ISSN 1330–0008
CODEN FIZAE4

LETTER TO THE EDITOR

FORMATION OF BIPOLARONS: A SMALL-CLUSTER STUDY

ŽELJKO CRLJEN

Department of Theoretical Physics, Rudjer Bošković Institute, P.O. Box 1016, 10 000 Zagreb, Croatia

Received 30 December 1997; revised manuscript received 21 May 1998
Accepted 24 June 1998

The effect of electron-phonon coupling on the formation of bipolarons is considered in both adiabatic and antiadiabatic regimes. Within the two-site Holstein-Hubbard model, it is shown that fast phonons can influence the formation for both repulsive and attractive effective on-site interactions.

PACS numbers: 71.38.+i, 63.20.Kr UDC 538.915
Keywords: bipolarons, electron-phonon coupling

It is widely accepted that the description of the electronic structure and properties of high-temperature superconductors requires tight-binding models. The presence of electron-phonon interaction is also recognized, particularly in the low hole-doping regime [1]. An obvious question is how much the presence of electron-phonon coupling influences the properties of these models and accounts for the physics of the materials the models describe. important is the In the scenario of preformed pairs [2], coupling of the pair's electrons to lattice vibrational modes might result in an increase of the binding energy of the pair or in a reduction of the binding energy. In addition, the value of the superexchange interaction J might also depend on the electron-phonon interaction.

The electron-phonon interaction, even if it appears not to be a mechanism responsible for superconductivity, might be a clue for the understanding of the stability of pairs and have a significant consequences in the models used.

We approach this problem by examining the Holstein-Hubbard model, in which correlated electrons are assumed to be locally coupled to a dispersionless phonon mode in a wide range of parameter's space. This has previously been considered in the adiabatic limit $\omega \to 0$ [3–4], when it was found that superexchange does not depend on the electron-phonon coupling, as the time is too short for the lattice to follow the virtual electron-hopping processes. The non-adiabatic limit has been addressed in Ref. 5, where a non-trivial dependence of J on electron-phonon coupling has been shown within a variational approach.

In this letter, we will use the exact diagonalization for small clusters, truncating the Hilbert space [6] by allowing only a finite maximum number of phonons per mode. The Holstein-Hubbard model is defined by the Hamiltonian

$$\begin{aligned} H \quad &= \omega \sum_i (a_i^+ a_i + \tfrac{1}{2}) - g \sum_\sigma (n_{i\sigma} - \langle n \rangle)(a_i^+ + a_i) \\ &-t \sum_{\langle i,j \rangle,\sigma} (c_{i\sigma}^+ c_{j\sigma} + c_{j\sigma}^+ c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow}. \end{aligned} \tag{1}$$

where $c_{i\sigma}^+$ and $c_{i\sigma}$ are the creation and annihilation operators for electrons of spin σ and a_i^+ and a_i are creation and annihilation operators for local phonons. In the sum, the indices $< i, j >$ run over the nearest-neighbour sites. The model describes tightly-binding electrons interacting locally with the effective interaction U that is assumed to be attractive or repulsive. Their coupling to the Einstein oscillator of frequency ω is taken via the fluctuations of the electron density $n_{i\sigma} - \langle n \rangle$ around the mean electron density $\langle n \rangle$. This eliminates the trivial coupling of the zero-momentum phonon mode to the total electron density. We use units such that $\hbar = 1$.

The simplest way to examine the model is to consider two electrons at a two-site cluster. Inspite of its simplicity, the system does have basic features that give an insight into the important physical quantities, such as the superexchange and the average distance between electrons (which could be related to the stability of electron pairs). For a sufficiently weak electron-phonon coupling and a large positive U, the electronic configuration with only a single electron per site will predominate. For a larger coupling constant g, one observes a transition to a local bipolaron. The energy difference then has the meaning of the bipolaronic binding energy. One can easily follow the development of the system as a function of the coupling constant g, from an electron's singlet state with each electron at different sites to a local bipolaronic state, where both electrons are localized at the same site.

For the two-electron problem, we choose the basis set that is a product of electronic and phononic states. The wave function is of the form:

$$\begin{aligned} \Psi_m = \sum_{n=0}^{\infty} \quad &(\beta_{m,n}^S |S> |n>_{ph} + \beta_{m,n}^+ |+> |n>_{ph} + \beta_{m,n}^- |-> |n>_{ph} \\ &+ \beta_{m,n}^{T_{-1}} |T_{-1}> |n>_{ph} + \beta_{m,n}^{T_0} |T_0> |n>_{ph} + \beta_{m,n}^{T_1} |T_1> |n>_{ph}) \end{aligned} \tag{2}$$

where $m = 0, 1, 2, 3, ..$ and 0 describes the ground state. $|n>_{ph}$ is an n^{th} excited oscillator state. Electron states are an intersite singlet

$$|S> = \frac{1}{\sqrt{2}} (c_{1,\uparrow}^+ c_{2,\downarrow}^+ - c_{1,\downarrow}^+ c_{2,\uparrow}^+)|0>, \tag{3}$$

polar states

$$|\pm>=\frac{1}{\sqrt{2}}(c^+_{1,\uparrow}c^+_{1,\downarrow}\pm c^+_{2,\uparrow}c^+_{2,\downarrow})|0> \tag{4}$$

and triplet states

$$\begin{aligned}&|T_0>=\tfrac{1}{\sqrt{2}}(c^+_{1,\uparrow}c^+_{2,\downarrow}+c^+_{1,\downarrow}c^+_{2,\uparrow})|0>\\&|T_1>=c^+_{1,\uparrow}c^+_{2,\uparrow}|0>\\&|T_{-1}>=c^+_{1,\downarrow}c^+_{2,\downarrow}|0>\end{aligned} \tag{5}$$

It has turned out that less than 50 phonons are needed to ensure the stability in the diagonalization for small clusters.

The energy of the ground state is calculated as a function of the electron-phonon coupling g/t. In Fig. 1a, ground-state energy is shown for a positive and large value of U for a range of phonon frequencies from adiabatic to antiadiabatic region. In the weak-coupling regime ($g/t<1$), the ground-state energy shows little dependence on the coupling strength. In the electronic configuration of the system, a single electron per site dominates, giving a singlet ground state. It is evident that the difference in energy E_1-E_0 between the lowest triplet state E_1 and the ground-state singlet E_0 can be interpreted as the effective exchange interaction J [7]. Note that a triplet state does not couple to phonons with our choice of the Hamiltonian.

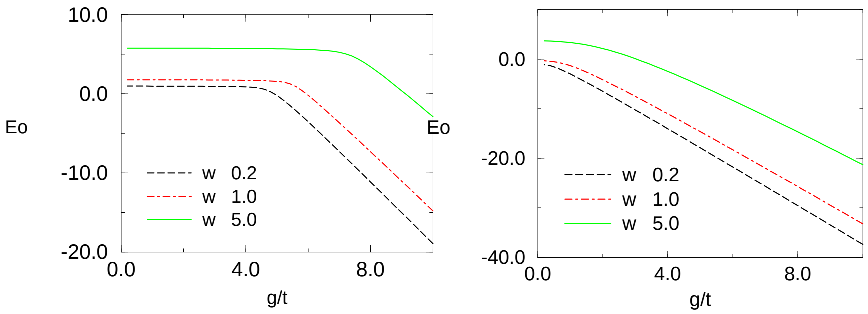

Fig. 1: Ground state energy from diagonalization of the Holstein-Hubbard model for two sites versus electron-phonon coupling g. (w= $\omega/\mid t\mid$, ω is phonon frequency.) a) $U/\mid t\mid=+18$. b) $U/\mid t\mid=-0.5$.

In Fig.2 an effective exchange interaction J is plotted for several values of ω/t. One should note that the result agrees well with the prediction of Ref. 4 that J does not depend on electron-phonon coupling in the adiabatic limit. The adiabatic result $J=4t^2/U$ appears to hold for $\omega\approx t$. What one learns from Fig. 2 is that an increase of electron-phonon coupling enhances superexchange very little until the coupling becomes strong enough to cause a transition to an on-site bipolaron. Then the energy difference E_1-E_0 becomes large, and this is accompanied with the complete domination of the polar state in the electronic part of the ground-state wave function Ψ_0. Also, the interpretation of E_1-E_0 as superexchange loses its meaning. It rather means the bipolaron binding energy [8].

From Fig. 1, one can see a dramatic collapse of the system to a strongly bound state at particular values of g/t. It shows that for a larger phonon frequency ω, the transition happens at larger values of g, extending the range of the adiabatic behaviour well into the strong coupling regime.

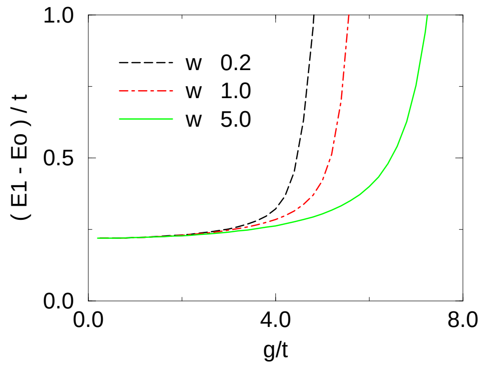

Fig. 2: Energy difference between triplet E_1 and ground-state singlet E_0 versus electron-phonon coupling. $U/\mid t\mid = +18$. (w= $\omega/\mid t\mid$, ω is phonon frequency.)

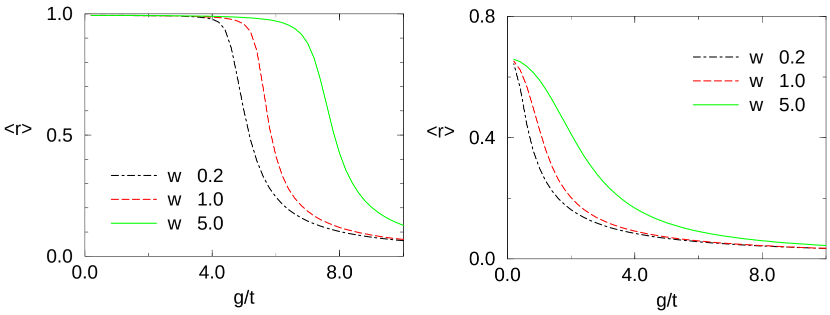

Fig. 3: Average distance between electrons, normalized to the size of the system, versus electron-phonon coupling g (w= $\omega/\mid t\mid$, ω is phonon frequency.) a) $U/\mid t\mid = +18$. b) $U/\mid t\mid = -0.5$.

‘OCIn Fig. 3, the change of the average distance between electrons, measured in units of the size of the system, is plotted as a function of the electron-phonon coupling constant g. In Fig. 3a, one can see that for a large and positive value of U and a sufficiently weak coupling constant g, the system prefers a singlet ground state, as expected. The average distance between electrons is as large as the size of the system. A large enough value of g is needed to overcome the repulsive potential U and to localize electrons around one center of the system. It is evident that the crossover from the weak-coupling ($g/t \ll 1$) to the strong-coupling ($g/t \gg 1$) regime depends on the adiabaticity of the system. For faster phonons, the transition to a localized state of electrons is postponed to a larger value of g. This seems to agree well with the prediction of the Lang-Firsov approach [9] which gives the effective on-site interaction as $U_{eff} = U - 2g^2/\omega$, a result that is valid in the extreme antiadiabatic limit ($\omega/t \gg 1$). The transition shows up in various correlation functions, the analysis of which will be presented elsewhere.

For large and negative values of U, electrons would be localized at one center, even in a weak-coupling regime.

An interesting feature emerges for a small and negative value of U. In Fig. 1b, the ground-state energy is plotted for a set of phonon frequencies and for an attractive on-site electron-electron interaction $U = -0.5$ (measured in units of $\mid t \mid$). It shows a transition to a strongly bound state. It is also evident that for a weak-coupling value of g, even though U is negative, the system is not entirely bound at one site. In the first place, that is a consequence of the hopping term in the Hamiltonian, but it also shows a dependence on the phonon frequency. The effect is better seen through the average distance between electrons as shown in Fig. 3b. The attraction and consequently the localization of electrons at one center is in a sense reduced by a fast phonon.

In summary, it has been shown that the presence of the electron-phonon interaction leads to an increase of the effective exchange interaction in a two-site model. The effect can be observed experimentally as an isotopic dependence of the measured value of J [10]. It is also shown that the value of the coupling constant at which a transition occurs to an on-site bipolaron depends on the phonon frequency. A tendency is shown that fast phonons oppose the transition. They seem to act so as to preserve the single-site occupancy. The effect can be seen even for a negative on-site electron-electron interaction U. One may expect that for a small on-site effective interaction fast phonons may lead to an anharmonic lattice fluctuation, suggesting possible polaronic effects well into the regime of existing local bipolarons.

A similar conclusion about the interplay of the electron-phonon coupling and phonons has been presented in Ref. 11. There, a formation of a single polaron was considered within the variational approach, and it is shown that fast phonons do oppose that formation.

In conclusion, it appears that a two-site model considered here agrees well with the adiabatic results and resembles the behaviour of the Holstein-Hubbard model in the antiadiabatic region. It gives a consistent meaning to the results in the whole region of phonon frequencies from the weak- to the strong-coupling regime, a result that is rather difficult to achieve using standard analytical techniques.

This work was supported by the Ministry of Science and Technology of the Republic of Croatia under contract no. 00980101.

References

1) X. X. Bi and P. C. Eklund, Phys. Rev. Lett. **70** (1993) 2626;
P. Calvani, M. Capizzi, S. Lupi, P. Maselli, A. Paolone and P. Roy, Phys. Rev. **B 53** (1996) 1;

2) I. O. Kulik, Int. J. Mod. Phys. **1** (1988) 851;
N. F. Mott, Adv. in Phys. **39** (1990) 55;
A. S. Alexandrov, J. Ranninger and S. Robaszkiewicz, Phys. Rev. B **33** (1986) 4526;

3) T. Holstein, Ann. Phys. **8** (1959) 325; ibid **8** (1959) 343;

4) R. Micnas, J. Ranninger and S. Robaszkiewicz, Rev. Mod. Phys. **62** (1990) 113;

5) D. Ihle and H. Fehske, J. Phys. **A 28** (1995) 275;

6) J. Ranninger and U. Thibblin, Phys. Rev. **B 45** (1992) 7730;

7) J. Ranninger, Z. Phys. **84** (1991) 167;
W. Stephen, M. Capone, M. Grilli and C. Castellani, Phys. Lett. **A 227** (1997) 120;

8) Since in our model the triplet state does not couple to phonons, one can set E_1 to 0 and take $E_1 - E_0$ as binding energy of two polarons at the same site. Our polar state is a bipolaron of the Anderson-type with an attractive interaction due to the electron-phonon coupling that overcomes the on-site Coulomb repulsion;

9) I. G. Lang and Yu. A. Firsov, Zh. Eksp. Teor. Fiz. **43** (1962) 1843 (Sov. Phys. JETP **16** (1963) 1301);

10) I thank the referee for drawing my attention to the paper by J. S. Zhou and J. B. Goodenough, Phys. Rev. Lett. **80** (1998) 2665, which appeared after the submission of this manuscript. There it was found that the dynamic Jahn-Teller deformations introduce vibrational modes into the spin-exchange interaction of perovskite manganites. A mass-dependent trapping out of mobile polarons is confirmed. This seems to be in accordance with the analysis of the present paper although a careful analysis is needed.

11) H. Fehske, D. Ihle, J. Loss, V. Trapper and H. Buttner, Z. Phys. **94** (1994) 91.

FORMIRANJE POLARONA: STUDIJ MALIH NAKUPINA

Učinak elektron-phonon vezanja na formiranje bipolarona razmatra se kako u adijabatskom tako i u antiadijabatskom režimu. U okviru Holstein-Hubbardovog modela s dva centra pokazano je da brzi fotoni mogu utjecati na ovo formiranje kako za odbojna tako i za privlačna međudjelovanja među česticama jednog centra.