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LETTER TO THE EDITOR

The coherence and dynamics of polarons in the presence of disorder

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Abstract. The effects of disorder on polaron dynamics and stability are studied by considering a correlated electron–phonon model on a three-site cluster. Using both analytical and numerical techniques, it is demonstrated how disorder affects the particle-like motion of the polaron and ultimately breaks down its coherent structure.

Strongly correlated electron–phonon systems constitute complex many-degrees-of-freedom systems where non-linearity and non-adiabaticity characterize distinctive, particularly *polaronic*, aspects of collective behaviour. In many physically interesting systems, a further complication is caused by *disorder* which combines with non-linearity, often in a competing fashion [1]. Thus, polarons represent a coherent particle-like motion of correlated electronic and lattice distortions, whereas disorder tends to produce localized wave-functions on quite different spatial and temporal scales—either for polaronic or for single-electron states.

In this letter, we focus on the important issue of disorder and how it interacts with polaron formation and dynamics, which has been little studied except by approximate scaling theories at mean-field level [2]. In particular, the question of when the polaron ceases to be a composite particle (of an electron and phonons) due to disorder is a central concern and is studied below within a specific cluster model. Moreover, since we consider a small (three-site) cluster, an exact diagonalization analysis can be made numerically exact. Thus non-linear and non-adiabatic dynamics is described precisely. We note that spatially extended systems are of course of interest, but there analytical approaches are usually limited to adiabatic and mean-field approximations [3] and numerical works rely on either quantum Monte Carlo [4] or variational [5] methods.

Below, we introduce specific measures of polaron coherence to establish our main result: the effects of disorder (both diagonal and off-diagonal) on polarons can be understood in terms of two important energy scales, ϵ_T and w, where ϵ_T is the polaron-tunnelling energy (i.e. the polaron bandwidth in our small cluster) and w is the bare electron bandwidth for the lowest-energy 'band' (i.e. in the absence of electron–phonon interactions). The tunnelling energy specifies the typical energy scale of disorder at which the coherent motion of polarons is suppressed and they are localized as composite particles. The bandwidth w, on the other hand, gives the energy scale at which the polaron ceases to be a composite particle of an electron and phonons; i.e. the dressing of the electron with phonons strongly decreases.

As a prototype of polaronic behaviour, we consider a three-site model [6] with two phonon modes, also known as a molecular-crystal Hamiltonian. It can be written in the

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form

$$H = H_{\rm el} + H_{\rm el-ph} + H_{\rm ph} \tag{1}$$

where

$$H_{\rm el} = \sum_n \epsilon_n \rho_n + U \sum_n \rho_{n\uparrow}\rho_{n\downarrow} + \sum_{\langle nn'\rangle\sigma} t_{nn'}(c^\dagger_{n\sigma}c_{n'\sigma} + {\rm HC}) \tag{2a}$$

$$H_{\rm el-ph} = \lambda_s(a_s + a_s^\dagger)(\rho_1 - \rho_2 + \rho_3) + \lambda_a(a_a + a_a^\dagger)(\rho_3 - \rho_1) \tag{2b}$$

$$H_{\rm ph} = \hbar\omega_s a_s^\dagger a_s + \hbar\omega_a a_a^\dagger a_a. \tag{2c}$$

Here, $c^\dagger_{n\sigma}$ creates an electron of spin σ at site n, $\rho_{n\sigma} = c^\dagger_{n\sigma}c_{n\sigma}$, and $\rho_n = \sum_\sigma \rho_{n\sigma}$. The notation $\langle nn'\rangle$ refers to the bonds and $t_{nn'}$ is the hopping matrix element between sites n and n'. An on-site electron–electron interaction of strength U is included for generality. The isolated three-site cluster has two phonon modes for displacements along the cluster axis that do not change the centre of mass. These bare modes are assumed to be harmonic with well defined parity. Usually, the symmetric and the antisymmetric phonon modes are referred to as Raman and infrared active. These modes are described by boson operators $a_{\rm s}$ and $a_{\rm a}$ with bare frequencies $\omega_{\rm s}$ and $\omega_{\rm a}$, where s (a) denotes the symmetric (antisymmetric) mode, respectively. The corresponding linear electron–phonon coupling constants are $\lambda_{\rm s}$ and $\lambda_{\rm a}$ ($\geqslant 0$). The above model has been used elsewhere [6] to explain some of the novel structural and optical features of the axial oxygen (O(4)) and the chain copper (Cu(1)) cluster—arranged as O(4)–Cu(1)–O(4) and located between CuO_2 planes in the high-temperature superconductor $YBa_2Cu_3O_7$. There $n = 1, 3$ denote the axial O(4) sites and $n = 2$ is the chain Cu(1) site.

Despite the above model's apparent simplicity, it can describe a wide variety of interesting phenomena, ranging from polaron formation and tunnelling to multi-polaron interactions. Rather than considering all these aspects, we focus here on a polaron- tunnelling regime [6]. In this regime for sufficiently large values of λ_a, the model dynamically generates a new length scale associated with a double-well structure in the antisymmetric phonon mode coordinate, $u_{\rm a} = a_a + a_a^\dagger$. The motion of the lattice is strongly correlated with the electron motion, corresponding to polaron formation, and a new timescale describing polaron tunnelling is generated. Furthermore, as the system's parameters move from the weak-coupling to the strong-coupling regime, the energies of the symmetric states show pronounced minima in the intermediate-coupling regime (onset of polaron tunnelling), whereas the energies of the antisymmetric states decrease in a regular fashion with increasing values of $\lambda_{\rm a}$ [6].

To model disorder, we assume that the system has two electrons with opposite spins ($S_z = 0$) on a linear cluster, which is parametrized so that $t_{13} = 0$, $t_{12} = t$, $t_{23} = t + \delta$, $\epsilon_{1,3} = \epsilon_0 \pm \Delta/2$, and $\epsilon_2 = 0$. We also consider the parameter regime where $0 \leqslant t \ll \epsilon_0, U - \epsilon_0$. Large, positive values of the on-site electron–electron interaction, U, and large positive average energies of sites 1 and 3, given by ϵ_0, inhibit bipolaron formation at low energies and the low-energy physics is characterized by polarons. The symmetry-breaking fields Δ and δ describe the disorder—diagonal and off-diagonal, respectively. These, as well as other parameters, are varied so that the salient disorder-induced features can be studied transparently. Thus, we first set $\lambda_{\rm s}$ to zero because the symmetric mode plays only a minor role in the polaron physics below.

While the electronic part of the Hamiltonian (2*a*) can be readily diagonalized numerically, it is already too complicated to be solved analytically for two electrons in the general case. However, an effective Hamiltonian can be derived easily when

$0 \leqslant t, \Delta, \delta \ll \epsilon_0, U - \epsilon_0$, allowing a straightforward physical interpretation. In this parameter regime, the hopping term is a small perturbation which can be eliminated by a unitary transformation: $\tilde{H} = \mathrm{e}^{-S} H \mathrm{e}^{S}$. By elimination to second order in t/ϵ_0 and $t/(U - \epsilon_0)$, we arrive at the electronic part of the effective Hamiltonian:

$$\tilde{H}_{\mathrm{el}} = \sum_{\substack{n=1,3 \\ \sigma=\pm}} \epsilon_\sigma^{(n)} d_{n\sigma}^\dagger d_{n\sigma} + \sum_{\sigma=\pm} \tau_\sigma (d_{1\sigma}^\dagger d_{3\sigma} + HC) \tag{3}$$

where the effective site energies and hopping matrix elements are defined as

$$\epsilon_\sigma^{(n)} = \epsilon_n - \frac{t_{\bar{n}2}^2}{\epsilon_{\bar{n}}} - 2(1+\sigma)\frac{U t_{n2}^2}{U^2 - \epsilon_n^2}, \tag{4a}$$

$$\tau_\sigma = -\tfrac{1}{2} \sum_{n=1,3} \frac{t_{12} t_{23}}{U - \epsilon_n} (1 + \sigma U/\epsilon_n) \tag{4b}$$

and $\bar{n} = 4 - n$. The new fermion operators are $d_{n\pm} = (c_{n\uparrow} \pm c_{n\downarrow})/\sqrt{2}$. The electronic part is thus reduced to a two-site problem with one 'd particle' in the Fock space of the effective Hamiltonian. Similarly, we can construct the effective electron–phonon interaction. For $\lambda_{\mathrm{s}} = 0$, this becomes

$$\tilde{H}_{\mathrm{el-ph}} = \lambda_{\mathrm{a}} (a_a + a_a^\dagger) \sum_{\sigma=\pm} (d_{3\sigma}^\dagger d_{3\sigma} - d_{1\sigma}^\dagger d_{1\sigma}). \tag{5}$$

It is now straightforward to understand how the polaron is affected by weak disorder ($0 \leqslant \Delta, \delta \ll \epsilon_0, U - \epsilon_0$): (i) For diagonal disorder ($\delta = 0$), the phonon coordinate u_{a} acquires a negative expectation value, meaning that the polaron begins to localize around site 3; (ii) for off-diagonal disorder ($\Delta = 0$), the on-site interaction has a critical value U_{c}, which separates the behaviour into two distinct regimes—if $U < U_{\mathrm{c}}$, the polaron tends to localize around site 3; however, if $U > U_{\mathrm{c}}$, the polaron localizes first around site 1 and then, for sufficiently large values of δ ($> \delta_{\mathrm{c}}$), it localizes around site 3. The reason for this behaviour for very large values of U and for $\delta \neq 0$ is that it is energetically more favourable for an electron to be at site 1 because of virtual hopping processes between the 2 and 3, which are not affected by the strong electron–electron interaction. Equation (4*a*) allows us to evaluate U_{c} as $U_{\mathrm{c}}/\epsilon_0 = 2 + \sqrt{5}$.

The above analysis is sufficient to describe polaron localization in the presence of weak disorder; it cannot be used to explain how disorder affects the internal stability (coherence) of the polaron. For this, we rely on numerical analysis, namely exact diagonalization of the Hamiltonian, (1) and (2). For these calculations, we choose representatively $\epsilon_0/t = 4$, $\hbar\omega_{\mathrm{a}}/t = 0.08$, $\lambda_{\mathrm{s}} = 0$, and vary the remainder of the parameters.

We begin with diagonal disorder which is conceptually easier to understand. To monitor the stability and localization of the polaron, we consider two diagnostic quantities.

First, we measure the correlation between the electrons and the phonon coordinate in the ground state. Defining deviations of the operators as $\delta O = O - \langle O \rangle$ and denoting $\rho_{13} = \rho_1 - \rho_3$, we introduce the correlation factor

$$\mathcal{R} = \frac{\langle \delta\rho_{13} \delta u_{\mathrm{a}} \rangle}{\sqrt{\langle (\delta\rho_{13})^2 \rangle \langle (\delta u_{\mathrm{a}})^2 \rangle}}. \tag{6}$$

Although the expectation values may be taken relative to any state, we consider here only the ground-state expectation values which will describe the polaronic state. The closer $\mathcal{R}$ is to unity, the more correlated are the electron and phonon dynamics, implying strong polaronic binding of the electron to its phonon cloud. In contrast, $\mathcal{R} = 0$ signals non-polaronic behaviour, where the motions of electrons and phonons are completely decoupled.

Second, we consider the dressing of electrons by phonons in terms of the overlap factors between the ground states of the system in the absence and in the presence of the electron–phonon interaction. For the ground states, the polaronic dressing of electrons is conveniently defined by the overlap factor

$$Z = |\langle\Psi_0(\lambda_a = 0, \Delta)|\Psi_0(\lambda_a, \Delta)\rangle|^2 \tag{7}$$

where $|\Psi_0(\lambda_a, \Delta)\rangle$ is the ground state of the system for the parameters shown. $Z = 1$ signifies no phonon dressing, and decreasing Z implies increasing dressing.

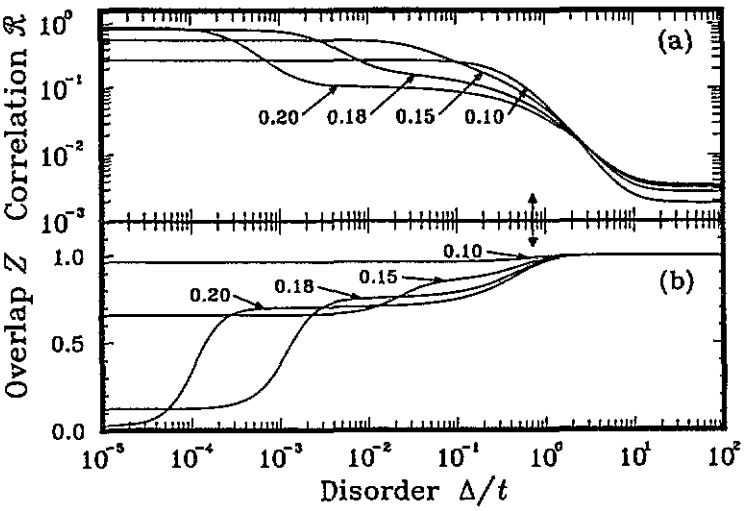

Figure 1. (*a*) The correlation factor $\mathcal{R}$ and (b) the ground-state overlap factor Z as functions of the diagonal disorder parameter Δ for $U/t = 16$ and for the electron–phonon coupling constant $\lambda_a/t = 0.10$, 0.15, 0.18, and 0.20. In the absence of disorder, the corresponding tunnelling energies ϵ_T/t are 5.3×10^{-2}, 1.5×10^{-2}, 1.2×10^{-3}, and 1.1×10^{-4}, respectively. The double-headed arrow marks the energy scale w (see text).

Our results for diagonal disorder are summarized in figure 1, which shows $\mathcal{R}$ and Z as functions of the disorder strength Δ for $U/t = 16$ and for various values of the electron–phonon coupling constant λ_a. Both $\mathcal{R}$ and Z exhibit a crossover behaviour at a larger value of Δ and another one for a smaller value when λ_a is large enough that the system is in the polaron-tunnelling regime. These results can be understood in terms of two characteristic energy scales: the polaron-tunnelling energy, ϵ_T, and w, the energy-splitting of the lowest-energy spin-singlet states (with opposite parity), which plays the role of the lowest-energy bare electron bandwidth in our finite cluster. For $U/t = 16$ and in the absence of disorder, $w/t = 0.72$. As the symmetry-breaking disorder field Δ is increased, the first crossover at $\Delta \sim \epsilon_T$ describes the localization of the polaron to essentially one site. As Δ is increased further so that $\Delta \sim w$, $\mathcal{R}$ decreases sharply to a small value and Z approaches unity. This signals the breaking of the composite character of the polaron, so that the electron is no longer coherently dressed by phonons.

Next, we consider off-diagonal disorder whose influence is illustrated in figure 2. Again, $\mathcal{R}$ and Z are plotted as functions of the disorder strength δ for $U/t = 16$ and for various values of the electron–phonon coupling constant λ_a. As for diagonal disorder, both quantities show two crossovers: one for disorder-induced localization and one for polaron breakdown. Note that the chosen value of U is less than the critical U_c for the localization transition defined above. If we choose instead $U > U_c$, we find intriguing behaviour for $\mathcal{R}$, namely

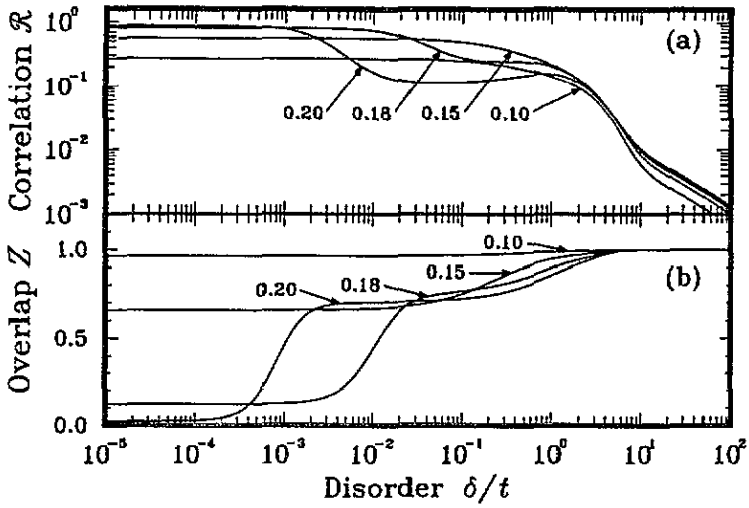

Figure 2. (*a*) The correlation factor $\mathcal{R}$ and (*b*) the ground-state overlap factor Z as a function of the off-diagonal disorder parameter δ for $U/t = 16$ and for the electron–phonon coupling constant $\lambda_a/t = 0.10$, 0.15, 0.18 and 0.20.

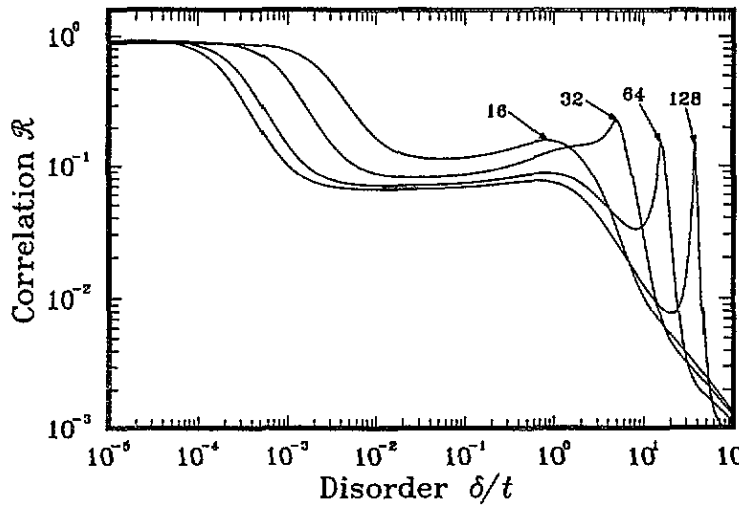

Figure 3. The correlation factor $\mathcal{R}$ as a function of the off-diagonal disorder parameter δ for the electron–phonon coupling constant $\lambda_a/t = 0.20$ and $U/t = 16$, 32, 64, and 128.

a sharp peak at δ_c, where the localization transition occurs; see figure 3. This peak signals the delocalization of the polaron, as can be verified by noting that the polaron-tunnelling energy has a minimum at that particular value of δ, and $\langle\rho_1\rangle = \langle\rho_3\rangle$ for the ground state. Note that, as seen from (4*a*), δ is not directly equal to the characteristic energy scale of off-diagonal disorder, as Δ is in the case of diagonal disorder (above).

Finally, we assess the above approximation of neglecting the symmetric phonon mode, which was made for numerical convenience. Although it is intuitively clear that the symmetric phonons do not qualitatively affect our conclusions, it is still important from a physical point of view to determine whether they are involved in dressing the electrons, and whether they show any correlation with the polaron formation through

the antisymmetric phonons. We consider the correlation factor $\mathcal{R}'$ between the 'polaron operator', $A_{\rm pol} = \rho_{13}u_{\rm a}$, and the symmetric phonon coordinate, $u_{\rm s} = a_{\rm s} + a_{\rm s}^{\dagger}$. In the absence of disorder and as a function of $\lambda_{\rm a}$ for $\lambda_{\rm s} \neq 0$, $\mathcal{R}'$ shows a clear maximum at intermediate values of $\lambda_{\rm a}$ for which the polaron, and thus the dynamic double well, begins to form. In this strongly non-linear regime with large-amplitude fluctuations, $u_{\rm s}$ thus has a highly non-trivial behaviour even though it is not directly involved in the polaron formation. Further, this behaviour has physically observable implications, for example, in dynamic structure factors, such as those measured in neutron scattering [7]. Also, we found that $\mathcal{R}'$ decreases to zero as $\lambda_{\rm a} \to 0$ or $\lambda_{\rm a} \to \infty$.

In conclusion, we have studied the interplay of polaron dynamics, coherence, and disorder which are widely important issues, applying also to magnon–phonon or exciton–phonon systems [8]. By considering the effects of disorder in a polaron-tunnelling regime for our three-site cluster, we have identified two crossover transitions. The first one, at small strengths of symmetry-breaking disorder fields, distinguishes a particle-like motion of polarons from localized polarons, and the second one, at larger strengths, distinguishes polarons as composite entities from uncorrelated electrons and phonons. Diagonal and off-diagonal disorder both lead to crossover behaviours although they have different effects: diagonal disorder can be understood as tending to make the electron immobile (by increasing its effective mass), whereas off-diagonal disorder can be viewed as decreasing the electron's effective mass by increasing its hopping rate. Both types of disorder cause the electronic and phonon time scales to be so different that polaron formation is inhibited.

We emphasize that the polaron study presented here is for a very small (three-site) cluster—clearly if the polaron formation and localization length scales involve more sites, a larger cluster is needed to resolve the competitions between disorder and polaron dynamics. In particular, for an infinite system, the hierarchy (continuum) of energy and length scales may result in new functional forms for the crossover energies, associated with the binding energies and the correlation lengths of polarons. Finally, we note that experimentally relevant optical signatures of disorder effects on polaron dynamics have been described elsewhere [7].

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