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Self-trapping versus trapping: Application to hole transport in DNA

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We address the problem of interplay between self-trapping effects and effects of an external potential, which may be relevant for many physical systems, such as polarons in solids or a Bose-Einstein condensate with attraction. If the potential consists of two different wells, the system initially localized in the shallower well may relax into the deeper well, or may not if stabilized by the self-trapping effect. We show how this picture can be applied to interpret results of recent experiments on electron transfer in the DNA molecule [Giese *et al.*, Nature **412**, 318 (2001)]. The results of our calculations agree well with the experimental findings, giving evidence that hole transport in DNA involves polaronic effects.

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I. INTRODUCTION

The phenomenon of self trapping (ST) is well known in many fields of physics. It is often mentioned when one deals with charge carriers or excitons in solids, which interact with the crystal lattice. Bose-Einstein condensate (BEC) with attraction between constituting particles may also be considered a system with ST.

One of the aspects of this phenomenon is the interplay between the effect of interactions responsible for ST, and the effect of an external potential applied to the system (confinement, external field, or impurity potential). One example of this is polaron formation in the presence of an impurity. Depending on the dimensionality of the system, its parameters, and the type of the impurity, the electronic state may shrink into a small polaron, or form a finite-radius polaron [1]. Another example is BEC with attraction in a magnetic trap, where the confining potential may prevent the cloud from collapsing [2].

A specific motivation for studying this problem is experiments on charge transport along a DNA molecule. 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), having different ionization potentials. Thus, if one removes an electron from the chain, the resulting hole feels the on-site potentials $V_G < V_A < V_C < V_T$. The overlap of electronic π orbitals of the neighboring bases tends to delocalize the carrier along the chain [3,4]. The dependence of this overlap on the interbase distance couples the hole motion to the lattice displacements, which in one-dimensional systems leads to the carrier ST [5]. Thus, one may hope to describe a charge on the DNA chain analogously to polarons in conducting polymers [4].

There is a large body of work in which transport of holes in DNA has been studied by monitoring their progress between different traps on the chain ([6] and references therein). A single guanine on a chain consisting only of adenines acts as a trap since $V_G < V_A$; two adjacent guanines represent then a different trap with a deeper level, etc. It was found that when two traps are connected by a long bridge sequence of A's, after a hole tunnels through the first 3 A's it moves through many later A's with essentially no further attenuation [6]. Several mechanisms have been proposed for hole transport through the bridge: incoherent hopping [7], fluctuation-induced hopping [8], and bandlike transport [9]. In the present paper, we show how the experimental results of Ref. [6] can be interpreted in the polaron model of Ref. [4].

This brings us into the general framework discussed in the beginning: if the polaron picture is relevant for DNA, hole transfer is a result of the competition between the effect of the trapping potential of guanines and the self-trapping effect due to the interaction with lattice. The former provides the driving force for the hole transfer from a single G trap to the deeper GGG trap, while the latter tends to keep the carrier where it is, i.e. on the single G. In this context one may ask several questions. When will the hole relax from a shallower trap (G) to a deeper trap (GG or GGG), and when will the shallower-trap state be stabilized by ST? What is the characteristic energy of this stabilization?

The same questions may be relevant for a completely different physical system, such as BEC in a double-well trapping potential. This system was studied in the context of phase coherence effects between the two condensates [10], but we are not aware of any work analyzing the stability of stationary states in different wells in the presence of an energy relaxation mechanism.

The arguments we give below are of quite general character, as long as systems whose stationary states are described by the stationary nonlinear Schrödinger equation with external potential, or a similar one, are considered. Important is that we will always remain at the level of classical field equations, neglecting the quantum nature of the crystal lattice vibrations (which is justified if the phonon frequency is small) or quantum corrections to the Gross-Pitaevski equation for the condensate wave function.

Focusing on stationary states, we do not address kinetic problems, like dc conductivity in DNA. Kinetics is strongly dependent on fluctuations and dissipation present in the system. For polymers and especially for DNA these processes are complex and different for different experimental condi-

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tions. One of the goals of the present paper is to get some insight into the behavior of the system regardless of the specific nature of fluctuations and dissipation.

II. GENERAL PICTURE

The phenomenon of self-trapping may occur when a charge carrier (an excess electron in the conduction band or a hole in the valence band) interacts with a deformable medium (crystal lattice). The charge polarizes the medium whose deformation, in turn, results in an effective potential acting on the charge, the total energy of the system being lower than for a free (delocalized) state; the carrier ‘‘digs’’ a well for itself. The interaction can often be formally described by an effective potential $v(\mathbf{r})$ acting on the carrier. This potential is produced by the deformable medium and it depends on the medium (lattice) degrees of freedom.

For simplicity we assume to be in one dimension. Considering states with only one carrier, we describe the carrier by the wave function $\psi(x,t)$. Assuming the lattice to be heavy, we treat the corresponding degrees of freedom classically. This leads to the Schrödinger equation for the particle wave function

$$i\hbar\frac{\partial\psi}{\partial t}=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)+v(x,t)\right]\psi. \tag{1}$$

Here, m is the carrier (effective) mass, $V(x)$ is an external potential acting on the carrier (e.g., due to traps, impurities, external electric field, etc.), and $v(x,t)$ is the effective potential due to the lattice. To determine the dynamics of the coupled system, in addition to Eq. (1) one should supply the equations of motion for the lattice degrees of freedom, which determine the behavior of the potential $v(x,t)$. The arguments we give below are quite general, but in order to make the algebra as simple and illustrative as possible we consider equations for acoustic phonons with the sound velocity c [11]

$$\frac{1}{c^2}\frac{\partial^2 u}{\partial t^2}=\frac{\partial^2 u}{\partial x^2}+\gamma\frac{\partial}{\partial x}|\psi|^2, \tag{2}$$

where $u(x,t)$ is the field of the lattice displacements, γ is the electron-phonon coupling constant, and the lattice potential is related to the displacements by $v(x)=\gamma\partial u/\partial x$ (deformation potential). The Lagrangian corresponding to these equations is given by

$$L=\int\left[\frac{i\hbar}{2}(\psi^*\dot{\psi}-\dot{\psi}^*\psi)-V(x)\psi^*\psi-\gamma\psi^*\psi\frac{\partial u}{\partial x}+\frac{\dot{u}^2}{2c^2}\right.$$
$$\left.-\frac{1}{2}\left(\frac{\partial u}{\partial x}\right)^2\right]dx. \tag{3}$$

Consider stationary solutions of Eqs. (1) and (2)

$$\psi(x,t)=\psi(x)e^{-i(\epsilon/\hbar)t},\quad u(x,t)=u(x),$$

where ϵ is the electronic energy and $\psi(x)$ may be considered real without loss of generality. Using the equation of motion for the lattice degrees of freedom, one can eliminate the latter. Namely, from Eq. (2) we obtain that in a stationary state the displacement $u(x)$ can be expressed in terms of the hole wave function as

$$\frac{\partial u}{\partial x}=-\gamma|\psi(x)|^2. \tag{4}$$

The total energy of the stationary state can be formally obtained from the Lagrangian (3) and can be expressed in terms of $\psi(x)$

$$E[\psi]=\int\left[\frac{\hbar^2}{2m}\left(\frac{\partial\psi}{\partial x}\right)^2+V(x)\psi^2-\gamma^2\psi^4\right]dx, \tag{5}$$

where the last term represents the additional energy of the system due to the interaction of the carrier with the medium. Minimizing $E[\psi]$ with respect to $\psi(x)$ one obtains the equation for the wave function of the stationary polaron.

The energy functional (5) coincides also with that for BEC with attraction. Choosing the appropriate units for the energy, we write it in a generic form

$$E[\psi]=\int\left[\left(\frac{\partial\psi}{\partial x}\right)^2+V(x)\psi^2-\frac{g}{2}\psi^4\right]dx, \tag{6}$$

where all the quantities are dimensionless and g is the nonlinear coupling constant. For BEC, one usually normalizes the wave function to the total number of particles, here we prefer to keep the normalization to unity

$$\int\psi^2(x)dx=1, \tag{7}$$

relevant for polarons. Changing the normalization of ψ corresponds to simple rescaling of g.

Suppose that the potential $V(x)$ consists of two different potential wells, and for each well there is a stationary state with the wave function localized around the well. The deeper of these two states represents the ground state of the system, the shallower one is an excited state. It is convenient to interpret this picture geometrically, viewing each wave function $\psi(x)$ as a point in the functional space. Then the ground state of the system is the global minimum of the functional $E[\psi]$ in this space, while the excited state may be either a local minimum or an unstable stationary point. If the dynamics of the system is governed only by the equations of motion considered above, the system can remain in the excited state forever. However, if one includes fluctuations and dissipation, the character of the excited state becomes very important. For a local minimum small perturbations will not drive the system out of the vicinity of the stationary point (i.e., the particle stays in the shallow well), while in the case of an unstable point dissipation may make the system fall into the global minimum (i.e., the particle moves to the deep well).

Thus, the first question we ask ourselves is whether a stationary point $\psi_0(x)$ of the functional (6) is stable or not. The wave function satisfies the stationary nonlinear Schrödinger equation

$$\frac{1}{2}\frac{\delta E}{\delta\psi}=\left[-\frac{\partial^2}{\partial x^2}+V-g\psi_0^2\right]\psi_0=\epsilon_0\psi_0. \tag{8}$$

The Lagrange multiplier ϵ_0 takes care of the constraint (7) and corresponds to the electronic energy for polarons and the single-particle energy (chemical potential) for BEC. Around the stationary point the energy functional (6) may be expanded to the second order as

$$E[\psi]\approx E[\psi_0]+\int\left[\frac{1}{2}\frac{\delta^2 E}{\delta\psi(x)\delta\psi(x')}-\epsilon_0\right]\times\delta\psi(x)\delta\psi(x')dx\,dx', \tag{9}$$

where the derivative is taken at the point ψ_0, and the variation $\delta\psi$ is orthogonal to ψ_0 (see the Appendix for details). When dealing with the quadratic form (9) $\delta\psi$ can be treated as a vector in the linear space orthogonal to ψ_0. If for some direction $|\delta\psi\rangle\perp|\psi_0\rangle$ the quadratic form is negative, the stationary point is unstable [12]. The vector minimizing the quadratic form (the "worst" fluctuation) must be an eigenvector of the corresponding matrix

$$\mathcal{H}|\delta\psi\rangle=\delta\epsilon|\delta\psi\rangle+\lambda|\psi_0\rangle, \tag{10}$$

where $\mathcal{H}$ is the linear operator whose kernel is given by the square bracket in Eq. (9)

$$\mathcal{H}_x=[-\nabla^2+V(x)-3g\psi_0^2(x)-\epsilon_0], \tag{11}$$

$\delta\epsilon$ is the corresponding eigenvalue, and $\lambda|\psi_0\rangle$ is an arbitrary vector parallel to $|\psi_0\rangle$, which is cancelled when Eq. (10) is projected on the subspace orthogonal to $|\psi_0\rangle$. From Eq. (10) the condition for the eigenvalues $\delta\epsilon$ follows:

$$\langle\psi_0|(\mathcal{H}-\delta\epsilon)^{-1}|\psi_0\rangle=0. \tag{12}$$

If the smallest eigenvalue $\delta\epsilon_{min}<0$, then the stationary point is unstable. The corresponding eigenvector determines the direction of the "worst" fluctuation

$$|\delta\psi\rangle=(\mathcal{H}-\delta\epsilon_{min})^{-1}|\psi_0\rangle. \tag{13}$$

Applied to the case of the two traps, this criterion means that the state in the shallower well may be stabilized, if the ST potential $-3g\psi_0^2$ manages to "deepen" the shallow well sufficiently. Note that conceptually the same picture describes the stabilization of a finite-radius polaron in a three-dimensional (3D) solid by an impurity potential [1], which prevents it from shrinking into a small polaron, or the stabilization of BEC with attraction by the trap potential [2], which would collapse in free space. In the latter case, the excitation $\delta\psi$ with the energy $\delta\epsilon_{min}$ approaching zero at the onset of the collapse, is the breathing mode [13]. Note also that for the translationally invariant case $V(x)=0$ one can differentiate Eq. (8) with respect to x to see that the function

$$\delta\psi\propto\frac{\partial\psi_0}{\partial x}\perp\psi_0$$

satisfies Eq. (10) with zero eigenvalue $\delta\epsilon=0$ (an analog of neutral equilibrium in mechanics). This solution corresponds to spatial translation of the polaron [14], which apparently costs no energy.

III. APPLICATION TO DNA

Now we apply the above considerations to a polymer chain with one excess hole (for DNA we assume that the hole is confined to one strand). The electronic wave functions on adjacent bases overlap, which leads to nonzero values of the hole transfer integrals $t_{n+1,n}$ between the sites $n+1$ and n (the off-diagonal elements of the hole Hamiltonian). This overlap is affected by various motions of the bases. The vibrational degrees of freedom that couple efficiently to the transfer integral are the relative base pair displacements along the stack $u_{n+1}-u_n$ (lattice strain) and the relative twist angles $\theta_{n+1}-\theta_n$ [15]. However, the base displacements u_n and the twist angles θ_n are not independent of each other, since rigidity of the sugar-phosphate backbone imposes a constraint that relates them [16]. Hence, we consider only the dependence $t_{n+1,n}(u_{n+1}-u_n)$ which has the sense of an effective coupling. Assuming that the displacements are small, we approximate this dependence by a linear one,

$$t_{n+1,n}(u_{n+1}-u_n)=t_0-\alpha(u_{n+1}-u_n), \tag{14}$$

where t_0 is the transfer integral for zero displacements and α is the effective coupling constant. The calculation is simplified by assuming t_0 and α to be the same for all neighboring bases. The assumptions made above lead us to the Su-Schrieffer-Heeger (SSH) Hamiltonian [17] for an undimerized chain

$$H=\sum_n V_n\psi_n^*\psi_n-\sum_n[t_0-\alpha(u_{n+1}-u_n)](\psi_n^*\psi_{n+1}+\psi_{n+1}^*\psi_n)+\sum_n\left[\frac{p_n^2}{2M}+\frac{K}{2}(u_{n+1}-u_n)^2\right], \tag{15}$$

where ψ_n is the hole wave function, V_n is the on-site trapping potential (determined by the ionization potential of the nth base), p_n is the momentum conjugate to the displacement u_n, and M and K are the mass and the elastic constant associated with the vibrations considered. Application of this Hamiltonian to DNA was discussed in detail in Ref. [4].

This Hamiltonian yields the following equations of motion for the hole wave function $\psi_n(t)$ and the lattice displacements $u_n(t)$:

$$i\hbar\dot{\psi}_n=V_n\psi_n-[t_0-\alpha(u_{n+1}-u_n)]\psi_{n+1}-[t_0-\alpha(u_n-u_{n-1})]\psi_{n-1}, \tag{16}$$

$$M\ddot{u}_n=K(u_{n+1}-2u_n+u_{n-1})+\alpha[-\psi_{n+1}^*\psi_n+\psi_n^*\psi_{n-1}+\text{c.c.}], \tag{17}$$

where "c. c." stands for the complex conjugate.

Considering stationary solutions

$$\psi_n(t)=\psi_n e^{-i(\epsilon/\hbar)t}, \quad u_n(t)=u_n,$$

we eliminate the strain using Eq. (17),

$$u_{n+1}-u_n=\frac{2\alpha}{K}\psi_{n+1}\psi_n, \tag{18}$$

which is an analog of Eq. (4). Substituting u_n into the Hamiltonian (15), instead of the functional (6) we obtain the energy functional for DNA

$$E[\psi_n]=2+\sum_n\left[V_n\psi_n^2-2\psi_n\psi_{n+1}-\frac{g}{2}\psi_n^2\psi_{n+1}^2\right]. \tag{19}$$

Here, energy is measured in units of the transfer integral t_0, while the dimensionless coupling constant g is expressed in terms of the electron-lattice coupling constant α and the lattice elastic constant K as $g=4\alpha^2/(Kt_0)$. The constant two is added to choose the zero energy to be the extremum of the free valence band in an undistorted chain with $V_n=0$, because we are dealing with holes.

In the experiment of Ref. [6] there were two traps of one and three guanines, respectively, separated by a sequence of l adenines. We model them by shifting down V_n for $n=0,l+1,l+2,l+3$ by an amount Δ (the difference between the ionization potentials of A and G). For each trap there is a bound state corresponding to a stationary point of the functional (19) in our model. Obviously, the energy is lower in the second trap (GGG), corresponding to the global energy minimum. As explained in the previous section, the bound state in the first trap (single G) may correspond to a local minimum of the functional (19) or it may be an unstable stationary point. In the latter case at least one fluctuation should have negative excitation energy. This is the first thing we are going to analyze.

When the state in the single G trap is stable (a local energy minimum), another important question arises. If the shallow state is stable, how high is the energy barrier separating the two minima of the energy in the phase space, or in other words, what is the minimal energy cost of a fluctuation that can move the system from one stationary state to the other? Strictly speaking, we should return to the full phase space considering the energy as a function of ψ_n, ψ_n^*, u_n, and p_n. However, it is clear that the energetically "cheapest" path should be quasistatic: the system should not "spend" energy received from the thermal bath on kinetic energy. Next, the highest point of the "cheapest" path must necessarily be a saddle point of the full energy functional, and Eq. (18) holds in saddle points. Therefore, it is sufficient to consider just the energy functional (19) instead of the full Hamiltonian (15). Thus, our second task will be to find and compare saddle points of the energy functional (19).

Intuitively, for sufficiently large bridge length l (such that the two states overlap weakly) one can imagine two possible trajectories of the relaxation. One corresponds to the hole jumping out of the first trap, traveling across the bridge, and falling into the second trap. Obviously, such a pathway will always "cost" some energy $\sim\Delta$, thus we do not expect it to cause instability. Still, in the stable situation, the highest point of this trajectory may be the lowest saddle point. Another possible pathway is to tunnel to the second trap through the exponential tail of the wave function, when first a small "fraction" of the hole appears in the second trap, then it grows with time until all of the wave function leaks into the second trap, the value of the wave function on the bridge being always small.

The values of microscopic parameters for charge carriers in DNA have not been agreed upon by the community yet. We use the values $t_0\approx 0.2$ eV, $\alpha\approx 0.4$ eV/Å, and $K\approx 0.85$ eV/Å^2, which allowed us to reproduce the experimental results of Ref. [18] for the differences in energies of the hole stationary states in different traps [19]. These values correspond to a coupling constant g in Eq. (19) of about four. For $g=4$, the energy of the static self-localized polaron state on a chain without traps (or on a very long bridge) is $\epsilon=-0.60$ (purely electronic energy), $E=-0.23$ (total energy), measured in units of t_0. The length determining the exponential tail of the wave function is of the order of the lattice constant (the polaron wave function extends over a few lattice sites), so discreteness of the model is essential for this value of g. The largest lattice strain $u_{n+1}-u_n$ is in the center of the polaron and for these parameters it is about 0.25 Å, which is much smaller than the lattice constant in DNA (3.4 Å). The corresponding change in the transfer integral $\alpha(u_{n+1}-u_n)$ is about half t_0; in the rest of the polaron it is smaller. Although using the linearized dependence (14) formally introduces some error, we believe, however, that this error is less significant than the indeterminacy in the parameters for DNA. The values of the ionization potentials for G and A are not known precisely. Several numbers were reported so far for their difference, varying in the range 0.2–0.5 eV; this corresponds to $\Delta\sim 1-2$. In Ref. [18] we could reporoduce the experimental results of Ref. [19] using $\Delta\approx 1$. In the absence of information about the precise value of Δ we consider it a parameter and analyze the situation for different values of l and Δ.

The state in the first trap becomes unstable at sufficiently large Δ, when the effect of the trap potential overcomes the ST. The stability analysis following the procedure described in the previous section shows that the critical value of the potential is $\Delta_{inst}\approx 2.1$ (which corresponds to ≈ 0.4 eV for our choice of t_0), and is almost independent of l. The wave function of the unstable direction $\delta\psi_n$ corresponds to tunneling: it has a negative peak at the position of the first trap (a "fraction" of the particle is removed), a positive peak at the position of the second trap (a "fraction" of the particle is added), and it is negligible on the bridge. Only at $l=3$ the critical value of Δ becomes $\Delta_{inst}\approx 1.8$, while for $l=2$ the first trap state is unstable for any Δ.

The fact that the critical value Δ_{inst} is independent of l for large l may seem counter-intuitive. Note, however, that even for a very large separation, displacing an infinitesimal fraction of the polaron from the first to the second trap may be energetically advantageous if the second trap is deep enough. What does depend on l is the characteristic time in which the instability develops and most of the wave function leaks into the deeper trap. This time is determined by the tail of the

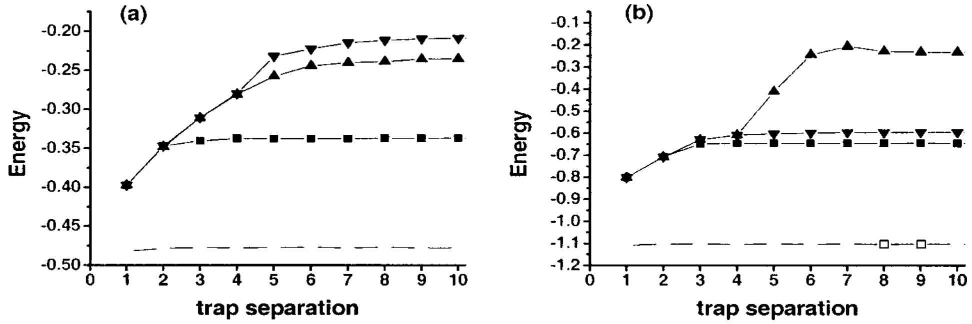

FIG. 1. The energies of the stationary points corresponding to the states in the shallow and the deep trap (solid and open squares, respectively) and of the saddle points corresponding to tunneling and propagation across the bridge (down and up triangles, respectively) versus the trap separation l for $g=4$, $\Delta=0.3$ (a); and $\Delta=1.0$ (b).

wave function, and thus grows exponentially with l, in agreement with the Marcus-Levich-Jortner relation for the tunneling rate [7].

For $\Delta<\Delta_{inst}$ the shallow trap state is stable, and even tunneling requires some activation energy. It is interesting to compare the two trajectories connecting the two stationary states (tunneling and propagation across the bridge, as mentioned above). We look for saddle points of the functional (19) numerically minimizing $\Sigma_n(\partial E/\partial\psi_n)^2$, and establish their character looking at the shape of the wave function corresponding to each point. We find that for Δ smaller than some value Δ_{tun} the on-bridge saddle point has lower energy. For $l>4$ $\Delta_{tun}\approx 0.42$ and is independent of l. At $l=4$ and smaller the two saddle points actually merge, the character of the single saddle point at $l=3,4$ and of the unstable direction at $l=1,2$ being tunnelinglike, since the corresponding wave functions have two maxima at the positions of the traps. These results are illustrated by Fig. 1, where we plot the energies of the stationary states in the two traps and the energies of the two saddle points as functions of l for $\Delta=0.3$ and $\Delta=1.0$.

We see that the typical energy difference between the stationary state in the first trap and the lowest saddle point is $\delta E\sim 0.1$, which for $t_0\approx 0.2$ eV is of the order of room temperature. This means that the probability to reach the saddle point should not be suppressed by the thermal exponential factor. However, besides the latter, this probability is determined by the statistical weight, or the width of the corresponding valley of the energy surface in the system phase space, and the availability of fluctuations capable of bringing the system there. Due to complexity of the system, it is difficult to say anything quantitative about this, but intuitively it is clear that even when the tunneling saddle point has a lower energy, it may be hardly reachable if the separation l is large. Thus, comparing the energies of the two saddle points does not yield the final conclusion, which one the system would actually prefer. Of course, when only the tunneling saddle point is available, the system has no choice.

The value of l at which the two saddle points merge can be related to the polaron size in a simple way: a polaron can exist on the bridge as long as the bridge length is larger than, or at least comparable to, the characteristic polaron size. For a short bridge the wave function is concentrated around one of the traps (for the bound states) or both of them (for the tunneling saddle point). This also explains why we have not found any significant dependence of the critical bridge length on the trap depth. Our results for the critical bridge length agree reasonably well with the experimental findings of Ref. [6], where the switching between the two transition mechanisms was observed at $l=3$. The smaller experimental value (for $g=4$ our calculations gave $l=4$) suggests that the coupling constant g should be larger than we assumed. Indeed, we find agreement with the experiment for $g\approx 5.2$. This supports the idea of a polaron mechanism of charge transport along a DNA chain made of the same base [20] versus the hopping mechanism [7].

In our model of DNA we have considered hole self trapping due to interaction with vibrations only. In principle, other polarizable degrees of freedom may also contribute to this effect. As the experiments of Ref. [6] were performed in a water solution of NaCl, a possible candidate is interaction of the hole with the polar solvent (water) and ions (Na^+, Cl^-) present in the solution, leading to additional fourth-order terms in the energy functional (19). Our estimates [21] have shown that they can affect polaron energetics substantially (increasing the binding energy), but at the same time, the shape of the polaron is not strongly changed. This means that the calculated critical bridge length is not expected to change much either and the agreement of our results with experiment should be preserved.

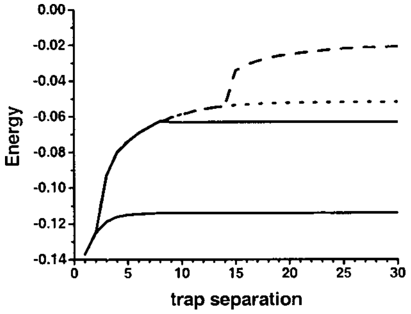

FIG. 2. The energies of the stationary points corresponding to the states in the shallow and the deep trap (upper- and lower-solid lines, respectively) and of the saddle points corresponding to tunneling and propagation across the bridge (dotted and dashed lines, respectively) versus the trap separation l for $g=1$ and $\Delta=0.15$.

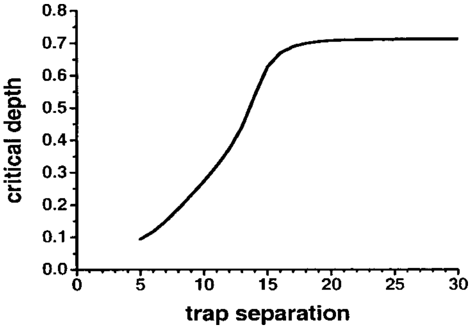

FIG. 3. The critical trap depth at which the stationary state in the smaller trap becomes unstable as a function of the trap separation l for $g=1$.

Smaller values of the coupling constant g can also be of interest, as they are relevant for conjugated polymers, where large polarons are the predominant excitations (in polymers with nondegenerate ground state) [22]. Traps may be due to interaction with the local environment, chain distortion, etc. For $g=1$, representative of many conjugated polymers, the continuum approximation works already quite well (if the traps are not very deep), and the corresponding energy functional is given by Eq. (6), which is the continuum limit of Eq. (19). Looking at the functional (6), one may note that changing g is equivalent to a rescaling of energies and lengths. Roughly speaking (because for $g=4$ the continuum approximation does not work well), we may expect that passing to $g=1$ should decrease the characteristic energies by a factor of four, and stretch the characteristic lengths by a factor of two. This can be seen in Fig. 2, which is the analog of Fig. 1 for $g=1$ and $\Delta=0.25$. The energies of the two saddle points for $l>14$ interchange at $\Delta_{tun}\approx 0.11$; for $l\leqslant 14$ the points merge. The dependence of the critical value Δ_{inst} on l is plotted in Fig. 3.

IV. CONCLUSIONS

In conclusion, we have considered a polaron on a polymer chain containing two different traps. In the presence of a relaxation mechanism the polaron, initially localized near the shallower trap, may fall into the deeper trap. On the other hand, the state in the shallower trap may be stabilized by ST. The conditions of stability of the shallow-trap state were analyzed in the present paper.

When the shallow state is stable, it may be viewed as separated by a barrier in the system configuration space from the deep state. The energy necessary for the system to relax into the deep state (to be supplied by thermal fluctuations), is determined by the lowest saddle point on the energy surface in the configuration space connecting the two energy minima corresponding to the two states. Two relevant saddle points correspond (i) to the polaron jumping out of the first trap and traveling as a whole across the bridge into the second trap, and (ii) to the tunneling between the traps. Comparison of our results from the SSH model for DNA to the experimental results gives evidence for relevance of the polaron mechanism for charge transport in DNA.

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APPENDIX

Here we discuss the details of derivation of Eq. (9). The goal is to obtain the expansion of the functional (6) in the vicinity of the stationary point ψ_0 to the second order. The situation is not straightforward because ψ is subject to the constraint (7), which defines a hypersphere in the functional space. The sphere is a curved space, and this curvature should be taken care of when considering the second-order terms of the expansion. It is convenient to consider a hyperplane tangent to the hypersphere at the point ψ_0 and defined by $(\psi-\psi_0)\perp\psi_0$. Points of this hyperplane can be represented as $\psi_0+\delta\psi$, where $\delta\psi$ spans a linear subspace $\delta\psi\perp\psi_0$. Then $\delta\psi$ can be used to label points on the sphere in the vicinity of ψ_0, thus serving as local coordinates on the sphere. The natural mapping is just the orthogonal projection on the plane. A point ψ on the hypersphere whose projection on the hyperplane is $\psi_0+\delta\psi$, is given by

$$\psi(x)=\left[1-\frac{1}{2}\int|\delta\psi(x')|^2dx'\right]\psi_0(x)+\delta\psi(x) \tag{A1}$$

to the second order in $\delta\psi$. Generally, the energy functional in the vicinity of ψ_0 can be approximated to the second order in $\psi-\psi_0$ as

$$\begin{aligned}E[\psi]\approx E[\psi_0]&+\int\frac{\delta E}{\delta\psi(x)}[\psi(x)-\psi_0(x)]dx\\&+\frac{1}{2}\int\frac{\delta^2E}{\delta\psi(x)\,\delta\psi(x')}[\psi(x)-\psi_0(x)]\\&\times[\psi(x')-\psi_0(x')]dx\,dx'.\end{aligned} \tag{A2}$$

Now, restricting ourselves to points on the hypersphere, expressing ψ in terms of $\delta\psi$ from Eq. (A1), and using the fact that $\delta E/\delta\psi=2\epsilon_0\psi_0$ [Eq. (8)], we arrive at Eq. (9). As $\delta\psi$ lies in a linear space, the expression (9) can be treated as a quadratic form and the linear eigenvalue problem can be posed.

[1] D. Emin and T. Holstein, Phys. Rev. Lett. **36**, 323 (1976).
[2] Yu. Kagan, G. V. Shlyapnikov, and J. T. M. Walraven, Phys. Rev. Lett. **76**, 2670 (1996).
[3] G. B. Schuster, Acc. Chem. Res. **33**, 253 (2000).
[4] E. M. Conwell and S. V. Rakhmanova, Proc. Natl. Acad. Sci. U.S.A. **97**, 4556 (2000).
[5] D. Emin, Phys. Rev. B **33**, 3973 (1986).
[6] B. Giese, J. Amaudrut, A.-K. Köhler, M. Spormann, and S.

Wessely, Nature (London) **412**, 318 (2001).

[7] M. Bixon, B. Giese, S. Wessely, T. Langenbacher, M. E. Michel-Beyerle, and J. Jortner, Proc. Natl. Acad. Sci. U.S.A. **96**, 11 713 (1999).

[8] R. Bruinsma, G. Grüner, M. R. D'Orsogna, and J. Rudnick, Phys. Rev. Lett. **85**, 4393 (2000).

[9] F. C. Grozema, Yu. A. Berlin, and L. D. A. Siebbeles, J. Am. Chem. Soc. **122**, 10 903 (2000).

[10] G. J. Milburn, J. Corney, E. M. Wright, and D. F. Walls, Phys. Rev. A **55**, 4318 (1997).

[11] A. S. Davydov, *Solitons in Molecular Systems* (Kluwer Academic Publishers, Dordrecht, 1991).

[12] Strictly speaking, when considering polarons, one has to consider the full configurational space of the system which includes the lattice degrees of freedom changing independently of $\psi(x)$. In principle, there could be unstable directions corresponding to a certain change of the lattice configuration not allowed by the condition (4). However, this turns out not to be the case: it can be shown that none of the independent fluctuations of the lattice $\delta u(x)$ can lead to an instability. Formally speaking, the full quadratic form [analogous to Eq. (9)] turns out to be positive definite on independent vectors δu. Physically, this fact is the consequence of stability of the lattice itself.

[13] R. J. Dodd, M. Edwards, C. J. Williams, C. W. Clark, M. J. Holland, P. A. Ruprecht, and K. Burnett, Phys. Rev. A **54**, 661 (1996).

[14] R. Rajaraman, *Solitons and Instantons: An Introduction to Solitons and Instantons in Quantum Field Theory* (North-Holland, Amsterdam, 1987).

[15] H. Sugiyama and I. Saito, J. Am. Chem. Soc. **118**, 7063 (1996).

[16] S. Cocco and R. Monasson, J. Chem. Phys. **112**, 10 017 (2000).

[17] W. P. Su, J. R. Schriffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[18] F. D. Lewis, X. Li, J. Liu, R. T. Hayes, and M. R. Wasielewski, J. Am. Chem. Soc. **122**, 12 037 (2000).

[19] E. M. Conwell and D. M. Basko, J. Am. Chem. Soc. **123**, 11 441 (2001).

[20] S. V. Rakhmanova and E. M. Conwell, J. Phys. Chem. B **105**, 2056 (2001).

[21] D. M. Basko and E. M. Conwell, Phys. Rev. Lett. **88**, 098102 (2002).

[22] D. K. Campbell, A. R. Bishop, and K. Fesser, Phys. Rev. B **26**, 6862 (1982).