First excited state calculation using different phonon bases for the two-site Holstein model

Jayita Chatterjee and A. N. Das

Saha Institute of Nuclear Physics
1/AF Bidhannagar, Calcutta 700064, India

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Abstract

The single-electron energy and static charge-lattice deformation correlations have been calculated for the first excited state of a two-site Holstein model within perturbative expansions using different standard phonon bases obtained through Lang-Firsov (LF) transformation, LF with squeezed phonon states, modified LF, modified LF transformation with squeezed phonon states, and also within weak-coupling perturbation approach. Comparisons of the convergence of the perturbative expansions for different phonon bases reveal that modified LF approach works much better than other approaches for major range of the coupling strength.

*Electronic Address: moon@cmp.saha.ernet.in
†Electronic Address: atin@cmp.saha.ernet.in
I. INTRODUCTION

The simplest model to study the nature and properties of polarons as a function of electron-phonon (e-ph) interaction is the Holstein model [1] which consists of tight binding electrons coupled through a site diagonal interaction term to dispersionless phonons. The ground state properties of this model has been extensively studied during recent years. In the antiadiabatic limit the confinement of the lattice deformation around the charge carrier for large e-ph interaction gives rise to small polarons whose nature and dynamics is generally studied using the Lang-Firsov (LF) method based on the canonical LF transformation [2]. For weak and intermediate e-ph coupling the LF method is not appropriate. For that region the importance and superiority of the modified LF (MLF) and the MLF with squeezed transformation (MLFS) over the LF method have been pointed out in previous works [3–5]. The results of exact diagonalization studies [6] of a two-site Holstein model indicate the failure of the standard (zero phonon averaging) classical LF approach even in the strong coupling antiadiabatic limit and the authors of Ref. [6] asserted that perturbation approach within the LF scheme is not meaningful. Marsiglio [7] studied the Holstein model in one dimension with one-electron up to 16 site lattices using numerical diagonalization technique and concluded that neither the Migdal approximation [8] nor the usual small-polaron approximation is in quantitative agreement with the exact results for intermediate coupling strength. So at present the Holstein model cannot be described by any single conventional analytical method for the entire range of the coupling strength either in the adiabatic or in antiadiabatic limit. In a recent work [9] we addressed this problem and considering a two-site system we developed a perturbation expansion using MLF phonon basis and the results obtained thereby are in good agreement with the exact numerical results for the entire range of the coupling strength for an intermediate value of hopping ($t \sim \omega_0$). Subsequently, we presented a detailed comparison for the convergence of perturbation corrections to the ground state energy and wave function for the same system [10] using different phonon bases obtained through the LF, modified LF (MLF) and modified LF with squeezing transformations (MLFS). The results
showed that for weak and intermediate coupling the perturbation corrections within the MLF and MLFS methods are much smaller and the convergence of the perturbation expansion is much better compared to the LF method. For strong coupling all the methods become equivalent and a good convergence in the perturbation expansion for the ground state is achieved. In this paper we have studied the convergence of the perturbation expansion for the energy and the correlation function for the first excited state of a two-site single electron system using different phonon bases obtained through the LF, MLF, MLFS, LF with squeezing (LFS) transformations, and also within weak-coupling expansion.

In Sec. II we define the model Hamiltonian, describe different variational phonon bases states that we have considered and present the expressions for the energy, wave function and static correlation functions calculated within the perturbation method for the first excited state. In Sec. III we present the results obtained by different methods and discuss about the convergence of the perturbation series, hence the applicability of the methods in different regions of the e-ph coupling strength for different hopping parameters and conclusions.

II. FORMALISM

The two-site single-polaron Holstein Hamiltonian is

\[ H = \sum_{i,\sigma} c_{i\sigma} n_{i\sigma} - \sum_{\sigma} t(c_{1\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma}) + g\omega_0 \sum_{i,\sigma} n_{i\sigma}(b_i + b_i^\dagger) + \omega_0 \sum_i b_i^\dagger b_i, \]

where \( i = 1 \) or \( 2 \), denotes the site. \( c_{i\sigma} \) (\( c_{i\sigma}^\dagger \)) is the annihilation (creation) operator for the electron with spin \( \sigma \) at site \( i \), and \( n_{i\sigma} \) (\( =c_{i\sigma}^\dagger c_{i\sigma} \)) is the corresponding number operator. \( g \) denotes the on-site e-ph coupling strength, \( t \) is the usual hopping integral. \( b_i \) and \( b_i^\dagger \) are the annihilation and creation operators, respectively, for phonons corresponding to interatomic vibrations at site \( i \), and \( \omega_0 \) is the phonon frequency. For the one-electron case spin index is redundant here, hence omitted in the following.

The Hamiltonian (1) can be divided into two independent parts: one part describing symmetric in-phase vibrations coupled to the total number of electrons and the other asymmetric out of phase vibrations coupled to the electronic degrees of freedom. The first part describes
just a shifted harmonic oscillator while the solution of the second part is a nontrivial problem. The Hamiltonian for the second part is given by

$$H_d = \sum_i \epsilon n_i - t(c_1^\dagger c_2 + c_2^\dagger c_1) + \omega_0 g_+ (n_1 - n_2) (d + d^\dagger) + \omega_0 d^\dagger d,$$

where $g_+ = g/\sqrt{2}$ and $d = (b_1 - b_2)/\sqrt{2}$.

For a perturbation method it is desirable to use a basis where the major part of the Hamiltonian becomes diagonal. The phonon bases chosen in the MLF or MLFS approach consist of variational displacement oscillators and can produce retardation effect even in the zeroth order of perturbation unlike the LF approach, hence these bases are better choices for perturbative calculation when the coupling strength is not very strong. We now use the MLF transformation where the lattice deformations produced by the electron are treated as variational parameters. For the present system,

$$\tilde{H}_d = e^R H_d e^{-R},$$

where $R = \lambda(n_1 - n_2)(d^\dagger - d)$, and $\lambda$ is a variational parameter related to the displacement of the $d$ oscillator. The transformed Hamiltonian is then obtained as

$$\tilde{H}_d = \omega_0 d^\dagger d + \sum_i \epsilon_p n_i - t[c_1^\dagger c_2 \exp(2\lambda(d^\dagger - d)) + c_2^\dagger c_1 \exp(-2\lambda(d^\dagger - d))] + \omega_0(g_+ - \lambda)(n_1 - n_2)(d + d^\dagger),$$

where $\epsilon_p = \epsilon - \omega_0(2g_+ - \lambda)\lambda$.

Now we will make a squeezing transformation to Hamiltonian (4)

$$\tilde{H}_{sd} = e^S \tilde{H}_d e^{-S},$$

where $S = \alpha(d_1 d_2 - d_1^\dagger d_2^\dagger)$. This new phonon basis is squeezed with respect to the previous basis. The transformed Hamiltonian (5) takes the form

$$\tilde{H}_{sd} = \omega_0 d^\dagger d[\cosh^2(2\alpha) + \sinh^2(2\alpha)] + \omega_0 \cosh(2\alpha) \sinh(2\alpha)(dd + d^\dagger d^\dagger) + \sum_i \epsilon_p n_i - t[c_1^\dagger c_2 \exp(2\lambda_c (d^\dagger - d)) + c_2^\dagger c_1 \exp(-2\lambda_c (d^\dagger - d))] + \omega_0(g_+ - \lambda)(n_1 - n_2)(d + d^\dagger) \exp(2\alpha) + \omega_0 \sinh^2(2\alpha).$$
where $\lambda_e = \lambda e^{-2\alpha}$. For the single polaron problem we choose the basis set

$$|\pm, N\rangle = \frac{1}{\sqrt{2}} (c_1^\dagger \pm c_2^\dagger) |0\rangle e |N\rangle$$  

(7)

where $|+\rangle$ and $|-\rangle$ are the bonding and antibonding electronic states and $|N\rangle$ denotes the $N$th excited oscillator state in the MLFS, MLF, LFS or LF bases depending on the method considered. It may be noted that the MLFS basis turns into the MLF basis when $\alpha = 0$, and into the LFS basis if $\lambda = g_+$. The MLF basis turns into the LF basis when $\lambda = g_+$, and it turns into the weak coupling expansion for $\lambda = 0$. We consider the diagonal part of Hamiltonian (6) as the unperturbed Hamiltonian ($H_0$) and the remaining part of the Hamiltonian, $H_1 = \tilde{H}_{sd} - H_0$, as a perturbation $[9,10]$. The unperturbed energy of the state $|\pm, N\rangle$ is given by

$$E^{(0)}_{\pm,N} = \langle N, \pm | H_0 | N, \pm \rangle = \omega_0 [\sinh^2(2\alpha) + N (\sinh^2(2\alpha) + \cosh^2(2\alpha))]$$

$$+ \epsilon_p \mp t_e \left[ \sum_{i=0}^{N} \frac{(2\lambda_e)^{2i}}{i!} (-1)^i Nc_i \right]$$  

(8)

where $t_e = t \exp (-2\lambda_e^2)$. The general off-diagonal matrix elements of $H_1$ are given in Refs. $[9,10]$. As noted in our previous work $[3]$ the unperturbed first excited state wave function should be built up as a linear combination of $|+, 1\rangle$ and $|-, 0\rangle$. The unperturbed energies of the states $|+, 1\rangle$ and $|-, 0\rangle$ are $(\epsilon_p + \omega_0 - t_e (1 - 4\lambda^2) + 3\sinh^2(2\alpha))$ and $(\epsilon_p + t_e + \omega_0 \sinh^2(2\alpha))$, respectively within the MLFS approach, and the off-diagonal matrix element between these two states is $(2\lambda_e t_e + \omega_0 (g_+ - \lambda)e^{2\alpha})$. The unperturbed energies of these two states cross at an intermediate value of $g_+$ for $2t > \omega_0$. So, following degenerate perturbation theory linear combinations of the states $|+, 1\rangle$ and $|-, 0\rangle$ are formed to obtain two new elements of basis states so that $\tilde{H}_{sd}$ becomes diagonal in the sub-space spanned by these two states. The unperturbed first excited state is given by

$$|\psi_{1}^{(0)}\rangle = \frac{1}{\sqrt{(a^2 + b^2)}} [a|-, 0\rangle + b|+, 1\rangle]$$  

(9)

The ratio $(c)$ of the coefficients $b$ to $a$ and the unperturbed energy $(\alpha)$ of the first excited state may be found out from the relation
\[ c = \frac{\alpha - H_{11}}{H_{12}} = \frac{H_{12}}{\alpha - H_{22}} \]  

(10)

where \( H_{11}, H_{22}, H_{12} \) are the matrix elements of \( \tilde{H}_d \) in the subspace of \(|-, 0\) and \(|+, 1\rangle\). Eq.(10) gives two roots of \( \alpha \), the lower value of \( \alpha \) (say, \( \alpha_1 \)) corresponds to the first excited state.

Our chosen phonon basis within the MLFS method have two variational parameters \( \lambda \) and \( \alpha \), proper choices of them will make the perturbative expansion convergent. In our previous works [9,10] we find that the minimization of the unperturbed ground state energy of the system yields phonon bases (within the MLF and MLFS) for which the perturbative expansion for the ground state shows satisfactory convergence. The corresponding values of \( \lambda \) and \( \alpha \) are given by \( \lambda = \frac{\omega_0 g_+}{\omega_0 + 2e_c} \) and \( \alpha = \frac{1}{4}\sinh^{-1}[2\lambda(g_+ - \lambda)] \). For the study of the first excited state we will use the same basis as we have used for the ground state. The first-order correction to the first excited state wave function is obtained as,

\[ |\psi_1^{(1)}\rangle = \frac{1}{\sqrt{1 + c^2}} \left[ \sum_{N=2,4,..} \frac{W_e}{(\alpha_1 - E_0^{(N)})} |-, N\rangle + \sum_{N=3,5,..} \frac{W_o}{(\alpha_1 - E_0^{(N)})} |+, N\rangle \right] \]

(11)

where \( W_e = W + \sqrt{N} \omega_0 c (g_+ - \lambda) e^{2\alpha} \delta_{N,2} + \sqrt{N(N-1)} \frac{\omega_0}{2} \sinh(4\alpha) \delta_{N,2}, \)

\( W_o = W + \sqrt{N} \omega_0 (g_+ - \lambda)e^{2\alpha} \delta_{N,1} + \sqrt{N(N-1)} \frac{\omega_0}{2} c \sinh(4\alpha) \delta_{N,3}, \)

and \( W = t_e \frac{(2\lambda e)^N}{N!} (1 + 2\lambda e_c - \frac{e_c^N}{2}). \)

Second-order correction to the first excited state energy is given by,

\[ E_1^{(2)} = \frac{1}{1 + c^2} \left[ \sum_{N=2,4,..} \frac{|W_e|^2}{(\alpha_1 - E_0^{(N)})} + \sum_{N=3,5,..} \frac{|W_o|^2}{(\alpha_1 - E_0^{(N)})} \right] \]

(12)

Using our previous prescription [10] successive higher order corrections to the wave function \((|\psi_1^{(N)}\rangle\)) as well as to the energy \((E_1^{(N)})\) are calculated.

The static correlation functions \( \langle n_1 u_1 \rangle_0 \) and \( \langle n_1 u_2 \rangle_0 \), where \( u_1 \) and \( u_2 \) are the lattice deformations at sites 1 and 2, respectively, produced by an electron at site 1, are the standard measure of polaronic character, and indicate the strength of polaron induced lattice defor-
motions and their spread. The operators involving the correlation functions may be written as

\[ n_1 u_{1,2} = \frac{n_1}{2} [(a + a^\dagger) \pm (d + d^\dagger)e^{2\alpha} - 2 (ng_+ \pm \lambda(n_1 - n_2))] \] (13)

The final form of the correlation functions are obtained as

\[ \langle n_1 u_1 \rangle_0 = \frac{1}{2} \left[ -(g_+ + \lambda) + \frac{A_1 e^{2\alpha}}{N_{G1}} \right] , \]
\[ \langle n_1 u_2 \rangle_0 = \frac{1}{2} \left[ -(g_+ - \lambda) - \frac{A_1 e^{2\alpha}}{N_{G1}} \right] , \] (14)

where \( N_{G1} = \langle \psi_1 | \psi_1 \rangle \), \( A_1 = \langle \psi_1 | n_1 (d + d^\dagger) | \psi_1 \rangle \) and \( | \psi_1 \rangle \) is the perturbed wave function of the first excited state.

**IV. RESULTS AND DISCUSSIONS**

The perturbation corrections to the energy and wave function of the first excited state are estimated up to the sixth and fifth-orders, respectively, within the LF, LFS, MLF, MLFS methods, and weak-coupling perturbative method considering 25 phonon states (which is sufficient for \( g_+ \leq 2.2 \)) in the transformed phonon basis.

In Fig. 1 the perturbation corrections to the energy of the first excited state are plotted as a function of \( g_+ \) for \( t/\omega_0 = 1.1 \). The perturbation corrections in energy are smaller within the MLF and MLFS than the LFS and LF methods. For the LF, LFS, and MLFS methods the convergence of the corrections is weaker in a range of \( g_+ \) where third and fourth or fifth and sixth-order corrections are comparable. Within MLF approach energy perturbation corrections show satisfactory convergence in the entire region of \( g_+ \) and the energy of the first excited state, when computed considering up to the fifth or sixth-order corrections, becomes identical with the exact result of Ref. [6].

The shape of the correlation function \( \langle n_1 u_2 \rangle_0 \) is much more sensitive to the corrections to the wave function than \( \langle n_1 u_1 \rangle_0 \) which indicates that convergence of \( \langle n_1 u_2 \rangle_0 \) is a clear signature for convergence of the wave function. In Fig. 2 we plot the correlation function...
\( \langle n_1 u_2 \rangle_0 \) obtained by considering up to the different orders of perturbation corrections to the wave function against \( g_+ \). The LF method shows a bad convergence for low values of \( g_+ \), while a good convergence beyond \( g_+ = 1.0 \). The convergence within the LFS method is not satisfactory over a wide region of \( g_+ \). The MLF method shows very good convergence for low values of \( g_+ (\leq 1.0) \) as well as for high values of \( g_+ (\geq 1.3) \). Convergence within the MLFS is excellent for low values of \( g_+ \), but then for a wide region of intermediate values of \( g_+ \) the convergence is not satisfactory. When compared with exact results of \( \langle n_1 u_2 \rangle_0 \) (taken from the Ref. [8]), it is found that the MLF results up to the fifth order perturbation are identical with the exact results except in the region \( 0.9 < g_+ < 1.3 \) where a slight departure in values from the exact results is seen.

In Fig. 3 we plot the perturbation corrections of different orders to the first excited state energy and the the correlation function \( \langle n_1 u_2 \rangle_0 \) evaluated by considering up to different orders of perturbation corrections to the wave function against \( g_+ \) within the weak-coupling perturbative expansion for \( t/\omega_0 = 1.1 \). The odd order corrections to the energy within the weak-coupling expansion are zero. The energy corrections of any (even) order increases monotonically with \( g_+ \), since the entire e-ph interaction is treated as a perturbation within the weak-coupling scheme. The correlation function within the weak-coupling perturbation procedure shows good convergence for low values of \( g_+ \), as expected. However even in this region, convergence within the MLF and MLFS methods is found to be slightly better than that obtained within the weak-coupling scheme.

In Fig. 4 we show the energy corrections and correlation function, calculated by considering different order of corrections, within the MLF method for \( t/\omega_0 = 0.6 \). The figure shows that the perturbation corrections of successive orders are really very small and shows perfect convergence for the entire region of \( g_+ \). The correlation function calculated considering up to second order correction to the wave function would reproduce almost the exact result in this limit. For lower values of \( t \) obviously the convergence within the MLF scheme would be much better. We have also studied the perturbation corrections to the energy and the
correlation function $\langle n_1 u_2 \rangle_0$ for the first excited state in the adiabatic region of hopping ($t/\omega_0 = 2.1$) within MLF approach and found that energy convergence is quite good for the entire range of $g_+$ whereas convergence of corrections to the wave function is fairly well except for intermediate range of coupling.

In conclusion, our study on the first excited state of a two-site single electron Holstein model shows that the perturbation method based on the MLF variational phonon basis is better than the other methods (LF, LFS, MLFS) if the entire range of $g_+$ is considered. The MLF method could yield exact results for the entire range of $g_+$ in the antiadiabatic cases ($t/\omega_0 \leq 0.6$) and for a major region of $g_+$ (covering both low and high values of $g_+$) for intermediate hopping ($t/\omega_0 = 1.1$). For small values of $g_+$ both the MLFS and MLF methods show excellent convergence, convergence is found to be even better than that within the weak-coupling perturbation method. Our previous study on the ground state and the present study on the first excited state thus establish that the perturbation method based on the MLF phonon basis could satisfactorily describe the ground state as well as the first excited state of the two-site system for major region of the $e$-ph coupling strength.
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Figure captions:

FIG. 1. Variation of the perturbation corrections $E_1^{(n)}$ to the first excited state energy as a function of the coupling strength $(g_+)$ for $t/\omega_0 = 1.1$ in (a) LF, (b) LFS, (c) MLF, and (d) MLFS methods. $E_1^{(n)}$ is the $n$th order perturbation correction to the first excited state energy.

FIG. 2. Plot of the correlation function $\langle n_1 u_2 \rangle_0$ calculated up to different order of perturbations in the wave function vs $g_+$ for $t/\omega_0 = 1.1$ within different methods (a) LF, (b) LFS, (c) MLF, and (d) MLFS. The labels (2), (3), .... denote the curves obtained by considering up to the second-order, third-order, .... corrections to the wave function, respectively.

FIG. 3 Convergence within weak-coupling expansion for $t/\omega_0 = 1.1$: (a) the perturbation corrections to the first excited state energy and (b) correlation function $\langle n_1 u_2 \rangle_0$ calculated up to different order of perturbations in the wave function, as a function of $g_+$.

FIG. 4 Convergence within MLF approach for $t/\omega_0 = 0.6$: (a) the perturbation corrections to the first excited state energy and (b) correlation function $\langle n_1 u_2 \rangle_0$ calculated up to different order of perturbations in the wave function, as a function of $g_+$. 
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