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Extended Holstein polaron model for charge transfer in dry DNA*

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The variational method is applied to the study of charge transfer in dry DNA by using an extended Holstein small polaron model in two cases: the site-dependent finite-chain discrete case and the site-independent continuous one. The treatments in the two cases are proven to be consistent in theory and calculation. Discrete and continuous treatments of Holstein model both can yield a nonlinear equation to describe the charge migration in an actual long-range DNA chain. Our theoretical results of binding energy $E_{\rm b}$, probability amplitude of charge carrier ϕ and the relation between energy and charge–lattice coupling strength are in accordance with the available experimental results and recent theoretical calculations.

Keywords: Holstein polaron model, dry DNA, charge transfer, variational method
PACC: 8715K, 7138, 8710, 7290

1. Introduction

The research on the processes of biochemistry and biophysics in DNA is the most important and basic topic in bioscience.[1−17] Charge migration in DNA has become a great interesting subject, which is partially motivated by various potential applications ranging from functional nanoscale electronic devices to the long-range effects of radiation damage. Recent experimental and theoretical studies have suggested the relevance of polaron effects to the charge migration in DNA. One of the most promising models is the linear molecular crystal model given by Holstein. Charge transfer (CT) through DNA molecules has been widely studied for a large number of DNA molecules in solution because CT mechanisms have important implications in the damage and repair of this biological system. The conductivity of the 'solid-state' thin films of DNA-based compounds was also studied. In modelling charge migration in DNA, it is therefore of critical importance that the structure degrees of freedom must be adequately taken into account. Several mechanisms have been proposed for charge migration and transport in DNA. In saline solution, counterions may play an essential role.[13,14] In the absence of salt (the dry condition), the mechanisms responsible for bandlike electronic transport,[16] small polaron motion,[15,17−19] and variable range hopping[20] between localized states have been proposed. In particular, efficient long-range hole migration can oxidize sensitive parts of the DNA sequence (cluster of two or three guanine bases), resulting in increasing the probability for mutations and carcinoid-genesis. A specific motivation for studying this problem is experiments on charge transport along a DNA that is an array of stacked base pairs in the interior of the α double helix with a stacking distance of about 3.4 Å.[4] The overlapping π orbitals of the base pairs provide a pathway for the charge carriers to enter the stack. Each of the two DNA strands may be viewed as a chain, each site of which is one of the four bases: guanine(G), adenine(A), cytosine(C), and thymine(T), which have different ionization potentials. The polaron scenario of charge migration has recently found a significant support in conductivity experiments on homopolymer poly(dG)–poly(dC) and poly(dA)–poly(dT) DNA.[5]

Recently, Alexandre *et al*[12] have discussed such a problem by *ab initio* calculations of positively charged fragments of dry poly(dC)–poly(dG) DNA.

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They found a strong hole–lattice coupling and clear evidence for the formation of small polarons. The largest geometric distortions occurred 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 holes localize. In the strong charge–lattice coupling B regime, the polaron binding energy $E_{\rm b}$ changes little and is saturated for very small-fragment sizes. It illustrates a stable small polaron state existing. But for a small B value(large polaron limit), the calculated value of $E_{\rm b}$ decreases strongly with site number n. Thus then arises a question whether the polaron state is stable or not when the number of base pairs becomes large enough, especially for small values of B. The basic motivation of the present work is to carry out a complete quantitative treatment of Holstein Hamiltonian, and then try to seek a concise analytical solution for the stable small polarons in a DNA chain by using variational method. Finally, we make a continuous transformation to the finite-sites system in order to generalize the finite-sites molecular chain problem to a concise long-range continuum one.

2. Variational theory

Polaron formation is expected when an electron or hole is added to a one-dimensional or quasi-one-dimensional chain or stack. The lack of constraint on the motion of atoms or molecules in one dimension allows a distortion along the chain or stack that decreases the energy of the added carrier. The combination of free carrier with distortion, the polaron, has been studied extensively. The essential ingredients of a Hamiltonian that gives rise to polarons are (i) wavefunction overlap of nearest neighbours, quantified by the transfer integral t; (ii) electron–phonon coupling to allow the formation of the distortion; and (iii) an elastic restoring force that keeps the distortion finite.[18]

The system Hamiltonian of a DNA chain, embodying the elements of the charge, the vibration of the molecule lattice points and their coupling interaction, can be given by

$$H = -t\sum_i (C_i^\dagger C_{i+1} + C_i^\dagger C_{i-1}) + \omega\sum_i b_i^\dagger b_i + g\sum_i C_i^\dagger C_i (b_i^\dagger + b_i), \quad (1)$$

where $C_i(C_i^\dagger)$ is the annihilation (creation) operator of the electron at site i, $b_i(b_i^\dagger)$ is the annihilation (creation) operator of localized phonon at site i. t is the hopping (transfer) integral of electron and ω is the frequency of localized phonon, g is the charge–lattice coupling constant. $-tC_i^\dagger C_{i+1}$ is the first-neighbour electron hopping term. g is the charge–lattice coupling constant. $\hbar = 1$ and $\omega = \sqrt{\kappa/m}$, with m being nucleotide mass. The first term on the right-hand side in Hamiltonian (1) is a tight-binding term describing the charge (hole) hopping between adjacent base pairs. The second term describes the phonon energy of the system and the last term describes the interaction between the charge and localized phonons.[21−24]

From Hamiltonian (1) we can see that the electron couples linearly with the oscillator and the number of phonons is nonconservative due to $[b^\dagger b, H] \neq 0$. Therefore it is particularly appropriate to write the wavefunction of an n-site system in the coherent-state space. Thus the trial variational wavefunction of the Hamiltonian (1) could be assumed to be in the following form:[25]

$$|\,\rangle = \sum_i \phi_i C_i^\dagger \exp\Big\{\sum_j \alpha_j b_j^\dagger - \frac{1}{2}\alpha_j^2\Big\}|0\rangle, \quad (2)$$

where ϕ_i is the probability amplitude for the charge carrier at the ith base pair. α_j is the displacement amplitude of phonon, and $a_j^\dagger$ and a_j are creation and annihilation operators of phonon, respectively. The sum is performed over the base pairs of the molecule chain. $|0\rangle$ is the state with no phonons.

The system energy is given by the expectation value of Hamiltonian (1) as follows:

$$E = \frac{\langle|H|\rangle}{\langle|\rangle} = \frac{1}{\sum_i \phi_i^2}\Big\{-t\sum_i(\phi_i\phi_{i+1} + \phi_i\phi_{i-1}) + 2g\sum_i \alpha_i\phi_i^2\Big\} + \omega\sum_i \alpha_i^2. \quad (3)$$

The variational operation of the energy expression (3) with respect to α_i , $\partial E/\partial\alpha_k$ produces

$$\alpha_k = -\frac{g}{\omega\sum_i \phi_i^2}\phi_k^2. \quad (4)$$

Inserting the expression (4) into the expression (3) yields

$$E = \Big[-t\sum_i(\phi_i\phi_{i+1} + \phi_i\phi_{i-1}) - \frac{g^2}{\omega}\frac{\sum_l \phi_l^4}{\sum_l \phi_l^2}\Big] \Big/ \sum_i \phi_i^2, \quad (5)$$

where E is the total energy of the system. Obviously, Eq.(5) is a nonlinear equation. Defining $E/t = \epsilon$ and

$B = g^2/t\omega$, Eq.(5) can be rewritten as

$$\epsilon = \frac{E}{t} = \Big[-\sum_i (\phi_i\phi_{i+1} + \phi_i\phi_{i-1}) - B\frac{\sum_l \phi_l^4}{\sum_l \phi_l^2}\Big] \Big/ \sum_i \phi_i^2. \quad (6)$$

3. Results and discussion

We notice that Eq.(5) is a set of nonlinear equations, and they can be solved only numerically. Numerical calculations are carried out by the simulated annealing (SA) technique.[25,26] The SA technique is a generalization of the Monte Carlo method that is used for solving frozen states in many-body systems. It has been proved to be a successful method of studying the ground states of many-body systems. The process can be continued until the energy does not change. Usually the choice of initial values is based on physical considerations. Since we are interested in localized states, we choose the wavefunction amplitude at a localized point to be close to 1, and almost 0 at all other points. It has been verified that in most cases the localized state is independent of these particular initial values.

We first study the energy spectrum as a function of molecule pairing site number n in terms of Eqs.(5) and (6). The charge amplitude probability function $\phi_i (i = 1, ..., n)$ and total energy E can be obtained self-consistently. Calculations are performed at different coupling strength values, $B = 1, 10, 64$, and 100, separately. Results are plotted in Fig.1.

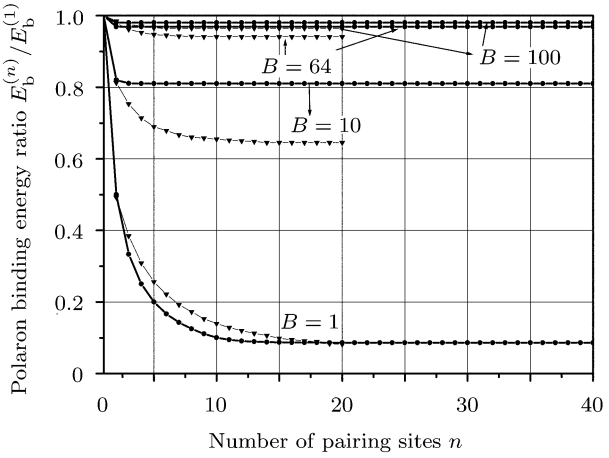


Fig.1. Comparison of polaron binding energy ratio $E_b^{(n)}/E_b^{(1)}$ as a function of the number of basic pairs n from our calculation with that from Ref.[12], under different charge–lattice coupling strengths.

We see that the system energy has almost no change with the base pairing site number n when the number of sites is larger than 10, illustrating that system energy is stable and saturated in the situation with sizes of DNA chain $n > 10$. The stronger the charge–lattice coupling is, the more stable the energy is, suggesting that the width of polaron is narrower. Calculations of hundreds sites can also be performed easily. A comparison between our calculation and recent result work in Ref.[15] is also shown in Fig.1 as shown in inverted triangle curves. We can see that our calculations not only are in agreement with those in Ref.[15], but also show a significant improvement. Based on Eqs.(5) and (6), we obtain an energy of 0.29 eV for the polaron formation, nearly independent of chain size, and the activation energy for polaron hopping can be estimated at about 0.14 eV, consistent with the available experimental value.[5]

Figure 2 demonstrates the results of three types of energies: the hopping energy, phonon energy and interacting energy between the charge and the lattice, and the total energy of the system as a function of charge–lattice coupling strength B. An interesting characteristic can be found that each curve of the three energies has a clear turning point, but the curve of their summation, i.e. their total energy, has not such a point. In other words, we cannot observe an abrupt change in the total energy curve. It implies that some intrinsic properties may hide in the macrocosm consequence of the system, which is possibly due to the collective contribution of charges, lattice imperfections and their interaction in a Holstein Hamiltonian described system.

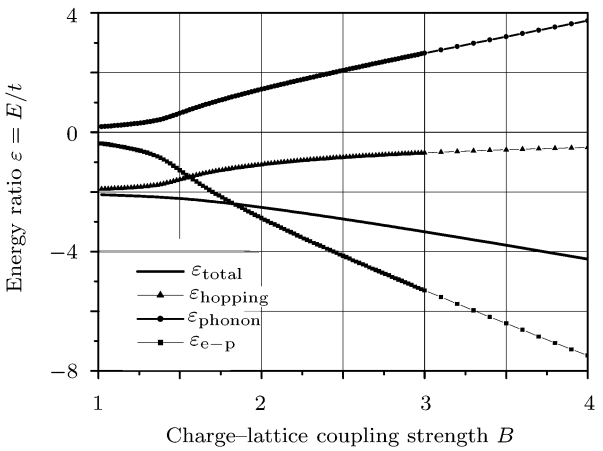


Fig.2. The energy ratio $\epsilon = E/t$ against coupling strength B. Here $\epsilon_{\rm phonon}$ is phonon energy, $\epsilon_{\rm hopping}$ is the hopping energy, $\epsilon_{\rm e-p}$ is electron–phonon interaction energy, and $\epsilon_{\rm total}$ is total energy of the system.

Figure 3 shows the profile of polaron wavefunc-

tions ϕ_n (the probability amplitude for the charge carrier) varying with site number n at different coupling strengths. The very narrow and sharp peak curve of wavefunction ϕ_n corresponds to the stronger charge–lattice coupling constant B. The curve will become broadened when the charge–lattice coupling strength is taken as small values. It is also indicated that the probability amplitude of polaron is still stable when the pair site number n becomes large enough. This means that the polaron formed in such a DNA system is related to the competition between the charge transfer and the charge–lattice coupling strength in a DNA chain. This fact may provide the physical explanation to the results in Fig.2.

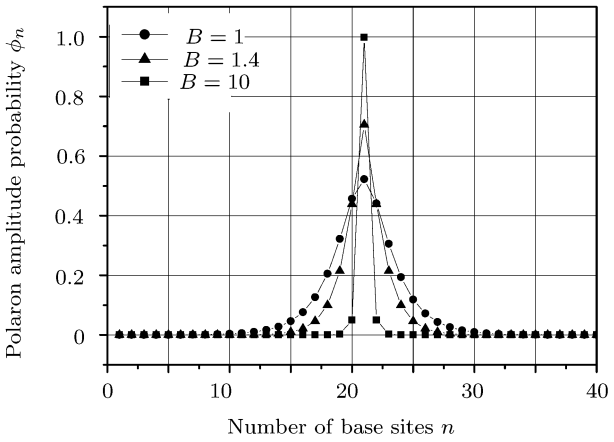


Fig.3. The probability amplitude of charge carrier ϕ_n as a function of the number of basic pairs n at different charge–lattice coupling strengths B.

The next important step is to make a continuous transformation on Eq.(5). Considering that the interval between any two nearest sites approaches zero, we thus have $\phi_{k+1} + \phi_{k-1} \longrightarrow \partial^2\phi/\partial x^2 + 2\phi$, and Eq.(5) then becomes

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} + (2 + \epsilon - W)\phi + B\phi^3 = 0, \tag{7}$$

where $W = \frac{B}{2}\int_{-\infty}^{\infty}\phi(x)^4\mathrm{d}x$. Equation (7) is a typical well-known nonlinear Schrödinger equation. It has an exact soliton solution

$$\phi = A\mathrm{sech}[\mu x], \tag{8}$$

where the coefficients A and μ in wavefunction (8) can be determined from nonlinear equation (7) and the normalized condition $\int\phi(x)^2\mathrm{d}x = 1$ to be $A = \sqrt{-(2 + \epsilon - W)/B}$ and $\mu = \sqrt{-(2 + \epsilon - W)}$, respectively. Finally, the system energy can be given by

$$E = -\Big(2 - \frac{B}{12} + \frac{B^2}{16}\Big)t. \tag{9}$$

A comparison between discrete and continuous considerations made based on the present theory is given by studying the profile of total energy E as a function of number of pairing sites n at different charge–lattice coupling strengths ($B = 3.52$ for $t = 0.12$ eV and $g = 0.6$ eV/Å; $B = 2.47$ for $t = 0.16$ eV and $g = 0.58$ eV/Å; and $B = 2.30$ for $t = 0.23$ eV and $g = 0.67$ eV/Å, where ω is taken as 0.85 eV/Å^2[18]) as plotted in Fig.4.

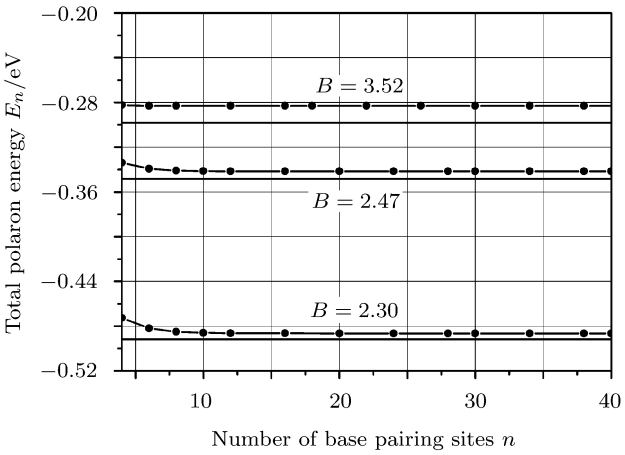


Fig.4. Comparison of discrete and continuous calculations of polaron energy versus the number of base pairs n. The dotted lines are for the results of discrete calculation and the black lines for continuous one.

It indicates that the system energies in the two cases are almost the same when the site number exceeds 10, and there shows a slight difference between the energy values when charge–lattice coupling strength B is comparatively large, and the energy from the continuous calculation is lower than that from the discrete calculation. The calculated energies in the two cases are in agreement with each other in the range of intermediate charge–lattice coupling constant, but show an obvious discrepancy in the larger B regime. This conclusion is within our anticipation, because, when the charge–lattice coupling constant is large, the width of the polaron becomes narrow and the continuous approximation holds true. These results are in agreement with recent results quantitatively.[27−29] This illustrates that the approximation of continuous transformation can work well in the range from weak to intermediate charge–lattice coupling strengths.

It should be noted that the solution (8) of Eq.(7) appeared also in the pioneer work of Holstein.[21−24] However, his deriving process was based on several assumptions and quite different from the starting point

of the present paper. Here the Eq.(7) is derived directly from the trial wavefunction (2), and the soliton solution (8) is deduced from nonlinear equation (7).

4. Conclusions

We use variational method to study the quantized Holstein small polaron model in discrete and continuous treatments for the possible application in describing the charge transfer behaviour in a dry DNA chain. The extended Holstein small polaron model is studied based on complete quantization, which is different from the studies in the recent papers. The combination of our trial wavefunction with the variational method can be used successfully to study the quasi-one-dimensional molecular chain with many lattice sites. Our calculation of binding-energy as a function of base site number has a clear improvement compared with the recent result in Ref.[12]. The obtained analytical soliton-like solution illustrates that the charge transfer in a quasi-one-dimensional chain exhibits a nonlinear behaviour. It is in coincidence with the results in Ref.[24,30]. The continuous theory provides a basic understanding, in physics, of the charge transfer phenomena in a long-range DNA chain. The coincident results of discrete and continuous treatments imply that we can use the continuous theory to predict more physical problems about charge transfer in a double helix structure DNA chain. A detailed investigation on influence of trapping potential of GG and GGG guanine sequences in the DNA chain will appear in another paper.

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