Polaronic optical absorption of the Holstein and Su-Schrieffer-Heeger models

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The optical conductivity of a polaronic charge carrier in the intermediate and strong-coupling regimes is calculated for a tight-binding electron using exact diagonalization. Two different simple models of the electron-phonon coupling are considered: the Holstein model, with coupling of the lattice displacement to the local electron density, and the Su-Schrieffer-Heeger type of coupling arising from modulation of the electronic overlap integral. The two models are shown to exhibit a similar polaronic absorption band. However, the Su-Schrieffer-Heeger form of coupling gives rise to a second strong absorption band not present in the Holstein model. This additional feature corresponds to transitions from the ground state of bonding character on a shortened bond to excited states of anti-bonding character on the same shortened bond.

I. INTRODUCTION

Electrons may acquire polaronic character when they strongly interact with phonons in such a way that the effect of the interaction is not merely a perturbative correction to the free electron. More specifically, if the electron-phonon (e-ph) interaction is sufficiently strong a cross-over occurs from the quasi-free electron limit in which the e-ph interaction weakly renormalizes the free-electron properties, to the polaronic state in which the electron is strongly bound to a potential well generated by the lattice distortion induced by the electron itself.

The possible relevance of polaronic phenomena to the high $T_c$ superconductors suggested by the observation of polaronic features in the optical response of lightly doped cuprates has generated renewed interest in the theoretical study of the conditions for and consequences of polaron formation. The strong-coupling nature of the polaron state severely limits the possibilities for reliable analytic approaches, in particular in the intermediate coupling region near the cross-over. For example, while quite accurate variational wave functions may be formulated, it is not feasible to calculate dynamical properties within this approach. The numerical exact diagonalization of small clusters on the other hand, allows the exact calculation of both static and dynamic properties with the only limitations being the finite memory available on the computer. We therefore use exact diagonalization to determine the optical conductivity for small one-dimensional clusters. Since the polaron becomes well localized for sufficiently strong coupling, finite-size effects may be controlled to a large extent by appropriate choice of the model parameters.

In this paper we study the optical response of the Holstein model and the Su-Schrieffer-Heeger (SSH) model. These models are the most used for electrons interacting with phonons via a short range e-ph interaction; we study the analogies and the differences between the optical absorption features for the two models.

The Holstein model is described by the Hamiltonian

$$\mathcal{H} = -t \sum_{\langle ij \rangle} c_i^\dagger c_j + \omega_0 \sum_i a_i^\dagger a_i + g \sum_i c_i^\dagger c_i \left( a_i + a_i^\dagger \right)$$

(1)

and the Su-Schrieffer-Heeger model by the Hamiltonian

$$\mathcal{H} = -t \sum_{\langle ij \rangle} c_i^\dagger c_j + \omega_0 \sum_i a_i^\dagger a_i$$

$$+ \frac{g}{\alpha} \sum_i \left[ \left( c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i \right) \left( a_i^\dagger + a_i \right) - a_i^\dagger - a_i \right].$$

(2)

We use units such that $\hbar = c = a = 1$, where $a$ is the lattice spacing. In both models the free electron part (first term) corresponds to hopping to a nearest neighbour site with hopping integral $t$, which we will take as our unit of energy. Since we restrict ourselves to the single electron case we will suppress electron spin indices. The second term describes free Einstein dispersionless phonons ($\omega(q) = \omega_0$) on each site. The e-ph term introduces a coupling between the phonon field and the local electron density (Holstein model) or the covalent bond operator $c_i^\dagger c_j$ (SSH model). Note that this model differs from the conventional SSH model in having local Einstein phonon modes rather than acoustic phonons. To compare and contrast the optical absorption of the two models we avoided unnecessary differences between them, in order to identify the differences deriving from the different e-ph coupling.

The Holstein e-ph coupling arises from the dependence of the atomic potential energy on the ionic displacement. This coupling is relevant in physical systems in which the screening is very weak, as is believed to be the case in the high $T_c$ superconductors with small doping. On the other hand, the SSH coupling arises if one assumes that the hopping integral depends on the distance between the ions. Despite the fact that the physical origin of the two terms is different we will use the same notation for the bare coupling constant ($g$) for both models, in order to underline the general character of the physical processes under consideration. One may define two independent dimensionless couplings, $\alpha = g/\omega_0$ and $\lambda = g^2/(2\omega_0)$ where $d$ is the dimensionality. In a previous paper we studied the conditions for the formation of small polarons...
for both models, finding that for the Holstein model the carriers have polaronic character if $\lambda > 1$ if the phonon frequency $\omega_0$ is smaller than $t$ (adiabatic regime), while the criterion is $\alpha > 1$ if the phonon frequency is larger than the hopping integral (antiadiabatic regime). Note that since polaron formation is not a phase transition, but rather a cross-over, there is some ambiguity in the definition of the exact numerical value of the critical value for polaron formation. For the SSH model the relevant parameter is $\lambda$ regardless of the value of the adiabatic ratio $\omega_0/t$. $\lambda = 0.2$ is the critical value for a significant polaronicity of the ground state of this model.

One important and direct consequence of the different nature of the electron-phonon coupling in the two models is obvious in the strong-coupling limit: the local character of the Holstein coupling drives the system towards polaron states localized on a single site, while the covalent coupling in the SSH model leads the system to localize the electron on a bond, forming an even symmetry state localized on two neighbouring sites. We shall see that this difference between “site” and “bond” polarons manifests itself in very obvious differences in the optical absorption spectra of the two models.

II. FORMALISM

The real part of the conductivity for a one-dimensional tight-binding model at zero temperature may be expressed in terms of the Kubo formula

$$\sigma(\omega) = D\delta(\omega) + \Im \langle 0|J^\dagger \frac{1}{\omega - H + E_0 - i\delta} J|0 \rangle,$$

where $J$ is the current operator.

The coefficient of the zero-frequency delta function contribution $D$ is usually called the Drude weight: it is given by

$$D = -\frac{\pi e^2}{2} \langle H_t \rangle - \sum_{n \neq 0} \frac{|\langle \phi_0|J|\phi_n \rangle|^2}{E_n - E_0}. \tag{4}$$

If the Drude weight $D$ is non-zero the system is a perfect conductor; this will generally be the case in such models with periodic boundary conditions (PBC) and no disorder at zero temperature.

In the Holstein model $J$ is

$$J_H = i\epsilon t \sum_i \left( c_{i+1}^\dagger c_i - c_i^\dagger c_{i+1} \right) \tag{5}$$

while for the SSH model it is

$$J_{SSH} = i\epsilon \sum_{i>0} \left[ t - g(a_{i+1}^\dagger + a_{i+1} - a_i^\dagger - a_i) \right] \times \left( c_{i+1}^\dagger c_i - c_i^\dagger c_{i+1} \right). \tag{6}$$

The fact that $J_{SSH}$ contains an explicit coupling to the phonon degrees of freedom is physically simple to understand: in this case the bond-length is modified by the lattice distortion, so that the change in electric dipole moment associated with the hopping of an electron is modified proportionally. Here we have neglected in both cases the direct coupling of the electric field to the ions which is of order $\sqrt{m/M}$, where $m$ and $M$ are the electron and ion masses. We are interested only in the features resulting from the $e$-$ph$ coupling, not in the direct excitation of the bare phonons. Equations (3), (4), (5) and (6) may be derived following the standard approach used for example in the case of the Hubbard model.

The use of the Lanczos algorithm to evaluate correlation functions such as (3) is well established. In the present models one must introduce a cutoff in the occupation of the phonon modes in order to represent the Hamiltonian as a finite matrix. We have checked that the results presented here are not significantly affected by this cutoff by comparing results for different cutoffs. The finite-frequency part of (3) has previously been studied by Alexandrov et al. for the Holstein model.

We have used both periodic and open boundary conditions for our numerical calculations. With open boundary conditions (OBC) the system is like a molecule; in this case free acceleration is impossible and the Drude weight $D$ is always zero. With PBC $D$ may be determined either by studying the dependence of the ground state energy on an adiabatic change of boundary condition, equivalent to a static uniform vector potential, or by making use of the $f$-sumrule which relates the integrated conductivity to a ground state expectation value. For the Holstein model the latter is

$$\int_0^\infty \sigma(\omega)d\omega = -\frac{\pi e^2}{2} \langle H_t \rangle, \tag{7}$$

while, given the explicit form for the current for the SSH model Eq. (4) the sumrule for the SSH model is given by

$$\int_0^\infty \sigma(\omega)d\omega = -\frac{\pi e^2}{2} (H_t + H_{e-ph}). \tag{8}$$

The $e$-$ph$ coupling term appears in the sumrule for the SSH model in the same way the hopping term does: this is a direct consequence of the origin of this term, arising from a modulation of the hopping integral. We have made use of the sumrule to determine $D$.

III. THE OPTICAL EXCITATION OF SMALL POLARONS: SIMPLE LIMITS

The optical excitation of a small polaron for the Holstein model has been studied by Emin by means of general arguments in the adiabatic limit and calculated by means of exact diagonalization by Alexandrov et al. for the more general case. The physical origin of the optical absorption of a small polaron can be easily described in the adiabatic limit $\omega_0 = 0$ invoking the Franck-Condon
principle. The ground state is given by an electron localized on a single site, which is strongly displaced from its equilibrium position, while all the other sites are not displaced. The electron can be excited to a neighboring site without changing the lattice configuration by the application of the current operator. The difference in energy between the two states is the lowering of the electronic energy associated with the small polaron formation $2E_b$, where $E_b = 2\lambda T$ is the small polaron binding energy.

The physical mechanism we have described is not peculiar to the extreme adiabatic limit $\omega_0 = 0$, and is not strongly affected by the introduction of the lattice dynamics via a finite value of the phonon energy $\omega_0$. Note that the current operator (10) acts only on the electronic degrees of freedom. Hence the current operator connects only states having the same lattice configuration, or at least having a non-zero overlap as far as the phononic state is concerned. Thus the physical picture we introduced for the extreme adiabatic limit can be extended to finite frequencies.

The small polaron optical conductivity is then characterized by an absorption band centered at $2E_b$, well described by Reik’s formula

$$\sigma(\omega) = \frac{\pi e^2}{2E_b T} \frac{1 - e^{-\beta\omega}}{\omega} \exp \left[ - \frac{(\omega - 2E_b)^2}{8E_b T} \right].$$

(9)

The width of the band is proportional to $\sqrt{E_b T}/t$, which, in the small $T$ limit reduces to $\sqrt{E_b \omega_0}/t = g/t$, while the maximum of the intensity is proportional to $t^2/E_b T$, which reduces to $t^2/g^2$ in the small $T$ limit.

The SSH model optical conductivity can also be studied starting from adiabatic arguments invoking the Franck-Condon principle, but now taking into account the bond nature of the polaronic state. The ground state is characterized by a short bond on which the electron is localized. The short bond is generated by the shift of two neighboring sites towards one another by equal amounts. The electronic ground state is the even combination of the two local states.

The optical absorption can happen in two different channels: a “Holstein-like” one in which the electron is excited onto a different bond that is not shortened, and a local channel in which the electron is excited from the even symmetry ground state into the local odd symmetry state on the short bond. The first kind of excitation is analogous to the excitation of the Holstein polaron and is expected to generate a band similar to the one previously described, centered at $2E_b$ (even if in this case $E_b$ is not simply given by the Lang-Firsov result $g^2/\omega_0$).

The local excitation energy is given by the difference in electronic energy between the even parity ground state and the odd parity state, keeping the lattice configuration fixed. While the “Holstein-like” excitation is characterized by the fact that the electron is excited from a state in which it gains an energy $2E_b$ from the local distortion to a state in which the electron energy is not affected by the lattice configuration, the “local” transition carries the electron from a state in which the distortion lowers the energy by an amount $2E_b$ to a state in which the electron energy is raised by the same amount $2E_b$. Hence the energy difference involved in the optical transition is $4E_b$.

If we introduce a finite phonon frequency this absorption peak broadens into a “band” exhibiting phonon features separated by the typical phonon frequency $\omega_0$.

For the special case of only two sites the SSH model can be analytically solved for arbitrary $\omega_0$ by means of a modified Lang-Firsov transformation that acts on the bond variable. After performing the modified Lang-Firsov transformation we obtain for the two site cluster

$$\sigma_{2s}(\omega) = \frac{\pi e^2}{4} \sum_{n=0}^{\infty} (2t + n\omega_0) e^{-8\alpha^2} \frac{(8\alpha^2)^n}{n!} \delta(\omega - (2t + n\omega_0)).$$

(10)

The conductivity of the two site cluster given by (10) consists of a succession of Dirac delta functions at frequencies separated by the phonon frequency $\omega_0$. Once the Dirac delta functions are substituted by Lorentzians the analytical formula (10) gives the same result as the numerical calculations: a single absorption band centered at $\omega = 2t + 8g^2/\omega_0$, with width proportional to $g/t$ and intensity proportional to $t/g + 4g/\omega_0$. Of course the other “Holstein-like” absorption feature which we argued should be present due to the transfer of the electron from the shortened bond to a neighboring undistorted one cannot occur for a two site system where there is only one bond. This implies that the sumrule (3) which is given by

$$\int_0^{\infty} \sigma(\omega)d\omega = \frac{\pi e^2}{2} \left( t + \frac{4g^2}{\omega_0} \right)$$

(11)

is exhausted by this feature. This is consistent with the width and intensity described above.

We expect the physics of the polaronic absorption for the SSH model to be much more dependent on the adiabatic ratio than is the case for the Holstein model. The dependence of the current operator on the phonon operators makes it possible to have an optical transition which does not leave the lattice configuration unaltered, especially if the phonon frequency is comparable or even greater than the hopping integral. This point will be discussed further in light of the numerical results.

### IV. EXACT DIAGONALIZATION RESULTS

In Fig. 1 we show the optical conductivity for the Holstein and SSH models for different lattice sizes with open boundary conditions, for a single particle with a phonon frequency $\omega_0 = 0.2t$. The lattice sizes range from two to four sites from top to bottom, with the left column presenting results for the Holstein model and the right column analogous results for the SSH model. We consider only one-dimensional systems, but due to the local
nature of the polarons we are considering and the arguments we previously introduced we do not expect the dimensionality to play a crucial role. Therefore, even if the numerical calculations refer to the one-dimensional case, the physical ideas we are describing are more general.

![Graph](image)

FIG. 1: Finite frequency optical conductivity for the Holstein model (H, left column) and the SSH model (SSH, right column) for different lattice sizes: from top to bottom 2, 3 and 4 sites.

We have chosen the coupling for the two different models in order to have the low energy feature for the SSH model centered at the same frequency as the feature in the Holstein model. For the Holstein model this coupling is intermediate, which can be seen both from the asymmetry of the absorption band and the significant size dependence of the spectrum. With a further increase in the coupling strength this absorption band becomes very similar to that expected from simple analytic approaches, as was previously found in ref. For the SSH model on the other hand, we are already deeper in the polaronic regime. This is clear from the fact that the low energy feature for the SSH model does not change significantly from 3 to 4 sites while the one in the Holstein case changes more noticeably. If one increases the coupling strength further however, there is the risk of obtaining unphysical results for the SSH model. Due to the linearized form of the e-ph coupling, when the displacement becomes sufficiently large the effective hopping matrix element may pass through zero and change sign. In a more complete treatment of the e-ph coupling this would be counteracted by non-linear terms. In the present work we avoid the unphysical region of this simple version of the model by restricting the coupling strength. The numerical calculations have been performed with a maximum allowed number of phonons \( n_{\text{max}} = 50 \) for the two and three site calculations and \( n_{\text{max}} = 20 \) for the four site calculations.

While the results for the Holstein model do not depend strongly on the number of sites, the SSH two-site model has a very different behaviour compared to the larger systems. The two-site SSH model, as we have anticipated in the previous section shows just a single feature centered at \( \omega = 2t + 8g^2/\omega_0 \), associated with a local transition from the even parity ground state to odd parity excited states. Increasing the number of sites a lower energy feature appears centered at half the centre of the high energy "local" feature. It is generated by the excitation of the electron from one bond to a neighbouring one. It is worth noting that the two features do not change significantly going from 3 sites to 4 sites, despite the fact that the model has a non-local e-ph coupling.

To summarise the results up to this point: the most noticeable feature of the optical conductivity of a single SSH polaron in the (quasi-)adiabatic limit is the presence of two optical absorption bands generated by different optical excitation processes, one corresponding to the feature found in the Holstein model, and the other at twice the energy corresponding to a local excitation on the distorted bond.

Further information about the different way in which the polaron excitation occurs in the two models can be extracted from an analysis of the optical spectra as functions of the e-ph coupling. This may be most clearly seen by examining the various contributions to the sumrule. As a consequence of the self-trapping, the electronic kinetic energy is strongly suppressed in the strong coupling limit; Eq. (7) implies that the total weight of optical excitations decreases with increasing coupling for the Holstein model. On the other hand the optical sumrule for the SSH model Eq. (8) also involves the e-ph term, which increases with increasing coupling constant.

As mentioned in Section II, the Lanczos algorithm allows us to calculate exactly the finite-frequency part of the conductivity, which coincides with the total conductivity for OBC. Using PBC, the additional information from the sumrule allows the Drude weight to be determined. In Fig. 2 we show for the Holstein model the total sumrule, the Drude weight and the incoherent integrated weight for a four-site cluster with PBC and a phonon frequency \( \omega_0 = 0.2t \). The total sumrule sharply decreases as soon as \( \lambda \sim 1 \); this sharp decrease is driven by the fall of the Drude weight, which rapidly approaches zero. Note further that even if, for \( \lambda > 1 \), the polaronic peak given by Reik’s formula appears besides the Drude weight, its weight also decreases as \( t/g \) as \( g \) increases in the strong-coupling regime.
FIG. 2: Spectral weights for the Holstein model for a four site cluster with PBC. The solid line is the total sumrule Eq. (7); the dashed line is the Drude weight; the dotted line is the integrated weight of the finite frequency polaronic absorption feature.

FIG. 3: Spectral weights for the SSH model for a four site cluster with PBC. The solid line is the total sumrule Eq. (8); the dashed line is the Drude weight; the dotted line is the integrated weight of the low energy “Holstein-like” polaronic absorption feature; the dot-dashed line is the high energy local bonding-antibonding transition.

In Fig. 3 we present similar information for the SSH model, showing the results for a four-site cluster with PBC for a phonon frequency $\omega_0 = 0.2t$. The total sumrule monotonically increases with the coupling, which indicates that the increase of the $e$-$ph$ term overcompensates the decrease of the hopping term. A detailed analysis of the different contributions to the optical sumrule shows that the Drude weight rapidly decreases for this kind of $e$-$ph$ coupling as well as for the Holstein one, whereas the polaronic structures increase their total weight as the coupling increases.

We have separately integrated the optical conductivity for the two different optical absorption bands characteristic of the SSH case, obtaining in both cases an increase in total optical weight with coupling. As far as the high-energy, local feature is concerned this result is consistent with Eq. (10), which predicts an increasing value for the intensity of the optical absorption as a function of the $e$-$ph$ coupling. The low-energy feature for the SSH model on the other hand, which we attributed to the same kind of optical excitation that generates the absorption band for the Holstein model, also shows an increase of total weight with increasing $g$, whereas the Holstein structure has a decreasing weight as the coupling increases. This difference does not undermine the similarity between the two features, but simply underlines the nature of the $e$-$ph$ coupling term for the SSH model: the dipole moment associated with this type of transition is an increasing function of the coupling, so that quite naturally the absorption is expected to increase with coupling.

A further aspect to be considered is the dependence of the conductivity on the phonon frequency. As we already stated, the independence of the current operator for the Holstein model on the phonon operators is responsible for the “survival” of the adiabatic small polaron excitation process with increasing phonon frequency. For the SSH model this argument does not work, so we expect that the physical picture we have drawn using the adiabatic approximation will not hold for a sufficiently large value of the adiabatic ratio $\omega_0/t$. The dependence of the current operator on the difference of the phonon displacements makes it possible to consider an optical transition that modifies, even strongly, if $\omega_0/t$ is sizeable the lattice configuration. The short bond can be enlarged as the electron is excited to a neighbouring bond and the adiabatic picture can break down.

In Fig. 4 we study the effect of increasing phonon frequency on the optical conductivity for a four-site OBC cluster keeping $\lambda$ constant. The value of the coupling

FIG. 4: Finite frequency optical conductivity of the SSH model for a four site cluster using $\lambda = 0.225$. The solid line is for $\omega_0/t = 0.2$ and the dashed line is for $\omega_0/t = 0.8$.

In Fig. 4 we study the effect of increasing phonon frequency on the optical conductivity for a four-site OBC cluster keeping $\lambda$ constant. The value of the coupling
(λ = 0.225) is large enough to show clear polaronic features in the adiabatic regime. The two optical features are very evident for the smaller of the two frequencies shown ω0/t = 0.2, whereas for the larger phonon frequency ω0/t = 0.8 the absorption bands are broadened and overlap significantly. Larger phonon frequency also results in a more evident phonon structure, which contributes to hide the two features. For an adiabatic ratio ω0/t = 1 there is almost no sign of two distinct optical structures. Note that for larger phonon frequency size effects are also more important: for ω0/t = 0.8 the difference between the high energy region of the 4-site result shown and the 2-site case is much larger than is the case for the results for ω0/t = 0.2 in Fig. 1.

V. CONCLUSIONS

In this paper we have studied the optical conductivity of the Holstein and SSH models in the intermediate and strong-coupling polaronic regime. The optical absorption of a polaron arising from e-ph coupling of the SSH type has been shown to exhibit marked differences from the well-known Holstein polaron. These differences have been shown to be a consequence of the nature of the polarons in the two models, which is in turn a consequence of the different way the electrons are coupled to the phonons. Whereas the Holstein small polaron consists of an electron bound to a single distorted site, the SSH polaron may be described as an electron localized on a shortened bond.

The absorption in the Holstein model is due to processes where the electron is excited from the distorted site to a neighbouring undistorted site. A feature in the optical conductivity centered at a frequency ω = 2E_p, i.e. twice the polaron binding energy, is associated with this kind of process. In the SSH model corresponding processes exist where the electron is transferred from the distorted bond to a neighbouring undistorted bond, leading to a very similar absorption feature. On the other hand, a different channel for the polaron excitation in the SSH model is available. The ground state is an even parity, bonding state localized on a shortened bond. Due to the existence of local excited states of anti-bonding (odd) symmetry on the “short” bond, there is an additional strong absorption feature at twice the energy of the familiar “Holstein-like” absorption. The higher energy of this feature may be understood to arise from the anti-bonding nature of these final states with respect to the shortened bond. This anti-bonding character leads to the raising of the energy of the state by the same amount by which the polaronic ground state energy is lowered, whereas the “Holstein-like” transition occurs from a low energy state to a zero energy state as far as the electron-phonon interaction energy is concerned. Although all numerical calculations were performed for one-dimensional systems, due to the local nature of the physics we have described, the dimensionality is not expected to play a crucial role and similar features would be expected also in higher dimensional systems.

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