. By using these results one can give alternative explanations for Peierls distortions and conductivity in PA by using the chemist's picture of resonance structures, rather than the picture of electron pairs delocalized in the crystal orbitals issued from band theory (21).

If the C–C bonds were equal in PA, then the CDW structure I_1 , which does not favor the Peierls distortions, should have been forbidden; therefore, the remaining structures such as I_x (. . . -, +, +, -, -, +, + . . .), which are allowed, can easily cause a shortening and an elongation of the C–C bonds by both the (+, -) attractions and (+, +), or (-, -), repulsions.

Band theory predicts that the PA with equal the C–C bond lengths should be a conductor. Since, as is well known (5), the predominance of CDWs is a strong factor against conduction, the fact that resonance structure I_1 is zero explains in terms of resonating structures this (hypothetical) conductivity. Similarly, the fact that in PA (with alternating bond lengths) the contribution of structure I_1 is important explains also its very low conductivity.

The well-known increasing conductivity of PA by doping (22) can also be explained from the decrease of the contribution of the CDW resonance structure, I_1 . Let us consider the case that the doping is p-type (e.g., the dopants are electron acceptors). Such a type of doping favors resonance structures which exhibit negative charges to the

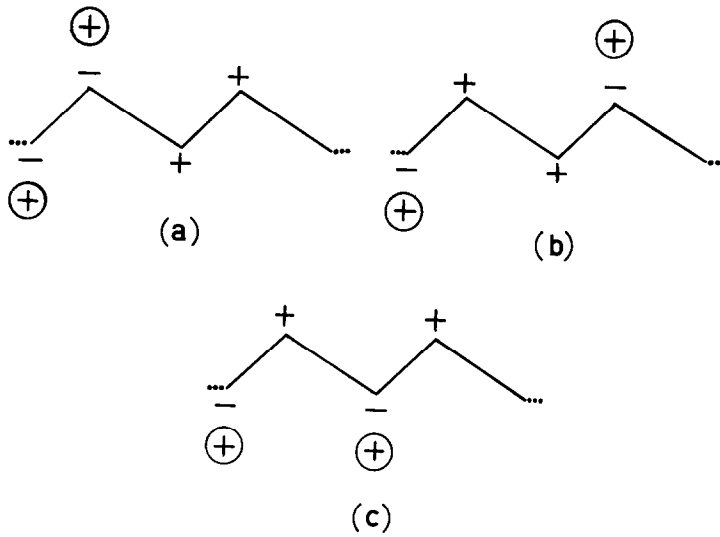


FIG. 4. Ionic structures which are favored from various arrangements of p-type dopants: in (a) and (b) the dopants are located at both sides of the polyacetylenic chain (realistic cases), while in (c) only at one side (nonrealistic case).

neighbouring to the dopants carbon atoms, as it is shown in Figs. 4a and 4b (the positive charges in cycles represent schematically the dopants); these structures exhibit an *asymmetric* distribution of the (+) and (-) charges and are quite numerous in PA. In the undoped PA they have small contributions due to the repulsions of (+, +) or (-, -) charges, whereas the CDW structure I_1 , as mentioned in a previous section, has the most important contribution. In the doped PA the contribution of I_1 must decrease according to the following reasons:

(i) Since the wavefunction Φ is normalized to 1, the increment by doping of the contributions of the numerous structures with the asymmetric (+) and (-) charge distributions leads to a decrease of the contribution of I_1 .

(ii) Since I_1 exhibits all the (+) and (-) charges in separate sides of a polyacetylenic chain, the only possible arrangement of the dopants around this chain which could favor

structure I_1 is a *symmetric* one, shown in Fig. 4c: the dopants are located only at the one side of the polyene. However, this arrangement is not realistic, the main reason being (apart from the dopant-dopant repulsions) the fact that one polyacetylenic chain is not alone inside the solid, and dopants are present at least in two sides (in-plane or/and out-of-plane) of each chain; all these arrangements of the dopants are asymmetric and therefore decrease the contribution of the CDW structure I_1 , which has the *most* symmetric distribution of (+) and (-) charges.

More often the effect of the p-type doping is strong enough so that one can consider that there is a transfer of the entire positive charges to PA (22b). In this case, the CDW resonance structure is destroyed due to the insertion of the additional charges in the polyacetylenic chain. In other words, the electronic configuration shown in Fig. 4c is not favored, not only for the above reasons,

but also due to the strong electron transfer from PA to the dopants. Of course, similar arguments are also valid for the case of n-type doping (e.g., when the dopants are electron-donating systems).

3. Conclusion

As in molecular chemistry delocalized MO-wavefunctions are not easily interpreted. In solid state chemistry the picture resulting from the band theory can also be difficult to be understood by an experimental chemist; this is essentially due to the fact that the picture of electron pairs delocalized over the whole molecule is far from the chemist's usual thinking in terms of bonds. On the other hand, band calculations are very familiar in solid state chemistry, in various approximation levels (22, 23). By using Moffitt's theorem we hope to benefit from both

(i) the facility in calculations using the Band theory, and

(ii) the chemical interpretation which is based on the picture of local structures.

In the case of PA we have showed how one can understand the Peierls distortions and the very low conductivity of undoped PA, as well as the effect of the doping on its conductivity, by examining the contributions of chemical structures as I_1 , I_x , etc., directly from the delocalized crystal orbitals. This type of decomposition of crystal orbitals to resonance structures will be further used in order to understand the (anti)ferromagnetic properties of other interesting systems such as the nonclassical polymers (24).

Acknowledgments

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