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Small Polarons in Dry DNA

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We report *ab initio* calculations for positively charged fragments of dry poly(dC)-poly(dG) DNA, with up to 4 C-G pairs. We find a strong hole-lattice coupling and clear evidence for the formation of small polarons. The largest geometry distortions occur in only one or two base pairs. They involve the stretching of weak bonds within each base pair, increasing the distance of positive hydrogens, and decreasing that of negative oxygens, to the region in which the hole localizes. We obtain an energy of $\sim$0.30 eV for the polaron formation, nearly independent of the chain size. From it, we can estimate an activation energy for polaron hopping of $\sim$0.15 eV, consistent with the available experimental value.

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The phenomenon of charge transport in DNA has been attracting the attention of both biologists and physicists. From the biology side, there is evidence that charge injection can be associated with damage, mutation, and repair processes in DNA [1–5]. From the physics side, recent developments in nanotechnology now allow the measurement of currents through single DNA molecules in dried samples [6–10]. Several mechanisms have been proposed for charge migration and transport in DNA. In a saline solution, calculations suggest that counterions play an essential role [11,12]. In the absence of salt, for the dry conditions relevant to most of the proposed nanotechnology setups, mechanisms that do not involve counterions, such as bandlike electronic transport [13], variable range hopping [14], and small polaron motion [3,15,16], have been proposed. Detailed electrical transport measurements through DNA molecules of identical base pairs poly(dA)-poly(dT) and poly(dG)-poly(dC) have been reported recently [10]. These results fit very well a model in which the conduction is due to thermal motion of small polarons, which are negatively charged in poly(dA)-poly(dT) and positively charged in poly(dG)-poly(dC).

The physics of polarons is that of an electron (hole), added to an otherwise empty (filled) band, and coupled to lattice deformations [17,18]. There are two important parameters in the problem: the width W of the conduction or valence bands (for electron or hole polarons, respectively), and the polaron binding energy E_b, defined as the reduction of the ground-state energy upon inclusion of the electron-lattice coupling. Two limiting cases appear naturally: the so-called small (for $W \ll E_b$) and large (for $W \gg E_b$) polarons. In the small polaron (or strong coupling) limit, Holstein [19] has shown that, at high enough temperatures, the conduction occurs by thermal hopping of the localized polarons, with a characteristic activation energy E_a. In this regime, it was also shown that the adiabatic description, that we use and which considers the nuclei as classical objects, is valid and leads to the same value of E_a as the full quantum description.

In this paper, we investigate the polaron formation in dry DNA by applying *ab initio* calculations to both neutral and positively charged fragments of dry poly(dG)-poly(dC). The fragments have one to four cytosine-guanine pairs, labeled $(CG)_1$ to $(CG)_4$. We find clear evidence of strong hole-lattice coupling and of the formation of small polarons. This evidence arises from several observations: (i) the small variation of the polaron binding energy E_b as a function of the DNA fragment size, suggesting that it is very localized; (ii) the fact that the energy E_b gained by localizing the hole is an order of magnitude larger than the energy of hole hopping, i.e., the bandwidth W of the uppermost valence band; (iii) the explicit localization of the hole wave function; and (iv) the localization of the structural deformations produced by the hole and their strong spatial correlation with the hole wave function.

In our method [20,21], we use density functional theory [22] within the spin-polarized generalized gradient approximation (GGA) [23], separable [24] norm-conserving pseudopotentials [25], and a double-ζ basis set of numerical atomic orbitals of finite range. Polarization functions were included for phosphorous and for the atoms involved in the hydrogen bonds. The geometries were optimized until the residual forces were less than 0.02 eV/Å for fragments $(CG)_1$ to $(CG)_3$, and 0.04 eV/Å for $(CG)_4$. For each base located at the edges of the DNA fragments, one backbone atom was held fixed in the same position as in the infinite, periodic, DNA [9]. The broken bonds at the fragment edges were saturated with hydrogen atoms. We consider the DNA in its acidic form; that is, the phosphate groups have protons as counterions, as in phosphoric acid. The isolated fragments were treated as molecules, with periodic boundary conditions. To minimize the interaction between adjacent images, we used enough empty space and appropriate corrections [26]. This methodology [20,21] was optimized for large systems and has been successfully applied to investigate polarons in carbon nanotubes [27], as well as biological systems, including neutral, periodic DNA [9,28]. In the present work, the existence of an unfilled band prevents the use of an order-N electronic functional [29,30], and the required spin-resolved density further complicates the convergence, limiting the size of the accessible DNA fragments. Therefore, we must pay special attention to possible finite size effects, when extrapolating any conclusions to infinite DNA.

To calculate the hole polaron binding energy E_b, we first relax the geometry of the neutral fragment, starting from that of the infinite, periodic DNA [9]. Second, we remove one electron and find the total energy E_0^+ of the ionized fragment, but with the fixed geometry of the neutral fragment. Finally, we relax the geometry of the ionized fragment, to find its ground-state energy E_{relax}^+. The polaron binding energy is then $E_b \equiv E_0^+ - E_{\text{relax}}^+$. In relaxing the ionized fragment, we start from the geometry of the neutral fragment. This assures that $E_{\text{relax}}^+ < E_0^+$ and $E_b > 0$. We have found that other starting points can lead to local metastable minima with higher energies.

Calculated values of E_b, for different parameters and fragment sizes, are shown in Table I. E_b changes by less than 0.04 eV with variations in force tolerance and cutoff radii, showing that these precision parameters are reasonably well converged. In fact, all the values of E_b in Table I are within 0.30 ± 0.06 eV. This value is already by itself a strong evidence of a large hole-lattice coupling and of the formation of small polarons, since it makes $E_b/W \sim 8$, where $W = 0.04$ eV is the calculated width of the uppermost valence band in neutral DNA [9].

In order to extrapolate the calculated value of E_b to infinite DNA, we must consider possible finite size effects. It may be argued that, if the hole is repelled by the chain edges, and affected by the chain asymmetry, then, even in $(\text{CG})_4$, there might be a unique preferred site for the hole. This possibility cannot be ruled out until we can perform calculations for larger fragments and, in fact, the results in Table II do show some weak edge and asymmetry effects. However, a strong preference for the hole position would make it difficult to understand the small variation of E_b as a function of chain size. In contrast, such a small variation of E_b is consistent with the formation of a small polaron, well confined already within the fragments considered, and which would be very similar in infinite DNA. To illustrate this further, we have performed finite-chain calculations with the linear molecular crystal model of Holstein [17], defined by the Hamiltonian

$$H = -t\sum_i (c_i^\dagger c_{i+1} + \text{H.c.}) - A\sum_i x_i c_i^\dagger c_i + \frac{1}{2}K\sum_i x_i^2, \tag{1}$$

where $-tc_i^\dagger c_{i+1}$ is a first-neighbor electronic hopping term, $-Ax_i c_i^\dagger c_i$ is an on-site coupling between a geometric displacement x_i and the electron (or hole) presence at site i, and the last term is an elastic energy associated with the atomic displacements. Figure 1 shows the exact solutions of (1) for finite size systems. E_b is plotted as a function of the number of sites, n, for different values of the parameter $B = 8E_b^{(1)}/W$, where $E_b^{(1)} = A^2/2K$ is the polaron formation energy for a single-site chain and $W = 4t$ is the bandwidth in the absence of deformations. For small values of B (large polaron limit), E_b decreases strongly with n. For large B, E_b changes little and saturates for very small-fragment sizes. In particular, the curve that corresponds to the first-principles values $E_b^{(1)} = 0.32$ eV and $W = 0.04$ eV ($B = 64$) is shown in Fig. 1 as black dots. In it, E_b changes by only ~6% and has converged already for $n = 4$. This is consistent with the first-principle results of Table I.

TABLE I. Polaron binding energies E_b, in eV, in the DNA fragments $(\text{CG})_1$ to $(\text{CG})_4$. The tolerance in the final forces was 0.04 eV/Å in (a) and 0.02 eV/Å in (b)–(e). In (c)–(d) the cutoff radii of the basis functions are increased by 20% and 40%, respectively, relative to (a)–(b).

	$(\text{CG})_1$	$(\text{CG})_2$	$(\text{CG})_3$	$(\text{CG})_4$
(a)	0.32	0.28	0.34	0.24
(b)	0.31	0.30	0.31	
(c)	0.35	0.28		
(d)	0.33			

We now consider the spatial distribution, among the base pairs, of the hole wave function, defined as the lowest unoccupied molecular spin orbital of the charged fragment (notice that this corresponds qualitatively to the highest occupied orbital in the neutral fragment). Table II gives the norm of the hole wave function, projected on each guanine site, for each stable fragment, as well as for the metastable polaron $(\text{CG})_4^*$, which is in a local minimum with a total energy 0.08 eV above that of $(\text{CG})_4$ [31]. It was obtained by replacing, in the starting geometry, the first CG pair of the relaxed neutral $(\text{CG})_4$ fragment, by the relaxed $(\text{CG})^+$ monomer. The Table shows several clear results. First, in all the fragments, over 95% of the hole wave function is localized on the guanines. Second, for $(\text{CG})_3$, $(\text{CG})_4$, and $(\text{CG})_4^*$, the hole is strongly localized [near $G2$ for $(\text{CG})_3$ and $(\text{CG})_4$, and near $G3$ for $(\text{CG})_4^*$]. Third, although the difference between $(\text{CG})_4$ and $(\text{CG})_4^*$ reveals a small asymmetry effect, the

TABLE II. Projected norm $q(Gn)$ of the hole wave function on each guanine Gn. A metastable polaron of the $(\text{CG})_4$ fragment (see text) is labeled as $(\text{CG})_4^*$.

	$(\text{CG})_1$	$(\text{CG})_2$	$(\text{CG})_3$	$(\text{CG})_4$	$(\text{CG})_4^*$
$q(G1)$	0.96	0.51	0.25	0.13	0.06
$q(G2)$		0.44	0.56	0.45	0.35
$q(G3)$			0.18	0.27	0.42
$q(G4)$				0.12	0.17

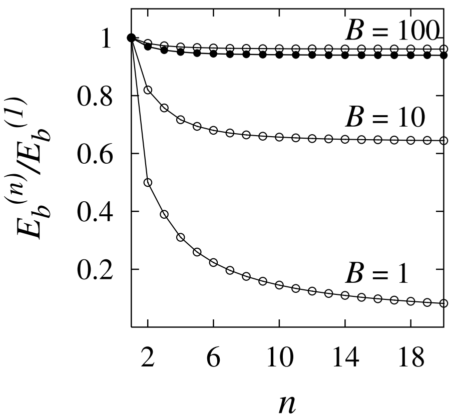

FIG. 1. Polaron binding energies $E_b^{(n)}$, calculated with the Holstein Hamiltonian of Eq. (1), as a function of the number n of base pairs of the chain, and normalized to the case $n = 1$. The curves correspond to different values of the parameter $B = A^2/Kt$. The black dots correspond to $B = 64$, obtained from the values of E_b and t calculated from first principles.

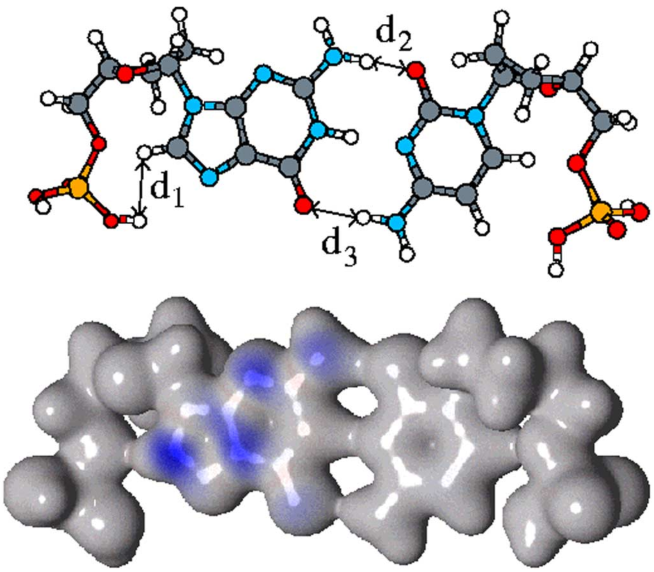

FIG. 2 (color online). Upper part: structure of a single DNA base pair with the guanine on the left. d_1, d_2, and d_3 are the interatomic distances that change the most after charging the system. Lower part: isosurface of constant electron density for the same system, colored from grey to dark grey (blue online) proportionally to the square of the hole wave function.

very fact that $(CG)_4^*$ is (meta)stable means that the hole prefers to be centered in either site, rather than spreading itself over the whole system. This shows that the finite size effects, due to our small-fragment sizes, cannot account for our observation of small polaron formation. Finally, it is clear that in none of the fragments [except the trivial $(CG)_1$ case] is the hole wave function completely localized in a single nucleotide.

Let us now consider the spatial distribution of the hole wave function at the atomic level, and its relationship with the structural deformations of the nucleotides. Long-range polaron deformations, such as electron-libron coupling [33], have been proposed in the past. We clearly cannot rule out such deformations with our small-fragment calculations but in fact the deformations that we observe are short ranged even compared to the fragment sizes. Figure 2 clearly shows that the hole wave function is localized on the guanine side. It also shows the bond distances d_1, d_2, and d_3 that change the most upon removing one electron. They correspond to soft bonds, located near sites with a significant amplitude of the hole wave function. These deformations represent a strong indication of an electrostatic mechanism for the polaron formation, since positively charged hydrogen atoms are repelled by the hole, and negatively charged oxygen atoms are attracted. Because of the softness of the bonds affected, the charged atoms undergo considerable displacements which, in turn, stabilize electrostatically the hole, forming the polaron.

The relationship between the hole distribution and the change in the bond distances d_1, d_2, and d_3 is presented in Fig. 3 for $(CG)_4$. The upper panel shows the norm of the hole wave function projected on the guanine bases. The lower panels show the respective changes in the distances d_1, d_2, and d_3 of each guanine. It can be seen in all cases that the magnitude of the distortion is directly related to the amount of charge on the guanine. Such a strong correlation is fully consistent with the small polaron model of Eq. (1), which predicts a proportionality $x_i = (A/K)q_i$.

The experiments of Yoo *et al.* [10] for the *I-V* characteristics of poly(dC)-poly(dG) indicate an activation energy $E_a = 0.12$ eV for polaron motion above 200 K. In this (high temperature) regime, and in the limit of a dispersionless phonon band, the Holstein model of Ref. [19] predicts that $E_a = E_b/2$. Thus, if we suppose that our value of $E_b \sim 0.30$ eV for $(CG)_1$ to $(CG)_4$, is also representative for long DNA, this relation and the results

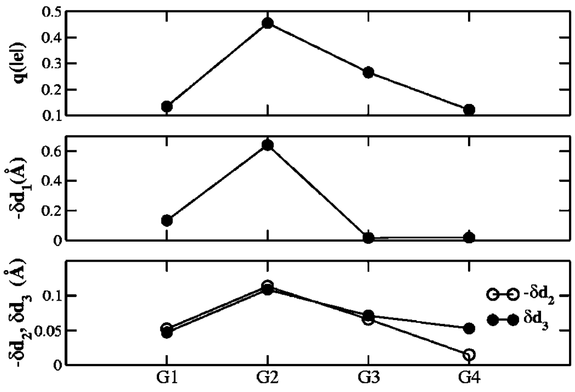

FIG. 3. Upper panel: amount of hole charge on each guanine for the four-base-pair DNA fragment. Lower panels: corresponding changes in the distances d_1, d_2, and d_3.

of Table I allow us to estimate a hopping activation energy of ~0.15 eV, consistent with the experimental value. Although the combined uncertainties of the experiment, the *ab initio* calculations, and the models used, are likely to make this agreement partly accidental, the similar magnitudes of the two values provide additional support for the small polaron model.

Finally, it can be mentioned that Yoo *et al.* [10] estimated a value of 25 Å (seven base pairs) for the mean polaron hopping length. This value seems surprising for very small polarons, which would be expected to jump mainly to nearest neighbor sites. However, tunneling electron transfer processes can occur for extremely long distances, even if the initial and final states are very localized. In DNA deposited over a substrate, [10], it is likely that many of the guanine deformations, required to trap the polaron, are constrained by interactions with the substrate, so that only a small fraction of the base pairs is suitable to host the polaron. Hopping would then occur only among these special sites, explaining the long observed hoppings.

In conclusion, using *ab initio* calculations, we have determined the hole polaron structure and binding energy in small fragments of dry poly(dC)-poly(dG) DNA. We find that the geometric changes induced by the hole are mainly confined to one or two guanines, affecting mostly the lengths of weak bonds, which change to minimize the electrostatic interaction of the hole with positive hydrogen and negative oxygen atoms. We also find a strong correlation between these geometry relaxations and the weight of the hole wave function, in agreement with a simple polaron model. The large binding energies obtained, and their constancy as a function of fragment size, constitute strong evidence of a large hole-lattice coupling and of the formation of small polarons. Extrapolating our results to long DNA, we estimate an activation energy for polaron hopping that is consistent with the available experimental value.

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