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The Electronic Structure of Polymers by the FSGO (Floating Spherical Gaussian Orbital) Method

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Non-empirical band-structure calculations have been performed on polyethylene using two basis sets introduced by Christoffersen. Both basis sets had to be optimised with respect to the carbon-carbon framework bond in order to yield solutions within the nearest-neighbour approximations. The valence bands of polyethylene are well reproduced by both basis sets whilst the conduction bands are only in fair agreement with those produced by conventional gaussian calculations. The use of the "unsplit" basis set was considered unsatisfactory for the representation of the core bands. The effect of increasing the number of interacting unit cells on the energy terms is discussed. Some of the energy terms converge when five unit cells are used and almost all of the terms reach a constant value when nine unit cells are employed.

Key words: Floating Spherical Gaussian Orbitals – Band structure calculations – Polyethylene.

1. Introduction

The Floating Spherical Gaussian Orbital (FSGO) method has met with some degree of success in the field of large-scale molecular calculations, mainly as a result of the extensive work of Christoffersen [1–8]. It might be considered, therefore, that the advantages afforded by the use of FSGO basis sets in molecular calculations might be exploited in the field of polymer band structure computations since here, as has been shown [9, 10], the total unit cell basis size is found to be severely restricted by the number of electronic repulsion integrals involved and the time taken to evaluate them.

The FSGO method was applied by Erickson and Linnett [11] to the case of solid lithium hydride. The particular MO approach to the solid state adopted by

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Erickson and Linnett, however, was limited to the derivation of the chemical properties (charge distribution, etc.) of the origin unit cell and yielded no information concerning the energy band structure. This model, often referred to as the "cluster" model, might equally well be applied to linear polymers, admitting a Madelung effect on increasing the number of interacting cells. However, a generally more useful model is that which employs Bloch functions as bases and gives rise to the energy band structure in addition to the molecular unit cell properties.

This approach has been used by André and his coworkers to determine the band structures of regular polymers [12]. These authors have also calculated the related X-ray diffraction structure factors for polymers [13]. In the present paper we report the use of FSGO's, produced by the Christoffersen approach, in the determination of the band structure of polyethylene as test case.

2. Method, Results, and Discussion

The method employed a modification of the full *ab initio* formalism due to André [14] to accommodate an FSGO basis set. Possible FSGO bases are those of Whitten [15], Archibald et al. [16], or Christoffersen [8] or a contracted set [17]. The exclusive use of spherical GTO's in the conventional *ab initio* scheme would, it might be anticipated, alleviate the problem of integral evaluation to roughly the same proportion as in molecular calculations. Whether the associated expected reduction in computing time would be sufficient to enable more detailed calculations to be carried out on larger systems remains to be seen.

In the application of the LCAO method to multi-atomic systems, use is generally made of basis sets which have been specifically derived for each isolated atom. In most cases it is assumed that such representations may be employed, unaltered, in polyatomic species. For cases in which very restricted basis sets are chosen, however, re-optimisation within a molecular environment is clearly advantageous. In some instances, for example that of the 2*p* orbitals of beryllium, the basis set must be derived, at least in part, in the molecular field [18].

The philosophy outlined above has been applied with some success by Christoffersen to the problem of accurately representing the electronic structure of large molecules for which it is necessary to employ very restricted FSGO atomic basis sets. As long as such "pre-optimisation" procedures can be carried out without too much effort (and it has been shown by Christoffersen that this is possible if the molecular fragments are very small), then their use is justified.

2.1. *Band Structure of Polyethylene by the Christoffersen* FSGO *Method*

The FSGO technique described by Christoffersen, in which bases developed for molecular fragments are incorporated in larger molecules, has been successfully applied to the case of the ethane molecule [3] using a GTO parameter set optimized for the methane molecule. Of particular interest are the manner in which the hydrogen atomic 1*s* orbitals are allowed to float from their nuclei

Table 1. The FSGO basis sets used in the polyethylene calculations

Basis set	Split [3]	Optimised split	Unsplit [3]	Optimised unsplit
α_C	27.385	27.385	9.304	9.304
α_C	4.874	4.874	—	—
$\alpha_{C\text{–}H}$	0.358	0.358	0.358	0.358
$R_{0(C\text{–}H)}$	1.249	1.249	1.234	1.234
$\alpha_{(C\text{–}C)}$	0.358	0.38	0.358	0.45
$R_{0(C\text{–}C)}$	1.249	0.76	1.249	0.68

towards the carbons until an energy minimum is reached and the improvement in the total molecular energy obtained on substitution of a "split" carbon atom core orbital for the single FSGO centred on the carbon atom.

The "split" and "unsplit" basis sets detailed in Table 1 were employed in the model of polyethylene together with the nearest-neighbour approximation. This resulted in negative eigenvalues for the overlap matrix when an attempt was made to carry out the reduction of the pseudo-eigenproblem to the standard eigenproblem. This is symptomatic of an imbalance of overlap terms around the origin cell, i.e. it stems from the cut-off imposed by the nearest-neighbour approximation. The problem can be alleviated only by increasing the number of interacting unit cells, at the expense of further computational effort. Before suspending the nearest-neighbour approximation, however, a further optimisation of the unit-cell parameter set was attempted.

2.2. Optimisation of Christoffersen Carbon–Carbon Bond FSGO'*s*

In Christoffersen's work on the ethane molecule, the FSGO lobe functions for the carbon–carbon bond were not optimised independently, but were taken from parameters obtained previously for the carbon–hydrogen bond in methane. Although economical in computational effort, this does appear to make a rather unrealistic assumption about the nature of the carbon–carbon bond in ethane. Hence, a source of the "cut-off" problem mentioned above may be exaggerated inter-cell interactions, in particular between lobe functions in adjacent cells. One might, therefore, expect that any lowering in the lobe-nuclear separation, R_0, will increase the separation of lobe functions in adjacent cells and will be likely to negate the possibility of negative overlap.

A set of FSGO MO calculations was therefore performed on ethane, with the object of optimising the FSGO's located in the carbon–carbon bonding region for both the "unsplit" and the "split" Christoffersen bases. The optimum values of α(C–C) and R_0(C–C) found for the "split" and "unsplit" bases reported by Christoffersen are given in Table 1.

The optimum position of the "unsplit" basis carbon–carbon FSGO was found to be slightly closer to the nucleus than that derived for the "split" basis lobe function in the ethane molecule, whilst both values are only slightly more than half the lobe–nuclear displacement employed by Christoffersen in his calculations. The optimised FSGO's are less diffuse than the Christoffersen functions and this behaviour is again more marked in the case of the "unsplit" basis set. The energy function was also observed to be more sensitive to unit variation of the exponent α than to R_0.

2.3. *Band Structure Calculations for Polyethylene Employing Optimised Christoffersen* FSGO *Basis Sets*

Calculations were performed on the polyethylene model using the Christoffersen "unsplit" and "split" core basis sets, in which the exponents and positions of the carbon–carbon FSGO's had been optimised, as reported in the previous section. The implication of these basis sets in the polyethylene unit cell are that the FSGO's directed along the carbon–carbon backbone are drawn in more closely to

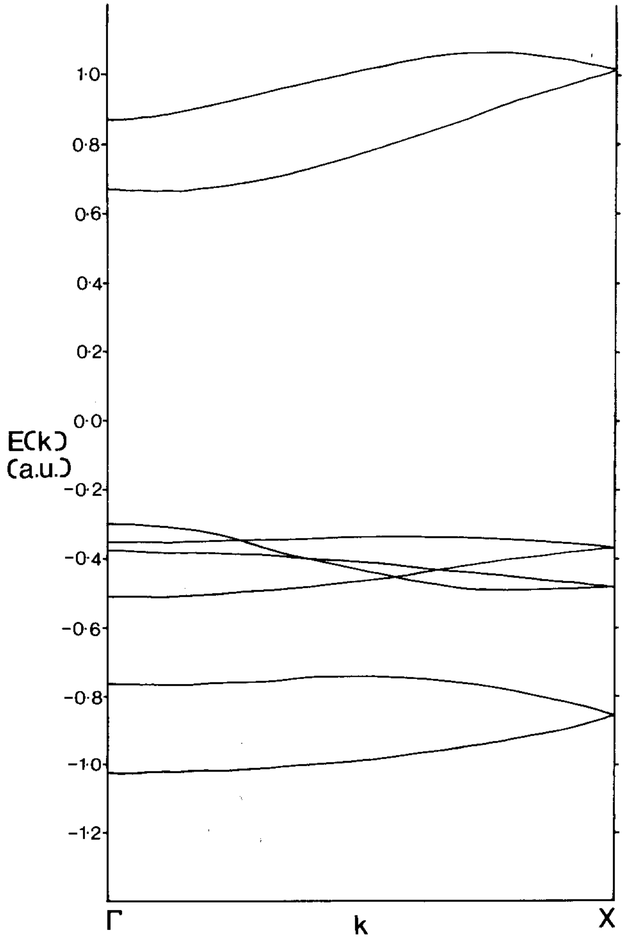

Fig. 1. The energy-band diagram for polyethylene obtained from the "unsplit" basis and nine interacting unit cells

their parent carbon atoms and are less diffuse; hence, weaker inter-cell interactions are anticipated.

In both sets of calculations, stable convergence of the SCF solution was obtained within the nearest-neighbour scheme. This contrasts with the failure of the unoptimised Christoffersen FSGO bases to yield a solution and justifies the additional computational effort required to optimise the ethane carbon–carbon FSGO's.

Figs. 1 and 2 show the valence and conduction band structures derived from the optimised bases. The important energy functions are given in Table 2.

The Koopmans' ionisation potential is found to be largely invariant to improvement of the core representation, although the energy gap, E_g, is lowered slightly. The core bands Γ_1 and Γ_2 and the total energy per unit cell E_T, however, show a strong dependence on the accuracy of the carbon 1s representation. This trend has

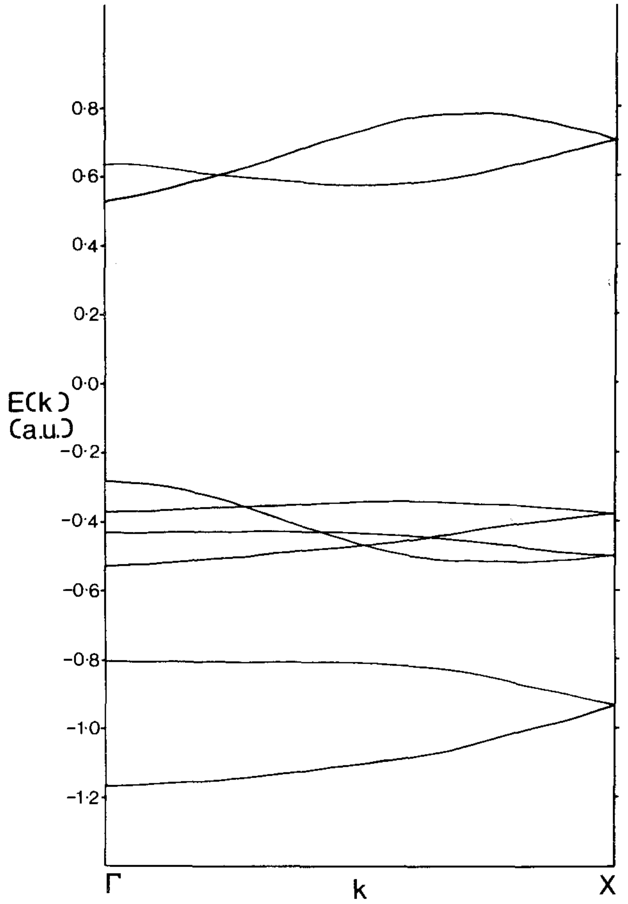

Fig. 2. The energy-band diagram for polyethylene obtained from the "split" basis and nine interacting unit cells

Table 2. The effect of the number of interacting unit cells on the more important energy terms (in a.u.) of the polyethylene chain obtained from the split and unsplit basis sets

	Split basis set				Unsplit basis set			
No. of Cells	3	5	7	9	3	5	7	9
Total Energy	−74.651	−74.373	−74.250	−74.179	−67.353	−67.080	−66.963	−66.900
Ionisation Potential ($-E_{\Gamma_8}$)	0.360	0.315	0.297	0.287	0.366	0.327	0.310	0.301
Band Gap ($E_{\Gamma_9}-E_{\Gamma_8}$)	0.790	0.826	0.826	0.826	0.978	0.974	0.973	0.972
E_{Γ_1}	−11.164	−11.116	−11.099	−11.089	−9.477	−9.437	−9.421	−9.412
$E_{\Gamma_1}-E_{\Gamma_2}$	0.008	0.005	0.005	0.005	0.158	0.159	0.159	0.159
Valence Band Width	0.248	0.241	0.241	0.241	0.392	0.396	0.396	0.396
Conduction Band Width	0.341	0.233	0.233	0.233	0.214	0.215	0.215	0.216

already been observed for conventional Gaussian basis sets [10]. A Γ-point separation of approximately 0.15 a.u. between E_{Γ_1} and E_{Γ_2} is observed, whilst the separation observed in the case of the "split" basis set is (0.008 a.u.) and constitutes a significant improvement over that found for the "unsplit" basis. Hence, the $E_{\Gamma_1}-E_{\Gamma_2}$ band gap produced from the latter calculation may stem from a deficiency in the "unsplit" basis set itself. This suspicion is confirmed to some extent by the structure and overall k-dependence exhibited by the "unsplit" core bands, compared with the essentially flat nature of the corresponding "split" bands.

The valence band structures are topologically similar to those obtained from conventional Gaussian orbital calculations [9, 10]. There is a two-band region centred about -1.0 a.u. and a four-band domain spanning 0.24 a.u. and 0.22 a.u. for the "split" and "unsplit" basis, respectively. Since the FSGO basis sets chosen for the calculations yielded only two bands covering an energy range of 0.40 a.u. and 0.23 a.u. for the "unsplit" and "split" basis, respectively, then the conduction band region is necessarily poorly represented. A conventional Gaussian orbital basis calculation produces a six-band region spanning 0.5 a.u. [10]. The shape of the conduction bands computed by the "unsplit" basis is in fair agreement with those of the conventional Gaussian basis calculation, whilst the "split" basis does not adequately reproduce the form of the conduction bands of previous calculations.

Fortunately both bases, by virtue of their small size and economy of computing requirements, are amenable to further investigation with regard to the dependence of the wavefunction on the number of interacting cells included in the calculation. This refinement has not been entirely possible, within accessible computational resources, for the bases used up until now for polyethylene, although systems involving up to five interacting cells have been investigated [18]. Previously, when the band structures obtained for polyethylene using three and five interacting cells were compared, the overall characteristics of the bands were found to be unaltered but the energy terms were, in general, raised on increasing the number of cells. This was interpreted as an indication that the nuclear-repulsion term decays more slowly with distance than all other terms in the Hamiltonian and thereby ensures that the energy terms arising from any model which fails to attain asymptotic Madelung convergence are lower than the true Madelung value. It is clear that the Variational Principle does not apply in this case.

Table 2 shows the effect, on some of the more relevant energy terms, of increasing the number of interacting unit cells considered in the band-structure determination from three (nearest-neighbour model) to nine cells.
For the "split" basis set the total energy per unit cell is in the region of -74.179 a.u. while the frontier (occupied) band approaches a value of about -0.287 a.u. Similarly, the energy gap E_g and the lower core band Γ_1 approach 0.83 a.u. and -11.089 a.u., respectively. For the "unsplit" basis set the $E_{\Gamma_1}-E_{\Gamma_2}$ band gap is found to converge on 0.159 a.u. and fails to reduce to zero. This indicates the gap

to be a characteristic of the basis set used, as was originally suspected, and so is not a consequence of the interaction cut-off imposed. It is reasonable to conclude, therefore, that some interaction persists between the core representations of the 1*s* orbitals. From this point of view, therefore, the "unsplit" basis set is unsatisfactory.

The convergence of the Koopmans' ionisation potential to 0.287 a.u. (7.81 eV) compared to the experimental value of 0.31 a.u. (8.5 eV) [19] encourages the belief that the high ionisation potential obtained [9, 10] calculationally for polyethylene stems from the approximation of considering only the nearest-neighbour inter-cell interactions.

The Mulliken population analysis yields similar electron populations for both basis sets, while increasing neighbour interactions exert only a small influence on the electron distribution. The core orbitals centred on carbon contain slightly less than two electrons (1.97). The carbon–carbon framework bonding orbitals possess 0.99 electrons while the orbital representing the carbon–hydrogen bonding holds 2.02 electrons. Thus the classical picture of the bonding in polyethylene is upheld.

3. Conclusions

The Christoffersen FSGO method requires a great deal of judgement in its application, as compared with the Whitten approach. The Christoffersen model departs from the latter schemes in that single FSGO's are employed, in general, in bonding regions and that FSGO's on hydrogen nuclei are neglected. This latter approximation automatically overcomes computational difficulties to some extent but raises the issue of whether the bond associated with this atom is now correctly represented. Successful application of the Christoffersen method has indicated that, providing the single FSGO in the bonding region is fully optimised, the representation is adequate.

We here have shown that an enhancement to the Christoffersen FSGO MO method, at the expense of some further computational effort, is the optimisation of the carbon–carbon lobe functions in ethane. This has been seen to improve the molecular wavefunction and energy expectation value and to be essential if a stable SCF solution is to be obtained in the nearest-neighbour approximation for a polymeric species.

Hence, we believe that the application of the Christoffersen FSGO method to polymer band-structure calculations presents the only real opportunity, in the foreseeable future, of performing *ab initio* LCAO computations on large polymeric systems. This, however, assumes, as an essential preliminary, the rigorous optimisation, using FSGO MO methods, of the Gaussian basis sets which span the polymeric unit cell.

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