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Finite-temperature two-state small-polaron dynamics: averaged Hamiltonian approach

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Abstract. We study small-polaron self-trapping properties in the two-state molecular crystal model by employing a finite-temperature variational non-adiabatic approach that is an extension to the semiclassical adiabatic Pekar theory. We find two distinct regions in the space of coupling constant versus adiabaticity parameter that are separated by a temperature-dependent critical line. In these regions the response of the lattice to the motion of the particle is quite different. We find conditions that allow for the determination of the character of the motion and the localization transition as a function of the physical parameters of the system and temperature.

1. Introduction

The motion of particles and quasi-particles such as electrons, excitons, etc, that strongly interact with lattice vibrations is typically accompanied by a local lattice distortion of the host [1–9]. The dynamical properties of the resulting polarons are in general quite different from those of the bare quasi-particles. There are two physical parameters that determine the different polaron properties that depend on the bare particle band width: $2J$ (where J is the intersite matrix element), and the maximal phonon energy $\hbar\omega_B$. It is useful to define an 'adiabaticity parameter' $B = 2J/\hbar\omega_B$ in order to discuss the different extreme limits. In the non-adiabatic limit ($B \ll 1$) the lattice distortion follows the particle motion instantaneously, resulting in an effective mass increase and a reduction in the effective tunnelling matrix element. Upon increase in the coupling between the quasi-particle and the lattice vibrations, the tunnelling rate reduces further; the polaron motion then exhibits a transition from the quasi-free propagation in the form of Bloch states (small-polaron band states) to a self-trapped-like state. While being in this state a small polaron can still propagate but in an incoherent fashion, i.e. through uncorrelated jumps between adjacent lattice sites [3–6].

In the adiabatic regime ($B \gg 1$) the lattice distortion has a large inertia and it fails to follow the particle motion; it forms an essentially static potential well where the particle may be trapped. Depending on the value of the coupling constant, the spatial extent of the lattice distortion may vary from being spread over few sites (weak-coupling limit) to being localized on only a single site (adiabatic small polaron) [3–8].

In the large number of studies of the polaron problem, different types of approach have been used for treating the vibrational degrees of freedom [1–9]. The two extreme cases of non-adiabatic and adiabatic conditions are well understood through the specific

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approximate techniques. In the former case, one applies a unitary transformation that partially diagonalizes the original Hamiltonian while the subsequent treatment is done through a perturbation expansion in the small parameter B [4–6]. In the adiabatic limit, on the other hand, the phonon system is effectively classical and one can apply the semiclassical variational method of Landau and Pekar [1] and Holstein [3] or its time-dependent extension, the Davydov [9] *ansatz* (DA). Since the applicability of both these methods is restricted to very small parameter regions of the system, it is of fundamental interest to develop a method that will work for an extended parameter regime and also interpolate between the two limits. This is important from the point of view of real systems applications since many systems lie in the intermediate regime [10].

In a recent paper [11] some of us used the time-dependent version of the Buimistrov–Pekar [12] theory that interpolates between non-adiabatic and adiabatic limits in the context of a two-state system in order to understand the precise nature of the self-trapping phenomenon in particular regions of the parameter space and how it determines the nature of polaron states. We found that, at zero temperature ($T = 0$) and irrespective of the type of coupling, the parameter space of the system, comprised by the coupling constant versus the adiabaticity parameter, is divided in two regions; in each one of these the system exhibits distinct dynamical behaviours. The first is dominated by the quantum nature of the phonon field and self-trapping is achieved through the reduction in the effective tunnelling matrix element. In the second region the classical nature of phonons prevails, and the system dynamics and localization transition are described by the discrete non-linear Schrödinger equation. These results may be relevant to the understanding of the underlying transport mechanisms in the phenomena involving charge and energy exchange between two molecules embedded in condensed media where strong interaction with environment may significantly affect transport processes [13–15].

An extension of these results to realistic problems demands the additional study of how temperature affects these predictions. This is the purpose of this paper in which we study how temperature modifies the self-trapped states and the conditions for their occurrence. In our study of the temperature effect we use a variational method referred to as the averaged Hamiltonian approach introduced by Davydov [9] and subsequently used extensively in the study of the temperature stability of molecular solitons [16–18]. In the following section we introduce our model and apply the variational approach, leading to specific conditions for the temperature dependence of the self-trapped state. Subsequently we analyse these results.

2. The model and variational method

The essential features of the system may be described on the basis of the two-site truncation of the Fröhlich Hamiltonian:

$$H = -J(a_1^+ a_2 + a_2^+ a_1) + \frac{1}{N^{1/2}} \sum_{n=1,2,q} F_q \exp(\mathrm{i}qnR_0) a_n^+ a_n (b_q + b_{-q}^+) + \sum_q \hbar\omega_q b_q^+ b_q \qquad (1)$$

where J defines the intersite tunnelling matrix element and $b_q^+(b_q)$ are Bose operators creating (annihilating) phonon quanta in mode q with frequency ω_q. The operators $a_n^+(a_n)$ denote the presence (absence) of the particle (electron, exciton, etc) on a particular site and R_0 is the lattice constant. Each particular application is specified by the explicit q-dependence of the coupling parameter F_q and phonon dispersion. In the present paper we shall focus our attention on the simplest case where the Hamiltonian (1) corresponds to

Holstein's [3] molecular crystal model (MCM) with $F_q = F \equiv$ constant and $\omega_q = \omega_0 \equiv$ constant.

The basis of our approach is a slightly modified version of the Davydov so-called D_1 *ansatz* with normalized trial state given as

$$|\psi_\nu(t)\rangle = \sum_{n=1,2} \psi_n(t) U_1(t) U_2 a_n^+ |0\rangle_e \otimes |\nu\rangle_{ph}, \quad \sum_{n=1,2} |\psi_n|^2 = 1. \tag{2}$$

Here ψ_n denotes the probability of amplitude of the occupation of the nth site, and $|\nu\rangle = \prod_q |\nu_q\rangle (|\nu_q\rangle = (\nu_q!)^{-1/2} (b_q^+)^{\nu_q} |0\rangle_{ph})$ represents the thermally populated multiphonon states where ν_q represents the phonon population in the qth mode. Unitary operators $U_1(t)$ and U_2 are given by

$$\begin{aligned} U_1 &= \exp\left(\sum_q [\beta_q(t) b_q^+ - \beta_q^*(t) b_q] \right) \\ U_2 &= \exp\left(\sum_{q,n} [f_q \exp(\mathrm{i}qnR_0) a_n^+ a_n (b_q - b_{-q}^+)] \right) \qquad (f_q = f_{-q}^*). \end{aligned} \tag{3}$$

The operators U_1 and U_2 are introduced in order to incorporate formally the two types of lattice response to the tunnelling particle in the theoretical description of the system. The time-dependent amplitudes $\beta_q(t)$ describe the slow (i.e. the classical) component of the phonon field engaged in the creation of lattice distortion. The remaining contribution arising from the 'fast' phonons is measured by the value of the variational parameter f_q which characterizes the degree of reduction of the effective tunnelling frequency. Note that an analogous variational procedure has been performed before by Toyozawa [5, 6] and Emin [7] but without taking into account the classical part of the phonon field.

According to the papers of Brown and Ivić [19], the equations of motion for these variables follow from the set of the Hamilton's equations:

$$\mathrm{i}\hbar \dot{\beta}_q(t) = \frac{\partial \mathcal{H}(\theta)}{\partial \beta_q^*(t)} \qquad \mathrm{i}\hbar \dot{\psi}_n(t) = \frac{\partial \mathcal{H}(\theta)}{\partial \psi_n^*(t)}. \tag{4}$$

Here $\mathcal{H}(\theta)$ represents the averaged Hamiltonian which, in the present context, plays the role of the Hamilton function: $\mathcal{H}(\theta) = \sum_\nu \rho_\nu \mathcal{H}_{\nu\nu}$ and $\mathcal{H}_{\nu\nu} = \langle \psi_\nu | H | \psi_\nu \rangle$, where ρ_ν is the phonon density matrix. The explicit expression for $\mathcal{H}(\theta)$ is

$$\begin{aligned} \mathcal{H}(\theta) = &-J \exp(-x)(\psi_1^* \psi_2 + \psi_2^* \psi_1) \\ &+ \frac{1}{N^{1/2}} \sum_{n=1,2,q} (F_q - \hbar\omega_q f_q) \exp(\mathrm{i}qnR_0)(\beta_q + \beta_{-q}^*) |\psi_n|^2 \\ &+ \sum_q \hbar\omega_q (|\beta_q|^2 + |f_q|^2 + \tilde{\nu}_q) - \frac{1}{N^{1/2}} \sum_q (F_q f_q^* + F_q^* f_q). \end{aligned} \tag{5}$$

Here $x = 2\sum_q |f_q|^2 (2\tilde{\nu}_q + 1)[1 - \cos(qR_0)]$ represents a temperature-dependent 'dressing' parameter ($\tilde{\nu}_q = [\exp(\hbar\omega_0/\theta) - 1]^{-1} \equiv \nu$ denotes the average phonon number, while $\theta = k_B T$).

The dynamics of the system are described by the set of evolution equations

$$\begin{aligned} \mathrm{i}\hbar \dot{\psi}_m &= -J \exp(-x) \psi_p + \frac{1}{N^{1/2}} \sum_q (F_q - \hbar\omega_q f_q) \exp(\mathrm{i}qnR_0)(\beta_q + \beta_{-q}) \psi_m \\ \mathrm{i}\hbar \dot{\beta}_q &= \hbar\omega_q \beta_q + \frac{1}{N^{1/2}} \sum_{n=1,2} |\psi_n|^2 (F_q^* - \hbar\omega_q f_q^*) \exp(-\mathrm{i}qnR_0). \end{aligned} \tag{6}$$

In this equation, $p = 2$ for $m = 1$, and $p = 1$ for $m = 2$. As before [11], here we have disregarded the possible time dependence of the parameter f_q, being primarily interested in the most significant effect reflecting the quantum nature of phonons: the reduction in the effective tunnelling matrix element. We shall find f_q self-consistently by minimizing the energy of the system which corresponds to the stationary value of $\mathcal{H}(\theta)$ after the substitution of static solutions for ψ_n and β_q in equation (5). Eliminating the static phonon amplitudes β_q from the above system and using the normalization constraint for ψ_n, we find that

$$\psi_{1,2} = \frac{1}{\sqrt{2}}\left[1 \pm \sqrt{1 - \left(\frac{J\exp(-x)}{\varepsilon}\right)^2}\right]^{1/2}. \tag{7}$$

ε is given here, in the context of the analysis of the small-polaron properties in terms of Holstein's model, simply by

$$\varepsilon = \hbar\omega_0 \left|\frac{F}{\hbar\omega_0} - f\right|^2. \tag{8}$$

We have anticipated here that the variational parameter f_q is q independent which is not an additional approximation but follows straightforwardly from the direct calculations [11]. Substituting (7) into the expression for the $\mathcal{H}(\theta)$ we obtain

$$E(\theta) = -\frac{J^2\exp(-2x)}{2\varepsilon} - E_B + \sum_q \hbar\omega_q \tilde{v}_q \tag{9}$$

where $E_B = (1/N)\sum_q |F_q|^2/\hbar\omega_q \equiv F^2/\hbar\omega_0$ denotes the small-polaron binding energy. In order to simplify further calculations we follow the procedure as in [11] and choose the variational parameter in the following form:

$$f = \frac{1}{N^{1/2}}\frac{F}{\hbar\omega_0 + a(2\nu+1)} \tag{10}$$

with the new variational parameter a. Minimizing the energy (9) with respect to a we obtain $a = 2\varepsilon$ together with the stability condition $1 + (a\partial x/\partial a)_{a=2\varepsilon}\rangle > 0$. Substituting the above expression into equation (8) and into the expression for the dressing parameter, we obtain

$$\begin{aligned} \varepsilon &= \frac{\hbar\omega_0}{2\nu+1}\left[S(\theta)\left(1 + \sqrt{1 - \frac{1}{S(\theta)}}\right) - \frac{1}{2}\right] \\ x &= S(\theta)\left(1 - \sqrt{1 - \frac{1}{S(\theta)}}\right) - \frac{1}{2} \end{aligned} \tag{11}$$

where $S(\theta) = (E_B/\hbar\omega_0)(2\nu+1) \equiv S(2\nu+1)$ denotes temperature renormalized coupling constant. The stability condition for these solutions $\hbar\omega_0/4\varepsilon < 1$ is always satisfied if $S(\theta) > 1$. The condition for the applicability of the semiclassical approximation can be found from equation (7): $J\exp(-x) < \varepsilon$ or in terms of the coupling constant and adiabaticity parameter:

$$B < \frac{2}{2\nu+1}\left[S(\theta)\left(1 + \sqrt{1 - \frac{1}{S(\theta)}}\right) - \frac{1}{2}\right]\exp\left[S(\theta)\left(1 - \sqrt{1 - \frac{1}{S(\theta)}}\right) - \frac{1}{2}\right]. \tag{12}$$

As was emphasized in [11], this condition is the consequence of the symmetry-breaking nature of the proposed trial state which was formally introduced assuming the non-vanishing value of the classical component of the phonon field β_q. If this condition is violated, the semiclassical approximation is no longer valid and one must set $\beta_q = 0$,

while the variational procedure should be carried on in a typical mean field manner. It assumes self-consistent determination of the variational parameter by minimizing the free energy corresponding to the transformed Hamiltonian $\tilde{H} = U_2^+ H U_2$ [15]. This results in $a = 2J\exp(-x)\tanh\{[J\exp(-x)]/\theta\}$, while the stability condition now becomes

$$1 + a\frac{\partial x}{\partial a}\left[1 + \frac{a}{2\theta\sinh^2\{[J\exp(-x)]/\theta\}}\right]_{a=2J\exp(-x)\tanh\{[J\exp(-x)]/\theta\}} > 0. \tag{13}$$

In this case the dressing parameter cannot be found in closed form; however, it is possible to express the coupling constant as a function of x with temperature and adiabaticity as parameters:

$$S = \frac{x}{2}\left[1 + B\exp(-x)\tanh\left(\frac{\alpha B\exp(-x)}{2}\right)\coth\left(\frac{\alpha}{2}\right)\right]^2\tanh\left(\frac{\alpha}{2}\right) \tag{14}$$

with the stability condition specified as

$$1 - \frac{2x}{1 + [2\tanh(\alpha/2)]/\alpha B\exp(-x)}\left[1 + \frac{\alpha B\exp(-x)}{2\cosh[B\exp(-x)]}\right] > 0 \tag{15}$$

where $\alpha = \hbar\omega_0/\theta$.

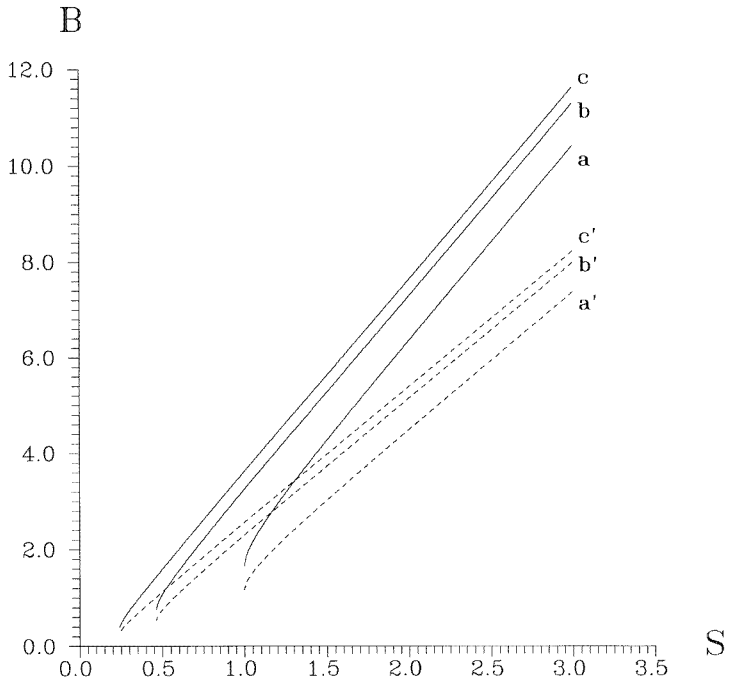

Figure 1. Symmetry-breaking versus symmetry-preserving regions (curves a–c) and localization boundaries (curves a′–c′) in the S–B plane for the three different temperatures: lines a and a′, $\alpha = \infty$; lines b and b′, $\alpha = 1$; lines c and c′, $\alpha = 0.5$ ($\alpha = \hbar\omega/\theta$).

3. Results and discussion

Our results are visualized in figures 1–3. In figure 1 we have plotted the so-called symmetry-breaking boundaries (the origin of this term was explained in [11]), curves a, b and c, for

a few different temperatures measured in units of $\hbar\omega_0$. Obviously there is no substantial qualitative difference in the form of these lines at finite temperatures compared with the zero-temperature case. Thus above some critical value of the coupling constant $S_c = (2\nu + 1)^{-1}$, which is determined by the condition of the non-negativity of the expression under the square root in equations (11) and (12), the parameter space of the system (S–B plane) is divided into two regions: a symmetry-preserving region lying above these lines with system dynamics being governed by the quantum nature of phonons, and a symmetry-breaking region with phonons behaving in a classical manner. Increasing the temperature lowers the value of the critical coupling constant and therefore enhances the classical nature of phonons, enlarging the symmetry-breaking region. Behaviour of the dressing parameter as a function of the temperature and coupling constant in the symmetry-breaking region (figure 2) supports the above conclusion. Similarly to the zero-temperature case (line a in figure 2), dressing does not depend on adiabaticity and it is most significant in the weak-coupling limit, rapidly vanishing with increase in the coupling constant. According to the explicit temperature dependence of the effective coupling constant it follows that the temperature increase causes an increase in $S(\theta)$ which results in an additional decrease in the magnitude of the dressing parameter (lines b and c in figure 2).

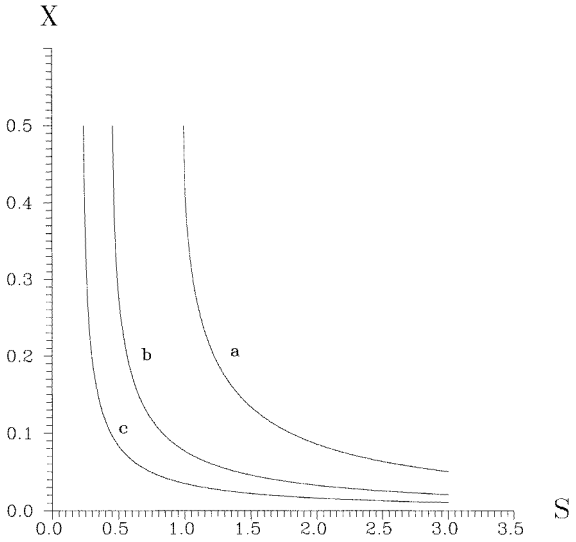

Figure 2. The influence of the temperature on the dressing parameter x as a function of the coupling constant S in the symmetry-breaking region: curve a, $\alpha = \infty$; curve b, $\alpha = 1$; curve c, $\alpha = 0.5$.

In order to examine small-polaron dynamics, and self-trapping in particular, in the symmetry-breaking region one must analyse the long-time behaviour ($t \to \infty$) of the intersite transition probability $P(t) = |\psi_1(t)|^2 - |\psi_2(t)|^2$. According to the numerous analytical and numerical studies of the time evolution of $P(t)$ in various contexts [20, 21], it follows that, depending on the values of the system parameters, $P(t)$ in the long-time limit, irrespective of the type of the coupling, may decay either into one of its stationary (minimum-energy states) $P(\infty) = \pm\sqrt{1 - [J\exp(-x)/\varepsilon]^2}$ (self-trapping) or it may tend to $P(\infty) = 0$ (delocalization). Therefore in the long-time limit the equation of motion for $P(t)$, which in the general case may have a quite complicated form, can be approximated

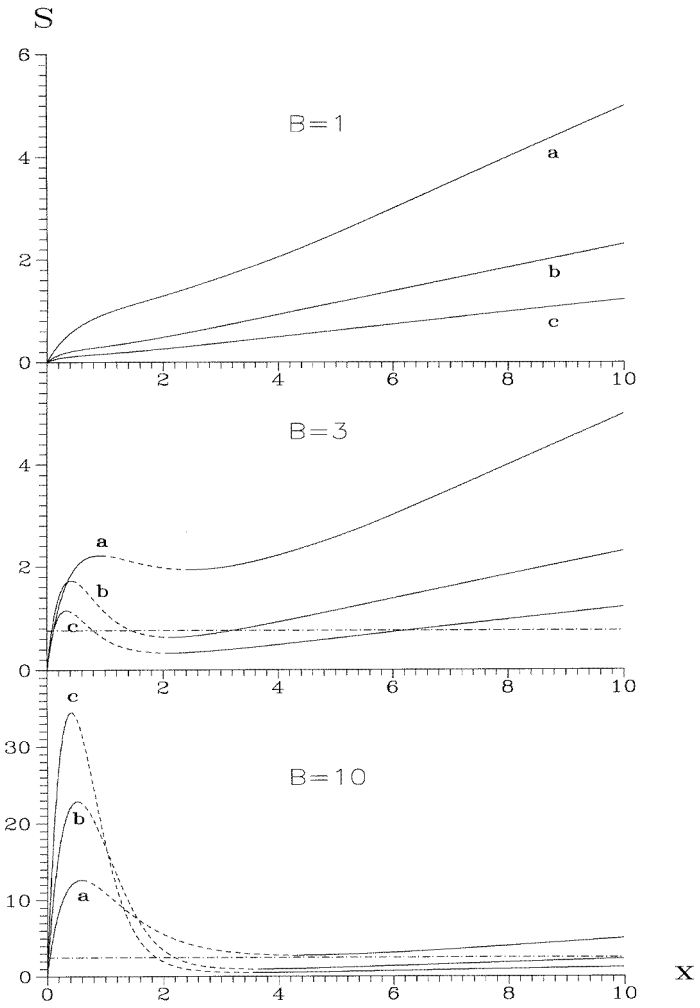

Figure 3. Behaviour of the dressing parameter as a function of the coupling constant in the symmetry-preserving region for three different temperatures: curve a, $\alpha = \infty$; curve b, $\alpha = 1$; curve c, $\alpha = 0.5$.

as follows [11, 20]:

$$\ddot{P} + \frac{1}{2}\left[1 - \left(\frac{\varepsilon}{J\exp(-x)}\right)^2\right]P + \frac{1}{2}\left(\frac{\varepsilon}{J\exp(-x)}\right)^2 P^3 + D(P)\dot{P} = 0 \tag{16}$$

where $D(P)$ represents the non-linear friction coefficient responsible for driving the system towards the above-mentioned equilibrium states. Its explicit form for the present analysis is irrelevant.

The self-trapping transition in this case may be understood on the basis of the well known classical analogy where equation (16) describes the motion of the classical particle

in the double-well potential:

$$U(P) = \tfrac{1}{2}(P^2 - 1)\left[1 - \frac{1}{2}\left(\frac{\varepsilon}{J\exp(-x)}\right)^2 + \frac{1}{2}\left(\frac{\varepsilon}{J\exp(-x)}\right)^2 P^2\right]. \quad (17)$$

As shown in [11] the localization is determined by the height of the 'potential barrier' $U(0) = -\frac{1}{2}\{1 - \frac{1}{2}[\varepsilon/J\exp(-x)]^2\}$. Thus, for $U(0) < 0$ which implies that $1 < \varepsilon/J\exp(-x) < \sqrt{2}$, transfer is possible while self-trapping arises when $U(0) \geq 0$. It implies the localization condition $\varepsilon/J\exp(-x) > \sqrt{2}$ or in terms of the coupling constant and adiabaticity

$$B < \frac{\sqrt{2}}{2\nu + 1}\left[S(\theta)\left(1 + \sqrt{1 - \frac{1}{S(\theta)}}\right) - \tfrac{1}{2}\right]\exp\left[S(\theta)\left(1 - \sqrt{1 - \frac{1}{S(\theta)}}\right) - \tfrac{1}{2}\right]. \quad (18)$$

Therefore, analogously to the previously examined case [11], the symmetry-breaking region for it is divided in two parts and self-trapping is determined by the above inequality. It defines the line in the S–B plane and localization arises if the system parameters correspond to those points lying below this, say, the localization boundary. In order to see how the temperature influences the self-trapping condition in figure 1 together with the symmetry-breaking boundaries at finite temperatures we also plotted lines a′, b′ and c′. It follows that an increase in temperature favours enlargement of the localization region compared with the zero-temperature case.

Thus we can conclude that temperature plays a twofold role in the particle tunnelling in the symmetry-breaking region. On the one hand it supports tunnelling through a decrease in the dressing parameter (increase in the effective tunnelling frequency), and on the other hand it favours localization, enlarging the region of parameter space where it may occur.

Both effects arise due to the classical nature of phonons which, as pointed out in [11], is the consequence of the increase in the level of excitation of phonon modes, which become macroscopically (classically) populated in the strong-coupling case. A rise in the temperature produces a similar effect by additionally increasing the number of phonons in each mode and in this way it enhances the 'classicity' of the phonon field. Consequently, dressing (the result of the quantum nature of phonons) is most significant in the weak-coupling limit ($S(\theta) \sim 1$), becoming negligible in the strong-coupling limit.

Furthermore the rise in the temperature and increase in coupling strength increase the number of phonons engaged in the creation of potential well which accompanies particle motion. This implies an increase in the height of the 'potential barrier' $U(0)$ for the double-well potential (17). We can estimate $U(0)$ in the strong-coupling limit ($S \gg 1$) at $T = 0$ as $U_0(0) \sim -\frac{1}{2}[1 - 2(2S - 1)^2/B^2]$ while in the high-temperature case we have $U_\infty(0) \sim -\frac{1}{2}[1 - 8S^2/B^2]$. Thus $U_\infty(0) - U_0(0) \sim 4S/B^2$, which means that the high temperature induces an additional increase in the height of $U(0)$ and in this way favours localization.

Therefore, if the system parameters S and B fall into that part of parameter space lying below the symmetry-breaking boundaries, the semiclassical approximation is satisfactory and small-polaron dynamics are well described in terms of the discrete non-linear Schrödinger equation. For the present two-site problem, it finally results in a non-linear evolution equation for the transition probability (16). According to [11], the dynamics of the system, as described by that equation, exhibit a self-trapping transition which, depending on the values of S and B, may be achieved in two different ways. Thus, when these parameters lie in the area between the symmetry-breaking and localization boundaries, the particle initially localized on one site ($P(0) = \pm 1$) in the beginning oscillates between

these localized states with a transition into oscillations around one of the minimal energy states: $P_{1,2} = \pm\sqrt{1 - [J\exp(-x)/\varepsilon]^2}$, in the long-time limit. When S and B lie below the localization boundary, $P(t)$ rapidly stabilizes into $P = \sqrt{1 - \{[J\exp(-x)]/\varepsilon\}^2}$ if $P(0) = 1$ or $P = -\sqrt{1 - \{[J\exp(-x)]/\varepsilon\}^2}$ when $P(0) = -1$.

Note that the above analysis does not take into account the effect of the so-called phonon-induced (phonon-assisted) hopping [22], which has quite the opposite effect so that in the final instance the temperature could destroy localized states. Localization breakdown has been examined recently by May and Schreiber [23] within the framework of the density matrix theory. Their results cannot directly apply in our case since only one aspect of phonon field, the quantum aspect, has been considered. However, we believe that the combination of the present variational approach and density matrix theory could be used in order to analyse localization breakdown in the symmetry-breaking region.

In the symmetry-preserving region the dressing parameter increases with rise in the temperature and increase in the coupling constant (figure 3). Here we have plotted the set of adiabatic curves $S = S(x)$ for a fixed adiabatic parameter, for several different temperatures. The dotted part of these adiabatic curves represents those points in parameter space where the stability condition (15) is not satisfied. Looking at these curves as a functional dependence of the dressing parameter on the coupling constant $x = x(S)$ with α and B being the parameters, we observe that the finite-temperature behaviour of x exhibits qualitatively the same character as in the zero-temperature case. Thus, for $B < B_c$, which is different for each temperature, x exhibits a gradual rise with increasing coupling constant. When B exceeds its critical value, x for each value of S has three values, but only two of them correspond to the stable minimum-energy eigenstates of the system.

This two-minima structure of the ground-state energy (free energy at $T \neq 0$) as a function of the variational parameter was usually assigned to the occurrence of two types of small-polaron state: the free state (small x) and the self-trapped state (large x) with an abrupt (discontinuous) localization transition [5–7]. However, these conclusions are in sharp contradiction to the exact numerical studies of the two-state MCM [24–28] which does not predict a two-minima structure for E_{GS} and consequently no discontinuous transition of the free states to the self-trapped states can be expected. Thus the two-minima structure of E_{GS} is just an artefact of the oversimplified variational procedure. In fact in the improved variational approaches it disappears [24, 27]. In this way the possibility of discontinuous self-trapping was eliminated while the quasi-particle effective mass exhibits a continuous although sudden increase as a function of coupling constant. In our notation the dressing parameter corresponds to $\ln(m_{eff}/m)$ in [24] (m_{eff} and m denote the masses of the dressed and the bare quasi-particle, respectively). This behaviour was usually considered to be a gradual self-trapping transition due to the reduction in the effective tunnelling matrix element. In the light of the present results, however, we must question this interpretation which ignores the possibility of the manifestation of the classical features of the phonon field. Namely, from $S(x)$ in figure 3, one should exclude the points where condition (12) is satisfied and which therefore corresponds to the symmetry-breaking phase. Thus, using this condition, which in the strong-coupling limit may be roughly approximated as $B < 4S$, we obtain that the physically meaningful region in the S–x plane lies below the line $S = B/4$ (chain curve in figure 3). At $T = 0$, this excludes the second minimum falling into the large-x range, and the possibility of the self-trapping due to the 'dressing' mechanism is eliminated. Consequently we expect that in the symmetry-preserving region (at $T = 0$) in the adiabatic limit ($B > 1$) the self-trapping transition cannot occur while in the non-adiabatic limit ($B < 1$) it arises through a continuous rise in the dressing parameter. This conclusion is

supported by exact numerical examinations of E_{GS} [25–28] which are, for the corresponding values of the system parameters, in very good agreement with the semiclassical (adiabatic) estimates. Thus localization due to the 'dressing' mechanism should be expected in the non-adiabatic limit only and it appears when x approaches infinity which corresponds to $S = x/2(T = 0)$ or $S = x\alpha/2(T \to \infty)$. Following Emin [7] we may formulate the localization condition using relation (15):

$$\begin{aligned} &1 + B\exp(-2S) \geq 0 \qquad (T = 0) \\ &1 + [B\exp(-4S/\alpha)]^2(1 - 16S/\alpha) \geq 0 \qquad (T \to \infty). \end{aligned} \tag{19}$$

A temperature rise favours self-trapping providing high values of the dressing parameter even for very small values of the coupling constant (figure 3). Furthermore in the adiabatic limit, where at zero temperature we do not expect any localization, our analysis indicates, as shown in figure 3, that a temperature rise could induce self-trapping through a discontinuous increase in the quasi-particle effective mass. However, in the framework of the present method we are not in a position to conclude whether such predictions could be accepted as a real physical possibility or simply reflect the limited validity of the present variational approach. This problem will be examined separately with the help of improved variational methods, in connection with the analysis of the small-polaron properties, its dynamics in particular, in the symmetry-preserving region.

In order to estimate the region of parameter space where the above predictions could apply, we need to compare the present results with those previously obtained by means of different approaches. Comparing the ground-state energy resulting from our method with that obtained by means of the fully semiclassical treatment [25] we find that the present approach predicts lower estimates for the ground-state energy if the following relation holds:

$$\exp\left[-S\left(1 - \sqrt{1 - \frac{1}{S}}\right) + \frac{1}{2}\right] > 1 + \sqrt{1 - \frac{1}{S}} - \frac{1}{2S}. \tag{20}$$

It provides superiority of the present method with respect to the strict semiclassical approach in the whole parameter space. Furthermore, comparison of the ground-state energies obtained by the pure semiclassical treatment with that following from the simple 'dressing' *ansatz* in the recent paper [29] shows that the condition for the superiority of semiclassical approach with respect to the 'dressing' approach is almost equivalent to our relation (12). Having in mind the very good agreement of the semiclassical calculations with exact numerical data [25–29], we may conclude that the present method gives a satisfactory description of the two-site small-polaron model in the symmetry-breaking region. On the other hand the validity of our predictions is limited in the symmetry-preserving region in the high adiabatic limit which demands improved treatment.

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