Polaron features of the one-dimensional Holstein Molecular Crystal Model

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The polaron features of the one-dimensional Holstein Molecular Crystal Model are investigated by improving a variational method introduced recently and based on a linear superposition of Bloch states that describe large and small polaron wave functions. The mean number of phonons, the polaron kinetic energy, the electron-phonon local correlation function, and the ground state spectral weight are calculated and discussed. A crossover regime between large and small polaron for any value of the adiabatic parameter $\omega_0/t$ is found and a polaron phase diagram is proposed.
**Introduction.** In the last decade the idea that the interaction of the charge carriers with the lattice distortions plays an important role in determining the electronic and magnetic properties of the doped cuprates and manganese oxide perovskites has gained ground more and more. Both the infrared spectroscopy and the transport measurements, involving the colossal magneto-resistance and high $T_c$ superconductivity, have pointed out the presence of polaron carriers in cuprates and manganites.

This large amount of experimental data has aroused a renewed interest for the Holstein molecular crystal model that is the simplest model for the study of the interaction of a single tight-binding electron coupled to an optical local phonon mode.

For the Holstein Hamiltonian the two standard analytical approaches, based on weak (WCPT) and strong (SCPT) coupling perturbation expansions, fail to describe the region, of greatest physical interest, characterized by intermediate couplings and by electronic and phonon energy scales not well separated. This regime has been analyzed employing several techniques based on Quantum Monte Carlo simulations, numerical exact diagonalizations of small clusters (EDSC), dynamical mean field theory (DMFT), density matrix renormalization group and variational approaches. The general conclusion is that the ground state energy and the effective mass in the Holstein model are continuous functions of the electron-phonon coupling. The ground state properties can change significantly, increasing the strength of the interaction, but without breaking the translational symmetry: there is a smooth crossover between a polaron ground state with slightly renormalized mass at weak electron-phonon (e-ph) coupling and a polaron ground state with a narrow bandwidth at strong e-ph coupling.

In this scenario it has been shown that the Global Local variational method (GLVM) and the Density Matrix Renormalization Group (DMRG) approach present some advantages on other methods. In fact, they provide a very high numerical accuracy when compared, for instance, to the Quantum Monte Carlo method (QMC) that provides a numerical accuracy of order of $0.1 - 0.3\%$. Furthermore the validity of these methods is not limited by the use of very small clusters as in the numerical exact diagonalization. On the other
hand we note that: 1) a solution of the GLVM for any particular \( k \) value (\( k \) is the wave number of the polaron Bloch state) is obtained by minimizing with respect to a very large number of parameters, that depends on the number of lattice sites and that increases dramatically with increasing the number of space dimensions from one to three; 2) the DMRG method involves a truncation of the boson Hilbert space and it is based on a heavy numerical technique.

Recently we have proposed a new variational approach\(^1\) that is based on a linear superposition of Bloch states that describe large and small polaron wave functions. This approach allows an immediate physical interpretation of the intermediate regime, does not involve a truncation of the boson Hilbert space and requires a very little computational effort involving a very small number of variational parameters that does not depend on the number of lattice sites and on the dimensionality of the system.

The aim of this paper is to show that a further improvement of this method allows to give a highly accurate description of the polaron features for any value of the parameters of the Holstein molecular crystal model. In particular, the comparison of our results with the DMRG and GLVM data points out that the ground state energies obtained within our approach are lower than the GLVM energies, the difference being about 0.01\%, and slightly upper than the DMRG energies, the difference being about 0.005\%. This agreement strengthens our idea that the true wave function is very close to a superposition of the Bloch translationally invariant wave functions that provide a very good description of the two asymptotic regimes.

**The model.** The Holstein molecular crystal model is described, with standard notations, by the Hamiltonian\(^3\)

\[
H = -t \sum_{<i,j>} c_i^\dagger c_j + \omega_0 \sum_q a_q^\dagger a_q + \frac{\omega_0 g}{\sqrt{N}} \sum_{i,\vec{q}} c_i^\dagger c_i \left[ e^{i\vec{q} \cdot \vec{R}_i} a_{\vec{q}} + h.c. \right].
\]

(1)

As trial wave functions we consider translationally invariant Bloch states obtained by taking a superposition of localized states centered on different lattice sites in the same
manner in which one constructs a Bloch wave function from a linear combination of atomic orbitals (see also ref.15):

$$|\psi^{(i)}_k\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}_n} e^{i\vec{k} \cdot \vec{R}_n} |\psi^{(i)}_k(\vec{R}_n)\rangle$$  \hspace{1cm} (2)

where

$$|\psi^{(i)}_k(\vec{R}_n)\rangle = \sum_{\vec{R}_m} c^{\dagger}_{m+n} \phi^{(i)}_k(\vec{R}_m) e^{\sum_q \left[f^{(i)}_{q,\vec{R}_m}(\vec{k}) a_q e^{i\vec{q} \cdot \vec{R}_n} - h.c. \right]} |0\rangle$$  \hspace{1cm} (3)

and

$$f^{(i)}_{q,\vec{R}_m}(\vec{k}) = f^{(i)}_{q}(\vec{k}) + \frac{g}{\sqrt{N}} d^{(i)}(\vec{k}) e^{i\vec{q} \cdot \vec{R}_m}.$$  \hspace{1cm} (4)

In the Eq.(3) the apex i=l, s indicates the large and small polaron wave function, |0⟩ denotes the electronic and boson vacuum state, \(\phi^{(i)}_k(\vec{R}_m)\) are variational parameters that satisfy the relation:

$$\sum_{\vec{R}_m} |\phi^{(i)}_k(\vec{R}_m)|^2 = 1 ,$$  \hspace{1cm} (5)

d\(^{(i)}(\vec{k})\) are two variational parameters and \(f^{(l)}_{q}(\vec{k})\) and \(f^{(s)}_{q}(\vec{k})\) represent the phonon distribution functions that are determined by minimizing the expectation value of the Hamiltonian \(H\) on the states (2) and by performing, respectively, the limit \(g \rightarrow 0\) and \(g \rightarrow \infty\).

In this paper we assume:

$$\phi^{(l)}_k(\vec{R}_n) = \alpha^{(l)}_k \delta_{\vec{R}_n,\vec{0}} + \beta^{(l)}_k \delta_{\vec{R}_n,\vec{\delta}} + \gamma^{(l)}_k \delta_{\vec{R}_n,\vec{\eta}} + \varepsilon^{(l)}_k \delta_{\vec{R}_n,\vec{\theta}} + \zeta^{(l)}_k \delta_{\vec{R}_n,\vec{\vartheta}}$$  \hspace{1cm} (6)

and

$$\phi^{(s)}_k(\vec{R}_n) = \alpha^{(s)}_k \delta_{\vec{R}_n,\vec{0}} + \beta^{(s)}_k \delta_{\vec{R}_n,\vec{\delta}} + \gamma^{(s)}_k \delta_{\vec{R}_n,\vec{\eta}} \hspace{1cm} (7)$$

Here \(\beta^{(i)}_k, \gamma^{(i)}_k, \varepsilon^{(l)}_k\) and \(\zeta^{(l)}_k\) are variational parameters, while \(\alpha^{(i)}_k\) are determined in such a way the Eq.(3) is satisfied. The symbols \(\vec{\delta}, \vec{\eta}, \vec{\theta}\) and \(\vec{\vartheta}\) indicate, respectively, the nearest, the next nearest neighbors and so on. This choice takes into account the broadening of the
electronic wave function to the nearest neighbors and to the next nearest neighbors for the small polaron and to fourth neighbors for the large polaron.

We also note that these wave functions can be systematically improved by adding further terms in Eq.(6) and Eq.(7). This allows to obtain better and better estimates of the polaron energy in the two asymptotic limits.

A careful inspection of these two wave functions shows that, far away from the two asymptotic regimes, they are not orthogonal and that the off-diagonal matrix elements of the Holstein Hamiltonian are not zero. It is then straightforward to determine variationally the polaron ground state energy by considering as trial state the linear superposition of the large and small wave functions:

$$|\psi_{k}^{s}\rangle = \frac{A_{k}^{s}|\psi_{k}^{(s)}\rangle + B_{k}^{s}|\psi_{k}^{(l)}\rangle}{\sqrt{A_{k}^{2} + B_{k}^{2} + 2A_{k}B_{k}S_{k}}}$$

where $|\psi_{k}^{(s)}\rangle$ and $|\psi_{k}^{(l)}\rangle$ are the normalized large and small polaron wave functions and $S_{k}$ is the overlap factor. In the Eq.(8) $A_{k}$ and $B_{k}$ are two additional variational parameters which provide the relative weight of the large and small polaron solutions in the ground state of the system for any particular value of $k$.

The minimization of the quantity $\langle \psi_{k}^{|H|\psi_{k}} / |\psi_{k}^{|\psi_{k}} \rangle$ with respect to the eight variational parameters $[\beta_{k}^{(s)}, \gamma_{k}^{(s)}, d^{(s)}(k)]$ and $[\beta_{k}^{(l)}, \gamma_{k}^{(l)}, e_{k}^{(l)}, \epsilon_{k}^{(l)}, d^{(l)}(k)]$ has been performed by making use of a routine based on a standard Newton algorithm. In this paper we will limit our attention to the one-dimensional ground state ($k = 0$).

**Numerical results.** In Fig.1a we plot the polaron ground state energy as a function of the e-ph coupling constant, in one dimension, for different values of the adiabatic parameter $\omega_{0}/t$. Our variational proposal recovers the second order weak and strong perturbation results in the two asymptotic regimes and, as it is clear from Table 1, provides a highly accurate estimate of the polaron ground state energy in the intermediate regime, that is the region of greatest physical interest from both experimental and theoretical point of view.

Although the polaron wave function is a translationally invariant Bloch state, in the strong coupling limit the polaron localization (small polaron) appears through a large en-
hancement of the effective mass and through the change in the behavior of the correlation function between the electron and lattice (see Fig.1c). In literature there is unanimous agreement on the conditions leading to the small polaron formation. It requires \( g > 1 \) and \( \lambda > 1 \), where \( \lambda \) indicates the ratio between the small polaron binding energy and the energy gain of an itinerant electron on a rigid lattice. It is also unanimously recognized that decreasing the value of the adiabatic parameter \( \omega_0/t \) the transition toward the small polaron formation becomes sharper and sharper.

In Fig.1b, 1c, 1d we report the numerical results of the mean phonon number, \( N \), the e-ph local correlation function (the lattice local distortion) scaled with the strong coupling result \( 2g \), \( S \), and the polaron kinetic energy, \( K \), in units of the bare electronic kinetic energy, as a function of the e-ph coupling constant for different values of the adiabatic parameter \( \omega_0/t \). For weak coupling \( K \) is very close to one and \( N \) is about zero: the electron is slightly affected by the interaction with the phonons and drags with itself a phonon cloud that gives rise to a weak renormalization of the bare electron mass. \( S \) is in agreement with the result of the weak coupling perturbation theory and confirms that in this regime the extension of the polaron is large compared with the lattice parameter of the crystal. The non-adiabatic limit deserves to be mentioned, where also for weak e-ph coupling the extension of the polaron can be less than the lattice parameter due to the small value of the transfer integral \( t \). Increasing the strength of the e-ph interaction the average number of phonons and the lattice local distortion increase, the kinetic energy reduces and asymptotically tends to the values predicted by the strong coupling perturbation theory (\( N \rightarrow g^2, K \rightarrow e^{-g^2}, S \rightarrow 1 \)). In this case the lattice displacement is different from zero only on the cell where there is an electron. It is worth to point out the behavior of the ratio \( B/A \) that indicates the relative weight of the small and large polaron components in the wave function \( |\psi_{\vec{k}}\rangle \): by increasing the strength of the e-ah interaction it increases and in the crossover regime is of the order of the unity indicating that both the wave functions contribute to the formation of the so-called intermediate polaron. By decreasing the adiabatic parameter \( \omega_0/t \), the width of the region characterized by values of \( B/A \) of order of unity decreases confirming that in the adiabatic
regime the transition toward the small polaron formation becomes sharper and sharper as it is also evident from the $K$, $S$ and $N$ behaviors.

The conclusions previously drawn and the use of the expressions "large, small and intermediate polarons" are based, in agreement with previous numerical works, on the analysis of the polaron ground state properties. On the other hand the spectral weight $Z$ associated with the ground state, $Z = |\langle \psi_{\vec{k}=0} | c_{\vec{k}=0}^\dagger | 0 \rangle|^2$, is not entered in the discussion. This factor represents the renormalization coefficient of the one-electron Green function and gives the fraction of the bare electron state in the polaron trial wave function. $Z$ is plotted in Fig.2a. It is evident that even in the adiabatic regime the transition toward the small polaron formation is accompanied by a very smooth decrease of the ground state spectral weight. There is a large region of $g$ values where the ground state is well described by an electron with a still weakly renormalized mass but this state is characterized by a spectral weight considerable smaller than the unity: this implies that an essential part of the single-particle spectral weight lies at higher energies. In particular, in the adiabatic regime although the ground state properties, as the kinetic energy and the mean number of phonons, change sharply in a narrow range of $g$ values, the transfer of spectral weight toward the higher energy bands takes place in a smooth and soft way. The analysis of the spectral weight attached to the polaron lowest energy band allows to distinguish in the phase diagram three different regimes (see Fig.2b): 1) the weak coupling regime or the large polaron phase where the ground state is well described by an electron with weakly renormalized mass and $Z$ is of order of unity ($0.9 < Z \leq 1$). In this limit the polaron quasi-particle is well defined and it is characterized by coherent motion; 2) the intermediate polaron phase characterized by ground state spectral weight significantly smaller than the unity but not negligible ($0.1 < Z < 0.9$) and by renormalized mass larger than the bare electronic mass, but not in a dramatic way; 3) the strong coupling regime or the small polaron phase where the spectral weight $Z$ is negligible ($0 \leq Z < 0.1$); in this limit the well known polaron band collapse takes place while the polaron extension is of order of the lattice constant. Here the main part of spectral weight is located at the excited states, indicating that the coherent motion is suppressed rapidly.
with increasing the temperature. Consequently we can define two different regimes: for electronic and phonon energy scales not well separated ($\omega_0/t \simeq 1$), the intermediate polaron phase is well described by a linear superposition of the two wave functions $|\psi^{(l)}_k\rangle$ and $|\psi^{(s)}_k\rangle$ and all the ground state properties, see for instance the kinetic energy behavior in Fig.1d, have intermediate values between small and large polaron phases. On the other hand, in the extreme adiabatic regime the intermediate polaron phase is described by the wave function $|\psi^{(l)}_k\rangle$ but is characterized by a small values of the ground state spectral weight in the single-particle spectrum. In this regime the two ways of characterizing the intermediate polaron, based on the analysis of the ground state properties and distribution of the spectral weight in the single-particle spectrum, are different. However, the latter way seems to be more suitable to individualize the different polaron regimes in the phase diagram, being based on the analysis of a property involving the weight of the ground state in the single-particle spectrum.

The existence of a intermediate regime can have interesting consequences on the infrared absorption of manganites where it has been shown that the conductivity spectra in the metallic region is characterized by the presence of a Drude peak at low frequencies and a broad mid-infrared band around 0.1 eV. In fact this features can be explained assuming (as generally expected) that the absorption is due mainly to polarons in the intermediate regime. Here since the calculated spectra weight is equally distributed between ground and all the excited states, the infrared absorption is expected to exhibit two structures with almost equal intensity: the coherent (ground-state intraband conductivity) and the incoherent (interband conductivity) contributions.

In conclusion, in this paper we have further improved a recently developed variational approach to investigate the polaron features of the one-dimensional Holstein molecular crystal model. It has been shown that a simple linear superposition of Bloch states that describe the small and large polaron solutions provides an highly accurate estimate of the ground state energy that is successfully compared with the best results available. It has been also pointed out that a crossover regime exists between the large and small polaron phases for
any value of the adiabatic parameter $\omega_0/t$. It is characterized by a soft transfer of spectral weight from the ground state toward the higher energy bands.

**TABLE 1 CAPTIONS**

Tab.1. The ground state energies as calculated by various methods at $\omega_0/t = 1$ and for two different values of the e-ph coupling constant. The energies (first and second columns) are given in units of $\omega_0$.

**FIGURE CAPTIONS**

Fig.1. The polaron ground state energy (Fig1.a), the average number of phonons (Fig.1b), the e-ph local correlation function (Fig.1c), the polaron kinetic energy (Fig.1d), in one dimension, are reported as a function of the electron-phonon coupling constant for different values of the adiabatic parameter $\omega_0/t$: $\omega_0/t = 2.5$ (solid line), $\omega_0/t = 1$ (dashed line), $\omega_0/t = .5$ (dotted line), $\omega_0/t = .25$ (dashed-dotted line). The results obtained within the approach discussed in this paper are compared with the GLVM data (diamonds), kindly provided by A. Romero, and the DMRG data (circles), kindly provided by E. Jeckelmann. The energies are given in units of $\omega_0$. The squares indicate the values of $S$ within the weak coupling perturbation theory.

Fig.2. In Fig 2.a the ground state spectral weight is reported as a function of the e-ph coupling constant for the same values of the adiabatic parameter of Fig.1. In Fig.2b the polaron phase diagram is plotted. The dashed line is characterized by $Z = .9$ and separates the large polaron regime from intermediate and small polaron phases. The dotted line is characterized by $Z = .1$ and separates the small polaron regime from the large and intermediate phases. The dashed-dotted line indicates the points in the phase diagram with $Z = .5$. 

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| $g = 1$  | $g = \sqrt{2}$ | Type of Method                      |
|---------|----------------|-------------------------------------|
| -2.000  | -2.500         | $2^{nd}$ order SCPT (Ref. 4)        |
| -2.4    | -2.89          | DMFT (Ref. 9)                       |
| -2.44721| -2.89442       | $2^{nd}$ order WCPT (Ref. 3)        |
| -2.46770| -2.98850       | Previous paper (Ref. 14)            |
| -2.46931| -2.99802       | GLVM (Ref. 11) ($N = 32$)           |
| -2.46962| -2.99833       | this paper ($N = 32$)               |
| -2.46968| -2.99883       | DMRG (Ref. 10) ($N = 32$)           |
| -2.471  | -2.999         | QMCM (Ref. 6)                       |
| -2.47142| -3.00027       | this paper ($N = 6$)                |
| -2.471  | -3.000         | EDSC (Ref. 8) ($N = 6$)             |

Table 1
