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## A Numerical Renormalization Group Approach for Calculating the Spectrum of a Vibronic System Occurring in Molecules or Impurities in Insulators

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### Abstract

Theoretically, in order to describe the behavior of a spectrum, a mathematical model which could predict the spectrum characteristics is needed. Since in this study a Two-state system has been used like models which was introduced previously past and could couple with the environment, the former ideas have been extended in this study. we use the second quantized version for writing this Hamiltonian. First, the Hamiltonian of a rotational system is considered in a classic scale, afterwards it is brought to a quantum scale. In the first step, the vibrations and quantum rotation is illustrated for two atom molecules. Then it is devoted to Two-state system and dissipative Two-state system.

In the second step, the rotation of a molecular group in a hindering potential is studied in the classic and quantum scales. Finally, at the present of strong coupling constant the Hamiltonian has been applied and a numerical renormalization group approach has been used for numerical solution. Then, by using Hubbard operators, dynamical functions of this operators are written. The fourier transform of the Greens function is developed, then density of state is calculated.

**Keywords:** Inelastic neutron scattering, Two state system, Second quantized, Hubbard operators, Numerical solution

### 1. Introduction

The study of the rotational motion of the molecules ( $O_2, CH_4$ ), molecular groups ( $-CH_3$ ), ( $NH_3$ ) and ions ( $CN^-, CH_4^+$ ) in solids has developed into an active field, both experimentally and theoretically. Over the past 30 years such systems have attracted considerable experimental interest, stimulated

by the development of high resolution inelastic neutron scattering (INS) spectra, which detect transitions, with very small amounts of energy transfer. In these systems, due to the presence of other molecules and particles, the molecules experience an orientational potential as they rotate in the field of the environment [1,2].

Many attempts have been made to provide theoretical basis to explain temperature dependence of the (INS) spectrum, but none

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of them have given a satisfactory comprehensive theory for both the quantum and classical behaviour of such systems. Here, an iteration scheme which makes use of a numerical renormalization group approach is used [3, 4]. The strong coupling constant of electron-phonon interaction is considered first and then put in a form, so that the rest of the modes can be treated perturbationally. In this model, phonon modes are coupled in a chain-like fashion/cluster, so that they can be treated iteratively [5].

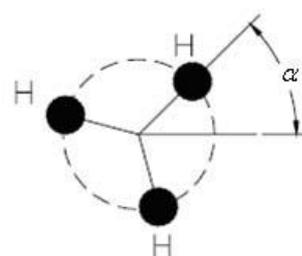
To realize the scheme, a set of orthogonal basis states is generated using the Lanczos algorithm [6]. The method works by making a successive choice of basis vectors. The initial normalized basis vector is  $X_i$  and the states  $H^n X_i, n=1,2,3,\dots$  are generated, where  $H$  is the original matrix. The matrix is in block form. The nonzero off-diagonal blocks linking  $n$ -phonon states with  $n+1$  phonon states.

## 2. The methyle group ( $-CH_3$ )

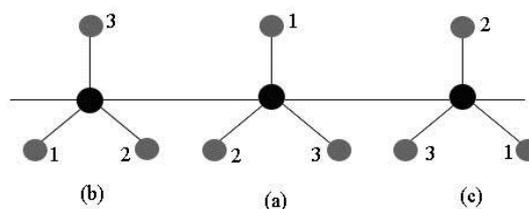
we concentrate on the one-dimensional rotational (torsional) motion of the Methyl group ( $-CH_3$ ), in the solid. The molecular environment of the group in the solid causes a hindering potential preventing its free rotation, this rotational motion is described by a signal angular coordinate  $\varphi$  in a hindering potential  $V(\varphi)$ . Because the energy involved in the rotational motion is small relative to that of the covalent bonds joining the group, the system can be regarded as a rigid unit with a moment of inertia,  $I$ . Therefore, the internal vibration of the molecule can be neglected. An impression of the molecular situation may be obtained from Fig. 1 [1,2,7,8].

Due to the symmetry of the group there

are three equivalent orientations. Let us rotate the molecule as shown in Fig. 2 so that (a) represents an equilibrium orientation of the system each equilibrium orientation corresponds to a pocket potential, therefore, the number of pockets in the potential is determined by the symmetry of the rotating group. There are three potential pockets for the one dimensional rotors  $CH_4$  and  $NH_4$  and 12 pockets for 3-dimensional rotors  $CH_4$  and  $NH_4^+$ .



**Fig. 1.** View of ( $-CH_3$ ) group or ( $NH_3$ ) molecule along the threefold axis of the molecule, with some of molecules in their equilibrium positions in solids.



**Fig. 2.** A proper rotation of the methyl group through  $-\frac{2\pi}{3}$  (b)  $\frac{2\pi}{3}$  (a), does not change the configuration of the system. Therefore, a rotation of methyl group through  $120^\circ$ , Converts one orientational state into another

Even permutations of the three identical particles correspond to a proper rotation of the molecule and does not change the framework, therefore, the three orientations shown in Fig. 2 are all equivalent and they are all equilibrium orientations of the molecule, if one of them is in equilibrium.

The three odd permutations can be neglected as this would change framework.

If the proton spin is neglected we are not able to distinguish the particles, and consequently the molecular orientations belonging to the different permutations are indistinguishable. The situation also occurs in the case of the  $CH_4$  and  $NH_4$  tetrahedral where these systems are treated as rigid units. Here 12 even permutation of four identical particles do not change the framework, and 12 odd permutations are neglected as they change the configuration.

### 3.The rotational potential $H_r$

The rotation of methyl group may be discussed in terms of the following Hamiltonian:

$$H_r = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \alpha^2} + V(\varphi) \quad (1)$$

where  $V(\varphi)$  must respect the indistinguishability of the protons [9].

At low temperature two extreme cases of rotational motion are understood:

Case 1 If the orientational potential is small in comparison with rotational constant  $B$  ( $B = \frac{\hbar^2}{2I}$ , where  $I$  is the moment of inertia of the rotating molecule) the molecule behaves like a free or almost free rotor, therefore, the eigenfunctions of  $H_r$  are approximately the pure rotational function  $(2\pi)\exp(im\varphi)$ , where  $m$  is the rotational quantum number.

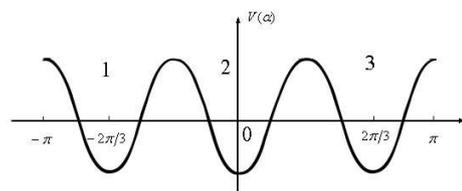
Case 2 If the orientating potential is strong in comparison with the rotating constant  $B$ , then the molecules perform small angular oscillations (also called libration) around their equilibrium orientations. The excitation spectrum is determined by the rotational constant  $\frac{\hbar^2}{2I}$ .

In the range of intermediate potential strengths, the librational states of individual oscillators split into several sublevel by the tunnelling motion between different equilibrium orientations. Therefore, the potential has strong influence on the energy levels if it strong in comparison with the rotational constant.

The potential of our system shows 3 deep minima at angular positions  $\varphi = -\frac{2\pi}{3}, 0, \frac{2\pi}{3}$  and as a function of rotational angle  $\varphi$ ,  $V(\varphi)$  fulfills the relation:

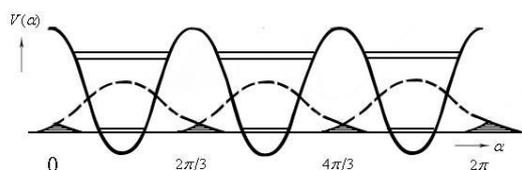
$$V(\varphi - \frac{2\pi}{3}) = V(\varphi) = V(\varphi + \frac{2\pi}{3}) \quad (2)$$

The equivalence of three minima (potential pockets) is illustrated in Fig. 3 [10].



**Fig. 3.** Due to the threefold symmetry of the  $CH_3$  group the angular potential  $V(\varphi)$  is period  $\frac{2\pi}{3}$  irrespective of the site symmetry involved. The origin for  $\varphi$ , the rotation angle around the threefold symmetry axis of the methyl group, has been chosen such that  $V(\varphi)$  has a minima at  $\varphi=0$ . The number I, II and III denote the three pockets of the potential.

The rotor performing small torsional oscillations about one such minima (pocket or well) will give rise to a librational spectrum. For a final potential there is a final probability for quantum mechanical tunnelling through the potential barrier causing a splitting of the energy levels. This is illustrated in Fig. 4.



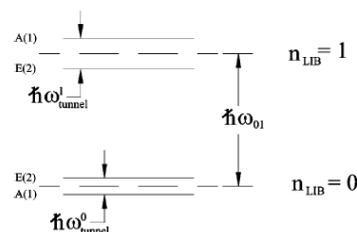
**Fig. 4.** Schematic drawing representing the tunnel splitting of the first libration state, The splitting is due to the overlap of wavefunctions (dashed region) in neighbouring potential Minima

Therefore, the pocket states are not stationary and they will oscillate with time because of the tunneling matrix elements between them. The tunnel splitting is proportional to the overlap between the two states  $\psi_I$  and  $\psi_{II}$ , (where the system is in two neighbouring minima) and if the lattice is not excited, the overlap  $\psi_I\psi_{II}$  is positive leading to a positive integral  $\langle \psi_I | \psi_{II} \rangle$ . If the translational motion of the molecules is neglected, then the total wavefunction depends on the rotational coordinate and on the sign coordinate of the three protons in the case of the methyl group (the allowed wavefunctions have to be totally symmetric under the even permutation of the three protons) and the four protons in the case of methane (the allowed wavefunctions have to be totally symmetric under the even permutation of the three protons).

The matrix elements of  $H$  ( $H_{ij}$ , with,  $i$  and  $j=I,II$  and  $III$ ) between these three states  $\psi_I$ ,  $\psi_{II}$  and  $\psi_{III}$  are not diagonal. From diagonalization of  $H_{ij}$ , one obtains a singlet A-state and a doublet E-state. Therefore, at low temperature, the methyl group exists in the form of three proton symmetry species A,  $E^a$  And  $E^b$ , according to the irreducible representations of the  $CH_3$  symmetry group

with the A states having nuclear spin 3/2 and E states having nuclear spin 1/2.

The mean energy of a set of these levels is known as the torsional energy of the methyl group and the splitting between A and E levels is known as the tunnelling splitting. The energy difference between the A and the two degenerate states  $E^a$  and  $E^b$ , which is denoted by,  $\hbar\omega_{tunnel}^0$  is referred to as the tunneling frequency in the rotational ground state energy. Splitting for the first excited torsional states has tunneling frequency  $\hbar\omega_{tunnel}^1$  Fig. 5 [11].



**Fig. 5.** low energy rotational states of a  $CH_3$  group, labeled by their symmetry. In general  $\hbar\omega_{01} \gg \hbar\omega_{tunnel}^1 \gg \hbar\omega_{tunnel}^0$ . A states have lower energy than the E states in the ground state, this is reversed in the first excited librational state.

#### 4. The potential energy $v(\varphi)$

The potential  $V(\varphi)$  which is periodic in  $3\varphi$  is written as:

$$V(\varphi) = \sum_{n=1}^{\infty} V_n \cos(3n\varphi + \eta_n) \quad (3)$$

with eigenfunctions  $|n,s\rangle$  of  $H_r$  corresponding to an energy  $E_{ns}$  where the label  $s$  is associated with the A,  $E^a$  And  $E^b$ , species and  $n$  is a torsional quantum number.

The peaks that are seen in the inelastic neutron scattering spectrum over a temperature range in these systems are identified by the transitions between the

levels of the torsional ground state that have been split by the rotational tunnelling.

The inelastic lines in the INS are due to transition between ground states  $|A\rangle \rightarrow |E^a\rangle, |E^b\rangle$  for the loss lines, and the inverse for the gain line, which for an isolated group would give sharp lines at energy  $\pm \hbar\omega_{tunnel}^1$ .

## 5. Experimental results

Here we present several experimental results which have been obtained by magnetic resonance and high resolution inelastic neutron scattering. Measurement have been performed whit powder samples of  $CH_3I$ . It is interesting to look at the temperature dependence of the quasi-elastic spectrum of the above molecule represented in fig 6. It is shown spectra of measurement at three different temperatures. On increasing the temperture the peaks become broaden [12].

## 6. The model hamiltonian

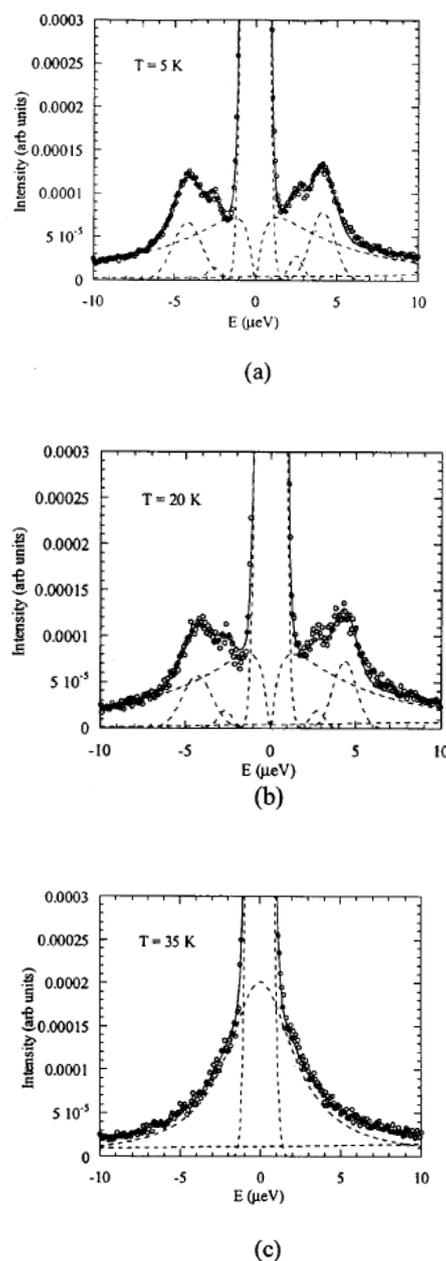
The theory is developed for a Hamiltonian of the form

$$H = \sum_{ns} E_{ns} X_{ns} + \quad (4)$$

$$\sum_k \omega_k b_k^+ b_k + \sum_{k, ns, n's'} \lambda_k^{ns, n's'} (b_k^+ + b_k) X_{n's'}$$

where,  $X_{n's'} = |ns\rangle\langle n's'|$  are Hubbard  $X$  – operators [13] and  $|ns\rangle$  are the eigenstates

of the uncoupled Hamiltonian. Also  $b_k^+, b_k$  are creation and annihilation operators for phonon of frequency  $\omega_k$  and  $\lambda_k^{ns, n's'}$  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.(4) is referred as interaction Hamiltonian [14].



**Fig. 6.** On increasing the temperture the peaks become broaden.

## 7. Conclusion

Transitions of the molecular groups in solids between rotational tunnelling states with energy differences in the range 1-100  $\mu$ V have been observed by neutron INS. These show in general shifting and broadening of the energy spectrum towards lower values as the temperature increases.

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 matrix form using products of suitable electron-phonon states as basis.

In applying the scheme to a multi-mode electron-phonon system, phonon modes are coupled in a chain like fashion. Then, a finite chain calculation in terms of X-Hubbard 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. In the case of a non-zero coupling constant, an effective Hamiltonian is calculated taking new basis states as a 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.

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