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Systematic *ab initio* Calculations on One- and Three-Dimensional Polyethylene

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The electronic structure of polyethylene has been re-examined using Gaussian basis sets in an *ab initio* solid-state method. Previous calculations were shown to possess a minor error in unit-cell coordinates and were corrected. Six basis sets were used and the results compared within the nearest-neighbour approximation. The effect on the calculation of increasing the number of interacting unit cells to five was studied. The latter produces no significant change in the C–H polarity; the overall conduction band width remains essentially the same but the Koopmans' ionization potential is displaced more towards the experimental value. An investigation was made into the effects of neighbouring strands on a central filament. We find that the Point Charge Perturbation model is a useful one in this context and yields a realistic interstrand distance. This is dominated by the hydrogen atoms. It is essentially unaffected by extension of the perturbing field to second neighbour strands.

Key words: Polyethylene, energy band structures and electron distribution of ~

1. Introduction

Polyethylene has been investigated theoretically by a number of semi-empirical techniques [1–13] and by a full *ab initio* method based on Gaussian-type orbitals [14]. Little realistic attention has, however, been given to the problem of neighbouring strands, the results derived applying only to a perfectly ordered single strand. In the present paper we give an account of calculations on polyethylene by an alternative *ab initio* technique and we examine the effect of neighbouring strands on the band scheme. In comparing our results with the only other *ab initio* treatment of this system [14], we also discovered an arithmetical error in the unit cell atomic coordinates of that paper.

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Assuming the computational scheme set down by Del Re, Ladik and Biczo [15] and incorporated by André in the POLYMOL suite to be correct, there are four readily confirmable sources of inaccuracy which might give rise to a discrepancy between the *ab initio* band structure of polyethylene, as calculated by André and that interpreted from experiment. We might investigate the dependence of the band structure on the unit cell geometry, on the effect of introducing a more reliable basis set, on the number of interacting unit cells considered in the computation, i.e., the validity of the "nearest-neighbour" approximation or on the effect of the neighbouring-strand interactions, i.e., proper consideration of the solid-state environment of the polymer chain.

It was evident, therefore, that a more thorough investigation of the *ab initio* method than that carried out by André was necessary before any true evaluation of the method could be made. Hence, we have recalculated the polyethylene band structure by a conventional GTO method.

2. Polyethylene Basis Sets and Unit Cell Parameters

Initially, four basis sets were employed in the band structure calculations within the nearest-neighbour approximation. In each basis set the atomic orbitals were represented by a linear combination of Gaussian orbitals. Basis sets I and II were identical to those used by André *et al.* [14] in their calculations with an expansion set labelled C(2, 2, 2)H(1) and C(5, 2, 3)H(3). (In the M(*a*, *b*, *c*)H(*d*) notation, *a*, *b*, and *c* represent separately the number of contracted Gaussians per 1*s*, 2*s*, and 2*p* atomic orbital of element M, while *d* indicates the number of primitive Gaussians simulating the hydrogen 1*s* atomic orbital.) Basis sets III and IV were identical in size to those of I and II, respectively, and were obtained by expanding Slater-type orbitals with a single zeta exponent [16] in terms of linear combinations of Gaussian orbitals [17]. Two further sets of calculations were carried out on the polyethylene model, using the basis sets C(4, 3, 2)H(3) and C(3, 3, 3)H(3) *via* the Stewart expansion technique [17]. This was done so as to explore the variation in band structures with different valence orbital representations. The polyethylene unit cell geometry employed in these calculations is shown in Fig. 1.

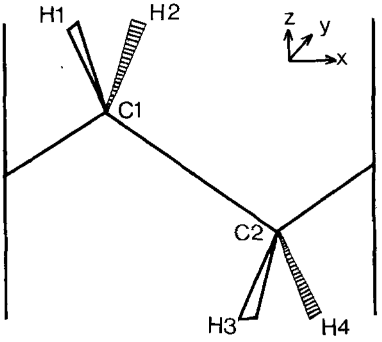

Fig. 1. The polyethylene unit cell

3. Results and Discussion

The results of the band-structure calculations are summarized in Table 1 and Fig. 2. Also included are André's results to illustrate the effect of an erroneous, shorter C–H distance on the band structure. If we begin by examining the blocked energy band diagrams (Fig. 2) we observe that correcting the C–H interatomic distance has the effect, for both André's basis sets, of increasing the band-gap E_g and reducing the ionization potential. Introduction of the expanded-STO bases, III and IV, continues to push these values in the same direction. As the value of

Table 1. The Koopmans ionization potential I.P., electronic energy band-gap Eg, total energy per unit cell E_T, the orbital energy $E(\Gamma_1)$, and atomic charges Z, of the polyethylene chain obtained using various basis sets

Basis set	I.P. (a.u.)	Eg (a.u.)	E_T (a.u.)	$E(\Gamma_1)$ (a.u.)	ZH	ZC
Basis I[a]	0.472	0.582	−70.488	−10.330	+0.124	−0.248
Basis I	0.447	0.594	−70.977	−10.309	+0.047	−0.094
Basis III	0.399	0.708	−74.992	−10.818	+0.181	−0.362
Basis II[a]	0.490	0.700	−77.524	−11.415	+0.281	−0.562
Basis II	0.457	0.703	−77.847	−11.391	+0.189	−0.378
Basis IV	0.433	0.740	−77.644	−10.996	+0.162	−0.324
Basis V	0.413	0.740	−77.621	−11.415	+0.149	−0.298
Basis VI	0.429	0.740	−77.285	−11.254	+0.152	−0.304

[a] Taken from Ref. [14].

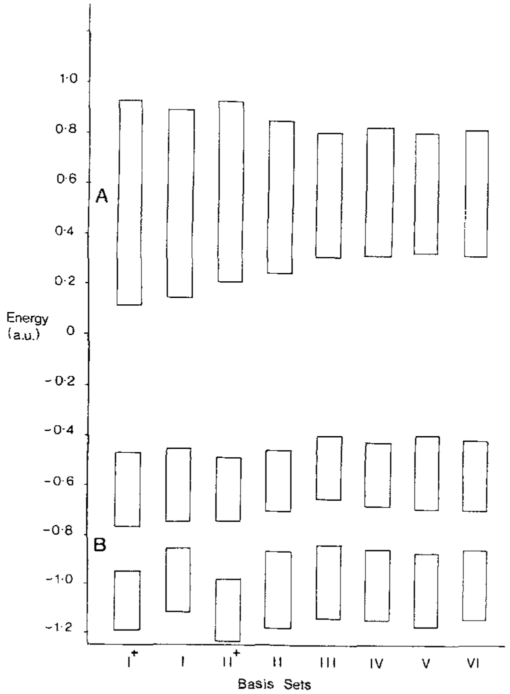

Fig. 2. Blocked band diagrams of polyethylene for basis sets I to VI (I^+ and II^+ are taken from Ref. [14])

the first ionization potential of polyethylene has been generally predicted, by extrapolation of known results for various alkanes, to lie in the region of 0.33 a.u. (9 eV), these results are, at first sight, very encouraging. The improvement in the total energy per unit cell, E_T, obtained using basis set III, is found to be greater than 4 a.u. and there is little doubt that this basis set, equal in size to that used by André (Basis Set I), constitutes a definite improvement.

The larger expanded STO basis IV, on the other hand, achieves nothing in the way of improvement in the total energy, although the same overall trend with respect to the ionization potential and band-gap is observed. It seems that the C(5, 2, 3)H(3) expansion, which this represents, does not constitute a correctly proportioned Gaussian basis set of the type normally derived using the expansion method and that the carbon 2*s* atomic orbital is inadequately represented (by two Gaussians in this instance) relative to the 2*p* and hydrogen 1*s* atomic orbitals.

The most obvious feature of the results of Bases V and VI is that neither of the new bases affords a total energy per unit cell lower than that given by expansion sets II and IV.

Rather large variations in the charge distribution are found in the course of what are really fairly small changes in geometry. Increasing the C–H distance from 0.898 Å to 1.08 Å for the smaller basis set (Basis Set I) reduces the hydrogen atom charge from +0.12 to +0.05, a comparatively large reduction in the amount of electron drift towards the carbon atom, with a corresponding decrease in the net negative charge on the carbon atoms. An equally marked variation is observed when the larger basis set is used (Basis Set II). Both sets of charges are accompanied by only slight lowering of the total energy.

Although the positions in the energy scale of all six valence bands Γ_3–Γ_8 vary, the general shapes of the bands are similar from one calculation to another and indeed show no significant disagreement with other band structures which have been obtained for polyethylene. The frontier band is observed to be the same throughout and appears to be predominantly carbon $2p_x$ in character at $\boldsymbol{k}=0$, the highest point in the valence band.

An interesting feature of the results, particularly relevant to the interpretation of the position of the highest occupied band Γ_8 as an ionization potential by the application of Koopmans' theorem [18], is that no strict correlation is observed to exist between this energy and any monitor of the accuracy of the wavefunction. Thus, although the Koopmans' ionization potential of polyethylene has been predicted by Delhalle *et al.* to lie in the region of 0.33 a.u. (9 eV) [19], the smallest expanded STO basis set used obtained a value somewhat higher than this, at 0.40 a.u. (see Table 1), and all other values obtained in more accurate calculations, employing larger basis sets, were actually in excess of this. Fujihara and Inokuchi [20] have estimated the valence band of polyethylene to lie at 0.31 a.u. (8.5 eV), on the basis of an experimental UPS investigation of solid polyethylene. Their value of 8.0 eV for the electronic energy band gap E_g shows a more marked disagreement with the results reported in this work. An XPS study by Wood *et al.* [8], also on solid polyethylene, predicts an equally low value for $E(\Gamma_8)$.

The photoelectron spectrum of polyethylene and the theoretical ionization potentials have been compared with the help of a density-of-states calculation [21, 22]. Excellent agreement is obtained when the theoretical energy scale is contracted by a slope factor of 1.43. It would appear that the disagreement between the calculated and observed ionization potential and band gap is not directly connected with the choice of basis set. The lack of direct correspondence between the theoretical electronic structure and the experimentally observed characteristic energies made it necessary to re-examine our model and, in particular, our use of both the nearest-neighbour approximation and the linear chain model.

4. Suspension of the Nearest-Neighbour Approximation

In the foregoing calculations the number of interacting unit cells was restricted to three. Considerable computational effort is required in order to extend the model to encompass a greater number of interacting cells. However, we considered this effort to be justified by the insight which is afforded by an extended model, into the nature of the approximations imposed in the nearest-neighbour scheme and the misinterpretations, if any, which might arise from its use.

The electronic band structure of polyethylene was calculated using Basis III with the number of interacting cells considered increased from three to five. The number of electronic repulsion integrals evaluated in this computation is scaled up by the ratio of the third power of the number of interacting cells, i.e., ca. 4.6.

Table 2. Comparison of results obtained using 3-unit cell and 5-unit cell models of the polyethylene chain for basis set III

Model	I.P. (a.u.)	Eg (a.u.)	E_T (a.u.)	$E(\Gamma_1)$ (a.u.)	ZH	ZC
3-unit cell	0.399	0.708	−74.992	−10.878	0.181	−0.362
5-unit cell	0.384	0.719	−74.794	−10.798	0.177	−0.354

The results obtained are summarized in Table 2. The relatively higher value of the total energy per unit cell found on increasing the number of interacting cells shows that the slower-decaying components of the total energy expression are those which are intrinsically positive; that is, the nuclear-repulsion and electronic-repulsion energy terms. Thus, the true value of the total energy per unit cell, for an infinite number of interacting units, is predicted to be less negative than that which is derived from the nearest-neighbour approximation. As has generally been found to be the case, this trend is also observed in the energies of the core bands, Γ_1 and Γ_2, corresponding to the non-bonding carbon atom 1*s* levels.

Comparing the energy band diagram shown in Fig. 4 with that given for the three-unit-cell case in Fig. 3, the direction and extent of this change of position of the energy bands is seen to be typical of the valence bands in general. Although more severe alterations in the positions of the conduction bands are noted, the overall

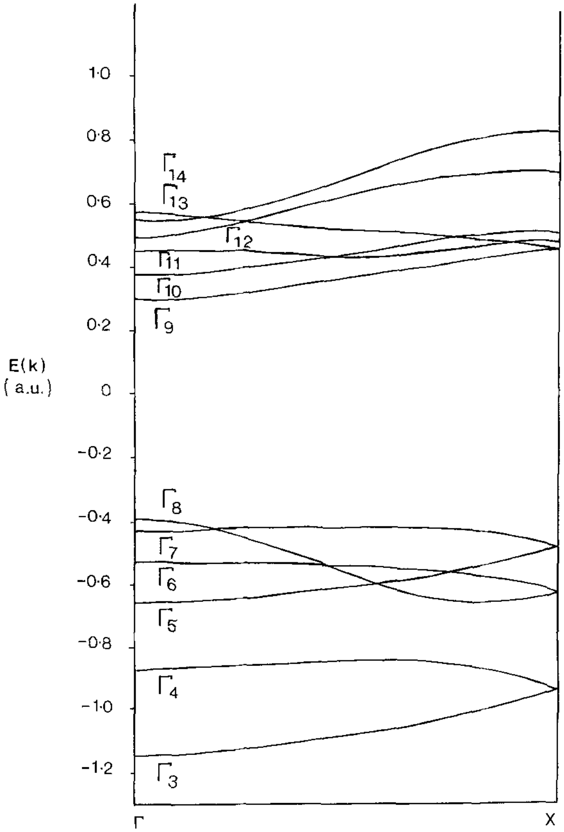

Fig. 3. The energy-band structure of polyethylene using a 3-unit cell model and basis set III

conduction band width is much the same as for the nearest-neighbour approximation. Since the band structure is raised in energy relative to the nearest-neighbour model, the value of the Koopmans' ionization potential tends towards the experimental value. The eigenvalues at $\boldsymbol{k}=\pi/a$ are now doubly degenerate, as expected from symmetry considerations, for the five-unit-cell case and this reflects an improvement to the model by the removal of the nearest-neighbour approximation.

Table 2 indicates that a reduction in the magnitude of the negative charge resident on the carbon atoms takes place on increasing the number of interacting cells. This reduction amounts to less than 2% of the "three-unit-cell" value, however, and is insignificant.

5. Simulation of the Solid-State Environment by Periodic Point Charges

A more realistic model for study would be solid polyethylene. However, as computations on the linear chain are only just possible, the treatment of a three-dimensional solid having a unit cell of comparable size is clearly out of the question. As an alternative, it is suggested that a model be employed in which the polyethylene chain is perturbed by a series of point charges representing the neighbour-

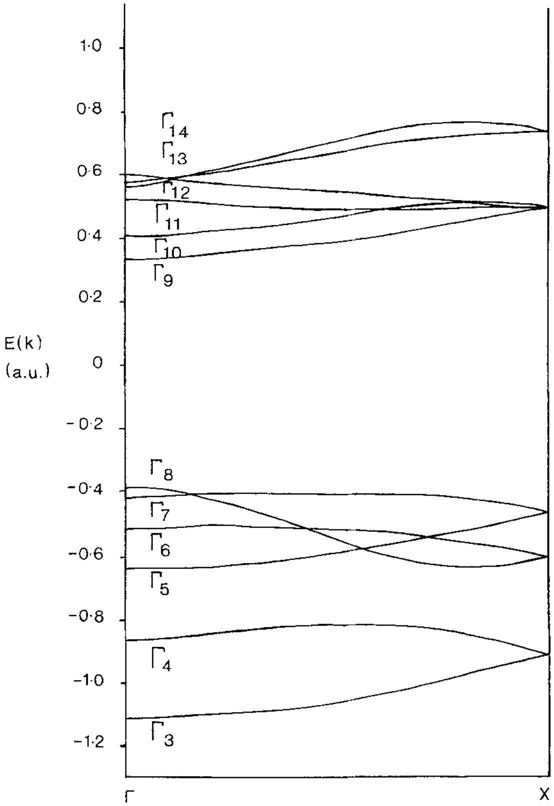

Fig. 4. The energy-band structure of polyethylene using a 5-unit cell model and basis set III

ing polymer strands, so that the overall effect as viewed from the main polymer strand is a simulation of the solid-state environment of the strand.

It has been suggested by Clementi [23] that a reasonable simulation of the effect of neighbouring molecules on the electronic energy band structure of a linear polymer chain may be obtained by the inclusion in the crystal orbital calculation of a perturbing field of point charges. He showed that, by including point charges in the unit cell of polyethylene, the energies of the bands are lowered or raised. If we apply his results to solid polyethylene, it can be envisaged that a value of $E(\Gamma_8)$ in the region of the experimental ionization potential can be obtained by the application of the correct perturbing field of surrounding negative charges. From Table 1, however, we can see that the hydrogen atoms for a variety of basis sets bear a positive charge. This would yield the interesting but unlikely situation in which alternative strands of polymer in the solid have oppositely-charged carbon-atom skeletons.

Thus we must have, as a first requirement, that the perturbing polymer strand resembles the main strand in charge distribution. In the present work a more precise investigation of the point charge perturbation technique, as applied to the polyethylene wavefunction, has been carried out and we have examined the effect of variation of the inter-strand distance as well as that of field strength.

6. The Point Charge Perturbation Model

The model employed in the present set of calculations is described diagrammatically by Fig. 5, in which C′ and H′ are point charges representing the constituent atoms of the neighbouring polymer strands. The distance between a given point charge and its equivalent point on the main strand is constant. The "skeleton" strands S1 and S2 are therefore identical in geometry to the main strand but are displaced a distance Δ a.u. along the positive and negative z-axes.

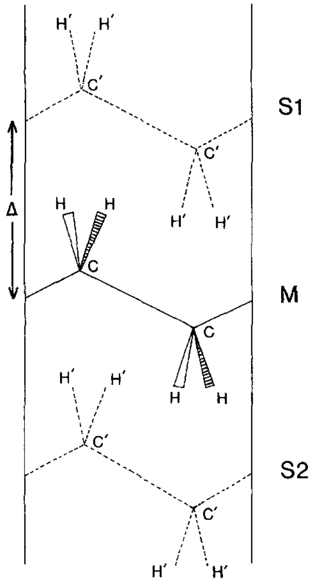

Fig. 5. The polyethylene unit cell for the point charge perturbation model

We permit the perturbing fields to interact with the main strand without allowing them to interact with each other. This very artificial restriction is essential to the integrity of the model in that the net field must only be observed by the single main strand whose electronic energy band structure is under investigation. Within the existing computational framework, this is achieved by the selection of only those perturbation terms which involve the origin cell of the main strand (M_0). The basis set chosen to span the main strand is the C(3, 3, 3)H(3) set introduced earlier.

7. The Perturbation Effect as a Function of Inter-Strand Displacement

It has been shown by Clementi [23] that the electronic properties of the polymer are generally found to vary in a regular fashion with the magnitude of the perturbing field. It might be anticipated, therefore, that an equally uniform effect will be observed on adjustment of the position of the field relative to the main polymer

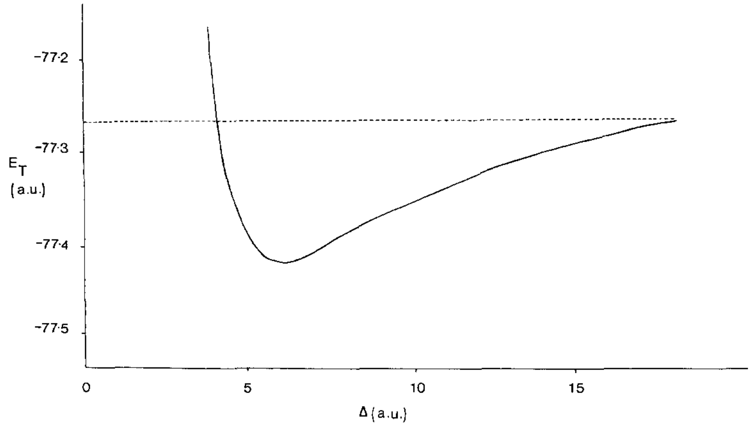

Fig. 6. Variation of the total energy per unit cell of polyethylene, E_T, with the strand displacement distance Δ

strand. The preliminary set of calculations investigate the validity of this assumption, employing the charge distribution obtained previously for the C(3, 3, 3)H(3) basis set, thereby maintaining as closely as possible the self-consistency principle expressed earlier. The set of calculations therefore describes the approach of the perturbing field, specified by C′ and H′ in Fig. 5, from infinity (represented by the original calculation on the unperturbed chain). Figs. 6, 7, and 8 show the effects of this change on the total energy per unit cell, the position of the highest occupied band at $k=0$, and the hydrogen atom electronic population, respectively. In each case the horizontal displacement axis has been drawn from the vertical axis point corresponding to infinite separation, or to the case of the unperturbed wavefunction.

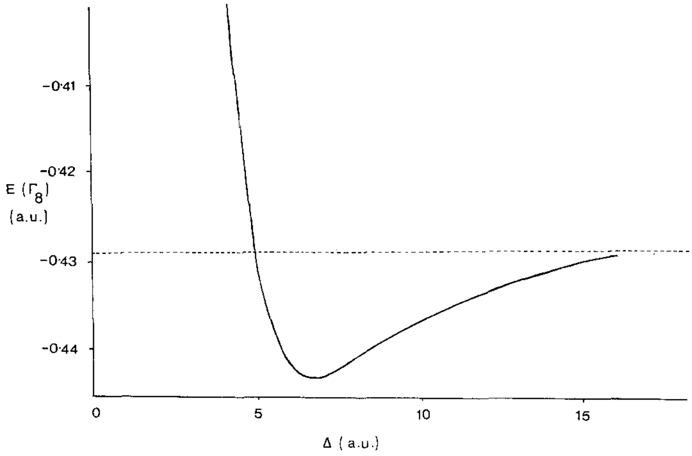

Fig. 7. Variation of the energy of the highest occupied band of polyethylene at $k=0$, $E(\Gamma_8)$, with the strand displacement distance Δ

The most striking feature of Figs. 6 and 7 is the overall Morse-curve form of the energy terms as functions of displacement showing, quite convincingly, that the model used does appear to be a stable one. Although the inter-chain distance in solid polyethylene has been reported by Bunn [24] to be 7.80 a.u., more recent work has favoured a lower value and, most significantly, Swan [25] has shown this particular dimension of the solid state unit cell to be temperature dependent. Extrapolation of Swan's results to allow comparison with the ground-state, absolute-zero situation assumed by the calculations suggests a value of the inter-chain distance of between 7.10 and 7.15 a.u. The minima obtained in Figs. 6 and 7, at 6.2 a.u. for the total energy and 6.9 a.u. in the case of the frontier energy band at $k = 0$, are in fairly good agreement with these results.

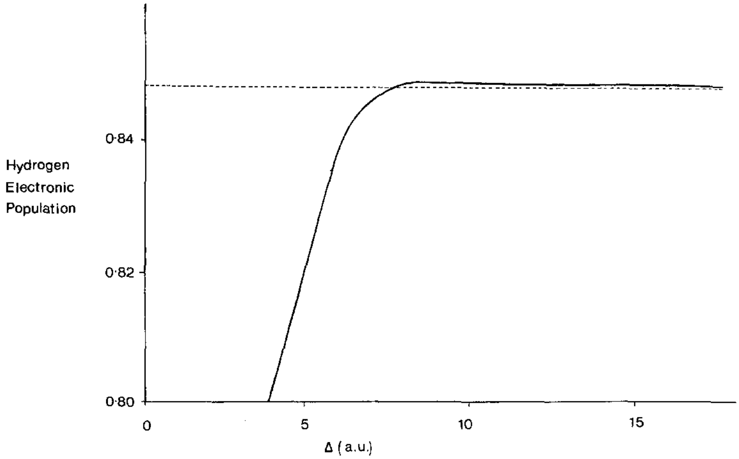

Fig. 8. Variation of the electronic population of hydrogen with the strand displacement distance Δ

Equally encouraging evidence with regard to the stability of the model is revealed on inspection of Fig. 8. The main-strand hydrogen atom electronic population is observed to remain virtually unchanged up to about 8.0 a.u. strand separation, at which point the self-consistency principle appears to begin to break down as slight electron drift toward the carbon atoms takes place. However, in the important region from 8.0 a.u. to 6.0 a.u. the total decrease in electron density on the hydrogen atom is only 0.0084, which represents a drop of less than 1%. The continued rate of drift of electron density from hydrogen to carbon as Δ is decreased below 6.0 a.u. is, also very low, and is found to be almost constant (about 0.2 e/a.u.) in this region although the corresponding values of E_T and $E(\Gamma_8)$ would indicate the system to be growing progressively less stable.

Thus all the results obtained indicate that the PCP model is a useful, stable model for the approximate representation of solid polyethylene and show that no significant change in charge distribution takes place on condensing to the solid from isolated polymer chains. With regard to the suggestion that neighbouring-strand interaction in the solid might account for the low ionization potential, we can discount this explanation on the basis of the properties of Fig. 6. Here it is shown that the ionization potential, given according to Koopmans' approximation by the modulus of the band energy at $\boldsymbol{k}=0$, increases as inter-strand separation is decreased, and begins to decrease only in the region in which the total energy function E_T indicates the system to be relatively unstable.

Several further avenues may be explored. Figs. 6 and 7 show that sizeable perturbations in E_T and $E(\Gamma_8)$ are obtained even at strand separations as great as 12–14 a.u. This range corresponds to roughly double the "stable" range previously found for the interstrand distance. With this in mind, we investigate the effect of introducing a more complete solid-state simulation in the form of a double perturbing layer of point charges. The extent to which the stability of the model is affected by allowing the self-consistency condition to lapse may be explored by altering the intensity of the field slightly while still employing the original main-strand wavefunction. Finally, it is useful to apply a perturbing field in which the polarity of the simulated carbon–hydrogen (C′–H′) bonds is reversed, a situation which would be necessary for good agreement with the observed ionization potential of polyethylene to be obtained.

8. Variation of the Perturbing Field Polarization

In the treatment introduced here, we have chosen two alternative field strengths based on C′ charges of -0.40 and -0.20, respectively stronger and weaker than the "self-consistent" distribution (C′ $= -0.30$) used in the foregoing set of calculations. As the H′ charge must vary accordingly, so that the net charge is zero, this is equivalent to altering the polarization of the C′–H′ bond in the perturbing strands. Figs. 9 and 10 show how the inter-strand interactions are affected by the change in polarization.

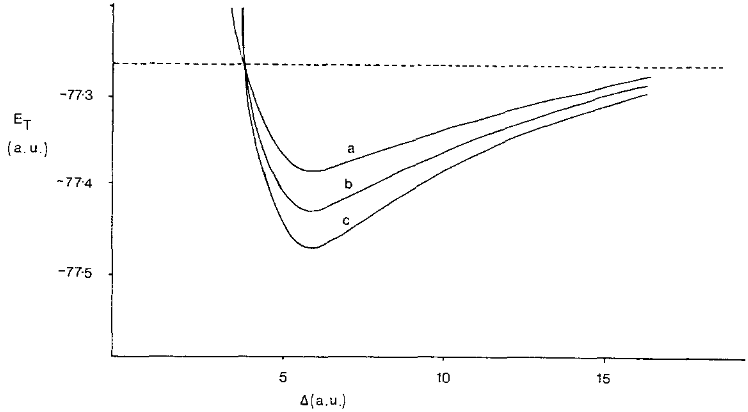

Fig. 9. Variation of the total energy per unit cell of polyethylene, E_T, with the strand displacement distance Δ. The charge on the carbon atoms of the strand is a) -0.20, b) -0.30 and c) -0.40

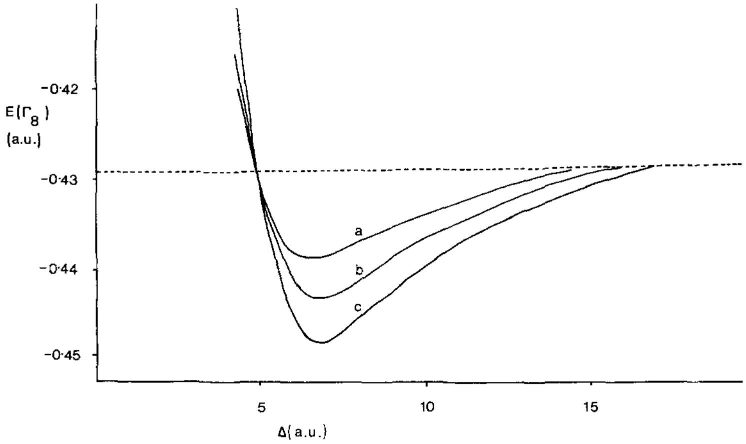

Fig. 10. Variation of the energy of the highest occupied band of polyethylene at $k=0$, $E(\Gamma_8)$, with the strand displacement distance Δ. The charge on the carbon atoms of the strand is a) -0.20, b) -0.30 and c) -0.40

As before, the main strand charge distribution was found to vary only slightly with inter-strand displacement and was also observed to be largely independent of the field polarization. In Fig. 9 the effect of increasing the internal field polarization is observed to be an overall lowering in the total energy Morse curve without any appreciable change in the position of the minimum. The stabilization of the total energy term would appear to increase linearly with the magnitude of the C′ charge and this effect must arise from the attraction between the positive H′ point charges and the electrons of the main strand. This would suggest, quite reasonably, that the hydrogen atoms on the polyethylene chain, rather than the carbon–carbon backbone, dominate the inter-strand forces and ultimately determine the chain separation in the solid.

The behaviour of the frontier energy band $E(\Gamma_8)$ at $k=0$ with respect to adjustment of the field polarization (Fig. 10) is identical to that of the total energy and is in agreement with the observations made by Clementi.

9. Reversed Field Polarization

Although we have already dismissed reversed-field polarization as an explanation of the ionization potential of polyethylene, it is nevertheless of interest to study the effect of such a field on the electronic properties of the main strand. In particular, as the positive H′ charge is seen to have a major influence on the position of the equilibrium inter-chain distance in the original "self-consistent" model (Figs. 6, 7), being balanced in the region $\Delta < \Delta_{\min}$ by the repulsion between the negative C′ charge and the main strand electrons, the substitution of a negative value for H′ is anticipated to have an interesting effect on the forms of the E_T and $E(\Gamma_8)$ curves.

The perturbing field charge distribution gives rise to the reversed-field effects depicted in Figs. 11 and 12. The total energy curve shown in Fig. 11 illustrates a

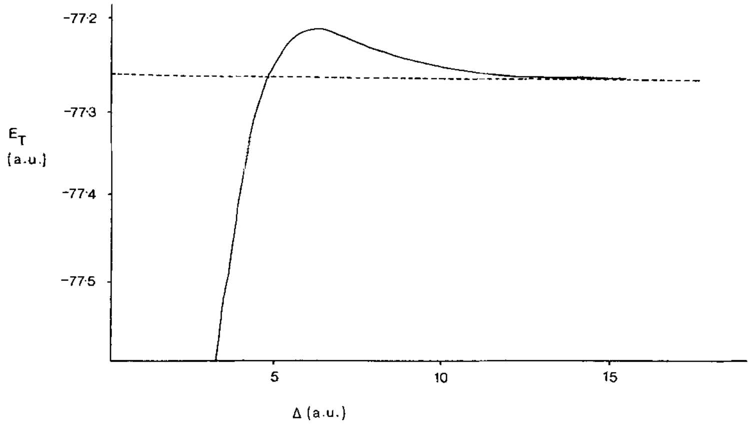

Fig. 11. Variation of the total energy per unit cell of polyethylene, E_T, with the strand displacement distance Δ for the reversed field polarization model

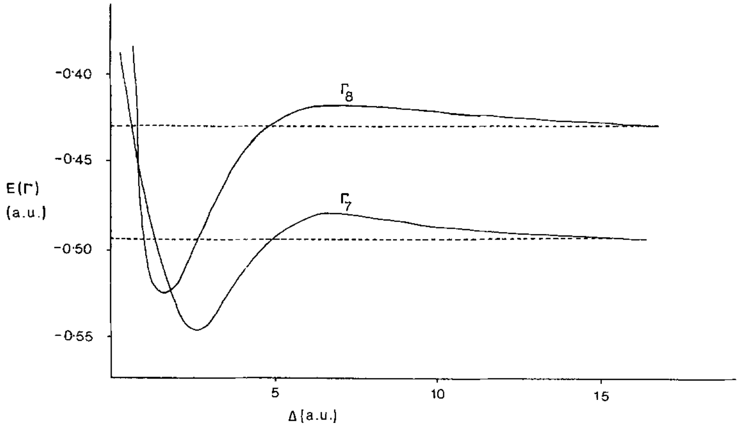

Fig. 12. Variation of the two highest occupied bands of polyethylene at $k=0$ with the strand displacement distance Δ for the reversed field polarization model

situation in which the PCP model has broken down. As Δ is reduced to the point of superimposition of the points C′ and H′ of the perturbing field, with their corresponding nuclei on the main strand, the dominant effect is the reinforcement of the carbon atom nuclear charge by that of C′, effectively increasing the main strand carbon atom nuclear charge to $+6.4$ on every carbon atom in the chain. The stabilization in the total energy term, without the moderating effect of nuclear repulsion precludes the possibility of a reasonable resultant being obtained.

In Fig. 12 the Δ-dependence of the second-highest-energy occupied band has been drawn in addition to that of Γ_8. Γ_7 is observed to become the frontier band at 2.0 a.u. strand separation, recrossing Γ_8 at $\Delta = 1.0$ a.u. There appears to be no significance in the fact that this crossing takes place, particularly in view of the obvious breakdown of the PCP model, other than that it explains the apparent discontinuity in the variation of the frontier band at $\boldsymbol{k}=0$ as Δ is reduced. A more interesting result is observed in the region of Δ from infinity to about 6.0 a.u. in which slight increases in both energy functions take place. This corresponds exactly to the effect noted by Clementi for the simpler case in which only a row of negative point charges was employed. The effect in the present case has been reduced by the opposing influence of the positive C′ point charges.

Therefore, in spite of the breakdown of the PCP scheme for this model, an important conclusion can be made by comparison of these results with those obtained by Clementi and with those described in previous sections. If a simple single chain of equally charged points is placed on either side of the main polymer chain, the effect of varying the magnitude and sign of the point charges has been shown by Clementi to be to raise and lower the energy bands of the polymer in an approximately linear manner. In this work it is deduced that a similar, though non-linear, effect will be observed on variation of the displacement of such a field from the main polymer chain. That is, the negatively charged field will cause the energy band structure to rise progressively as Δ is reduced, while the positively-charged field will cause it to fall. The effect of substituting a less simple field, containing charges of opposite signs and different magnitudes, is to introduce a less straightforward but possibly more realistic situation in which the raising of the energy bands is followed, as the inter-chain separation is decreased further, by a lowering of the energy band structure. The opposite effect has been noted in a previous section to take place when the "self-consistent" perturbing field is employed.

10. The Double Perturbing Layer

The final aspect of this model to be considered is that of introducing a second layer of perturbing point charges. This calculation follows from the earlier observation that a significant perturbation effect persisted at strand separations in the region 12.0–14.0 a.u., corresponding to twice the distance considered to be the probable equilibrium inter-chain displacement. The parameter Δ, which represents the main strand–perturbing strand displacement, is therefore taken to determine the distance between the first and second layer of perturbing strands.

The rules given for the single-layer model also apply to the double-layer scheme, only those interactions between the perturbing point charges and the main-strand origin cell M_0 being considered. Figs. 13 and 14 compare the effects of single- and double-layer fields on E_T and $E(\Gamma_8)$, respectively.

The overall effect of the second strand is shown to be to reinforce that of the neighbouring strand. Quite significantly, however, no variation in the position of the energy minimum is observed, suggesting that no further improvement in the agreement of the interstrand distance with the experimental value is likely to be obtained by extension of the model to include more distant polymer strands.

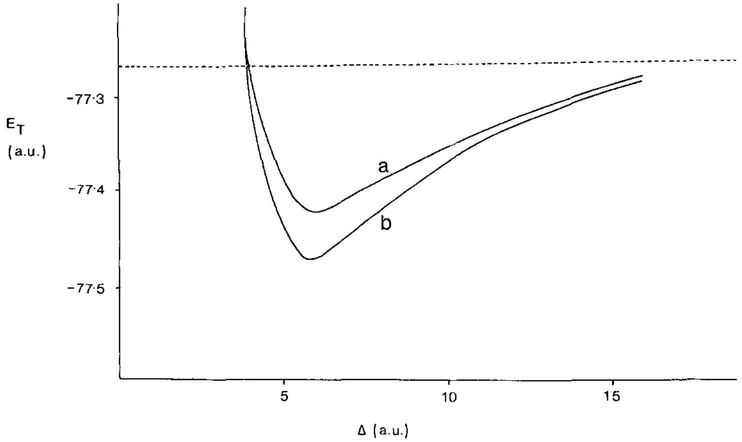

Fig. 13. Variation of the total energy per unit cell of polyethylene, E_T, with the strand displacement distance Δ for a) the single-layer model and b) the double-layer model

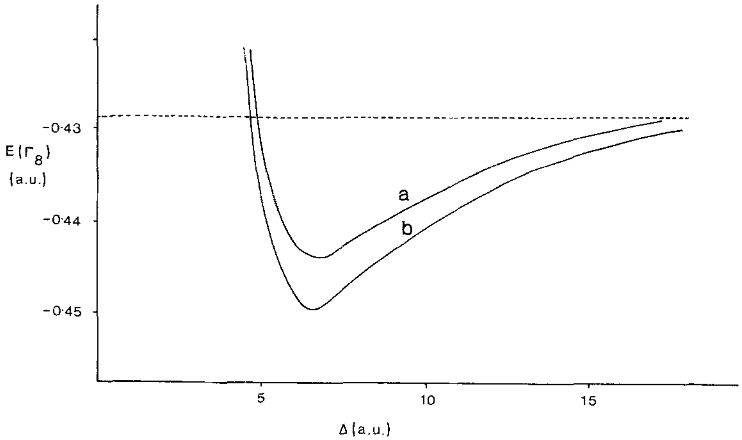

Fig. 14. Variation of the energy of the highest occupied band of polyethylene at $k = 0$, $E(\Gamma_8)$, with the strand displacement distance Δ for a) the single-layer model and b) the double-layer model

The point-charge perturbation model of solid polyethylene was originally invoked by us in order to explain the discrepancy between the experimentally observed ionization potential of solid polyethylene and that predicted by the band-structure calculations. It is evident from this work that the solid-state environment is less likely to raise the valence bands, as required to obtain better agreement, than to lower them.

Very little work has, as yet, been carried out on the investigation of the effects of electron correlation on the energy band structure of polymeric species. However, the introduction by Collins [26] of the "Screened-Exchange/Coulomb-Hole" (SECH) computational technique to a treatment of the diamond lattice has shown the exchange-integral correction to electron correlation to predominate for the valence bands, while the Coulomb-integral correction is more apparent in the conduction bands. As the screened-exchange term increases and the Coulomb-hole correction lowers, the energy relative to the Hartree-Fock value, the overall effect of correlation on the energy band structure, as observed by Collins, is therefore to reduce the theoretical ionization potential, bringing it into closer agreement with the lower experimental value.

Finally, McCubbin [27] has recently made some important projections concerning the effects of disorder on the energy band structures of polymers. In general, it has been found that the introduction of disorder, in the form of folds in the polymer strand (as known to take place at approximately 120 Å intervals in polyethylene [28]), has the effect of increasing the band gradients towards the points of high symmetry in the Brillouin zone and of broadening the bands over all. In polyethylene this "tailing", as it is called, takes place in the positive direction at the Γ-point and in the negative direction at the X-point, thereby reducing the Γ-point ionization potential.

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