Quantum theory of spectral distribution of isolated nonlinear vibration modes near the combination frequency

M. I. Dykman

Institute of Semiconductors, Academy of Sciences of the Ukrainian SSR, Kiev
(Submitted November 10, 1972)
Fiz. Tverd. Tela, 15, 1075-1079 (April 1973)

The time correlation function and its spectral representation for isolated (for example, local or quasilocal) nonlinear vibrations interacting with the medium are calculated at frequencies close to the combination frequencies. The case of an arbitrary relationship between the nonequidistant distribution of vibration levels (due to nonlinearity) and the reciprocal of their lifetime is considered. The Feynman method of time ordering of operators is used to eliminate the coordinates of the medium which is approximated by a set of harmonic oscillators. The spectral distribution obtained on the basis of this method in conjunction with the asymptotic perturbation theory represents an integral of an elementary function. The form of the spectral distribution and its fine structure are studied. When the nonlinearity is large, the spectrum consists of a series of lines whose widths are proportional to the number labeling each line. It is found that the spectrum exhibits a fine structure in a well-defined temperature range. Outside this range, the distribution is essentially smooth.

The dynamics of isolated nonlinear oscillators interacting with the medium is governed by their higher harmonics. They are especially important in the interpretation of absorption peaks at infrared frequencies which are observed in the neighborhood of double and combination frequencies of local and quasilocal vibrations in crystals.[1,2] The width and the profile of such peaks are governed by a finite lifetime of the vibration modes,[3-7] by the modulation of their bare frequencies ω_χ due to the interaction with the medium,[4-7] and by the nonequidistant nature of the separation of the levels $\Delta\omega$ which is due to anharmonicity of the isolated vibration modes.

Special cases of such vibrations have been studied theoretically. The absorption spectrum of local and quasilocal vibrations was studied in ref. 5 and 6 in a wide temperature range on the basis of the Green's function method. Two limiting cases were considered in refs. 5 and 6, i.e., $\Delta\omega \gg \Gamma$ (when the spectra exhibit a fine structure) and $\Delta\omega \ll \Gamma$ (identical broadened peaks appear in the neighborhood of combination frequencies), where Γ is the reciprocal of the lifetime of isolated vibrations. Another approach based on the asymptotic methods of nonlinear mechanics[7] yields relatively simple expressions governing the profile of the peaks for an arbitrary ratio $\Delta\omega/\Gamma$ but it is applicable only at high temperatures $kT \gg \hbar\omega_\chi$.

Our aim is to study the case of arbitrary ratios $Q^\pm_{\chi\chi'}(\omega)$ and arbitrary temperatures.

We shall calculate the spectral distribution $Q^\pm_{\chi\chi'}(\omega)$ governing the profile of the absorption peak at infrared frequencies[5] $\omega \approx \omega_\chi \pm \omega_{\chi'}$, which is due to isolated vibrations in noncentrosymmetric crystals:

$$Q^\pm_{xx'}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} Q^\pm_{xx'}(t)\exp(i\omega t)\,dt = \frac{1}{\pi}\mathrm{Re}\int_0^{\infty} Q^\pm_{xx'}(t)\exp(i\omega t)\,dt. \quad (1)$$

The time correlation function $Q^\pm_{\chi\chi'}(t)$ containing products of annihilation and creation operators a_{χ_1}, $a^+_{\chi_1}$ of isolated oscillators χ_1

$$\left.\begin{array}{l} Q^+_{xx'}(t) = \langle a_x(t)\,a_{x'}(t)\,a^+_x(0)\,a^+_{x'}(0)\rangle = Z^{-1}\mathrm{Tr}\,(a^+_x a^+_{x'} e^{-\lambda H} e^{iHt} a_x a_{x'} e^{-iHt}), \\[2mm] Q^-_{xx'}(t) = \langle a_x(t)\,a^+_{x'}(t)\,a^+_x(0)\,a_{x'}(0)\rangle = Z^{-1}\mathrm{Tr}\,(a^+_x a_{x'} e^{-\lambda H} e^{iHt} a_x a^+_{x'} e^{-iHt}) \end{array}\right\} \quad (2)$$

is related directly to the time correlation function $Q_\chi(t) = \langle a_\chi(t)\,a^+_\chi(0)\rangle$ at frequencies[5,7] $\omega_\chi \pm \omega_{\chi'}$.

The following notation is used in Eq. (2): H is the Hamiltonian of the system; $a_\chi = a_\chi(0)$, $\lambda = (kT)^{-1}$, $\hbar = 1$; and $Z = \mathrm{Tr}\,\exp(-\lambda H)$.

We shall consider a weakly coupled low-symmetry impurity center whose vibration frequencies ω_χ are nondegenerate $(\omega_\chi \neq \omega_{\chi'})$ and far from the combination frequencies $(\omega_\chi \neq \omega_{\chi'} \pm \omega_{\chi''})$. We shall approximate the medium by a system of harmonic oscillators k with frequencies ω_k belonging to a continuous spectrum.

The Hamiltonian of isolated vibration modes interacting with such a medium can be written in the form

$$H = H_0 + H_i; \qquad H_i = \sum_k H_k(a_k + a^+_k)$$

$$+ \frac{1}{2}\sum_{kk'} H_{kk'}(a_k + a^+_k)(a_{k'} + a^+_{k'});$$

$$H_0 = \sum_x \omega_x \hat{n}_x + \frac{1}{6}\sum_{xx_1x_2} V_{xx_1x_2}(a_x + a^+_x)$$

$$\times (a_{x_1} + a^+_{x_1})(a_{x_2} + a^+_{x_2}) + \frac{1}{2}\sum_{xx'} V_{xx'}\hat{n}_x\hat{n}_{x'}$$

$$+ \sum_k \omega_k \hat{n}_k; \qquad \hat{n}_x = a^+_x a_x; \qquad \hat{n}_k = a^+_k a_k;$$

$$H_k = \sum_x V_{xk}(a_x + a^+_x) + \sum_{xx'} V_{xx'k}(a_x + a^+_x)(a_{x'} + a^+_{x'});$$

$$H_{kk'} = \sum_x V_{xkk'}(a_x + a^+_x) + \sum_{xx'} V_{xx'kk'}(a_x + a^+_x)(a_{x'} + a^+_{x'}). \quad (3)$$

As already discussed, we shall assume that all the quantities V contain small parameters.

We shall calculate the quantity $Q^\pm_{\chi\chi'}(\omega)$ at frequencies $\omega \approx \omega_\chi \pm \omega_{\chi'}$, where it exhibits a maximum, on the basis of the asymptotic perturbation theory (see ref. 8). It follows from ref. 8 that $Q^\pm_{\chi\chi'}(t)$ should be calculated in the limit $t \gg t_0$, where $t_0 = \max\{\omega_m^{-1}, \omega_\chi^{-1}\}$, ($\omega_m$ is the maximum frequency of the continuous spectrum). The terms $\sim t_0/t$ can be neglected, which implies that the "nonresonance" terms in the Hamiltonian (for example, $a^3_\chi a^+_{\bar{\chi}}$) proportional to $V_{\chi\chi'}$ can be omitted. The nonresonance terms proportional to $V_{\chi\chi_1\chi_2}$ lead, in the second order of the perturbation theory, to the following renormalization of the parameters ω_χ and $V_{\chi\chi'}$:[1]

$$\bar{\omega}_x = \omega_x + \sum_{x_1x_2}\left[V^2_{xx_1x_2}\frac{\omega_{x_1} + \omega_{x_2}}{\omega_x^2 - (\omega_{x_1} + \omega_{x_2})^2} - \frac{V_{xxx_1}V_{x_1x_2x_2}}{\omega_{x_1}}\right] -$$

$$-\frac{1}{2}\sum_{x_1} V^2_{xxx_1}\left[\frac{\omega_{x_1}}{4\omega_x^2-\omega_{x_1}^2}-\frac{2}{\omega_{x_1}}\right],$$

$$\Gamma_{xx'}=V_{xx'}+\sum_{x_1}\left[\frac{V^2_{xx'x_1}\omega_{x_1}}{(\omega_x-\omega_{x'})^2-\omega_{x_1}^2}\right.$$

$$+\left.\frac{V^2_{xx'x_1}\omega_{x_1}}{(\omega_x+\omega_{x'})^2-\omega_{x_1}^2}-\frac{V_{xxx_1}V_{x_1x'x'}}{\omega_{x_1}}\right](2-\delta_{xx'}). \tag{4}$$

It is most convenient to calculate the function $Q^{\pm}_{xx'}(t)$ on the basis of the method described in ref. 8. Eliminating the vibrations belonging to the continuous spectrum by means of the Feynman ordering technique and using the asymptotic perturbation theory, we arrive at a system of partial differential equations[8] whose solution has the form

$$\left.\begin{array}{l}Q^{\pm}_{xx'}(t)=(1+\delta_{xx'})(\bar{n}_x+1)\left(\bar{n}_{x'}+\frac{1}{2}\pm\frac{1}{2}\right)\\[2mm]\qquad\exp\{-i(\tilde\omega_x\pm\tilde\omega_{x'})t\}\Psi^{-1}_{x\pm}(t)\\[2mm]\times\Psi^{-1}_{x'\pm}(t)\prod_{x_1}\Psi^{-1}_{x_1\pm}(t)\exp\left[\Gamma_{x_1}t-iP_xt\mp iP_{x_1}t\right.\\[2mm]\qquad\left.+\frac{i}{2}(\mathcal{V}_{xx_1}\pm\mathcal{V}_{x'x_1})t\right],\quad t\gg t_0;\\[3mm]\Psi_{x_1\pm}(t)=\mathrm{ch}\,a^{\pm}_{x_1}t+\left[1+i\frac{(\mathcal{V}_{xx_1}\pm\mathcal{V}_{x'x_1})}{2\Gamma_{x_1}}(2\bar{n}_{x_1}+1)\right]\frac{\Gamma_{x_1}}{a^{\pm}_{x_1}}\,\mathrm{sh}\,a^{\pm}_{x_1}t;\\[3mm](a^{\pm}_{x_1})^2=\Gamma^2_{x_1}+i\Gamma_{x_1}(\mathcal{V}_{xx_1}\pm\mathcal{V}_{x'x_1})(2\bar{n}_{x_1}+1)-\frac{1}{4}(\mathcal{V}_{xx_1}\pm\mathcal{V}_{x'x_1})^2;\\[3mm]\bar{n}_x=[\exp(\lambda\tilde\omega_x)-1]^{-1},\end{array}\right\} \tag{5}$$

where Γ_x and P_x are the reciprocal of the lifetime and the frequency shift of isolated vibration modes due to their interaction with the vibrations belonging to the continuous spectrum; they are proportional to the square of the parameters V_{xk} and $V_{xkk'}$ and are defined by Eqs. (16) and (29) of ref. 8.

Equation (5) is obtained under the assumption $V_{xx'k}=V_{xx'kk'}=0.$[2]

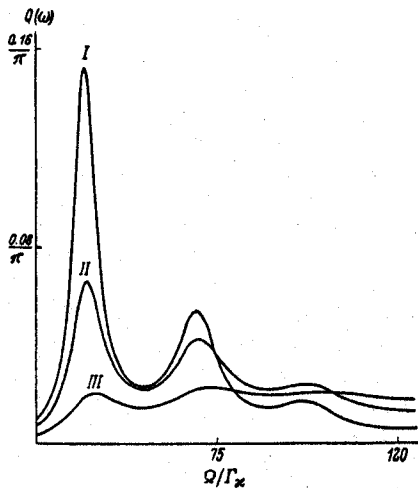Equation (5) represents an expression for the correlation function $Q^{\mp}_{xx'}(t)$ [for $Q^{-}_{xx'}(t)$ $x\neq x'$] in terms of elementary functions and it holds for an arbitrary relationship between the parameter $\tilde{V}_{x'x'}$ governing the nonequidistant distribution of the levels and the lifetime Γ_x (provided the conditions $|\tilde{V}_{xx}|/\omega_x$, Γ_x/ω_x, $|P_x|/\omega_x$, $|\tilde{V}_{xx}|\lambda$, $\Gamma_x\lambda\ll1$ are satisfied). The spectral distribution $Q^{\pm}_{xx'}(\omega)$ can be also transformed by means of Eqs. (1) and (5) to a single integral which can be easily evaluated on a computer for an arbitrary ratio $\tilde{V}_{xx_1}/\Gamma_{x_1}$ and arbitrary temperatures. The calculated values of $Q^{+}_{xx}(\omega)$ are shown in Fig. 1 for different values of the parameters $\tilde{V}_{xx}/\Gamma_x$, and n_x. In certain limiting cases, explicit analytic expressions can be obtained for the integrals in Eq. (1).

We shall first consider the case of a strong nonlinearity $|\tilde{V}_{xx_1}\pm\tilde{V}_{x'x_1}|\gg\Gamma_{x_1}(1+2n_{x_1})$, when the distribution (1) exhibits a clearly defined fine structure. In fact, expanding $\Gamma_{x_1}/(\tilde{V}_{xx_1}\pm\tilde{V}_{x'x_1})$ and retaining only the quadratic terms in the expansion, we can express the functions $\exp(a^{\pm}_{x_1}t)\,\Psi^{-1}_{x_1\pm}(t)$, $\Psi^{-2}_{x_1\pm}(t)\cdot\exp(2a^{\pm}_{x_1})$ and $\Psi^{-3}_{x_1\pm}(t)$ as infinite series in terms of $\exp(-a^{\pm}_{x_1}t)$. Introducing the Fourier transforms (1), we obtain

$$\left.\begin{array}{l}Q^{\pm}_{xx'}(\omega)=\frac{e^{(\tilde\omega_x\pm\tilde\omega_{x'})\lambda}}{\pi\prod_{x_1}(1+\bar{n}_{x_1})}\sum_{\ldots m_{x_1}=1\ldots}^{\infty}m_x\left(m_{x'}+\frac{1}{2}\mp\frac{1}{2}-\delta_{xx'}\right)\\[3mm]\times e^{-\lambda\sum_{x_1}\tilde\omega_{x_1}m_{x_1}}\frac{\Gamma^{\pm}_{m_{x_1}}\cos a^{\pm}_{m_{x_1}}-\Omega^{\pm}_{m_{x_1}}\sin a^{\pm}_{m_{x_1}}}{(\Gamma^{\pm}_{m_{x_1}})^2+(\Omega^{\pm}_{m_{x_1}})^2};\\[4mm]\Omega^{\pm}_{m_{x_1}}=\omega-\tilde\omega_x\mp\tilde\omega_{x'}+\frac{1}{2}(\mathcal{V}_{xx}+\mathcal{V}_{x'x'}\pm2\mathcal{V}_{xx'})\\[3mm]\qquad-\sum_{x_1}(\mathcal{V}_{xx_1}\pm\mathcal{V}_{x'x_1})m_{x_1}\\[3mm]\qquad-4\sum_{x_1}\frac{\Gamma^2_{x_1}}{\mathcal{V}_{xx_1}\pm\mathcal{V}_{x'x_1}}\bar{n}_{x_1}(\bar{n}_{x_1}+1)\\[3mm]\qquad\times(1+2m_{x_1}-\delta_{xx_1}\mp\delta_{x'x_1})-P_x\mp P_{x'};\\[3mm]\Gamma^{\pm}_{m_{x_1}}=\sum_{x_1}\Gamma_{x_1}[(1+2m_{x_1}-\delta_{xx_1}\mp\delta_{x'x_1})(1+2\bar{n}_{x_1})-1];\\[3mm]a^{\pm}_{m_{x_1}}=4\sum_{x_1}\frac{\Gamma_{x_1}}{\mathcal{V}_{xx_1}\pm\mathcal{V}_{x'x_1}}\left[m_{x_1}-\delta_{xx_1}\right.\\[3mm]\qquad\left.-\delta_{x'x_1}\left(\frac{1}{2}\pm\frac{1}{2}\right)-\bar{n}_{x_1}(1+\delta_{xx_1}+\delta_{x'x_1})\right].\end{array}\right\} \tag{6}$$

It follows from Eq. (6) that the fine structure lines are not necessarily Lorentzian, their widths are proportional to the numbers $\{m_{x_1}\}$ labeling the lines and increase with temperature. In the simplest one-dimensional case $[\tilde{V}_{xx'}=\tilde{V}_{xx}\delta_{xx'}$ and the substitutions $\Gamma_{x_1}=\Gamma_x\delta_{xx_1}$, $\alpha_{mx_1}=\alpha_{mx}\delta_{xx_1}$ should be formally made in Eq. (6)], the distribution $Q_{xx}(\omega)$ in the neighborhood of the frequency $2\omega_x$ represents (with an accuracy up to terms $\alpha_{mx}\sim\Gamma_x/\tilde{V}_{xx}$) a set of equidistant Lorentzian bands (for small m). The separation of such bands (obtained with the same accuracy) $2\tilde{V}_{xx}$ is twice the distance between the fine structure lines lying close to the fundamental frequency. The width of the m-th band $\Gamma_m=\Gamma_x[(2m-1)(1+2n_x)-1]$ is a factor of $\Gamma_x(1+2n_x)$ smaller than the width of the corresponding line in the neighborhood of the fundamental frequency $\Gamma_x[2m(1+2n_x)-1]$ and is given by the general formula of the Weisskopf–Wigner theory. However, the total width of the spectrum (6) correspond-

M. L. Dykman   736

ing to a one-dimensional system is greater than the spectrum of the fundamental frequency. This is due to the fact that the expression governing the intensity of the m-th line contains a factor quadratic in m and the separation of the lines is twice as large.

When the temperature is raised, the deviation of the line profile from the Lorentzian form and the overlap of individual lines increase (the overlap increases with increasing m), the fine structure disappears (which is demonstrated in Fig. 1), and Eq. (6) reduces to the expressions (17)-(18) of ref. 7 which were obtained on the basis of the classical statistics. It should be noted that the fine structure also practically disappears at very low temperatures since the expression for the intensity contains a rapidly decreasing factor $\exp(-\lambda \omega_{\varkappa} m)$.

For high transition probabilities when $|V_{\varkappa\varkappa_1} \pm V_{\varkappa'\varkappa_1}| \ll \Gamma_{\varkappa_1}$, we obtain the following result which is valid with an accuracy up to terms quadratic in $(V_{\varkappa\varkappa_1} \pm V_{\varkappa'\varkappa_1}) \cdot \Gamma_{\varkappa_1}$:

$$Q_{\varkappa\varkappa'}^{\pm}(\omega) = \frac{1+\delta_{\varkappa\varkappa'}}{\pi} (\hat{n}_{\varkappa}+1)\left(\hat{n}_{\varkappa'} + \frac{1}{2} \pm \frac{1}{2}\right)$$
$$\times\left\{ \frac{\Gamma_{\varkappa}+\Gamma_{\varkappa'}}{(\Gamma_{\varkappa}+\Gamma_{\varkappa'})^2+(\Omega_{\varkappa\varkappa'}^{\pm})^2} \right.$$
$$+ \sum_{\varkappa_1} \frac{(\mathcal{V}_{\varkappa\varkappa_1}+\mathcal{V}_{\varkappa'\varkappa_1})^2}{4\Gamma_{\varkappa_1}^2} \hat{n}_{\varkappa_1}(\hat{n}_{\varkappa_1}+1)(1+\delta_{\varkappa\varkappa_1}$$
$$+\delta_{\varkappa'\varkappa_1})\left[\frac{\Gamma_{\varkappa}+\Gamma_{\varkappa'}}{(\Gamma_{\varkappa}+\Gamma_{\varkappa'})^2+(\Omega_{\varkappa\varkappa'}^{\pm})^2} \right.$$
$$- \frac{\Gamma_{\varkappa}+\Gamma_{\varkappa'}+2\Gamma_{\varkappa_1}}{(\Gamma_{\varkappa}+\Gamma_{\varkappa'}+2\Gamma_{\varkappa_1})^2+(\Omega_{\varkappa\varkappa'}^{\pm})^2}$$

$$- 2\Gamma_{\varkappa_1} \frac{(\Gamma_{\varkappa}+\Gamma_{\varkappa'})^2-(\Omega_{\varkappa\varkappa'}^{\pm})^2}{[(\Gamma_{\varkappa}+\Gamma_{\varkappa'})^2+(\Omega_{\varkappa\varkappa'}^{\pm})^2]^2} \right]\right\};$$

$$\Omega_{\varkappa\varkappa'}^{\pm} = \omega - \bar{\omega}_{\varkappa} \mp \bar{\omega}_{\varkappa'} - P_{\varkappa} \mp P_{\varkappa'},$$

$$- \sum_{\varkappa_1}(\mathcal{V}_{\varkappa\varkappa_1} \pm \mathcal{V}_{\varkappa'\varkappa_1})\hat{n}_{\varkappa_1}(1+\delta_{\varkappa'\varkappa_1}+\delta_{\varkappa\varkappa_1})$$

$$- \frac{1}{2}(\mathcal{V}_{\varkappa\varkappa} \pm \mathcal{V}_{\varkappa'\varkappa'}+\mathcal{V}_{\varkappa\varkappa'} \pm \mathcal{V}_{\varkappa\varkappa'}). \tag{7}$$

The first term in braces in Eq. (7) corresponds to a Lorentzian distribution with a width $2(\Gamma_{\varkappa}+\Gamma_{\varkappa'})$. The second correction term is non-Lorentzian and increases when the temperature is raised ($\propto T^2$ at high temperatures). The broadening of the distribution (7) with respect to the Lorentzian distribution is of the modulation type.

The author is grateful to M. A. Krivoglaz for his interest in the present work and for his valuable remarks.

[1] W. Hayes, G. D. Jones, R. J. Elliott, and C. T. Sennett, in: Proc. Intern. Conf. on Lattice Dynamics, Copenhagen, 1963 (ed. by R. F. Wallis), Suppl. 1 to J. Phys. Chem-Solids, Pergamon Press, Oxford (1965).
[2] M. Waldner, M. A. Hiller, and W. G. Spitzer, Phys. Rev., 140, A172 (1965).
[3] S. I. Dudkin, Ukr. Fiz. Zh., 10, 873 1093 (1965).
[4] M. A. Krivoglaz and I. P. Pinkevich, Opt. Spektrosk., 23, 571 (1967).
[5] M. A. Krivoglaz and I. P. Pinkevich, Ukr. Fiz. Zh., 15, 1817 (1970).
[6] M. A. Krivoglaz and I. P. Pinkevich, Ukr. Fiz. Zh., 15, 2039 (1970).
[7] M. I. Dykman and M. A. Krivoglaz, Ukr. Fiz. Zh., 17, 1971 (1972).
[8] M. I. Dykman and M. A. Krivoglaz, Zh. Eksp. Teor. Fiz., 64, 993 (1973).