Effect of Overlap Integrals and Parametrization in Polymer Molecular Orbital Calculations

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ABSTRACT: The effect on the energy-band structure of the overlap integrals in polymer molecular orbital calculations is examined for the case of polyethylene. A simplified method of parametrization and calculation is suggested. The method is also applied to α-helical polyglycine and qualitatively reasonable results are obtained.

A polymer molecular orbital (PMO) theory has been formulated lately by several authors for calculating the energy-band structures of organic and biopolymers.[1–5] This theory resulted from combining the solid-state Block-type functions with MO–LCAO theory. It is applicable mainly to periodic polymers; however, it appears promising in the study of questions pertaining to polymer properties such as conductivity and structure–energy relationship. Actual application of the theory requires certain approximations to reduce the volume of computations to a tractable size. Therefore, some integrals are neglected and others are treated as semiempirical parameters. This procedure is brought from the MO–LCAO theories as applied to ordinary molecules. Ladik, *et al.*, have used Hückel-type approximations in studying the π-electronic structures of some biopolymers.[6] The extended-Hückel method has also been used by Imamura for determining the band structure of the valence electrons of polyethylene.[3] Recently the CNDO, INDO, and MINDO approximations have been incorporated in to PMO theory, and actual calculations have been performed for a few polymers such as polyacetylene, polyethylene, and polyglycine.[2–5] Except for the extended-Hückel method, these methods set the complex overlap integral matrix equal to the unity matrix, although some off-diagonal elements in this matrix have appreciable values, and the diagonal elements may have values quite different from unity (see eq 4). The effect of this approximation on the band structure has not yet been investigated. A methodic investigation of this question would be to use the same set of parameters in two calculations, one which neglects overlap and another which includes overlap. We have done a calculation on polyethylene including all valence electrons, with and without neglecting overlap integrals. We have used Hückel-type parameters and found that the neglect of overlap has a great effect on the energy-band structure in this case. A calculation on α-helical polyglycine is also reported.

Formulation and Parametrization

The polymer molecular orbitals of a periodic polymer are given by

$$\psi = \sum_{j=0}^{N-1} \sum_{\mu=1}^{n} c_\mu e^{ikj} \phi_{\mu j} \qquad (1)$$

where n is the number of atomic orbitals ϕ_μ in one elementary cell, N is the number of cells in the chain polymer, usually taken as infinite; and k is the wave number which varies from 0 to 2π. The problem amounts to determining the n coefficients C_μ for each polymer molecular orbital (PMO). The PMO's are grouped in n bands, each of which has N orbitals. The coefficients are the solutions of the matrix equation

$$\mathbf{\Gamma C} = \boldsymbol{\varepsilon}\boldsymbol{\sigma}\mathbf{C} \qquad (2)$$

where the elements of $\mathbf{\Gamma}$ and $\boldsymbol{\sigma}$ are given by

$$\gamma_{\nu\mu} = H_{\nu0,\mu0} + \sum_{l=1}(H_{\nu0,\mu l}e^{ikl} + H_{\nu0,\mu-l}e^{-ikl}) \qquad (3)$$

and

$$\sigma_{\nu\mu} = S_{\nu0,\mu0} + \sum_{l=1}(S_{\nu0,\mu l}e^{ikl} + S_{\nu0,\mu-l}e^{-ikl}) \qquad (4)$$

In these relations $H_{\nu0,\mu l}$ is the one-electron hamiltonian matrix element between atomic orbital ν in the zero cell and μ in the l cell. The zero cell is in the middle of the polymer. Similarly, $S_{\nu0,\mu l}$ is the overlap integral between the mentioned atomic orbitals. In the first-neighbor approximation, the expansions in eq 3 and 4 are limited to $l = 1$. The PMO energies $\boldsymbol{\varepsilon}$ and the coefficients $\mathbf{C}$ are functions of k. By varying k between 0 and π, the energy bands can be generated. The charge–bond order matrix elements are given by

$$p_{\nu,\mu} = \frac{2}{\pi}\int_0^\pi \text{real}\left[\sum_m^{\text{occ}} C_{\mu m}{}^* C_{\mu m}\sigma_{\nu\mu}\right]\text{d}k \qquad (5)$$

occ stands for occupied PMO's. These integrations may be performed by the gaussian numerical integration method. Therefore, eq 2 is solved for eight appropriate values of k, and the energy levels $\epsilon(k)$ are drawn as functions of k to produce the bands. From the sets of eight matrices of coefficients $\mathbf{C}(k)$ and $\boldsymbol{\sigma}(k)$, the integrals (5) may be calculated.

It is customary in the extended-Hückel approximation to set

$$H_{\nu0,\nu0} = -I_\nu$$

and

$$H_{\nu0,\nu l} = -0.5KS_{\nu0,\nu l}(I_\nu + I_\mu)$$

where I_ν is the ionization potential of the electron in the ν atomic orbital and $K = 1.75$. We found, however, that using the electronegativities instead of the ionization potentials gave more reasonable values for the energy gaps between the highest filled and the lowest unfilled bands in hydrocarbon polymers. Therefore, we used the relations

$$H_{\nu0,\nu0} = -0.5(I_\nu + A_\nu) \qquad (6)$$

and

$$H_{\nu0,\mu l} = 0.5S_{\nu0,\mu l}K(H_{\nu0,\nu0} + H_{\mu0,\mu0}) \qquad (7)$$

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TABLE I
ELECTRONEGATIVITIES IN EV

Type of orbital	Atom H	Atom C	Atom N	Atom O
s	7.176	14.051	19.316	25.390
p		5.572	7.275	9.111

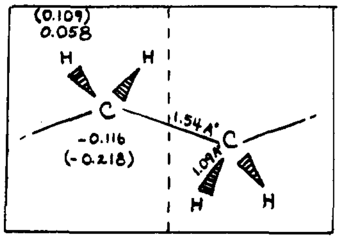

Figure 1. Polyethylene geometry and charge distribution. Charges in parentheses are obtained from calculation including overlap integrals.

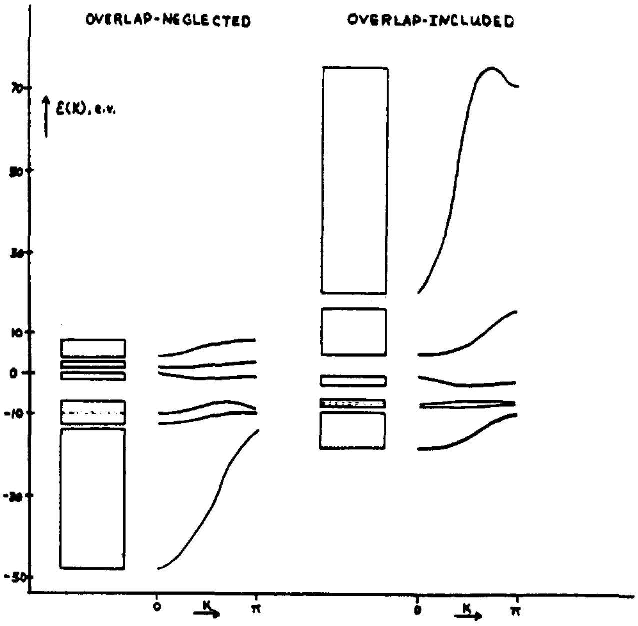

Figure 2. Energy-band structure of polyethylene.

where $K = 1.80$. The same parameters are used in both calculations, with and without neglecting overlap, in the hope of seeing the effect of neglecting overlap integrals on the energy band structure.

Overlap Neglected

Setting the complex overlap matrix equal to the unity matrix E, eq 2 reduces to

$$\Gamma C = \varepsilon C \tag{8}$$

which can be solved by a standard method. For this purpose, we have written a program which takes as input the overlap integrals $S_{\nu\mu}$ and electronegativities, calculates the energy bands by diagonalizing the complex (Hermitian) matrix Γ for eight values of k, and calculates the charge–bond order matrix **P**. The overlap integrals $S_{\nu\mu}$ are calculated from Slater orbitals by a separate program written by Pople, *et al.* In all our calculations, we used the first-neighbor approximation in calculating the elements in (3) and (4). The electronegativities used in the calculations are given in Table I.

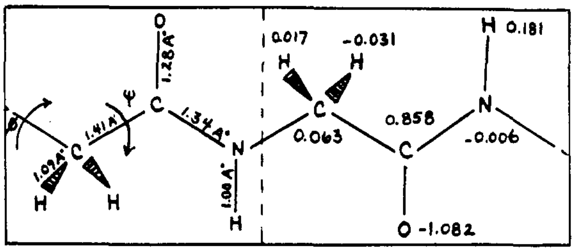

Figure 3. The geometry of α-polyglycine, $\phi = 132°$, $\psi = 123°$, and charge distribution obtained from calculations with overlaps neglected.

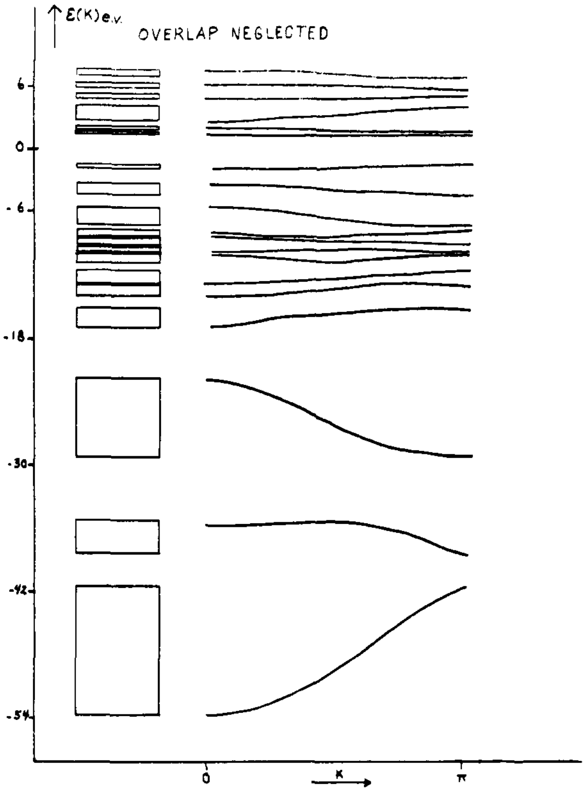

Figure 4. Energy-band structure of α-polyglycine calculated with overlaps neglected.

Overlap Included

We have transformed eq 2 in this case into an eigenvalue equation

$$\mathbf{HU} = \varepsilon \mathbf{U} \tag{9}$$

where

$$\mathbf{H} = \mathbf{T}^{+}\Gamma\mathbf{T} \tag{10}$$

T is a suitable transformation which is found by a standard procedure. We have also written and tested a program which carries on such a procedure.

Results

(i) Polyethylene. We have considered only the trans-planar form of polyethylene (Figure 1), where all bond angles are equal to 1.09°28′. The C–C bond length is 1.54 Å and C–H is equal to 1.09 Å. In the calculation with overlap neglected, the occupied bands are relatively wide while the unoccupied bands are narrower (Figure 2). This seems to be a common feature of all results obtained from calculations which neglect the overlap integrals such as the INDO or MINDO/2 calculation.[4–5] The energy gap between the highest filled and lowest unfilled bands is equal to $\Delta = 5.16$ eV. This value is not unreasonable and is considerably less than the gap calculated with more sophisticated approximations.[3–5] The charge distribution is given in Figure 1. The carbon atom has a negative charge $\delta-$, while the INDO and MINDO/2 calculations yield a slightly positive charge on carbon.[5]

The band structure obtained without neglecting overlap is also shown in Figure 2. Here, the unoccupied bands are larger than the occupied ones. A similar result was obtained by Imamura with a different set of parameters.[3] Therefore, the widening of the upper bands must be due entirely to the inclusion of overlap integrals. The energy gap Δ in this case is equal to 3.67 eV. This value would put polyethylene on the line between semiconductors and insulators. Experimental measurements of conductivity show that polyethylene is an insulator; therefore, the above-mentioned value of Δ seems rather unlikely. The charge distribution is also overestimated (Figure 1). The inclusion of more neighbors in calculating the elements in eq 3 and 4 does not seem to improve the results significantly, as is apparent from Imamura's work. It might be concluded that the results obtained neglecting overlap are more reasonable than the results of the other method.

(ii) Polyglycine. The qualitatively satisfactory results obtained in the case of polyethylene with the first method (overlap neglected) has encouraged us to further test the method on α-helical polyglycine, Figure 3. The energy band structure obtained is shown in Figure 4. This structure is similar to what is obtained from more sophisticated methods of calculation.[5] The energy gap width Δ is equal to 1.4 eV. According to this value polyglycine would be a semiconductor. Qualitatively speaking, this result should not be surprising, since DNA and proteins are known to be semiconductors. The experimental values reported for DNA vary from 1.8 to 5 eV.[7,8] Figure 3 shows the charge distribution. The signs of the charges agree with those obtained from INDO and MINDO/2 calculations.[5] The charges on the C–O bond seem, however, slightly overestimated.

Conclusion

The width of the energy gap between the higher occupied band and the lower unoccupied (conduction) band, Δ, is very sensitive to the parametrization procedures. The first method proposed in this work seems to give reasonable qualitative results. The quality of the calculated band structure might be further improved by properly rescaling the parameters in eq 6 and 7. Although we do not expect this method to give precise energy bands, in general, we do think that it would give a reasonable qualitative description of the electronic structure of the periodic and semiperiodic polymers which may be helpful in interpreting their chemical and physical properties.

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Statistical Mechanics of Random-Flight Chains. III. Exact Square Radii Distributions for Rings

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ABSTRACT: Analytical relations in the form of series containing $(N-1)/2$ terms have been derived for distribution functions of the square radius of gyration S^2 and of its random orthogonal components $S_k{}^2$ for random-flight ring chains with an odd number of bonds N. In the limit for $N \to \infty$, the convergence of the infinite series becomes slower as the argument $S_k{}^2$ approaches zero; therefore, for the region of very small $S_k{}^2$ a different asymptotic formula is recommended. As has been observed for linear chains, the convergence of the distribution functions with growing N to their limiting forms for $N \to \infty$ is fast; however, the distributions for rings are considerably sharper, with their maxima closer to the average values of the arguments, than is the case for linear chains.

The distribution of the square radius of gyration S^2 for random-flight chains is a function of primary importance for any size-dependent property of flexible macromolecules. Whereas many papers[1–11] have been published on analytical properties and numerical solutions of square radius distributions for linear chains, there seem to be no such data on molecules with other structures. During a recent study[12] of the shape characteristics of random-flight chains with various structures it occurred to us that the square radius distribution for ring macromolecules is especially easy to obtain in a simple form; rings with an odd number of bonds were the only structure with the characteristic function lacking branch points in the complex plane. In view of this unique property

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