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The Linear Combination of Localized Orbitals Methods (LCLO) for Polymers

I. Polyethylene

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The application of the Linear Combination of Localized Orbitals (LCLO) method to the band structure of polyethylene in the *T*, *TG*, *TGTG'* and *G* conformations is reported. The method uses full *ab initio* results on molecules to construct Fock matrix elements and deduce the energy bands. The main advantages of the technique are the low cost and the simplicity. Results are compared with those obtained from published *ab initio* and empirical calculations.

Key words: Linear combination of localized orbitals method, application to polymers

1. Introduction

During the past decade many calculations of realistic polymers have been published (a review on these works is attempted in Ref. [1]). On the one side, photoelectron spectroscopy has proven to be an essential tool for the study of the electronic levels of polymers and on the other it has required quantum calculations to help interpret the spectra [2]. Except for some cases [3-6] the studies were always confined to semi-empirical schemes developed in molecular quantum chemistry. However, a recent

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comparison [7] of ESCA (Electron Spectroscopy for Chemical Analysis) and theoretical data relative to the valence electronic structure of polyethylene tends to prove that *ab initio* results are more reliable and more complete than semi-empirical ones. These latter are often based on arbitrary simplifications which lead to unexpected and unaccountable results. Unfortunately *ab initio* methods, based on well-defined approximations, are very time-consuming and expensive when simply extended to polymers.

It is then highly desirable to dispose of a technique which offers the advantages of both semi-empirical (computationally fast) and *ab initio* (more reliable) schemes. B. J. Duke *et al.* [5, 6] have already proposed such a method based on the simulated *ab initio* molecular orbital technique [8] (SAMO). It is the purpose of this work to discuss a similar approach, i.e., the extension of the linear combination of localized orbitals [9, 10] (LCLO) to polymers.

The necessary equations of this method applied to stereoregular polymers are deduced in Sect. 2, and Sect. 3 summarizes the steps leading to the density of states distributions. Sect. 4 is devoted to a comparison of the results on polyethylene in its T conformation (PE-T) with previous *ab initio* computations [3, 5] and some experimental data [7, 11]. Finally, in Sect. 5 the influence of the conformational changes (T, G, $TGTG'$ and TG) on the electronic levels' distributions of PE is investigated in comparison with previously published extended Hückel results [12].

2. The LCLO Method for Polymers

In the original paper describing the linear combination of localized orbitals method [9] the usual molecular orbitals, ϕ_n, solutions of the monoelectronic equation

$$h^{\mathrm{SCF}}\phi_n = \phi_n E_n \tag{1}$$

are expanded in terms of localized functions, θ_p,

$$\phi_n = \sum_a \theta_a T_{an} \tag{2}$$

resulting from the Magnasco and Perico localization technique [13, 14]. Introducing Eq. (2) in expression (1), the following relation is obtained:

$$\sum_a h^{\mathrm{SCF}} \theta_a T_{an} = \sum \theta_a T_{an} E_n \tag{3}$$

In the matrix form, we have

$$F' T_n = S' T_n E_n \tag{4}$$

where F' is the Fock matrix between localized function (θ_a). These are orthogonal by construction ($S' = 1$). The transferability of the F' elements and their use in constructing the F' matrix of other molecules is discussed in Refs. [9] and [10].

It is straightforward to introduce the translational symmetry and to build up the Fock matrix elements between localized functions θ_a^0 and θ_b^j respectively centered on bonds, inner-shell or lone-pairs in the original unit cell ($j = 0$) and in the cell j:

$$F'^{j}_{ab} = \langle \theta^{0}_{a} | \hat{F} | \theta^{j}_{b} \rangle \tag{5}$$

Similarly the dependence of the Fock matrix on the wave number k is given by the usual trigonometric series,

$$F'(k) = \sum_{j=-N}^{+N} F'^{j} \exp(ikja) \tag{6}$$

where $2N + 1$ is the total number of interacting cells and a the cell parameter. The band structure is obtained by solving the classical eigenvalue problem:

$$F'(k)T_n(k) = T_n(k)E_n(k) \tag{7}$$

Some differences between SAMO and LCLO procedures are to be pointed out. First, SAMO matrix elements are constructed from hybridized atomic functions giving estimates of virtual orbitals (conduction bands). On the other hand, matrix elements of the LCLO method are derived from the Magnasco and Perico localization in such a way that the dimensions of the F' matrices are limited to the total number of "bonds between pairs of well-defined atoms, of inner-shells and of lone-pairs on well-defined atoms" [13–14].

Furthermore, the orthogonality property of these localized functions solves an ordinary eigenvalue problem (Eq. 6), reducing somewhat the numerical effort. The non-existence of conduction bands is not a real limitation of this method since these virtual bands are very much dependent on the basis set and on the number of interacting cells [3, 5]. Good estimates of conduction bands require large reference molecules and extended bases for constructing the localized Fock elements. Such an effort, even at the molecular level, is certainly a barrier for the interest in these methods (SAMO or LCLO).

3. Density of States Calculations

The density of electronic states, $\mathscr{D}(E)$, for a unit length polymer is the number of states per unit energy interval [15, 16],

$$\mathscr{D}(E) = \frac{1}{\pi} \sum_{n=1}^{n_0} \left| \frac{dk}{dE_n(k)} \right|_E \tag{7a}$$

where for the cases considered herein, n runs over all doubly occupied valence bands (n_0). In practice, one constructs frequency histograms, $D(E_i)$, to approximate the density of states distributions. It corresponds to an average, over a finite interval ΔE, of $\mathscr{D}(E)$ at discrete values E_i,

$$(E_i) = \frac{1}{\Delta E} \int_{E_i - \Delta E/2}^{E_i + \Delta E/2} \mathscr{D}(E')dE' \tag{8}$$

$\mathscr{D}(E)$ is the limiting function of $D(E)$ when ΔE goes to zero. The density of states distributions presented in this work are obtained with $\Delta E = 0.01$ a.u. Five histograms are computed simultaneously with the same value of ΔE but shifted in the energy scale from each other by an amount of $\Delta E/5$ to produce smooth distributions. When $D(E_i)$ is convoluted with a Gaussian function of 0.7 eV width at half-height, the resulting distribution, $D_C(E_i)$ can be considered

$$D_C(E_i) = \int_{-\infty}^{+\infty} D(E)\exp[-(E-E_i)^2/2\sigma^2 dE] \tag{9}$$

as a theoretical simulation of an XPS experimental spectrum. To be closer to the experimental shape of the spectra, one should also include cross-section effects [17]. The procedure we have used to generate $D(E_i)$ is the sampling method, which can be formally summarized as follows

$$D(E_i) = \sum_{n=1}^{n_0} \sum_{k=1}^{Nk} \delta^{\Delta E}[E_n(k) - E_i)] \tag{10}$$

(N_k being of the order of $20 \cdot 10^3$), where $\delta^{\Delta E}$ is an appropriate Kronecker-delta defined by

$$\delta^{\Delta E}[E_n(k) - E_i] \begin{cases} = 1 & \text{if } |E_i - E_n(k)| \leqslant E/2 \\ = 0 & \text{otherwise} \end{cases}$$

A more detailed description of the numerical steps can be found in Ref. [15].

4. Polyethylene in the *T*-Conformation

The aim of this section is to compare, as far as possible, the results of the LCLO method on the occupied valence bands of polyethylene with previously reported calculations of the same type. These latter have only been performed on polyethylene in its *T*-conformation, PE-*T* (Fig. 1a). In Ref. [9] it is suggested that there is no need to consider

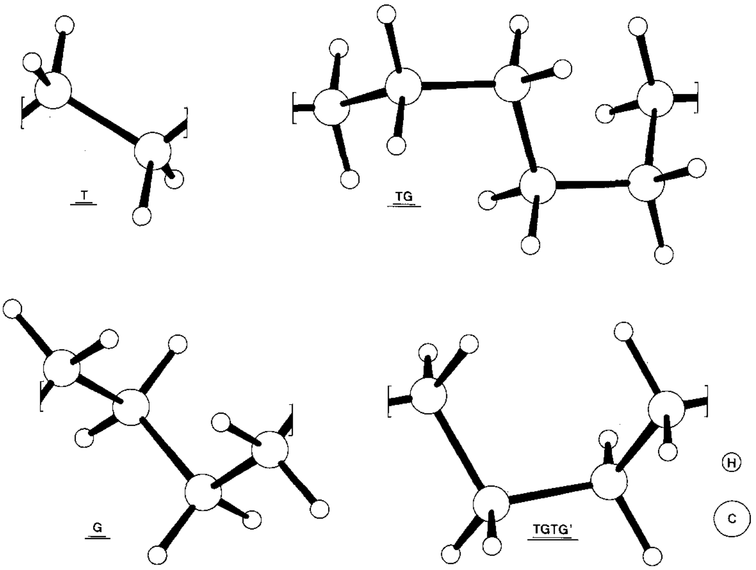

Fig. 1. *T*, *TG*, *G* and *TGTG'* conformations of polyethylene

more than three bond lengths of interaction to reproduce quite satisfactorily the *ab initio* results on the reference molecules. In our case (PE-T) it corresponds practically to nearest neighbor interactions ($N = 1$ in Eq. (6)). *Ab initio* calculations on the reference molecules (also called "pattern molecules" [5]) were initially performed with the $7s/3p$ Clementi basis set [9]. This ensures a proper comparison between these results and the previous ones of André and Leroy [3] obtained with the same atomic basis set for polyethylene.

Table 1 contains the F^{ij} elements used in the present calculation of the band structure of PE-T (F^2 matrix has only one non-zero element: $F^2_{43} = -0.010$ a.u.).

Fig. 2 shows the band structure (Fig. 2a), the density of electronic states (Fig. 2b) and the convoluted density of states (Fig. 2c). For the sake of comparison the present results, as well as those obtained from *ab initio* [3], SAMO [5] and extended Hückel [12], are collected in Table 2.

From a qualitative point of view (Fig. 2 and similar figures in Refs. [2], [3], [5] and [18]) an overall agreement between *ab initio*, SAMO, extended Hückel and LCLO

Table 1. Polyethylene Fock matrix elements, F^{ij}_{ab}, between orbitals centered in the origin unit cell and orbitals centered in the cell j (a and b are bonds, lone-pairs, inner-shells). In atomic units

	$1sC_1$	$1sC_2$	C_1C_2	C_2C_1	C_1H_1	C_1H_2	C_2H_3	C_2H_4
$1sC_1$	−11.235							
$1sC_2$	0.019	−11.235						
C_1C_2	−0.615	−0.615	−0.840					
C_2C_1	0.050	−0.615	−0.128	−0.840			$F'_{ab}(0)$	
C_1H_1	−0.640	0.052	−0.134	−0.012	−0.735			
C_1H_2	−0.640	0.052	−0.134	−0.012	−0.136	−0.735		
C_2H_3	0.052	−0.640	−0.134	−0.134	−0.014	0.042	−0.735	
C_2H_4	0.052	−0.640	−0.134	−0.134	0.042	−0.014	−0.136	−0.735
$1sC_1$	0.000							
$1sC_2$	0.019	0.000						
C_1C_2	0.050	0.000	0.040					
C_2C_1	−0.615	0.050	−0.128	0.040			$F'_{ab}(1)$	
C_1H_1	0.000	0.000	0.000	0.000	−0.011			
C_1H_2	0.000	0.000	0.000	0.000	0.000	−0.011		
C_2H_3	0.052	0.000	−0.012	0.000	−0.014	0.042	−0.011	
C_2H_4	0.052	0.000	−0.012	0.000	0.042	−0.014	0.000	−0.011
$1sC_1$	0.000							
$1sC_2$	0.000	0.000						
C_1C_2	0.000	0.050	0.040					
C_2C_1	0.000	0.000	−0.010	0.040			$F'_{ab}(-1)$	
C_1H_1	0.000	0.052	−0.012	−0.134	−0.011			
C_1H_2	0.000	0.052	−0.012	−0.134	0.000	−0.011		
C_2H_3	0.000	0.000	0.000	−0.012	0.000	0.000	−0.011	
C_2H_4	0.000	0.000	0.000	−0.012	0.000	0.000	0.000	−0.011

Table 2. Band structure of polyethylene computed with *ab initio* [3], SAMO [5], extended Hückel [12] and LCLO methods (in atomic units)

	Ab initio	SAMO		Extended Hückel	LCLO	Experimental
		$N = 1$	$N = 2$			
Ionization potential	0.489	0.439	0.469	0.443	0.484	0.312 [5]
1*s* band width	0.001	0.0001	0.00001	-	0.022	
C–C band width	0.250	-	-	0.324	0.347	0.287 [2]
C–H band width	0.266	-	-	0.180	0.249	~0.184 [2]
Total valence band width	0.741	0.782	0.754	0.618	0.694	0.55 – 0.61

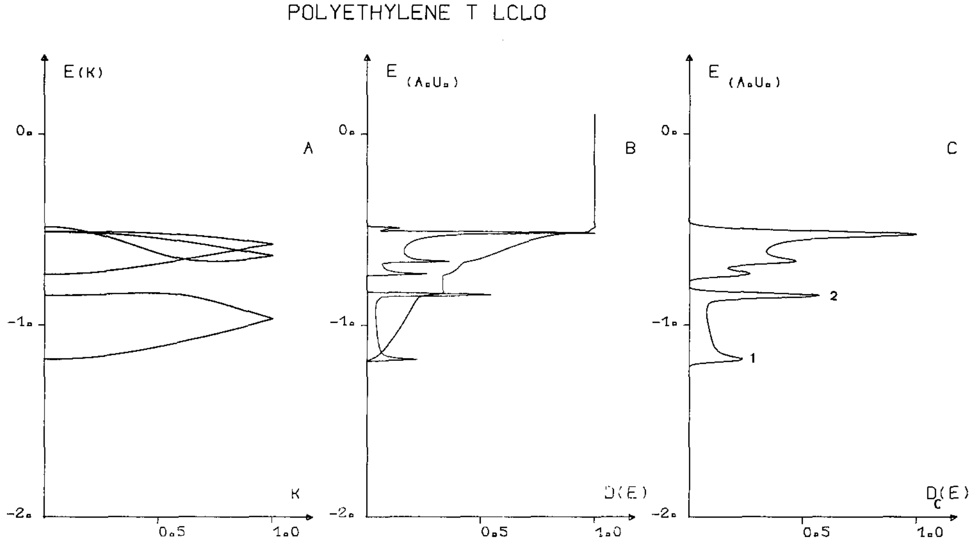

Fig. 2. Band structure (A), density of electronic states and its integral (B) and convoluted density of states of *T* polyethylene. Energy side in atomic units

energy band structures is observed. Density of states distributions, which are even more sensitive to band structure changes, reveal deviations in the relative heights of the C–C peaks for each method. The ratios of peak heights are 2.4, 2.7 and 3.2 respectively for LCLO, *ab initio* and extended Hückel results. This is consistent with the C–C band widths reported in Table 2, since the smaller energy range will correspond with peaks of larger intensity. When qualitatively compared to experiment, the energy range covered by the C–C bonds is too small for *ab initio* results [3] and too large for LCLO ones. As already noticed, the peaks of the density of states corresponding to the *ab initio* band structure are sharper and higher than those of the LCLO method. The reduced number of interacting cells ($N = 1$) taken into account in the calculation of André and Leroy [3] is certainly responsible for that situation which will improve with greater values of N. This is suggested in the paper of Duke and O'Leary [5] where two calculations are reported, respectively, with $N = 1$ and $N = 2$. The graphs of these bands tend to prove that the C-C region enlarges slightly when going from $N = 1$ to $N = 2$. The LCLO C-C band width is more difficult to interpret. With the same number of interacting cells as for the *ab initio* calculation [3] ($N = 1$), one ends up with an energy range 1.4 times greater. Without any other data it is hard to decide whether it is due to the smallness of the reference molecules [9], i.e. CH_4, C_2H_6, C_3H_8, C_4H_{10} and $i \cdot C_4H_{10}$, which constitute the basis of the localized Fock matrix elements used herein, or due to the orthogonality of the localized functions. Investigations are actually in progress on larger molecules, C_8H_{18}, to discover the nature of the discrepancy. Except for the highest occupied C-H band near the center of the Brillouin zone ($k \simeq 0$), the C-H bands and their energy domain are very similar to the *ab initio* ones (cf. Table 2). In the latter case, comparison with the experiment is complicated. Due to the relatively small cross-sections of the C_{2p} [18] orbitals, which mostly contribute to the monoelectronic functions, $\phi_n(r, k)$, describing the C-H bands, it comes out that the associated XPS intensity is very small [7] and no precise estimation of the C-H band widths is really possible.

5. Band Structure of Polyethylene Versus Conformational Changes

In 1971, Morosi and Simonetta [19] published a conformational study of polyethylene using the CNDO/2 method extended to stereoregular polymers but no comment on the monoelectronic levels distributions has been made. A recent work [12] showed that conformational changes could induce sensible modifications on the XPS spectrum and suggested possible applications to stereoisomers. These calculations have been performed in the framework of the extended Hückel method generalized for polymers (EHCO). Since this latter technique has proven to be successful in computing band structures and density of states comparable to ESCA [7] and because, at the time being, no *ab initio* results are available on those conformations, we will be content with a qualitative comparison of LCLO and EHCO data. We want to particularly prove that the LCLO method, whatever its formal simplicity, is able to produce information for specific conformational changes. The elementary cells and the molecular geometries adopted for the conformations of polyethylene are depicted in Fig. 1. Polyethylene T contains one $-CH_2-CH_2-$ group in the unit cell, the $TGTG'$ and G have two such groups and TG is made of four $-CH_2-CH_2-$ groups in each repeating cell. Figs. 3 to 5 show the band structure, the density of states and the convoluted density of states respectively for the G, TG and $TGTG'$ conformations. Since the geometry is not explicitly introduced, the existence or the non-existence of "conjugated bonds" [9] in the chain is the only parameter we use to take the conformation into account. It is, of course, a very rough method but surprisingly enough it turns out to be sufficient to give correct behavior to the monoelectronic energies in the Brillouin zone. Table 3 collects the most significant characteristics of the C-C and C-H bands obtained with the LCLO and EHCO methods. When comparing Figs. 2 to 5 of this work to those of Ref. [12] one observes good agreement between the shape of the EHCO valence bands and the present ones. It is possible to state more precisely the agreement when examining the values of Table 3. The ionization potentials, roughly minus the value of the highest occupied level, vary in the same way as the ones of the EHCO method. No comparison of the $1s_C$ band widths is possible but they are not modified by the conformational changes. This confirms the results [21] obtained with the Siegbahn model potential. The C-C, the C-H and the total valence band widths follow also the same trends as the EHCO results. There is one small exception for the C-H band width of

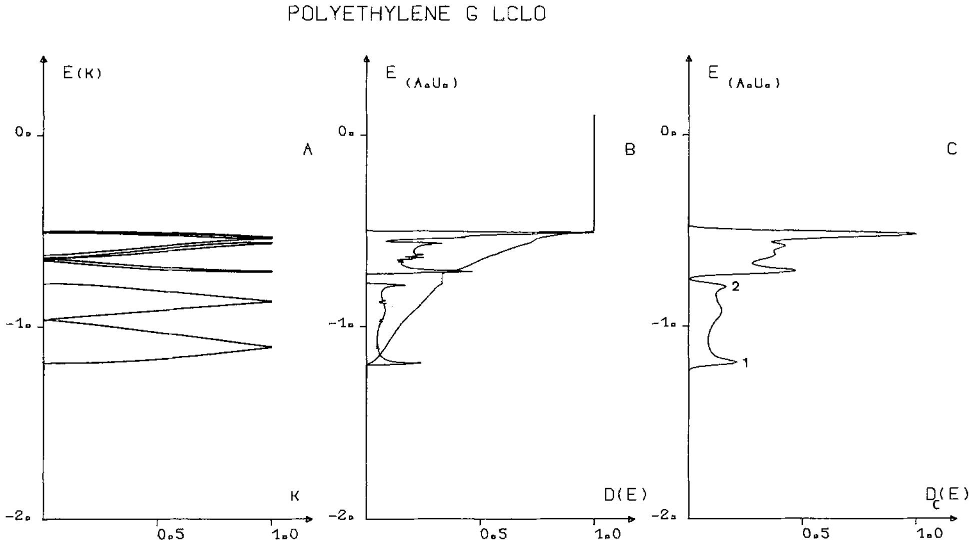

Fig. 3. Band structure (A), density of electronic states and its integral (B) and convoluted density of states (C) of the *G* polyethylene. Energy side in atomic units

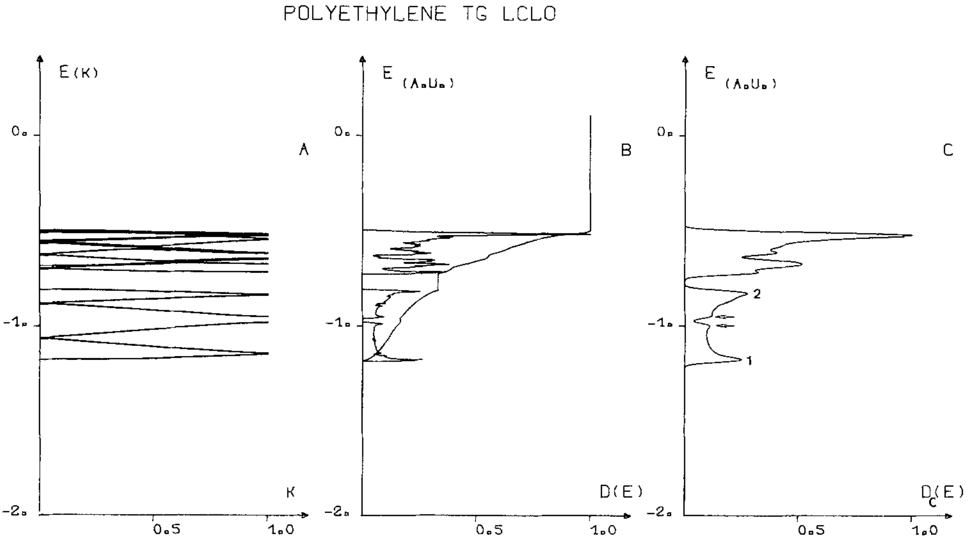

Fig. 4. Band structure (A), density of electronic states and its integral (B) and convoluted density of states (C) of *TG* polyethylene. Energy side in atomic units

the *G* conformation (0.2128 a.u.). If one compares the results for the convoluted density of states, the same agreement is also obtained for the intensity ratio between the two peaks at the boundaries of the C-C clumb, its width and the gap (Figs. 2c to 5c), still with an exception for the *G* conformation where $I_1/I_2 = 1.29$. It would be interesting to see whether or not it is due to the procedure used in taking care of the geometry changes.

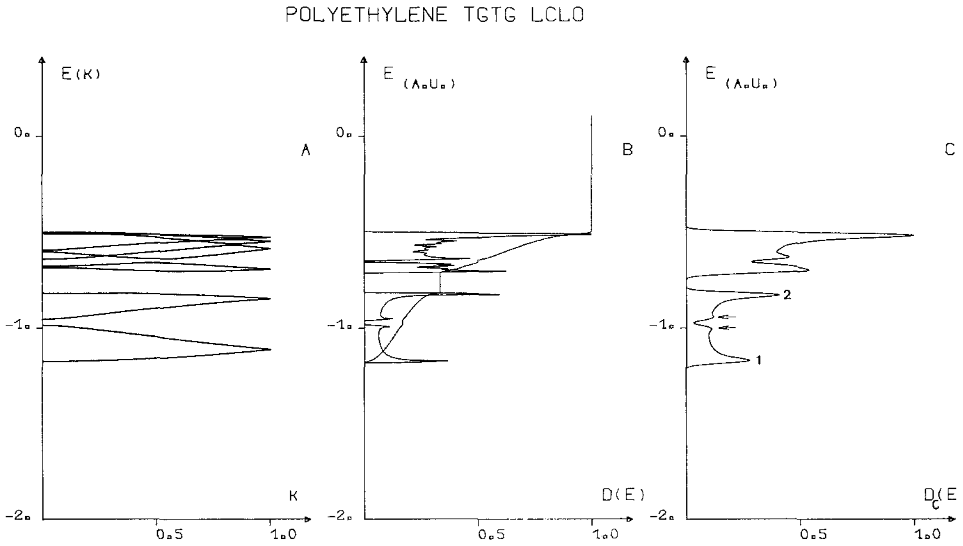

Fig. 5. Band structure (A), density of states and its integral (B) and convoluted density of states (C) of *TGTG'* polyethylene. Energy side in atomic units

Table 3. LCLO and EHCO band structures of polyethylene in the following conformations: *T*, *G*, *TGTG'* and *TG* (in atomic units)

	LCLO				EHCO			
	T	*G*	*TGTG'*	*TG*	*T*	*G*	*TGTG'*	*TG*
Ionization potential	–0.4840	–0.5010	–0.4981	–0.4959	–0.4429	–0.4739	–0.4700	–0.4675
1s band width	0.0217	0.0224	0.0224	0.0224	–	–	–	–
C–C band width	0.3473	0.4144	0.3562	0.3732	0.3277	0.3896	0.3577	0.3656
C–H band width	0.2490	0.2128	0.2047	0.2179	0.1798	0.1512	0.1323	0.1387
Total valence band width	0.6930	0.6874	0.6746	0.6830	0.6176	0.5978	0.5951	0.5977
I_1/I_2[a]	0.376	1.290	0.682	0.909	0.316	0.845	0.748	0.933
$I_2 - I_2$[b]	0.342	0.376	0.342	0.352	0.316	0.372	0.340	0.346
Gap[c]	–	–	–	–	–	–	0.050	0.054

[a] Ratio between heights of peaks 1 and 2 in Figs. 2c to 5c.

[b] Distance between these peaks.

[c] Estimated from both positions marked by an arrow in Figs. 4c and 5c.

6. Conclusions

The LCLO method uses the transferability of both diagonal and off-diagonal matrix elements of the Fock operator over localized molecular orbitals from small molecules to the polymer. Its aim, as for the SAMO method, is mainly to mimic the results of full *ab initio* computation on a polymer. In this case the Fock matrix elements are averaged over an initial reference set of molecules. According to the particular polymer geometry it is also possible to improve the results by calculating the electronic structure and the localized orbitals from a better suited set of pattern molecules. This approach is currently under investigation.

Concerning the present results, one can conclude, in the following way:
- the general shape of the band structures as well as of the density of states distribution and their associated functions are correctly reproduced;
- even with a rough simulation of the conformational changes it is possible to obtain the principal characteristics of the band structures;
- one can obtain direct information on the core levels (and also on the shifts due to the chemical environment);
- the trouble with this method and also with the SAMO technique is the tedious manipulation of the numerous matrix elements required to build the F^j molecules.

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