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Interchain electron states in polyethylene

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We present a theoretical study of the nature of the lowest empty conduction-band states in crystalline polyethylene (PE), conducted through density-functional electronic structure calculations. Results reveal that the wave function of the conduction-band edge is of *interchain* character, as opposed to the *intrachain* character of all the filled valence-band states. Thus, while a hole added to neutral PE will mainly belong to the PE chain backbone bonds, an added electron in PE will mostly reside between the chains, and far from the existing bonds. Moreover, the added electron state charge centroid is predicted to move further out from the chain backbone towards the low-density interstitial region, if and when the chains are pried apart. This suggests that injected electrons will naturally flow to low-density regions inside real PE, and that the experimentally established propensity of PE to expel electrons out of the bulk, should be directly related to the interchain nature of the conduction states.

I. INTRODUCTION

Understanding the nature of the electronic states corresponding to the valence-band top (hole states), and to the conduction-band bottom (electron states) is of paramount importance in all semiconductors and insulators. Key properties, including in the first place the conduction process in transport, but also impurity trapping, self-trapping, and charge-induced degradation processes, depend intimately on that nature. In particular, in insulating polymers—materials of choice for high voltage applications—it is necessary to understand conduction states, since electrons are most often the relevant carrier underlying both transport and electrical breakdown behavior.

Strikingly, however, there appears to be very little specific work dealing with insulating polymers and aimed precisely at understanding the nature of *conduction* states. Even in polyethylene (PE), chemically the simplest, and certainly the most popular insulating polymer for high voltage ac and dc applications, only the *valence*-band states have been reasonably well characterized. Experimentally, that was achieved by means of *k*-resolved photoemission;[1] theoretically, through various types of electronic structure calculations.[2–4] From these studies, the valence bands can be seen to be made up of both C-C and C-H bonding states, which propagate and disperse relatively strongly along each chain, but do that very poorly, if hardly at all, between the chains. We shall henceforth refer to this kind of behavior of electronic states as *intrachain*. By comparison, the conduction states, in spite of their obviously larger importance for transport, seem to have received much less attention; and their nature is presently unclear. The purpose of this work is to fill this important gap.

There are, to be sure, certain technical reasons that make a study of the empty conduction states of polymers more difficult than that of valence states. Thus, in PE for example, low-energy electron transmission and secondary electron emission data have long been available,[5] but *k* resolved inverse photoemission data have not. On the theory side also, it is generally difficult to calculate proper quasiparticle states. The usual default empty states found in electronic structure calculations do not enjoy the same variational quality and significance as the filled ones. Most calculation methods suffer from a ‘‘gap problem:’’ the calculated insulating band gaps are systematically inaccurate, either too large (as in the case of Hartree-Fock, or linear combination of atomic orbitals/tight-binding methods), or too small [as in the case of density functional theory in the local-density approximation (LDA)]. A wrong energy gap will, in turn, lead, at least in all cases where valence and conduction states are of similar nature, to an error in the form of the wave function at band edges. In a LDA calculation, the problem will generally be worse for conduction states, which are in a sense unphysical, for unlike valence states they do not directly determine

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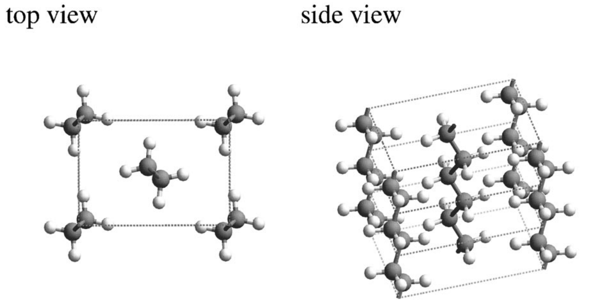

FIG. 1. Side and top views of the crystal structure of polyethylene. The structure is base-centered orthorhombic, with lattice parameters $a=7.4$ Å, $b=4.93$ Å, and $c=2.534$ Å (Ref. 6). The two independent chains of the orthorhombic unit cell are oriented along the c axis and are rotated by $\pm 42°$ with respect to the b axis, respectively.

the ground-state electron density and thus the total energy. Needless to say, all these potential difficulties hardly diminish the importance of understanding conduction states of insulating polymers, whose study remains mandatory.

The scope of this paper is to present a fresh theoretical investigation of the empty electronic states of crystalline PE, chosen as the prototype insulating polymer for both fundamental and technological reasons. Of course, real solid PE that one can make in the laboratory is far from crystalline, encompassing both amorphous regions and crystalline lamellas in an extremely complex texture. Technological PE, moreover, possesses additional complications, including those related with cross-linking chemicals. All the same, it can hardly be overemphasized how a good starting knowledge of the electronic properties of the ideal crystalline state is of primary importance. The crystalline electronic states will be related to, and to some extent will determine, those of real PE used in applications. Moreover, there is no hope of eventually understanding electrons in real PE if we do not even begin to fathom their nature in the much simpler crystalline state.

The method of calculation will be based on the gradient-corrected LDA (LDA/GGA). Despite the gap problem, there are, in the case of PE, good reasons to believe that conduction states are, in fact, well described. The reason is that, as it will turn out, the nature of the lowest conduction states in this case is very different from that of valence states, so that an error in the calculated gap does not reflect strongly on the conduction state wave functions, and on their band dispersion.

II. CALCULATIONS

High-density crystalline PE possesses a based-centered orthorhombic (bco) unit cell with lattice parameters $a=7.4$ Å, $b=4.93$ Å, and $c=2.534$ Å, as found from x-ray diffraction data.[6] The bco unit cell consists of four CH_2 units arranged in two chains whose axes are parallel to the c axis. Looking down the c axis, the chains form a ''herringbone structure'' (Fig. 1), i.e., they lie on planes alternatively rotated by a setting angle of about $\pm 42°$ relative to the b axis.

We undertook first-principle electronic structure calculations of PE, using state-of-the-art density-functional methods, based on plane-wave expansions and pseudopotentials. The choice of a large plane wave basis set in our calculations was particularly important, in order to capture the best possible real nature of conduction states. Restricted local basis sets, very effective for describing localized valence states, should be considered here with suspicion, as they may fail to properly describe the more extended, higher energy conduction states.

Calculations were carried out within the LDA/GGA.[7] Becke-Perdew[8] and Becke-Lee-Yang-Parr gradient corrections (GC) (Ref. 9) were used as two alternative choices for the exchange-correlation term of the total energy functional. Both these functionals are known to be relatively accurate in describing both electronic and structural properties of carbon-based systems, either solid or molecular.[10] Martins-Troullier pseudopotentials[11] were used to describe the ion-electron interactions for both C and H atoms. Wave functions were expanded in plane waves, with a plane-wave energy cutoff of 40 Ry, checked to ensure a sufficient convergence for our purposes. K-point sampling of the Brillouin zone was tried with increasing density of points, and the degree of convergence was checked. Results reported here were obtained using a 3×3 k-point mesh in the (a,b) plane, and 10 k points parallel to the c axis, on account of the larger band dispersion along chains. In all calculations, intrachain atomic positions (bond lengths and bond angles) were optimized by relaxing positions to obtain minimal energy, by means of a standard minimization algorithm. Interchain distances, as discussed elsewhere,[10] cannot be obtained in this manner because of the lack of van der Waals forces in the LDA/GGA functional. Instead, the interchain distances were assigned parametrically a grid of values starting with the experimental distance of true crystalline PE, and increasing to larger and larger distances, to mimic eventually the limiting case of a single isolated PE chain.

Comparison of our calculated PE relaxed structure with that of $C_{36}H_{74}$ (Ref. 12)—a long alkane which has been extensively studied as it is much easier to crystallize than PE, but whose electronic and structural properties are believed to be very close to those of PE — is in very good agreement ($\sim1\%$). We obtained bond lengths $r_{CC}=1.534$ Å, $r_{CH}=1.11$ Å, against experimental values of[12] $r_{CC}=1.53$ Å, $r_{CH}=1.09$ Å, and bond angles $\theta_{CCC}=113.3°$, $\theta_{HCH}=105.3°$, against experimental values of $\theta_{CCC}=112.3°$, $\theta_{HCH}=109.5°$. This proves that we have obtained an excellent description of the chemical bonding, which determines intrachain properties. We found very little dependence of the intrachain properties upon the GC scheme chosen. The calculated electronic structure for BLYP is shown in Fig. 2. As found in previous LDA calculations,[4,3] valence bands are in good agreement with photoemission data.[1] The calculated gap is 6.4 eV, against an experimental value, well established for the alkane $C_{36}H_{74}$ of 8.8 eV.[13] As anticipated, this discrepancy reflects a typical weakness of the LDA, which systematically underestimates gaps. Whether this is of consequence or not for the conduction state description will, however, depend on their nature relative to that of the valence states, which we considered next.

Figure 3 shows the square amplitude of the conduction $|\psi^{cond}_{k=0}|^2$ and valence $|\psi^{val}_{k=0}|^2$, band-edge wave functions

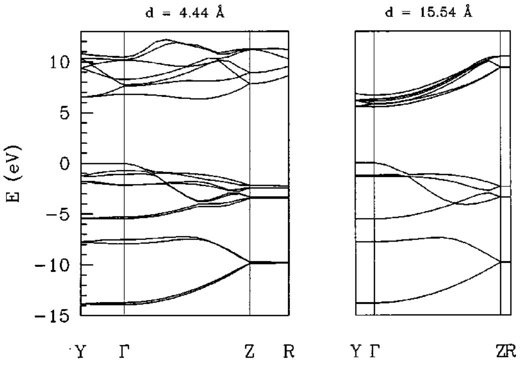

FIG. 2. Left panel: Band dispersion of crystalline PE along symmetry directions; right panel: same as left panel but for an interchain spacing expanded by a factor 3.5. Notice the effect of the increased spacing on the conduction bands, which clearly show a free-electron-like behavior (only partially visible for the conduction bands at equilibrium distance, left panel).

(electron and hole states, respectively) corresponding in Fig. 2 to the lowest empty band and the highest filled band at $k = (0,0,0)$. The valence state amplitude, as expected, is strictly localized on the chains. The conduction state amplitude on the contrary is dramatically spread out, and has its maximum *between* the chains.

In contrast with the intrachain character of the valence state, we shall refer to this kind of behavior of the conduction edge state as *interchain*—by analogy with the so-called interlayer states, found in some layer compounds.[14,15]

III. INTERCHAIN STATES IN POLYETHYLENE

Quite generally, we may define an interchain state as one (i) whose wave-function amplitude is maximum away from the chains; (ii) whose band-bottom energy tends essentially towards vacuum zero from above when the chains are moved apart; and (iii) whose band dispersion (k dependence) parallel as well as perpendicular to the chains is strong and free-electron-like, at least as the interchain distance is sufficiently increased.

If indeed, as it seems to be the case in PE, an interchain state might constitute the lowest conduction band, then one could expect that a conduction electron in its lowest energy state should naturally be channeled *out* of the crystal, since the lowest allowed electron energy inside the solid is higher, by virtue of (ii), than the zero of energy in the outside vacuum. This property corresponds to negative electron affinity (NEA), a rare but well characterized property of some materials. NEA is found, for example, on hydrogen-saturated diamond (111) surfaces,[16] and in hexagonal BN.[14] Because it involves both the solid and the vacuum, electron affinity, like work function, is a surface property. Thus, strictly speaking NEA cannot be ascertained with pure bulk calculations of the type carried out here; and, in fact, work is now in progress in our group to carry out a much more demanding surface calculation aimed at establishing the polymer electron affinity. Still, it can be argued qualitatively that since the lowest bulk conduction-state has interchain nature, as defined above, then the property of NEA must follow, at least for any surface the does not cut across the chains (planes). In fact, from the property that the conduction band bottom energy decreases steadily towards vacuum zero as the chains (planes) are separated, it follows that at any such surface, there will be states of zero or possibly even negative energy (e.g., image charge states) which do not penetrate deep inside the crystal, because the conduction-band bottom energy is higher. That being so, a bulk conduction electron will be naturally channeled to the surface, and out of the crystal, which signifies precisely NEA. In Pate's language,[16] this would be a case of *intrinsic* NEA.

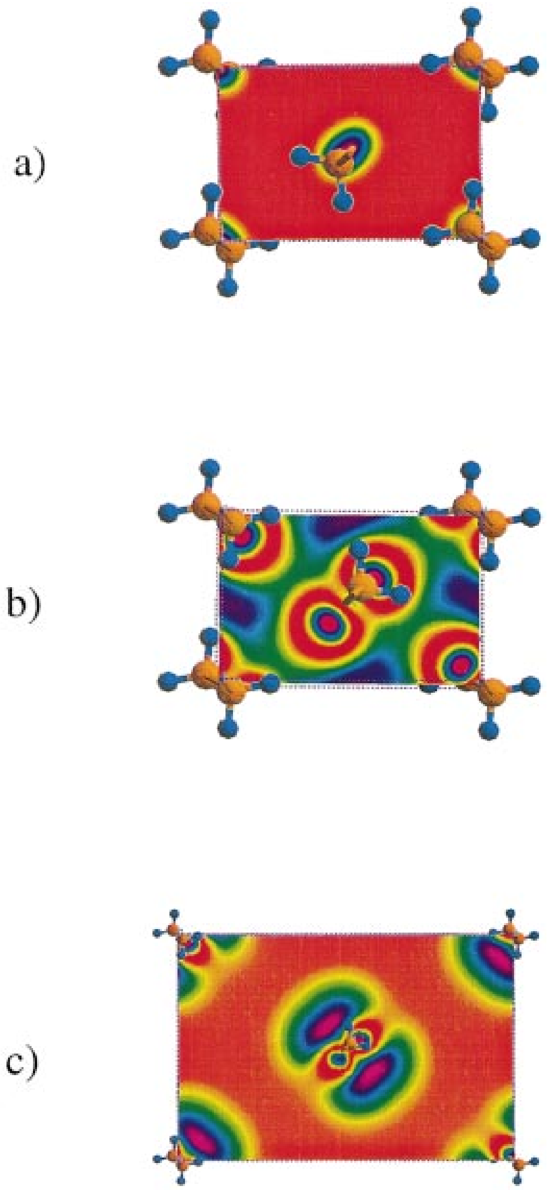

FIG. 3. (Color) (a) Charge density three-dimensional (3D) plot of $|\psi^{val}_{k=0}|^2$ for crystalline PE. Density increases from red to indigo in rainbow order. Notice that the density is all intrachain. (b) Same as above for the corresponding conduction state, $|\psi^{cond}_{k=0}|^2$. Notice the large maximum in the middle of the unit-cell edges, between next-nearest-neighbor chains. There is a second maximum close to the central chain, where, however, only ≈10% of the wave function is found. (c) Charge density 3D plot of the conduction state, $|\psi^{cond}_{k=0}|^2$, for an interchain spacing expanded by a factor 3.5 (corresponding to the right panel in Fig. 2). Here the large interchain wave-function maximum is clearly observable.

Let us return to our calculated conduction-band dispersion, shown in Fig. 2(a). First we may note that the absolute band-bottom energy is positive, but this in itself is of no significance, as all calculated bulk band energies lack reference to the vacuum zero. We shall return to this point later, however. Low-lying conduction states are dense, and as a whole they appear to disperse approximately parabolically and isotropically for momenta both parallel and perpendicular to the chains, suggestive of free-electron-like behavior. The similarity with a free-electron band, indicating an effective mass close to one, is indeed suggestive of an interchain state. The valence band is by contrast remarkably anisotropic, with an effective mass along the chains which is about one-half that of conduction states, but about 100 times larger perpendicular to the chains.

These tentative hints obtained by studying band dispersion are, as noted above, much strengthened after inspection of the squared wave-functions amplitudes of Fig. 3. The valence state is clearly intrachain, since the wave function vanishes everywhere except for the vicinity of C-C and of C-H bonds on the chain, but the conduction state behaves differently, with maxima well removed from the chains. From Fig. 3(b) it is also evident that maxima are located in between two neighboring equivalent chains, as in point (ii). In order to obtain further confirmation of this fact, we examined the evolution of this state in a series of successive calculations, realized by expanding artificially and progressively the interchain distances. We expanded the *a* and *b axis* magnitudes by a factor α, while keeping the *c*-axis length, which controls intrachain properties, unchanged. As the expansion factor α increased from 1 to 3.5, the valence states hardly changed, whereas the first conduction state gradually expanded outwards from the chains, eventually stabilizing to a well developed maximum located very far [~ 5 Å, Fig. 3(c)] outside the chains. Moreover we found that the energy of this state extrapolates from above for $\alpha \rightarrow \infty$ to an energy E_∞ which is very close to zero, in fact slightly negative ($E_\infty = -0.14$ eV). We note here that, once the interchain distances are being so expanded, the bulk calculation comprises an increasing portion of vacuum. There is an accumulation of empty states towards the energy of true vacuum zero, which as a result is in this limit becomes well defined. Returning to the conduction-band edge state, we can conclude, when its characters are compared with our definitions (i)–(iii), that the lowest conduction state of PE definitely is of interchain character.

Moreover, the small negative E_∞ and the related large stabilization distance of ~ 5 Å indicates that the binding of an additional electron to a single PE chain will not be strong and chemical, but weak and physical. Once chains are assembled together to form bulk PE (whose spacing, 4.44 Å is much less than ~ 10 Å) this electron state becomes confined, literally squeezed, between the chains. The additional kinetic energy due to the confinement must raise the band-bottom energy to a positive value relative to vacuum zero. The slightly negative E_∞, found on separating chains, in turn foreshadows the presence of surface states, most likely image charge states, physically bound with an energy of perhaps 0.5–1 eV (since a single chain binds with at least 0.14 eV) to the basal plane of the semi-infinite PE crystal.

IV. CONSEQUENCES FOR REAL POLYETHYLENE: DISCUSSION

The conclusions of this work on the nature of the empty electronic states in PE is rich of potentially important consequences for our future understanding of the electrical behavior of real PE. Particularly relevant are the implications on the microscopic nature of space-charge regions in PE, and on electron mobility, which we can briefly address.

Because the nature of the empty states in crystalline PE is interchains, one can argue that an added electron will prefer to move to a low-density region, such as the outer wall of a cavity, or a crystalline-amorphous interface, where it can have a lower energy than in the dense regions. An electron injected inside real, inhomogeneous PE will be quite naturally channeled towards these low-density regions, and become spontaneously trapped there. Due to the local inhomogeneity in the density of PE, electrons that make up space charges, for example, will be nonuniformly distributed at the microscopic level. Counter-intuitively, they will tend to accumulate where the local PE density is lowest, not highest. In particular, we predict that crystalline regions, such as the interior of lamellas, should be essentially empty of space-charge electrons.

External physical actions such as pressure, which act to increase density, should reduce the size and number of low-density pockets, and therefore also their ability to trap electrons. This may be related to the improved electrical behavior known for PE under pressure.[17]

The interchain character of the conduction state implies a strong electromechanical effect. An added electron in PE will tend to mechanically push away the neighboring chains, so as to create for itself a lower density region where it can have lower energy. Hence the added electron will, in principle, act as a local negative pressure, and disfavor compactness in its neighborhood.

An electron in PE cannot be expected to be able to move freely, as in a true conduction-band. The conduction-band bottom energy being high, trapping will be favored. Trapping will not only occur at chemical defects, but also at a variety of physical defects, including low-density pockets, interfaces, etc., which can act as traps in virtue of the interchain nature of conduction states. The exceedingly low electron mobilities observed in PE ($\mu \sim 10^{-7}$–10^{-12} cm^2 V^{-1}s^{-1}) are compatible with this picture (though, of course, they do not prove it).

Moreover, the temperature dependence of the mobility is generally activated,[18] with activation energies of the order of 0.7–1.1 eV. One can interpret this activation energy as a trapping energy of the relevant electron below the free bulk conduction band. Considering that the experimental magnitude of NEA and the energy of the conduction-band minimum about vacuum zero are about 0.4-0.5 eV,[5] this range of activation energies imply traps located at an energy of 0.1–0.6 eV below vacuum zero. This is precisely the energy range suggested, above, e.g., for surface and interface states. It seems, therefore, entirely possible that the physical defects could represent an important class of traps which limit mobility in PE.

In conclusion, we have found that interchain electron states exist in polyethylene, where they should constitute the lowest conducting states. The predictions based on this concept appear to agree with a variety of available evidence[17] in real PE. A more detailed first-principle study of electron affinity, electron trapping, and other related processes will be the subject of forthcoming investigations.

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