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Mobile Bipolaron—Strong Coupling Approach

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We explore the properties of the bipolaron in a 1D Holstein–Hubbard model with dynamical quantum phonons. We apply strong coupling theory to investigate the intersite bipolaron. We investigate the influence of the Hubbard interaction on the bipolaron binding energy, effective mass, and phase diagram. We compare our analytic results to recent numerical calculations [1]. In the intermediate and strong coupling regimes, a bipolaron is stable beyond the naive stability limit $U_0 = 2\omega g^2$. The intersite bipolaron has a significantly reduced mass compared to the single site bipolaron, and is stable in the strong coupling regime up to $U_c \sim 4\omega g^2$.

KEY WORDS: Bipolaron; polaron; electron-phonon coupling; superconductivity.

Although there is a generally accepted belief that in high-T_c superconductors (HTSC) a dominantly electronic interaction is responsible for the unusually high transition temperatures, the interplay between the electron–phonon interaction and the strong electron–electron interaction nevertheless plays a significant role in determining the physical properties of these strongly correlated systems [2,3]. Although theoretical study of lattice effects in strongly correlated materials is steadily growing [4–6], understanding of the influence of the Hubbard interaction U on bipolaron formation is still incomplete. In particular, it is known that in the strong coupling regime bipolarons have an extremely large effective mass [1,7,8], which represents one of the main objections [8,9] against the theory of small bipolaron superconductivity [10]. Recent calculations in the adiabatic (static phonon) limit show that a first-order phase transition exists between the on-site ($S0$) and intersite ($S1$) bipolaron [11]. The properties of the $S1$ bipolaron were also investigated by an approximate variational method [12].

Our recent numeric calculations [1] based on a new numerical approach [14,15] show that the effective mass of $S1$ can be many orders of magnitude smaller than the $S0$ bipolaron mass. In this article, we focus on strong coupling theory applied to the $S0$ and the intersite $S1$ bipolaron. We show that the effective $S1$ bipolaron mass scales with the same exponent—that is, e^{-g^2}—as the polaron mass and that the stability criteria of $S1$ bipolaron in strong coupling limit has a simple asymptotic form: $U_c = 4\omega g^2$. With dynamic quantum phonons, there is a crossover rather than a phase transition between the $S0$ and the $S1$ regimes.

We consider the Holstein–Hubbard Hamiltonian [13]

$$H = -t \sum_{js} (c^\dagger_{j+1,s} c_{j,s} + H.c.) - g\omega \sum_{js} c^\dagger_{j,s} c_{j,s} (a_j + a^\dagger_j) + \omega \sum_j a^\dagger_j a_j + U \sum_j n_{j\uparrow} n_{j\downarrow} \quad (1)$$

where $c^\dagger_{j,s}$ creates an electron of spin s and $a^\dagger_j$ creates a phonon on site j. The last term in Eq. (1) represents the on-site Coulomb repulsion. We consider the case in which two electrons with opposite spins couple to dispersionless optical phonons.

We start by applying second-order strong coupling perturbation theory to the $S0$ bipolaron. Following Lang and Firsov [16], we use the canonical transformation $\tilde{H} = e^s H e^{-S}$, where $S = q\ \Sigma_{js} n_{js} (a_j - a^\dagger_j)$. The transformed Hamiltonian takes the following form:

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$$\tilde{H} = H_0 + V$$
$$H_0 = \omega \sum_j a_j^\dagger a_j - \omega g^2 \sum_j n_j + (U - 2\omega g^2) \sum_j n_{j\uparrow} n_{j\downarrow}$$
$$V = -te^{-g^2} \sum_{js} (c_{j+1,s}^\dagger c_{j,s} e^{-g(a_{j+1}^\dagger - a_j^\dagger)} e^{g(a_{j+1} - a_j)} + H.c.) \quad (2)$$

where $n_j = n_\uparrow + n_\downarrow$. The first term in H_0 is the energy of the phonon excitations, and the second is the energy gained by the oscillator that is displaced by the force of the electron. In the limit where $g \to 0$ and $\omega \to \infty$ while ωg^2 remains a constant, the phonon interaction is instantaneous, and the Holstein–Hubbard model maps onto a negative U Hubbard model with an effective Hubbard interaction $\tilde{U} = U - 2\omega g^2$. In 1D, a bound state exists as long as $\tilde{U} < 0$.

In the strong coupling limit, V in Eq. (2) is considered a perturbation. It represents the hopping of electrons, including possible creation and destruction of phonon excitations. The $S0$ state $\phi_0 = c_{0\uparrow}^\dagger c_{0\downarrow}^\dagger |0\rangle$ has the lowest energy to zeroth order in V when $\tilde{U} < 0$. In perturbation theory to second order, the energy of the $S0$ bipolaron is computed as an infinite sum of diagrams (Fig. 1).

$$E_{bi}^{S0}(k) = U - 4\omega g^2 + 4t^2 e^{-2g^2} \sum_{n,m=0}^{\infty} \frac{g^{2(n+m)}}{n!m!} \frac{1 + (-1)^{n+m} \cos k}{\tilde{U} - (n+m)\omega} \quad (3)$$

In the first step, one of the two electrons hops from the original doubly occupied site to a neighboring site, creating m and n additional phonons on the original and neighboring site, respectively (see Fig. 1). In the next step, there are two distinct processes: (a) the original electron hops back, erasing the created phonon excitations; and (b) the second electron follows the first, erasing the phonons. Although in both cases the system returns to the original $S0$ bipolaron configuration, there is an important difference between the two sets of diagrams. In the second case, the $S0$ bipolaron is shifted by one lattice spacing. Those diagrams lead to dispersion [k dependence in Eq. (3)], which further leads to the effective mass renormalization. Note that there is an additional minus sign in this case that is responsible for a large effective mass (see below).

To calculate the binding energy $\Delta = E_{bi} - 2E_{po}$, we also compute the polaron energy up to second order in V

$$E_{po}(k) = -\omega g^2 - 2t \cos k e^{-g^2} - \frac{2t^2 e^{-2g^2}}{\omega} \sum_{n=1} \frac{g^{2n}}{nn!} (2^n + \cos(2k)) \quad (4)$$

The energy minimum is in both cases at $k = 0$. The effective mass $m^{-1} = \partial^2 E(k)/\partial k^2$ of a polaron and a bipolaron can be obtained in an analytical form from Eqs. (3,4) by calculating the infinite sums [1,6,7]

$$m_{po}^{-1} = 2te^{-g^2} \left[1 + \frac{4t}{\omega} e^{-g^2} (\text{Ei}(g^2) - \gamma - \ln g^2) \right] \quad (5)$$

$$m_{bi}^{S0^{-1}} = \frac{4^2}{\omega} e^{-\left(2g^2 - \frac{\tilde{U}}{\omega} \ln 2^{g^2}\right)} \left[\Gamma\left(-\frac{\tilde{U}}{\omega}\right) - \Gamma\left(-\frac{\tilde{U}}{\omega}, 2g^2\right) \right] \quad (6)$$

where γ is Euler's constant, $\text{Ei}(x)$ is the exponential integral, and $\Gamma(x)$ and $\Gamma(a, x)$ are gamma and incomplete gamma functions, respectively.

Taking the asymptotic limit ($g \to \infty$) in Eqs. (5, 6), one finds (see also Ref. [7])

$$m_{po}^{-1} \simeq 2t \left(1 + \frac{4t}{\omega g^2} \right) e^{-g^2} \quad (7)$$

$$m_{S0}^{-1} \simeq \frac{\sqrt{\pi} 4t^2}{\omega g} \left(1 - \frac{1}{\sqrt{\pi} g} \right) e^{-4g^2} \quad (8)$$

where the limit $U \to 0$ was taken in Eq. (8). Clearly, at large g, m_{s0} is roughly a factor $\exp(3g^2)$ larger than m_{po}.

One would naively expect that within the strong

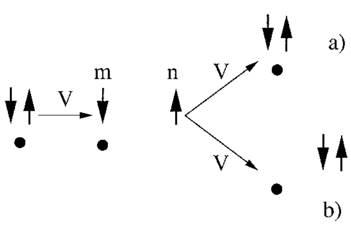

Fig. 1. Diagrams that contribute to second-order perturbation theory for the $S0$ bipolaron.

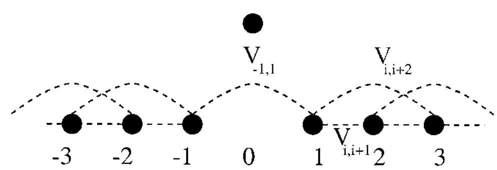

Fig. 2. Pictorial representation of the secular equation $|V_{ij} - \delta_{ij} E_{bi}^{S1}| = 0$. Taking into account translation invariance, we fix one of the spins at the origin (site 0). Dots numbered $\{-3, \ldots, 3\}$ represent functions ϕ_i, $V_{i,j}$ and are matrix elements up to second order in strong coupling theory. The function ϕ_0 enters the calculation only through the virtual process that contributes to $V_{-1,1}$.

coupling approximation, a bipolaron unbinds when $\tilde{U} \geq 0$. This is false: A bound bipolaron may exist even for $\tilde{U} \geq 0$. In this regime, a set of degenerate states $\phi_i = c^\dagger_{0\uparrow} c^\dagger_{i\downarrow}|0\rangle$ for $i \neq 0$, written in a translationally invariant form, represents states with minimum energy of H_0. The energy of an $S1$ bipolaron is obtained by solving the secular equation $|V_{ij} - \delta_{ij} E^{S1}_{bi}| = 0$, where matrix elements $V_{ij} = \langle\phi_i|V|\phi_j\rangle$ are calculated up to second order in V. The secular equation can be viewed as a tight-binding model in which degenerate wave functions $|\phi_i\rangle$ are connected with off-diagonal matrix elements (Fig. 2).

$$V_{i,i+1} = -(1 + e^{ik})\, te^{-g^2} \tag{9}$$

$$V_{i,i+2} = -(1 + e^{2ik})\, t^2 e^{-2g^2} \sum_{n=1}^{\infty} \frac{g^{2n}}{n!} \frac{1}{n\omega},$$
$$\sim -(1 + e^{2ik}) \frac{t^2}{\omega g^2} e^{-g^2} \tag{10}$$

$$V_{1,-1} = -t^2 e^{-2g^2} \left[\sum_{n=1}^{\infty} \frac{(2g^2)^n}{n!} \frac{2e^{-ik}}{\tilde{U} + n\omega} + \frac{g^{2n}}{n!} \frac{1 + e^{-2ik}}{\tilde{U} + n\omega} \right] \sim -\frac{2t^2}{U} e^{-ik} \tag{11}$$

On-site energies of the tight-binding model in Fig. (2) are diagonal matrix elements

$$V_{i,i} = -4t^2 e^{-2g^2} \sum_{n=1}^{\infty} \frac{(2g^2)^n}{n!} \frac{1}{n\omega} \sim -\frac{2t^2}{\omega g^2} \tag{12}$$

$$V_{1,1} = -2t^2 e^{-2g^2} \left[\sum_{n=1}^{\infty} \left[\frac{(2g^2)^n}{n!} \left(\frac{1}{n\omega} + \frac{1}{\tilde{U} + n\omega} \right) + \frac{g^{2n}}{n!} \frac{\cos k}{n\omega} \right] + \frac{1}{\tilde{U}} \right] \sim -t^2 \left(\frac{1}{\omega g^2} + \frac{2}{U} \right) \tag{13}$$

The forms for general site i are used except where specific forms are listed for sites $i = 1, -1$. The approximate expressions of the above matrix elements are valid in the limit $g \to \infty$. Note that the strong coupling expansion is an expansion in $t^2/\omega g^2$, and not in $t \exp(-g^2)$, as one would naively expect from the first-order expression. Eigenvectors of the secular equation represent the wavefunction of the $S1$ bipolaron written in the basis ϕ_i.

The main source of the binding in this formalism arises because the overlap between the two states where electrons are on neighboring sites in different spin configurations $V_{1\text{-}1}$ is much larger than all other off-diagonal matrix elements. Although in the limit when $g \to \infty$, $V_{1-1} \propto -t^2/U$, the second largest (first-order) matrix elements $V_{i,i+1} \propto t \exp(-g^2)$ for $i \neq \{0, -1\}$. In the singlet configuration, $\phi_1^{S=0} = (\phi_1 + \phi_{-1})/\sqrt{2}$, the diagonal correction to the energy is given by $V_{11} + V_{1-1}$. There is also a contribution to V_{11} that resembles a retardation effect, in which one electron hops, creating one or more phonon quanta on the site that it has left, and then the second electron follows, absorbing phonons. This effect, however, decreases with g exponentially as $t^2/(\omega g^2) \exp(-g^2)$, and is not strong enough to bind two polarons in the triplet configuration.

The effective $S1$ bipolaron mass is expected to be much smaller than m^{S0}_{bi}. Approximating the $S1$ bipolaron wave-function with only $\phi_1^{S=0}$ (omitting the exponential tail), the effective mass is

$$m^{-1}_{S1} \simeq \frac{2t^2 e^{-2g^2}}{\omega} \left[\frac{2\omega}{\tilde{U}} + \sum_{n=1} \frac{g^{2n}}{n!} \left(\frac{2}{\tilde{U}/\omega + n} + \frac{1}{n} \right) \right]$$
$$\sim 2t^2 e^{-g^2} \left[\frac{2}{U - \omega g^2} + \frac{1}{\omega g^2} \right] \tag{14}$$

As in the case of Eqs. (5, 6), m_{S1} can also be expressed in terms of gamma and exponential integral functions. However, the second approximate form in Eq. (14) provides greater physical intuition. There are three distinct processes contributing to m_{S1}: an $S1$ pair can move by one lattice site through an intermediate doubly occupied state with n phonons [terms that contain U in Eq. (14)], or through an intermediate state with only phonon degrees of freedom (terms without U). In the first process, the spins either exchange or do not exchange. The main difference between m_{S0} and m_{S1} is that the latter is of the order of the polaron mass.

In Fig. 3, we present numerical results for binding energy $\Delta = E_{bi} - 2E_{po}$ vs. U. For a discussion of numeric results in the weak and intermediate coupling regimes, see Ref. [1]. Comparison with strong coupling results for $g = 2$ using Eqs. (3, 4) and perturbation theory that involves states ϕ_i shows good agreement with numeric results.

Figure 4 plots the bipolaron mass in units of the polaron mass [1]. We plot the ratio $R_m = m_{bi}/(2 * m_{po})$ vs. U for different values of ω and g. At fixed $\omega = 1$, the bipolaron mass ratio increases by several orders of magnitude with increasing g at $U = 0$. The increase can be understood within the strong coupling theory.

Increasing U has a dramatic effect on the mass ratio R_m in the $S0$ regime. A sharp decrease of R_m is observed. Note that the scale in Fig. 4 is logarithmic. Near the strong coupling regime ($g = 2$) and for small U, good agreement is found between the numerical

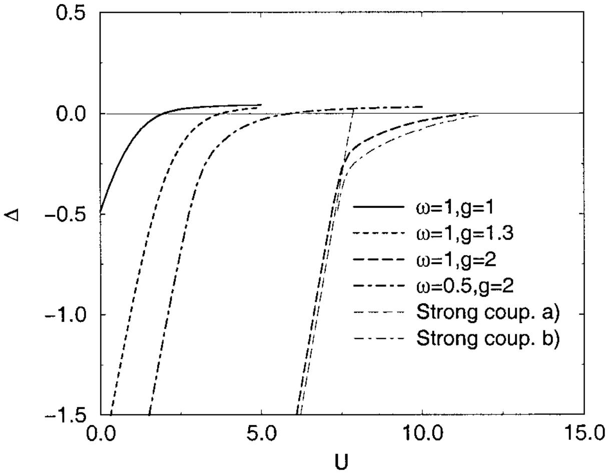

Fig. 3. Binding energy Δ vs. U, where $\Delta < 0$ for a bound state. Thick lines are numerical results ($N_h = 18$ generations used in the variational space). Thin lines are strong coupling expansion results for $g = 2$, $\omega = 1$ obtained from a) Eqs. (3, 4) and b) including degenerate states ϕ_i as well as ϕ_0. Hopping $t = 1$ in this and all subsequent numerical calculations.

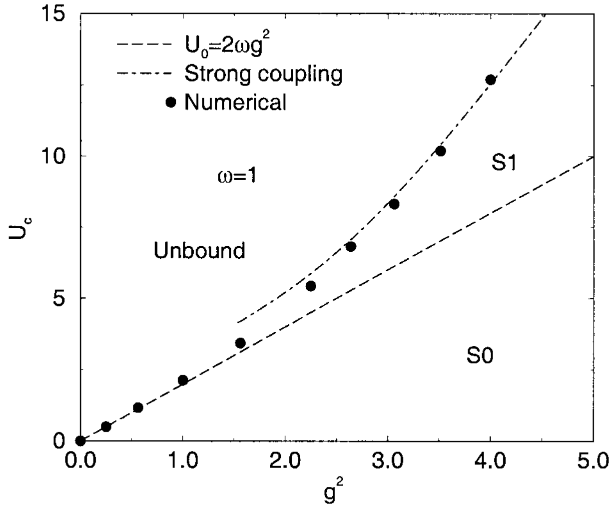

Fig. 5. Phase diagram calculated at $\omega = 1$. Numerical results are represented by full circles. The dashed line represents the limit of stability of a $S0$ bipolaron in the strong coupling limit, i.e., $U_c = 2\omega g^2$. The dot-dashed line represents the degenerate strong coupling perturbation result that asymptotically approaches $U_c = 4\omega g^2$.

and the strong coupling result obtained from Eqs. (5, 6). The difference between these results increases as U approaches $U_0 = 8$, where the perturbation theory based on the $S0$ bipolaron breaks down. In the $S1$ regime, for $U > U_0$, R_m is small, as predicted by the strong coupling result.

We conclude with the phase diagram $U_c(g)$ shown in Fig. 5 at fixed $\omega = 1$. Numeric results, shown as circles, indicate the phase boundary between two dissociated polarons and a (bipolaron) bound state. The dashed line, given by $U_0 = 2\omega g^2$, is a reasonable estimate for the phase boundary at small g. At large g, the dashed line roughly represents the crossover between a massive $S0$ and lighter $S1$ bipolaron. The $S1$ region grows with increasing g. The dot–dashed line is the phase boundary between $S1$ and the unbound polaronic phase, as obtained by degenerate strong coupling perturbation theory. Numeric results approach this line at larger g. The dashed line asymptotically approaches $U_c = 4\omega g^2$, which can be understood within the strong coupling approach: Because all the off-diagonal matrix elements except V_{1-1} scale as $\exp(-g^2)$, we can work in the static limit where the condition for a bound state is given by $V_{11} + V_{1-1} < V_{ii}$. Keeping only terms of the order $t^2/\omega g^2$ and setting $k = 0$, the matrix elements can be expressed as $V_{11} = V_a + V_b$, $V_{1-1} = V_b$ and $V_{ii} = 2V_a$; $i > 1$, with

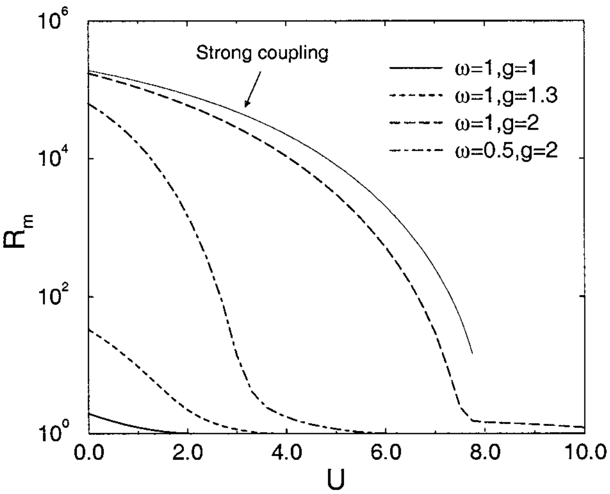

Fig. 4. The mass ratio $R_m = m_{bi}/(2 * m_{po})$ vs. U. Numerical results are shown as thick lines. The thin line is the strong coupling expansion result.

$$V_a = \frac{-2t^2e^{-2g^2}}{\omega}\sum_{n=1}\frac{(2g^2)^n}{n!n} \sim -\frac{t^2}{\omega g^2} \tag{15}$$

$$V_b = \frac{-2t^2e^{-2g^2}}{\omega}\sum_{n=0}\frac{(2g^2)^n}{n!}\frac{1}{\frac{\tilde{U}}{\omega}+n} \sim -\frac{2t^2}{U} \tag{16}$$

In the large-g limit, this yields the inequality $U < 4\omega g^2$.

In conclusion, using strong coupling perturbation theory and precise numerical calculations [1], we demonstrate that near the strong coupling limit a mobile $S1$ bipolaron exists with an effective mass of the order of a polaron mass. The wavefunction of the intersite $S1$ bipolaron is a spin singlet with extended s-wave spatial symmetry. Taking into account the asymptotic stability criterion $U_c = 4\omega g^2$, it is clear that a triplet $S1$ bipolaron that corresponds to the $U \rightarrow \infty$ solution is not bound. In the static limit it can be shown that bound states of three or more polarons are not stable in the $S1$ regime, thus ruling out phase separation in the strong coupling regime of the Holstein–Hubbard model.

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