

Electronic structures of polyethylene and polytetrafluoroethylene

Michael Springborg

Nordisk Institut for Teoretisk Atomfysik (NORDITA), Blegdamsvej 17, DK-2100 København Ø, Denmark,
Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-7000 Stuttgart 80, Federal Republic of Germany,
and Center for Materials Science, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

Milos Lev

Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-7000 Stuttgart 80, Federal Republic of Germany

(Received 17 January 1989)

Results of first-principles calculations on polyethylene [poly-(CH₂)] and polytetrafluoroethylene [poly-(CF₂)] are reported. We have optimized the carbon-carbon bond lengths for polyethylene, and using the optimized value we have considered structures in which the carbon backbone is assumed helical both for polyethylene and for polytetrafluoroethylene. The calculated bond lengths and valence-band structures are compared with those of other theoretical approaches and with experimental data. It is finally discussed why polyethylene has a planar carbon backbone whereas polytetrafluoroethylene is nonplanar.

I. INTRODUCTION

Due to the simplicity of the chemical unit of polyethylene, CH₂, this polymer is a standard test case for new developments in techniques for calculating the electronic structure of polymers, and there exist a number of papers reporting results of calculations at different levels of sophistication, including semiempirical calculations,¹⁻¹⁴ parameter-free Hartree-Fock calculations,^{8,15-23} Hartree-Fock calculations with perturbational inclusion of correlation effects,²⁴ and parameter-free calculations within the density-functional formalism.^{25,26} In contrast to polyacetylene with the even simpler chemical unit, CH, polyethylene is a large-gap insulator, so the problems related to slow lattice-sum convergences of the orbitals near the optical gap are small for polyethylene.

Recently, Seki and co-workers^{27,28} have performed angle-resolved photoemission experiments on CH₃(CH₂)₃₄CH₃, and from the results they derived the valence-band structures of polyethylene. This was the first direct observation of the valence-energy-band dispersions of an organic solid. In their first paper²⁷ they compared their bands with a large number of theoretical band structures. They concluded that rescaling and shifting those calculated by Karpfen¹⁹ (who used an *ab initio* Hartree-Fock approach) gave the best reproduction of their data, and that the agreement with the bands derived from the density-functional calculations^{25,26} was very poor.

We have recently developed a first-principles, density-functional method for performing self-consistent calculations on isolated, helical, periodic, infinite polymers,^{29,30} and will here report its applications to polyethylene. One of the purposes of the present paper is to demonstrate that this method gives valence-band structures in good agreement with the experimental ones, and, therefore, that the above mentioned failures of the density-

functional calculations in reproducing the experimental valence bands are related neither to the density functional formalism nor to the local approximation.

Whereas the carbon backbone of polyethylene is planar (i.e., the angle γ between adjacent planes of three neighboring carbon atoms is $\gamma = 180^\circ$), its fluorine-substituted derivative polytetrafluoroethylene ("Teflon," poly-CF₂) has a nonplanar carbon backbone with $\gamma \approx 160^\circ - 165^\circ$. Another purpose of the present paper is a first-principles examination of this structural difference between the two polymers.

In Sec. II we briefly introduce our computational method, which has been described in detail elsewhere.²⁹ In Sec. III we report our optimized value of the carbon-carbon bond lengths for polyethylene with a planar carbon backbone and compare it with other theoretically optimized values^{11,19} as well as with experimental values.³¹⁻³⁵ We also report calculated valence-band structures and compare them with the experimental ones.^{27,28} Seki *et al.*²⁷ have given a detailed account of most of the previous theoretically derived band structures and a comparison with those is therefore not included here. We neglect the formal lack of correspondence between the calculated single-particle eigenvalues within the density-functional formalism and electronic excitation energies, since experience has shown this to be a good approximation. We also present the total-energy and band structures as a function of γ . In Sec. IV we similarly report our results on the total energy and band structures as a function of γ for polytetrafluoroethylene. Here the results are compared with those of other theoretical approaches^{2,6,21,26,36,37} and with experimental photoelectron spectra.^{38,39} The two compounds are compared in Sec. V, and we conclude in Sec. VI.

II. METHOD OF COMPUTATION

The self-consistent calculations are performed within the density-functional formalism^{40,41} using the local ap-

proximation of von Barth and Hedin.⁴² The eigenfunctions to the single-particle Schrödinger-like equations are expanded in linear muffin-tin orbitals (LMTO's) as described in detail elsewhere.^{29,30} An LMTO is defined as follows: The three-dimensional space is divided into (nonoverlapping) muffin-tin spheres—each with a nucleus at its center—and the interstitial region containing no nuclei. Basis functions, electron densities, and potentials are expanded numerically inside the spheres and analytically outside them. An atom-centered LMTO is then defined as being the (numerical) eigenfunction to the spherically symmetric potential of the sphere of the atom of interest matched continuously and differentially to a spherical Hankel function (times a spherical harmonic) on the sphere boundary. Inside any other sphere the Hankel function is replaced by the numerical functions of that sphere such that the function is smooth everywhere in space.

For a single, infinite, periodic, helical polymer the primitive symmetry operation is a combined translation of h and rotation of v . Here the zigzag symmetry (e.g., of planar polyethylene) can be represented by a helical structure with $v = \pi$. For the polymer we define Bloch waves formed by the atom-centered LMTO's defined in *local* right-handed coordinate systems with the z axis parallel with the polymer axis and the x axis pointing away from it. Thus, for $(CR_2)_x$ (R being hydrogen and fluorine for polyethylene and polytetrafluoroethylene, respectively) one unit cell contains only one CR_2 unit.

The angle γ between two adjacent planes of three neighboring carbon atoms is related to v through⁴³

$$\cos v = \frac{1}{2}(1 - \cos \gamma)(1 - \cos \alpha) - \cos \alpha$$

with α being the C—C—C bond angle.

The sizes of the muffin-tin spheres were kept constant for all calculations of each polymer, and we furthermore used the same size of the carbon spheres for both compounds. The $1s$ electrons of carbon and fluorine were treated within a frozen-core approximation. The basis sets contained s , p , and d functions on all sites. It consisted of two functions per atom and (l, m) set, but nearly linear dependent linear combinations were excluded.

Since the present approach requires a full self-consistent calculation for each set of nuclear coordinates it is a tremendous task to explore all details of the total energy as a function of nuclear configurations. We have therefore chosen to vary only a few coordinates keeping the rest fixed at reasonable values. For polyethylene with a planar backbone we varied only the C—C bond lengths believing that variations in this geometrical parameter would lead to the largest changes in the physical properties of the material. In the rest of the calculations [both for $(CH_2)_x$ and for $(CF_2)_x$] we fixed the value of this parameter at the optimized value (i.e., the value that gave the lowest total energy in the first set of calculations) and varied only γ . For polyethylene this is a reasonable approximation when γ deviates only little from 180° . For polytetrafluoroethylene this approximation might be worse since we use a bond length optimized for another polymer. However, since the C—C bonds are formed by almost ideal carbon sp^3 hybrids the replacement of hy-

drogen with fluorine is expected to lead only to minor modifications in the C—C bond lengths. We therefore believe the essential physical properties of both polymers to be explored throughout this limited set of calculations.

The geometrical parameters were chosen as follows. The two planes defined by one carbon atom and its two nearest carbon neighbors and the same carbon atom and its two nearest hydrogen or fluorine neighbors were assumed to be perpendicular. Moreover, the pairs of two hydrogen (or fluorine) atoms were assumed to be placed symmetrically about the plane of the three neighboring carbon atoms. We kept the C—C—C and H—C—H bond angles fixed at the experimental values for polyethylene,^{31–34} i.e., 112° and 107° , respectively. These values are close to the ideal value, 109.5° , for tetrahedrally coordinated carbon atoms. For polytetrafluoroethylene the F—C—F bond angles were kept also at 107° . For the C—H and C—F bond lengths we chose the values 2.02 a.u. and 2.48 a.u., respectively.

III. RESULTS FOR POLYETHYLENE

For fixed bond angles and C—H bond lengths we varied the C—C bond lengths for the polyethylene structure with a planar zigzag carbon backbone. The lowest total energy was found for C—C bond lengths of 2.87 a.u. This value is in good agreement with the experimental values 2.89 a.u. from x-ray scattering^{31–34} and 2.98 a.u. from neutron scattering,³⁵ as well as with the theoretical values 2.91 a.u. from semiempirical calculations,¹¹ and 2.95 a.u. from *ab initio* Hartree-Fock calculations.¹⁹

In Fig. 1 we depict our calculated valence-band structures for the optimized structure together with the latest experimental data by Fujimoto *et al.*²⁸ as read off from their figure. The experimental data have been shifted upwards by 2 eV. Furthermore, the band structures of Fig. 1 correspond to only considering translational symmetry, such that one unit cell contains two CH_2 units.

Unfolding the bands of Fig. 1 for a helical structure that has a unit cell with one CH_2 unit we recognize three valence bands of which the lowest one and that band defining the top of the valence bands are of σ symmetry with respect to reflection in the plane of the carbon nuclei. The other band is of π symmetry.

Except for the constant shift of 2 eV the overall agreement between theory and experiment is good. The data of Fujimoto *et al.*²⁸ are an extension of those published by Seki *et al.*²⁷ and do not change the conclusions of Seki *et al.* Since, furthermore, Seki *et al.*²⁷ have given a very detailed comparison between their data and a large number of theoretical band structures we will here only describe the general trends of the results of the other theoretical approaches. For more details the reader is referred to Ref. 27.

We calculate the total valence-band width to be 17.4 eV, in good agreement with the experimental value of 16.2 eV.²⁷ Most of the *ab initio* Hartree-Fock calculations yield a total valence band width of about 20 eV, whereas the various semiempirical "neglect-of-differential-overlap" methods [complete neglect of differential overlap (CNDO), modified neglect of diatomic

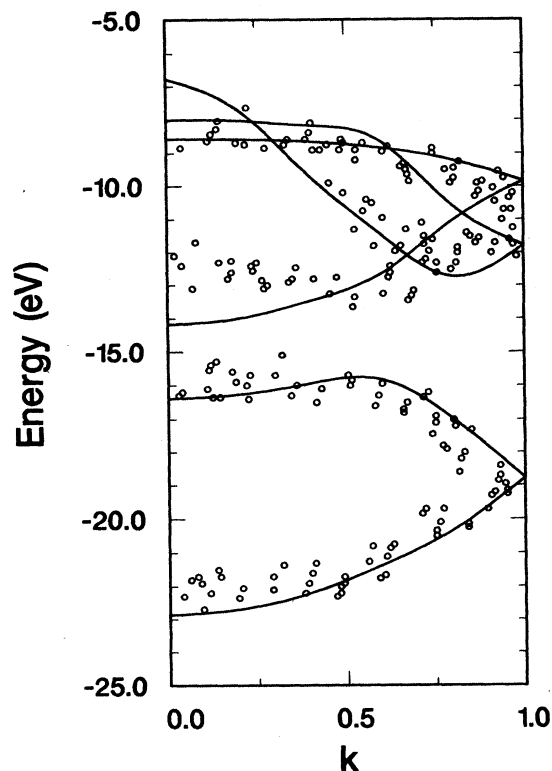


FIG. 1. The calculated (solid curves) band structures for the optimized structure of planar polyethylene shown as functions of a dimensionless k variable with $k=0$ being the zone center and $k=1$ the zone edge. The Brillouin zone is that corresponding to a unit cell of two CH_2 units. Also shown (the circles) are the angle-resolved photoemission data by Seki and co-workers (Refs. 27 and 28). The latter have been shifted upwards in energy by 2 eV.

overlap (MNDO), modified intermediate neglect of differential overlap (MINDO), and intermediate neglect of differential overlap (INDO)] predict the width to be much too large, i.e. 30–40 eV. On the other hand, the Hückel calculations give roughly the correct width, about 17 eV. Finally, the earlier density-functional calculations yield 17.9 eV (Ref. 25) and 14.8 eV (Ref. 26), which is in reasonable agreement with the experimental value. As demonstrated by Seki *et al.*,²⁷ most of the calculations giving reasonable total bandwidths predict other quantities (like the width of the two lowest valence bands, that of the four upper valence bands, or the gap between the two sets of valence bands) at significant variance with the experimental values.

The width of the lowest valence band we calculate to be 7.2 eV (experimental value: 7.2 eV), and the total width of the upper two valence bands is found to be 8.9 eV (experimental: 6.7 eV). The finding that the upper width is larger than the lower is in contrast with the result of most other calculations.

Experimentally it is found that the bottom of the upper valence bands is not at the zone center (see Fig. 1). This is in disagreement with our findings as well as with those of the other theoretical approaches. This indicates that the interpretation of the experimental data may not be fully

correct. Especially, the determination of the so-called inner potential in the solid (see Refs. 27 and 28) might be connected with some uncertainty.

We calculate the ionization potential to be 5.1 eV, which is considerably smaller than the experimental values 9.6–9.8 eV,^{8,44,45} whereas Seki *et al.*²⁷ report a value of 8.8 eV, which according to them is to be increased by 0.5 eV in order to be compared with the results of calculations on a single chain. The *ab initio* Hartree-Fock calculations yield 10–13 eV, the semiempirical CNDO, MNDO, INDO, and MINDO give 9–12 eV (except for three at 4.9, 7.0, and 8.3 eV, respectively), the Hückel calculations give 12–13 eV, and, finally, the density functional calculations give 11.3 and 12.8 eV, respectively.

Thus, our absolute position of the band structure seems to be off by approximately 2–4 eV. However, a comparison with the even simpler compound polyacetylene, $(\text{CH})_x$, supports our results. *Trans*-polyacetylene is planar with a zigzag carbon backbone and one hydrogen atom per carbon atom in the same plane. The uppermost valence band is formed by carbon p orbitals perpendicular to the plane of the nuclei, and is thus of π symmetry. The orbitals of this band are fairly delocalized and do not have a counterpart for polyethylene. The rest of the valence bands are formed by localized orbitals of σ symmetry and can accordingly be compared with the bands for polyethylene. For this compound one of us has recently reported results of calculations similar to those reported here.^{46,47} The ionization potential was found to be in good agreement with the experimental value. Furthermore, for both polyacetylene and polyethylene the bottom of the valence bands is formed essentially by carbon s orbitals and is at -22 to -23 eV. Finally, the top of the σ valence bands for polyacetylene is very flat and at approximately -8.5 eV, which is in good agreement with the flat parts of the uppermost valence bands for polyethylene. Therefore, we find the results on polyacetylene and on polyethylene to be in agreement with each other. Since the results on polyacetylene are consistent with experimental findings we suggest the reported experimental ionization potential to be related to the second and third highest valence bands, which have large flat parts in a small energy interval, and not to the highest valence band, which gives only a small density of states at the top of the valence electron energies. This reinterpretation will bring the discrepancy between our calculated and the experimental ionization potential down to about 2 eV consistent with that for the photoemission data.

In the next set of calculations we fixed also the C—C bond lengths (at the optimized value, i.e. 2.87 a.u.) but assumed the dihedral angle between two neighboring planes of three neighboring carbon atoms to deviate from 180° . In Fig. 2 we show the resulting relative total energy per CH_2 unit. Both Imamura¹ and Morokuma² have reported results of similar calculations but with semiempirical methods (extended Hückel in Ref. 1, and CNDO in Ref. 2). Their total energies are much less sensitive to variations in γ than ours are. Thus, for $\gamma=150^\circ$ we found a relative total energy of roughly 2 eV, whereas Imamura found 0.2 eV and Morokuma found 0.05 eV. We have no

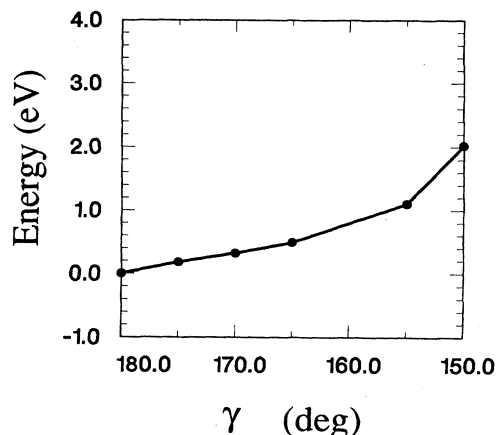


FIG. 2. Relative total energy per CH_2 unit for polyethylene as a function of the dihedral angle γ between two neighboring planes of three neighboring carbon atoms. Straight lines are drawn connecting the data points.

direct explanation of this discrepancy, but the results to be reported in the next section on polytetrafluoroethylene suggest that the semiempirical methods significantly underestimate the total-energy variations upon screwing the polymer.

In Fig. 3 we depict the band structures for three selected values of γ (175° , 165° , and 155° , respectively). For $\gamma = 175^\circ$ [Fig. 3(a)] we easily see how the bands 2 and 3 show an avoided crossing and comparing with Fig. 1 we see that for $\gamma = 180^\circ$ they become of different symmetry (σ and π) and are crossing. As γ is reduced the splitting between them is increased, and for $\gamma = 155^\circ$ we in total have three well separated valence bands. As functions of decreasing γ the orbitals interact less as can be visualized

from the bandwidths. For instance, for $\gamma = 160^\circ$ (155°) the total valence-band width is 16.6 eV (16.3 eV), the width of band 1 is 6.8 eV (6.6 eV), and the total width of bands 2+3 is 7.9 eV (7.5 eV). These values should be compared with those quoted above for $\gamma = 180^\circ$ (17.4 eV, 7.2 eV, and 8.9 eV, respectively).

IV. RESULTS FOR POLYTETRAFLUOROETHYLENE

For polytetrafluoroethylene we fixed all geometrical parameters except for the dihedral angle γ as described in Sec. II.

In Fig. 4 we show the valence-band structures for $\gamma = 180^\circ$ (i.e., the structure with the planar zigzag carbon backbone) as well as for $\gamma = 165^\circ$.

The σ_1 and π_1 bands in Fig. 4(a) are mainly formed by the symmetric and antisymmetric combinations of atomic fluorine $2s$ orbitals. The σ_2 band corresponds to the lowest valence band of polyethylene, and is largely formed by carbon orbitals. The other two valence bands of polyethylene (see Figs. 1 and 3) have large hydrogen components and have therefore no direct counterparts for polytetrafluoroethylene.

When reducing γ from 180° no bands may cross as for instance shown in Fig. 4(b), but otherwise the differences between Fig. 4(a) and Fig. 4(b) are only small.

The total valence-band width is calculated to be 25.4 eV for $\gamma = 180^\circ$ and 25.0 eV for $\gamma = 165^\circ$.

Other theoretical calculations on the valence band structures of polytetrafluoroethylene include extended Hückel calculations by McCubbin,³⁶ CNDO calculations by Morokuma,² semiempirical so-called simulated *ab initio* molecular-orbital (SAMO) calculations by Duke and O'Leary,⁴⁸ *ab initio* Hartree-Fock calculations by Otto *et al.*,²¹ and density-functional calculations by Falk and

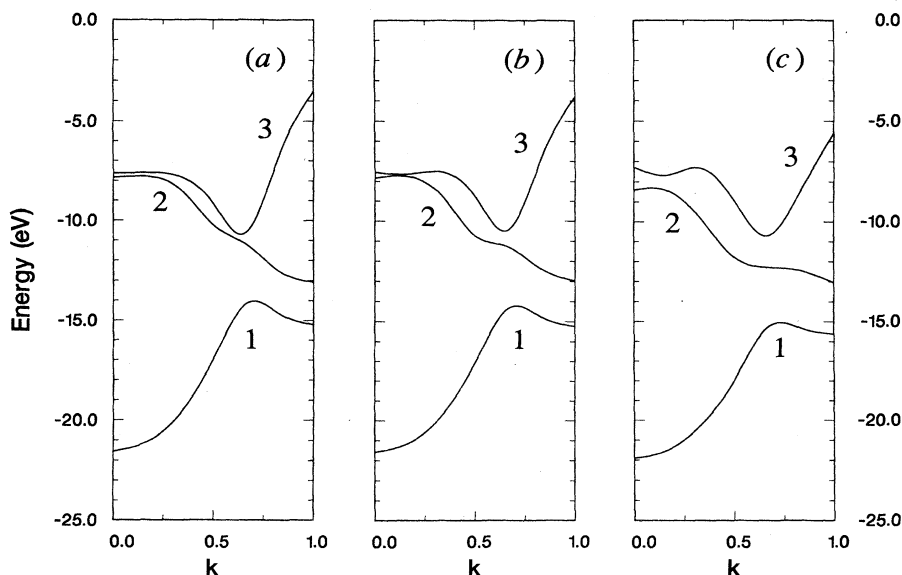


FIG. 3. Valence-band structures for polyethylene for different values of the dihedral angle γ : (a) $\gamma = 175^\circ$, (b) $\gamma = 165^\circ$, and (c) $\gamma = 155^\circ$. The unit cell contains one CH_2 unit, and $k = 0$ ($k = 1$) corresponds to the zone center (zone edge).

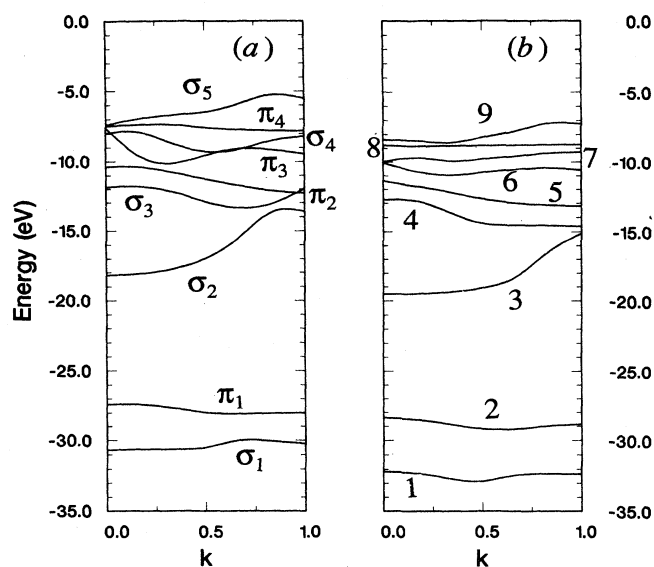


FIG. 4. Valence-band structures for polytetrafluoroethylene for two values of the dihedral angle γ : (a) $\gamma = 180^\circ$ and (b) $\gamma = 165^\circ$. The unit cell contains one CF_2 unit, and $k = 0$ and $k = 1$ correspond to the zone center and zone edge, respectively.

Fleming,³⁷ and by Kasowski *et al.*²⁶ For a helical geometry McCubbin reported a total valence-band width of 31 eV, whereas Morokuma found it for $\gamma = 180^\circ$ to be over 40 eV, and Duke and O'Leary reported 35 eV also for $\gamma = 180^\circ$. The Hartree-Fock approximation inherent in the SAMO and CNDO approaches used above explains the larger bandwidths of those compared with ours. Similarly, the *ab initio* Hartree-Fock valence-band width of Otto *et al.* is larger (about 33 eV) than ours.

It is more surprising that the density-functional calculations by Falk and Fleming lead to a valence-band width of over 30 eV, but as argued elsewhere,⁴⁶ their results on polyacetylene disagree in many respects with results of other methods and with experiments. In their discussion of the valence bands for $\gamma = 180^\circ$ Kasowski *et al.* have excluded the two lowest bands. The remaining ones are found to have a total width of 14.8 eV, somewhat larger than the 12.9 eV we find. Since the experimental valence bands for polyethylene agreed well with ours but to a lesser extent with those of Falk and Fleming and of Kasowski *et al.*, we believe our valence bands for polytetrafluoroethylene to be the most accurate ones obtained within the density-functional formalism.

Pireaux and co-workers have in two papers^{38,39} reported results of theoretical extended Hückel calculations and experimental x-ray photoelectron spectra (XPS) on polytetrafluoroethylene. Their calculations were for a planar carbon backbone, whereas in the experiments, of course, the backbone was helical. They reported a calculated total width of the two lowest valence bands to be 2.2 eV according to theory compared to a 3.7 eV experimental width. Our results indicate that this width depends on γ , being 3.3 eV for $\gamma = 180^\circ$ and 4.5 eV for $\gamma = 165^\circ$, in good agreement with the experimental values.

There are larger discrepancies regarding the absolute position of these two bands: the Hückel calculation gave around -40 eV, experiments around -35 eV, and we find roughly -30 eV. We find the total width of the upper seven valence bands to be about 13 eV; the XPS results gave approximately 14 eV, and the Hückel calculations gave also about 13 eV. In contrast to this, the *ab initio* Hartree-Fock calculations by Otto *et al.*²¹ predicted this width to be significantly larger (roughly 19 eV) as often is the case for Hartree-Fock calculations. The total valence-band width we find to be 25–26 eV, in reasonable agreement with the theoretical result of Pireaux *et al.*^{38,39} and in good agreement with their experimental result (30 eV and 27 eV, respectively), and smaller than the value (33 eV) by Otto *et al.*²¹ Thus, except for a constant shift that might be related to both experimental and theoretical uncertainties we find good agreement between our calculated valence bands and the XPS data of Pireaux *et al.*^{38,39}

In Fig. 5 we plot the relative total energy per CF_2 unit as a function of γ . We notice that there is a minimum for γ slightly less than 180° although the optimal value of γ is larger than the experimental one. Compared with the similar curve for polyethylene (Fig. 2) the total energy is here found to depend more strongly on γ .

Similar curves for the total energy as a function of γ have been presented by Morokuma² obtained with the semiempirical CNDO method and by Otto *et al.*²¹ calculated with the *ab initio* Hartree-Fock method. Morokuma finds essentially no difference between the results for polyethylene and polytetrafluoroethylene, and, furthermore, a much weaker dependence on γ . Also Otto *et al.* find a weaker dependence on γ but have only presented results for polytetrafluoroethylene. Both predict a local maximum for γ around 120° , but that of Otto *et al.* is approximately 1 order of magnitude larger than that of Morokuma. Thus, the results by Morokuma seem to predict too weak dependencies of the total energy on γ . The bond lengths used by Otto *et al.* were slightly larger than those used by us, i.e. 2.91 a.u. for C—C bonds and 2.60 a.u. for

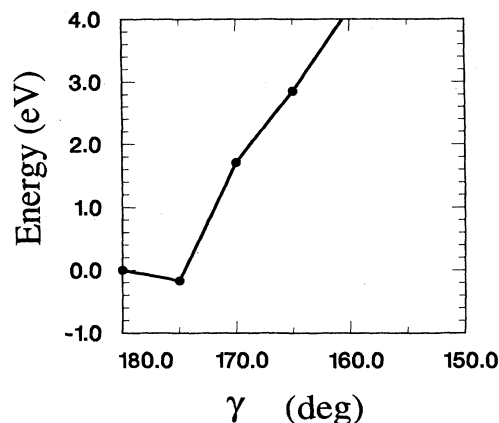


FIG. 5. Relative total energy per CF_2 unit for polytetrafluoroethylene as a function of the dihedral angle γ . Straight lines are drawn connecting the data points.

C—F bonds versus 2.87 a.u. and 2.48 a.u., respectively. This difference explains at least partially the differences in the relative total-energy curves.

We would finally like to point out that the curves in Figs. 2 and 5 are to be taken with some caution: In a complete investigation all the other geometrical parameters (i.e., C—C and C—F or C—H bond lengths and C—C—C and F—C—F or H—C—H bond angles) should be relaxed for each fixed value of γ .

V. COMPARISON BETWEEN POLYETHYLENE AND POLYTETRAFLUOROETHYLENE

The most striking difference between polyethylene and polytetrafluoroethylene is the planar versus twisted carbon backbones. We will here discuss some of the similarities and differences that might be of relevance in understanding this structural difference.

Polytetrafluoroethylene has a larger carbon-to-side-group electron transfer than polyethylene has because of the strong fluorine electronegativity. This also shows up in the calculated numbers of valence electrons inside the carbon muffin-tin spheres for the two compounds (since we use the same size of the spheres), being (for $\gamma = 180^\circ$) 1.90 and 1.81, respectively. Thus, although polytetrafluoroethylene contains *more* electrons per unit cell than polyethylene, *less* are inside the carbon spheres. Therefore, one might speculate that by decreasing γ the electrostatic repulsion between the side-groups is reduced. However, this is only partly true, since simultaneously with the increase in some side-group-side-group distances others decrease. In this context some of the most important interatomic distances are those between the atoms attached to next-nearest carbon neighbors. For polyethylene these are 4.76 a.u. and 5.76 a.u. for $\gamma = 180^\circ$ changing to 4.96 a.u. and 4.83 a.u. for $\gamma = 160^\circ$. For polytetrafluoroethylene these equivalently change from 4.76 a.u. and 6.21 a.u. for $\gamma = 180^\circ$ to 5.04 a.u. and 5.01 a.u. for $\gamma = 160^\circ$. Thus we do not believe a simple electrostatic repulsion to be the sole reason for the preference of a helical form for polytetrafluoroethylene.

The ionic radius of a F^- ion is 2.57 a.u. (Ref. 49) which is larger than half of the smaller of the above mentioned interatomic distances for the fluorine atoms in polytetrafluoroethylene. Thus, the fluorine atoms are expected to interact with each other. This is also evident from the γ dependence of the σ_1 - π_1 splitting mentioned in the preceding section. However, the bond length of the F_2 molecule (2.67 a.u., Ref. 50) is considerably smaller than the present F—F interatomic distances, but for a partially negatively charged F_2 molecule we expect a significant increase in the bond length. Thus, upon varying γ the electronic orbitals of the fluorine atoms of next-nearest carbon neighbors interact differently in contrast to polyethylene for which those of the hydrogen atoms do not interact. These variations in the interactions of the orbitals will cause small but noticeable variations in the electronic distributions. We can quantify these variations by using the number of valence electrons inside the muffin-tin spheres. For polyethylene and

$\gamma = 180^\circ$ (160°) these numbers are 1.90 (1.90) electrons inside each carbon sphere and 0.31 (0.32) electrons inside each hydrogen sphere. These numbers are contrasted by the equivalent numbers for polytetrafluoroethylene: For $\gamma = 180^\circ$ (160°) we find 1.81 (1.85) electrons inside each carbon sphere and 3.34 (3.35) electrons inside each fluorine sphere. Thus, there is a non-negligible interaction leading to a noticeable redistribution of the electron density for polytetrafluoroethylene not recovered for polyethylene. In total we believe the combined effect of the electrostatic interactions and the orbital interactions to be the reason for the structural difference between the two compounds.

VI. CONCLUSION

We have applied the first-principles, full potential, density-functional, LMTO method for helical polymers on various geometries of polyethylene and of polytetrafluoroethylene.

For a polyethylene structure with a planar carbon backbone we have optimized the C—C bond lengths keeping all other bond lengths and all bond angles fixed. The optimized value was found to be within a few percent of experimental values and of other theoretical values.

The valence-band structures for the optimized polyethylene structure are—except for a constant shift of about 2 eV—in good agreement with experimental angle-resolved photoemission data in contrast to most other theoretical approaches. By comparing with the results of similar calculations on polyacetylene we argued that the absolute position of the bands for polyethylene as derived from the experimental data might be reconsidered. As a consequence of the observed good agreement the earlier reported failures of density-functional methods in obtaining valence-band structures agreeing with the experimental bands is not to be ascribed the density-functional formalism or the local approximations hereto.

By allowing the structures to be helical we found—within a very limited variation in the geometrical parameters—the structure with a planar carbon backbone to have the lowest total energy for polyethylene.

This was contrasted by results of similar calculations on polytetrafluoroethylene for which a structure with a small helical distortion away from that with a planar carbon backbone was found to have the lowest total energy.

We argued that not only electrostatic interactions but also orbital interactions were responsible for this structural difference between the two compounds.

Finally, the band structures of polytetrafluoroethylene were found to be in good agreement with XPS data, except for a constant shift.

ACKNOWLEDGMENTS

The authors acknowledge a careful reading of the manuscript by Dr. Robert C. Albers. Furthermore, one of us (M.S.) was supported by the Danish Natural Science Research Council.

*Present address.

- ¹A. Imamura, *J. Chem. Phys.* **52**, 3168 (1970).
²K. Morokuma, *J. Chem. Phys.* **54**, 962 (1971).
³E. Clementi, *J. Chem. Phys.* **54**, 2492 (1971).
⁴M. H. Wood, M. Barber, I. H. Hillier, and J. M. Thomas, *J. Chem. Phys.* **56**, 1788 (1972).
⁵D. L. Beveridge, I. Jano, and J. Ladik, *J. Chem. Phys.* **56**, 4744 (1972).
⁶B. J. Duke and B. O'Leary, *Chem. Phys. Lett.* **20**, 459 (1973).
⁷M. J. S. Dewar, S. H. Suck, and P. K. Weiner, *Chem. Phys. Lett.* **29**, 220 (1974).
⁸J. Delhalle, J. M. André, S. Delhalle, J. J. Pireaux, R. Caudano, and J. J. Verbist, *J. Chem. Phys.* **60**, 595 (1974).
⁹P. N. Dyachkov and A. A. Levin, *Theor. Chim. Acta (Berlin)* **36**, 181 (1975).
¹⁰M. J. S. Dewar, Y. Yamaguchi, and S. H. Suck, *Chem. Phys. Lett.* **50**, 259 (1977).
¹¹M. J. S. Dewar, Y. Yamaguchi, and S. H. Suck, *Chem. Phys.* **43**, 145 (1979).
¹²J. M. André, L. A. Burke, J. Delhalle, G. Nicolas, and Ph. Durand, *Int. J. Quantum Chem. Symp.* **13**, 283 (1979).
¹³P. G. Perkins, A. K. Marwaha, and J. J. P. Stewart, *Theor. Chim. Acta (Berlin)* **57**, 1 (1980).
¹⁴B. J. Duke, *Int. J. Quantum Chem. Symp.* **16**, 391 (1982).
¹⁵D. R. Armstrong, J. Jamieson, and P. G. Perkins, *Theor. Chim. Acta (Berlin)* **50**, 193 (1978).
¹⁶J. L. Brédas, J. M. André, and J. Delhalle, *Chem. Phys.* **45**, 109 (1980).
¹⁷D. R. Armstrong, J. Jamieson, and P. G. Perkins, *Theor. Chim. Acta (Berlin)* **57**, 43 (1980).
¹⁸R. S. Weidman, K. L. Bedford, and A. B. Kunz, *Solid State Commun.* **39**, 917 (1981).
¹⁹A. Karpfen, *J. Chem. Phys.* **75**, 238 (1981).
²⁰H. Teramae, T. Yamabe, and A. Imamura, *Theor. Chim. Acta (Berlin)* **64**, 1 (1983).
²¹P. Otto, J. Ladik, and W. Förner, *Chem. Phys.* **95**, 365 (1985).
²²R. J. Meier, *Chem. Phys. Lett.* **138**, 471 (1987).
²³D. J. Wyble, M. Seel, and J. T. Waber, *Solid State Commun.* **64**, 827 (1987).
²⁴S. Suhai, *Int. J. Quantum Chem. Symp.* **18**, 161 (1984).
²⁵J. E. Falk and R. J. Fleming, *J. Phys. C* **6**, 2954 (1973).
²⁶R. V. Kasowski, W. Y. Hsu, and E. B. Caruthers, *J. Chem. Phys.* **72**, 4896 (1980).
²⁷K. Seki, N. Ueno, U. O. Karlsson, R. Engelhardt, and E.-E. Koch, *Chem. Phys.* **105**, 247 (1986).
²⁸H. Fujimoto, T. Mori, H. Inokuchi, N. Ueno, K. Sugita, and K. Seki, *Chem. Phys. Lett.* **141**, 485 (1987).
²⁹M. Springborg and O. K. Andersen, *J. Chem. Phys.* **87**, 7125 (1987).
³⁰M. Springborg, *J. Chim. Phys.* (to be published).
³¹C. W. Bunn, *Trans. Faraday Soc.* **35**, 482 (1939).
³²H. M. M. Shearer and V. Vand, *Acta Crystallogr.* **9**, 379 (1956).
³³P. W. Teare, *Acta Crystallogr.* **12**, 294 (1959).
³⁴S. Kavesch and J. M. Schultz, *J. Polym. Sci. A2* **8**, 243 (1970).
³⁵G. Avitabile, R. Napolitano, B. Pirozzi, K. D. Rouse, M. W. Thomas, and B. T. M. Willis, *J. Polym. Sci., Polym. Lett. Ed.* **13**, 351 (1975).
³⁶W. L. McCubbin, *Chem. Phys. Lett.* **8**, 507 (1971).
³⁷J. E. Falk and R. J. Fleming, *J. Phys. C* **8**, 627 (1975).
³⁸J. J. Pireaux, J. Riga, R. Caudano, J. J. Verbist, J. M. André, J. Delhalle, and S. Delhalle, *J. Electron Spectrosc. Relat. Phenom.* **5**, 531 (1974).
³⁹J. Delhalle, S. Delhalle, J. M. André, J. J. Pireaux, J. Riga, R. Caudano, and J. J. Verbist, *J. Electron Spectrosc. Relat. Phenom.* **12**, 293 (1977).
⁴⁰P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
⁴¹W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
⁴²U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
⁴³M. Springborg and R. O. Jones, *J. Chem. Phys.* **88**, 2652 (1988).
⁴⁴J. J. Pireaux, S. Svensson, E. Basilier, P.-Å. Malmqvist, U. Gelius, R. Caudano, and K. Siegbahn, *Phys. Rev. A* **14**, 2133 (1976).
⁴⁵J. J. Pireaux, R. Caudano, and J. Verbist, *J. Electron Spectrosc. Relat. Phenom.* **5**, 267 (1974).
⁴⁶M. Springborg, *Phys. Rev. B* **33**, 8475 (1986).
⁴⁷M. Springborg, *Phys. Rev. B* **37**, 1218 (1988).
⁴⁸B. J. Duke and B. O'Leary, *Int. J. Quantum Chem. Symp.* **18**, 407 (1984).
⁴⁹L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1960).
⁵⁰K.-P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).