

## **Comparisons among some theoretical studies of electrical conductivity in polymers**

**G.P. Das and J.E. Mark**

Chemistry Department and the Polymer Research Center, University of Cincinnati, Cincinnati, OH 45221, USA

### ABSTRACT

The following three theoretical schemes for the study of electronic band structures in polymers are compared: (a) Extended Huckel, (b) Valence Effective Hamiltonian, and (c) Ab-Initio. In the last category, both the conventional approach and a novel approximate scheme are compared with the other methods.

### I. INTRODUCTION

In a polymer, as in a crystal, the interaction of the repeat units leads to the formation of electronic bands. Since in polymers the translational symmetry is only in one direction, however, one expects a one-dimensional band in contrast with the 3-dimensional ones occurring in crystals.

There is strong interest in the theoretical understanding of electrical conductivity in organic polymers since several polymers have been shown to behave as semiconductors. Moreover, in the presence of suitable dopants, they become good conductors. The basic mechanism by which electricity is transported in these systems is far from clear. It is not even certain that the models that are successful with respect to the inorganic semiconductors (or, for that matter, the inorganic conductors) are applicable to organic polymers. In polyacetylene (PAC), for example, there is strong evidence (1) that the conductivity carriers are largely solitons (electron-phonon distortion waves) rather than free (or semi-free) electrons, as in metals and inorganic semiconductors.

Thus far theoretical calculations (2-6) on the electronic band structures (prompted by the availability of experimental information) have largely been based on semi-empirical methods (2-3) such as the Extended Huckel Theory (EHT), and more recently the Valence Effective Hamiltonian (VEH) method (5). Because of prohibitive computing expenses, ab-initio calculations in this area are rare. Nonetheless, all-electron crystal-orbital SCF calculations (6) on infinite chain polyene and polyethylene have been reported. However, apart from the fact that these calculations are based on a theory that is parameterless, their quality is uncertain since ab-initio SCF wavefunctions are notoriously inadequate in covalent systems for most properties. A semi-empirical Pariser-Parr-Pople (PPP) variant (4) of this theory has also been tried on the same systems.

In what follows we consider an approximate ab-initio framework (7) that treats a system by computing "local" wavefunctions for various components of the system and then uses the resulting cumulative field to determine the valence and conduction bands generated by the most itinerant electrons (i.e. those having the smallest ionization potential). We consider this approach in detail in Sections II and III and present the corresponding results along with both the semi-empirical, VEH and other available ab-initio results in the following sections.

## II. DESCRIPTION OF THE APPROXIMATE AB-INITIO THEORY

In this model (7) we view the given molecular system (e.g. the repeat unit of a given polymer) as consisting of simple fragments (very often single atoms or pairs of atoms). We surround each fragment by its nearest neighbor fragments and call it a "subsystem". We now assign a basis space to represent the orbitals of this subsystem. It is necessary to include functions that are common between the fragments (particularly those that are required to represent the itinerant electrons).

We write the total energy of a subsystem in the form

$$E^s = \sum_a^{(s)} E_a + \sum_{a>b}^{(s)} E_{ab} + P \sum_{a>b}^{(s)} \sum_{i,j} \langle ia/jb \rangle^2 \quad (1)$$

The first summation corresponds to the individual energies of the fragments, the second represents the interactions between the fragments, and the third (with  $P \gg 0$ ) is introduced to prevent orthogonality "collapse".

The wavefunction to be used for the subsystem is of the unrestricted Hartree-Fock (UHF) type and is variationally determined, leading to a minimum energy. Once all the subsystems have been optimized, the total energy for the complete system is taken as

$$E = \sum_a E_a + \sum_{a>b} \{ E_{ab} - \left( \sum_j \sum_{i \in \text{core}} \epsilon_{ia} \langle ia/jb \rangle^2 + \sum_i \sum_{j \in \text{core}} \epsilon_{jb} \langle ia/jb \rangle^2 \right) \} \quad (2)$$

the last term (with  $\epsilon_{ia}, \epsilon_{jb}$  as the core orbital energies of the fragments a and b) representing an approximation to the energy correction arising from the non-orthogonality of the orbitals between the fragments.

## III. EQUATIONS DETERMINING ELECTRONIC BANDS OF POLYMERS

We shall treat the most itinerant electrons as the only members forming the electronic bands of direct importance to the conduction of electricity. In all the cases considered here, the  $\pi$ -electrons appear to fall in this category.

We flank the repeat unit by the nearest fragments coming from the two adjoining repeat units. The  $\pi$ -electron Hamiltonian is constructed by

taking the fragment  $\pi$ -orbitals as the functional basis and using the one- and two-electron integrals over these orbitals computed for each subsystem. Thus if  $\{\chi_i\}$  are functions centered on the fragments  $\{i\}$  of a subsystem, then the one- and two-electron integrals involving these functions are approximated as

$$\begin{aligned} \langle \chi_i | h | \chi_j \rangle &\equiv \langle \chi_i | T + V_1 + V_2 + \dots | \chi_j \rangle \\ &\quad (s) \\ &\approx \langle \chi_i | T + \sum_k V_k | \chi_j \rangle = \langle \chi_i | h^{(s)} | \chi_j \rangle \end{aligned} \quad (3)$$

and

$$\langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_k \chi_l \rangle = J_{ijkl}^{(s)} \quad (4)$$

where the integrals  $\langle \chi_i | h^{(s)} | \chi_j \rangle$  and  $J_{ijkl}^{(s)}$  are those that are given from the subsystem (s);  $V_k$ 's include the two-electron Coulomb and exchange terms coming from the  $k$  and core electrons.

The  $\pi$ -electron problem is now solved by assuming an "auf-bau" - type MO wavefunction

$$\Psi_\pi = \pi_1^2 \pi_2^2 \dots \quad (5)$$

where the orbitals  $\pi_1, \pi_2, \dots$  etc. are completely delocalized. The wavefunction is variationally optimized via the Fock equation

$$F^{\text{mono}} | \pi_i \rangle = \epsilon_i | \pi_i \rangle \quad (6)$$

We now consider the HOMO and LUMO orbitals

$$\begin{aligned} \phi_{\text{HOMO}} &= \sum_{k=1}^n c_k \chi_k \\ \phi_{\text{LUMO}} &= \sum_{k=1}^n d_k \chi_k \end{aligned} \quad (7)$$

Using these as the basis for the polyatomic  $\pi$ -Hamiltonian we approximate the corresponding matrix elements as

$$\langle \phi_{\text{HOMO}}^i | F^{\text{poly}} | \phi_{\text{HOMO}}^i \rangle = \epsilon_{\text{HOMO}}^{(\text{mono})}$$

$$\begin{aligned}
\langle \phi_{\text{LUMO}}^i | F^{\text{poly}} | \phi_{\text{LUMO}}^i \rangle &= \epsilon_{\text{LUMO}}^{(\text{mono})} \\
\langle \phi_{\text{HOMO}}^i | F^{\text{poly}} | \phi_{\text{HOMO}}^{i+1} \rangle &= c_n c_2 F_{nn}^{\text{mono}} \\
&\quad + c_{n-1} c_1 F_{n-1, n-1}^{\text{mono}} + (c_n c_1 + c_{n-1} c_2) F_{n, n-1}^{\text{mono}} \\
\langle \phi_{\text{HOMO}}^i | F^{\text{poly}} | \phi_{\text{LUMO}}^{i+1} \rangle &= c_n d_2 F_{nn}^{\text{mono}} \\
&\quad + c_{n-1} d_1 F_{n-1, n-1}^{\text{mono}} + (c_n d_1 + c_{n-1} d_2) F_{n, n-1}^{\text{mono}}
\end{aligned} \tag{8}$$

etc. Similar equations apply for the overlap matrix  $S^{\text{poly}}$ . Polyatomic Fock equations of the following form

$$F^{\text{poly}} C^{\text{poly}} = C^{\text{poly}} S^{\text{poly}} E^{\text{poly}} \tag{9}$$

are now solved leading to the electronic valence and conduction bands. No self-consistency is attempted in this last step, assuming that the off-diagonal elements in Eq (8) are small (which is generally borne out).

#### IV. APPLICATIONS

We have considered in this work the polymer systems PAC, cis-polybenzobisoxazole (PBO) and trans-polybenzobisthiazole (PBT). We present below the various computational details regarding these systems leading to their ab-initio electronic bands.

##### (a) Structural Details

The polymer PAC in the "trans" form consists of two alternating weak and strong carbon-carbon bonds with lengths  $R_{\text{C}=\text{C}} = 1.34 \text{ \AA}$ ,  $R_{\text{C}-\text{C}} = 1.44 \text{ \AA}$  and  $R_{\text{C}-\text{H}} = 1.12 \text{ \AA}$ . The bond angles  $\theta(\text{C}=\text{C}-\text{C}) = 127^\circ$  and  $\theta(\text{C}=\text{C}-\text{H}) = 118^\circ$  (2).

The structural and conformational information on PBO and PBT are taken from the reported X-ray structural data (8). Both X-ray and electron-diffraction studies (9) indicate that the polymers are planar in the crystalline state.

##### (b) Selection of Fragments

In PAC there is just one identifiable fragment. Although only one subsystem  $\text{C}_3\text{H}_3$  has been used, the band calculations have been performed with  $\text{C}_3\text{H}_3$ ,  $\text{C}_5\text{H}_5$  and  $\text{C}_7\text{H}_7$  as the repeat units using  $\text{C}_3\text{H}_3$ -based integrals. This is described in Figure 1 (a). These calculations are meant to assess the kind of accuracy one can expect for the larger systems PBO and PBT.

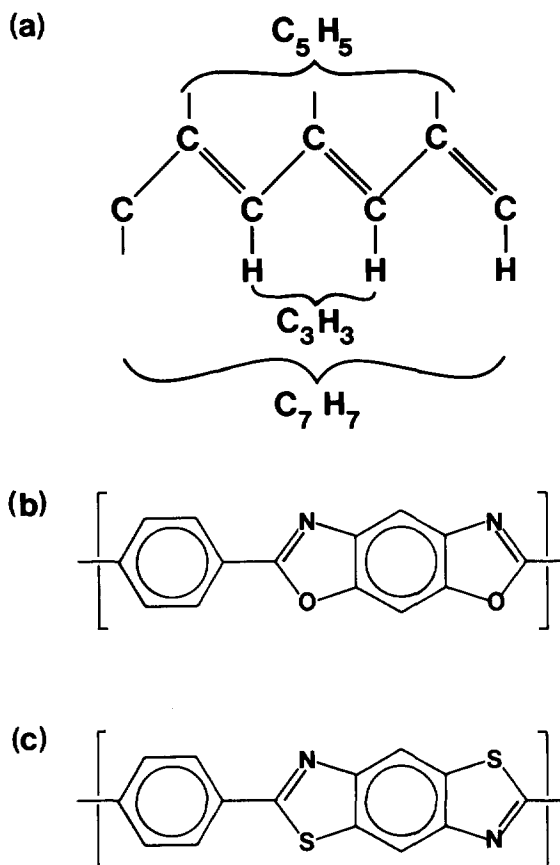


Figure 1. (a) A section of the PAC chain, with delineation of the three sequences considered in the calculations. (b) The repeat unit of the cis-PBO chain. (c) The repeat unit of the trans-PBT chain.

In the PBO and PBT repeat units shown in Figure 1 (b) and (c), only seven fragments are identified, ignoring small differences in the environments of some of the fragments. These are shown in Figure 2.

### (c) Computational Details

The Huzinaga (9s4p)/(3s2p) GTO basis has been used throughout for all the first-row atoms while for hydrogen a (4s)/(1s) set has been found adequate. For sulfur an Effective Core Potential (ECP) set (3s2p)/(2s2p) has been used (10).

In the UHF calculations a spin-arrangement allowing the least amount of orthogonality effect has been consistently used. No actual energy minimization to determine the optimal spin-arrangement has, however, been carried out.

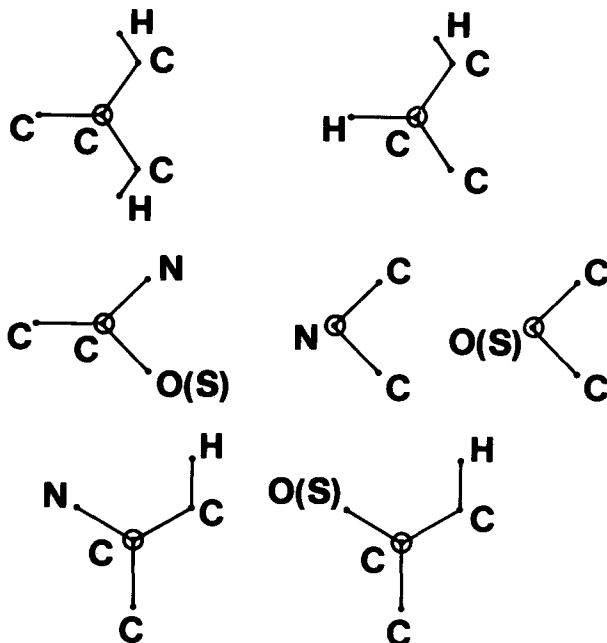


Figure 2. "Subsystems" in PBO (and PBT); the central fragments are circled.

#### (d) Results

Tables I and II summarize the results for PAC, PBO and PBT. Three sets of results are shown for PAC coming from  $C_3H_3$ ,  $C_5H_5$  and  $C_7H_7$ . The total polymer length has been taken as thirty times the repeat unit. The VEH calculations for PBO and PBT have been performed using the VEH program kindly provided by J. L. Bredas (11) and modified for compatibility with the computing facilities at the University of Cincinnati. The program has been checked for the known cases of polypyrimidine and others.

#### V. CONCLUSIONS

We have compared in this work results based on an approximate first-principle theory with those based on semi-empirical theory as well as accurate SCF-calculations (for PAC). Our results are in fair-to-good agreement with those derived on the basis of EHT but deviate markedly from all other methods. In the case of PAC our band gap value, which is twice as large that as given by EHT, is not necessarily in disagreement with experiment (which puts the band gap value in the neighborhood of 1.4 - 1.9 eV), since the semi-conductivity in PAC may not be due to excitation of electrons into the conduction band.

Table I. Results for PAC<sup>a</sup>

Method	Band Gap	Ionization Potential (IP)
LCGO-SF-CO (6)	6.1	8.4
PPP (4)	5.1	6.3
EHT (2)	1.3	
VEH (5)	~6.1	~8.4
This work	$C_3H_3$	3.9
	$C_5H_5$	3.0
	$C_7H_7$	3.1
Experimental	1.6 - 1.9	

<sup>a</sup>All energies in this and the following Table are in eV.

Table II. Results for PBO and PBT

Properties	This Work		EHT (3)		VEH	
	PBO	PBT	PBO	PBT	PBO	PBT
IP	11.7	9.3	11.7	~10.0	9.5	9.0
Band gap	2.7	2.2	1.7	1.8	.6	1.1
$\pi$ -BW <sup>a</sup>	1.0	1.6	.25	.4	~.01	.01
$\pi^*$ -BW	1.3	.3	.25	.4	~0	.36

<sup>a</sup>Band width.

The high value of the bandgap from the LCGO-SF-CO calculations may point to a breakdown of the SCF approximation for these materials and since the VEH method is tied to such wavefunctions, it is likely that VEH will fail where the SCF approximation itself is suspect.

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