

Lattice Anharmonicity and Optical Absorption in Polar Crystals. III. Quantum Mechanical Treatment in the Linear Approximation

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A quantum mechanical calculation is given for the effect of lattice anharmonicity on the optical constants of an ionic crystal in the reststrahl region of the spectrum. A modification of the Kubo formalism for treating transport coefficients is employed. Only cubic anharmonic terms in the Hamiltonian are considered. In agreement with the correspondence principle, the present results in the limit of high temperatures reduce to those of the classical treatment which was given in a previous paper. A comparison is made between the present calculation and that of Born and Huang. The available experimental data are discussed.

1. INTRODUCTION

THE first extensive theoretical treatment of lattice anharmonicity and its influence on the optical properties of polar crystals was carried out by Born and Blackman¹ and by Blackman² using a classical mechanical approach with cubic anharmonic terms in the lattice Hamiltonian. They found that the optical properties in the vicinity of the reststrahl frequency are in large measure determined by a frequency-dependent damping constant which is proportional to the absolute temperature. In a recent paper (hereafter referred to as II) Maradudin and Wallis³ have re-examined the classical problem using modern techniques for handling irreversible processes in many-body systems and have obtained results in substantial agreement with those of Born and Blackman.

A quantum mechanical treatment of anharmonic lattice vibration absorption has been developed by Born and Huang⁴ who considered cubic anharmonic terms in detail. The damping constants which occur in their theory turn out to be proportional to the cube of the absolute temperature in the high-temperature limit. The fact that the quantum mechanical damping constants of Born and Huang do not have the same temperature dependence in the high-temperature limit as the classical damping constants is somewhat disturbing in view of the correspondence principle. Furthermore, there are certain other features of the Born-Huang theory which are not entirely satisfactory and which will be discussed in detail later.

Recently, experimental investigations have been carried out by Heilmann⁵ for LiF and by Hass⁶ for NaCl on the infrared lattice vibration spectra at high temperatures. In both cases for temperatures near the

melting points, the data relatively close to the reststrahl frequency are described by a damping constant which is approximately proportional to the square of the absolute temperature. These experimental results therefore do not agree with either the classical theory of Born and Blackman or the quantum mechanical theory of Born and Huang.

In view of the various discrepancies discussed above, we have developed a new quantum mechanical theory which has the virtue of clearly reducing to the classical result in the high-temperature limit. The methods are generalizations of those employed in II.

2. THEORETICAL DEVELOPMENT

We consider a diatomic ionic lattice which satisfies periodic boundary conditions. The Hamiltonian for the lattice is assumed to have the form

$$H_L = H_0 + H_A, \quad (1)$$

where

$$H_0 = \frac{1}{2} \sum_{l\kappa\alpha} m_\kappa \dot{u}_\alpha(l\kappa)^2 + \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa; l'\kappa') u_\alpha(l\kappa) u_\beta(l'\kappa'), \quad (1a)$$

$$H_A = \frac{1}{6} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l''\kappa''\gamma} \Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') \times u_\alpha(l\kappa) u_\beta(l'\kappa') u_\gamma(l''\kappa''). \quad (1b)$$

The quantity $u_\alpha(l\kappa)$ is the α Cartesian component of the displacement of the κ th atom in the l th unit cell from its equilibrium position, and m_κ is the mass of the κ th kind of atom in a unit cell. The indices l and κ range over N unit cells and two atoms per unit cell, respectively. The quantities Φ are general force constants for the crystal. In principle H_A , the anharmonic part of the Hamiltonian, would include quartic and higher order terms which could be treated in the theory to be developed. We shall restrict ourselves, however, to the cubic terms given in Eq. (1b).

It is convenient to introduce the normal coordinate

¹ M. Born and M. Blackman, *Z. Physik* **82**, 551 (1933).

² M. Blackman, *Z. Physik* **86**, 421 (1933); *Phil. Trans. Roy. Soc. (London)* **A236**, 103 (1936).

³ A. A. Maradudin and R. F. Wallis, *Phys. Rev.* **123**, 777 (1961).

⁴ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

⁵ G. Heilmann, *Z. Physik* **152**, 368 (1958).

⁶ M. Hass, *Phys. Rev.* **117**, 1497 (1960).

transformation

$$\mathbf{u}(l\kappa) = (Nm_\kappa)^{-\frac{1}{2}} \sum_{\mathbf{k}j} \mathbf{e}(\kappa|\mathbf{k}j) Q(\mathbf{k}j) \exp[2\pi i \mathbf{k} \cdot \mathbf{x}_l], \quad (2)$$

where the normal coordinates $Q(\mathbf{k}j)$ satisfy the condition

$$Q(\mathbf{k}j) = Q^*(-\mathbf{k}j), \quad (2a)$$

the $\mathbf{e}(\kappa|\mathbf{k}j)$ are the components of an eigenvector normalized to unity for the dynamical matrix of the crystal and the quantity \mathbf{x}_l is the position vector for the origin of the l th unit cell. The indices \mathbf{k} and j specify the wave vector and branch of the normal mode. The harmonic and anharmonic parts of the Hamiltonian can now be written in the forms

$$H_0 = \frac{1}{2} \sum_{\mathbf{k}j} \{ \dot{Q}(\mathbf{k}j) \dot{Q}(-\mathbf{k}j) + \omega^2(\mathbf{k}j) Q(\mathbf{k}j) Q(-\mathbf{k}j) \}, \quad (3a)$$

$$H_A = \frac{1}{3} \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} \sum_{jj'j''} V(\mathbf{k}j, \mathbf{k}'j'; \mathbf{k}''j'') \times Q(\mathbf{k}j) Q(\mathbf{k}'j') Q(\mathbf{k}''j''), \quad (3b)$$

where $\omega(\mathbf{k}j)$ is the normal mode frequency and $V(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')$ is a new anharmonic coefficient whose explicit form is given in II.

The calculation of the optical constants of the crystal is based on a modified version of the Kubo formalism⁷ for calculating transport coefficients. We assume that the interaction between the lattice and the electromagnetic radiation contributes a term to the Hamiltonian of the form

$$H_I = - \sum_{l\kappa} \epsilon_\kappa \mathbf{u}(l\kappa) \cdot \mathbf{E}_{l\kappa}(t), \quad (4)$$

where ϵ_κ is the charge on the ion of type κ and $\mathbf{E}_{l\kappa}(t)$ is the electric vector of the radiation at the ion $l\kappa$. In the following development we shall neglect the finite wave vector of the radiation and write

$$H_I = -\mathbf{M} \cdot \mathbf{E}(t), \quad (5)$$

where \mathbf{M} is the dipole moment operator and $\mathbf{E}(t)$ is now independent of position. In terms of the normal coordinates $Q(\mathbf{k}j)$ the dipole moment operator can be written as

$$\mathbf{M} = N^{\frac{1}{2}} \sum_j \mathbf{M}_j Q(0j), \quad (6)$$

where

$$\mathbf{M}_j = \sum_\kappa m_\kappa^{-\frac{1}{2}} \epsilon_\kappa \mathbf{e}(\kappa|0j). \quad (6a)$$

In II it was shown that the Kubo formalism⁷ can be used to express the components $\chi_{\mu\nu}$ of the complex dielectric susceptibility tensor in the form

$$\chi_{\mu\nu} = \lim_{\epsilon \rightarrow 0^+} \frac{1}{ZV} \text{Tr} \int_0^\infty d\tau \times e^{-i\omega\tau - \epsilon\tau} e^{-\beta H_L} \int_0^\beta d\lambda \dot{M}_\nu(-i\lambda\hbar) M_\mu(\tau), \quad (7)$$

where Z is the partition function, V is the volume of the crystal, ω is the frequency of the radiation, $\beta = 1/kT$, and $\dot{M}_\nu(-i\lambda\hbar)$ is the time derivative of the ν th component of the dipole moment operator evaluated at the imaginary time $-i\lambda\hbar$. The time-dependent components of the dipole moment operator which appear in Eq. (7) are obtained formally from Eq. (6) by treating the normal coordinates as time-dependent Heisenberg operators. It is to be emphasized that the time dependence of these operators is to be calculated using only the Hamiltonian H_L for the lattice and neglecting the interaction term H_I . Evaluation of $\chi_{\mu\nu}$ according to Eq. (7) enables one to calculate the optical constants of the crystal as indicated in II.

It is instructive to consider the structure of Eq. (7). The dielectric susceptibility is expressed as the thermal average of the product of a certain function and the Laplace transform of the dipole moment operator. We shall find it advantageous to calculate the Laplace transform of $M_\mu(\tau)$ directly rather than to calculate $M_\mu(\tau)$ first and then take its Laplace transform. This procedure is related to the use of the resolvent formalism as discussed by Van Hove⁸ and elaborated by Teitler and Wallis.⁹ If one is interested in a result valid to the lowest non-vanishing order in the anharmonic coupling, one can neglect the anharmonic terms in H_L where the latter appears explicitly in Eq. (7) and in evaluating $\dot{M}_\nu(-i\lambda\hbar)$. The anharmonicity need be considered only in the calculation of the Laplace transform of $M_\mu(\tau)$.

In place of the normal coordinate operators $Q(\mathbf{k}j; t)$ it is convenient to use the creation and annihilation operators $a^*(\mathbf{k}j; t)$ and $a(\mathbf{k}j; t)$ defined by

$$Q(\mathbf{k}j; t) = [\hbar/2\omega(\mathbf{k}j)]^{\frac{1}{2}} [a^*(-\mathbf{k}j; t) + a(\mathbf{k}j; t)], \quad (8a)$$

$$\dot{Q}(\mathbf{k}j; t) = [\hbar\omega(\mathbf{k}j)/2]^{\frac{1}{2}} [a^*(-\mathbf{k}j; t) - a(\mathbf{k}j; t)]. \quad (8b)$$

The time dependence of the operators $a^*(\mathbf{k}j; t)$ and $a(\mathbf{k}j; t)$ is determined for our purposes by the Heisenberg equations of motion

$$i\hbar \dot{a}^*(\mathbf{k}j; t) = [a^*(\mathbf{k}j; t) H_L - H_L a^*(\mathbf{k}j; t)], \quad (9a)$$

$$i\hbar \dot{a}(\mathbf{k}j; t) = [a(\mathbf{k}j; t) H_L - H_L a(\mathbf{k}j; t)]. \quad (9b)$$

The following commutation relations are satisfied by the operators a and a^* :

$$a(\mathbf{k}j; t) a^*(\mathbf{k}'j'; t) - a^*(\mathbf{k}'j'; t) a(\mathbf{k}j; t) = \delta_{\mathbf{k}\mathbf{k}'} \delta_{jj'}, \quad (10a)$$

$$a(\mathbf{k}j; t) a(\mathbf{k}'j'; t) - a(\mathbf{k}'j'; t) a(\mathbf{k}j; t) = 0, \quad (10b)$$

$$a^*(\mathbf{k}j; t) a^*(\mathbf{k}'j'; t) - a^*(\mathbf{k}'j'; t) a^*(\mathbf{k}j; t) = 0. \quad (10c)$$

Using Eqs. (3), (8), and (10) one can transform Eqs. (9) to

$$i\hbar \dot{a}^*(-\mathbf{k}j; t) = -\hbar\omega(\mathbf{k}j) a^*(-\mathbf{k}j; t) - A(\mathbf{k}j; t), \quad (11a)$$

$$i\hbar \dot{a}(\mathbf{k}j; t) = \hbar\omega(\mathbf{k}j) a(\mathbf{k}j; t) + A(\mathbf{k}j; t), \quad (11b)$$

⁸ L. Van Hove, *Physica* **21**, 517 (1955).

⁹ S. Teitler and R. F. Wallis, *J. Math. Phys.* **1**, 372 (1960).

⁷ R. Kubo, *J. Phys. Soc. Japan* **12**, 570 (1957).

where

$$A(\mathbf{k}j; t) = \left(\frac{\hbar}{2}\right)^{\frac{3}{2}} \sum_{\mathbf{k}'j'\mathbf{k}''j''} \frac{V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')}{[\omega(\mathbf{k}j)\omega(\mathbf{k}'j')\omega(\mathbf{k}''j'')]^{\frac{1}{2}}} \\ \times [a^*(-\mathbf{k}'j'; t)a^*(-\mathbf{k}''j''; t) + a(\mathbf{k}'j'; t)a^*(-\mathbf{k}''j''; t) + a^*(-\mathbf{k}'j'; t)a(\mathbf{k}''j''; t) \\ + a(\mathbf{k}'j'; t)a(\mathbf{k}''j''; t)]. \quad (12)$$

Equations (11) can be simplified by means of the transformation

$$a(\mathbf{k}j; t) = c(\mathbf{k}j; t)e^{-i\omega(\mathbf{k}j)t}, \quad (13a)$$

$$a^*(-\mathbf{k}j; t) = c(\mathbf{k}-j; t)e^{-i\omega(\mathbf{k}-j)t}, \quad (13b)$$

where

$$c(\mathbf{k}-j; t) = c^*(-\mathbf{k}j; t), \quad (14a)$$

$$\omega(\mathbf{k}-j) = -\omega(\mathbf{k}j). \quad (14b)$$

After introducing the notation

$$F(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') = \left[\frac{|\omega(\mathbf{k}j)|}{|\omega(\mathbf{k}'j')||\omega(\mathbf{k}''j'')|} \right]^{\frac{1}{2}} \\ \times V(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j''), \quad (15)$$

$$i\hbar s\gamma_{\mathbf{k}j}(s) = \left(\frac{\hbar}{2}\right)^{\frac{3}{2}} \frac{1}{\omega(\mathbf{k}j)} \sum_{\mathbf{k}'j'\mathbf{k}''j''} \left\{ \frac{F(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')c_0(\mathbf{k}'j')c_0(\mathbf{k}''j'')}{s + i[\omega(\mathbf{k}'j') + \omega(\mathbf{k}''j'') - \omega(\mathbf{k}j)]} \right. \\ \left. + F(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')[c_0(\mathbf{k}'j')\gamma_{\mathbf{k}'j''}(s') + \gamma_{\mathbf{k}'j'}(s')c_0(\mathbf{k}''j'')] \right\}, \quad (18)$$

where

$$\gamma_{\mathbf{k}j}(s) = \mathcal{L}[c_1(\mathbf{k}j; t)] = \int_0^\infty dt c_1(\mathbf{k}j; t)e^{-st}, \quad (19a)$$

$$s' = s + i[\omega(\mathbf{k}'j') + \omega(\mathbf{k}''j'') - \omega(\mathbf{k}j)]. \quad (19b)$$

Equation (18) is a linear integral equation for the quantities $\gamma_{\mathbf{k}j}(s)$. As such it lends itself to an iterative solution.

Before taking up the iteration of Eq. (18) we shall return to the discussion of Eq. (7). As has been noted previously, the integral over λ need be evaluated only in the harmonic approximation, if results correct to the lowest non-vanishing order in the anharmonicity are desired. Utilizing Eqs. (6) and (8) one obtains

$$\dot{M}_\nu(t) = i \sum_j M_{\nu j} [N\hbar\omega(0j)/2]^{\frac{1}{2}} \\ \times [a^*(0j; t) - a(0j; t)]. \quad (20)$$

The expressions for $a^*(0j; t)$ and $a(0j; t)$ which satisfy the harmonic equations of motion are

$$a^*(0j; t) = a^*(0j; 0)e^{i\omega(0j)t}, \quad (21a)$$

$$a(0j; t) = a(0j; 0)e^{-i\omega(0j)t}. \quad (21b)$$

A straightforward evaluation using Eqs. (20) and (21)

we can write the equations of motion as the single equation

$$i\hbar \dot{c}(\mathbf{k}j; t) = \left(\frac{\hbar}{2}\right)^{\frac{3}{2}} \frac{1}{\omega(\mathbf{k}j)} \\ \times \sum_{\mathbf{k}'j'\mathbf{k}''j''} F(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \\ \times c(\mathbf{k}'j'; t)c(\mathbf{k}''j''; t) \\ \times e^{-i[\omega(\mathbf{k}'j') + \omega(\mathbf{k}''j'') - \omega(\mathbf{k}j)]t}, \quad (16)$$

where j, j' , and j'' now take on both positive and negative values.

It is convenient to linearize Eq. (16) by the substitution

$$c(\mathbf{k}j; t) = c_0(\mathbf{k}j) + c_1(\mathbf{k}j; t), \quad (17)$$

where $c_0(\mathbf{k}j)$ is a time-independent solution to the harmonic equations of motion and $c_1(\mathbf{k}j; t)$ is a time-dependent anharmonic correction which is taken equal to zero at $t=0$. If one substitutes Eq. (17) into Eq. (16), neglects higher powers of the quantities c_1 than the first, and takes the Laplace transform \mathcal{L} of the resulting equation, one gets

yields

$$\int_0^\beta \dot{M}_\nu(-i\lambda\hbar)d\lambda \\ = i \sum_j M_{\nu j} [N/2\hbar\omega(0j)]^{\frac{1}{2}} \{ a^*(0j; 0)[e^{\beta\hbar\omega(0j)} - 1] \\ + a(0j; 0)[e^{-\beta\hbar\omega(0j)} - 1] \}. \quad (22)$$

Referring back to Eq. (7) we see that the basic problem is to evaluate the thermal averages

$$\frac{1}{Z} \text{Tr}\{e^{-\beta H_0} a^*(0j; 0)\gamma_{0j}(s)\} = \langle a^*(0j; 0)\gamma_{0j}(s) \rangle, \quad (23a)$$

$$\frac{1}{Z} \text{Tr}\{e^{-\beta H_0} a(0j; 0)\gamma_{0j}(s)\} = \langle a(0j; 0)\gamma_{0j}(s) \rangle, \quad (23b)$$

where the anharmonic term in the Boltzmann factor

has been omitted as discussed previously. Since

$$a^*(0j; 0) = c_0(0 - j) = c_0^*(0j), \quad (24a)$$

$$a(0j; 0) = c_0(0j), \quad (24b)$$

the evaluation of Eq. (23) requires the thermal averages

$$\langle c_0^*(\mathbf{k}j)c_0(\mathbf{k}'j') \rangle = \begin{cases} n_{\mathbf{k}j} \\ n_{\mathbf{k}j} + 1 \end{cases} \delta_{\mathbf{k}\mathbf{k}'} \delta_{jj'} \quad \text{for } \begin{cases} j > 0 \\ j < 0 \end{cases}, \quad (25a)$$

$$\langle c_0(\mathbf{k}j)c_0^*(\mathbf{k}'j') \rangle = \begin{cases} n_{\mathbf{k}j} + 1 \\ n_{\mathbf{k}j} \end{cases} \delta_{\mathbf{k}\mathbf{k}'} \delta_{jj'} \quad \text{for } \begin{cases} j > 0 \\ j < 0 \end{cases}, \quad (25b)$$

$$\langle c_0(\mathbf{k}j)c_0(\mathbf{k}'j') \rangle = \langle c_0^*(\mathbf{k}j)c_0^*(\mathbf{k}'j') \rangle = 0, \quad (25c)$$

where

$$n_{\mathbf{k}j} = [e^{\beta\hbar|\omega(\mathbf{k}j)|} - 1]^{-1}. \quad (25d)$$

We return now to the iterative solution of Eq. (18). The iterative procedure leads to a large number of terms which are conveniently classified according to diagrams. The situation is very similar to the classical case discussed in II in that the same types of diagrams

occur. The principal difference between the classical and quantum mechanical cases is that in the latter, one must use the correct commutation rules when the order of two operators is interchanged. We shall restrict ourselves to a few qualitative observations and a statement of results and refer the reader to II for details.

The character of the basic thermal averages specified by Eq. (25) leads to the vanishing of a great many of the terms which arise when the iterative solution for $\gamma_{0j}(s)$ is substituted into Eq. (23). Of the remaining terms only certain ones correspond to contributions which dominate at long times. Since we are interested in the stationary state driven by the radiation field, we retain only the terms which lead to the dominant long-time behavior. Finally, a number of terms appearing in higher order may be neglected if a result correct only to the lowest non-vanishing order in the anharmonic coupling is desired. The terms which remain after these approximations are made correspond to the so-called ring diagrams and form a geometric series which can be summed exactly. The results for the required thermal averages can be written as

$$\begin{aligned} \mathcal{L}\langle c_0^*(0j)c(0j; t) \rangle &= \mathcal{L}\langle c_0^*(0j)c_0(0j) \rangle + \langle c_0^*(0j)\gamma_{0j}(s) \rangle \\ &= (n_{0j}/s) \sum_{p=0}^{\infty} G_1^p \\ &= n_{0j}/s(1 - G_1), \end{aligned} \quad (26)$$

where

$$G_1(s) = -\left(\frac{\hbar}{2}\right) \sum_{\mathbf{k}'j'\mathbf{k}''j''} \frac{F(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')F(-\mathbf{k}''j''; \mathbf{k}j; -\mathbf{k}'-j')}{ss'\omega(\mathbf{k}j)\omega(\mathbf{k}''j'')} (n_{\mathbf{k}'j'} + \frac{1}{2}), \quad (26a)$$

$$s = i[\omega + \omega(\mathbf{k}j)] + \epsilon, \quad (26b)$$

$$s' = s + i[\omega(\mathbf{k}'j') + \omega(\mathbf{k}''j'') - \omega(\mathbf{k}j)], \quad (26c)$$

and

$$\mathcal{L}\langle c_0(0j)c^*(0j; t) \rangle = (n_{0j} + 1)/s(1 - G_2), \quad (27)$$

where

$$G_2(s) = \left(\frac{\hbar}{2}\right) \sum_{\mathbf{k}''j'\mathbf{k}'j''} \frac{F(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')F(-\mathbf{k}''j''; -\mathbf{k}j; -\mathbf{k}'j')}{ss''\omega(\mathbf{k}j)\omega(\mathbf{k}''j'')} (n_{\mathbf{k}'j'} + \frac{1}{2}), \quad (27a)$$

$$s = i[\omega - \omega(\mathbf{k}j)] + \epsilon, \quad (27b)$$

$$s'' = s + i[\omega(\mathbf{k}'j') + \omega(\mathbf{k}''j'') + \omega(\mathbf{k}j)]. \quad (27c)$$

Utilizing the preceding results the complex dielectric susceptibility can be written in the form

$$\begin{aligned} \chi_{\mu\nu} &= \frac{i}{2v_a} \sum_j \frac{M_{\mu j} M_{\nu j}}{\omega(0j)} \left\{ [e^{\beta\hbar\omega(0j)} - 1] \frac{n_{0j}}{s[1 - G_1(s)]} \right\}_{s=i[\omega+\omega(0j)]+\epsilon} \\ &\quad + \frac{i}{2v_a} \sum_j \frac{M_{\mu j} M_{\nu j}}{\omega(0j)} \left\{ [e^{-\beta\hbar\omega(0j)} - 1] \frac{(n_{0j} + 1)}{s[1 - G_2(s)]} \right\}_{s=i[\omega-\omega(0j)]+\epsilon}, \end{aligned} \quad (28)$$

where v_a is the volume of a unit cell. If one substitutes the expression for n_{0j} specified by Eq. (25d) into Eq. (28)

and makes use of the relation

$$\lim_{\epsilon \rightarrow 0^+} \frac{1}{x - i\epsilon} = \mathcal{P}\left(\frac{1}{x}\right) + i\pi\delta(x), \quad (29)$$

where \mathcal{P} denotes the principal part, one obtains

$$\chi_{\mu\nu} = \frac{1}{2v_a} \sum_i \frac{M_{\mu j} M_{\nu j}}{\omega(0j)} \left\{ \frac{1}{\omega + \omega(0j) + \Delta\omega(0j) + i\Gamma(0j)} - \frac{1}{\omega - \omega(0j) - \Delta\omega(0j) - i\Gamma(0j)} \right\}. \quad (30)$$

The frequency shifts $\Delta\omega(0j)$ and damping constants $\Gamma(0j)$ are given by

$$\Delta\omega(0j) = \left(\frac{\hbar}{2}\right) \sum_{\mathbf{k}'j'\mathbf{k}''j''} \frac{|V(0j; \mathbf{k}'j'; \mathbf{k}''j'')|^2}{\omega(0j) |\omega(\mathbf{k}'j')| |\omega(\mathbf{k}''j'')|} (n_{\mathbf{k}'j'} + \frac{1}{2}) \mathcal{P} \frac{1}{\omega - \omega(\mathbf{k}'j') - \omega(\mathbf{k}''j'')}, \quad (31a)$$

$$\Gamma(0j) = \left(\frac{\pi\hbar}{2}\right) \sum_{\mathbf{k}'j'\mathbf{k}''j''} \frac{|V(0j; \mathbf{k}'j'; \mathbf{k}''j'')|^2}{\omega(0j) |\omega(\mathbf{k}'j')| |\omega(\mathbf{k}''j'')|} (n_{\mathbf{k}'j'} + \frac{1}{2}) \delta[\omega - \omega(\mathbf{k}'j') - \omega(\mathbf{k}''j'')]. \quad (31b)$$

In obtaining Eq. (31) we have replaced the dummy variables j', j'' by $-j', -j''$.

The form for $\chi_{\mu\nu}$ specified by Eq. (30) is the same as that found in II for the classical case, but the expressions for $\Delta\omega(0j)$ and $\Gamma(0j)$ are different. In the high-temperature limit, however, one sees from Eq. (25d) that

$$n_{\mathbf{k}'j'} \rightarrow kT/\hbar |\omega(\mathbf{k}'j')|,$$

and

$$\Delta\omega(0j) \rightarrow \frac{kT}{2} \sum_{\mathbf{k}'j'\mathbf{k}''j''} \frac{|V(0j; \mathbf{k}'j'; \mathbf{k}''j'')|}{\omega(0j)\omega^2(\mathbf{k}'j')\omega(\mathbf{k}''j'')} \mathcal{P} \frac{1}{\omega - \omega(\mathbf{k}'j') - \omega(\mathbf{k}''j'')}, \quad (32a)$$

$$\Gamma(0j) \rightarrow \frac{\pi kT}{2} \sum_{\mathbf{k}'j'\mathbf{k}''j''} \frac{|V(0j; \mathbf{k}'j'; \mathbf{k}''j'')|}{\omega(0j)\omega^2(\mathbf{k}'j')\omega(\mathbf{k}''j'')} \delta[\omega - \omega(\mathbf{k}'j') - \omega(\mathbf{k}''j'')], \quad (32b)$$

in agreement with the classical expressions in II. The present quantum mechanical theory therefore satisfies the requirement of the correspondence principle that it reduce to the classical result in the limit of high temperatures.

In the low-temperature limit $T \rightarrow 0$ the classical expressions for $\Delta\omega$ and Γ vanish. The quantum mechanical expressions given by Eq. (31) possess zero-point contributions, so that $\Delta\omega$ and Γ need not vanish as $T \rightarrow 0$.

3. COMPARISON WITH THE BORN-HUANG THEORY

In order to facilitate comparison of the present results with those of Born and Huang⁴ a brief review of the latter theory is presented. Born and Huang calculate the time-dependent wave functions which satisfy the time-dependent Schrödinger equation involving the complete Hamiltonian $H = H_0 + H_A + H_I$. Perturbation theory is employed with the eigenfunctions of the harmonic Hamiltonian H_0 taken as the basis. From the time-dependent wave functions Born and Huang calculate the thermal average of the expectation value of the electric dipole moment operator. The complex dielectric susceptibility is then obtained.

It is convenient to discuss the Born-Huang procedure in terms of second order perturbation theory involving the two perturbing terms H_A and H_I . From an initial state i the radiation may produce transitions to inter-

mediate states $\pm j$ followed by anharmonic transitions to the final state f . Alternatively, anharmonicity may produce transitions to intermediate states t followed by radiative transitions to the final state f . One of the weaknesses of the Born-Huang theory is that transitions from states t to states f are omitted. As pointed out by M. Lax,¹⁰ the omission of these transitions leads to incorrect results in the wings of the absorption region. In the present calculation all necessary intermediate states are included and the correct behavior in the wings is obtained.

The damping constants which occur in the Born-Huang theory describe the damping of individual quantum states and are calculated using a "reduced" anharmonic Hamiltonian given by

$$H_A^{\text{red}} = \sum_j Q(0j) \sum_{\mathbf{k}'j'\mathbf{k}''j''} V(0j; \mathbf{k}'j'; -\mathbf{k}''j'') \times Q(\mathbf{k}'j') Q(-\mathbf{k}''j''). \quad (33)$$

This reduced anharmonic contribution to the Hamiltonian is linear in the normal coordinates $Q(0j)$ which appear in the radiation interaction term H_I . Although Born and Huang offer a qualitative justification for using the reduced Hamiltonian, it does not occur in a natural way in their derivation. From a pragmatic

¹⁰ See A. A. Maradudin and R. F. Wallis, Phys. Rev. **120**, 442 (1960), footnote 13.

point of view, however, the reduced Hamiltonian leads to the very desirable result that the Born-Huang damping constants are intensive quantities as they should be. If the full anharmonic Hamiltonian were used in the Born-Huang procedure, the damping constants would turn out to be extensive properties. Brout¹¹ has noted this type of situation and has proposed that only differences of such damping constants should appear in intensive physical quantities. The Born-Huang theory, however, does not satisfy this criterion, for sums as well as differences of damping constants occur in their results.

The damping constants which occur in the present quantum mechanical theory have the necessary intensive character. This result is obtained by using the full anharmonic Hamiltonian and without an *ad hoc* introduction of a reduced Hamiltonian.

Another unsatisfactory feature of the Born-Huang theory is the proportionality of the damping constants to T^3 in the high-temperature limit. As a result the temperature dependence of the optical constants at high temperatures is not consistent with that obtained classically, in violation of the correspondence principle. As has been pointed out previously, the present theory does not suffer from this difficulty.

The two procedures under discussion in principle should lead to the same result if each were carried through exactly. In practice only terms which dominate at long times are retained in each case. Further approximations involve the omission of various terms which

arise in the perturbation procedures used in the two methods. It is of interest to note that the approximations enter the Born-Huang theory primarily in the calculation of the time-dependent wave functions for the various quantum states, whereas they enter the present theory in the calculation of the dielectric susceptibility itself. Although the Born-Huang procedure may lead to results for the wave functions which are satisfactory on an individual basis, it is not clear that their result for the dielectric susceptibility is consistent to the desired degree of approximation.

4. COMPARISON WITH EXPERIMENT

In the high-temperature limit the quantum mechanical theory for anharmonic lattice vibration absorption developed in this paper confirms the classical result that cubic anharmonic terms lead to frequency shifts and damping constants proportional to the first power of the absolute temperature. As mentioned in the introduction, the experimental data for LiF and NaCl near their respective melting points are described by damping constants which are more nearly proportional to the square of the absolute temperature. This discrepancy between theory and experiment suggests that cubic anharmonic terms alone are not adequate, at least in the cases of NaCl and LiF. Near the melting point of a crystal it seems reasonable that quartic and possibly higher order terms should be important. The effect of quartic anharmonic terms on infrared lattice vibration absorption is being investigated by D. W. Jepsen.

¹¹ R. Brout, Phys. Rev. **107**, 664 (1957).