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Polarons on a one-dimensional non-linear lattice with two structural phases

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Abstract. The case of polaron and bipolaron formation due to electron–phonon coupling was studied on a lattice with soft non-linear intersite interactions. The ground state of a system that consists of one or two electrons coupled to a non-linear lattice was obtained numerically. The binding energy of the bipolaron was examined as a function of the degree of the non-linearity of the lattice. A model was investigated where the interatomic interactions in the lattice are described by a double-well potential. This type of non-linear interaction strongly influences the bipolaron formation and generally improves its stability and increases its binding energy by permitting a local structural change of the lattice.

1. Introduction

The localization of electrons on one-dimensional lattices due to electron–phonon coupling has been extensively studied [1] over the last decades. Emin and Holstein [2] have shown that the ground state of a system that consists of an electron coupled with a linear lattice is either an extended Bloch-type function, or a polaron, namely a state where the electron is trapped permanently by a strong local deformation of the lattice. For a perfectly periodic quantum mechanical system the polaron is always extended [1], although its effective mass can be very large. In such a case a small amount of disorder will localize the polaron.

The Emin and Holstein model, where the interatomic lattice interactions are linear, is physically meaningful as an aproximation in the case of weak deformation of the lattice, corresponding to weak coupling. If stronger electron–phonon coupling is considered, non-linear terms should be included in the lattice Hamiltonian, which can introduce a variety of new structural and dynamical features in the model.

Experimental evidence suggests that the introduction of electron–phonon coupling in an anharmonic lattice creates a model with many interesting features. The strong electron–phonon interactions are increasingly recognized as essential in understanding the properties of high-T_c superconducting materials [3]. Recent ion channelling [4] and neutron scattering [5] experiments give evidence for large anharmonic lattice fluctuations in several of the cuprates, where the coupling of the 'breathing' modes to the electron system leads to local, phonon-driven, charge instabilities. Based on these findings, the existence of polaronic and bipolaronic electronic states was extensively examined [6]. Furthermore, both traditional high-T_c superconductors and the new ones (ceramic cuprates, fullerides [7]) exhibit structural instabilities and/or structural phase transitions, suggesting that the lattice is anharmonic and soft. Thus it is important to study the influence of anharmonicity on the effects of the electron–phonon interaction.

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In the present work the formation of polarons and bipolarons is examined in a one-dimensional (1D) non-linear lattice. The 1D feature was selected, in spite its limitations, becauses it simplifies the numerical work and permits the investigation of a finite system of meaningful size.

Using the model presented here, we attempt to understand the influence of structural instabilities of a lattice on the formation of polarons and bipolarons. The lattice interatomic interaction is modelled by a double-well potential. In this way the lattice has two structural phases corresponding to two possible lattice constants. Therefore the creation of a polaron or bipolaron can be accompanied by a local structural deformation, if the related distortions are strong enough. Hence, the soft non-linear model described in detail in section 2, even though it is 1D, includes a variety of interesting structural and dynamical properties related to the formation of polarons and bipolarons.

The stability of a bipolaron in this system is an important property of the model. For this reason it is examined systematically in section 3 on a finite system by an exact diagonalization method. Our results show that the soft non-linear interaction of the model favours a binding between two polarons stronger than that of the linear system.

2. Description of the model

We are interested in studying the ground state properties of a system that consists of one or two extra electrons coupled to a 1D lattice. We consider first the case of a single electron in the band, so that it can be described as a spinless particle. The Hamiltonian of the system consists of three parts. The first one describes the electrons in a tight-binding approximation:

$$H_{\mathrm{el}} = \sum_n [\epsilon_0 c_n^\dagger c_n - J c_n^\dagger (c_{n-1} + c_{n+1})] \tag{1}$$

where ϵ_0 is the on-site electron energy when the lattice does not interact with the electron, J is the nearest-neighbour intersite energy, and $c_n^\dagger$, c_n are the creation–annihilation operators for the electron. Using the above notation the one-electron state can be described by the wave function

$$|\psi\rangle = \sum_n \psi_n c_n^\dagger |0\rangle \tag{2}$$

where the coefficients ψ_n are normalized to unity, so $\rho_n = |\psi_n|^2$ describes the probability of finding the electron at the nth site of the lattice.

The second part describes the lattice Hamiltonian in the adiabatic limit:

$$H_{\mathrm{latt}} = \sum_n V(y_{n+1} - y_n) \tag{3}$$

where y_n denote the displacements of the lattice particles, and V is an interatomic potential.

Finally the third part describes the electron–phonon interaction:

$$H_{\mathrm{el-ph}} = \chi(y_{n+1} - y_{n-1}) c_n^\dagger c_n \tag{4}$$

where χ is the electron–phonon coupling constant.

It is convenient to scale the above semi-classical model so that $J = 1$ and $V(r)$ satisfies the conditions

$$V(0) = 0 \qquad V''(0) = 1. \tag{5}$$

By applying these scaling tranformations and replacing the displacements y_n with the relative displacements Δ_n

$$\Delta_n = y_n - y_{n-1} \tag{6}$$

the above Hamiltonian takes the form

$$H = \sum_n [e_0 c_n^\dagger c_n - c_n^\dagger (c_{n-1} + c_{n+1}) + V(\Delta_n) + \sqrt{\lambda}(\Delta_n + \Delta_{n-1}) c_n^\dagger c_n] \tag{7}$$

where λ is the dimensionless electron–phonon coupling constant used in the theory of superconductivity and e_0 is the scaled on-site electron energy. Since we examine the electron–phonon interaction in a system without disorder, e_0 is uniform in all sites. Therefore the first term of the Hamiltonian (7) can be neglected. Hence the Hamiltonian of the model is reduced to

$$H = \sum_n [-c_n^\dagger (c_{n-1} + c_{n+1}) + V(\Delta_n) + \sqrt{\lambda}(\Delta_n + \Delta_{n-1}) c_n^\dagger c_n]. \tag{8}$$

If two electrons with opposite spins are considered, the electron state can be described by the wave function

$$|\psi\rangle = \sum_{n,m} \psi_{n,m} c_{n\uparrow}^\dagger c_{m\downarrow}^\dagger |0\rangle \tag{9}$$

where the coefficients $\psi_{n,m}$ are normalized to unity. Therefore, the electron probability at the nth site of the lattice is given by

$$\rho_n = \sum_m |\psi_{n,m}|^2 + |\psi_{m,n}|^2. \tag{10}$$

In the two-electron case an extra term must be introduced into the Hamiltonian to describe the electron–electron repulsion. A simple way to express this repulsion is to consider only on-site repulsion between the two electrons, as in the Hubbard model. Therefore the new Hamiltonian is

$$H = \sum_n [-c_{n,\sigma}^\dagger (c_{n-1,\sigma} + c_{n+1,\sigma}) + U c_{n\uparrow}^\dagger c_{n\uparrow} c_{n\downarrow}^\dagger c_{n\downarrow} + V(\Delta_n) + \sqrt{\lambda}(\Delta_n + \Delta_{n-1}) c_{n,\sigma}^\dagger c_{n,\sigma}] \tag{11}$$

where U is the on-site electron–electron repulsion energy.

In order to determine the ground state for this system with one or two electrons, we have to diagonalize the Hamiltonian (11) and simultaneously optimize the result with respect to Δ_n. Numerically, this can be accomplished for a finite lattice by a modified Lanczos technique. Starting with a arbitrary configuration for the relative displacements Δ_n, we calculate by exact diagonalization the ground state wave function and the local electron

densities, ρ_n. The local electron densities are related to the displacements Δ_n via the optimization conditions

$$\frac{\partial H}{\partial \Delta_n} = \frac{dV(\Delta_n)}{d\Delta_n} + \sqrt{\lambda}\,(\rho_{n+1} + \rho_n) = 0. \tag{12}$$

Equations (12) can be solved with respect to Δ_n, while the constraints imposed by the boundary conditions of the finite system are also taken into account. In this work we consider periodic boundary conditions for the finite lattice. This imposes the following constraint for the relative displacements Δ_n:

$$\sum_n \Delta_n = 0. \tag{13}$$

Therefore the optimization conditions (12) are solved under the constraint (13).

In the special case where $V(\Delta_n)$ is the harmonic potential, equations (12) are linear with respect to Δ_n and can be solved analytically. This possibility also exists if $V(\Delta_n)$ is a cubic or quartic polynomial. In this work we chose to study a lattice with a double-well intersite interaction. Specifically we used the piecewise quadratic potential

$$\begin{aligned} V(\Delta) &= \tfrac{1}{2}\Delta^2 && \text{if } -x_0 \leqslant \Delta \\ V(\Delta) &= b - \tfrac{1}{2}k\,(\Delta + a)^2 && \text{if } -2a + x_0 \leqslant \Delta \leqslant -x_0 \\ V(\Delta) &= \tfrac{1}{2}(\Delta + 2a)^2 && \text{if } \Delta \leqslant -2a + x_0 \end{aligned} \tag{14}$$

where $k = 2b/(a^2 - 2b)$ and $x_0 = ka/(k+1)$. The parameter k must be a positive number, therefore $b < (a^2/2)$. The function (14) has two free parameters, which control its non-linear character. The parameter a controls the distance between the two minima of the double well, while the parameter b controls the barrier height. Therefore the model (11) allows an arbitrary flattening of the potential in the region $-2a \leqslant \Delta \leqslant 0$ by varying the barrier height without changing the distance between the two minima (figure 1).

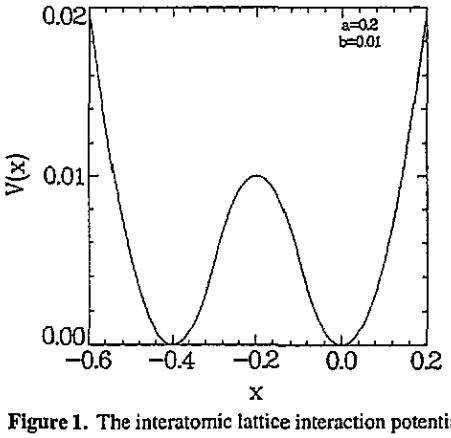

Figure 1. The interatomic lattice interaction potential as a function of the relative displacement. The parameters of the model are selected as a=0.2 and b=0.01.

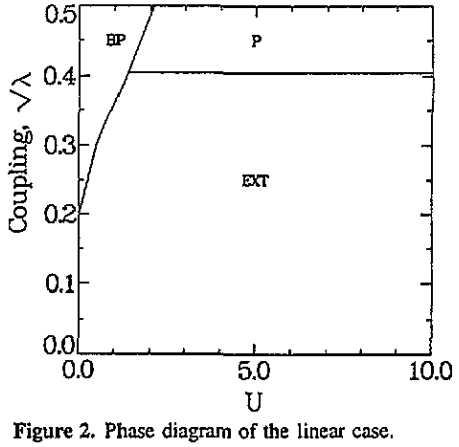

Figure 2. Phase diagram of the linear case.

The double-well potential (11) enriches the problem of polaron formation by introducing an extra structural feature of the lattice, which, in this case, has two possible lattice constants corresponding to two different phases. The barrier height, b, is the most important of the two parameters of the model, since it directly controls the critical value of the electron–phonon coupling for changing the lattice constant locally. The existence of two local structural phases in this model creates a variety of local minima, therefore one must use the optimization method described above, carefully, in order to obtain the ground state of the system.

The properties of the model are further enriched if periodic boundary conditions are considered. This assumption imposes the constraint that the total length of the lattice is fixed. Therefore the regions of the lattice with short lattice constant cannot be arbitrarily large. Moreover, the above constraint causes important finite-size effects, since the compression of a number of bonds is accompanied by the elongation of the rest of the lattice. The size of the distortion of these expanding bonds depends on the total length of the lattice. This feature of the model should not be considered as a weakness beacause it introduces in a simple fashion the local character of the structural change of the lattice.

3. Polaron formation

In this work, we attempt to study the polaron and bipolaron formation due to electron–phonon coupling in a lattice that exhibits two structural phases. This type of lattice is modelled by the system described in section 2. In this model there are three physical parameters: the electron–phonon coupling constant $\sqrt{\lambda}$, the barrier height b, and the on-site electron–electron repulsion U. As a result a variety of microphase transitions can be observed in this three-dimensional (3D) phase diagram, which will be examined in detail. Our computations were performed on a 1D finite lattice with 144 sites. This size of the lattice offers the possibility for a systematic numerical study of its phase diagram. The stability of the bipolaron which is expressed by its binding energy, was also studied as a function of these three parameters. The binding energy of the bipolaron is defined as

$$E_B = E_2 - 2E_1 \tag{15}$$

where E_2 is the bipolaron ground state energy and E_1 is the polaron ground state energy.

There are three distinct phases on the phase diagram described above. The first one is the 'extended' state, where the localization length is longer than the size of the finite lattice considered. This pseudoextended state mimics a 3D feature on a 1D lattice. This state generally exists for small values of the parameter $\sqrt{\lambda}$. If the electron–phonon coupling increases, the electrons become localized, but they can either form two separate polarons, or bind together to form a bipolaron. The competition between the electron–electron repulsion U and the non-linear parameter b controls this second transition.

We examine first the linear case of this model, corresponding to large b. In this case the phase diagram of the two-electron system is two-dimensional and is shown in figure 2. There it is shown that the phase transition between the two-isolated-polaron state (P) and the bipolaron state (BP) strongly depends on the repulsion parameter U. The electron–phonon coupling also influences the stability of the bipolaron, which increases with its strength. The transition between the 'extended' and the localized state obviously depends only on

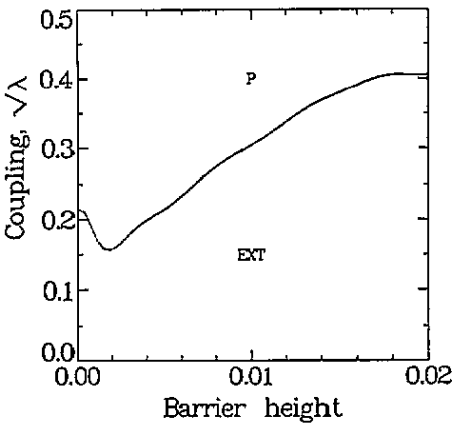

Figure 3. Phase diagram of the single-electron system. The dashed line corresponds to the region of strongly soft non-linearity, where the curvature, k, of the barrier is small ($k \simeq 0.1 \ll 1$). In this region the behaviour of the model is not well understood.

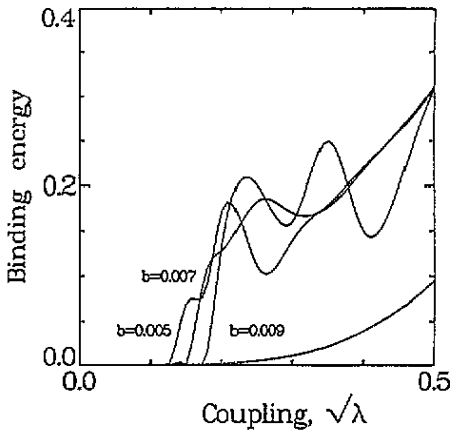

Figure 4. The bipolaron binding energy as a function of the electron–phonon coupling, $\sqrt{\lambda}$, for the case where U=0. The dashed line corresponds to the linear model.

$\sqrt{\lambda}$ for the single-polaron case, while for the bipolaron case, the electron–electron repulsion facilitates the delocalization of the electrons. A similar phase diagram is presented in [8].

In the non-linear case the phase diagram is enriched with the third parameter b, which describes the barrier height (figure 1). The parameter a is choosen to be equal to 0.2 length units, so the distance between the two minima of the function (14) is 0.4 length units. Under this assumption the acceptable range for the parameter b is the interval [0, 0.02). Therefore the maximum value of b corresponds to 232 K, if J is 1 eV. This restriction is imposed by the form of the non-linear potential (14), where k is positive. In order to explore the three-parameter phase diagram of the model, we first examine the case of a single electron in the lattice. The corresponding phase diagram is presented in figure 3. Our calculations show that the value of the electron–phonon coupling $\sqrt{\lambda}$ necessary for creating a small polaron (localized state) decreases with the barrier height b. In other words the soft non-linearity of the model that permits a structural deformation of the lattice facilitates the electron localization. For very small barriers ($b < 0.001$), the segment of the potential function with negative curvature covers most of the region between the minima, while its curvature, k, approaches zero. As a result a large number of configurations become degenerate with respect to the lattice energy. This unnatural feature of the model is pictured in figure 3, where an unexpected behaviour is observed at low values of b (dashed line). For large b ($b \simeq 0.02$) the behaviour of the system becomes similar to that of the linear case. In the two-electron case the above result also describes the transition between the isolated polaron state (P) and the 'extended' state (EXT).

For small values of the electron–electron repulsion U, a bipolaron state exists for sufficiently large values of the electron–phonon coupling. Figure 4 presents the dependence of the bipolaron binding energy on $\sqrt{\lambda}$ where U was selected to be equal to zero for several values of the barrier height. The dashed curve corresponds to the linear case. Figure 4 shows that the bipolaron binding energy is strongly influenced by the non-linear lattice interactions. Specifically, a sharp increase of the binding energy occurs in the case of the narrow polaron, for small values of b, because the strongly localized electrons cause a local change of the lattice constant. In other words, the formation of a narrow polaron is generally

accompanied by a lattice distortion. If this distortion is large, the corresponding bonds are compressed to the shorter minimum (at position $-2a$ in figure 1) causing a local structural change. Since the increase of the electron density also increases the lattice deformation, the bipolaron formation is favoured by this property of the model and its stability improves.

The large fluctuations of the binding energy shown in figure 4 are a result of the discrete character of the examined system. The binding energy depends on the ground state energy E_2 and E_1 of the two-electron system and of the single electron system, respectively (definition (15)). Both E_1 and E_2 depend on the size of the compressed region of the lattice. The extent of the compressed region increases as the electron–phonon coupling increases. The size of the compressed region is measured by the number of compressed bonds, which is an integer. Therefore the widening of the compressed region takes place in discrete steps. Since the size of the compressed region increases in discrete steps at different rates for the one-electron and two-electron cases, the binding energy, E_B, fluctuates.

For small values of b, the formation of a polaron creates a region of the compressed phase in the lattice, as we explained earlier. It is easy to show that the deformation at the boundaries between the two regions with different lattice constant has the largest contribution to the elastic energy of the lattice. Therefore the soft non-linearity increases the stability of the bipolaron, since a stronger repulsion U is required to break the compressed region of the lattice into two. This result is better demonstrated by studying the $\sqrt{\lambda}$ versus U phase diagram for a typical value of the parameter b equal to 0.005 (figure 5). On this phase diagram, we observe that the critical value of U for the bipolaron–polaron transition moves to higher values in comparison to the linear case. Moreover, the bipolaron state increases its stability at the expense of the 'extended' state as well. Therefore, a bipolaron is the ground state of the system for smaller values of $\sqrt{\lambda}$ and larger values of U in comparison to the linear case (figure 2).

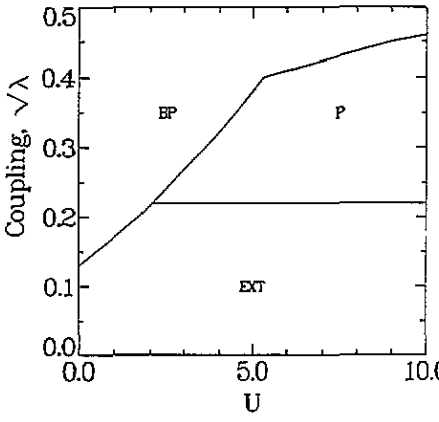

Figure 5. Phase diagram, $\sqrt{\lambda}$ versus U, for the non-linear system, where b=0.005 and a=0.2.

The non-linear interactions in the lattice produce interesting behaviour only when polarons are formed, since the 'extended' state corresponds to a uniform uncompressed lattice. For this reason we study the bipolaron binding energy as a function of the non-linear parameter b, while U=0 and $\sqrt{\lambda}$=0.3. These values of the electron–phonon coupling and the electron–electron repulsion do not permit the 'extended' state to be the ground state of the system for all values of b, as figures 2 and 5 show. The results are plotted in figure 6. In the same figure we plot the size of the region of the compressed phase as a function of the number of compressed bonds for the bipolaron and single-polaron cases. Because of

the discrete character of the lattice, the size of the compressed phase region is a multi-step function. Consequently, the binding energy is also a function of the same type, as shown in figure 6. Regardless of its step-like shape, the bipolaron binding energy shows a maximum as a function of b at the value of approximately 0.012. The existence of a maximum of the binding energy for moderately large values of the barrier height, b, is an important result of this numerical study. In other words, there is an optimum value of b, where the bipolaron effects on the lattice are stronger than those of the single polaron. The maximum value of the binding energy is considerably larger than the binding energy corresponding to the linear case, indicated by the dashed line in figure 6(b). Even though these results are obtained for a specific model, where the finite-size effects are important, they generally demonstrate the role of structural instabilities of the lattice, described by a soft non-linearity, in improving the bipolaron stability.

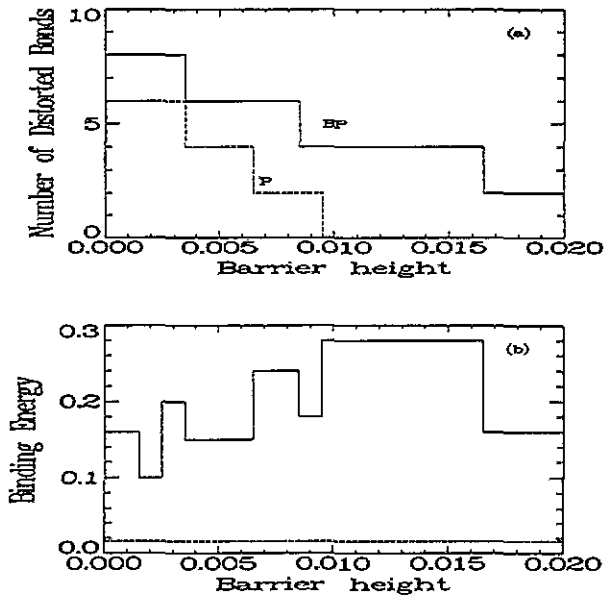

Figure 6. (a) The size of the compressed phase region as a function of the non-linear parameter b for the bipolaron case (continuous line) and for the single-polaron case (dashed line). (b) The bipolaron binding energy as a function of the non-linear parameter b. The rest of the parameters of the model are selected as follows: U=0, $\sqrt{\lambda}$=0.3 and a=0.2.

Another way to examine the bipolaron stability for the non-linear system is to study the U versus b phase diagram for $\sqrt{\lambda}$ equal to 0.45. For this value of $\sqrt{\lambda}$, the electrons are localized for all values of U and b. Therefore, on this phase diagram we study the transition from the bipolaron to the single-polaron state. Figure 7 shows that the non-linear interaction generally increases the critical value of U for the polaron–bipolaron transition, although in a non-monotonic way. For large values of b the critical electron–electron repulsion for this transition tends towards the corresponding value of the linear system (dashed line). Nevertheless, the restriction imposed by the assumption that k is positive in formula (14) limits the acceptable range of the parameter b to lower values. The discrete character of the system examined produces effects on the transition line similar to those observed for the binding energy in figure 6. At selected regions on the b axis a very strong repulsion

for the electrons is needed to break the bipolaron. This behaviour is a result of the short range of the repulsion. Because of the on-site repulsion between the two electrons, the polarons can strongly reduce the repulsion energy by retaining a short distance from each other equal to 2–4 lattice sites, while their corresponding compressed regions of the lattice remain connected (figure 8).

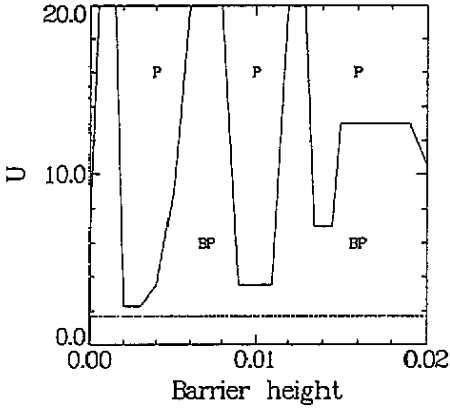

Figure 7. Phase diagram, U versus b, for the non-linear system, where $\sqrt{\lambda}=0.45$ and $a=0.2$.

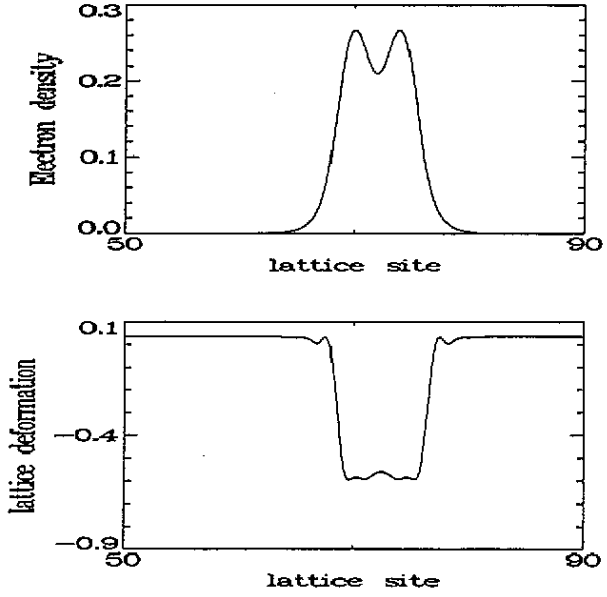

Figure 8. Profiles of the electron density and the lattice deformation for the case where $\sqrt{\lambda}=0.45$, $U=10$, $b=0.006$, $a=0.2$.

The above numerical results demonstrate the influence of a soft non-linearity on the bipolaron formation. It was shown that the bipolaron state resists transitions towards either an 'extended' state or isolated polarons in a non-linear lattice with two structural phases more strongly than in the linear lattice.

4. Conclusions

The ground state of a system with one or two electrons coupled to a finite non-linear lattice with periodic boundary conditions was studied numerically by an exact diagonalization method. The lattice intersite potential is described by a double-well function, which introduces a soft non-linearity to the lattice model, as observed experimentally in almost all the high-T_c materials (cuprates, fullerides). This function was constructed in such a way that the potential can become arbitrarily soft. Therefore, the lattice exhibits two structural phases, namely the normal and the compressed one.

The localization of an electron in this type of lattice, in other words the formation of a polaron, is accompanied by a local structural change of the lattice, if the intersite potential is sufficiently soft. The two local configurations of the lattice structure tend to separate in order to minimize the lattice energy. This property of our model improves the stability of a bipolaron and increases its binding energy by forcing the two electrons to remain bound. As a result, stronger repulsion between the electrons is required to break the bipolaron.

Even though the same feature of the model can cause clustering of more than two electrons, the formation of large clusters of electrons could be supressed because of the increased electron–electron repulsion among the electrons. Unfortunately, detailed numerical studies of a lattice of the same size as that studied above with more than two electrons are not possible because of the large dimension of the electron wave function.

The increased binding of the electronic pair, due to soft anharmonicity of the lattice, may possibly account (at least partly) for the elevation of the critical temperature for superconductivity in cuprates and fullerides. To explore this possibility, further investigations should be conducted on the dynamic properties of the polarons and the bipolarons formed on an anharmonic lattice, in order to examine their stability from the dynamical point of view and determine their effective mass.

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