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Abstract
We studied the behaviour of an injected electron–hole pair in crystalline polyethylene theoretically. Time-dependent adiabatic evolution by *ab initio* molecular dynamics simulations show that the pair will become self-trapped in the perfect crystal, with a trapping energy of about 0.38 eV, with formation of a pair of trans-gauche conformational defects, three C_2H_4 units apart on the same chain. The electron is confined in the interchain pocket created by a local, 120° rotation of the chain between the two defects, while the hole resides on the chain and is much less bound. Despite the large energy stored in the trapped excitation, there does not appear to be a direct non-radiative channel for electron–hole recombination. This suggests that intrinsic self-trapping of electron–hole pairs inside the ideal quasi-crystalline fraction of polyethylene might not be directly relevant for electrical damage in high-voltage cables.

1. Introduction

Thanks to its large band-gap ($\sim$8.8 eV), to its chemical inertness, and to its easy processing, polyethylene (PE) is the material of choice in extruded electric cables for high-voltage applications. The highly insulating properties of PE, however, do not prevent a tiny flow of charge carriers, both electrons and holes, injected at the very high electric fields realized under normal high-voltage operation conditions. Understanding and controlling this flow is of course extremely important for improving the cable performances. For example, dielectric breakdown depends crucially on the mobility of the injected charge carriers. Ageing and eventual failure of the cable is also believed to be connected to local damage induced by charge flow and/or recombination [1]. From a physicist's perspective, it is of primary importance to understand the basic electronic properties of PE which underlie the observed phenomenology. In particular, it is crucial to explore the detailed nature of the electronic states corresponding to the highest valence-band states (holes), to the lowest conduction-band states (electrons), and to the simultaneous presence of holes and electrons whose bound state we will refer to with the standard name of excitons [2].

Excitons are particularly interesting in this context, as it is known [3] that under high field *and* polarity reversals, electroluminescence—the field-induced emission of photons—is observed with particular intensity, plausibly due to radiative electron–hole recombination. However, electroluminescence is also known to open the way to electric damage. When in fact the electron–hole recombination energy, amounting to several electronvolts, is released in a non-radiative channel, it is suddenly turned into ion kinetic energy, and will most likely fuel important local structural and eventual electric damage. The possible existence of channels for this kind of damage is as yet unexplored.

Recently, considerable progress was made in the understanding of the nature of, separately, electron and hole states in PE. Photoemission studies [4] agree well with electronic structure calculations [5–7] in showing that the filled valence bands are made up of C–C (and of C–H) bonding states, propagating very effectively along the polymeric chain, but rather ineffectively between the chains. We shall refer to states of this kind, that are heavily chain-localized, as *intrachain* states. The lowest empty conduction band states were found, in contrast (so far only theoretically), to propagate quite well in all directions in three-dimensional space, and also to display a maximum amplitude no longer on the chains, but rather in the empty space between the chains. Such a state was referred to as an *interchain* state [7, 8]. The interchain nature of the conduction states is held responsible for some uncommon physical properties such as the *negative electron affinity* or NEA [9], characteristic of PE.

An extra electron injected in a soft insulator like bulk PE will not remain indefinitely free, delocalized, and conduction band-like. As in other soft materials, the extra electron can be expected to cause some kind of spontaneous static distortion of the lattice—a small polaron—whose effect will be to trap the electron itself in the volume encompassed by the deformation (*self-trapping*). Detailed calculations [10] indicated the existence of such a polaron state in bulk crystalline PE. It consists of a short PE chain segment—limited by a pair of *trans-gauche* conformational defects—which undergoes a large rotational distortion, with the extra electron locally bound, and self-trapped. No self-trapping, conversely, was found for holes, owing presumably to the stiffness of the C–C and C–H covalent bonds in the chains onto which the hole intrachain wavefunction is localized.

The scope of this work is to address the issue of how a bound electron–hole pair—an exciton—will behave in this respect once injected in PE. Electron–hole pairs can be created through electrical injection of hot carriers. Although ordinary carrier mobility in real PE is extremely small, of order 10^{-10} cm^2 V^{-1}, some electrons and holes do nonetheless get injected at opposite electrodes when the field overcomes the threshold for space charge formation. Once inside, electrons and holes drift toward one another. Due to their (screened) Coulomb attraction they will as soon as possible merge to form bound exciton pairs. Excitons can of course also be created optically [11], by absorption of UV photons of energy higher than the PE energy gap.

These considerations and the related questions call for an investigation of the electron–hole pair (*exciton*) state in crystalline PE, in particular of its accompanying structural deformation, and of its possible self-trapped state in the perfect material. We approached this problem theoretically, making use, as in our previous electron and hole studies, of constrained density functional electronic structure calculations that possess enough quantitative accuracy to be predictive.

We will present material in the following order. First we shall describe in section 2 the methods and computational techniques used. In section 3 we will study the exciton in perfect crystalline PE, and demonstrate its self-trapping, the associated distortion similar to some extent but not identical to that of the isolated electron. Section 4 will be devoted to discussion of the possible consequences, and to our conclusions.

2. Computational techniques

We carried out first-principle electronic structure calculations of PE, using density-functional methods [12], based on plane-wave expansion and pseudopotentials. Technical details are identical to those given in previous papers [16, 7, 10]. It should be stressed that the choice of a large plane wave basis set in these calculations is particularly important, in order to capture the best possible real nature of conduction states. Restricted local basis sets, otherwise very effective for describing chemical bonding and well localized valence states, should be considered with suspicion, as they may easily fail to describe the extremely extended, plane wave-like *interlayer* conduction states properly [7]. Calculations were carried out within the BLYP gradient corrected energy functional [13]. The ion–electron interactions were described by norm-conserving Martins–Troullier pseudopotentials [14]. Wavefunctions were expanded in plane waves, with a plane wave energy cutoff of 40 Ryd. Structural optimization and molecular dynamics (MD) simulations were carried out with a steepest descent and a Car–Parrinello algorithm [15], respectively. The time step for the Car–Parrinello dynamics was set to 5 atomic units (0.6 fs) and the electronic mass to 200 atomic units. *Ab initio*, finite-temperature MD simulations were carried out with the help of a Nosé thermostat with a fictitious mass corresponding to a frequency of 40 THz.

The van der Waals attraction between the chains—a numerically small but qualitatively important contribution to the stability of PE which is not accounted for by quasi-local approximations to the DFT functional such as BLYP—was included empirically through an extra two-body interatomic potential with a parameterized r^{-6} tail of the form

$$V_{\text{vdw}} = -\frac{1}{2} \sum_{i,j} \frac{C_{i,j}}{r_{i,j}^6} f_{\text{c}}(r_{i,j}), \tag{1}$$

where f_{c} is a function cutting off at short distance. All the parameters entering (1) were given the same values as in Serra *et al* [16], optimized to correctly reproduce the equilibrium structure, stability, elastic constants and thermal properties of neutral PE. This ensures that we begin with a sound overall physical description of PE, prior to the excitation, consisting of the simultaneous introduction of an electron and a hole.

A first basic question of the present excited-state calculations is how in fact to introduce the electron–hole pair. A natural choice would be to introduce a triplet exciton. Theoretically, a triplet exciton is the $S = 1$ ground state, and it can in principle be introduced in a calculation by forcing a total spin of one in a spin-polarized calculation [17]. Experimentally, triplet excitons could be created by impact energy-loss exchange processes of low-energy electrons [18], whereby an incoming spin-down electron will fall in energy to occupy an empty conduction state, while kicking away a spin-up electron, and thus creating a spin-up valence hole. Although its actual energy location and lifetime are presently unknown, a long-lived *triplet $S = 1$ exciton* must surely exist in PE, as in all other molecular solids, with an excitation energy below the ordinary, singlet excitation gap. Practical and computational limitations force us however to abandon this costly spin-polarized procedure, and to consider a simpler alternative solution. We mimic here the presence of an exciton by simply constraining an occupancy of one, instead of two, for the highest pair of occupied Kohn–Sham eigenvalues in a non-spin-polarized calculation (constrained DFT). Spin-contamination problems (related to the fact that such an exciton is, in a non-polarized calculation, neither a singlet nor a triplet pure state [19]) are expected to be minor in this case. In fact the hole and the electron states, one intrachain and the other interchain, overlap poorly in space, making the contribution of electron–hole exchange relatively small, and negligible with respect to the large exciton creation energy of many electronvolts (approximately equal to the band gap of about 8.8 eV). This kind of approximation

will of course not hold any more when, as for example in aromatics, both electron and hole states share the same electronic nature; or else when, even in impure PE, the electron and hole may both become tightly localized onto some chemical defects. However, in the present case of defect-free PE we believe that this represents a highly reasonable approximation. It can also be noted that the probable slight overestimate of excitation energy relative to the true triplet state will cancel at least a fraction of the well-known DFT energy gap deficit, thus representing a small improvement, rather than a deficiency.

First of all we carried out the electronic structure calculations and the structural optimization in this model exciton state. A sophisticated many-body description (GW-Bethe–Salpeter [20]) of the electron–hole interaction would be desirable to describe the excitonic energies, but the associated structural relaxations can be obtained quite accurately within a constrained DFT approach, as reported for the self-trapped exciton in a conjugated organic polymer [21]. Subsequently, starting from this state we also carried out a reasonable number of Car–Parrinello molecular dynamics steps, in order to explore effectively the potential energy surface of the system.

3. Results

Perfect crystalline PE possesses a base-centred orthorhombic crystal structure with lattice parameters $a = 4.93$ Å, $b = 7.4$ Å and $c = 2.534$ Å [22]. The unit cell contains two polymer chains, running parallel to the c-direction. The two chains are rotated by $\pm 42°$ around the c-axis, and the CH_2 units are in a trans-planar conformation; namely, the carbon skeleton forms a zig-zag chain lying entirely on a plane (see figure 1 of [7]).

The calculated DFT/BLYP energy band gap for ground-state PE is 6.46 eV [16], in perfect agreement with previous calculations [4, 6] but somewhat smaller than the experimental gap of about 8.8 eV. Due to that, the energy available to create a distortion, in our approximation, will represent a lower bound to that in real PE. We modelled the system with four parallel chains, each seven $-CH_2–CH_2-$ units long, in a periodically repeated simulation cell. We first performed a calculation starting from the perfect crystalline PE configuration. However, the self-trapped state of the excess electron is known to involve a structural rearrangement of the chains [10], and this rearrangement might be hindered by energy barriers when starting from ideal perfect crystalline PE. To circumvent that, we also performed a series of calculations starting from distorted atomic configurations morphologically similar to that of the self-trapped electron. In particular, we created two gauche defects on the same chain at a distance of one, two, three, and four C_2H_4 units, the chain segment between the two defects being rotated by 120° with respect to the crystalline PE structure.

We start by describing first the results obtained for the undistorted structure. We first relaxed the structure by steepest descent, both in the ground state and in the excited state. In both cases, deviations from the trans-planar conformation were negligible. The ground-state HOMO–LUMO gap of 6.46 eV is slightly reduced to 6.36 eV: after excitation the hole Kohn–Sham (KS) eigenvalue 0.09 eV above the top of the valence band, and the electron KS eigenvalue 0.01 eV below the bottom of the conduction band. The resulting reduction of the energy gap is 0.1 eV. Such a small value may be due to the well-known gap problem of LDA. We did not attempt to perform GW-BS [20] calculations in order to compute the exciton binding energy. Starting from this relaxed static structure, we next performed a molecular dynamics simulation at 300 K. The atomic positions oscillated about the trans-planar conformation and no defects were spontaneously created. The behaviour with simulation time of the electron and hole Kohn–Sham eigenvalues is shown in figure 1: the hole eigenvalue oscillates with a magnitude of about 0.5 eV, but the gap remains substantially unchanged for the duration
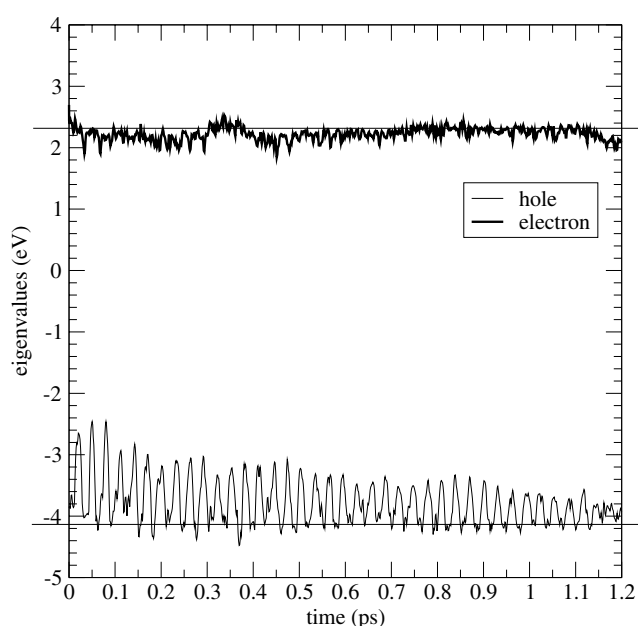
Figure 1. Kohn–Sham (KS) eigenvalues of crystalline PE as a function of time, during a constant-temperature molecular dynamics run. The two horizontal lines represent the band edges.

Table 1. Self-trapped exciton: energy difference with respect to the undistorted case.

Number of rotated C_2H_4 units	Energy difference with respect to the undistorted case (eV)
1	1.22
2	1.55
3	**−0.38**
4	−0.05

of the simulation (1.5 ps), showing no evidence for self-trapping, at least in this relatively short time.

Similar results were found in the simulations which started from the distorted structures. Annealing the system by molecular dynamics at room temperature for 0.3 ps led to states where the distortion persisted, suggesting that each distortion is a local minimum of the energy landscape, and that different minima are separated by energy barriers that will take a long time to cross. In order to determine the energetically favoured structure, we optimized by steepest descent the atomic positions of each distorted structure with $n = 1, \ldots, 4$ rotated C_2H_4 units. The total energy calculated at the local minimum of each distorted structure is reported in table 1. We found in this way that the self-trapped exciton with lowest energy consisted of *three* rotated C_2H_4 units (figure 2). Comparison with the self-trapped electron case (without hole), where the distortion consisted of seven rotated units, supports the notion that the electron–hole attraction contributes substantially to the electron localization, reducing the self-trapped polaron size from seven for the electron to three for the electron–hole pair. While in the electron-only case the singly occupied electron level sank about 0.5 eV below the conduction band bottom, that level (upper singly occupied level) is found here to lie a mere 0.04 eV below the conduction band, most likely on account of the extra kinetic energy
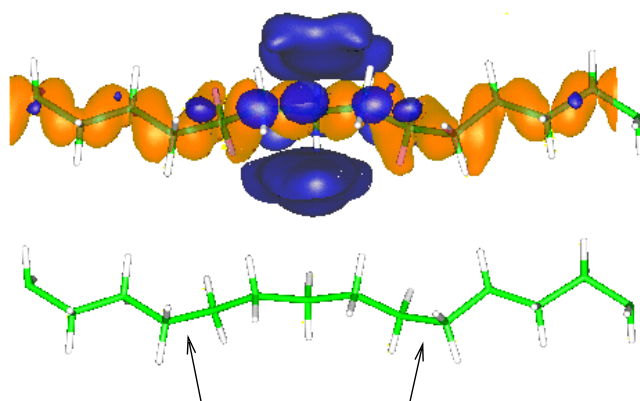
Figure 2. Iso-density surface of the self-trapped exciton; hole-state in light grey; electron state in dark grey. The bare polymeric chain is shown on the left for the sake of clarity. The two small arrows indicate the position of the gauche defects.

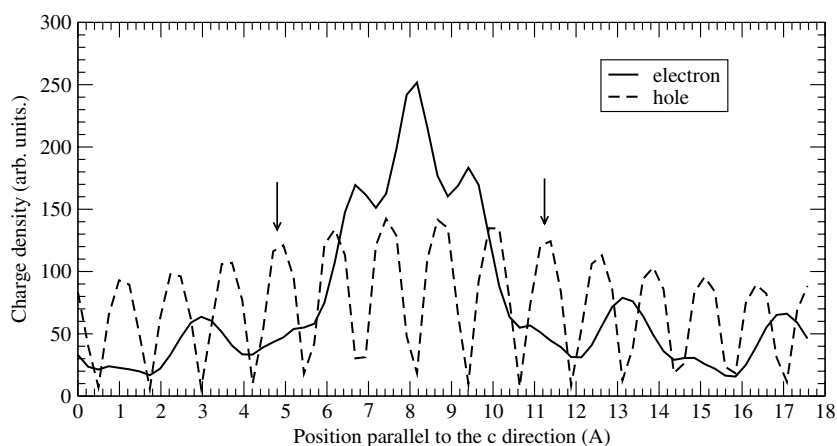(This figure is in colour only in the electronic version)

Figure 3. Charge density profile parallel to the *c*-direction. Small arrows indicate the position of the gauche defects.

required by localization in the smaller three-unit pocket [10]. The hole energy level (lower singly occupied level) is 0.01 eV above the top of the valence band, corresponding to a much weaker localization of the hole wavefunction in the neighbourhood of the trapped and strongly localized electron, as seen in figure 3. The remainder of the total energy gain is thus to be ascribed to the screened electron–hole Coulomb attraction. Figure 3 shows the electron and hole charge-density profile parallel to the *c*-direction; the dashed line is the square modulus of the hole wavefunction; the maxima correspond to the centre of the C–C bonds. The solid line is the square modulus of the electron wavefunction; the position of the gauche defects is indicated by the two short arrows. The hole is only slightly affected by the presence of the electron but tends to be more localized in the proximity of the electron, due to Coulomb attraction.

Figure 2 shows the iso-density surfaces of the hole and electron states together with the polymeric chain. The electron state is clearly *interchain* and is trapped in the volume encompassed by the deformation.

4. Discussion and conclusions

Our calculations indicate that *self-trapped electron–hole pairs* should exist in crystalline polyethylene, with a distortion pattern qualitatively similar to—although quantitatively different from—that of the self-trapped electron. The necessary energy to detrap the exciton (consisting of reduction of band gap, increase of kinetic energy due to confinement, creation of two gauche defects, rotation of a segment of chain and electron–hole Coulomb interaction) is about 0.3–0.4 eV. The exciton state, although very high in absolute energy, is apparently long-lived, displaying no apparent direct channel for non-radiative recombination. This suggests that exciton self-trapping in ideal quasi-crystalline PE might not be directly relevant for electrical damage and implies that release of the energy (several electronvolts) stored in the electron–hole pair should take place in other forms. Likely candidates for that would seem conformational or chemical defects, possibly via a combination of non-radiative and radiative decay processes. Further studies will be needed to explore such more complex scenarios.

Acknowledgments

References

[1] Dissado L A and Fothergill J C 1992 *Electrical Degradation and Breakdown in Polymers* (Stevenage: Peter Peregrinus)
[2] Ceresoli D, Righi M C, Tosatti E, Scandolo S, Santoro G and Serra S 2001 Electron–hole trapping and self-trapping in polyethylene *Electrons and Photons in Solids, a Volume in Honor of Franco Bassani* (Pisa: Scuola Normale Superiore di Pisa)
[3] Laurent C, Mayoux S and Noel S 1983 *J. Appl. Phys.* **54** 1532
Lebey T and Laurent C 1990 *J. Appl. Phys.* **68** 275
[4] Seki K, Ueno N, Karlsson U O, Engelhardt R and Koch E E 1986 *Phys. Chem.* **105** 246
[5] Miao M S, Van Camp P E, Van Doren V E, Ladik J J and Mintmire J W 1996 *Phys. Rev.* B **54** 10430
[6] Montanari B and Jones R O 1997 *Chem. Phys. Lett.* **272** 347
[7] Serra S, Tosatti E, Iarlori S, Scandolo S and Santor G 2000 *Phys. Rev.* B **62** 4389
[8] Cubero D, Quirke N and Coker D F 2003 *Chem. Phys. Lett.* **370** 21
[9] Righi M C, Scandolo S, Serra S, Iarlori S, Tosatti E and Santoro G 2001 *Phys. Rev. Lett.* **87** 76802
[10] Serra S, Tosatti E, Iarlori S, Scandolo S and Santoro E 2002 *Chem. Phys. Lett.* **360** 487
[11] Bassani F and Pastori Parravicini G 1975 *Electronic States and Optical Transitions in Solids* (Oxford: Pergamon)
[12] Hohenberg P and Kohn W 1964 *Phys. Rev.* B **136** 864
Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133
[13] Becke A 1988 *Phys. Rev.* A **38** 3098
Lee C, Yang W and Parr R 1988 *Phys. Rev.* B **37** 785
[14] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[15] Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471
[16] Serra S, Iarlori S, Tosatti E, Scandolo S and Santoro G 2000 *Chem. Phys. Lett.* **331** 339
[17] Bernasconi M, Chiarotti G L, Focher P, Parrinello M and Tosatti E 1997 *Phys. Rev. Lett.* **78** 2008
[18] Bocchetta C J, Tosatti E and Yin S 1987 *Z. Phys.* B **67** 89
[19] Frank I, Hutter J, Marx D and Parrinello M 1998 *J. Chem. Phys.* **108** 4080
[20] Ismail-Beigi S and Louie S G 2003 *Phys. Rev. Lett.* **90** 076401
[21] Artacho E, Rohlfing M, Côté M, Haynes P D, Needs R J and Molteni C 2004 *Phys. Rev. Lett.* **93** 116401
[22] Bunn C W 1939 *Trans. Faraday Soc.* **35** 482
Kavesh S and Schultz J M 1965 *J. Polym. Sci.* A **2** 1133