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Self-trapping vs. non-trapping of electrons and holes in organic insulators: polyethylene

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Abstract

We show, by electronic structure based molecular dynamics simulations, that an extra electron injected in crystalline polyethylene should fall spontaneously into a self-trapped state, a shallow donor with a large novel distortion pattern involving a pair of *trans-gauche* defects. Parallel calculations show instead that a hole will remain free and delocalized. We trace the difference of behavior to the intrachain nature of the hole, as opposed to the interchain one of the electron, and argue that applicability of this concept could be more general. Thus electrons (but not holes) should tend to self-trap in saturated organic insulators, but not for example in aromatic insulators, where both carriers are intrachain. © 2002 Elsevier Science B.V. All rights reserved.

There is a resurgent interest in the electronic properties of organic insulators and molecular crystals, both from the point of view of fundamental physics [1,2], and for their seemingly enormous application potential [3–6]. Understanding the precise nature of charge carriers, i.e., electron and hole states, is of primary importance. Under what conditions will carriers undergo free band propagation, or will instead become self-trapped [7], and why and how, is a basic issue, among other things, for both semiconductor or insulator applications. Recent femtosecond spectroscopy experiments [8] in ultra-thin heptane layers, C_7H_{16} on Ag(1 1 1) suggested for example that the lowest electronic states of such a system are, most probably, shallow self-trapped polarons; but the reasons for that, the exact nature of such states, and of the accompanying lattice distortion are thus far unknown. Ionic solids have provided perhaps the earliest examples of self-trapping [7]. Hard solids, such as valence semiconductors, do not lead to self-trapping, due to the large energy cost of the accompanying lattice distortion. In soft solid insulators such as polymers and molecular

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crystals, it is generally unclear whether self-trapping should occur or not. A case study is therefore extremely useful, as it will provide elements for a broader understanding.

To address a specific and relevant case, we performed extensive first-principle molecular dynamics simulations of the simplest saturated organic polymer, polyethylene (PE), which is also a prototype wide-gap insulator with a number of important technological applications. For electrical applications, in particular, it is important to understand the mechanisms of charge transport, trapping, and accumulation, all very crucial ingredients for the design of materials with a large threshold to dielectric breakdown. Despite a large amount of experimental work, largely carried out on heavily non-crystalline technological materials [9,10], the details of the conduction mechanisms for carriers (electrons or holes), and the nature of the traps which affect carrier propagation are only poorly understood. From a fundamental viewpoint, the crystalline state is clearly to be understood first, and here we shall concentrate on that.

PE crystallizes with a base-centered orthorhombic cell with lattice parameters [11,12] $a = 7.4$ Å, $b = 4.93$ Å and $c = 2.534$ Å. The $(CH_2)_n$ chains are oriented along the c-axis of the orthorhombic cell, with two independent $(CH_2)_n$ chains per unit cell, (see Fig. 1), forming a setting angle of ±42° with respect to the a-axis. The chain backbone carbons are connected by strong sp^3 bonds, closely resembling those of diamond, but in the a–b plane, chains are softly held together by weak attractive (van der Waals) forces, giving PE its well-known flexibility, soft elasticity, and low melting point. One is led to suspect free propagation for a carrier whose wavefunction would mostly reside on the bond chains (intrachain character), but self-trapping for one whose weight would lie mostly between the chains (interchain character). Electronic structure studies of neutral PE [13], indicated that the Bloch functions for states at the top of the valence band (hole), and at the bottom of the conduction band (electron) differ precisely in this respect, possessing intrachain and interchain character, respectively. In view of that, self-trapping in crystalline PE seems much more likely for electrons, than for holes. Our calculations and simulations fully confirm these expectations, and moreover provide a remarkable picture of the spontaneous PE chain distortion and of the ensuing electron self-trapped state in the polymer. The understanding thus gained appears quite useful in predicting the self-trapping behavior of other organic insulators.

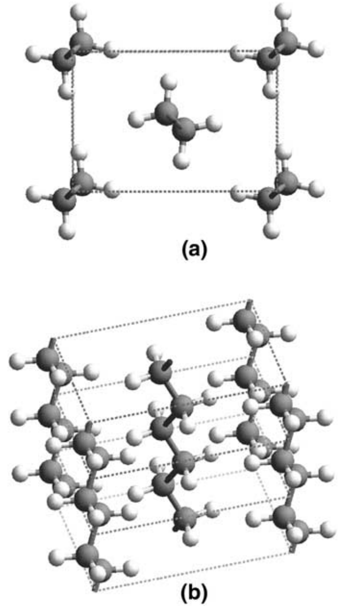

Fig. 1. Top (a) and side (b) views of the orthorhombic unit cell of crystalline PE.

We pursued the ground state of one added carrier in PE, by means of electronic structure-based molecular dynamics simulations with the Car-Parrinello (CP) technique, using state-of-the-art density functional methods, supplemented by phenomenological but realistic van der Waals forces. To improve on the accuracy of the total energy functional for PE, where the electron density varies strongly in space, we supplemented the exchange-correlation term of the local density approximation (LDA) [14,15] functional with Becke–Lee, Yang, and Parr gradient corrections [16,17]. Martins–Troullier pseudo-potentials [18] were used to describe the interactions of valence electrons with the carbon cores and with the protons. Moreover, for a good description of the conduction states a plane wave expansion with a large cutoff of 40 Ry was used. Within this scheme, extensively tested for neutral PE [19], comparison of the calculated relaxed structure against X-ray data for *n*-hexatriacontane $C_{36}H_{74}$ (an alkane whose crystal structure properties are believed to be very close to those of PE) [11,12] gave very good agreement ($\sim$1%) for both bond lengths and bond angles, ensuring an excellent description of the intrachain bonding properties. The electronic structure of neutral PE calculated with this scheme is also in excellent agreement with valence photoemission data [20], as well as with previous LDA calculations [21,22]. The calculated band gap is 6.43 eV, in relatively poor agreement with experiment [20] (8.8 eV). This typical weakness of LDA is of no consequence for the present scope, as it does not affect the accuracy of the energy. Moreover, the dispersion and the electron–phonon coupling (deformation potential) of the band states are expected to be quite accurately described. The van der Waals physical attraction between the chains – a numerically small, but qualitatively important contribution to the stability of the system, is not accounted for by the LDA-type functionals. It was included in our simulations through addition to the first principle electronic forces, of a phenomenological two-body r^{-6} potential term, of carefully optimized strength as described in [19]. Extensive simulations with this hybrid scheme proved capable of correctly reproducing not just equilibrium structure and stability, but also the elastic and thermal properties of neutral PE [19].

For present purposes, an extra electron was introduced in the system, neutralized by a uniform positive background. The simulation was run starting from the equilibrium configuration of neutral PE [19]. An initial simulation cell comprised four PE chains, each chain seven C_2H_4 units long (altogether, 56 C and 112 H atoms). Temperature was controlled, and raised by steps up to 300 K. The time evolution, especially at 300 K, appeared at first somewhat chaotic. The long PE chains underwent large time-dependent deformations, often leading to patterns characterized by the rotation by 120° of a single chain segment. The added electron wavefunction was correspondingly influenced by this evolution, and when occasionally the length of the rotated segment became sufficiently large, the electron would become localized. The total trapping energy (the mean potential energy difference between the delocalized state and the trapped state), was generally small, below 0.1 eV. We shall refer to this kind of self-generated defect – a rotated chain segment, with one trapped electron – as a self-trapped polaron (STP) [1]. Analysis of these STP configurations showed that the two junctions between the rotated segment and the unrotated part of the chain (see Fig. 2) have a clear nature of 'trans-gauche defects', well known to represent local minima in the space of defect configurations of PE [23–25]. In the ground state, the PE chains are in the all-trans configuration, where neighboring CH_2 units form an angle of 180°, as opposed to a gauche configuration, where they form an angle of $\pm 60°$. In the STP, the rotated segment is just a piece of gauche chain between two opposite trans-gauche defects. The added electron is trapped in the proximity of the gauche segment (Fig. 2).

The onset of the distortion was directly caused by the added electron. No such defect appeared, for example, in similar simulations, even at higher *T*, performed for neutral PE [19]. The structure of the STP, however, was not stable in time: it disappeared after short intervals, of the order of 400 fs, and reappeared later on different chains, consistent with thermal behavior of a very low binding energy defect. When we gradually reduced *T*, and let the system anneal towards its overall energy minimum, the STP became stable; but, somewhat surprisingly, the rotated segment length grew throughout the whole simulation cell. In other words, the two trans-gauche defects approached and annihilated each other through the periodic boundary conditions, resulting simply in one of

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[1] Actually, our calculations do not by themselves demonstrate self-trapping. They just show that in this approximation the electron acts to break the static lattice translational symmetry, becoming localized at its self-generated local distortion. Quantum mechanical hopping of the whole object to an equivalent neighboring lattice site is always in principle possible, and so long as that process is nonzero, the effective mass remains finite [7] and there is no self-trapping. In the present case however the distortion is so very massive, that the lattice overlap part of the wavefunction must cause the mass to diverge exponentially. Hence we may speak of a genuine self-trapping.

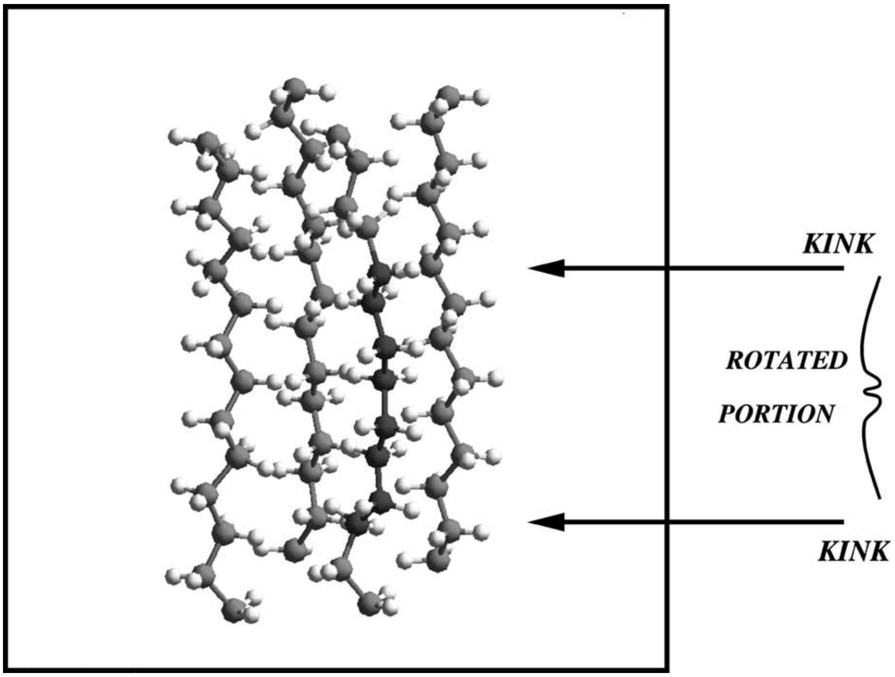

Fig. 2. Ball-and-stick picture of the distortion of PE caused by one added electron in the initial stage of polaron formation (small simulation cell, 7 units long). A portion of one chain (in red) is rotated by ~ 120° through formation of two trans-gauche defects (marked by arrows).

the four chains completely and uniformly rotated by roughly 120° degrees, i.e., *gauche*, relative to its standard orientation. The energy gain with respect to the $T = 0$ undistorted case (where the electron is freely propagating) became correspondingly larger, about 0.3 eV. The extra electron was bound in a state lying in the gap, 0.55 eV below the conduction band bottom. In space, it appeared to be well localized along (x, y), occupying, roughly speaking, the empty space made available by the chain rotation. Such a strong (x, y) localization justifies the use of a relatively small cell with just four chains. The situation is the opposite along z. Due to disappearance of the trans-gauche defects, the electron is still propagating along z, but that is clearly an artifact of a short cell. In a longer cell the cost of rotating a very long chain would grow without limit, and in reality trans-gauche defects and self-trapping along z will come back to represent the true electron ground state. In conclusion the simulation, in spite of the inadequate size, provides the idea, as well as the numerical parameters, of the following simple model of electron self-trapping in crystalline PE.

The electron STP involves overturning a chain segment L C_2H_4 units long, and binding an electron next to it. We write the energy difference between the STP, and undistorted free electron case

$$\Delta E_L = 2E_d + L\delta_1 - V_0 + \frac{\hbar^2}{2m^*}\frac{\pi^2}{(Lc)^2}, \tag{1}$$

where $2E_d$ is the energy cost of the two trans-gauche defects, δ_1 is the energy cost (per C_2H_4 unit) for rotating one chain, $-V_0$ measures the electron level in the gap relative to the conduction band bottom ($V_0 = 0.55$ eV from our simulation), and $\frac{\hbar^2}{2m^*}\frac{\pi^2}{(Lc)^2}$ is the kinetic energy due to z-confinement of an ideal one-dimensional electron in a region of length Lc. By separately calculating the energy increase of neutral PE upon rotation of one entire chain by 120°, we found $\delta_1 \approx 49$ meV. The trans-gauche cost is known, $E_d \approx 8.5$ meV [19,22]. Minimizing ΔE_L with respect to L, we find an energy minimum for

$$L_0 = \left[\frac{\hbar^2\pi^2}{m^* c^2 \delta_1}\right]^{1/3} \approx 6.5 \quad (m^* \approx 1,\ \text{see Ref. [13]}). \tag{2}$$

The electron STP is predicted to overturn $L_0 \sim 6$–7 CH_2 units, a value accidentally close the cell size $L = 7$ used in the simulation. This may explain why in the simulation the STP eventually spread over the whole chain. The model predicts a total self-trapping energy gain $\Delta E = \approx -0.1$ eV, relative to the free band state. In spite of a massive lattice distortion involvement, the STP is predicted to behave as a shallow electron trap. This comes about because the electronic binding energy term $-V_0$ is weak. That is due in turn to the interchain location of the electron, the interchain region being one where the nuclear attractive potentials are weak. On the other hand, the weakness of binding is not sufficient to avert self-trapping, because of the softness of the interchain potentials, reflected by the small δ_1.

To check the predictions of this model, we performed a new simulation using again a cell with four PE chains, but now $14C_2H_4$ units long, a safely large size. To be sure, we could not similarly increase the cell size transverse to the chains. Luckily, however, there is no strong indication of need in that direction, as the trapped electron appears to fit completely inside the steric pocket provided by the single overturned chain. On the other hand, the energy required to overturn more than one chain is manifestly too large. Thus we expect the new cell to be now adequate. In the initial state half the cell ($L_2 = 7$) was undistorted, and in the remaining half ($L_1 = 7$) one chain was rotated, STP-like, the two regions joined through a pair of trans-gauche defects. Molecular dynamics annealing was used to relax this initial configuration, and to allow the distorted region L_1 to grow or shrink relative to L_2. Relaxation, although very slow and painstaking, eventually converged to a fully relaxed STP state whose final picture is shown in Fig. 3. The equilibrium value L_0 of the rotated segment length L_2 remained ≈ 7, and the final overall energy gain of the STP was 0.13 eV, in substantial agreement with expectations based on (1). While substantial error bars should be attached to these numbers, as both simulation size and time were pushed to our limits, we found residual forces in the simulation to be generally small, of order 0.5 meV/Å, and a very sluggish relaxation behavior. Both facts indicate beyond doubt the neighborhood of a local energy minimum, well described by our STP state.

As the next step, we repeated a batch of similar simulations for a hole added to PE. Here we failed to detect any self-trapping, and the hole remained freely propagating, in both small and large simulation cells, with or without temperature. We further checked whether hole trapping could at least be provoked by a less crystalline environment, such as a bent chain, or built-in trans-gauche defects, or else by introducing an interface through a model lamella. In no cases did we find trapping or self-trapping, at least within our system sizes (of course some form of weak localization is to be expected for an infinitely long bent chain [26], but that will take place on a very different scale). Lack of hole self-trapping is in line with expectations based on the intrachain (on-bond) nature of the hole wavefunction [13]. In a one-dimensional model of the chain, an ideal point-like hole-binding distortion of strength f would cause an energy gain $\Delta E_h = (1/2)kf^2 - hf^2$, where the first term is the elastic cost, the second the hole binding energy for a delta-function potential. Both are proportional to f^2, so that $\Delta E_h < 0$, the condition for hole self-trapping, can only be satisfied if the stiffness k is sufficiently small. In the light of this model, our negative results mean that the C–C bond stiffness prevent hole self-trapping in PE.

Self-trapping of electrons, but not of holes, is most probably a feature shared by other saturated organic insulators, where strong bonds push the intrachain antibonding states above the conduction band bottom, and the affinity level is again intermolecular or interchain. Evidence for shallow electron self-trapping has recently been found in *n*-heptane bilayer–Ag(1 1 1) interfaces [8]. Even though in *n*-heptane the chain rotation and trans-gauche defects do not necessarily take place in the same manner as in PE due among other things to the chain shortness we speculate that the interchain nature of the electron may be responsible for self-trapping there too.

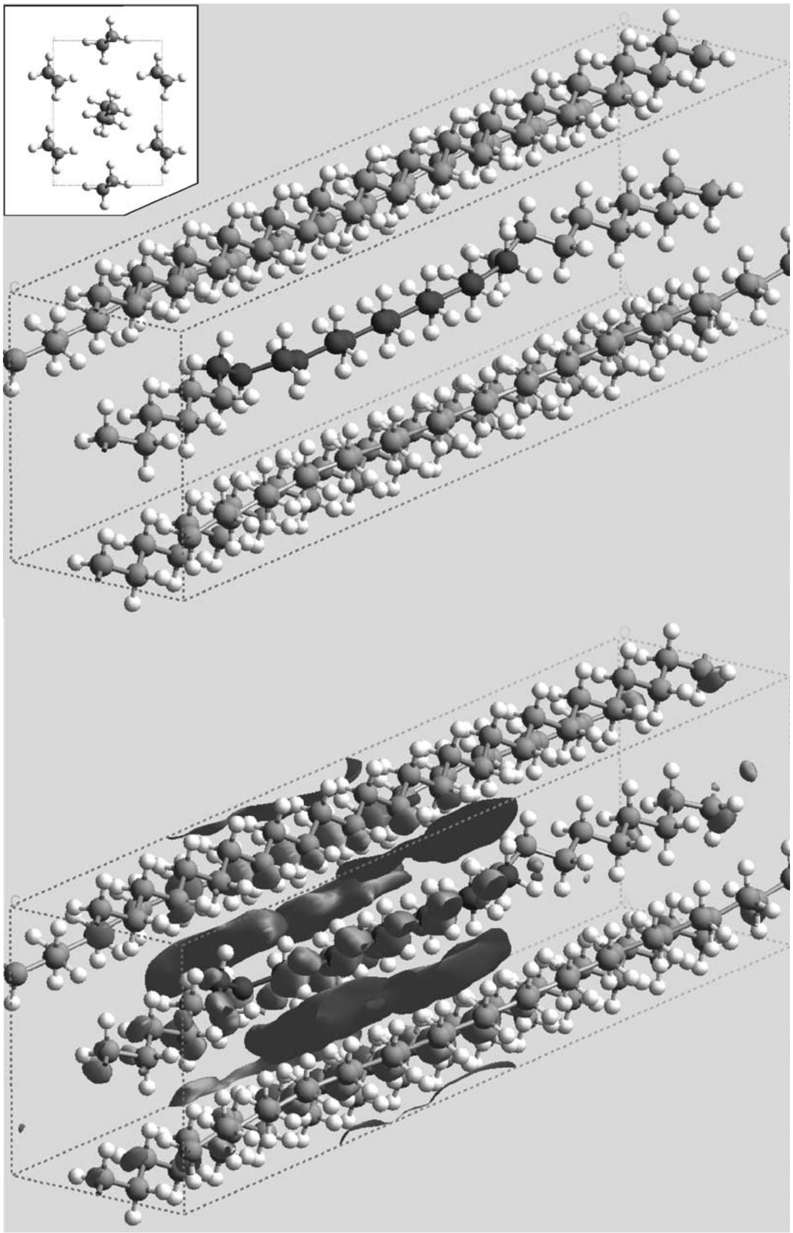

Fig. 3. (Top) final relaxed structure for the STP state of PE obtained for a large simulation cell with $14C_2H_4$ units. The twisted chain portion is colored in red. (Bottom) visualization of the electron wavefunction squared amplitude in the self-trapped polaron. Note the interchain nature and the confinement near the twisted chain segment. (Inset) top view of the relaxed structure for the supercell used in the simulation.

In unsaturated, aromatic insulators, conversely, both the electron and the hole, of π and $\pi*$ nature, respectively, are clearly intrachain, and in that case self-trapping can be avoided. That is consistent with the excellent band-like mobilities recently reported, for example, in pentacene [6].

The STP nature of the ground state of an added electron should have experimentally observable consequences also in PE, as well as in long alkanes (longer than *n*-heptane) such as hexatriacontane. Transport must of course be crucially affected by formation of STPs, since electron motion will only be possible in the free conduction band, the total effective mass of the STP being very large. If, as we find, the electron ground state is a STP, and the propagating band state corresponds to an excitation $|\Delta E|$, conduction will only take place following thermal promotion of the electron out of its STP cage. Therefore, in ideal crystalline PE devoid of any extrinsic deep traps, electron mobility should be activated, with activation energy $|\Delta E| \approx 0.13$ eV controlled by STP formation. However, the ubiquitous presence of deep traps in the real material, where activation energies are typically as large as ≈ 0.7–1.1 eV [10], is likely to make an attempt to verify this predicted transport property of ideal PE a rather difficult one. Again, long alkanes might offer a better testing ground in that respect.

In conclusion, we have found that a hole will not self-trap in polyethylene, but an electron will, the STP predicted to involve a gauche chain segment several units long, acting as a shallow trap. The occurrence or not of self-trapping is related to the contrasting interchain or intrachain nature of the two carrier states. That concept leads more generally to expect electron self-trapping in other saturated organic insulators, but not in unsaturated ones.

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