A renormalization scheme for calculating the spectrum of a vibronic system occurring in molecules or impurities in insulators

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Abstract

An iteration scheme which makes use of a numerical renormalization group approach is used to calculate the spectrum of vibronic levels. This spectrum resulted from dynamic effects occurring in certain molecules or impurities in insulators.

The Hamiltonian of these systems is expressed in the matrix form, using products of suitable electron–phonon states as a basis. In applying this method to multimode electron–phonon systems, phonon modes are coupled in a chain-like fashion. Then a finite chain calculation in terms of Hubbard X-operators is explored by setting up the vibronic Hamiltonian.

Calculations are based on Lanczos algorithm, in which only the nearest neighbor matrix elements along the chain need to be taken into account. The iterative scheme is then applied to a two-level electronic system coupled to phonons. A single-particle Green’s function corresponding to a two-level system is applied to calculate the spectral density of states, which, coupled to single mode is carried out. The strength of lines in density of states is affected by the coupling constant as well as the temperature dependence of some measurable quantities.

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1. Introduction

Different types of systems in which localized electronic states can be strongly coupled to vibronic modes (phonons) may occur in insulators or certain molecules. In these systems, quantum mechanical tunneling between equivalent configurations may occur in which the spectrum of vibronic levels can be calculated. The Hamiltonian of the system can be expressed in matrix format, using products of suitable electron–phonon states as a basis. Subsequently the matrix elements are numerically diagonalized, giving the vibronic levels.

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Here, an iteration scheme, which makes use of a numerical renormalization group approach, is used [1,2]. The strong coupling constant of electron–phonon interaction is considered first and then put in a specific format, in a way that the rest of the modes could be treated perturbationally. In this model, phonon modes are coupled in a chain-like fashion/cluster, so that they can be treated iteratively [3] (Fig. 1).

To realize the scheme, a set of orthogonal basis states are generated using the Lanczos algorithm [4]. The method works by making a successive choice of basis vectors by repeatedly operating with the matrix on any suitable initial vector. The initial normalized basis vector is $X_1$, states $H^nx_1$, $n = 1,2,3,...$ are generated, where $H$ is the original matrix. The choice of $X_1$ is important. Here $X_1$ is selected to be the phonon state, which is linearly coupled to the electronic system

$$X_1 = \sum_k \tilde{\alpha}_k |k\rangle = \sum_k \tilde{\alpha}_k b_k^+ |0\rangle$$ (1)

where $b_k^+$ represents creation operator for a phonon mode.

The Hamiltonian composed of the electronic system linearly coupled to this mode is set up in matrix form using uncoupled electron and phonon states as a basis. The matrix is in block form with blocks of elements corresponding to a particular number of phonons excited and nonzero off-diagonal blocks linking $n$ phonon states with $n+1$ phonon states. This matrix has to be truncated, so that it includes blocks up to some specific number of phonon excitations.

2. Theoretical model

The theory is developed for a Hamiltonian of the form

$$H = \sum_{nn'n''} E_{nn'n''} X_{nn'n''} + \sum_k \omega_k b_k^+ b_k + \sum_{k,l,n,n',s'} \gamma_k^{n,n',s'} (b_k^+ b_{n's'} + b_{n's'}^+ b_k) X_{n'n''}$$ (2)

where $X_{n'n''} = |ns\rangle \langle n's'|$ are Hubbard $X$-operators [5] and $|ns\rangle$ are the eigenstates of the uncoupled Hamiltonian. Also $b_{k}^+$ and $b_k$ are creation and annihilation operators for phonon of frequency $\omega_k$ and $\tilde{\alpha}_k^{n,n',s'}$ is the matrix element of the interaction term between states $|ns\rangle$ and $|n's'\rangle$ divided by $\sqrt{2\omega_k}$, where the third term in Eq. (2) is referred as interaction Hamiltonian.

Due to exploring an iterative scheme, a canonical transformation is used with new creation and annihilation operators $B_k^+$, $B_k$, where

$$\lambda B_k = \sum_k \tilde{\alpha}_k b_k^+ b_k, \quad B_k = \sum_k \tilde{\alpha}_k b_k, \quad \lambda = \sqrt{\sum_k \tilde{\alpha}_k^2}, \quad \tilde{\alpha}_k = \lambda/\tilde{\alpha}_k$$ (3)

In the new representation, the new phonon states are denoted by

$$B_k = \sum_k \tilde{\alpha}_k b_k^+ b_k, \quad |2\rangle = \tilde{\alpha}_k^{1} |1\rangle, \quad B_{s'} = \delta_{s'0}$$ (4)

with $\tilde{\alpha}_k^{1}$ real. The diagonal term $\sum_k \omega_k b_k^+ b_k$, which may be denoted by $H_p$, is transformed to a non-diagonal form as $\sum_{ss'} D_{ss'} B_{s'}^+ B_s$ with $D_{ss'} = \sum_k \omega_k \tilde{\alpha}_k^{s's'}$, where $\tilde{\alpha}_k$ and $\tilde{\alpha}_k^{s's'}$ are denoted by components of the column vectors $|s\rangle$ and $|s'\rangle$, respectively. The form of the proposed iterative scheme for the Hamiltonian is illustrated in Fig. 2 showing the electronic part coupled to a cluster of phonon modes with diagonal matrix elements $D_{ss'}$ and non-diagonal ones $D_{ss'} + \tilde{\alpha}_k^{s's'}$.

For a calculation based on Lanczos algorithm, $\tilde{\alpha}_k$’s can be chosen so that only the nearest neighbor matrix elements are needed to be taken into account. To do so, a complete set of orthogonal basis states $\{1\rangle, \{2\rangle, \{3\rangle, \ldots, n\rangle, \ldots\}$ can be generated with the first vector defined by $|1\rangle = B_1^+ |0\rangle = \sum_k \tilde{\alpha}_k b_k^+ |0\rangle$, where $|0\rangle$ is the vacuum state for the phonon Hamiltonian. The vector $|1\rangle$ is equal to $\frac{\tilde{\alpha}_k}{\tilde{\alpha}_k^{1}} |1\rangle$ corresponding to frequency $D_{11} = \sum_k \omega_k b_k^+ b_k$.

The second vector $|2\rangle$ is chosen to be orthogonal to $|1\rangle$ with the coupling constant $D_{12} = \sqrt{\sum_k \omega_k^2 \tilde{\alpha}_k^2 - D_{11}^2}$. Also, the third vector $|3\rangle$ is chosen to be orthogonal to vectors $|1\rangle$ and $|2\rangle$. The procedure is continued to obtain the general form of vectors which correspond to $|n-2\rangle$, $|n-1\rangle$, $|n\rangle$ modes, along the chain. Then the $|n+1\rangle$th phonon state may be written as follows

$$|n+1\rangle = D_{n+1,n}^{-1} (\tilde{D} |n\rangle - n_{n+1} |n\rangle - n_{n-1} |n-1\rangle)$$ (5)

where $\tilde{D} = \sum_{ss'} D_{ss'} B_{s'}^+ B_s$, $D_{11} = \langle 1 |\tilde{D}|1\rangle, D_{12} = \langle 1 |\tilde{D}|2\rangle$ and so on.

The general form of $H_p$ on the basis of the new representation having only the nearest-neighbor modes coupled to each other may be written as

$$H_p = \sum_{n=1} D_{n+1,n} B_{n+1}^+ B_n + \sum_{n=2} D_{n-1,n} (B_n^+ B_{n-1}^+ + B_{n-1}^+ B_n)$$ (6)

For $\lambda = 0$, one has $H_p = \sum_{n} E_{ns} X_{ns} + H_p$ with eigenstates $|n\rangle$, where $\gamma$ labels the electronic part and $n$ represents the phonon excitation number.

In the following section, the iteration scheme is applied to a two-level electronic system coupled to a chain of phonons.

3. Application to a quantum two-level system

The scheme is performed in two stages: (a) the first mode of frequency $D_{11}$ is taken into account and the Hamiltonian
matrix $H$ plus the first phonon mode along the chain which is directly coupled to it is diagonalized. (b) the diagonalized states of the first stage are used as a basis to take account of the next mode along the chain. This is then diagonalized and a new Hamiltonian is constructed by using these to include the next mode along the chain and so on. As one moves along the chain, the number of basis states involved increases and the matrix gets larger. As an approximation in calculating the lower energy states, the basis is truncated and only a limited number of states are remained in each stage. This scheme is simplified because we have only nearest-neighbor coupling of modes along the chain.

The model Hamiltonian is given by

$$H = \sum_{j=0}^{n-1} E_j (c_j^+ c_j + \text{h.c.}) + \sum_k \lambda_k (b_k^+ b_k + b_k^* b_k) + \sum_k \omega_k (b_k^+ b_k)$$

(7)

where the creation and annihilation operators, $c_a^+, c_a$ and $c_b^+, c_b$ correspond to the electronic states at sites $a$ and $b$, respectively, with an overlap matrix element $t$.

The Hamiltonian is written in a slightly different form by introducing bonding and antibonding operators, $C_{1,0} = (c_a + c_b)/\sqrt{2}$ with $+ \rightarrow 1$, $- \rightarrow 0$.

In terms of these operators and on the new basis states we get

$$H = (E_0 + t) C_1^+ C_0 + (E_0 - t) C_0^+ C_0 + \sum_{n=1}^{n-1} D_{n-1,n} B_n^+ B_n$$

$$+ \sum_{n=1}^{n} D_{n-1,n} B_n^+ B_n + B_n^+ B_{n+1}$$

$$+ \lambda (B_1^+ + B_1) (C_1^+ C_0 + C_0^+ C_0)$$

(8)

By keeping the first mode and ignoring the rest to diagonalize the Hamiltonian, one may write

$$H_1 = (E_0 + t_0) X_0 + (E_0 - t_0) X_1 + \lambda (B_1^+ + B_1) (1 X_0 + 0 X_1)$$

$$+ D_{11} B_1^+ B_1$$

(9)

In this stage one may distinguish two different cases

(a) $\lambda = 0$, $|n_f\rangle = \langle n | B_1^+ | 0 \rangle |g\rangle$, $|g\rangle = 0, 1$, where $g = 1 \rightarrow +$ parity and $0 \rightarrow -$ parity, which bears similarity to a spin up and spin down system. Then the set of basis vectors $|n_f\rangle$ is broken down into two subgroups belonging to $H_0$ as

$$S_{\pm} = \{ |n_f\rangle, \quad \gamma \rightarrow n \text{ even}, - \rightarrow n \text{ odd} \}$$

(10)

(b) in the case of $\lambda \neq 0$, using $|r\rangle$ to represent the basis states, one may write $|r\rangle$ as a linear combination of diagonal states (i.e. $S_1$)

$$|r\rangle = \sum_{n_f} q_{n_f}^r |n_f\rangle, \quad \text{for a plus block}$$

(11)

where $r$ represents the phonon excitation number and $z$ denotes the parity of states. Also, for a negative block one may write $|s\rangle$ as a linear combination of $S_2$ as follows:

$$|s\rangle = \sum_{n_f} q_{n_f}^s |n_f\rangle$$

(12)

The optical transitions between these quantum two-level systems are proportional to the imaginary part of the Fourier transform of the corresponding Green’s function, which is calculated in the following section.

4. One-particle Green’s function

A single-particle Green’s function corresponding to a quantum two-level system coupled to a single phonon mode may be written as

$$G(t) = \langle 0 | X_1(t) : 1 X_0(0) \rangle$$

(13)

where

$$1 X_0 = \sum_{r,s,t} \left( \sum_{n \text{ even}} q_{n_f}^{r,s} q_{n_s}^{s,t} r X_s + \sum_{n \text{ odd}} q_{n_f}^{r,s} q_{n_s}^{s,t} s X_s \right)$$

The spectrum density of states, $\rho(\omega)$, can be calculated from the following response function

$$G_{01}(\omega + i\delta) = \frac{1}{2\pi} \left[ \frac{[0 X_0 - 1 X_1]}{\omega - (t_1 - t_0) + i\delta} \right]$$

(14)

$$\rho(\omega) = -\frac{1}{\pi} \text{Im} G(\omega + i\delta)$$

(15)

The function $\rho(\omega)$ represents a number of sharp lines which are spread over the range of energy at positions $\Delta E = |r_s - s_t|$. The strength of lines in the density of states is affected by the coupling constant as well as the temperature dependence of some measurable quantities [6].

5. Conclusions

In this paper, an iteration scheme which makes use of a numerical renormalization group approach has been used to calculate the spectrum of vibronic levels due to dynamic effects which occurred in certain molecules or impurities in insulators. The Hamiltonian of these systems is expressed in the matrix form using products of suitable electron–phonon states as basis.

In applying the scheme to a multimode electron–phonon system, phonon modes are coupled in a chain-like fashion.
Then, a finite chain calculation in terms of Hubbard X-operators is explored by setting up the vibronic Hamiltonian, and a set of orthogonal basis states is generated by making use of Lanczos algorithm, where only nearest neighbor matrix elements along the chain need to be taken into account.

The iterative method is then applied to a quantum two-level system coupled to phonons. Two different cases have been considered: (a) the coupling constant is set to be zero, leading to a set of basis vectors for an uncoupled Hamiltonian. (b) In the case of a nonzero coupling constant, an effective Hamiltonian is calculated taking new basis states as linear combinations of the diagonal subsets.

The spectral density of states is worked out from a single Green function corresponding to a two-level system. A number of sharp lines which are spread over the range of energy represent the spectral density of states, and the strength of lines is affected by the coupling constant as well as temperature dependence of some measurable quantities.

References