Optical conductivity of polarons: Double phonon cloud concept verified by diagrammatic Monte Carlo simulations

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We study theoretically a fundamental issue in solids: the evolution of the optical spectra of polaron as the electron-phonon coupling increases. By comparing the exact results obtained by the diagrammatic Monte Carlo method and the data obtained through exact diagonalization within an appropriate subspace of the phononic wavefunctions, the physical nature of the crossover from weak to strong coupling is revealed. The optical spectra are well understood by the quantum mechanical superposition of states with light and heavy phonon clouds corresponding to large and small polarons, respectively. It is also found that the strong coupling Franck-Condon regime is not accessible at realistic values of the coupling constant.

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I. INTRODUCTION

Polaron physics plays a crucial role in describing magnetoresistive perovskites,[1] high-temperature superconductors,[2,3] molecular semiconductors,[4] fullerenes,[5] polar semiconductors,[6] etc. However, in spite of a lot of efforts, there are still only a few well grounded results concerning spectral properties, optical conductivity (OC), and Lehman spectral function of polaronic systems at any coupling. Even the simplest model for a periodic system, i.e., the Holstein model, is not an exception, and the nature of its spectral response at all couplings is still a puzzle, in particular in the nearly adiabatic case, the most frequently encountered regime in experiments.

In contrast to Frochlich-like models,[7] which simplify the manifold of all momenta of the lattice system by using continuum approximation, the Holstein model takes into account the true momentum space of the system.[8] Here the tight-binded charge carrier is coupled with an optical local phonon mode:

$$H = -t \sum_{<i,j>} c_i^\dagger c_j + \omega_0 \sum_i b_i^\dagger b_i + g\omega_0 \sum_i c_i^\dagger c_i (b_i^\dagger + b_i),$$

where t is the nearest-neighbor hopping amplitude, $c_i^\dagger$ (c_i) denotes the electron creation (annihilation) operator in the site i, and $b_i^\dagger$ (b_i) creates (annihilates) a phonon in the site i with frequency ω_0. The strength of electron-phonon interaction is characterized by the dimensionless coupling parameter $\lambda = g^2\omega_0/2tD$ expressed in terms of the coupling constant g and system dimensionality D.

There are many methods able to calculate the ground-state properties of the Holstein polaron (see Ref. 9 for an incomplete list). In particular, adiabatic and some variational calculations lead to a discontinuous transition between weak and strong coupling regimes as electron-phonon interaction increases.[10] The quantum correction to this picture is a singular perturbation, and essentially nonperturbative. A naive picture is that the discontinuous transition becomes a crossover by quantum mixture of states describing asymptotic regimes. On the other hand, the situation changes drastically if some spectral properties, e.g., OC, are considered. The main problem is due to the infinite dimensional phononic Hilbert space that has prevented an in-depth analysis so far. The full phonon basis exact diagonalization (ED) method[11] is basically valid only for 1D and 2D systems and suffers from effects caused by the very small size of the considered clusters, normally limited to ten sites. The dynamical mean-field theory,[12] though it is exact in an infinite dimension system, leaves doubts about applicability to realistic 3D, 2D, and especially 1D systems. Finally, containing no approximation, diagrammatic Monte Carlo (DMC) methods[3,13] provide approximation-free results for infinite systems of any dimension. However, none of the above methods help physical intuition or provide an understanding of the nature of OC and/or excited states in the weak, strong, and especially the traditionally most puzzling intermediate coupling regime. An exception is momentum average[14] approach. It suggests an analytic formula and explicitly relates the shape of OC in the strong coupling regime to the phononic cloud dragged by polaron moving through the crystal. Unfortunately, the intermediate coupling regime, the most interesting one from an experimental point of view, is a puzzle for the momentum average approach too.

II. POLARON OPTICAL CONDUCTIVITY

In the present paper, we present the exact DMC results for the OC of the 1D system for any interaction value ranging from the weak- to the strong-coupling regime. The regular part of the OC, a typical experimental probe of a physical system, is defined[15] as

$$\sigma_{\rm reg}(\omega) = \pi \sum_{n\neq 0} \frac{|\langle\psi_n|j|\psi_0\rangle|^2}{\omega_n}[\delta(\omega-\omega_n)+\delta(\omega+\omega_n)].$$

Here

$$j = iet \sum_{<i,j>} c_i^\dagger c_j(\vec{R}_i - \vec{R}_j) \qquad (1)$$

is the current operator, $\vec{R}_i$ is the position vector of the site i, e is charge, $|\psi_n\rangle$ and E_n are the exact eigenstates and eigenvalues, respectively, and $\omega_n = (E_n - E_0)$. The lattice parameter a and Planck constant $\hbar$ are set to unity.

To disclose the nature of the OC we introduce two contrasting physical pictures of a polaronic phonon cloud: i) a weak-coupling phonon cloud (WCPC) that allows for a very good description of the weak-coupling regime; ii) a strong-coupling phonon cloud (SCPC) that is able to reproduce accurately the properties of the strong-coupling regime. The surprising result obtained by our analysis of the exact DMC data is that a straightforward linear superposition of the weak- and strong-coupling phonon clouds, i.e., double phonon cloud (DPC), is capable of describing polaron properties in any coupling regime. Comparison of the exact results with those obtained by the DPC analysis points out that the Franck-Condon approach, based on the factorization of the wave functions associated to charge and lattice degrees of freedom and on optical transitions in a frozen lattice, fails at all couplings except for strong and unrealistic values of charge-lattice interaction, i.e., at couplings where one can use the crudest photoemission approximation (PA) that describes the photoionization process toward the free-electron continuum: Within the Franck-Condon approach one replaces the exact excited charge states within the ground-state lattice potential well with the free electron states in the absence of electron-phonon interaction.

The phonon cloud in the weak-coupling regime is not characterized by strong local deformations, and, thus, we set that the WCPC consists of up to $n \leqslant \mathcal{N}_{wc}$ phonons situated at arbitrary sites (upper panel in Fig. 1). To the contrary, the lattice deformation is well localized in the strong-coupling regime, and, thus, we construct the phonon SCPC as $n \leqslant \mathcal{N}_{sc}$ phonons located at three nearest-neighbor sites. Due to the nonlocal nature of the current operator Eq. (1), it is crucial that the deformed neighboring sites are situated in the arbitrary place with respect to the charge carrier (two lower panels in Fig. 1). We found that $\mathcal{N}_{\rm wc} = 5$ and $\mathcal{N}_{\rm sc} = 50$ is enough to describe successfully the system in the range of the λ values

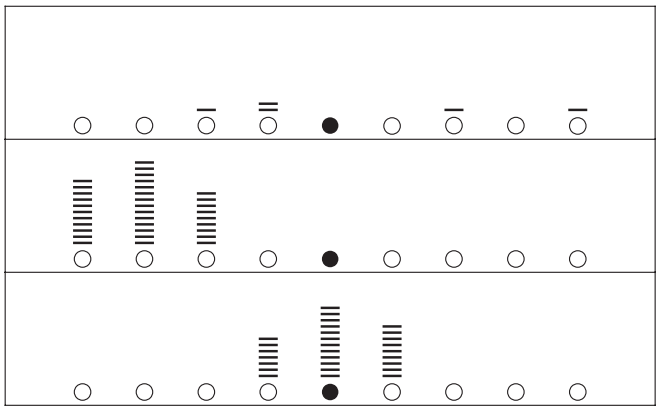

FIG. 1. The empty (full) circles stand for the lattice sites (electron); the dashes denote phonons. The upper panel represents a typical WCPC, and the two lowest panels show possible realizations of the SCPC.

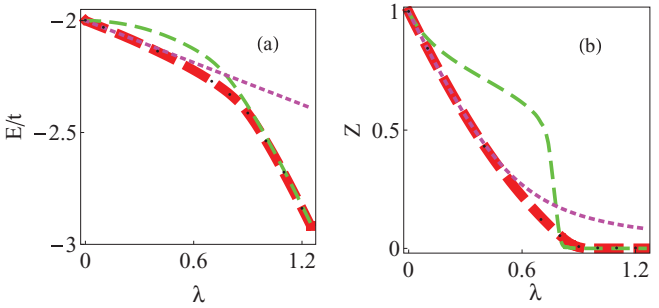

FIG. 2. (Color online) (a) Energy versus λ in the DMC (black dots), DPC (dashed thick red line), lowest order perturbation (Ref. 16) (dotted magenta line), and Franck-Condon (dashed thin green line) approaches; (b) ground-state spectral weight versus λ in the DMC (black dots), DPC (dashed thick red line), WCPC (dotted magenta line), and momentum average (0) approaches (dashed thin green line).

considered in the following and concerning the 1D case with $\omega_0/t = 0.1$ (the lattice size is 80).

First, we compare the ground-state properties obtained by DPC model and those coming from the exact DMC method and demonstrate a good agreement [see Figs. 2(a) and 2(b)]. A very good agreement is seen even in the intermediate coupling regime suggesting that the DPC combination of the weak- and strong-coupling phonon clouds provides an accurate description in the whole range of coupling parameters. Indeed, there are domains of λ values where both strong- and weak-coupling phonon cloud models fail, but, nevertheless, the results using the DPC model are still in good agreement with exact ones. Not only ground-state properties but also the Lehman spectral function is well reproduced by the DPC picture (Fig. 3). One can see the obvious failure of the simplest variant of the momentum average approach [i.e., momentum average (0) that takes into account only lattice deformations located at one lattice site at a time] in describing the ground-state spectral weight Z [see Fig. 2(b)]. This failure explicitly demonstrates that in the intermediate coupling regime the phonon wave functions are characterized by lattice distortions involving many sites at the same time.

Good agreement of the OCs obtained by perturbative and DMC approaches at $\lambda = 0.01$ [see Fig. 4(a)] indicates that the final states of the optical transition do not contain more than

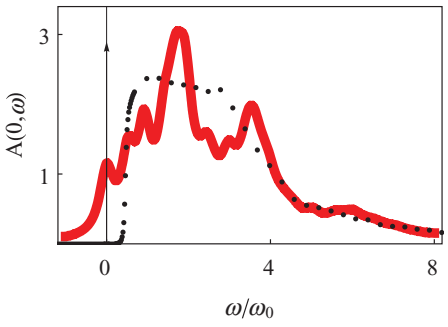

FIG. 3. (Color online) Lehman spectral function in the DMC method (black dots for incoherent part and vertical black arrow for δ-functional polaron state) and in DPC approach (solid red line).

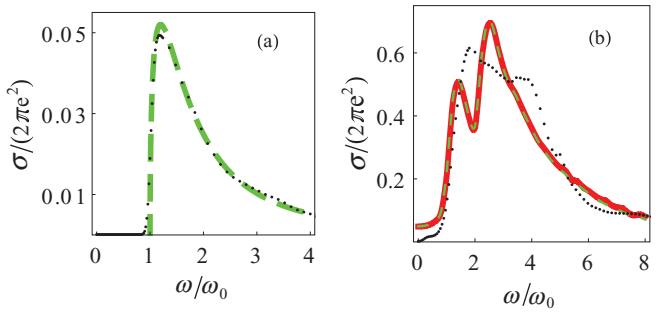

FIG. 4. (Color online) OC in DMC method (black dots) at $\lambda = 0.01$ (a) and $\lambda = 0.4$ (b). Dashed green line is lowest perturbative result (Ref. 16) in (a). Dashed thin green (solid thick red) line in (b) is the result of WCPC (DPC) approach.

one phonon. To the contrary, evident rise of OC at $2\omega_0$ for $\lambda = 0.4$ [see Fig. 4(b)] manifests the importance of the processes where correlation between two successively emitted phonons is present. The agreement between the WCPC approximation and the DPC approach indicates that the contribution of the strong-coupling counterpart of the phonon cloud is still negligible at $\lambda = 0.4$.

In Fig. 5, the exact data for the OC in the intermediate coupling regime ($\lambda \approx 0.8$) are compared with the results following from the WCPC, SCPC, and DPC conceptions of the phonon clouds. The intermediate coupling regime is a stumbling stone for most of the methods because any approach, starting from the characteristic features of either the weak- or strong-coupling regime, fails there. The results in Fig. 5 clearly reveal the reason for such difficulties, showing that the phonon cloud in this regime is a *superposition* of the WCPC and SCPC contributions. The dominating hump of the OC splits into two peaks: The former one is located at the energy determined by the weak-coupling counterpart of the lattice deformation and the higher energy structure is governed by the strong-coupling component of the phonon cloud. Indeed we note that if the OC obtained in the framework of the Franck-Condon concept is shifted toward lower frequencies, we recover the peak of the OC governed by strong-coupling lattice deformation (see insets in Fig. 5). Hence, the OC in the intermediate coupling

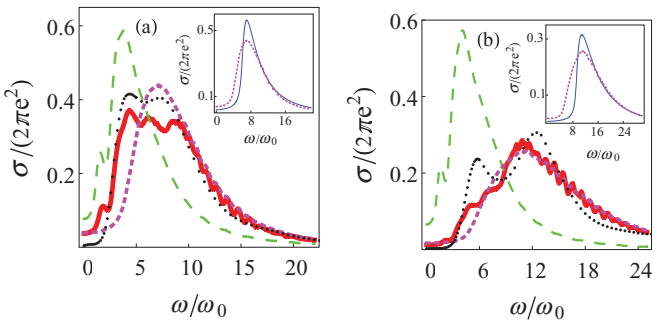

FIG. 5. (Color online) OC in DMC (black dots), DPC (solid red thick line), WCPC (dashed green line), and SCPC (dotted magenta line) approaches at $\lambda = 0.77$ (a) and $\lambda = 0.87$ (b). Insets show comparison of OCs in SCPC and Franck-Condon (solid blue line) approaches. The OC in the Franck-Condon approach is shifted down by energy $\approx 5\omega_0$.

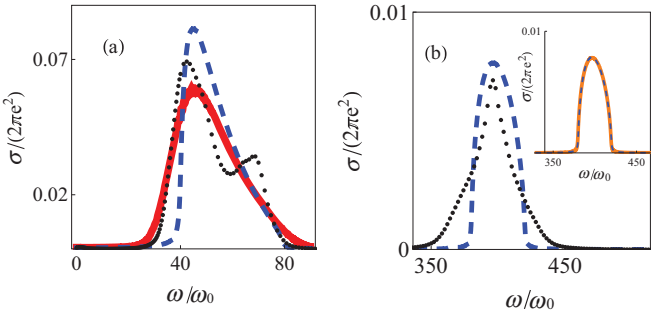

FIG. 6. (Color online) OC in DMC (black dots), DCP (solid red thick line), and Franck-Condon (dashed blue line) approaches at $\lambda = 1.5$ (a) and $\lambda = 10$ (b). Inset in (b) shows OC in Franck-Condon approach and photoemission curve (solid orange line).

regime is not yet described by the Franck-Condon processes where optical excitations correspond to electronic excitations in the rigid lattice. The highest energy peak of the OC in the intermediate coupling regime can be interpreted as the result of light absorption in two successive steps: The lattice is frozen during the electronic transition at the first stage and then it relaxes and adapts itself to new electron configuration.

By increasing λ there is a net transfer of spectral weight toward higher frequencies, and at $\lambda = 1.5$ only the higher energy contribution survives [see Fig. 6(a)]. In this regime the energy of lattice relaxation from the frozen Franck-Condon state is almost zero and the energies of the main peak of the OC in the DMC, DPC, SCPC, and Franck-Condon approaches are the same. On the other hand, there are differences in the tails of the OC calculated in the above techniques, indicating the residual role played by the nonadiabatic transitions even in the strong-coupling regime. Finally, the crudest PA approximation is valid at extremely large couplings [see inset in Fig. 6(b)].

In Fig. 7, we plot the energy of lattice relaxation from the frozen Franck-Condon state ΔE. According to the previously described physical scenario, we find that it becomes negligibly small only in the very strong coupling regime at $\lambda > 1.2$. On the other hand, the polaron mass at such couplings is three orders of magnitude larger than the bare mass. Such an effective mass, to the best of our knowledge, was never observed in any physical system.

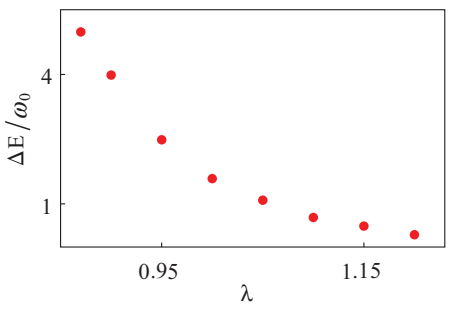

FIG. 7. (Color online) Energy of lattice relaxation from the frozen Franck-Condon state to the relaxed excited configuration of the SCPC state.

III. DETAILS OF THE METHOD

In the following, we will describe in detail the above introduced double phonon cloud (DPC) approach, based on a limited phonon basis and the exact diagonalization. Limited phonon basis, including not the whole manifold of the phonon states but only the essential ones, enables studies of large systems up to about 100 sites. The proposed approach allows us to investigate successfully any electron-phonon coupling at any adiabatic ratio.

First of all, we take into account the translational invariance of the Hamiltonian and perform an exact diagonalization of the Hamiltonian based on the Lanczos algorithm, requiring that the states have a definite momentum.[17] Each of the basis vectors is a linear superposition with appropriate phases of the translational copies (charge carrier and lattice configurations are together rigidly translated) of a state having the electron fixed at a site and phonon quanta located around it.

The *weak-coupling counterpart* is restricted to at the most five phonons situated at up to five different sites which, in turn, are arbitraryly located with respect to the charge carrier. The phononic Hilbert subspace corresponding to the WCPC is generated by the following elements:

$$|ph\rangle^{(\mathrm{WCB})}_{[j],[n_j]} = \prod_{h=1}^{5} \frac{(a^{\dagger}_{j_h})^{n_{j_h}} |0\rangle_{j_h}}{\sqrt{n_{j_h}!}} \prod_{i\neq[j]} |0\rangle_i \,. \qquad (2)$$

Here i, j_h label the lattice sites, $[j] = (j_h, h = 1, \ldots 5)$ represents a set of five different sites, $|0\rangle_i$ is the i-site phonon vacuum state, and the integers $n_{j_h} = 0, \ldots . 5$ are such that $\sum_h n_{j_h} \leqslant 5$. In any basis element, there are up to five phonons distributed on at the most five different sites: All the others sites are not deformed. In this way the scattering processes between the charge carrier and lattice for up to five phonons in q space are exactly treated. This basis is able to recover the self-consistent Born approximation and goes beyond it including vertex corrections.

The *strong-coupling counterpart* in the direct space representation contains the following set of states:

$$|ph\rangle^{(\mathrm{SCB})}_{j,n_j,n_{j'}} = \frac{(a^{\dagger}_{j})^{n_j} |0\rangle_j}{\sqrt{n_j!}} \prod_{j'} \frac{(a^{\dagger}_{j'})^{n_{j'}} |0\rangle_{j'}}{\sqrt{n_{j'}!}} \prod_{i\neq(j,j')} |0\rangle_i \,. \qquad (3)$$

Here j' indicates the nearest neighbors of the j site, and $n_{j'}$ represents the number of phonons on such sites. In any basis element there is a cluster with at the most three deformed nearest-neighbor sites which are located at an arbitrary position with respect to the electron. We found that the sufficient basis for all of the above studied couplings is limited to $(n_j + \sum_{j'} n_{j'}) \leqslant 50$. We note that by restricting the cluster with excited phonons to one site, one comes to the simplest formulation of the momentum average approximation, i.e., momentum average (0).[18]

The *DPC approach* is based on the idea that the physical properties for any value of the electron-phonon interaction can be described by diagonalizing the Hamiltonian in the phononic Hilbert subspace generated by both above introduced sets of states (excluding obvious double counting).

IV. CONCLUSIONS

In conclusion, we have shown that the ground state, Lehman spectral function, and OC of the polaron at any coupling are well described in terms of superposition of two phonon clouds: The former one is spatially extended and contains small number of phonons, whereas the latter one is well localized and includes a large number of vibrational quanta. Surprisingly, the lattice deformation around the polaron in the puzzling intermediate coupling regime appears to be not a peculiar characteristic of this particular regime but a mere superposition of quantum states representing two asymptotic couplings. The accuracy of the results obtained in the present paper confirms the usefulness of DPC method, which uses not the whole manifold of the phonon states but only the essential ones. This DPC method enables the study of large systems, which are inaccessible by the classic exact diagonalization method. Comparing the results for OC of this method with those obtained by the approximation-free diagrammatic Monte Carlo method validates both the suggested double phonon cloud concept and the numeric method based on it. This method can be further applied to problems of nonequilibrium dynamics[19] where such methods as diagrammatic Monte Carlo fail.

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