Mobile small polaron

A.S. Alexandrov[1] and P.E. Kornilovitch [2]
[1] *Department of Physics, Loughborough University, Loughborough LE11 3TU, United Kingdom*
[2] *Blackett Laboratory, Imperial College, London SW7 2BZ, United Kingdom*
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Extending the Fröhlich polaron problem to a *discrete* ionic lattice we study a polaronic state with a small radius of the wave function but a large size of the lattice distortion. We calculate the energy dispersion and the effective mass of the polaron with the $1/\lambda$ perturbation theory and with the exact Monte Carlo method in the nonadiabatic and adiabatic regimes, respectively. The "small" Fröhlich polaron is found to be lighter than the small Holstein polaron by one or more orders of magnitude.

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A free electron interacting with the dielectric polarisable continuum was studied by Pekar [1] and Fröhlich [2] in the strong and weak coupling limit, respectively. This is the case of carriers interacting with optical phonons in ionic crystals under the condition that the size of the self-trapped state is large compared to the lattice constant so the lattice discreteness is irrelevant [3]. The most sophisticated treatment of this "*large*" or "continuum" polaron is due to Feynman and co-workers [4] with the path-integral method, substantially extended in the past decade [5]. This treatment leads to a mass enhancement, but not to a hopping conduction or to a narrow polaron band.

When the electron-phonon coupling constant λ is large, all the states in the Brillouin zone are involved in the formation of the polaron wave function, so the polaron radius becomes comparable with the lattice constant a and the continuum approximation is no longer valid. Basic features of the *small* polaron were well recognised a long time ago by Tjablikov [6], Yamashita and Kurosawa [7], Sewell [8], Holstein [9], Lang and Firsov [10] and others, and are described in several review papers and textbooks [11–15]. So far, analytical and numerical studies have been mainly confined to the Holstein model with a short-range electron-phonon interaction. Exact diagonalization of several vibrating molecules coupled with one electron [16,17], variational [18,19] and Monte Carlo calculations [20] revealed an excellent agreement with analytical results of Holstein [9] and Lang and Firsov [10] for the energy of the ground state and first excited states at large λ. Polaron mass is very large in the Holstein model, unless phonon frequencies are extremely high. The size of the region, where the small Holstein polaron is localised, is about the same as the size of the lattice distortion, each of the order of the lattice constant. Both sizes are almost identical also for the large Fröhlich polaron, but much larger.

In this Letter we study a problem of the lattice polaron with a long-range Fröhlich interaction [21]. This quasiparticle has a small (atomic) size of the electron localization region but a large size of the lattice distortion. While the large Fröhlich polaron is heavier than the large Holstein polaron, the *small* Fröhlich polaron (SFP) turns out to be much lighter than the small Holstein polaron (SHP) with the same binding energy. We argue that SFPs are relevant quasiparticles in the cuprates.

A quite general electron-phonon lattice Hamiltonian with one electron and the "density-displacement" type of interaction is given by [9,12,15]

$$H = -\sum_{\mathbf{nn}'} t_{\mathbf{nn}'} c^\dagger_{\mathbf{n}'} c_{\mathbf{n}} + \sum_{\mathbf{q}\alpha} \hbar\omega_{\mathbf{q}\alpha}(d^\dagger_{\mathbf{q}\alpha} d_{\mathbf{q}\alpha} + 1/2) - \sum_{\mathbf{mn}\alpha} f_{\mathbf{m}\alpha}(\mathbf{n}) c^\dagger_{\mathbf{n}} c_{\mathbf{n}} \xi_{\mathbf{m}\alpha}. \quad (1)$$

Here α corresponds to the different phonon modes, $\xi_{\mathbf{m}\alpha}$ is a normal coordinate at site $\mathbf{m}$, and $f_{\mathbf{m}\alpha}(\mathbf{n})$ is the *force* between the electron at site $\mathbf{n}$ and the normal coordinate $\xi_{\mathbf{m}\alpha}$.

If characteristic phonon frequencies are large compared to the electron kinetic energy, $\hbar\omega > t$, (nonadiabatic regime) then one can apply a powerful analytic method, based on the Lang-Firsov canonical transformation [10] and subsequent $1/\lambda$ perturbation technique. Introducing the phonon operators as $\xi_{\mathbf{m}\alpha} = \sum_{\mathbf{q}}(u_{\mathbf{mq}\alpha} d^\dagger_{\mathbf{q}\alpha} + u^*_{\mathbf{mq}\alpha} d_{\mathbf{q}\alpha})$ with $u_{\mathbf{mq}\alpha} = \hbar^{1/2}(2NM\omega_{\mathbf{q}\alpha})^{-1/2} e^{i\mathbf{qm}}$, N the number of sites, and M the ion mass, one obtains the transformed Hamiltonian

$$\tilde{H} = e^{-S} H e^{S} = -\sum_{\mathbf{n}'\neq\mathbf{n}} \hat{\sigma}_{\mathbf{n}'\mathbf{n}} c^\dagger_{\mathbf{n}'} c_{\mathbf{n}} - E_p \sum_{\mathbf{n}} c^\dagger_{\mathbf{n}} c_{\mathbf{n}} + \sum_{\mathbf{q}\alpha} \omega_{\mathbf{q}\alpha}(d^\dagger_{\mathbf{q}\alpha} d_{\mathbf{q}\alpha} + 1/2). \quad (2)$$

Here $S = \sum_{\mathbf{mnq}\alpha} (\hbar\omega_{\mathbf{q}\alpha})^{-1} u_{\mathbf{mq}\alpha} f_{\mathbf{m}\alpha}(\mathbf{n}) c^\dagger_{\mathbf{n}} c_{\mathbf{n}} d^\dagger_{\mathbf{q}\alpha} - h.c.$, and E_p is the familiar polaronic shift,

$$E_p = \sum_{\mathbf{mm}'\mathbf{q}\alpha} \frac{1}{2NM\omega^2_{\mathbf{q}\alpha}} f_{\mathbf{m}\alpha}(0) f_{\mathbf{m}'\alpha}(0) \cos \mathbf{q}(\mathbf{m}-\mathbf{m}'). \quad (3)$$

The polaronic shift is the natural measure of the strength of the electron-phonon interaction. It defines the electron-phonon coupling constant as $\lambda = E_p/zt$, where z is the lattice coordination number. The first term in Eq. (2) contains the transformed hopping integral $\hat{\sigma}_{\mathbf{nn}'}$, which depends on the phonon operators as

$$\hat{\sigma}_{\mathbf{nn}'} = t_{\mathbf{nn}'} \exp\left[\sum_{\mathbf{mq}\alpha} \frac{f_{\mathbf{m}\alpha}(\mathbf{n}) - f_{\mathbf{m}\alpha}(\mathbf{n}')}{\hbar\omega_{\mathbf{q}\alpha}} \times (u_{\mathbf{mq}\alpha} d^{\dagger}_{\mathbf{q}\alpha} - u^{*}_{\mathbf{mq}\alpha} d_{\mathbf{q}\alpha})\right]. \quad (4)$$

At large λ the hopping term in Eq. (2) can be treated as a perturbation. Introducing a set of N zero-order Bloch eigenstates (all with the same energy $-E_p$) $|\mathbf{k},0\rangle = N^{-1/2}\sum_{\mathbf{n}} c^{\dagger}_{\mathbf{n}} \exp(i\mathbf{k}\cdot\mathbf{n})|0\rangle$, one readily calculates the lowest energy levels in a crystal. Up to the second order in the hopping integral, the result is

$$E(\mathbf{k}) = -E_p - \sum_{\mathbf{n}\neq 0} t_{\mathbf{n}0}\, e^{-g^2(\mathbf{n})} \exp(-i\mathbf{k}\cdot\mathbf{n}) - \sum_{\mathbf{k}', n_{\mathbf{q}\alpha}} \frac{|\langle \mathbf{k},0| \sum_{\mathbf{nn}'} \hat{\sigma}_{\mathbf{nn}'} c^{\dagger}_{\mathbf{n}'} c_{\mathbf{n}} |\mathbf{k}', n_{\mathbf{q}\alpha}\rangle|^2}{\hbar \sum_{\mathbf{q}\alpha} \omega_{\mathbf{q}\alpha} n_{\mathbf{q}\alpha}}. \quad (5)$$

Here $|\mathbf{k}', n_{\mathbf{q}\alpha}\rangle$ is an excited state of the unperturbed Hamiltonian with one electron and at least one phonon, $n_{\mathbf{q}\alpha}$ is the phonon occupation number. The second term in Eq. (5), which is linear with respect to the bare hopping $t_{\mathbf{nn}'}$, determines the dispersion of the polaron band with a band-narrowing exponent (at zero temperature)

$$g^2(\mathbf{n}) = \sum_{\mathbf{q}\alpha} \frac{1}{2NM\hbar\omega^3_{\mathbf{q}\alpha}} \times \sum_{\mathbf{mm}'} [f_{\mathbf{m}\alpha}(0) f_{\mathbf{m}'\alpha}(0) - f_{\mathbf{m}\alpha}(0) f_{\mathbf{m}'\alpha}(\mathbf{n})] \cos\mathbf{q}(\mathbf{m}-\mathbf{m}'). \quad (6)$$

The third term in Eq.(5), quadratic in $t_{\mathbf{nn}'}$, yields a negative almost $\mathbf{k}$-*independent* correction of the order of $1/\lambda^2$ to the polaron level shift. It is unrelated to the polaron effective mass and the polaron tunneling mobility.

In general, there is no simple relation between the polaronic shift E_p and the exponent g^2 which describes the mass enhancement, as one can see from Eq. (3) and Eq. (6). We now consider the case of a single dispersionless phonon mode $\omega_{\mathbf{q}\alpha} = \omega$ and the nearest-neighbor hopping with an amplitude t. One obtains

$$E_p = \frac{1}{2M\omega^2} \sum_{\mathbf{m}} f^2_{\mathbf{m}}(0), \quad (7)$$

$$g^2 \equiv g^2(1) = \frac{1}{2M\hbar\omega^3} \sum_{\mathbf{m}} \left[f^2_{\mathbf{m}}(0) - f_{\mathbf{m}}(0) f_{\mathbf{m}}(1)\right]. \quad (8)$$

The effective mass renormalisation is $m^*/m = e^{g^2}$, where m is the bare band mass and $1/m^* = \partial^2 E(\mathbf{k})/\partial(\hbar k)^2$ with $k \to 0$. If the interaction is local, $f_{\mathbf{m}}(\mathbf{n}) = \kappa\delta_{\mathbf{mn}}$ (Holstein model), then $g^2 = E_p/(\hbar\omega)$. In general, one has $g^2 = \gamma E_p/(\hbar\omega)$ with a numerical coefficient $\gamma = 1 - \sum_{\mathbf{m}} f_{\mathbf{m}}(0) f_{\mathbf{m}}(1)/\sum_{\mathbf{m}'} f^2_{\mathbf{m}'}(0)$, which is less than unity for the canonical Fröhlich interaction [22].

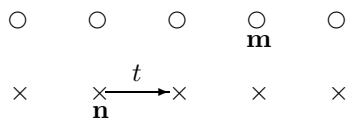

FIG. 1. One-dimensional model of the small Fröhlich polaron on chain (×) interacting with all ions of chain (○).

To calculate γ explicitly we introduce one and two-dimensional lattice models with a long-range Coulomb interaction between an electron and ions (see Fig.1). The electron in a Wannier state on a site $\mathbf{n}$ of the infinite chain (plane) (×) interacts with the vibrations of *all* ions of another chain (plane) (○) polarised in the direction perpendicular to the chains. A strong coupling of carriers with c-axis polarised phonons ($\hbar\omega \simeq 75$ meV) has been established experimentally in $YBa_2Cu_3O_{6+x}$ [23]. Because of a low c-axis conductivity and high phonon frequency, this coupling is not screened representing an example of a long-range Fröhlich interaction. In this way our model mimics a hole on the CuO_2 plane (chain ×) coupled with the c-axis apical oxygen vibrations (chain ○) in the cuprates. The corresponding force is given by

$$f_{\mathbf{m}}(\mathbf{n}) = \frac{\kappa}{(|\mathbf{m}-\mathbf{n}|^2+1)^{3/2}}. \quad (9)$$

Here the distance along the chains $|\mathbf{m}-\mathbf{n}|$ is measured in lattice constants a, and the inter-chain distance is also $a = 1$. For this long-range interaction, one obtains $E_p = 1.27\kappa^2/(2M\omega^2)$, $g^2 = 0.49\kappa^2/(2M\hbar\omega^3)$, and $g^2 = 0.39E_p/(\hbar\omega)$. The effective mass renormalisation is much smaller than in the Holstein model, roughly as $m^*_{SFP} \propto \sqrt{m^*_{SHP}}$.

Our analytical consideration is applied if $\omega \geq t$, and $\lambda \gg 1$. To extend the results to the adiabatic case and to the intermediate coupling we apply a continuous-time path-integral Quantum Monte Carlo (QMC) algorithm, developed recently [24]. This method is free from any systematic finite-size, finite-time-step and finite-temperature errors and allows for exact calculation of the ground-state energy and the effective mass of the lattice polaron for any electron-phonon interaction. The method was tested on the one-dimensional (1D) Holstein model which has been extensively studied by other methods. Excellent agreement with exact diagonalization [16,17], density-matrix renormalization group [25] and

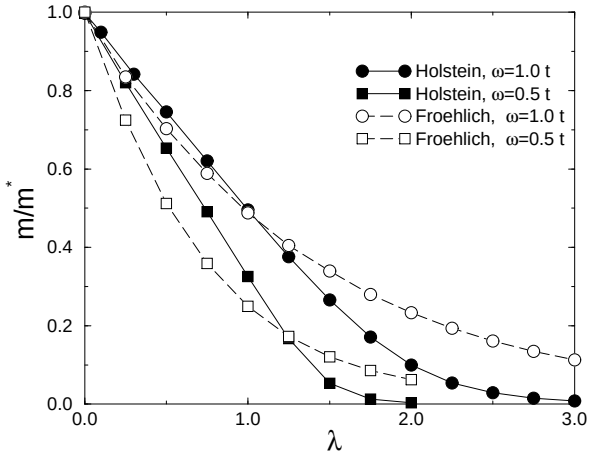

FIG. 2. Inverse effective polaron mass in units of $1/m = 2ta^2/\hbar^2$ for the one-dimensional Holstein and Fröhlich [Eq. (9)] models. Circles: $\omega = 1.0\,t$; squares: $\omega = 0.5\,t$.

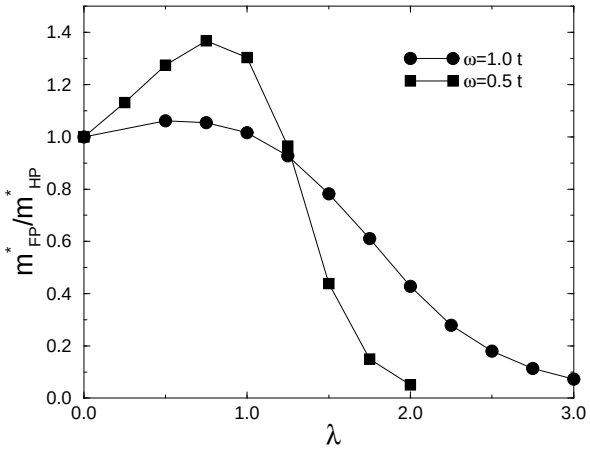

FIG. 3. The ratio of the effective masses of the Fröhlich and Holstein polarons in 1D. Fröhlich polaron is heavier at small $\lambda < 1.25$ but much lighter at $\lambda > 1.25$.

variational [18] results was found for both the ground-state energy and effective mass.

Exact polaron masses of the one-dimensional model defined by Eq. (9) and Fig. 1, are compared with 1D Holstein polaron masses in Fig. 2. For both phonon frequencies $\hbar\omega = 1.0\,t$ and $0.5\,t$ we found SFP to be *heavier* than SHP at small $\lambda < 1$, but *much* lighter than SHP in the strong-coupling regime $\lambda > 1.5$. The mass ratio reaches 1 order of magnitude at $\lambda = 2.75$ for $\hbar\omega = 1.0\,t$ and at $\lambda = 1.75$ for $\hbar\omega = 0.5\,t$. This is in accordance with our analytical approach in the $\hbar\omega > t$ regime. Thus the mass ratio m^*_{FP}/m^*_{HP} is a non-monotonic function of λ (see Fig. 3). This is a consequence of the fact that $m^*_{FP}(\lambda)$ is well fitted by a single exponential function, $\exp(0.73\lambda)$ for $\hbar\omega = 1.0\,t$ and $\exp(1.40\lambda)$ for $\hbar\omega = 0.5\,t$. This is not so for the Holstein polaron, in which case a crossover between two regimes occurs at $\lambda \sim 1.5$. It is interesting that the numerical exponents found are only slightly smaller than that follow from the Lang-Firsov transformation, $\exp(0.78\lambda)$ and $\exp(1.56\lambda)$ respectively. This shows the excellent accuracy of this transformation even in the intermediate region of parameters, $\lambda \sim 1$ and $\hbar\omega/t \sim 1$. Note, however, that the exact exponent deviates more and more from the Lang-Firsov approximation with a decreasing adiabatic ratio $\hbar\omega/t$. This is in agreement with the exact diagonalization of a two-site model [16], where it was shown that the Lang-Firsov approximation overestimates the polaron mass in the adiabatic regime.

We also compared our exact QMC masses with the canonical weak- [2] and strong-coupling [1] continuum polaron theory, where the bandwidth is assumed to be infinite. To make such a comparison meaningful we determine the Fröhlich coupling constant α in such a way, that the ground-state energy E_0 of the continuum approximation is the same as the one in our model. Then we calculate the continuum-case mass and compare with our $m^*_{SFP}(\lambda)$. In the Fröhlich weak-coupling regime one has $E_0 = -\alpha\,\hbar\omega$ and $m^*_c = (1 + \alpha/6)\,m$. This mass appears to be well below our m^*_{FP} for $\lambda < 1$. For instance, for $\lambda = 0.5$ and $\hbar\omega = t$, the continuum mass is $m^*_c = 1.119\,m$ while our result is $m^*_{FP} = 1.422\,m$. However, in the strong-coupling regime, $\lambda > 1$, the continuum approximation overestimates the mass. Using Pekar's ground state energy, $E_0 = -0.1085\alpha^2\,\hbar\omega$, and mass $m^*_c = 0.021\alpha^4\,m$ for $\lambda = 2$ and $\hbar\omega = t$ we find $m^*_c = 17.2\,m$ which is much larger than our mass, $m^*_{FP} = 4.29\,m$. This difference does not depend very much on the dimensionality of the polaron. We notice also that if we take into account the intermediate coupling corrections to the ground state energy of the strong-coupling Pekar polaron, $E_0 = -(0.109\alpha^2 + 2.836)\hbar\omega$ [26], a continuum polaron mass $m^*_c = 1.074\,m$ turns out to be much lighter than the exact one for the same λ. These estimates underline the crucial role of a finite bandwidth.

To check that the light small Fröhlich polaron is not an artifact of one dimension we calculated its mass for the *two*-dimensional (2D) version of the model (9) and compared it with the 2D Holstein polaron (see Fig. 4). At $\lambda > 1$ the mass ratio m^*_{SFP}/m^*_{SHP} (see inset) shows even more sharp fall than in 1D. While SFP is 2.5 times heavier than SHP at $\lambda = 1.0$, they are equal at $\lambda = 1.1$, and SFP is 36 times lighter at $\lambda = 1.3$ (at this coupling $m^*_{SHP} = 400$ but $m^*_{SHP} = 11$). The reason for such a dramatic change is the *very* large mass of 2D SHP. At the same time, the mass of SFP grows exponentially but smoothly, similar to the 1D case. The best fit to QMC data is $\exp(1.62\lambda + 0.19\lambda^2)$.

The physical reason for the small mass of SFP lies in

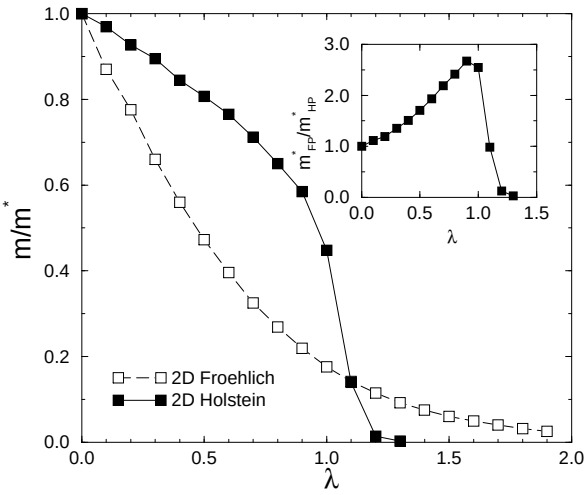

FIG. 4. Inverse effective polaron mass in units of $1/m = 2ta^2/\hbar^2$ for the two-dimensional Holstein and Fröhlich [Eq. (9)] models. $\hbar\omega = 0.5\,t$. Inset: Ratio m^*_{FP}/m^*_{HP}.

the form of electron-phonon interaction. A long-range interaction of the type of Eq. (9) induces a lattice distortion which undergoes *less* changes when the carrier hops to the neighboring site, than a distortion induced by a short-range interaction. Namely, relative changes are essential for the polaron mass. One should also emphasize the new type of internal structure of SFP, which is best understood in the extreme strong-coupling limit, $\lambda \to \infty$. In this limit the Lang-Firsov transformation is exact, and the polaron is localised on one site $\mathbf{n}$. Hence, the size of its wave function is the atomic size. On the other hand, the lattice deformation, which is proportional to the displacement force $f_{\mathbf{m}}(\mathbf{n})$, spreads over a large distance. Its amplitude falls with the distance as $|\mathbf{m}-\mathbf{n}|^{-3}$ in our model. Thus we have a new situation when the size of the polaron and the size of lattice deformation are very different. Our findings suggest to generalise the definitions of the polaron and polaron "cloud" to include this new possibility.

In conclusion, we have studied the small polaron problem with the long-range Fröhlich interaction. This polaron has a small (atomic) size of the wave function but a large size of the lattice deformation. The "*small* Fröhlich polaron". propagates in a narrow band with the effective mass much smaller than that of the Holstein small polaron with the same binding energy. We argue that small Fröhlich (bi)polarons [22] as well as large Fröhlich (bi)polarons [27,28,5] are relevant quasiparticles in the cuprates, describing holes in the CuO_2 plane coupled with the lattice distortion by a long-range interaction.

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