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THz oscillating currents enhanced by long-range correlations in DNA

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ABSTRACT

Recently synthetic homopolymer DNA molecules have been theoretically demonstrated to support oscillating polarons when they are subjected to an external electric field (Bloch oscillations). Environment effects might introduce randomness in the molecular levels that, in general, destroy the coherence necessary to support this periodic dynamics. In this sense the existence of long-ranged correlations in DNA as well as its influence on its properties has been widely discussed. We demonstrate that the polaron performs Bloch oscillations even in disordered DNA molecules provided long-range correlations arise in the sequence of molecular levels. We predict the occurrence of THz alternating currents across the DNA molecules, opening the possibility of new applications in molecular electronics.

1. Introduction

Conducting properties of single DNA molecules have been studied for some years now due to their potential applications. Recent experiments suggest that DNA molecules may play an important role in future nanoelectronics. Thus, depending on the particular DNA sequence, environment conditions or contacts effects, different conducting behaviors have been established for the DNA [1]. The most promising DNA molecules seem to be DNA homopolymers as poly(G)–poly(C), whose semiconducting behavior has been theoretically and experimentally established [2–18].

However, since DNA is easily deformable, its structural deformations should be taken into account for an accurate description of its charge transport properties [19]. Charge coupling with such DNA distortions can create a polaron and enhance its mobility. This process reminds the multiple-step hopping mechanism also proposed to explain charge transport in DNA [20–22]. Thus, the behavior of the incoherent charge hopping can be understood as polaron diffusion. In this respect a variety of works have been devoted to the description of the polaron dynamics in DNA molecules [23–28].

For the particular case of DNA homopolymers subjected to a dc electric field, it was theoretically proven that, due to the periodicity of the nucleotide sequence, polarons might behave as electrons in biased periodic potentials. This means that they perform a periodic motion, in real and in k space, known as Bloch oscillations (BOs), whose amplitude and frequency can be established from semiclassical arguments [29,30]. Moreover, such a periodic motion leads to alternating currents in the THz range [31].

As we already mentioned, the particular nucleotide sequence as well as the environment conditions of DNA, which locally modify the base energy levels, strongly affect the transport properties. In this sense, it is well established the existence of long-range correlations in the energy landscape of natural DNA sequences [32–38] and therefore, a study of the polaron dynamics in such DNA molecules is in order. In particular, the energy distribution used in Ref. [39], which models long-range correlations, presents a number of interesting properties as reported in several works [39–44]. Despite disorder-induced dephasing effects, such correlated distributions support BOs when correlations are strong enough [42].

In this paper we study the polaron dynamics in DNA presenting long-range correlations. Contrary to what expected, long-range correlations in DNA enhance the periodic motion of the polaron under an applied electric field, leading to ac currents with a well-defined frequency in the THz range.

2. Model

The Peyrard–Bishop–Holstein (PBH) model maps the double stranded DNA helix onto a 1D lattice where every node represents a base pair [45]. A single degree of freedom is assigned to every site, which describes the stretching of the H-bonds within the two complementary bases, y_n. Notice that the stretch of the base pairs is the degree of freedom most strongly coupled to the electron system and therefore, the most capable of carrying polarons [46,47]. Moreover, due to the different time-scales of the carrier and the bases dynamics, the Hamiltonian of the PBH model can be cast within a semiclassical approximation [48]. The carrier is then treated quantum-mechanically, within the framework of the tight-binding approximation, while the lattice dynamics is taken into account classically. Under such considerations the Schrödinger

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equation for the carrier in a biased heterogenous molecule is given by [49]

$$i\hbar\frac{d\psi_n}{dt} = \mathscr{E}_n - Un\psi_n - T(\psi_{n+1} + \psi_{n-1}) + \chi y_n\psi_n, \tag{1}$$

where ψ_n is the probability amplitude for the charge carrier located at the nth nucleotide ($n = 1,\ldots,N$). The parameter $U = eFa$ is the potential energy drop across one period of the lattice ($a = 3.4$ Å in DNA) due to the applied electric field F. The hopping is restricted to nearest-neighbor nucleotides and its magnitude is given by $-T$. The last term in Eq. (1) is a Holstein-like on-site correction to describe the carrier–vibration coupling, whose strength is parameterized by χ [50]. It should be noted that *ab initio* estimations of the coupling constant χ are scarce and the results are strongly dependent on the sequence and number of nucleotides [28]. In this work our calculations were mostly performed with the constant $\chi = 0.3$ eV/Å which agrees with the experimental and theoretical results given in Refs. [47,51].

Long-range correlations are introduced in the on-site energies $\mathscr{E}_n = \bar{\mathscr{E}} + \varepsilon_n$ as follows [39]

$$\varepsilon_n = \sigma C_\alpha \sum_{k=1}^{N/2} \frac{1}{k^{\alpha/2}} \cos\left(\frac{2\pi kn}{N} + \phi_k\right), \tag{2}$$

where $C_\alpha = \sqrt{2}\left(\sum_{k=1}^{N/2} k^{-\alpha}\right)^{-1/2}$ is a normalization constant and $\phi_1,\ldots,\phi_{N/2}$ are $N/2$ independent random phases, N assumed to be even. They are generated using a uniform probability distribution within the interval $[0, 2\pi]$. Hereafter we set $\bar{\mathscr{E}} = 0$ without loss of generality and the standard deviation of the sequence (2), $\sigma = \langle\varepsilon_n^2\rangle^{1/2}$, is referred to as magnitude of disorder. Here $\langle\ldots\rangle$ denotes average over realizations of the random phases ϕ_n. The strength of the correlations in the energy sequence is defined by the exponent α which also describes its power-like spectral density $S(k) \sim 1/k^\alpha$ [39]. When the electron–vibration coupling is neglected ($\chi = 0$), the steady-state Schrödinger equation arising from (1) supports a set of extended states at the band center as well as other interesting properties, provided $\alpha > \alpha_c \approx 2$ [39–43]. Therefore, we consider two limiting cases in our study hereafter, the strongly correlated case $\alpha > \alpha_c$ and the weakly correlated one $\alpha < \alpha_c$.

Newton's equations of motion for the displacement y_n become

$$m\frac{d^2y_n}{dt^2} = -V_M'(y_n) - W'(y_n, y_{n-1}) - W'(y_n, y_{n+1}) - \chi|\psi_n|^2, \tag{3}$$

where m is the nucleotide mass and the prime indicates differentiation with respect to y_n. The Morse potential

$$V_M(y_n) = V_0[\exp(-\alpha y_n) - 1]^2 \tag{4}$$

takes into account the anharmonic interaction between complementary bases as well as the interaction with the sugar–phosphate backbone and the surrounding solvent. The interaction between nearest-neighbor nucleotides along the stacking direction is described by the potential [49]

$$W(y_n, y_{n-1}) = \frac{k}{4}(2 + e^{-\beta(y_n + y_{n-1})})(y_n - y_{n-1})^2. \tag{5}$$

Both potential terms depend on fitting parameters which were chosen to reproduce experimental DNA melting curves [52]. Hereafter we will use the following set of optimized parameters: $m =$ 300 amu, $V_0 = 0.04$ eV, $\alpha = 4.45$ Å^{-1}, $k = 0.04$ eV/Å^2, $\beta = 0.35$ Å^{-1} and $T = 0.1$ eV. The chosen value of the parameter V_0 is compatible with poly(A)–poly(T) synthetic DNA [53].

3. Stationary polaron solution

To obtain the initial polaron, we closely follow the procedure given in Ref. [50] in an unbiased homogeneous lattice ($U = 0$ and $\sigma = 0$), including a dissipative term of the form $-\gamma m dy_n/dt$ in Eq. (3), with $\gamma = 50$ THz. We solve the nonlinear Eqs. (1) and (3) using a Runge–Kutta method of 4th order under rigid boundary conditions, considering the homopolymer DNA case. Gaussian functions are used as the initial conditions for the lattice distortion and the carrier wave function. Due to the dissipation in the lattice, the extra energy of these unphysical initial functions will be removed in the energy minimization process. After a long enough time we get the minimal energy conformation of the charge-lattice system, which is the stationary polaron solution to start our dynamical study of the biased DNA molecules.

In Fig. 1, the stationary polarons for different values of χ in a system of $N = 750$ are shown. It is to be noticed that by increasing the strength of the charge-lattice coupling the localization of the steady states becomes larger.

4. Motion of the polaron in a biased and disordered DNA molecule

In this section we calculate the time-evolution of the polaron obtained in Section 3. We integrate (1) and (3) including disorder in the site energies of a biased lattice without dissipation. The numerical integration method as well as the boundary conditions used in this case are the same that those considered above. Our interest is to monitor the polaron motion in a biased and disordered DNA molecule in the two already mentioned limiting cases: strongly correlated (i.e. $\alpha = 5$) and weakly correlated (i.e. $\alpha = 1$) disorder. To this end, the modulus of the carrier wave function $|\psi_n|$ and the local lattice distortion y_n will be displayed by means of density plots.

Figs. 2 and 3 show the local lattice displacement (left panels) and the corresponding modulus of the carrier wave function (right

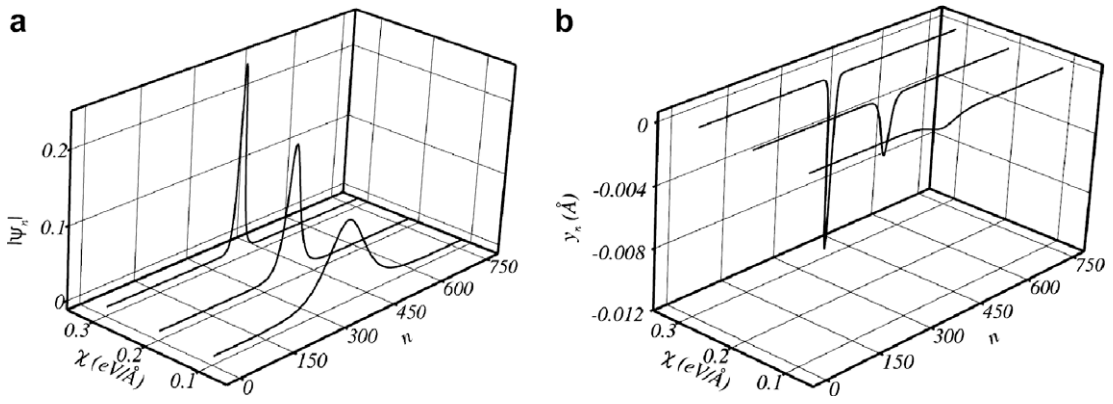

Fig. 1. (a) Modulus of the carrier wave function and (b) lattice displacement at $t = 0$ for different values of χ and $N = 750$.