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Complex band structures and decay length in polyethylene chains

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Abstract

The complex band structure of an isolated polyethylene chain is calculated within density functional theory (DFT). A plane wave basis and ultrasoft pseudopotentials are used. The results are compared with those obtained via a local basis set. We obtain a gap between the highest occupied molecular orbital (HOMO) and the antibonding unoccupied molecular orbitals of 9.3 eV and a non-resonant tunnelling β parameter of 0.9 per monomer, in reasonable agreement with experiment and with results obtained via local basis. Polyethylene is a negative electron affinity material and the actual gap should be the energy of the HOMO with respect to the vacuum level (in DFT approximation only about 5.14 eV). The Bloch states at imaginary k are mainly free-electron-like parabolic bands which are missing in the local basis. We present also the complex bands of bulk polyethylene in order to estimate the effects of the chain–chain interactions on the complex band structure. The relevance of these results for the tunnelling conduction of n -alkane chains is discussed.

1. Introduction

The conductance of interfaces, tunnel junctions or molecular chains connecting two tips is of paramount importance for areas such as nanoelectronics or molecular electronics. It is well known that, in order to understand the electronic and transport properties of surfaces and interfaces, the complex electronic band structure (CBS) of the constituent materials [1] may be as important as the real band structure. However, *ab initio* calculations of CBS are still rare.

Very recently the Bloch functions with complex wavevector k have been revived for calculation of the ballistic conductance of carbon nanotubes [2], because they provide an effective

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way to deal with open quantum systems and transmission coefficients within Landauer theory. Furthermore, the spin-dependent conductance of ferromagnetic/insulator/ferromagnetic junctions has been explained in relation with the complex bands of the insulator [3]. Inside an isolated surface or tip, the electronic wavefunctions can be written as a superposition of Bloch functions, including both real and complex k , namely both propagating and evanescent waves. The vacuum tunnelling between two tips arises as the overlap in the vacuum gap of two opposite evanescent waves. The electronic states of a nanowire, a nanotube, a long polymer bridged between two tips or of an insulating thin film sandwiched between two metallic contacts can all be expanded in Bloch states with both real and complex k . A detailed analysis of the CBS itself helps to explain the properties of the tunnelling current. For instance, in the theory of scanning tunnelling microscopy (STM), the exponential decay of the current with the tip surface distance depends on the metal work function which controls the decay length of the evanescent metal states in the vacuum.

This concept was applied in [4] to calculate the non-resonant tunnelling parameter β of n -alkane chains measured accurately in recent experiments [5, 6]. The resistance of alkanethiol chains of variable monomer numbers was measured by adsorbing the n -alkane chains on a gold (111) surface and contacting the other extreme with an atomic force microscopy (AFM) tip coated with gold. The pressure on the chains is kept constant by controlling the force exerted by the tip on the n -alkane film. The resistance depends strongly on the contact force, but at fixed force it depends exponentially on the chain length ($R = R_0 e^{\beta N}$, where N is the number of CH_2 monomers). The reported values of β range from 0.8 to 1.2 per monomer, depending on the contact force. Note that in vacuum, $\beta = \sqrt{\frac{8m}{\hbar^2} \Phi_{\text{Au}}} a = 3.0$, where ($a = 1.25 \text{ \AA}$ is the length of a monomer, $\Phi_{\text{Au}} = 5.3 \text{ eV}$ is the gold work function, m is the electron mass and \hbar is Planck's constant). The metal wavefunctions decay exponentially in the polymer and, at low tip-surface voltage, the current is due to non-resonant tunnelling because the Fermi energy of the gold contacts lies within the gap of the n -alkane chain [4]. The decay length $\beta = 2(\text{Im } k)a$ can be derived from the CBS of a polyethylene chain (the polymeric form of the n -alkane). For sufficiently long chains, only the slowest decaying state dominates the tunnelling current [4]. In the CBS, this state belongs to a loop that joins, at imaginary k , the highest occupied molecular orbital (HOMO) and an antibonding unoccupied molecular orbital (that we call here LUMO) of the polyethylene chain. Taking the Fermi level at the point where $d\epsilon/dk = 0$ a value of β close to 1.0 was found in the literature [4], based on CBS calculations done with two different local basis sets (a minimal one, s for H and sp^3 for C, and an extended one, sp^3 for H and sp^3d^5 for C). There, the decay length β was well converged with respect to the basis size, but the imaginary bands show a huge basis set dependence. This is the aspect that we address here. A local basis should work very well for the localized bonding and antibonding states of molecules, but problems could arise when considering saturated, wide gap molecular wires such as n -alkane chains. Here the antibonding empty states often fall above the zero of the electrostatic potential in the vacuum. It is known that, experimentally [9] as well as in density functional theory (DFT) [7, 8], polyethylene is a negative electron affinity material. While holes in the highest valence band are intra-chain bonding states, electrons in the lowest conduction band are delocalized inter-chain states while the empty antibonding states lie above the vacuum level. In a monolayer of n -alkane chains attached to the gold surface, both intra-chain and inter-chain states appear. The latter cannot easily be described and are sometimes missing altogether in local basis calculations. Ignoring these inter-chain states or vacuum states in conductance calculations may still work or it may not: our point is that they cannot be *a priori* neglected. Vacuum states between the HOMO and the LUMO, in general, will influence the complex band structure of the polymer in a way that needs to be addressed.

To clarify this point, we decided to study the complex electronic structure of an isolated periodic one-dimensional polyethylene chain and to compare the CBS obtained with a plane wave basis with those given by a local basis [4]. Our results confirm a very strong dependence of CBS upon the choice of the basis. In the plane wave basis, the decay length for non-resonant tunnelling is shown to be close to that obtained by the local basis but, connecting to the free-electron-like states present in the middle of the HOMO–LUMO gap, at imaginary k , a continuum of free-electron-like parabolic states appears. It is very difficult to describe these delocalized states with a local basis and in general they are substituted by a few basis-dependent states. Depending on the chemical potential, they might be relevant or not to conductance. For instance, they represent vacuum tunnelling processes for very short nanocontacts. Whatever the case, in order to discuss the tunnelling current, it is useful to keep in mind that they exist and that they might be important in some cases.

This paper is organized as follows. In section 2, we describe the method used to get the CBS of the polyethylene with a plane wave basis [10]. In section 3, we describe the geometry of the isolated chain and of the bulk polyethylene used in the calculation and the other technical details. In section 4, we present our calculated CBS, compare with previous calculations and discuss the consequences of our results on the tunnelling current of n -alkane chains. Finally, section 5 contains our conclusions.

2. Method

In this section, we describe briefly the method used to compute the CBS of a periodic system. The Bloch theorem allows us to label the one-electron states with a wavevector \mathbf{k} and a band index n . We are interested in Bloch functions with both real and complex \mathbf{k} . Within DFT in the local density approximation (LDA) these Bloch functions are solutions of the one-electron Kohn–Sham equations. To deal with ultrasoft pseudopotentials [11], we need to consider the generalized form of these equations [12] (atomic units $e^2 = 2m = \hbar = 1$ are used):

$$E\hat{S}|\psi_{\mathbf{k}}\rangle = [-\nabla^2 + V_{\text{eff}} + \hat{V}_{\text{NL}}]|\psi_{\mathbf{k}}\rangle, \quad (1)$$

where V_{eff} is the effective local potential (see [11, 12]), V_{NL} is the nonlocal part of the ultrasoft pseudopotential:

$$\hat{V}_{\text{NL}} = \sum_{Imn} D_{mn}^I |\beta_m^I\rangle \langle \beta_n^I|, \quad (2)$$

constructed using the set of projector functions β_m^I associated with atom I and \hat{S} is the overlap operator:

$$\hat{S} = 1 + \sum_{Imn} q_{mn}^I |\beta_m^I\rangle \langle \beta_n^I|. \quad (3)$$

The coefficients q_{mn}^I are the integrals of the augmentation functions defined in [11, 12]. It is convenient to rewrite equation (1) in the form

$$E|\psi_{\mathbf{k}}\rangle = [-\nabla^2 + V_{\text{eff}}]|\psi_{\mathbf{k}}\rangle + \sum_{Imn} (D_{mn}^I - Eq_{mn}^I) |\beta_m^I\rangle \langle \beta_n^I| \psi_{\mathbf{k}}. \quad (4)$$

In this equation we take the energy E as a fixed external parameter and the values of \mathbf{k} (in general complex numbers) are determined so that $|\psi_{\mathbf{k}}\rangle$ obeys the Bloch periodicity condition. This problem, formulated within the ultrasoft pseudopotential scheme, is not substantially different from the norm-conserving one solved in [2].

We solve this equation in a supercell geometry along the x and y directions. A wave propagating at energy E will have $\mathbf{k} = (\mathbf{k}_{\perp}, k)$. Due to the supercell geometry $\psi_{(\mathbf{k}_{\perp}, k)}$ will have the Bloch form along x and y :

$$\psi_{(\mathbf{k}_{\perp}, k)}(\mathbf{r}_{\perp} + \mathbf{R}_{\perp}, z) = e^{ik_{\perp}\mathbf{R}_{\perp}} \psi_{(\mathbf{k}_{\perp}, k)}(\mathbf{r}_{\perp}, z), \quad (5)$$

where \mathbf{k}_\perp is a real vector whereas k can be complex. Different \mathbf{k}_\perp do not mix and can be considered separately. From now on, we omit the \mathbf{k}_\perp on $\psi_{(\mathbf{k}_\perp, k)}$.

As in [2] we write the solution of the integro-differential equation (4) as a linear combination:

$$\psi_k(\mathbf{r}) = \sum_n a_{n,k} \psi_n(\mathbf{r}) + \sum_{Im} c_{Im,k} \psi_{Im}(\mathbf{r}), \quad (6)$$

where ψ_n are linearly independent solutions of the homogeneous equation:

$$E \psi_n(\mathbf{r}) = [-\nabla^2 + V_{\text{eff}}(\mathbf{r})] \psi_n(\mathbf{r}), \quad (7)$$

and ψ_{Im} is a particular solution of the inhomogeneous equation:

$$E \psi_{Im}(\mathbf{r}) = [-\nabla^2 + V_{\text{eff}}(\mathbf{r})] \psi_{Im}(\mathbf{r}) + \sum_{\mathbf{R}_\perp} e^{i\mathbf{k}_\perp \cdot \mathbf{R}_\perp} \beta_m^I(\mathbf{r} - \boldsymbol{\tau}^I - \mathbf{R}_\perp). \quad (8)$$

Both ψ_n and ψ_{Im} are (x, y) periodic as in equation (5). Summation over Im in equation (6) involves all the projectors in the unit cell and the coefficients $c_{Im,k}$ are determined by

$$c_{Im,k} = \sum_n [D_{mn}^I - E q_{mn}^I] \int [\beta_n^I(\mathbf{r} - \boldsymbol{\tau}^I)]^* \psi_k(\mathbf{r}) d^3r. \quad (9)$$

Note that the set of wavefunctions ψ_n is infinite. In practice the expansion $\psi_n(\mathbf{r}) = \sum_{\mathbf{G}_\perp} \psi_n(\mathbf{G}_\perp, z) e^{i(\mathbf{k}_\perp + \mathbf{G}_\perp) \cdot \mathbf{r}_\perp}$ over two-dimensional plane waves is used. If one considers only N_{2D} plane waves with $\mathbf{G}_\perp^2 \leq E_{\text{cut}}$ the number of ψ_n becomes finite and equal to $2N_{2D}$. As in [2], to find the functions ψ_n we discretize the unit cell along the z axis by dividing it into slices and replacing the $V_{\text{eff}}(\mathbf{r})$ in each slice by a z -independent potential. The ψ_n in the slices is a linear combination of two exponentials with coefficients obtained by a matching procedure.

The allowed values of k for a given energy E can be determined by imposing periodicity along z to the Bloch function and to its z derivative. If d is the cell length along z we have

$$\psi_k(\mathbf{G}_\perp, d) = e^{ikd} \psi_k(\mathbf{G}_\perp, 0) \quad (10)$$

$$\psi'_k(\mathbf{G}_\perp, d) = e^{ikd} \psi'_k(\mathbf{G}_\perp, 0). \quad (11)$$

Inserting equation (6) into (9)–(11) one can show that the last three equations are equivalent to the generalized eigenvalue problem:

$$AX = e^{ikd} BX, \quad (12)$$

where A and B are known matrices. We solve this problem to obtain in general a complex k and coefficients $X = \{a_{n,k}, c_{Im,k}\}$ for the generalized Bloch state ψ_k at a given energy E and \mathbf{k}_\perp .

Our CBS calculations proceed in two steps. First we compute with a standard electronic structure code (PWscf) [13] the ground state electronic structure of the system and we obtain the effective local potential $V_{\text{eff}}(\mathbf{r})$ and the screened coefficients D_{mn}^I . In a second step, we use the potential $V_{\text{eff}}(\mathbf{r})$ and the screened coefficients D_{mn}^I to compute the CBS applying the scheme described above.

3. Geometrical model and technical details

The n -alkane chains $[X(\text{CH}_2)_n\text{Y}]$ are made of CH_2 monomers with singly bonded carbon atoms and two terminating groups (indicated by X and Y). If grafted via a thiolic terminating group ($X = \text{SH}$) on the Au(111) surface, they can spontaneously assemble into a dense and ordered monolayer film to form an insulating layer [14]. We model the n -alkane chain with a periodic polyethylene chain [poly- CH_2] as depicted in figure 1(a). Since we shall compare

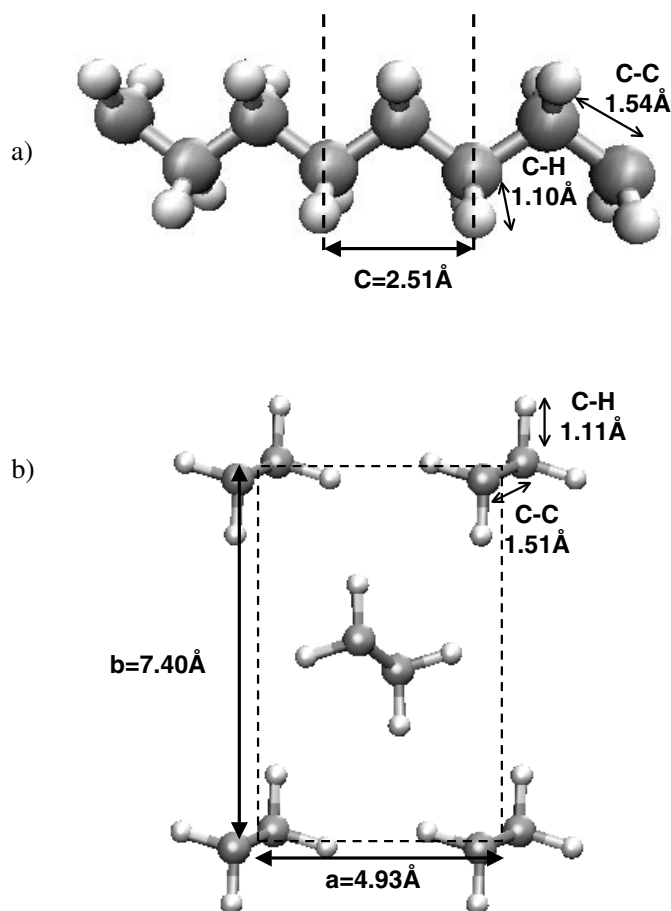


Figure 1. (a) Geometric structure of the polyethylene chain considered in this work. The geometry is kept close to the ideal tetrahedral one, with CC and CH bond lengths as in [4]. (b) Geometric structure of bulk polyethylene.

our results with [4], we choose the same geometry, C–C–C and H–C–H angles are those of the perfect tetrahedral structure (109.5°) and the C–C bond lengths and C–H bond lengths are, respectively, equal to 1.54 and 1.10 Å.

The chain is modelled with a tetragonal supercell. The chain is parallel to the z axis and periodically repeated along the x and y directions with a chain–chain distance a (10.58 Å) large enough to avoid replica interactions (tests with a larger supercell gave no relevant change of the results). The length of the unit cell c in the z direction is $c = 2.51$ Å (experimentally $c = 2.50$ Å). In order to estimate the influence of the chain–chain interaction, we also calculated for bulk polyethylene. The rhombohedral unit cell edges are $a = 4.93$ Å, $b = 7.40$ Å and $c = 2.534$ Å, as in [7], and the internal coordinates were allowed to relax. We found $d_{CC} = 1.51$ Å, $d_{CH} = 1.11$ Å, $\alpha_{CCC} = 114^\circ$ and $\alpha_{HCH} = 105^\circ$ (see figure 1(b)) to be compared with experimental values $d_{CC} = 1.53$ Å, $d_{CH} = 1.09$ Å, $\alpha_{CCC} = 113.3^\circ$ and $\alpha_{HCH} = 109.5^\circ$.

We calculated the electronic structure of these systems with the PWscf code [13] using the LDA with the parametrization of Perdew and Zunger [15]. The electron–ion interaction was described by ultrasoft pseudopotentials [13]. The wavefunctions were expanded in a plane

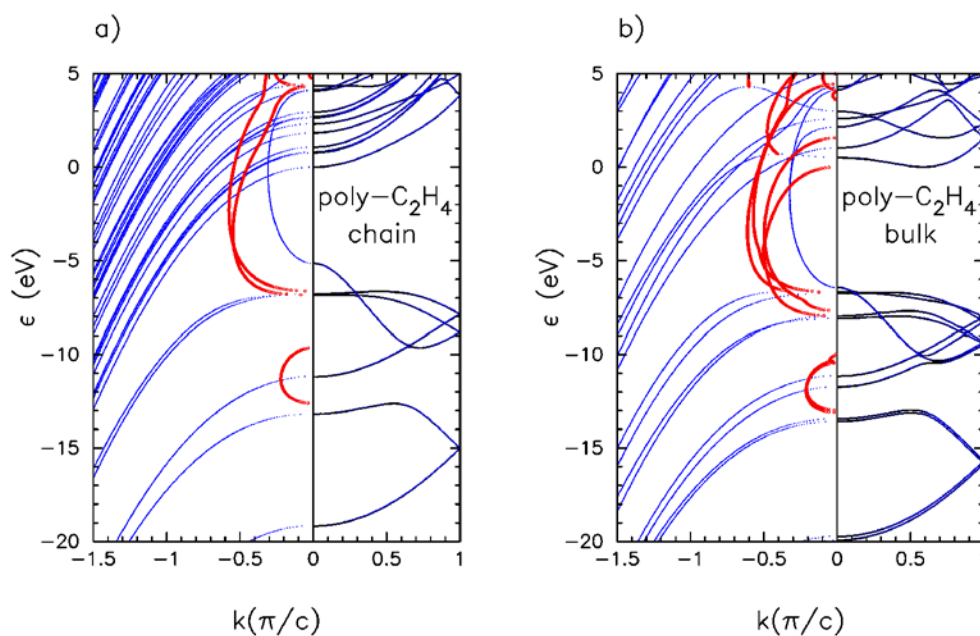


Figure 2. (a) Complex band structure of polyethylene. The right panel shows the real bands, while imaginary and complex bands are shown in the left panel. Small dots represent bands with purely imaginary k , while small circles represent Bloch states with complex k projected on the imaginary plane. (b) As in (a) for bulk polyethylene.

(This figure is in colour only in the electronic version)

waves basis with an energy cut-off of 25 Ryd. The cut-off for the charge density is 150 Ryd. The integrations on the Brillouin zone are done with a uniform mesh of 40 k points for the isolated chain and with a mesh of $3 \times 3 \times 10$ k points for the bulk.

The CBS calculation was subsequently carried out with the technique described above. The unit cell length c , in the z direction, is divided into 15 slices and the integrals are performed with 11 points in each slice (the slice thickness is 0.167 Å which is sufficient to describe accurately the slowly varying effective potential). The two-dimensional cut-off energy is taken as in the electronic structure calculation. We consider only the $k_{\perp} = \Gamma$ point. This is a very good approximation for the isolated chain, while it gives the complex band structure of bulk polyethylene only along one line in reciprocal space.

4. Results and discussion

The CBS calculated for the periodic isolated polyethylene chain and for the bulk polyethylene are shown in figures 2(a) and (b), respectively. The lowest unoccupied state, identifiable with the vacuum zero in the limit of infinite inter-chain spacing, is taken as the zero of the energy. In each figure, the right panel shows the bands at real k , the Bloch modes propagating along the z direction, whereas the left panel displays the bands obtained for complex k and Bloch modes evanescent (or exponentially diverging) in the z direction (note that for each solution k , at a given energy E , the complex conjugate k^* is also a solution). Bands with purely imaginary k are represented with small dots, while bands with complex k are projected on the imaginary k plane and indicated by small circles.

Table 1. Band properties of an isolated polyethylene chain and bulk polyethylene calculated in the present work compared with selected previous results.

References	Basis	Functional	Bandwidth (eV)	C–C bandwidth (eV)	Gap (eV)
Chain					
This work	Plane Waves	LDA	14.0	6.2	5.14
[7]	Plane waves	GGA	14.0	7.0	5.1
[17]	Plane waves	LDA	13.5	6.8	5.7
[17]	Plane waves	GGA	13.5	6.7	6.0
[4]	Local basis	?	13.5	7.0	9.0–10.25
[16]	Gaussian basis	LDA	14.0	6.1	8.0
Bulk					
This work	Plane Waves	LDA	13.6	7.0	6.4
[18]	Plane waves	LDA	14.2	8.1	6.7
[18]	Plane waves	GGA	13.7	7.1	6.2
[7]	Plane waves	GGA	14.0	7.0	6.4
Experimental			16.2 ^a	7.2 ^a	8.8 ^b

^a Reference [24].^b Reference [9].

The energy bands at real k of polyethylene (both for the bulk structure and for an isolated chain) have been reported in several papers [4, 7, 16–23]. The valence bands, C–C and C–H bonding states have also been compared with experimental angular-resolved photoemission data [16, 19, 21, 23]. In table 1, we compare our results with previous DFT calculations. All theoretical bandwidths are in substantial agreement with each other, weakly dependent on the basis set used or the actual geometry (isolated chain or bulk polyethylene). Our conduction bandwidths are 14.0 eV (chain) and 13.6 eV (bulk), in good agreement with previous calculations. All these results are also in reasonable agreement with the experimental value of 16.2 eV [19, 20, 24]. In all theoretical calculations, however, the absolute position of the occupied bands of the chain with respect to the vacuum level is too high compared with experiment. In the bulk, according to the photoemission data of [24], the HOMO level lies 10 eV below vacuum (8.8 eV below vacuum, according to [9]). DFT calculations, however, place the valence band top about 6.0 eV below vacuum. Thus, for example, a shift of 4.5 eV was needed in [16] to bring theory and experiment in closer agreement.

The theoretical bandgaps appear to be in disagreement with each other. For the chain there are two sets of values: depending on the exact geometry or exchange and correlation functional, gaps calculated with plane waves cluster around 5–6 eV [7, 17, 18], while gaps calculated with local basis are around 8–10 eV [4, 16]. We find an energy gap of 5.14 eV (for the isolated chain) which becomes 6.4 eV (in bulk polyethylene) in agreement with previous plane wave results [7, 17, 18]. Süle *et al* [22] have found that the bandgap depends on the basis-set quality. Variations of several electron volts have been attributed to the appearance in the gap of new states belonging to the continuum when the basis-set size is increased. The nature of the conduction band states obtained with plane waves has been discussed in detail by Serra *et al* [7]. In bulk polyethylene, the charge density associated to the Γ point wavefunction at the conduction band minimum shows clear maxima between the chains. Increasing the inter-chain distance, this state evolves to a free-electron-like state, or perhaps a surface state [8]. In addition a slab calculation has shown that, within GGA, polyethylene is a negative electron affinity material [8]. According to experiment [9] the electron conduction band lies at an energy

A above the vacuum level and A is about 0.5 eV above the vacuum. It is a characteristic feature of DFT in the LDA to yield gaps that are generally too small, with the exception of bonding and anti-bonding gaps. Comparing our complex bands with those obtained via a localized basis [4], it is possible to identify the reason for the different theoretical values for the bandgap. In the chain, the gap calculated by plane waves measures the position of the HOMO with respect to the vacuum level, while the gap calculated by local basis is very close to the energy of the HOMO with respect to an antibonding empty state (that we call LUMO). Actually free-electron-like states are poorly described by a local basis set and they barely appear within the HOMO–LUMO gap. Instead, in our calculation, the lowest conduction bands are parabolic, indicating free-electron-like states which, in bulk polyethylene, indicate inter-chain states [7, 8]. In a truly isolated polyethylene chain the vacuum zero energy identifies the onset of free-electron-like states. The LUMO, which is higher in energy than the vacuum zero, should appear as a resonant level in the density of states at positive energy. Since we are using a supercell geometry the density of free-electron-like states will, however, depend on the box size.

We now analyse the band structure at imaginary k and at complex k of the isolated chain and compare our results with those of [4]. At imaginary k the CBS is formed mainly by free-electron-like parabolas. The presence of the polyethylene chain splits the degeneracy of free-electron bands. In our calculation these bands are discrete, but at infinite box size, above the free-electron parabola departing from the Γ point at vacuum zero energy, they are a continuum of imaginary k states. The continuum of parabolic bands is not well reproduced with a local basis and actually the states that one obtains at imaginary k depends on the basis as shown in [4] where a minimal and an extended basis give totally different results. At the Γ point parabolic bands depart also from all the valence states except the HOMO. A loop starts from the HOMO and joins the LUMO of the molecule which is at 9.3 eV above the HOMO, 4.13 eV higher, in DFT, than the vacuum. We note that our HOMO–LUMO gap is correctly close to the local basis gap [4].

For complex k there are loops joining maxima and minima of the bands. The loop between -12.3 and -9.9 eV closes the gap between the C–C σ -bonding band and the C–H bonding states. Since these states are well reproduced by local basis, the shape and size of this loop is in good agreement with [4]. Two additional loops, also in good agreement with the local basis calculation, join maxima in the valence bands with minima in the conduction states. In the energy gap, these states have a decay length shorter than the loop joining the HOMO and the LUMO of the molecule.

The imaginary and complex k bands of bulk polyethylene are shown in figure 1(b). From the comparison of this result with the isolated chain, we can estimate the effect of the reduced inter-chain distance on the complex bands. As expected, the density of free-electron-like states is much reduced. Furthermore, since there are four monomers per unit cell, all the bands are doubled with small splittings in the valence bands and much larger splittings in the conduction bands. The loop which, in the isolated chain, joins the HOMO and the LUMO at imaginary k is now split into two loops through an avoided crossing with a parabolic band. The two loops that, at complex k , join valence and conduction bands are both split and, since the gap is now indirect, in a small energy window below the LUMO, the states in one of these loops have a longer decay length than those in the loop which joins the valence and conduction band at the Γ point.

In a typical experiment where the tunnelling decay length β of an n -alkane chain is measured, the molecule is adsorbed on an Au(111) substrate by terminating it with a thiol group. As shown in [4] the Fermi level of the gold substrate is between the HOMO–LUMO gap. Its real position is not known experimentally; theoretically it depends on the basis set used in the calculation. With plane waves, it is at about 3.5 eV [4] above the HOMO of the polymer.

It is reasonable to suppose that the presence of the thiol group, as well as the termination of the chain, are perturbations which decay much faster than the metal tunnelling states. With this hypothesis, the typical decay length of the tunnelling current can be approximated with the longest decay length of the evanescent Bloch states of the polyethylene chain at the Fermi energy. The important complex band determining the tunnelling decay length is therefore the loop joining the HOMO and LUMO states since it has the smallest $\text{Im } k$ at the Fermi level. Our value for $\text{Im } k$ is 0.36 \AA^{-1} , corresponding to $\beta = 0.9$ per monomer, in good agreement with experiment and with the calculation of [4–6], the small difference with [4] being due only to the choice of the Fermi level. Our CBS shows that local basis and plane waves give the same decay length for the non-resonant tunnelling regime if the chemical potential is much lower than the vacuum. According to a local basis calculation, increasing the substrate tip voltage, one would, however, expect to move the chemical potential of the metal and to enter into a resonant tunnelling regime where the current pass through the LUMO of the molecule [25]. According to our plane wave LDA calculation there is instead a range of voltages before the resonant tunnelling regime, where vacuum tunnelling should start to contribute to the current. The LDA underestimates the voltage necessary for this phenomenon to occur, since the HOMO is only 5.14 eV below the vacuum, while the correct gap should be of 8.8 eV [9] but, in negative electron affinity molecules, vacuum states do start to play a role before the LUMO. The LDA error in positioning the HOMO of the molecule must be kept in mind before comparing with experiment the conductance calculated with a plane wave basis. Nonetheless, negative electron affinity molecules such as the *n*-alkanes must be treated carefully, especially with local bases because the incorrect description of vacuum states may lead, not only to a complete lack of free-electron-like states in the HOMO–LUMO gap, but also to the presence of many fictitious states at imaginary k that are totally dependent on the choice of the basis set.

5. Conclusion

In this paper, the CBS of a periodic polyethylene chain has been calculated using a plane wave basis set and compared with the CBS obtained with a local basis [4]. We have shown that the tunnelling decay length β of *n*-alkane chains, here replaced by polyethylene, is independent of the choice of the basis, at least as long as, at low voltages, the tunnelling is dominated by a slowly decaying state which belongs to the loop joining, at imaginary k , the HOMO and LUMO states. Instead, our results show that the choice of the basis could be critical in large gap polymers with negative electron affinity molecules, particularly at large voltages. Future calculations of the conductance must be done carefully because of the presence of free-electron-like vacuum states within the HOMO–LUMO gap, signifying vacuum tunnelling besides intra-chain tunnelling. With a plane wave basis, the free-electron-like modes are taken into account but the density functional approximation puts the HOMO too close to the vacuum. With a local basis that treats correctly the bonding and antibonding states of the polymer the density functional problem remains. On top of that the free-electron-like states are replaced by basis-dependent levels.

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