Mobile small polaron

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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 of the polaron wave function, so the polaron radius becomes comparable with the lattice constant unless phonon frequencies are extremely high. The size of the energy of the ground state and first excited states at large λ becomes 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

\[ H = - \sum_{nn'} t_{nn'} c_{n}^{\dagger} c_{n'} + \sum_{q\alpha} \hbar \omega_{q\alpha} (d_{q\alpha}^{\dagger} d_{q\alpha} + 1/2) - \sum_{m\alpha} f_{m\alpha}(n) c_{n}^{\dagger} c_{n} \xi_{m\alpha}. \]  

Here α corresponds to the different phonon modes, ξ_{mα} is a normal coordinate at site m, and f_{mα}(n) is the force between the electron at site n and the normal coordinate ξ_{mα}.

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

\[ \hat{H} = e^{-S} H e^{S} = - \sum_{n \neq n'} \delta_{n n'} c_{n}^{\dagger} c_{n'} - E_{p} \sum_{n} c_{n}^{\dagger} c_{n} + \sum_{q\alpha} \omega_{q\alpha} (d_{q\alpha}^{\dagger} d_{q\alpha} + 1/2). \]  

Here S = \sum_{m\alpha q\alpha} (\hbar \omega_{q\alpha})^{-1} u_{m\alpha q} f_{m\alpha}(n) c_{n}^{\dagger} d_{q\alpha}^{\dagger} - h.c., and E_{p} is the familiar polaronic shift,

\[ E_{p} = \sum_{mm'\alpha q\alpha} \frac{1}{2NM\omega_{q\alpha}} f_{m\alpha}(0) f_{m'\alpha}(0) \cos q(m - m'). \]
The polaronic shift is the natural measure of the strenght 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 \( \hat{\sigma}_{nn'} \), which depends on the phonon operators as
\[
\hat{\sigma}_{nn'} = t_{nn'} \exp \left[ \sum_{m\neq q} \frac{f_{m\alpha}(n) - f_{m\alpha}(n')}{\hbar \omega_{q \alpha}} \times (u_{mq \alpha} d_{q \alpha}^\dagger - u^*_{mq \alpha} d_{q \alpha}) \right].
\]
(4)

At large \( \lambda \) 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 \(-E_p\)) \( |k, 0\rangle = N^{-1/2} \sum_n c_n^\dagger \exp(ik \cdot n)|0\rangle \), one readily calculates the lowest energy levels in a crystal. Up to the second order in the hopping integral, the result is
\[
E(k) = -E_p - \sum_{n \neq 0} t_{n0} e^{-\sigma^2(n)} \exp(-ik \cdot n) - \sum_{k', n_{q \alpha}} \left| \langle k, 0 | \sum_{m \neq q} \hat{\sigma}_{nn'} c_{n'}^\dagger c_n |k', n_{q \alpha}\rangle \right|^2 / \hbar \omega_{q \alpha} n_{q \alpha}.
\]
(5)

Here \( |k', n_{q \alpha}\rangle \) is an excited state of the unperturbed Hamiltonian with one electron and at least one phonon, \( n_{q \alpha} \) is the phonon occupation number. The second term in Eq. (3), which is linear with respect to the bare hopping \( t_{nn'} \), determines the dispersion of the polaron band with a band-narrowing exponent (at zero temperature)
\[
g^2(n) = \sum_{q \alpha} \frac{1}{2N M \hbar \omega_{q \alpha}} \times \sum_{mm'} [f_{m\alpha}(0)f_{m'\alpha}(0) - f_{m\alpha}(0)f_{m'\alpha}(n)] \cos q(m - m').
\]
(6)

The third term in Eq. (3), quadratic in \( t_{nn'} \), yields a negative almost \( k \)-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. (4). We now consider the case of a single dispersionless phonon mode \( \omega_{q \alpha} = \omega \) and the nearest-neighbor hopping with an amplitude \( t \). One obtains
\[
E_p = \frac{1}{2M \omega^2} \sum_m f_m^2(0),
\]
(7)
\[
g^2 = g^2(1) = \frac{1}{2M \omega^2} \sum_m [f_m^2(0) - f_m(0)f_m(1)].
\]
(8)

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

To calculate \( \gamma \) 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 \( n \) of the infinite chain (plane) \( (\times) \) interacts with the vibrations of all ions of another chain (plane) \( (\circ) \) polarised in the direction perpendicular to the chains. A strong coupling of carriers with \( c \)-axis polarised phonons \( (\hbar \omega = \sim 75 \text{ meV}) \) has been established experimentally in \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) [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 \( \times \)) coupled with the \( c \)-axis apical oxygen vibrations (chain \( \circ \)) in the cuprates. The corresponding force is given by
\[
f_m(n) = \frac{\kappa}{(m - n^2 + 1)^{3/2}}.
\]
(9)

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

Our analytical consideration is applied if \( \omega \gg t \), 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 [10,11], density-matrix renormalization group [23] and
varietal 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 state energy and effective mass.

Circles: $\omega = 1.0t$; squares: $\omega = 0.5t$.

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 $m_{\lambda}^\ast (\lambda)$ in the Fröhlich weak-coupling regime one has $E_0 = -\alpha \hbar \omega$ and $m_{\lambda}^\ast = (1 + \alpha/6) m$. This mass appears to be well below our $m_{FP}^\ast$ for $\lambda < 1$. For instance, for $\lambda = 0.5$ and $\hbar \omega = t$, the continuum mass is $m_{FP}^\ast = 1.119 m$ while our result is $m_{FP}^\ast = 1.422 m$. 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 $m_{FP}^\ast = 0.021\alpha^4 m$ for $\lambda = 2$ and $\hbar \omega = t$ we find $m_{FP}^\ast = 4.29 m$ which is much larger than our mass, $m_{FP}^\ast = 4.29 m$. 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 $m_{FP}^\ast = 1.074 m$ turns out to be much lighter than the exact one for the same $\lambda$. 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 [26] and compared it with the 2D Holstein polaron (see Fig. 3). At $\lambda > 1$ the mass ratio $m_{SF}^\ast / m_{SH}^\ast$ (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 $m_{SF}^\ast = 400$ but $m_{SH}^\ast = 11$). 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
the form of electron-phonon interaction. A long-range interaction of the type of Eq. (6) 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 $m_{FP}^*$ models. $\bar{\omega} = 0.5 t$. Inset: Ratio $m_{FP}^*/m_{HP}^*$.

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 are as well as large Fröhlich (bi)polarons 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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