Surface Polaron Formation in the Holstein model

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The effect of a solid-vacuum interface on the properties of a strongly coupled electron-phonon system is analyzed using dynamical mean-field theory to solve the Holstein model in a semi-infinite cubic lattice. Polaron formation is found to occur more easily (i.e., for a weaker electron-phonon coupling) on the surface than in the bulk. On the other hand, the metal-insulator transition associated to the binding of polarons takes place at a unique critical strength in the bulk and at the surface.

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I. INTRODUCTION

Convincing experimental evidence of polaronic behavior has been reported in materials such as the high-$T_c$ cuprates and manganites. For instance, the transition from the low temperature ferromagnetic metallic state to the paramagnetic insulating state in manganites is caused by the formation of combined structural/magnetic polarons. Signatures of small polarons have been observed in undoped cuprates.

From a theoretical point of view, polaron formation has been intensively studied using a number of approaches. An important role to improve our understanding of polaron phenomena has been recently played by Dynamical Mean-Field Theory (DMFT). DMFT is a powerful non-perturbative tool for strongly interacting systems. This technique, which becomes exact in the limit of infinite coordination number, reduces the full lattice many-body problem to a local impurity embedding in a semi-consistent effective bath of free electrons.

DMFT studies of the half-filled Holstein model in a Bethe lattice with a semi-elliptic free density of states have clarified the difference between the polaron crossover, i.e., the continuous and progressive entanglement between electrons and phonons, and the bipolaronic metal-insulator transition. If no symmetry breaking is allowed, for small e-ph couplings the ground state is metallic with Fermi liquid characteristic. Upon increasing the e-ph coupling, the carriers lose mobility, eventually acquiring polaronic character, with a finite lattice distortion associated to the electron motion. Polaron formation occurs as a continuous crossover. Once formed, polarons tend to attract and form a bound pair in real space, called bipolaron.

Within DMFT the bipolaronic binding gives rise to an insulating state of localized pairs, and bipolaron formation gives rise to a metal-insulator transition. The pairing transition does not coincide with the polaron crossover: Polarons are formed before (i.e., for a weaker coupling) the pairing transition occurs as long as the typical phonon frequency is smaller than the electronic energy scales (adiabatic regime).

On the other hand, fabrication of a variety of heterostructures and interfaces involving cuprates and manganites raises the question of whether the electronic behavior at the surface or interface is different from the bulk. Several studies have been devoted to the case of repulsive electron-electron interactions (Hubbard model) and to a vacuum-solid interface. Potthoff and Nolting, and Liebsch have argued that reduced coordination at the surface may enhance correlation effects. They also studied the magnetic ordering induced by enhanced correlation at the surface. Matzdorf et al. proposed that ferromagnetic ordering is stabilized at the surface by a lattice distortion. Surface ferromagnetism had been also discussed in a dynamical mean field theory of Hubbard model by Potthoff and Nolting.

Here we concentrate on the effect of a vacuum-solid surface on interacting electron-phonon systems, and we study the formation of polarons and the transition to a bipolaronic insulating state in the semi-infinite Holstein model at half-filling and zero temperature on the bipartite simple cubic (sc) lattice with nearest-neighbor hopping. While the occurrence of charge transfer is typical for a system with reduced translational symmetry, in our model at half-filling any charge transfer is excluded by the particle-hole symmetry, leading to a homogeneous charge distribution among the layers parallel to the surface, and local occupations near the surface do not differ from the average filling, $\langle n_\alpha \rangle = \langle n \rangle = 1$, where $\alpha$ labels each layer.

In addition to the geometrical effect of missing neighbors, the surface electronic structure of interacting electron systems is also complicated by the fact that the microscopic interactions in the vicinity of the surface have values which may significantly differ from those in the bulk. A relaxation of the surface layer, for example, changes the overlap between the one-particle basis states and thus implies a modified hopping integral. Within the Holstein model, the parameter modifications will be reflected in different values of the surface topmost layer hopping integrals and e-ph coupling strengths rel-
ative to the bulk ones. In this work we will not consider this effect, in order to focus on the more intrinsic effects that can give rise to different physics in the surface.

This paper is organized as follows: In Sec. II the model is introduced and the application of DMFT for surface geometry is briefly discussed. We mainly characterized the electronic and phononic properties by considering the layer quasiparticle weights, double occupancies and the phonon probability distribution function. The corresponding results are discussed in Sec. III. Finally Sec. IV is devoted to concluding remarks.

II. THE MODEL AND METHOD

The Holstein Hamiltonian is defined by:

\[ H = - t \sum_{<ij>\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c.c.) + g \sum_{i} (n_i - 1) (b_i^\dagger b_i + \Omega_0 \sum_{\delta} b_\delta^\dagger b_\delta), \]  

where \( c_{i\sigma} (c_{i\sigma}^\dagger) \) and \( b_i (b_i^\dagger) \) are, respectively, destruction (creation) operators for itinerant electrons with spin \( \sigma \) and local vibrons of frequency \( \Omega_0 = 0.2t \) on site \( i \), \( n_i \) is the electron density on site \( i \), \( t \) stands for the itinerant electrons hopping matrix elements between the nearest-neighbor sites, and \( g \) denotes the electron-phonon coupling. We fix the energy scale by setting \( t = 1 \).

To obtain the ground state properties of this model, we use the embedding approach introduced by Ishida and Liebsch\(^{15}\) to extend DMFT to inhomogeneous systems. In this scheme, the system is divided into two parts: The surface region which includes the first \( N \) layers, and the adjacent semi-infinite bulk region (substrate) which is coupled to it. Next, we represent the effects of the substrate on the surface region by a complex, energy-dependent, embedding potential acting on the Hamiltonian matrix of the surface region. The embedding method requires to consider a relatively small number of surface layers and it is therefore a computationally less expensive extension of DMFT in the presence of an interface as compared to the slab method, in which the inhomogeneous system is simply represented as a finite number of layers\(^{15}\).

Because of translational in the plane perpendicular to the interface, the embedding potential of the substrate is diagonal with respect to the two-dimensional wave vector \( \mathbf{k} = (k_x, k_y) \) and can be expressed as an \( N \times N \) matrix by

\[ S(\mathbf{k}, i\omega_n) = TG(\mathbf{k}, i\omega_n)T, \]  

where \( G(\mathbf{k}, i\omega_n) \) is the Green’s function of the substrate defined by

\[ G(\mathbf{k}, i\omega_n) = \left[ (i\omega_n + \mu)I - \epsilon(\mathbf{k}) - \Sigma(i\omega_n) \right]^{-1}. \]  

In here, \( \Sigma(i\omega_n) \) is the bulk self-energy, which in the framework of single-site DMFT, is independent of wave vectors, \( \mathbf{k} \), and \( \omega_n \) are the Matsubara frequencies. We obtain the self-energy by performing a standard DMFT calculation for the bulk crystal corresponding to the substrate. \( \mu \) is the chemical potential and \( \epsilon(\mathbf{k}) \) is the two-dimensional dispersion relation, which includes information about surface geometry. The \( \epsilon(\mathbf{k}) \) matrix for the surface cutting a simple cubic lattice along the \( z \) direction [sc(001) surface] takes the following form\(^{9}\):

\[ \epsilon(\mathbf{k}) = \begin{pmatrix} \epsilon_\parallel(\mathbf{k}) & \epsilon_\perp(\mathbf{k}) \\ \epsilon_\perp(\mathbf{k}) & \epsilon_\parallel(\mathbf{k}) \end{pmatrix}. \]  

The intralayer (parallel) hopping and the interlayer (perpendicular) hopping are specified by \( t\epsilon_\parallel(\mathbf{k}) \) and \( t\epsilon_\perp(\mathbf{k}) \), respectively, and are given by

\[ \epsilon_\parallel = -2[\cos(k_x) + \cos(k_y)], \quad |\epsilon_\perp(\mathbf{k})|^2 = 1. \]  

Finally, \( T \) is the hopping matrix between primitive cells of substrate and surface region. Since \( T \) is non-zero between nearest-neighbor layers of substrate and surface region, only the surface Green’s function\(^{16}\) of the substrate need to be considered in Eq. (2).

After constructing the embedding potential of the substrate, \( S(\mathbf{k}, i\omega_n) \), by way of a coupled-layer DMFT calculation in the surface region the self-energy matrix is determined self-consistently. This can be achieved via the following steps: (i) associating an effective impurity model with each layer in the surface region, solving them by using an impurity solver to find the layer-dependent local self-energies, \( \Sigma_{\alpha\beta}(i\omega_n) \), and constructing the surface region self-energy matrix which is diagonal in layer indices \( \alpha, \beta \) with the elements, \( \Sigma_{\alpha\beta}(i\omega_n) = \Sigma_{\alpha\beta}(i\omega_n)\delta_{\alpha\beta} \), (ii) calculating the on-site layer-dependent Green’s function via the following relation:

\[ \Sigma_{\alpha}(i\omega_n) = \sum_{\mathbf{k}} \left( \frac{1}{(i\omega_n + \mu)I - \epsilon(\mathbf{k}) - S(\mathbf{k}, i\omega_n) - \Sigma(i\omega_n)} \right)_{\alpha\alpha}, \]  

where \( N \times N \epsilon(\mathbf{k}) \) matrix is given by Eq. (4), (iii) implementing the DMFT self-consistency relation for each layer, \( G_{\alpha}(i\omega_n) = [G_{\alpha}^{-1}(i\omega_n) + \Sigma_{\alpha}(i\omega_n)]^{-1} \), which determines the bath parameters for the new effective impurity model. The cycles have to be repeated until self-consistency is achieved.

We use the exact diagonalization (ED) technique to solve the effective impurity model at zero temperature\(^{17}\), which works equally well for any values of the parameters and only involves a discretization of the bath hybridization function, which is described in terms of a finite and small set of levels \( n_s \) in order to limit the Hilbert space to a workable size. For the case of phonon degrees of freedom we considered here, the infinite phonon space is also truncated allowing for a maximum number of excited phonons \( N_{ph} \). The typical values we considered for the bath levels are \( n_s = 8 - 9 \) and typical maximum number of phonons are \( N_{ph} = 30 - 50 \). We tested that these numbers, indeed, provide converged results. Moreover, the number of surface layers is chosen to be \( N = 5 \) in all calculations.
II. QUASIPARTICLE WEIGHT FOR A CORRELATED INSULATOR

Fig. 1 shows the calculated quasiparticle weight \( z \) of the semi-infinite Holstein model at \( T = 0 \) in the metallic range as a function of layer index \( \alpha \). Crosses on the vertical axis on the right hand side indicate the bulk \( z \) corresponding to five given-values of \( g \). Lines are drawn as a guide to the eye.

III. RESULTS

As we anticipated in the introduction, all our calculations are performed for the case of uniform parameters. This assumption, together with the half-filling condition which enforces charge homogeneity, let us to single out the effect of the interface and to focus on the purely geometrical aspect of the problem. Fig. 1 shows the calculated quasiparticle weight \( z_{\alpha} \) of the semi-infinite Holstein model at \( T = 0 \) in the metallic range as a function of layer index \( \alpha \), where the outermost layer corresponds to \( \alpha = 1 \). \( z_{\alpha} \) measures the metallic nature of a system, \( z \) being one for a non-interacting metal and zero for a correlated insulator. In our case \( z = 0 \) implies a bipolaronic insulator. The crosses on the vertical axis on the right hand side indicate the \( z \) values of the bulk metal determined by a separate bulk DMFT calculation. For any value of the coupling, the quasiparticle weight of the surface layer \( z_{\alpha=1} \) is significantly reduced compared to \( z_{\alpha=2} \) and \( z_{\alpha=3} \) which can be understood as the effect of the reduced surface coordination number and enhanced effective correlations, in complete analogy to the results for repulsive interactions. The evolution as a function of the layer index depends instead on the coupling regime. For weak and moderate coupling, \( z_{\alpha} \) has a non monotonic behavior which is damped with increasing distance to the surface. For \( g \)-values closer to the critical coupling strength of the bulk bipolaronic transition, \( g_c \) ( \( g_c \approx 0.55 \) ) the behavior changes qualitatively. Here the layer dependence becomes monotonic, and the quasiparticle weight quickly approaches its bulk value with increasing \( \alpha \).

Fig. 2 illustrates the layer-dependent quasiparticle weight \( z_{\alpha} \) for the first three layers and the bulk quasiparticle weight as a function of \( g \). As expected, all the \( z \)'s monotonically decrease as a function of the \( e\)-ph coupling, and they eventually vanish. As can be seen in the figure, the differences between the \( z \) and the bulk \( z \) diminish with increasing distance from the surface and for the third layer, the quasiparticle weight is almost indistinguishable from the bulk \( z \) on the scale used. It is crucial to observe that the different \( z_{\alpha} \) all vanish at the same value of \( g \), which also coincides with the bulk critical coupling strength, \( g_c = g_{c,\text{bulk}} \).

If the surface and the bulk were decoupled, the reduced surface coordination number would tend to drive the surface to an insulating phase at a coupling strength lower than the bulk critical coupling \( g_c \). However, below \( g_c \) the bulk excitations, due to hopping processes between the surface and the bulk can induce a quasiparticle peak with a non-zero weight \( z_{\alpha=1} > 0 \) in the topmost layer and a real surface transition is not found; \( z_{\alpha=1} \) remain non-zero, although being very small, up to the critical coupling for bulk transition, \( g_c \). The investigation of the imaginary part of the layer-dependent self-energies, \( \Sigma_{\alpha}(i\omega_n) \) at \( \omega_n \to 0 \) (not shown) confirms the uniqueness of the critical strength \( g_c \). In the limit of \( \omega_n \to 0 \) and for all \( g < g_c \), the imaginary part of self energy vanishes for all layers as it must be for a Fermi liquid. In the coupling constants close to \( g_c \), and in the metallic regime, a significant layer dependence of \( Im\Sigma_{\alpha}(i\omega_n) \) for \( \omega_n \to 0 \) with a considerably larger slope in the first layer (\( \alpha = 1 \)) is seen, which reflects the enhanced correlation effects at the surface. In the insulating state, \( Im\Sigma_{\alpha}(i\omega_n) \) diverges for \( \omega_n \to 0 \). Therefore, there is
a unique critical strength $g_c$, at which all quasiparticle weight functions, $z_{\alpha}(g)$, simultaneously approach zero.

The layer-dependent average double occupancy, $d_{\alpha} = \langle n_{\alpha1} n_{\alpha1} \rangle$, is shown in the bottom panel of Fig. 2 as a function of $g$. For small $g$ and all layers, $d_{\alpha}$ increases gradually. At $g = g_c$ it rapidly reaches $\approx 1/2$. In the metallic region, the double occupancies are increased more rapidly at the topmost surface layer as compared with the interior of the system. Again, this is due to the stronger effective e-ph interaction which results from the narrowing of the non-interacting density of states at the surface.

We have thus far established that even in the presence of a surface, the half-filled Holstein model undergoes a single bipolaronic metal-insulator transition, despite the surface is less metallic than the bulk for any $g < g_c$. We now discuss how the surface influences the local lattice distortions, measured by the phonon probability distribution function (PDF), $P(x) = \langle \phi_0 | x | x \rangle \langle x | \phi_0 \rangle$, where $| x \rangle$ is the projection operator on the subspace for which the phonon displacement $\hat{x}$ has a given value $x$, and $| \phi_0 \rangle$ is the ground state vector. This quantity can be used to characterize the polaron crossover, which can be used to characterize the polaron crossover.

In the absence of e-ph interaction $P(x)$ is a Gaussian centered around $x = 0$. A small e-ph coupling slightly broadens the distribution which remains centered around $x = 0$, implying that the coupling is not sufficient to give rise to a finite polarization of the lattice. Continuously increasing the interaction one eventually obtains a bimodal distribution with two identical maxima at $x = \pm x_0$. Those maxima are indeed associated with empty and doubly occupied sites, and testify the entanglement between the electronic state and the lattice distortion, which is precisely the essence of the polaron crossover. Thus, the appearance of a bimodal shape in $P(x)$ is a marker of the polaron crossover.

Fig. 3 shows the polaron crossover for our semi-infinite Holstein model. For each layer the evolution as a function of the coupling follows the pattern we described above: The anharmonicity due to e-ph interaction increases with increasing coupling strength leading first to a non-Gaussian and finally to a bimodal PDF at all $g > g_{pol}$. This behavior signals the appearance of static distortions, even if we are neglecting any ordering between them. The strongest differences with respect to the bulk PDF are found for the top layer ($\alpha = 1$) PDF. The layer PDFs converge to the bulk PDF with increasing distance to the surface. Beyond the third layer the PDF is essentially identical to its bulk behavior. It is apparent from the data of Fig. 3 that the PDF at the topmost (surface) layer becomes bimodal at lower values of the coupling strength with respect to the internal layers. The surface can display polaronic distortions while the bulk is still undistorted (even if the local vibrations are strongly anharmonic).

IV. CONCLUDING REMARKS

We have investigated polaron formation and transition to the bipolaronic insulating state at solid-vacuum surface at zero temperature in the framework of the semi-infinite Holstein model at half-filling. Using the embedding approach to extend dynamical mean-field theory to layered systems, it is found that the bipolaronic insulating state occurs simultaneously at the surface and in the bulk, and it takes place exactly at the same critical coupling strength $g_{c, bulk}$ as for the infinitely extended system, $g_{c, bulk} = g_c$. When the system is metallic the topmost layer quasiparticle weight $z_1$ is smaller than the bulk value $z_{bulk}$, since a reduced surface coordination number implies a stronger effective correlation effects. Fixing the coupling at values quite smaller than $g_c$, the quasiparticle weight is an oscillating function of the layer index. As the distance from the surface increases, these oscillations fade away. For couplings close to the metal-insulator transition $z_\alpha$ instead monotonically increases by approaching the bulk. On the other hand, the polaron crossover occurs more easily at the surface with respect to the bulk. There is therefore a finite window of e-ph coupling in which the surface presents polaronic distortions, while the bulk has no distortions. As we already mentioned, this difference is not able to support a metallic bulk coexisting with an insulating surface.
Surface effects are expected to be the more pronounced the larger is the number of missing neighbors in the topmost layer. As we move from the sc(001) to the sc(011) and to the sc(111) surface geometries, the surface coordination numbers decrease from $n_{c}^{(001)} = 5$ to $n_{c}^{(011)} = 4$ to $n_{c}^{(111)} = 3$, respectively. Therefore, we expect to observe a narrowed topmost layer free density of state which results in an enhanced ratio between the e-ph coupling strength and the effective band width. Consequently, the e-ph interaction tends to be stronger at the surface. Clearly, according to this argument we expect the difference between the two coupling strengths for the polaron formation at the surface and in the bulk would become larger.

The present study has been restricted to uniform model parameters. This leaves several open questions like the possibility of coexisting different surface and bulk phases, if the model parameters at the vicinity of the surface are modified (See the comment made in this respect in Sec. I).

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