Relation between electron mass enhancement and potential shape: Numerical analysis of two-site anharmonic Holstein-Hubbard model

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Abstract. In order to promote our understanding on the emergence of magnetically robust heavy-electron state due to the interaction between conduction electrons and local anharmonic oscillations of guest atom in cage-structure materials, we investigate how the electron mass enhancement factor depends on the potential shape of the guest atom by analyzing numerically the two-site anharmonic Holstein-Hubbard model. It is found that the electron mass enhancement factor becomes maximum when the bottom of the potential becomes wide and flat. Such a potential is called a rattling type, which appears in the transition region between single-well and double-well types. Thus, the anharmonic oscillation in the rattling potential is considered to play a key role for the formation of the heavy-electron state in cage-structure compounds. We briefly discuss the reason why the electron mass enhancement factor becomes maximum in the rattling type potential region.

1. Introduction

Since the discovery of magnetically robust heavy-electron phenomenon in Sm-based filled skutterudite compound SmOs$_4$Sb$_{12}$ [1], the heavy-electron formation due to the electron-phonon interaction has attracted renewed attention in the research field of condensed matter physics [2, 3]. A traditional mechanism of the emergence of heavy-electron state has been based on quantum criticality induced by the competition between the Kondo effect and the Ruderman-Kittel-Kasuya-Yosida interaction [4]. However, it is difficult to explain the peculiar magnetically robust heavy-electron state on the basis of the standard Kondo effect originating from spin degree of freedom. Thus, the importance of the non-magnetic Kondo effect due to electron-phonon interaction has been pointed out [5, 6, 7], since local anharmonic oscillation of rare-earth atom, i.e., rattling, in the pnictogen cage has been considered to play a crucial role for understanding of electronic properties of filled skutterudites [8].

In fact, from the numerical evaluation of the Sommerfeld constant $\gamma$ under the magnetic field in the Anderson-Holstein model, it has been found that large $\gamma$ actually becomes magnetically robust [9, 10], when the bottom of the potential is relatively wide and flat, i.e., in the rattling region. It has been gradually recognized that magnetically robust heavy-electron phenomenon occurs due to rattling, but we are interested in new properties of electron-rattling coupled state. In particular, the analysis in the periodic system is further required. Then, the anharmonic Holstein model has been analyzed within the standard perturbation theory [11, 12], indicating...
that the electron mass enhancement becomes large when the bottom of the potential is changed to be wide and flat. However, when the potential exhibits the double-well structure, the mass enhancement becomes extremely large, suggesting that the perturbation calculation is invalid for the case of strong anharmonicity. It is still requested to promote further our understanding on the relation between the electron mass enhancement and the potential shape over beyond the perturbation calculation.

In this paper, we analyze the two-site anharmonic Holstein-Hubbard model by using an exact diagonalization method. It is observed that the electron mass enhancement factor is maximized at the rattling potential, the bottom of which becomes wide and flat. We can understand the increase in the electron mass enhancement factor when the potential shape is changed from the single-well to the rattling type on the basis of the strong-coupling tendency owing to the phonon softening [11, 12]. On the other hand, the decrease in the electron mass enhancement factor when the potential shape is changed from the rattling to the double-well type is considered to be interpreted as the effect of vertex corrections. We briefly discuss an effective method to understand the behavior of the electron mass enhancement factor in the double-well potential as one of future problems. Throughout this paper, we use such units as $\hbar=\kB=1$.

2. Model and Method

We introduce the two-site Holstein-Hubbard model, given by

$$H = -t \sum_{\sigma} (c_{i\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma}) + \sum_{i=1,2} [H_{\text{eph}}^{(i)} + H_{\text{ph}}^{(i)}],$$

where $t$ denotes the hopping amplitude of electrons, $c_{i\sigma}$ is an annihilation operator of electron at site $i$ with spin $\sigma$, and the second and third terms denotes the local electron interactions and the atom oscillations, given by

$$H_{\text{eph}}^{(i)} = \mu \rho_i + Un_i n_{i\uparrow} + gn_i Q_i, \quad H_{\text{ph}}^{(i)} = \frac{P_i^2}{2M} + V(Q_i),$$

respectively. Here, $\mu$ indicates the chemical potential, $n_{i\sigma}=c_{i\sigma}^\dagger c_{i\sigma}$, $\rho_i=n_{i\uparrow} + n_{i\downarrow}$, $U$ denotes the Coulomb interaction between electrons, $g$ is an electron-phonon coupling constant, $Q_i$ indicates the normal coordinate of oscillation of atom at site $i$, $P_i$ is the canonical momentum, $M$ denotes the reduced mass of oscillation, and $V(Q_i)$ is an anharmonic potential for atom, expressed by

$$V(Q_i) = k_2 Q_i^2 + k_4 Q_i^4,$$

where $k_2$ and $k_4$ denote the coefficients for second- and forth-order terms, respectively. In this paper, $k_2$ can be both positive and negative for the control of the anharmonicity, whereas $k_4$ is set to be positive to confine the oscillation in a finite space.

In order to investigate the potential shape, it is useful to introduce the length scale $Q_0=1/\sqrt{2M\omega}$, where $\omega$ is the phonon frequency and $Q_0$ denotes the amplitude of zero-point oscillation for harmonic oscillator. Then, we obtain

$$V(q_i) = \omega \left[ (\beta_2 + \frac{1}{4})q_i^2 + \beta_4 q_i^4 \right],$$

where $q_i=Q_i/Q_0$ and $\beta_2$ and $\beta_4$ are nondimensional anharmonicity parameters, defined by

$$\beta_2 = \frac{1}{4} \left( \frac{2k_2}{M\omega^2} - 1 \right), \quad \beta_4 = \frac{k_4}{4M^2\omega^2},$$

respectively. Note that the case of $\beta_2=\beta_4=0$ denotes the potential for the harmonic oscillator.
By further introducing the phonon operator $a_i$ through the relation $q_i=a_i+a_i^\dagger$, we obtain

$$H_{\text{eph}}^{(i)} = \mu \rho_i + U n_i n_i + \sqrt{\alpha \rho_i (a_i + a_i^\dagger)}, \quad H_{\text{ph}}^{(i)} = \omega \left[ a_i^\dagger a_i + \frac{1}{2} + \beta_2 (a_i + a_i^\dagger)^2 + \beta_4 (a_i + a_i^\dagger)^4 \right],$$

where $\alpha$ is the non-dimensional electron-phonon coupling constant given by $\alpha=g^2/(2\omega^3)$.

In order to investigate the electron mass enhancement due to the electron-phonon interaction, we numerically evaluate the Green’s function, defined by

$$G_k(i\omega_n) = -\int_0^{1/T} d\tau e^{i\omega_n \tau} \langle c_{k\sigma}(\tau) c_{k\sigma}^\dagger \rangle,$$

where $k$ denotes momentum, $T$ is a temperature, $\omega_n$ is the fermion Matsubara frequency given by $\omega_n=\pi T(2n+1)$ with an integer $n$, $c_{k\sigma}(\tau) = e^{iH\tau} c_{k\sigma} e^{-iH\tau}$, and $\langle \cdots \rangle$ denotes the operation to take the thermal average. After some algebraic calculations, we obtain the retarded Green’s function in the spectral representation as

$$G_k^R(\omega) = \int_{-\infty}^{+\infty} dE \frac{A_k(E)}{\omega + i\eta - E},$$

where $\eta$ is a positive infinitesimal and the spectral function $A_k(E)$ is given by

$$A_k(E) = \sum_{i,j} e^{(\Omega-E_j)/T} (e^{E/T} + 1) \delta(E+E_i-E_j) \langle \Psi_i | c_{k\sigma} | \Psi_j \rangle \langle \Psi_j | c_{k\sigma}^\dagger | \Psi_i \rangle.$$  \hspace{1cm} (9)

Here, $\Omega$ denotes the thermodynamic potential given by $\Omega=-T \ln(\sum_i e^{-E_i/T})$, $E_i$ is the eigenenergy of $H$, and the corresponding eigenstate is $| \Psi_i \rangle$. By introducing the electron self-energy $\Sigma_k^R(\omega)$, we obtain another expression for $G$ through the Dyson’s equation, given by

$$G_k^R(\omega) = \frac{1}{\omega - \varepsilon_k + \mu - \Sigma_k^R(\omega)},$$

where $\varepsilon_k$ denotes the electron energy of momentum $k$. In the two-site case, we obtain $\varepsilon_k=-t \cos k$ and the momentum $k$ takes 0 and $\pi$.

In the present research, first we evaluate the Green’s function and the spectral function with the use of the eigenvalues and eigenstates obtained by solving $H|\Psi_i\rangle=\varepsilon_i|\Psi_i\rangle$. Concerning the exact diagonalization method, there exists a disadvantageous point that only a small-size system is treated, while we can obtain the exact results for the case of strong anharmonicity in the strong-coupling and anti-adiabatic region beyond the perturbation theory on the basis of the Migdal’s theorem. Next, we calculate the self-energy $\Sigma$ from eqs. (8), (9), and (10). Then, we finally calculate the mass enhancement factor $Z_k$ by

$$Z_k = 1 - \frac{\partial}{\partial \omega} \text{Re} \Sigma_k^R(\omega) \big|_{\omega \to 0}.$$  \hspace{1cm} (11)

In actual calculations, the differentiation is replaced by $\text{Re} \Sigma_k^R(\delta \omega)/\delta \omega$ with a small energy $\delta \omega$. Note that $\delta \omega$ is chosen to be much smaller than $\omega$.

In the exact diagonalization calculation, we prepare the phonon basis $|n_1, n_2\rangle$, given by $|n_1, n_2\rangle = (1/\sqrt{n_1!n_2!})(a_i^\dagger)^{n_1}(a_i)_{n_2}|0\rangle$ with the vacuum $|0\rangle$. In actual calculations to solve the eigenvalue problem, each phonon basis is truncated at a finite number $N_{\text{ph}}$. In order to check the convergence, we have performed the numerical calculations for $N_{\text{ph}}$, up to 50. Concerning the electron number, throughout this paper, we consider the half-filling situation by controlling appropriately the value of the chemical potential $\mu$. 

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3. Calculated Results

Let us first discuss the variation of the potential shape as well as the change of the phonon energy spectra by the anharmonicity. Note that the phonon energy spectra are obtained by the diagonalization of $H_{ph}^{(i)}$. In Figs. 1(a)-1(e), we plot the potentials by solid curves for several values of $\beta_2$ for $\beta_4=0.01$. We observe the change of the potential from the single-well to double-well types. At the transition region from the single-well to the double-well types, i.e., $\beta_2 \approx -0.25$, we find the rattling type potential, the bottom of which is wide and flat.

Concerning the phonon energy spectra, we draw the horizontal broken lines at the positions of the eigenenergies in each potential. In Figs. 1(a) and 1(b) with the single-well potential, we observe the phonon energy spectra similar to that of the harmonic oscillator. Note, however, that the width in the spectrum of Fig. 1(b) is apparently smaller than that of Fig. 1(a), since in the narrow potential, the energy is totally increased due to the uncertainty principle. In Fig. 1(c), the bottom of the potential becomes relatively wide and flat, since the quadratic term disappears in this case. The width of the phonon energy spectrum becomes small and the zero-point energy is decreased in comparison with those observed in Figs. 1(a) and 1(b). These are characteristic points of the phonon energy spectrum in the rattling potential.

In Figs. 1(d) and 1(e), we find the double-well potentials. In Fig. 1(d), the double-well structure is shallow and the energy difference between the ground and the first excited states is small, but it can be still observed in the figure. On the other hand, in Fig. 1(e), the depth of the double well becomes large and at the bottom of the double well, we find the degenerate ground states, originating from left and right positions of the double well. In this case, the first excited state also seems to be degenerate. In Fig. 1(f), we show the eigenenergies vs. $\beta_2$ for $\beta_4=0.01$. For $\beta_2 > -0.5$, we find non-degenerate eigenenergies, characteristic to the single-well potential. However, for $\beta_2 < -0.5$, we observe the degeneracy in the ground and a few excited states due to the double-well structure.

Figure 1. Potential shapes and eigenenergies of local anharmonic oscillator for (a) $\beta_2=0.5$, (b) $\beta_2=0.0$, (c) $\beta_2=-0.25$, (d) $\beta_2=-0.4$, and (e) $\beta_2=-0.7$ with $\beta_4=0.01$. In (f), we plot the excitation energies vs. $\beta_2$ for $\beta_4=0.01$. Note that the energy scale of the local phonon problem is $\omega$, as easily understood from eq. (6).
and flat potential can be a source of the formation of the heavy-electron state. When we include the coupling between electrons mediated by anharmonic oscillation of atom, leading to the mass enhancement of electrons. When we include Coulomb interaction, the magnitude of the effective attraction is weakened by $U$, and the characteristic peak structure is expected to be reduced. Here, we note that the peak structure of $U=4$ is rather robust in comparison with that of $U=2$. When we turn our attention to $Z_k$ for $k=\pi$ (not shown here), it shows a minimum at the rattling potential region and the depth of the minimum becomes large with the increase in $U$, if we consider the average of $Z_{k=0}$ and $Z_{k=\pi}$, the peak structure at the rattling potential region is monotonically reduced with the increase in $U$. It is concluded that the Coulomb interaction totally suppresses the peak structure in the dependence of $Z_k$ on the potential shape.

4. Discussion and Summary
We have found that the electron mass enhancement factor $Z_k$ becomes maximum for the rattling type potential, which appears between the single-well and double-well type potentials. As for the increase in $Z_k$ when the potential shape is changed from the single-well to the rattling type, it is basically understood from the strong-coupling tendency of the phonon softening due to
anharmonicity, as has been emphasized in our previous papers [11, 12]. In fact, in Fig. 1(f), we have already observed that the phonon excitation energy becomes small, when $\beta_2$ is decreased in the region of $\beta_2 > -0.5$. In the present research, the behavior of $Z_k$ in the region of $\beta_2 > -0.2$ is considered to be understood by this strong-coupling tendency due to the anharmonicity.

On the other hand, concerning the decrease in $Z_k$ with the increase in $\beta_2$ in the region of the double-well type potential, it is difficult to understand it by the strong-coupling tendency. When we increase the raw value of the electron-phonon coupling constant $\alpha$, the effective attraction between electrons eventually overcomes the Coulomb interaction and the bipolaron formation is expected to occur at a certain value of $\alpha$, leading to the charge-density-wave state. However, in the present situation, the strong-coupling tendency is effectively controlled by the potential shape. The formation of the bipolaron state violates the local charge conservation and we expect that the Nambu-Goldstone mode occurs to resolve the bipolaron state. This is the effect of vertex corrections, which are ignored in the second-order perturbation theory in terms of $g$. In the exact diagonalization calculations, such vertex corrections are included, although the system size is small. Thus, in the region of $\beta_2 < -0.2$, $Z_k$ decreases due to the effect of vertex corrections in the higher-order perturbation terms for the self-energy.

Since it is difficult to include exactly the vertex corrections in the perturbation theory, it is necessary to consider another effective way to evaluate $Z_k$ in the double-well type potential. Here, we should note the degenerate ground state in the double-well type potential, as observed in Fig. 1(e). In this case, a simple perturbation calculation leads to the divergence in $Z_k$, as has been mentioned in the previous papers [11, 12]. When there exists the double-well structure, we should consider the extra degree of freedom concerning the position, right or left in the double-well type potential. It is necessary to construct the revised perturbation theory to evaluate the electron mass enhancement in the double-well type potential by including explicitly positional degree of freedom. It is one of future problems.

In summary, by exploiting the exact diagonalization method to analyze the two-site anharmonic Holstein-Hubbard model, we have shown that the electron mass enhancement factor $Z_k$ becomes maximum for the rattling type potential, appearing in the region between the single-well and the double-well type potentials. It is also found that the Coulomb interaction suppresses the characteristic peak structure in the dependence of $Z_k$ on the anharmonicity.

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