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Density functional study of crystalline polyethylene

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Abstract

Density functional calculations have been performed for single chains and the crystalline (orthorhombic) form of polyethylene (PE). The geometrical structures are optimized without constraints, and the exchange-correlation energy is calculated using local density (LD) and non-local (gradient-corrected, GC) approximations. Both give good descriptions of the structure of a single PE chain, but LD calculations overestimate the binding energies *between* chains, and GC calculations lead to no interchain binding at all. © 1997 Published by Elsevier Science B.V.

1. Introduction

The importance of molecules containing carbon is unquestioned. Carbon readily forms single and multiple bonds and is the basis of countless molecules with rings and with straight and branched chains. Hydrocarbons, particularly alkanes and alkenes, are prototype organic molecules, and their polymers are among the most important polymeric materials. It is understandable that polyethylene (CH₂)_n, with a relatively simple chain structure and great technological importance, has been used as a benchmark in the development of theoretical techniques. This is aided by the availability of much experimental data, including X-ray [1–4] and neutron diffraction [5] studies of the crystalline material. In the present work, we apply density functional (DF) techniques to polyethylene, both single chains and crystalline.

DF calculations provide an economical method for calculating structural and binding properties of molecules and clusters, as well as in traditional applications in condensed matter physics. Studies of C-containing molecules include carbon clusters [6]

and the energy surfaces of some reactions of organic molecules [7]. Recent work in our group has focused on the structures and energy barriers in small organic molecules (including ethylene) [8] and the relationship between the structures of a single chain of polypropylene and its constituent units [9]. In recent years there have been numerous DF studies using both the local spin density (LSD) approximation to the exchange-correlation energy and non-local modifications to it. Modifications involving gradients of the density often lead to better agreement with measured formation energies in small molecules [10], and the description of hydrogen bonds is much improved [11]. Work performed so far indicates that both LSD and gradient-corrected (GC) functionals give a reliable description of structures and rotation barriers in small organic molecules and in chains like polypropylene [9], although both approximations tend to underestimate reaction barriers [7].

DF calculations for a single chain of polyethylene were performed recently by Miao et al. [12], who used LSD approximations for exchange (XO) and for exchange and correlation. One goal of the present

work is to examine the description of *interchain* interactions in crystalline polyethylene provided by LSD and GC functionals. Recent studies on the interactions between rare gas atoms [13] and between two benzene molecules [14] show pronounced differences. In Section 2 we provide essential details of the calculations, and in Section 3 compare the results with experiment and previous calculations. We summarize and discuss our findings in Section 4.

2. Method of calculation

Polyethylene crystallizes in the orthorhombic structure shown in Fig. 1, which also defines the axes used in the present work. Carbon atoms are black, and hydrogen atoms are white.

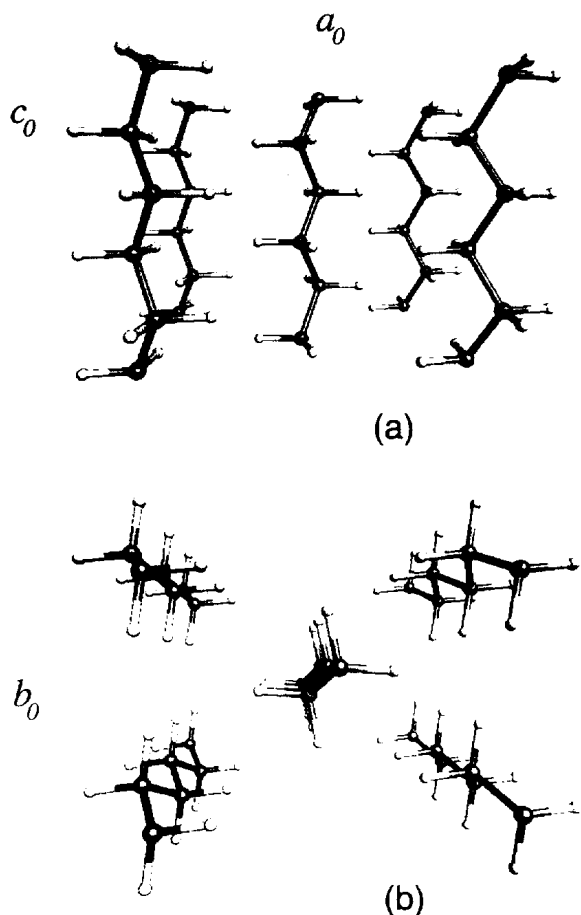


Fig. 1. Views of the orthorhombic structure of polyethylene along (a) b -axis, (b) c -axis (the axis of the polymer chains).

The method used in our earlier work on single chains of polypropylene [9] is used here. It assumes periodic boundary in three dimensions. The initial structure of the isolated chain had the experimental lattice constant along the chain and large lattice constants perpendicular to it, and the optimum geometry was found by minimizing the forces on all atoms. The calculation was repeated for different chain lengths to minimize the energy as a function of *all* atomic positions. An analogous procedure was used for crystalline PE, where the structural optimization is naturally much more time-consuming.

The electron-ion interaction is represented by ionic pseudopotentials for C and H that have the (non-local) form suggested by Troullier and Martins [15]. This is the same prescription we used previously [8,9]. The basis set is taken to be plane waves, and detailed tests of the convergence of this basis for CH and CH₂ [8], as well for PE in the present work, have shown that reliable energy differences can be obtained using a kinetic energy cutoff of 30 a.u. The integration in reciprocal space employed the special points technique [16], and the convergence of the total energy was tested with 3, 6, 12 and 24 such points. Six k -points give a well-converged total energy and were used to obtain the results presented here. We expect that a single k -point would give very similar geometries.

We have seen above that the choice of energy functional is an important consideration. The LSD approximation is based on accurate calculations of the exchange-correlation energy density in a homogeneous, spin-polarized electron gas, and we have also used a non-local, gradient-corrected functional with the exchange part due to Becke [17] and the correlation part due to Perdew [18] (the “BP” functional).

3. Results

3.1. Geometrical structures

The optimized structures calculated for a single chain with LD and GC approximations are compared in Table 1 with the results of other calculations [12,13,19,20] and with experimental values for crys-

Table 1

Measured structural parameters of crystalline PE and calculated structures for a single chain. Bond lengths are in Å, angles in degrees. Values marked with an asterisk (*) were assumed, and not measured or calculated directly

	r_{CC}	r_{CH}	α_{CCC}	α_{HCH}
X-rays ^a	1.53	–	112	–
X-rays ^b	1.534 ± 0.006	1.09 *	112.0 ± 0.3	109.5 *
X-rays ^c	1.533 ± 0.022	1.07 ± 0.022	111.9 ± 1.8	107.0 ± 1.8
X-rays ^d	1.527 ± 0.007	1.091 *	112 ± 0.8	–
neutrons (4 K) ^e	1.578(5)	1.06(1), 1.10(1)	107.7(5)	109.0(1.0)
neutrons (90 K) ^e	1.574(5)	1.07(1)	108.1(5)	110.0(1.0)
Hartree–Fock ^f	1.536	1.083	112.7	106.8
Hartree–Fock ^g	1.541	1.087	112.5	107.2
DF (PZ, XO) ^h	1.515, 1.534	1.10 *, 1.10 *	113.0, 113.0	109.7, 110.0
this work (LDA, GC)	1.512, 1.536	1.111, 1.111	114.3, 113.8	105.2, 105.6

^a Ref. [1].

^b Ref. [2], monoclinic *n*-hexatriacontane C₃₆H₇₄.

^c Ref. [3], orthorhombic *n*-hexatriacontane C₃₆H₇₄.

^d Ref. [4].

^e Ref. [5].

^f Ref. [19], 7s3p,4s basis.

^g Ref. [20], STO-3G basis.

^h Ref. [12], GTO basis.

talline PE. Gradient corrections lead to an increase of ~1% in the C–C bond length. In view of the experimental uncertainties, however, both approximations give reasonable agreement with the measured values and with the results of earlier calculations. Apart from a deviation of ~4° in the H–C–H bond angle, the present LD values are very close to the DF (LD) results of Miao et al. [12].

The optimization of the orthorhombic crystalline structure with the LD and GC approximations led to strikingly different results. The LD calculations yielded a well-defined minimum in the binding energy curve (Fig. 2), and the length of the unit cell parallel to the C-chains is in excellent agreement with all experimental data (Table 2). The structure of the chain is modified by the lower symmetry of the crystal, but the changes are small (r_{CC} is 0.007 Å less, there is a small splitting in the values of r_{CH} , and the bond angles are ~0.4° smaller). The inter-chain separations, however, are underestimated by ~9% (Table 2). The GC binding energy curve, by contrast, shows no minimum (Fig. 2). We have noted above that pronounced differences between LD and GC predictions also arise in the interactions between rare gas atoms [13] and between C₆H₆ molecules [14], and we return to this point below.

The differences between the descriptions of bonding provided by the LD and GC approximations are reflected in the density distributions, and we have studied these in detail for the experimental geometry. In isolated, homonuclear clusters of phosphorus and

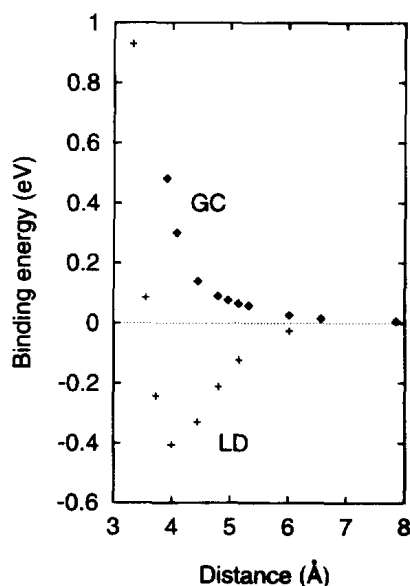


Fig. 2. Binding energy (per unit cell) as a function of interchain separation for LD (crosses) and GC (diamonds) approximations.

Table 2

Comparison of measured and calculated (LDA) lattice constants and interchain distances. The shortest distance between C atoms in different chains is $d_{(C\dots C)}$, and ϕ is the angle between the ac -plane and the plane of the C atoms in the chain. Distances are in Å, angles in degrees

Method	a_0	b_0	c_0	ϕ	$d_{(C\dots C)}$
X-rays ^a	7.40	4.93	2.534	48.8	4.13
X-rays ^b	7.42 ± 0.01	4.945 ± 0.01	2.546 ± 0.004	41.4	4.14
X-rays ^c	7.42 ± 0.01	4.96 ± 0.01	–	47.7	4.15
X-rays ^d	7.388 ± 0.008	4.929 ± 0.004	2.539 ± 0.002	45	4.59
neutrons (4 K) ^e	7.121 (2)	4.851 (2)	2.548(1)	41(1)	–
neutrons (90 K) ^e	7.161(2)	4.866(2)	2.546(1)	41(1)	–
this work	6.73	4.53	2.52	41.3	3.67

^a Ref. [1].

^b Ref. [2], monoclinic *n*-hexatriacontane $C_{36}H_{74}$.

^c Ref. [3], orthorhombic *n*-hexatriacontane $C_{36}H_{74}$.

^d Ref. [4].

^e Ref. [5].

arsenic the use of gradient corrections moves charge from the region near the centres of the atoms towards the outside of the clusters [21]. The differences are more subtle in crystalline PE, where there are two types of atom and interchain interactions are important. Although the density differences are small, the net effect of gradient corrections here is to lower the electron density both between the C atoms and between the chains. There is also an overall transfer of electrons from the neighbourhood of the C nuclei to that of the H nuclei. The differences in the densities are small, but suffice to give the qualitatively different descriptions of the interchain interactions found here.

3.2. Electronic structure

Recent advances in polymer electronic have focused attention on their excitation spectra and band structures. Polyethylene is no exception, and it was in fact the first organic polymer for which band structures were reported [22], based on angle-resolved photoemission from oriented films of *n*-hexatriacontane [$CH_3(CH_2)_{34}CH_3$]. While the identification of DF eigenvalues with excitation energies is not a rigorous procedure, the comparison is often valuable. We show in Fig. 3 the energy bands calculated for a single chain using both the LD and GC approximations, and the overall form in both is the same as found in the measurements [22] and in

previous band structure calculations [23,12]. A more detailed comparison also shows similarities. The total valence band width in single chain LDA calculations (13.5 eV), for example, is in reasonable agreement with calculated (17.4 eV [23], 14.0 eV [12]) and measured values (16.2 eV [22]). Gradient correc-

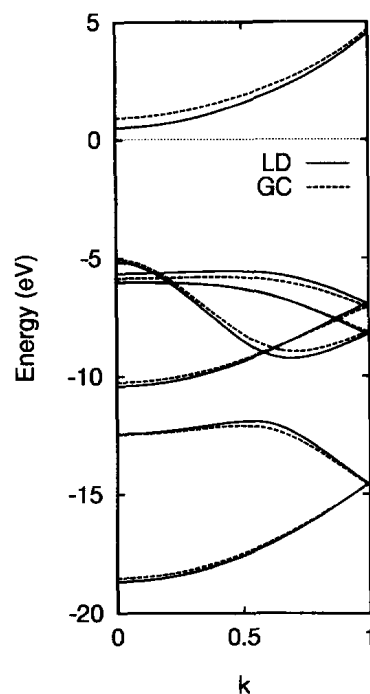


Fig. 3. Band structure of single chain of polyethylene calculated with LD (full curves) and GC (broken curves) approximations. Wave vector k in units of $(2\pi/c_0)$.

tions lead to a negligible change in the band width and an increase in the the gap between valence and conduction bands from 5.7 to 6.0 eV.

The interchain interactions in the crystalline form of PE lead to splittings of the bands and to modifications in the vibration frequencies. A study of both of these features should lead to insight into the nature of the interactions between the chains, and we are performing such a study now.

4. Discussion

Density functional (DF) calculations have been performed for single chains and for crystalline (orthorhombic) polyethylene. The calculated structures of the single chains agree well with earlier theoretical work and with X-ray and neutron diffraction data. This result is consistent with our earlier work on polypropylene. However, the experimental structure of the crystalline phase is reproduced neither by calculations using the LSD approximation to the exchange-correlation energy nor by gradient-corrected (GC) modifications to it. The former results in lattice constants perpendicular to the chains that are $\sim 9\%$ too short, while the latter results in a binding energy curve that has no minimum, i.e., there is no binding at all. Previous LDA calculations on the structures of *trans*-polyacetylene [24] and poly(*para*-phenylene) [25] did not show such effects, as the lattice constants were constrained to have the measured values.

A similar picture has been found in calculations on other systems whose binding is viewed to arise from “polarization” or “van der Waals” forces. In the rare gas dimers He_2 , Ne_2 , Ar_2 , HeNe , HeAr , and NeAr , Pérez-Jordá and Becke [13] found that the LD approximation yielded serious overestimates of the binding energies, while two generalized gradient approximations led to repulsive potential energy curves. Meijer and Sprik [14] have found the same effects in a study of intermolecular interactions in benzene, C_6H_6 . The three sets of results may disturb those who have felt that modifications based on the gradient of the density would correct for all of the well-known deficiencies of the LD approximation [26], and they provide a stimulus for developing further hybrid functionals with this goal. On the other hand,

we note that both LD and LD-GC approximations give reliable predictions of *intrachain* structures of polypropylene [9] as well as PE, and of numerous rotation barriers in small organic molecules [8]. It should perhaps come as no surprise that the relatively simple descriptions of exchange and correlation provided by current DF approximations does not provide reliable predictions of the weak *interchain* interactions.

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