Journal of the Nigerian Association of Mathematical Physics
Volume **18 (May, 2011), pp 107 - 110**

The Effect of Phonon Relaxation Process on Absorption Spectra.

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Abstract

In this work we study the effect of phonon relaxation process on the absorption spectra using the Green's function technique. The Green's function technique which is widely used in many particle problems is used to solve the Kubo formula which describes the optical absorption process. Finally the configurational diagram is used to explain the absorption and emission process.

Key words: Phonon relaxation process, absorption spectra, Green's function, Kubo formula, configurational coordinate diagram.

1.0 Introduction:

In physics, a phonon is a quasi particle characterized by the quantization of the modes of lattice vibrations of periodic elastic crystal structures of solids [1]. The study of phonons is an important part of solid state physics because phonons play a major role in many of the physical properties of solids, including thermal and electrical conductivity. A phonon is a quantum mechanical description of a special type of vibration motion known as normal modes in classical mechanics in which a lattice uniformly oscillates at the same frequency. While normal modes are wave like phenomena in classical mechanics, they have particle like properties in the wave particle duality description of quantum mechanics. In many materials like metals, superconductors and semi conductors, the coupling of an electron with phonons is called polaron. The electron-phonon interaction causes superconductivity in many metals and influences the transport properties of every metal. In pure semi conducting and ionic solids, the electron-phonon interaction usually dominates the transport properties. In most theoretical treatment of kinetic phenomena in pure metals and superconductors associated with the electron phonon interaction, only longitudinal phonons are taken into account [2]. The electron phonon interaction is decisive for many properties of metals [3] such as the electrical and thermal resistivity, and the renormalization of the linear electronic specific heat. In this work, we have shown clearly how the phonon relaxation process affects the absorption spectra by first diagonalising the Hamiltonian which describes a localized defect with several possible localized electronic states. Then the Green's function technique is used to solve the Kubo formula [4] which describes the optical absorption process.

2.0 Mathematical formulation

One important model is the Hamiltonian (2.1) which describes a localized defect with several possible localized electronic states, and where each of these states [4] may have a different matrix element for coupling to the phonon field:

$$H = \sum_q \omega_q a_q^\dagger a_q + \sum_i V_i \tag{2.1}$$

$$V_i = c_i^\dagger c_i \left[\varepsilon_i + \sum_q M_{qi}\left(a_q + a_q^\dagger\right)\right] \equiv h_i c_i^\dagger c_i \tag{2.2}$$

Here $a_q^\dagger$ (a_q) creates (destroys) phonons, ω_q is the frequency of the phonons, $c_i^\dagger (c_i)$ creates (destroys) conduction electrons, V_i is the perturbed energy, M_{qi} is a single state matrix element.

The Hamiltonian H is diagonalized using canonical transformation, that is

$$\bar{H} = e^S H e^S \tag{2.3}$$

$$S = \sum_i s_i = \sum_i c_i^\dagger c_i \sum_q \frac{M_{qi}}{\omega_i}\left(a_q^\dagger - a_q\right) \tag{2.4}$$

Afterward, (2.3) can be expanded [5] as follows

$$\bar{H} = e^s H e^{-s} = H + [S,H] + \frac{1}{2}\left[S,[S,H]\right] + \frac{1}{3!}\left[S,\left[S,[S,H]\right]\right] + \cdots \tag{2.5}$$

$$\bar{H} = e^s\left[\sum_q \omega_q a_q^\dagger a_q + \sum_i V_i\right]e^{-s} \tag{2.6}$$

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The transformation done on H must be in such a way that $S^{\dagger} = -S$ so that $e^{-s}e^{s} = 1$. Also using

$$e^{s}ABCD\cdots e^{-s} = (e^{s}Ae^{-s})(e^{s}Be^{-s})(e^{s}Ce^{-s})(e^{s}De^{-s})\ldots = \bar{A}\bar{B}\bar{C}\bar{D}\ldots \quad (2.7)$$

(2.6) becomes

$$\bar{H} = \sum_q \left(e^{s}\omega_q e^{-s}\right)\left(e^{s}a_q^{\dagger}e^{-s}\right)\left(e^{s}a_q e^{-s}\right) + \sum_i (e^{s}V_i e^{-s}) \quad (2.8)$$

If we expand the second part of (2.8) we have

$$e^{s}V_i e^{-s} = e^{s}\left[\varepsilon_i c_i^{\dagger}c_i + \sum_q M_{qi}\left(a_q + a_q^{\dagger}\right)c_i^{\dagger}c_i\right]e^{-s} \quad (2.8a)$$

$$e^{s}V_i e^{-s} = (e^{s}\varepsilon_i e^{-s})\left(e^{s}c_i^{\dagger}{}_i e^{-s}\right)(e^{s}c_i e^{-s}) + \sum_q \left(e^{s}M_{qi}e^{-s}\right)\left[\left(e^{s}a_q e^{-s}\right) + \left(e^{s}a_q^{\dagger}e^{-s}\right)\right]\left(e^{s}c_i^{\dagger}{}_i e^{-s}\right)(e^{s}c_i e^{-s}) \quad (2.8b)$$

Putting (2.8b) into (2.8) we have

$$\bar{H} = \sum_q \omega_q a_q^{\dagger}a_q + \sum_i (\varepsilon_i - \Delta_i)\, c_i^{\dagger}c_i \quad (2.9)$$

Since $\left(e^{s}a_q^{\dagger}e^{-s}\right) = a_q^{\dagger},\ \left(e^{s}a_q e^{-s}\right) = a_q$

Where $$\Delta_i = \sum_q \frac{M_{qi}^2}{\omega_q} \quad (2.10)$$

The Hamiltonian (2.1) is written with the electronic states not interacting with each other, except through the phonons. Any terms which permit a direct interaction between the states usually render the Hamiltonian unsolvable, at least exactly. For example, terms such as (2.11) are not included.

$$\left[c_i^{\dagger}c_j + c_j^{\dagger}c_i\right]\sum_q M_{q,ij}\left(a_q + a_q^{\dagger}\right) \quad (2.11)$$

Equation (2.11) permits the particle to change its state by emitting a phonon. In an optical absorption process, an electron may change its electronic state, say from *i* to *j*, by the absorption of a photon of frequency ω. This process is described by the Kubo formula, using the current-current correlation function. For optical frequencies such that βω»1, the formula is

$$Re\left(\sigma_{\alpha\beta}\right) = \frac{1}{2\omega}\int_{-\infty}^{\infty} dt e^{i\omega t}\langle j_{\alpha}(t)j_{\beta}(0)\rangle \quad (2.12)$$

where (α, β) are (x, y, z) indices. The relation βω»1 [4] is easily satisfied, since typically $\hbar\omega_i \approx$ 2-3ev is in the visible spectrum, while at room temperature $\beta = 40\text{ev}^{-1}$. For the transition between two localized states, the current operator is

$$j_{\alpha} = \sum_{ij} P_{ij,\alpha}c_i^{\dagger}c_j \quad (2.13)$$

The matrix element $P_{ij,\alpha}$ is treated as a constant in this problem. It plays no role in the many body Physics which follows. The correlation function is:

$$\langle j_{\alpha}(t)j_{\beta}(0)\rangle = \sum_{ijkl} P_{ij,\alpha}P_{kl,\beta}\langle c_i^{\dagger}(t)c_j(t)c_k^{\dagger}c_l\rangle \quad (2.14)$$

Using the Green's function technique, we can put

$$N = \langle c_i^{\dagger}(t)c_j(t)c_k^{\dagger}c_l\rangle = e^{\beta\Omega}Tr\left(e^{-\beta H}e^{iHt}c_i^{\dagger}c_j e^{-iHt}c_k^{\dagger}c_l\right) \quad (2.15)$$

Equation (2.15) is now solved exactly by inserting the unit operator $1 = e^{-s}e^{s}$ into the trace and using the cyclic property of trace, we have

$$N = e^{\beta\Omega}Tr\left(e^{-\beta\bar{H}}e^{i\bar{H}t}X_i^{\dagger}X_j c_i^{\dagger}c_j e^{-i\bar{H}t}X_k^{\dagger}X_l c_k^{\dagger}c_l\right) \quad (2.15)$$

The factors X_i result from the transformation of the particle operators:

$$\bar{H}_i = e^{s}c_i e^{-s} = c_i X_i \quad (2.16)$$

Where $$X_i = exp\left[-\sum_q \frac{M_{qi}}{\omega_q}\left(a_q^{\dagger} - a_q\right)\right] \quad (2.17)$$

The transformed Hamiltonian H in (2.9) is diagonal in the operator c and a_q. The time development of the correlation function may be found. The electron and phonon parts of the trace may be separated, which is permissible because the X_i operators do not depend on particle states:

$$N = e^{it(e_i - e_j - \Delta_i + \Delta_j)}N_{el}N_{ph}(t) \quad (2.18)$$

$$N_{el} = Tr\left[e^{-\beta H}c_i^{\dagger}c_j c_k^{\dagger}c_l\right] \quad (2.19)$$

$$N_{ph} = Tr\left[e^{-\beta H}X_i^{\dagger}(t)X_j(t)X_k^{\dagger}(0)X_l(0)\right] \quad (2.20)$$

Using Wick's theorem for the electron part, where the subscripts *ijkl* refer to the particle state.

$$N_{el} = Tr\left[e^{-\beta H}c_l^{\dagger}c_k c_k^{\dagger}c_l\right] = n_l(1 - n_k) \quad \text{Putting } j=k \text{ and } i=l \quad (2.21)$$

For the phonon part, the four operators can be paired and combined into two. This can be easily done since their exponents commute and we have.

$$N_{ph}(t) = exp\{-\varphi_{kl}(t)\} \quad (2.22)$$

where (2.23)

M_{qk} and M_{ql} are two single states matrix elements, usually M_{qk} and M_{ql} are not equal, at least not for all different wave vectors, so that phonon effects are present in the transition.

By putting (2.23) into (2.22) we have

(2.24)

Also putting (2.21) and (2.24) into (2.18) we have

(2.25)

Putting (2.25) into (2.14) we have the result for the correlation function for the conductivity

(2.26)

3.0 Discussion of Result

The model used in section 2.0 describes dynamic relaxation. In the initial state of the system, the electron is in a state *l*, and the phonons are relaxed about their equilibrium configuration for the state *l*. In the optical absorption the electron starts in state *l* and ends in state *k*. The phonons start with an equilibrium configuration about the point $Q^{(l)}_q$ but end the optical transition with the equilibrium configuration about the point $Q_q^{(k)}$. The phonon system must alter its equilibrium configuration during the transition. This change is a relaxation process, since it must relax to the new equilibrium configuration during the optical step. The effect of the phonon relaxation process on the absorption process is contained in (2.24). The process is indicated schematically in Figure 3.1 which shows a potential energy diagram for each oscillator coordinate Q_q. There are two parabolic curves, with parabolicity . The lower curve describes the ground state of the system. If there were no coupling to the particle in state *l*, the phonon parabola would be a minimum at the point $Q_q=0$. However, because of the coupling M_{ql} to this particle, the potential minimum is at $Q_q^{(l)}$. The upper curve describes the final state potential energy curves of the phonons plus particle. The particle energy is $_k$, and the curve crosses here because the phonon system has this energy when $Q_q=0$. This potential energy curve has the minimum at $Q_q^{(k)}$. This minimum has been shown on the other side of the axis to emphasize that it is usually a point different than the ground state minimum. Fig 3.1 is called the configurational coordinate diagram [6]

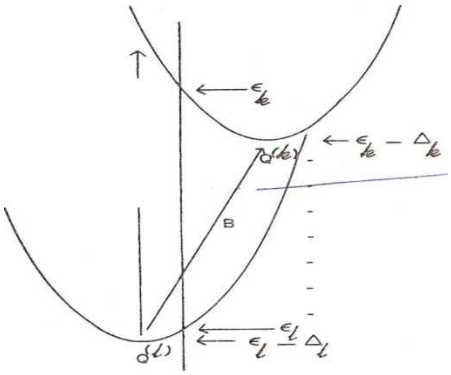

Fig 3.1 Configurational coordinate drawing of the independent boson model. The two parabolas represent the phonon potential energy of the initial and final electronic states in the transition. Transition path A IS most likely, while path B is less likely but gives the zero-phonon probability.

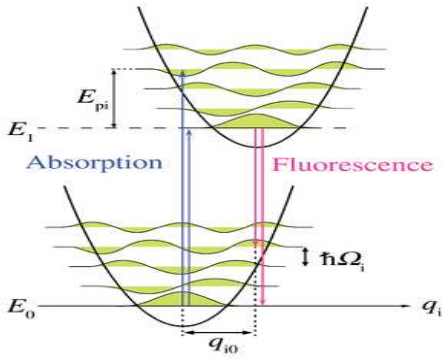

Figure 3.2. Energy diagram of an electronic transition with phonon coupling along the configurational coordinate q_i, a normal mode of the lattice. The upwards arrows represent absorption without phonons and with four phonons. The downwards arrows represent the symmetric process in emission

The phonon absorption and emission spectra is properly explained with the help of Fig. 3.2. The upper curve represents the final of the relaxation process, while the lower curve represents the initial state of the system. When relaxation from the lower curve to the upper curve takes place, the possibilities of absorption of dour phonons and without phonons are indicated by the upward arrows. Likewise during emission, we have the corresponding release of four phonons and also without phonons represented by the downward arrows. This process occurs during the interaction of electrons without phonons.

3.0 Conclusion

We have looked at the Hamiltonian which describes a localized defect with several possible localized electronic states. By diagonalising the Hamiltonian and also using the Green's function technique, we were able to describe the relaxation process from one state to the other and hence the effect on the absorption and emission spectra.

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