LIGHT ABSORPTION AND SCATTERING BY NONLINEAR LOCAL AND QUASI-LOCAL OSCILLATION

M. I. Dykman

Institute of Semiconductors
Ukrainian Academy of Sciences
Kiev, USSR

and

M. A. Krivograz

Institute of Metal Physics
Ukrainian Academy of Sciences
Kiev, USSR

The influence of nonlinearity of particular oscillators interacting with a medium (e.g., local or quasi-local vibrations) on their time correlation functions and spectral distributions is investigated. The modulational broadening which is not connected with the finite lifetime of the oscillator and the fine structure of the spectral distribution are considered.

The calculation of the line shape of light absorption or scattering by a particular oscillator κ interacting with a medium (e.g., a local or quasi-local vibration near a defect in a crystal) to a good approximation is reduced to the calculation of the spectral representation $Q_\kappa(\omega)$ of the time correlation function

$$Q_\kappa(t) = \langle q_\kappa(t) q_\kappa(0) \rangle \qquad (1)$$

of the oscillator κ under consideration with normal coordinate q_κ. The problem of determination of $Q_\kappa(t)$ arises also in the theory of

lasers [1-3] and plasma. It is connected with the general statistical-mechanical problem of investigating the process of approaching the equilibrium state in a subsystem.

The relaxation of a linear oscillator was considered in detail in [4-6]. In this case $Q_\kappa(\omega)$ has the well-known Lorentzian shape with the half-width equal to the reciprocal lifetime of the oscillation κ. However real local oscillations are to some degree nonlinear. It is essential to note that even small nonlinearity produces qualitative changes in the character of these oscillations and can significantly affect the shape of their spectral distribution.

In terms of classical theory these effects are due to the dependence of the nonlinear oscillator frequency on the amplitude and their continuous and random change in time (as a consequence of interaction with a medium). The time dependence of the frequency leads to a specific broadening of $Q_\kappa(\omega)$. This broadening is of a modulational nature and is not caused directly by the relaxation of the local oscillation, that is, by frictional forces.

In terms of the quantum theory, the nonlinearity leads to nonequal spacing of the energy levels of the oscillator. This is evident from Fig. 1, where ω_κ is the harmonic frequency, and V_κ is a parameter of nonlinearity. The transitions between adjacent levels have different frequencies. If $|V_\kappa| \gg I_\kappa$, where I_κ is the characteristic width of the energy level due to relaxation, then the lines corresponding to different transitions do not overlap and the spectral distribution has fine structure. If $|V_\kappa| < I_\kappa$, there appears a single distribution of essentially non-Lorentzian shape.

The calculation of $Q_\kappa(\omega)$ is rather complicated because a nonlinear oscillator has an infinite number of almost equidistant energy and the corresponding quantum states interfere. That is why the use of the Green's function method provides the opportunity to obtain $Q_\kappa(\omega)$ only in the extreme cases $|V_\kappa| \gg I_\kappa$ and $|V_\kappa| \ll I_\kappa$ [7,8]. The development of new asymptotic classical [9] and quantum [10,11] methods allowed us to determine $Q_\kappa(t)$ at arbitrary V_κ / I_κ (but $|V_\kappa|, I_\kappa \ll \omega_\kappa$). It was found, somewhat unexpectedly, that $Q_\kappa(t)$ had a simple form (an elementary function). At the same time a corresponding expression for $Q_\kappa(\omega)$ was rich enough to lead to various spectra of essentially non-Lorentzian shape, including those with fine structure.

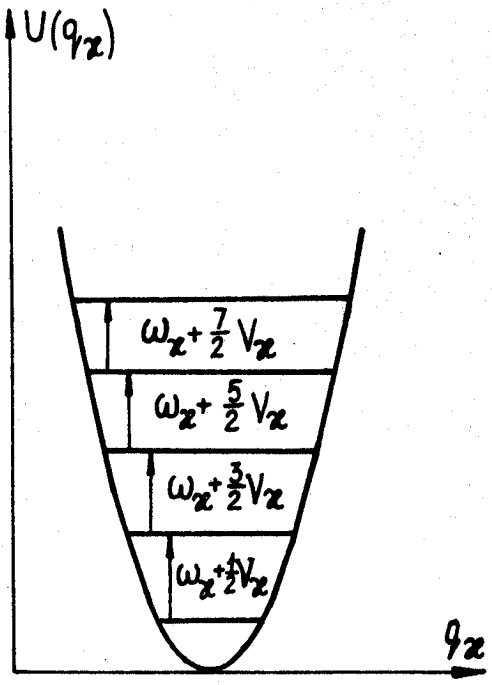

Fig. 1. Schematic of the nonlinear oscillator energy levels.

In this paper we give a short review of our results on the theory of nonlinear oscillators interacting with a medium obtained in [9-14].

The Hamiltonian of a single nonlinear oscillator, interacting with a medium, is of the form

$$H = \tfrac{1}{2}(p_\kappa^2 + \omega_\kappa^2 q_\kappa^2) + \tfrac{1}{4}\gamma_\kappa q_\kappa^4 + \tfrac{1}{2}\sum_k (p_k^2 + \omega_k^2 q_k^2) + \sum_k \epsilon_{\kappa k} q_\kappa q_k$$

$$+ \sum_{kk'} \epsilon_{\kappa kk'} q_\kappa q_k q_{k'}$$

Here q_κ and p_κ, q_k and p_k are the normal coordinates and momenta of the particular oscillation κ and of the medium vibration k; the frequencies ω_k belong to the continuous spectrum; γ_κ is the nonlinearity parameter ($V_\kappa = .75\ \hbar\gamma_\kappa / \omega_\kappa^2$); $\epsilon_{\kappa k}$ and $\epsilon_{\kappa kk'}$ determine the interaction with the medium linear in the

coordinate of the singled-out oscillator.

In classical considerations one can exclude continuous spectrum oscillations and thus obtain a nonlinear integro-differential equation for $q_\kappa(t)$ [see Eq. (5) in [9]]. This equation is essentially stochastic since the initial amplitudes and phases of the continuous spectrum oscillations are random quantities. Therefore, the application of the usual asymptotic methods of nonlinear oscillation theory is not enough for its solution. One must also make a rather complex, non-trivial averaging. A special stochastic asymptotic method [9] allows one to reduce the expression for $Q_\kappa(t)$ at large t to the explicit form:

$$Q_\kappa(t) = 2\mathrm{Re}[\exp(-i\tilde{\omega})_\kappa |t| \overline{Q}_\kappa(|t|)];$$

$$\overline{Q}_\kappa(t) = \frac{kT}{2\omega_\kappa^2} \exp(I_\kappa t)\left[\frac{I_\kappa(1+2i\alpha)}{a} \mathrm{sh}(at) + \mathrm{ch}(at)\right]^{-2} \qquad (3)$$

$$t \gg \omega_\kappa^{-1}; \quad a^2 = I_\kappa(1+4i\alpha); \quad \alpha = \frac{3kT}{8\omega_\kappa^3} \frac{\gamma_\kappa}{I_\kappa} .$$

Here

$$I_\kappa = \frac{\pi}{4} \sum_k \epsilon_{\kappa k}^2 \delta(\omega_\kappa - \omega_k) + I_{\kappa\ell}$$

(essentially $I_{\kappa\ell} \sim T \sum_{kk'} \epsilon_{\kappa kk'}^2 \delta(\omega_\kappa - \omega_k \pm \omega_{k'})$ for local vibrations) defines the broadening due to interaction with the medium and characterizes the inverse lifetime of the oscillatory states; the parameter $\alpha \sim \gamma T / I_\kappa$ describes the ratio between the nonlinearity and the relaxation broadening.

The light absorption or scattering line shape $Q_\kappa(\omega)$ is determined, according to (3), by a single parameter α and may be easily obtained by numerical Fourier-transformation at arbitrary α (Fig. 2). At $\alpha = 0$, $Q_\kappa(\omega)$ is a Lorentzian curve with the half width $2I_\kappa$. Such a distribution is typical for a linear oscillator, interacting linearly with a medium, when relaxation processes are simply reduced to an effective friction proportional to the velocity. However, at $\alpha \neq 0$ the picture becomes more complex

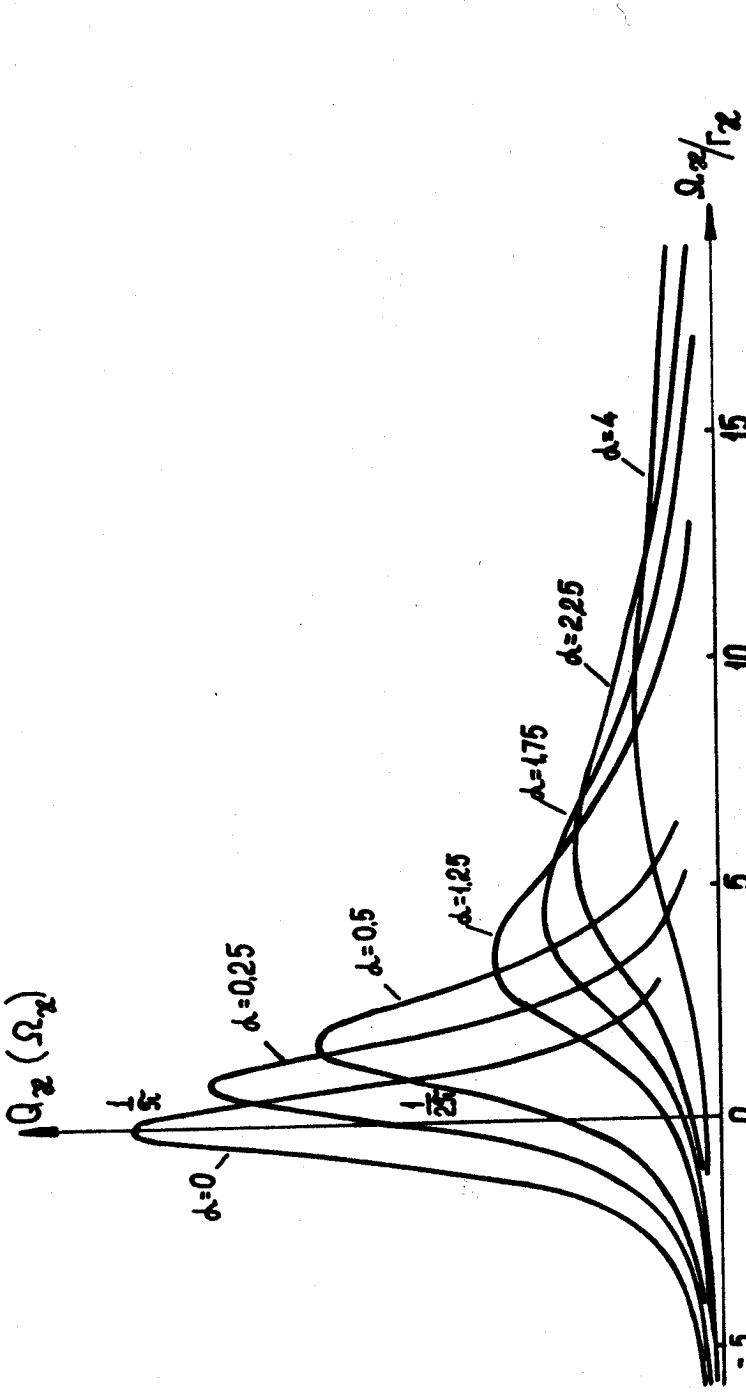

Fig. 2. Spectral distributions $Q_K(\omega)$ for different values of the dimensionless parameter α in the classical limit; $\Omega_K = \omega - \omega_K$, and the intensity is normalized to unity.

and the distribution becomes non-Lorentzian and asymmetric. As α grows, the asymmetry increases, the distribution width becomes larger and its maximum is shifted. At $|\alpha| >> 1$ the width is determined only by the nonlinearity parameter γ_κ and, therefore, has a purely modulational nature. The detailed analysis of the temperature dependence of the form and width of the spectral distribution for quasi-local and local vibrations is presented in [9].

If the condition $kT >> \hbar\omega_\kappa$ does not hold, then quantum considerations are needed. It is necessary also for the investigation of the spectral fine structure. The latter is connected with the discreteness of the energy levels, that is, with a pure quantum effect.

In order to calculate the time correlation function of impurity oscillations in quantum theory, a special asymptotic method was developed [10].

This method enabled the following expression for $Q_\kappa(t)$ to be obtained (cf. Eq. (4) in [10]):

$$Q_\kappa(t) = \exp\left[-i(\omega_\kappa - \tfrac{1}{2}V_\kappa)t + \frac{\hbar\omega_\kappa}{kT}\right](\bar{n}_\kappa+1)^{-1}$$

$$\times \sum_{m=1}^{\infty} mF(m,t)\exp\left(-\frac{\hbar\omega_\kappa m}{kT} - iV_\kappa mt\right), \quad t >> \omega_\kappa^{-1},$$

where $\bar{n}_\kappa$ is the Planck occupation number.

The Fourier transform of $F(m, m-1;t) = F(mt)\exp\left(-\frac{\hbar\omega_\kappa m}{kT}\right)$ is connected with a light absorption line, corresponding to the transition between the (m-1)-th and m-th oscillator levels. According to (4), $Q_\kappa(\omega)$ may be interpreted as the sum of partial spectra. As all energy levels are almost equidistant, the lines $[F(m,t)]$ with different m interfere and for $F(m, m-1;t)$ in [10, 11] an equation was obtained (cf. Eq. (6) in [11]) which is an analog of the quantum kinetic equation

$$\frac{\partial F(n,m;t)}{\partial t} = \sum_{j=-1}^{1} D_j(n,m)\exp\left[-iV_\kappa j(n-m)t\right]F(n+j, m+j;t). \quad (5)$$

D_j depend on the damping I_κ and frequency shift of the singled-out oscillator due to interaction with the vibrations of the continuous spectrum. It is possible to find a generating function for F and to show that it satisfies an equation in partial derivatives. It is essential that the exact solution of this equation may be obtained for our problem. It was found that in quantum theory the time correlation function may be formally described by the same formula as in classical theory. The only difference is that in the quantum case

$$\alpha = \frac{3\gamma_\kappa \hbar}{16\omega_\kappa^2 I_\kappa}(2\bar{n}_\kappa+1);\quad a^2 = I_\kappa^2\left[1+4i\alpha - \frac{4\alpha^2}{(2\bar{n}_\kappa+1)^2}\right]. \tag{6}$$

Detailed analysis of $Q_\kappa(\omega)$ as a function of temperature and the parameters of the interaction is given in [10] on the basis of (3), (6). We should note that the most interesting quantum effect, namely the fine structure of $Q_\kappa(\omega)$, appears at $|V_\kappa| \gg I_\kappa(2\bar{n}_\kappa+1)$ and exists within a limited temperature range. The fine structure may be due also to nonlinear interaction between the singled-out oscillator considered and another one [10].

The classical [9] and quantum [10] asymptotic methods allow also for consideration of the shape of $Q_\kappa(\omega)$ near combined frequencies of the singled-out oscillations [12, 13]. The effects of nonlinearity there are even more pronounced.

Some of the above-mentioned effects caused by nonlinearity have been already observed in experiments on infrared absorption by local and quasi-local oscillations. For example, the increase in temperature leads to strong asymmetry in the absorption lines in the systems NaCl:Cu^+ [15, 16] and KI:Ag^+ [17] (quasi-local oscillation) which is probably of a modulational nature. The width of the lines also grows strongly (by an order of magnitude for the former system at $kT \sim \hbar\omega_\kappa$). Fine structure was found in the spectrum of quasilocal oscillation in MnF_2:Eu^{2+} [18]. Its character and temperature dependence agree with theoretical results [10]. In [19] modulational broadening of the high-frequency local vibration of the impurity complex SO_4^{2-} and Ca^{2+} in a KCl crystal due to interaction with low-lying quasi-local oscillation was observed.

Even strong modulational broadening does not lead to a change of the infrared absorption peak intensity with temperature

[14]. With the use of the unambiguous procedure of separation of the peak in [14] an expression (Eq. (8) in [14]) for the peak intensity change containing only relaxation parameters was obtained. The strong temperature broadening of the absorption line under a slight change of its intensity, observed in [16], is typical for modulational broadening and may be used to distinguish it.

New effects arise in the case of nonlinear friction when the energy of interaction between a particular singled-out oscillation and a continuous spectrum of oscillations contains not only the above terms

$$q_\kappa\left(\sum_k \epsilon_{\kappa k} q_k + \sum_{kk'} \epsilon_{\kappa kk'} q_k q_{k'}\right)$$

but also the terms

$$q_\kappa^2 \sum_k \epsilon_{\kappa kk'} q_k$$

proportional to q_κ^2, corresponding to decay with participation of two quanta of the oscillator κ [11]. Here, in terms of classical theory, the friction coefficient depends on amplitude, i.e., it changes with time even for a linear singled-out oscillator. Therefore, $Q_\kappa(t)$ decays nonexponentially and its spectral representation is non-Lorentzian even for a linear oscillator.

In [11] the asymmetric complex $Q_\kappa(\omega)$ is investigated for an arbitrary ratio of the parameters of linear and nonlinear friction and nonequal spacing, on the basis of generalizations of Eq. (4) and (5). In the absence of nonequal spacing nonlinear friction leads to narrowing of $Q_\kappa(\omega)$ as compared to a Lorentzian curve with the same wings and integral intensity.

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