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Local Density Approximation Calculation of the Conformation and Electronic Structure of Poly(fluoroethylene)s

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A series of density functional calculations of the structural and electronic properties of all six different fluorinated polyethylenes with several different dihedral angles are performed using two different local density approximations (LDA's), the Gáspár−Kohn−Sham and the Perdew−Zunger ones. The geometrical parameters are optimized simultaneously for the stable conformation of poly(tetrafluoroethylene) and poly(difluoroethylene). The torsional potential curves for all the poly(fluoroethylene)s show an absolute minimum at dihedral angles other than 180°, corresponding to a nonplanar conformation. For poly(difluoroethylene), the absolute minimum is found at the gauche form. The valence and conduction bands as well as the Mulliken populations are calculated and compared with other theoretical calculations and experimental results.

I. Introduction

For several decades, simple polymers such as polyethylene and its fluorine derivatives have caused wide interest among physicists and chemists. Because of their technical and commercial importance, intensive theoretical and experimental research has been done on them. Owing to the simplicity of their chemical structure, these polymers are easy to be synthesized and prepared in a perfect crystalline state,[1] allowing the experimental determination of very precise structure parameters and theoretical calculations. The latter include the prediction of the geometry and electronic structure, and it serves in some cases as the tests for the theory itself.[2]

Unlike polyethylene, poly(fluoroethylene)s are mostly found stable in a crystalline state formed by helical chains.[1] Poly(tetrafluoroethylene) (PTFE) crystal[3−5] is well-ordered below $T = 19$ °C and is formed by 13/6 helical chains with a dihedral angle of 163.5°. A solid phase transition occurs at $T = 19$ °C, and the chain turns to 15/7 helix with a dihedral angle of 165.8°.[6] Poly(vinyl fluoride) (PVF) crystallizes in an orthorhombic state formed by planar chains,[7] whereas poly(vinylidene fluoride) (PVF2) has three crystalline states:[8−10] the orthorhombic state formed by slightly deflected planar chains, the monoclinic state consisting of glide-type chains, and another monoclinic one conformed by slightly deflected planar chains. Not many photoelectron spectra measurements for the band structure of poly(fluoroethylene)s are available, except the one for PTFE reported by Pireaux et al.[11,12]

The theoretical studies for the geometry and electronic structures of poly(fluoroethylene)s, ranging from semiempirical to first-principles methods, include the extended Hückel calculation by McCubbin,[13] the CNDO calculation by Morokuma,[14] the semiempirical simulated ab initio molecular orbital (SAMO) calculations by Duke and O'Leary,[15] and the ab initio calculations by Otto et al.[16] Density functional approaches have seldom been applied to polymers, like polyethylene or its fluorine derivatives, in contrast to the intensive applications of local density approximation (LDA) calculations for solids and small molecules. Falk and Fleming[17] presented a density functional (DFT) calculation for six poly(fluoroethylene)s using a linear combination of atomic orbitals−muffin tin potential (LCAO−MT) method. Later on, Kasowski et al.[18] reported an application of the extended muffin tin orbitals for a DFT calculation of polyethylene, PTFE, and polyacetylene. More recently, Springborg et al.[19] calculated both the geometry and electronic structures for polyethylene and PTFE using a LDA approach and an atom-centered linear muffin tin orbitals (LMTO) method.

In the previous works, we presented a full potential LDA calculation using both Gáspár−Kohn−Sham (GKS) and Perdew−Zunger(PZ) correlations for the geometry and the electronic structures of polyethylene[20] and polyparaphenylene.[21,22] Some rough discussion on the structures of PTFE was also presented within this LDA formalism.[23]

In this paper, we perform a series of LDA calculations, using both the GKS and the PZ exchange correlation functionals, of the geometry and the electronic structures of all six kinds of poly(fluoroethylene)s including poly(tetrafluoroethylene), poly(difluoroethylene) (PDFE), *syn*-poly(difluoroethylene) (sPDFE), poly(vinyl fluoride) (PVF), poly(vinylidene fluoride), and poly(trifluoroethylene) (P3FE). After a brief introduction to the method and basis sets, we first present our conformation results in section III and then the one-electron band structure as well as the Mulliken population in section IV. Finally, some conclusions are summarized in section V.

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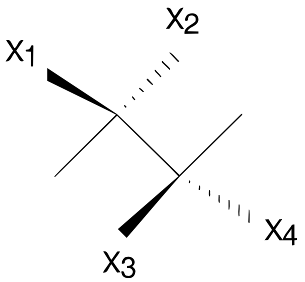
TABLE 1: Optimized Geometry Parameters for PTFE, Using Both the X_α and the PZ Local Density Approximations, in Comparison with the Fixed Parameters for LDF (LMTO) and LCAO−MT as Well as HF Calculations[a]

	X_α	PZ	HF	LDF (LMTO)	LCAO−MT
C−C bond length (Å)	1.57	1.54	1.54	1.52	1.54
C−F bond length (Å)	1.37	1.36	1.375	1.313	1.334
CCC bond angle (deg)	110.71	110.13	109.42		
FCC bond angle (deg)	109.39	109.43	109.42	107	
dihedral angle (deg)	163.7	163.7	163.7	175	109

[a] For the definition of the parameters, see Figure 1.



Polymer	Abbreviation	Chemical repeat unit	X1	X2	X3	X4
Polyethylene	PE	CH2	H	H	H	H
Polytetrafluoroethylene	PTFE	CF2	F	F	F	F
Poly(1,2-difluoroethylene)	PDFE	CHF	H	F	F	H
syn-Poly(1,2-difluoroethylene)	sPDFE	CHFCFH	H	F	H	F
Polyvinylfluoride	PVF	CHFCH2	H	F	H	H
Poly(vinylidene fluoride)	PVF2	CH2CF2	H	H	F	F
Polytrifluoroethylene	P3FE	CHFCF2	H	F	F	F

Figure 1. Unit cell and geometry of the poly(fluoroethylene)s. Thick C−X bonds point out from the plane of the paper, while dotted C−X bonds into the plane of the paper. X stands for the hydrogen or fluorine atom.

II. Theoretical Methods

Our calculations are performed using the local density functional approach based on a linear combination of Gaussian-type orbitals (LCGTO) originally developed for molecular systems[24,25] and extended to two-dimensional systems[26] and helical chain polymers.[27−30] For the exchange-correlation functional, two local density approximations were used: the Gáspár−Kohn−Sham exchange approximation[31,32] and the Kohn−Sham exchange functional together with the Perdew−Zunger[33] (PZ) analytic fit to the numerical electron-gas correlation results of Ceperley and Alder.[34]

The Gaussian orbital and auxiliary basis sets used were optimized for LDA calculations by Godbout et al.[35] Using Huzinaga's notation,[36] the hydrogen atom has a (41/1*) contraction pattern, and the carbon atom has a (7111/411/1*) contraction pattern. Auxiliary fitting functions consisting of four s functions and four sets of s, p, and d functions having the same exponents, denoted as (4,4;4,4) auxiliary basis, are used on the carbon atoms, while a (3,1;3,1) auxiliary basis is used for the hydrogen atoms.

The more detailed description of the methods can be found in our previous papers on the same series.[20−23,30]

III. Conformation Results

The configurations of the poly(fluoroethylene)s are shown in Figure 1. The geometry parameters are optimized for PTFE and for PDFE. For the other poly(fluoroethylene)s, the fixed geometry is taken from the reference and will be shown in subsection III.c.

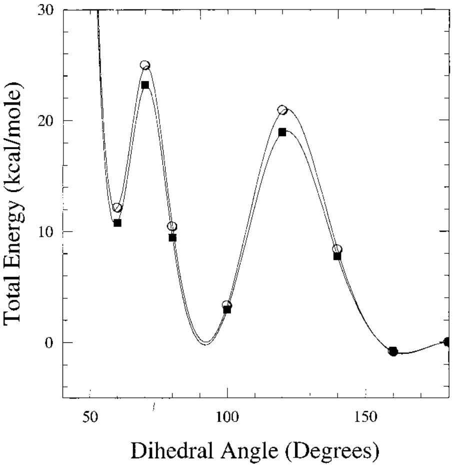


Figure 2. Torsional potential per CF_2 unit cell (kcal/mol) for single poly(tetrafluoroethylene) helical chain as a function of carbon backbone dihedral angle. Open circles and closed squares denote GKS and PZ results, respectively. The splines are used as a guide to the eye.

A. Poly(tetrafluoroethylene). The total energy of PTFE is minimized with respect to all the geometry parameters, including the carbon−carbon bond length, the carbon backbone bond angle, the carbon−fluorine bond length, the fluorine−carbon−carbon bond angle, and the dihedral angle of the backbone. The absolute minimum is at a dihedral angle of 163.7° corresponding to a slightly deformed planar conformation. The optimized geometrical parameters are listed in Table 1. As far as we know, there is not any experimental result for geometry parameters of PTFE available; neither is the first-principle calculation result. Similar to what we have found in the calculation for polyethylene (see ref 20), the GKS results of 1.57 Å for the C−C bond length is larger than the PZ results of 1.54 Å. Both these values are close to the values used as fixed parameters in previous HF[16] and LDA[19] calculations. It is worth noticing that both C−C bond lengths obtained by the GKS and PZ calculations for PTFE are about 0.03 Å larger than those for polyethylene reported in our previous article. This can be easily understood after taking into account that the repulsion between the fluorine atoms in PTFE is larger than that between the hydrogen atoms in polyethylene. The GKS and PZ calculations get similar optimized values for the other parameters, i.e., 1.37 Å (C−F bond length), 110.71° (CCC bond angle), 109.39° (FCC bond angle), and 163.7° (dihedral angle) for GKS and 1.36 Å, 110.13°, 109.43°, and 163.7° for PZ, respectively. The values of the FCC bond angle for PTFE are quite similar to those of the HCC bond angle of polyethylene.

The total energies as a function of the dihedral angle relative to the energy of the planar zigzag conformation for both the GKS and PZ LDA calculations are depicted in Figure 2. The two LDA calculations present similar energy curves except a constant shift that has been eliminated in Figure 2 since only the relative values to the planar conformation are interesting. Although the curve looks quite similar to that of polyethylene, there are several significant differences between them.

TABLE 2: Optimized Geometrical Parameters for PDFE, Using Both the X_α and the PZ Local Density Approximations

	X_α			PZ		
C−C bond length (Å)	1.535	1.550	1.534	1.510	1.522	1.511
C−F bond length (Å)	1.419	1.415	1.416	1.401	1.396	1.399
C−H bond length (Å)	1.121	1.118	1.123	1.108	1.105	1.109
CCC bond angle (Å)	111.22	113.02	116.84	111.47	113.62	116.65
FCC bond angle (deg)	109.3	108.47	107.79	109.30	108.70	107.80
HCC bond angle (deg)	109.88	109.45	107.95	109.78	109.39	108.30
dihedral angle (deg)	90.3	58.4	302.0	89.2	57.7	302.4

The most striking feature of the conformation of PTFE is the twisted carbon backbone. The absolute minima are at 163.7° for both GKS and PZ calculations. Their well heights relative to planar conformation are rather small, only 1.03 and 0.96 kcal/mol for GKS and PZ, respectively. This result is in a good agreement with the experimental measurement (see below) as well as the HF result of 163° obtained by Otto et al.[16] Springborg et al.[19] reported a LDA optimized dihedral angle of 175° using the linear muffin tin orbitals (LMTO) method. Confirmed by the spectroscopic measurements, PTFE in the crystalline state exhibits several phases. Under high pressure, there is one orthorhombic phase and one monoclinic phase both formed by planar zigzag chains. Under ambient pressure, PTFE crystal is well-ordered below $T = 19$ °C formed by twisted chains with a backbone dihedral angle of 163.5°. At the temperature of 19 °C, a phase transition occurs, which drives the helical chain to a 15/7 form with a dihedral angle of 165.8°.[6] In order to determine the origin of this transition, we present a detailed calculation for a PTFE single chain around the planar conformation and find that there is only one minimum. So it can be concluded that the phase transition at 19° is mainly caused by interchain interactions or the crystal packing, which always reduces the torsion of each chain and prefers a planar conformation.

Another important feature for the torsional potential of PTFE is that there are two distinct local minima in the gauche form, located at 90.33° and 58.4° for GKS as well as 89.2° and 57.7° for PZ, respectively. Single-point calculations show that the energies at 90.3° for GKS and 89.2° for PZ are about 1.8 kcal/mol, which are near to those in the planar zigzag conformation. But no gauche form was found experimentally.

B. Poly(difluoroethylene). The structural properties of poly(difluoroethylene) are studied in detail in this subsection. Since the substituent atoms binding to a backbone carbon are different, the unit cell loses its planar reflection symmetry. Thus starting from the planar zigzag conformation, the polymer will change to a different geometry under a left or a right screw operation. For this reason, we calculated the torsional potential from a dihedral angle of 40° to that of 320° rather than from 40° to 180° as in the cases of polyethylene and PTFE. All the other geometrical parameters are fixed during the calculation.

The torsional potential of PDFE is shown in Figure 3. The particular important feature of the potential is that the absolute minima are located at 302.0° for GKS and 302.4° for PZ, respectively, which correspond to a gauche form. The well depth of the absolute minimum relative to planar conformation is rather large, 4.0 kcal/mol for GKS and 4.32 kcal/mol for PZ, which means that the gauche minimum can be a very stable conformation even in the case of the crystalline state. Other two local minima are at dihedral angles from 50° to 100°, again corresponding to a gauche form. The well depths of these minima are 3.11 and 3.07 kcal/mol for GKS as well as 3.65 and 3.22 kcal/mol for PZ, respectively. A shoulder structure was found around the absolute minimum. The planar conformation corresponds to a maximum. Left and right from it, there are two local minima with smaller well depths of about 1.2−1.5 kcal/mol.

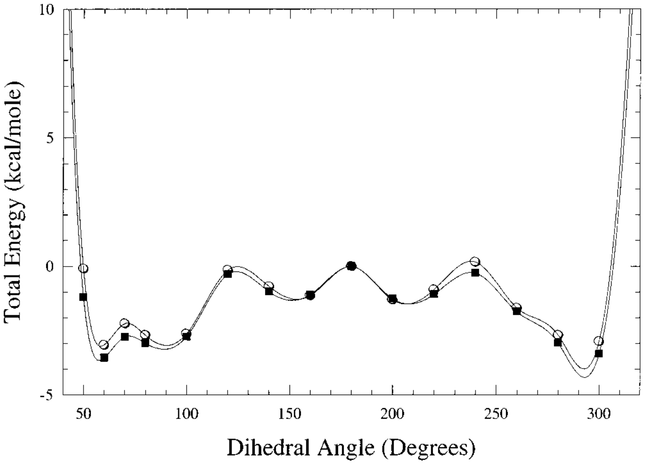


Figure 3. Torsional potential per CHF unit cell (kcal/mol) for a single poly(difluoroethylene) helical chain as a function of carbon backbone dihedral angle. Open circles and closed squares denote GKS and PZ results, respectively. The splines are used as a guide to the eye.

All the geometrical parameters are optimized at the three minima in the potential curve. The results are listed in Table 2. The C−C bond lengths are 1.54 Å at 90.3°, 1.55 Å at 58.4°, and 1.53 Å at 304° in the GKS case as well as 1.51 Å at 89.2°, 1.52 Å at 57.7°, and 1.51 Å at 302.4° in the PZ case. All these values are more or less smaller than that for PTFE but roughly close to that of polyethylene. In contrast to the C−C bond lengths, the C−F bond lengths for PDFE, 1.42 Å (GKS) and 1.40 Å (PZ) for the most stable conformation, are significantly larger than those for PTFE, i.e., 1.37 and 1.36 Å for GKS and PZ, respectively. The FCC bond angles are found to be similar to each other for PDFE and PTFE.

C. Other Poly(fluoroethylene)s. The conformations of all six different poly(fluoroethylene)s are studied in detail around the dihedral angle of 180°. The resulting torsion potential curves are presented in Figure 4 together with the potential curve of polyethylene. The geometry parameters are fixed as 1.54, 1.375, and 1.10 Å for C−C, C−F, and C−H bond lengths and 113°, 110°, and 110° for the CCC, FCC, and HCC bond angles. Only the PZ exchange correlation is used, since the GKS method provides very similar results with a constant shift for the total energy.

Three kinds of potential curves can be found in Figure 4. The potential curve for polyethylene has an absolute minimum at 180° corresponding to a planar conformation. In contrast to polyethylene, all its fluorine derivatives have a local or absolute minimum in the trans form but not at 180°, which means that their single chains should be stable in a nonplanar conformation. As shown in the previous subsections, PTFE has an absolute minimum at 163.7° whereas PDFE has a local minimum at about 150°, which is out of the frame of Figure 4. The torsional potential curves for another four poly(fluoroethylene)s are quite similar to each other. They all have a minimum at dihedral angles between 165° and 170°. The total energies of all these four polymers increase strongly for dihedral angles less than

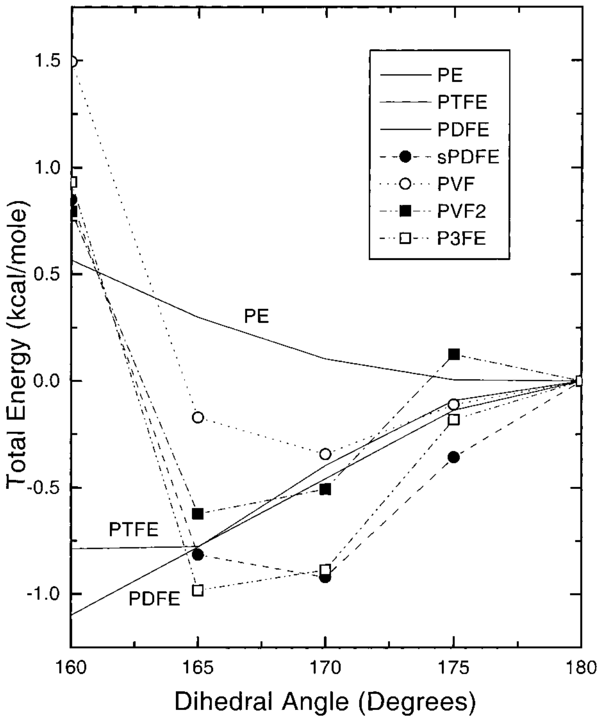


Figure 4. Relative total energy per unit for poly(fluoroethylene)s as a function of the dihedral angle, using PZ LDA. All the values are in kcal/mol units. The three solid lines are for PE, PTFE, and PDFE, respectively, as denoted in the figure, and the four dashed and dotted lines are for sPDFE (dashed line + filled circle), PVF (dotted line + open circle), PVF2 (dash−dotted line + filled square), and P3FE (dash−dotted line + open square).

165°. The well depths of the minima relative to the planar conformation are mostly less than 1 kcal/mol. The smallest depth, only 0.3 kcal/mol, occurs for poly(vinyl fluoride). The only known crystalline state of this polymer consists of chain in planar conformation. This is caused by the crystal packing effect, which always favors a less bulked structure. In another example, poly(vinylidene fluoride), with a corresponding well depth of 0.62 kcal/mol, was found to crystallize in a slightly deflected planar zigzag conformation.

IV. Electronic Structure

A. Energy Bands of Poly(tetrafluoroethylene). Figure 5 shows our calculated occupied and low-lying unoccupied bands for the stable conformation, using both the GKS and PZ LDA approaches. The conduction bands and valence bands are very well separated, and all the valence bands are below −5 eV. As shown in the rest of the article, the above description is true for the bands of all the poly(fluoroethylene)s studied. It is worth noticing that the absolute value is useless and only after a constant shift the band structure is comparable with experimental results. It can be seen that the nine occupied bands are separated into two groups. The lower group contains two bands mainly formed by the symmetric and the antisymmetric combination of fluorine 2s orbitals, while the upper group consists of seven bands formed by the carbon sp^3 hybrids and fluorine 2p orbitals. In general, the GKS and PZ band structures are in good agreement with each other except for a constant shift of about 1.0−1.5 eV.

The band characteristics, including the band gap, ionization energy, and the widths of the valence band and the conduction band, are calculated for two dihedral angles (180°, 163.7°) using both GKS and PZ exchange-correlation functionals. They are listed in the second horizontal part of Table 3. For the stable conformation at a dihedral angle of 163.7°, the calculated band gaps are 5.5 and 5.8 eV for GKS and PZ, respectively. These values are remarkably smaller than the HF results of 17.8 eV found by Otto et al.[16] and the CNDO results of 17.0 eV found by Morokuma.[14] Kasowski et al.[18] performed a LDA calculation using the extended muffin tin orbitals method and reported a gap value of 6.2 eV, whereas Falk and Flaming[17] found it to be 11.8 eV after a calculation using a linear combination of atomic orbitals−muffin tin (LCAO−MT) potential.

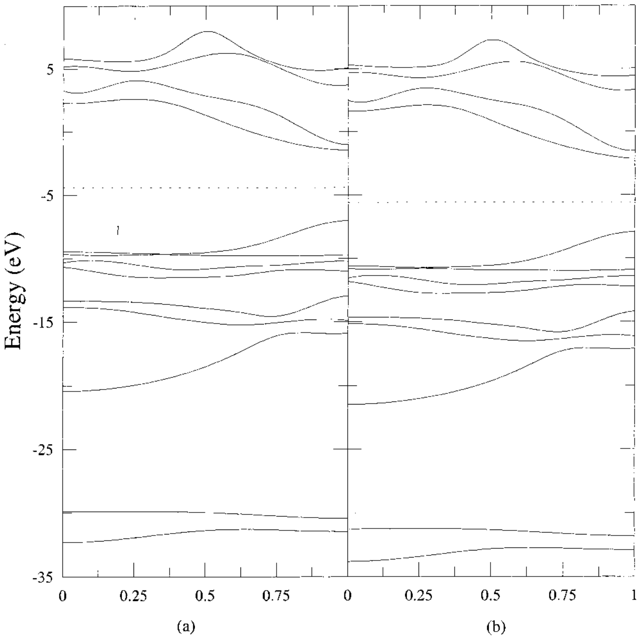


Figure 5. Valence and conduction band structure of PTFE at dihedral angle of 163.7° for (a) GKS and (b) PZ. Each vertical strip denotes half of the helical Brillouin zone, with the abscissa giving the scaled effective quasimomentum κ/π running from the zone center ($\kappa/\pi = 0$) at the left-hand side to the zone edge ($\kappa/\pi = 1$) at the right-hand side of each strip.

Our calculated total occupied band widths are 25.3 eV(GKS) and 25.9 eV(PZ), which are also in agreement with the LMTO results of 25.4 eV[19] but smaller than other LDA and semiempirical results, i.e., 36 eV for LCAO−MT (from Figure 7 in ref 17), 31 eV for extended Hückel (from ref 19), and 45 eV for CNDO (from Figure 10 in ref 14). The two groups of the occupied bands are separated by a gap of about 6 eV. The total widths of the two low-lying and the upper seven valence bands were calculated to be 2.4 eV (GKS) and 2.6 eV (PZ) and 13.4 eV (GKS) and 13.6 eV (PZ), respectively, which are in good agreement with experimental XPS spectra[11] values of 3.7 and 14 eV, respectively. Springborg et al.[19] reported values of 4.5 eV for the low-lying bands and 12.9 eV for the upper bands. For the total width of the upper seven bands, the extended Hückel calculations have given a result of 13 eV[13] while Kasowski et al.[18] found 14.8 eV. In contrast to this, the HF calculations by Otto et al.[16] presented a much larger value, roughly 19 eV. As a conclusion, it could be pointed out that HF calculations always give too large band widths and gaps (which can be corrected, however, by taking into account correlation[2]) while the LDA method usually provides a too small fundamental gap and also too small dispersions for the bands. The usual underestimate of the fundamental gap is caused partly by the neglect of the discontinuity of the exchange-correlation potential and partly by the use of the LDA. For obtaining a physically more correct gap, a quasiparticle calculation is requested. But it is out of the scope of this article since we

TABLE 3: Calculated Band Characteristics, Including the Minimum and Maximum Values and Band Widths of the Valence and the Conduction Bands and the Band Gap, for Polyethylene and all Poly(fluoroethylene)s, Together with a HF Result[a]

			valence band			conduction band			
polymers	methods	DA (deg)	min	max	width	min	max	width	gap
CH_2	DF(GKS)	180	−8.86	−5.37	3.48	2.29	5.34	3.05	7.67
	DF(GKS)	60	−7.93	−5.61	2.32	1.33	3.98	2.64	6.94
	DF(PZ)	180	−9.94	6.35	3.59	1.62	4.78	3.15	7.97
	DF(PZ)	60	−9.05	−6.58	2.48	0.62	3.30	2.78	7.09
	HF(C-10s5p)[b]	180	−16.61	−11.12	5.49	2.81	6.61	3.80	13.93
CF_2	DF(GKS)	180	−9.47	−7.05	2.42	−1.77	3.24	5.01	7.05
	DF(GKS)	163.7	−9.63	−6.94	2.69	−1.32	2.67	3.99	5.62
	DF(PZ)	180	−10.65	−8.27	2.38	−2.88	2.14	5.03	5.39
	DF(PZ)	163.7	−10.73	−7.88	2.85	−1.63	2.10	3.74	6.25
	HF(C-10s5p)	180	−18.37	−14.68	3.70	2.43	7.97	5.54	17.10
CHF	DF(GKS)	180	−7.63	−5.82	1.81	−0.87	2.61	3.48	4.95
	DF(GKS)	302.0	−8.30	−7.30	1.0	−0.08	2.61	2.69	7.22
	DF(PZ)	180	−8.75	−6.96	1.79	1.84	1.89	3.72	5.12
	DF(PZ)	302.4	−9.43	−8.37	1.06	−0.57	1.98	2.55	7.8
	HF(C-10s5p)	180.0	−14.59	−10.96	3.63	3.05	7.04	3.99	14.02
CHFCFH	DF(GKS)	180	−7.44	−5.82	1.62	−0.87	2.54	3.42	4.95
	DF(PZ)	180	−8.55	−6.96	1.60	−1.84	1.60	3.45	5.12
	HF(C-7s3p)[c]	180	−15.23	−13.36	1.87	6.27	10.56	4.30	19.62
$CHFCH_2$	DF(GKS)	180	−6.55	−5.31	1.24	1.48	2.76	1.29	6.78
	DF(PZ)	180	−7.62	−6.38	2.34	0.63	1.87	1.24	7.01
	HF(C-10s5p)	180	−12.68	−9.57	3.12	3.61	7.54	3.94	13.17
CF_2CH_2	DF(GKS)	180	−7.82	−5.91	1.91	0.62	2.08	1.46	6.53
	DF(PZ)	180	−8.93	−7.03	1.90	−0.26	1.07	1.33	6.78
	HF(C-10s5p)	180	−14.18	−11.07	3.11	3.46	8.43	4.97	14.53
$CHFCF_2$	DF(GKS)	180	−7.82	−5.91	1.91	0.62	2.08	1.46	6.53
	DF(PZ)	180	−9.05	−7.57	1.48	−2.39	−0.01	2.38	7.56
	HF(C-7s3p)	180	−15.97	−14.03	1.94	4.19	8.91	4.72	18.22

[a] All the values are in units of eV. [b] C-10s5p, Clementi's double-ζ basis set 10s5p. [c] C-7s3p, Clementi's basis set 7s3p.

have more interest in the features of the valence bands, especially how they change with the substitution of hydrogen with fluorine and the change of the dihedral angle.

B. Energy Bands of Poly(difluoroethylene). Figure 6 shows the energy bands of PDFE. Only the results obtained by use of PZ exchange-correlation functional are given, because as it is found from the calculations for PTFE in this paper and for polyethylene in a previous paper,[20] there is no significant difference for the bands calculated by either GKS or PZ exchange-correlation energy except a constant shift of about 1 eV. Only the bands for the dihedral angle of 302.4° corresponding to the most stable geometry in gauche form are shown.

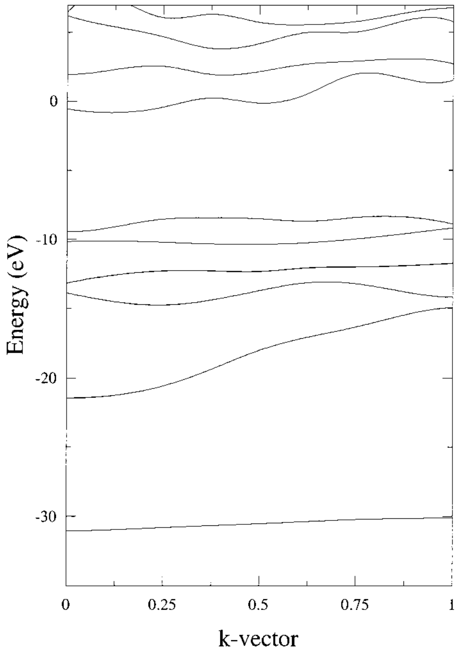


Figure 6. Highest filled and lowest unfilled bands of PDFE at dihedral angle of 302.4° for PZ LDA calculation. The notations are the same as those in Figure 5.

It is indicated in Figure 6 that the occupied bands for PDFE can also be sorted into two groups such as those of PTFE. The difference is that there is only one band at about −30 eV, which is rather flat and formed by fluorine 2s orbitals, and only five bands in the upper group, which are mainly formed by carbon sp^3 hybrids, hydrogen s, and fluorine 2p orbitals. Among them, the lowest band is largely formed by carbon orbitals and can be considered as a counterpart for the lowest occupied band of polyethylene.[20]

The important band characteristics, including the gap between the valence and the conduction bands, the valence and the conduction band widths, and the ionization energy, are listed in Table 3 for two different dihedral angles, 302° and 180°, corresponding to the stable and the planar zigzag conformations, respectively. The calculated band gaps are 7.22 eV (302°) and 4.95 eV (180°) for GKS and 7.80 eV (302.4°) and 5.12 eV (180°) for PZ, respectively. Considering the nonplanar chains are more stable than the planar chain, it is not so surprising to find that the band gaps for nonplanar conformations are considerably larger than for the planar conformation. This result coincides with the ionization energy values, 7.30 eV (302°) and 5.82 eV (180°) for GKS and 8.37 eV (302.4°) and 6.96 eV (180°) for PZ, respectively. For comparison, the PZ band gap for polyethylene is 7.97 eV while the ionization energy is 6.41 eV.

The total occupied band widths (PZ) are 23.3 and 22.6 eV for 180 and 302.4°, respectively. It seems that the occupied band region of PDFE is similar to that of PTFE[23] and is always about 11 eV larger than that of polyethylene.[20] The lowest occupied band is always very flat and seems not to change with the dihedral angle. The total widths of the upper five bands are calculated to be 13.74 and 13.04 eV for the dihedral angles of 180° and 302.4°, respectively (see Figure 6).

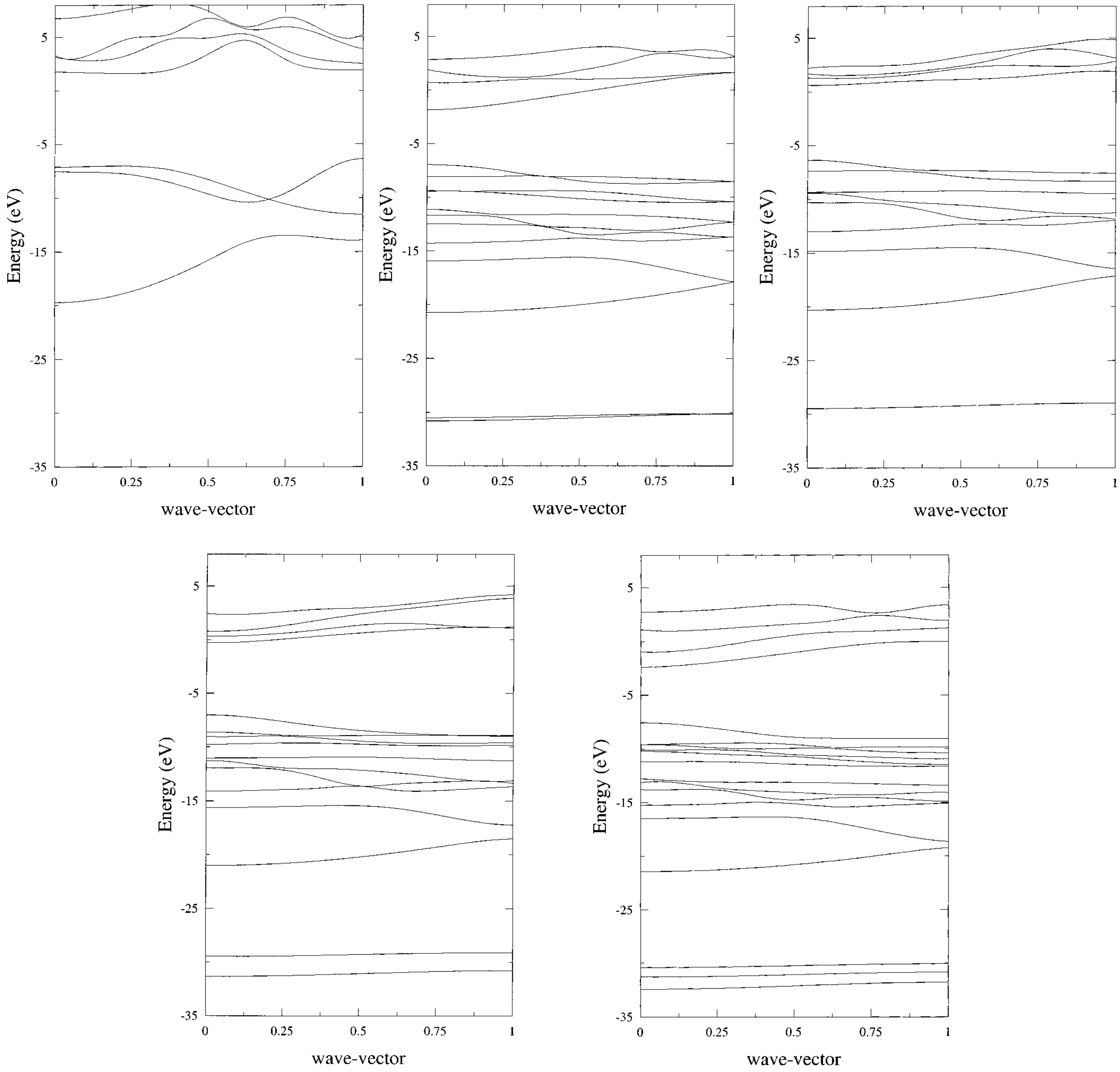


Figure 7. Comparison of the calculated occupied and unfilled bands of polyethylene (a), sPDFE (b), PVE (c), PVF2 (d), and P3FE (e) at a dihedral angle of 180°, using PZ LDA.

C. Energy Bands of Other Poly(fluoroethylene)s. The energy bands of all the poly(fluoroethylene)s except PTFE and PDFE are presented in Figure 7, together with the bands of polyethylene. Like in the previous section, only the PZ exchange-correlation functional is used. The results of PTFE and PDFE presented in the previous subsections will be used for discussing the influence of the fluorine substitution on the band structure. Noticing that the unit cells of these poly(fluoroethylene)s are enlarged to include two backbone carbon atoms rather than one, the bands are folded and their number is twice as big as before.

Some common characteristics of the band structures for all kinds of poly(fluoroethylene)s can be found in these figures. The occupied bands of these polymers are all located in the region from −5 to about −30 eV and can be distinguished into two groups. At about −30 eV, there are one, two, or three flat bands, depending on how many fluorine atoms are in one unit cell. These bands are all formed by the fluorine 2s orbitals, with σ or π symmetry. Compared to its fluorine derivatives, polyethylene has no corresponding band at the same region (see Figure 7a). The lowest occupied band of polyethylene is located in the region from −20 to −15 eV and mainly formed by the combination of the main chain carbon sp^3 hybrid orbitals. The corresponding bands for poly(fluoroethylene)s are found in the same region. The number of bands is identical to the number of carbon atoms in one unit cell. The other occupied bands are mainly formed by carbon sp^3 hybrid, fluorine 2p, and hydrogen 1s orbitals. These bands are distributed in the same region from about −5 to −15 eV and cross each other. The bands of *syn*-poly(difluoroethylene) (sPDFE) are doubly degenerate at the ends of the first Brillouin zone because of a glide-plane symmetry along the chain.

The characteristics of the valence band and conduction band as well as the gap between them can be found in Table 3 for

PE and all its six fluorine derivatives. Both GKS and PZ results are listed, and the band characteristics of PE, PTFE, and PDFE are calculated for both planar and nonplanar conformation for discussing the variation of band structure versus the helix of the chain. The HF results reported by Otto et al. are also listed in Table 3 for the convenience of comparison. It can be found in the table that for all kinds of poly(fluoroethylene)s and polyethylene itself, the locations of occupied bands obtained by LDA calculations are much higher than those by HF calculations, and the locations of the unfilled bands obtained by LDA calculations are much lower than those by HF calculations. Therefore the gap obtained from LDA calculations is always significantly smaller than that from HF calculations. On the other hand, the differences between the band widths obtained from two approaches are rather small. For example, the top of the valence band and the bottom of the conduction band as well as the band gap for PTFE in planar conformation are −8.27, −2.88, and 5.39 eV by LDA (PZ) calculation and −14.68, 2.43, and 17.10 eV according to the HF calculation. The valence and conduction band values of 2.38 and 5.03 eV for PZ are quite similar to the HF values of 3.70 and 5.54 eV, respectively. From Table 3, it can be found that the substitution of the hydrogen atom by fluorine changes significantly the bands. For example, the valence band widths (PZ) are 3.59, 2.48, 1.79, 1.60, 2.34, 1.90, and 1.48 eV for CH_2, CF_2, CHF, CHFCFH, $CHFCH_2$, CF_2CH_2, and $CHFCF_2$, respectively. Another factor that strongly affects the band structure is the dihedral angle. The PZ band gaps for PTFE are 5.38 and 6.25 eV for 180° and 163.7°, respectively. This strong dependence of the band structure on substituents and on the conformation shows a way to characterize the properties of these materials. The substitution by a side group is especially important if it can effect the conformation.

D. The Mulliken Populations for Poly(fluoroethylene)s. The Mulliken populations on carbon, fluorine, and hydrogen atoms for all the poly(fluoroethylene)s as well as for polyethylene are listed in Table 4, together with the previous LCAO−MT results of Falk and Fleming,[17] and CNDO and EH results of André and Delhalle.[37] The notation of the atoms at each position can be found in Figure 1. All the results are presented only for the planar conformation. For polyethylene, our calculation gives a reasonable net charge transfer of 0.29 from the hydrogen atoms to the carbons while both the LCAO−MT and the CNDO/2 calculations predicted a charge transfer from the carbon to the hydrogen. The EH calculations have given a charge transfer from hydrogen to carbon, but the value is much smaller than the LDA results. The same conclusions are found for the charge transfer results for PVF, PVF2, and P3FE. The charge density on hydrogen in all poly(fluoroethylene)s and in polyethylene is larger than 1 for the LCAO−MT calculation. The LDA calculations using either GKS or PZ exchange-correlation obtain quite similar Mulliken populations for all the atoms in all the polymers concerned.

The Mulliken populations (PZ) of carbon, fluorine, and hydrogen atoms for PTFE and PDFE as a function of dihedral angle are shown in Figure 8. Compared to the strong dependence of the band structure on the torsion of the backbone, the total charges on the atoms vary only slightly with the change of the dihedral angle. The curves all appear strongly correlated with the changes in the torsional potential curve. The minima of the charges on the carbon atom for both PTFE and PDFE always correspond to the maxima of the total energy, except the one around 50°, which is caused by the intramolecular interactions of the two neighboring loops due to the small dihedral angle.

TABLE 4: Mulliken Populations for Polyethylene and Its Fluorined Derivatives, Obtained by Both the X_α and the PZ Local Density Approximations, Compared with Other LDA (LCAO−MT)[a] and CNDO/2[b] as Well as EH[c] Results

polymers	methods	C1	C2	X1	X2	X3	X4
CH_2	X_α	6.29	6.29	0.86	0.86	0.86	0.86
	PZ	6.30	0.85	0.85	0.85	0.85	0.85
	LCAO-MT[a]	5.94	5.94	1.03	1.03	1.03	1.03
	CNDO/2[b]	5.99	5.99	1.00	1.00	1.00	1.00
	EH[c]	6.09	6.09	0.96	0.96	0.96	0.96
CF_2	X_α	5.69	5.69	9.16	9.16	9.16	9.16
	PZ	5.67	5.67	9.17	9.17	9.17	9.17
	LCAO−MT[a]	5.7	5.7	9.15	9.15	9.15	9.15
	CDO/2[b]	5.7	5.7	9.15	9.15	9.15	9.15
	EH[c]	4.61	4.61	9.7	9.7	9.7	9.7
CHF	X_α	5.96	5.96	0.84	9.2	9.2	0.84
	PZ	5.96	5.96	0.84	9.21	9.21	0.84
CHFCFH	X_α	5.96	5.96	0.84	9.20	0.84	9.20
	PZ	5.95	5.95	0.84	9.21	0.84	9.21
$CHFCH_2$	X_α	5.91	6.35	0.86	9.20	0.83	0.85
	PZ	5.90	6.34	0.86	9.22	0.83	0.86
	LCAO−MT[a]	5.42	6.08	1.15	9.21	1.06	1.07
	CNDO/2[b]	5.68	6.17	1.04	9.21	0.94	0.95
	EH[c]	5.3	6.13	0.97	9.71	0.95	0.94
CF_2CH_2	X_α	5.54	6.45	9.18	9.18	0.82	0.82
	PZ	5.52	6.45	9.18	9.18	0.82	0.82
	LCAO−MT[a]	5.0	6.25	9.3	9.3	1.08	1.08
	CNDO/2[b]	5.43	6.32	9.23	9.23	0.9	0.9
	EH[c]	4.56	6.16	9.7	9.7	0.94	0.94
$CHFCF_2$	X_α	6.06	5.56	0.83	9.19	9.18	9.18
	PZ	6.06	5.56	0.83	9.19	9.18	9.18
	LCAO−MT[a]	5.76	5.15	1.18	9.26	9.33	9.31
	CNDO/2[b]	5.99	5.57	0.93	9.13	9.18	9.19
	EH[c]	5.36	4.58	0.95	9.71	9.70	9.69

[a] See ref 17. [b] See ref 14. [c] See ref 13.

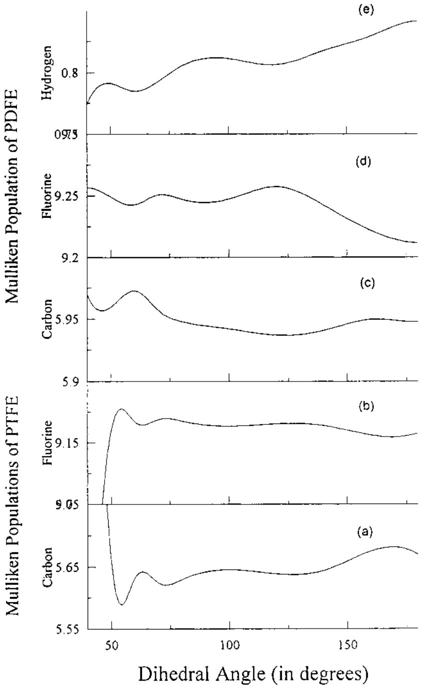


Figure 8. Comparison of the dependence of the Mulliken population on the dihedral angle in the case (a) of the C atom of PTFE, (b) of the F atom of PTFE, (c) of the C atom of PDFE, (d) of the F atom of PDFE, and (e) of the H atom of PDFE.

V. Conclusions

Using GKS and Perdew−Zunger exchange-correlation functionals, we present systematic LDA calculations on the conformation and electronic structure of various poly(fluoroethylene)s including poly(tetrafluoroethylene) (PTFE or CF2), poly(difluoroethylene) (PDFE or CHF), *syn*-poly(difluoroethylene) (syn-PDFE or CHFCFH), poly(vinyl fluoride) (PVF or $CHFCH_2$), poly(vinylidene fluoride) (PVF2 or CH_2CF_2), and poly(trifluoroethylene) (P3FE or $CHFCF_2$). The calculations for PTFE and PDFE are performed through a range of dihedral angles encompassing both the all-trans and all-gauche local minima, and for the other poly(fluoroethylene)s only through a range around the planar conformation.

The calculated stable conformation for PTFE is a slightly distorted planar zigzag with a dihedral angle of 163.7°, which is in good agreement with the experimental results on the crystalline state at low temperature. Two distinct local minima are found in the gauche form at around 70°. The stable conformation for PDFE is found in the gauche form at a dihedral angle of about 302°. All the other poly(fluoroethylene)s have a minimum other than 180°. In general, PZ geometries are similar to GKS ones. In comparison with the available experimental results, the PZ geometries are better.

The LDA (both GKS and PZ) one-electron band structure of PTFE is in good agreement with the experimental measurements and other theoretical results. The calculations on all the poly(fluoroethylene)s show that the band characteristics strongly depend on the nonplanar conformation and the side group substitutions. The reasonable Mulliken charge populations are constructed from the Kohn−Sham single-particle orbitals and give the right charge transfer.

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