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Theory of Impurity-Induced Infrared Absorption*†

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The problem of impurity-induced absorption of light due to a localized mode is studied on the basis of the Kubo linear-response theory. The equation of motion for the dipole-moment correlation function with respect to the localized mode is derived using Zwanzig's projection-operator method, and solved with the assumption that the anharmonic coupling between the localized mode and the remaining modes (the bath) is of the form $Q\Gamma$ and weak enough to allow a perturbation treatment. The variables Q and Γ represent the localized-mode normal coordinate and an arbitrary function of the bath coordinates, respectively. The first nonvanishing contribution is shown to be of second order in the coupling and to give an absorption band of Lorentzian shape whose width and shift are given by the real and imaginary parts of the half-interval Fourier transform of the correlation function $\langle[\Gamma,\Gamma(t)]\rangle^0$, where $\langle\cdots\rangle^0$ denotes an average over the canonical ensemble which represents the uncoupled bath. It follows directly from this result that the width and shift functions satisfy the Kramers-Kronig relations. In an Appendix, the width and shift expressions for the special case of an anharmonic crystal having up to quartic terms in the potential are derived and shown to be equivalent to Maradudin's calculation based on many-body diagram techniques.

1. INTRODUCTION

TRANSPORT properties depend upon the interaction or coupling between the constituent particles of the system and the manner in which energy is exchanged between them. In linear-response theory (LRT)[1] the transport coefficients are expressed in terms of correlation functions the calculation of which is often made difficult by the complicated nature in which exchange processes occur and the lack of sufficient data on molecular interaction.

Many workers have performed model calculations for lattice systems based on the LRT of Kubo[1] using an assumed form for the potential energy of the coupled system.[2] Further progress in the LRT of transport processes is expected to come from an analysis of the structure of correlation function formulas rather than from model calculations as pointed out by Zwanzig.[3]

The temperature dependence of the shape of an impurity-induced absorption band is a valuable source of information for molecular coupling. The impurity serves as a probe for studying the dynamical properties of the system when the band lies in an absorption-free region of the pure system.

The main goal of this paper is to provide a better understanding of molecular coupling by studying the optical absorption due to an impurity mode coupled linearly to the surrounding or bath. The system consists of a set of coupled oscillators to allow for energy exchange between bath and impurity. The coupling determines the absorption band shape.

Specifically, we consider the Hamiltonian of the system to be

$$H=H_I+H_B+\lambda\Gamma Q_I\,, \qquad (1.1)$$

where H_I is the Hamiltonian for an harmonic oscillator which represents the impurity mode, H_B is the Hamiltonian for the bath modes, and $\lambda\Gamma Q_I$ is the linear coupling term, assumed small. Here Γ is a function of the bath coordinates alone which are of quadratic or higher order and Q_I is the impurity mode normal coordinate.

According to the LRT of Kubo,[1] the electric susceptibility which describes light absorption is given by the Fourier transform of the autocorrelation function of the dipole moment of the system. For the calculation of the correlation function we find that Zwanzig's projection-operator technique[4] seems most effective. It is shown that the absorption band shape of an impurity mode coupled linearly to a heat bath is Lorentzian. This is true under mild assumptions: that the impurity absorption band does not overlap with other bands such as the restrahl band and that the coupling is weak. The width and shift of the absorption band are given by the real and imaginary parts of the half-interval Fourier transform of the autocorrelation function of Γ [see Eq. (6.10)] and thus it is a simple matter to see that the Kramers-Kronig relation holds between the width and shift as it should due to the linear approximation.

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[1] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[2] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273.

[3] R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965).

[4] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960); in *Lectures in Theoretical Physics*, edited by W. E. Britten, B. W. Downs, and J. Downs (Interscience Publishers, Inc., New York, 1961), Vol. 3.

This is a considerable simplification over the previous proof.[5,6]

We shall briefly outline the procedure to be followed in this paper. After a brief discussion of the Hamiltonian of the system, we proceed with a calculation of the electric susceptibility $\chi(\omega)$ making full use of the symmetry relations satisfied by the correlation functions appearing in $\chi(\omega)$, thereby simplifying the calculation. In fact, to get $\chi(\omega)$ we need the Fourier transform of only one function, namely, $G(t)=\langle aa^\dagger(t)\rangle$, where $a^\dagger$ and a are the creation and annihilation operators with respect to the localized mode, and $\langle\cdots\rangle$ represents the canonical ensemble average for the natural motion of the system. Next we transform an exact integro-differential equation derived for $G(t)$ into a form suitable for the weak-coupling approximation, i.e., exact up to the order of λ^2 in the coupling parameter λ. At this point we apply Van Hove's very elegant weak-coupling method[7] which involves the double limit, $\lambda\rightarrow 0$ as $t\rightarrow\infty$, with $\lambda^2 t$ kept finite. We also justify this procedure by solving the exact integro-differential equation for $G(t)$ directly. Comparison is also made with the work of Lax[8] in which he obtained a result similar to ours based on a zeroth-order Hartree approximation. We show that his result does not seem to prevail for arbitrary field strengths according to his supposition.[9]

2. HAMILTONIAN

Here we present the Hamiltonian in a form which determines the absorption band shape in the vicinity of the impurity mode frequency. The potential energy ϕ of an anharmonic crystal containing a substitutional point defect can be expanded in powers of the atomic displacements of q_i:

$$\phi=\frac{1}{2!}\sum_{ij}\phi_{ij}q_iq_j+\frac{1}{3!}\sum_{ijk}\phi_{ijk}q_iq_jq_k+\frac{1}{4!}\sum_{ijkl}\phi_{ijkl}q_iq_jq_kq_l+\cdots \qquad (i,j,k,l=1,2,\cdots,f)\,, \tag{2.1}$$

where f is the total number of degrees of freedom of the system. The coefficients ϕ_{ij}, ϕ_{ijk}, ϕ_{ijkl}, $\cdots$, are the quadratic, cubic, quartic, etc., atomic force constants.

In order to define the quantities involved in the present calculation we shall sketch a normal coordinate transformation which leads to the so-called creation and annihilation operators $a_i^\dagger$, a_i given by[10]

$$q_i=\left(\frac{\hbar}{2m_i}\right)^{1/2}\sum_{s=1}^{f}(\omega_s)^{-1/2}B_i^{(s)}(a_s+a_s^\dagger) \qquad (i=1,2,\cdots,f)\,, \tag{2.2}$$

where $B_i^{(s)}$ are the orthonormalized eigenvectors of the following eigenvalue problem:

$$\sum_{j=1}^{f}D_{ij}B_j^{(s)}=\omega_s^2B_i^{(s)}\,.$$

The matrix D is defined by

$$D_{ij}=\phi_{ij}/(m_im_j)^{1/2}$$

and m_i is the mass of the ith particle. By definition the matrix D is a $f\times f$ real, symmetric matrix with f eigenvalues $\{\omega_s^2\}$. The quantities ω_s are the normal mode frequencies of the system. The operators $a_i^\dagger$, a_i satisfy the commutation relations

$$[a_i,a_j^\dagger]=\delta_{ij}\,,\qquad [a_i,a_j]=[a_i^\dagger,a_j^\dagger]=0\,. \tag{2.3}$$

Since we are interested in the absorption due to the impurity mode whose frequency ω_I is larger than any other frequencies ω_b of the remaining modes (referred to as the bath), we shall write the Hamiltonian in the form

$$H=H_0+\lambda H'=H_I+H_B+\lambda H'\,, \tag{2.4}$$

$$H_I=\sum_I\hbar\omega_I(a_I^\dagger a_I+\tfrac{1}{2})\,, \tag{2.5}$$

$$H_B=\sum_b\hbar\omega_b(a_b^\dagger a_b+\tfrac{1}{2})\,, \tag{2.6}$$

$$H'=\sum_I\Gamma_IQ_I+\cdots\,, \tag{2.7}$$

where $\hbar$ equals Planck's constant divided by 2π and $Q_I=a_I^\dagger+a_I$. The perturbation term H' describes the coupling between various modes, and the first sum in H' arises from the terms which are linear in the impurity normal coordinates. In the following calculation we keep only this term and neglect the rest, which lead either to side-band structure[11] or to higher-order effects. The Γ_I depend upon the bath variables quadratically in the lowest order. The explicit expression is easily obtained by using the normal coordinate transformation given in Eq. (2.2) and using the orthonormal properties of the eigenvectors $B_i^{(s)}$. Then for Γ_I we have

$$\Gamma_I=\Gamma^{(2)}+\Gamma^{(3)}+\cdots\,, \tag{2.8}$$

where

$$\Gamma^{(n)}=(n+1)\sum_{S_1S_2\cdots S_n}{}'\,\Phi_{IS_1S_2\cdots S_n}Q_{S_1}Q_{S_2}\cdots Q_{S_n}\,. \tag{2.9}$$

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[5] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 19, p. 1.

[6] A. A. Maradudin, A. E. Fein, and G. H. Vineyard, Phys. Status Solidi **2**, 1479 (1962).

[7] L. Van Hove, Physica **21**, 517 (1955).

[8] M. Lax, J. Phys. Chem. Solids **25**, 487 (1964).

[9] P. T. Landsberg and E. A. B. Cole, Physica **37**, 309 (1967).

[10] A. A. Maradudin, Rept. Progr. Phys. **28**, 331 (1965).

[11] J. B. Page, Jr., and B. G. Dick, Phys. Rev. **163**, 910 (1967).

Here the prime on the summation denotes the condition $s_1 \neq I, \cdots, s_n \neq I$ and the factor $n+1$ accounts for this. The coefficients $\Phi_{Is_1 \cdots s_n}$ are linear combinations of the ϕ's given in Eq. (2.1). For completeness we have given the explicit dependence of Γ on the bath phonon coordinates. However, we may not need these expressions until we compare the present result with that of previous calculations, which we have done in the Appendix.

3. ELECTRIC SUSCEPTIBILITY

In order to calculate the impurity-induced absorption band shape we use the LRT of Kubo[1] in which the absorption coefficient $\alpha_{xx}(\omega)$ for an isotropic system interacting with light of frequency ω and plane polarized in the x direction is given by

$$\alpha_{xx}(\omega) = (4\pi\omega/c\eta(\omega))\chi_{xx}''(\omega)\,, \tag{3.1}$$

where

$$\chi_{xx}'' = -\mathrm{Im}\chi_{xx}$$

and is given in terms of the Fourier transform of the autocorrelation function of the dipole-moment operator M_x of the system in the x direction:

$$\chi_{xx}''(\omega) = \frac{(1-e^{\beta\hbar\omega})}{2\hbar V}\int_{-\infty}^{\infty} e^{-i\omega t - \epsilon|t|}\langle M_x M_x(t)\rangle dt\,. \tag{3.2}$$

Here V is the volume of the system, c is the velocity of light, $\eta(\omega)$ is the index of refraction, and ϵ is an infinitely small positive quantity. In the following we shall omit ϵ, it being understood that all infinite integrals are taken in the above Abel limit.[1]

The dipole moment M_x of the system in the x direction is defined by

$$M_x = \sum_i e_i q_x^{(i)}\,, \tag{3.3}$$

where the quantities e_i, $q_x^{(i)}$ are the effective charge and displacement in the x direction of the ith particle of the system. The Heisenberg operator $M_x(t)$ in Eq. (3.2) is defined by

$$M_x(t) = e^{iHt/\hbar} M_x e^{-iHt/\hbar}\,, \tag{3.4}$$

while $\langle \cdots \rangle$ denotes the canonical ensemble average for the natural motion of the system which is described by the Hamiltonian H, i.e.,

$$\langle X\rangle = \mathrm{Tr}e^{-\beta H}X/\mathrm{Tr}e^{-\beta H}, \quad \beta = 1/kT\,. \tag{3.5}$$

If we expand the dipole moment of the system in terms of $a_i^\dagger$, a_i defined by the normal coordinate transformation given in Eq. (2.2), then we find

$$\langle M_x M_x(t)\rangle \approx N_I \sum_i c_i^{(x)} \langle (a_i + a_i^\dagger)(a_i(t) + a_i^\dagger(t))\rangle$$
$$\approx N_I C(\langle a^\dagger a(t)\rangle + \langle a a^\dagger(t)\rangle)\,, \tag{3.6}$$

where the number of impurity ions N_I has been introduced to account for a finite concentration of noninteracting impurities. To obtain Eq. (3.6) we have neglected the cross terms and the correlation functions $\langle a_I a_I(t)\rangle$ and $\langle a_I^\dagger a_I^\dagger(t)\rangle$ which either lead to higher-order effects[10] or absorption removed from that of interest.[11] From general cubic-symmetry arguments we picked out only one of the three degenerate localized modes to determine $\langle M_x M_x(t)\rangle$ and for convenience dropped the subscript I on $a_I^\dagger$ and a_I. The constants in these expansions, $c_i^{(x)}$ and C, have been given for a rigid ion model by Maradudin.[5]

We can simplify Eq. (3.6) further by means of the following symmetry relation:

$$\mathrm{Re}\int_0^\infty \langle a^\dagger a(t)\rangle e^{-i\omega t}dt = e^{\beta\hbar\omega}\,\mathrm{Re}\int_0^\infty \langle a a^\dagger(t)\rangle e^{i\omega t}dt\,. \tag{3.7}$$

This symmetry relation may be verified easily in terms of the matrix representation which diagonalizes H using the properties of the Dirac delta function. Substituting Eq. (3.6) into Eq. (3.2) and using Eq. (3.7), we can write $\chi_{xx}''(\omega)$ in the form

$$\chi_{xx}''(\omega) = N_I C(\psi(\omega) - \psi(-\omega))\,, \tag{3.8}$$

where

$$\psi(\omega) = 2(1-e^{-\beta\hbar\omega})\,\mathrm{Re}\hat{G}(\omega) \tag{3.9}$$

and $\hat{G}(\omega)$ is the half-interval Fourier transform of $G(t)$:

$$\hat{G}(\omega) = \int_0^\infty G(t)e^{-i\omega t}dt\,,$$
$$G(t) = \langle a a^\dagger(t)\rangle\,. \tag{3.10}$$

Accordingly, the calculation of χ_{xx}'' has been reduced to the evaluation of one correlation function, namely, $G(t) = \langle a a^\dagger(t)\rangle$, which we shall consider in Sec. 4.

4. DERIVATION OF INTEGRO-DIFFERENTIAL EQUATION FOR $G(t)$

We shall now derive an integro-differential equation for the correlation function $G(t)$ using Zwanzig's projection-operator method,[4] which we have found to be the simplest and most direct for our purposes. Application of the method to our problem necessitates the choice of an appropriate projection operator which projects out that part of $a^\dagger(t)$ which contributes to $G(t)$, i.e.,

$$\langle a\mathbf{P}a^\dagger(t)\rangle = \langle a a^\dagger(t)\rangle = G(t)\,. \tag{4.1}$$

The relevant and irrelevant parts are defined by

$$a_R^\dagger(t) = \mathbf{P}a^\dagger(t)\,, \tag{4.2}$$

$$a^\dagger{}_{IRR}(t) = (1-\mathbf{P})a^\dagger(t)\,. \tag{4.3}$$

Consequently, $a^\dagger(t)$ can be written as the sum of its relevant and irrelevant parts,

$$a^\dagger(t) = a_R^\dagger(t) + a_{IRR}^\dagger(t)\,. \tag{4.4}$$

A suitable projection operator for our purposes is defined according to its action on any arbitrary operator X as follows:

$$\mathbf{P}X(t)=a^\dagger\langle aX(t)\rangle/\langle aa^\dagger\rangle. \tag{4.5}$$

This operator is certainly a projection operator since by definition

$$\mathbf{P}^2X(t)=\mathbf{P}X(t). \tag{4.6}$$

In order to obtain the equation of motion for $G(t)$ we shall make use of the Liouville equation for $a^\dagger(t)$ given by

$$\dot{a}^\dagger(t)=(i/\hbar)[H,a^\dagger(t)]=iLa^\dagger(t). \tag{4.7}$$

Following Zwanzig's procedure for the elimination of the irrelevant part $a_{IRR}{}^\dagger(t)$, we calculate the time derivative of $a_R{}^\dagger$ and $a_{IRR}{}^\dagger$ to obtain

$$\dot{a}_R{}^\dagger(t)=i\mathbf{P}La_R{}^\dagger(t)+i\mathbf{P}La_{IRR}{}^\dagger(t), \tag{4.8}$$

$$\dot{a}_{IRR}{}^\dagger(t)=i(1-\mathbf{P})La_R{}^\dagger(t)+i(1-\mathbf{P})La_{IRR}{}^\dagger(t), \tag{4.9}$$

where we have used Eqs. (4.4) and (4.7). Solving Eq. (4.9) formally for $a_{IRR}{}^\dagger(t)$ in terms of $a_R{}^\dagger(t)$ and substituting into Eq. (4.8), we arrive at

$$\dot{a}_R{}^\dagger(t)=i\mathbf{P}La_R{}^\dagger(t) - \int_0^t \mathbf{P}Le^{i(1-\mathbf{P})Lt'}La_R{}^\dagger(t-t')dt', \tag{4.10}$$

where we have used the following initial condition $[a_{IRR}{}^\dagger(0)=0]$, which is obvious from the definition of $\mathbf{P}$. From Eqs. (4.1) and (4.10) we immediately obtain

$$\dot{G}(t)=\langle a\dot{a}_R{}^\dagger(t)\rangle=igG(t)-\int_0^t K(t')G(t-t')dt'. \tag{4.11}$$

Here the quantity g is a function of temperature alone which is defined by

$$g=\langle\langle aLa^\dagger\rangle\rangle, \tag{4.12}$$

the kernel $K(t)$ is a function of time which is given by

$$K(t)=-\langle\langle(La)e^{i(1-\mathbf{P})Lt}(1-\mathbf{P})(La^\dagger)\rangle\rangle, \tag{4.13}$$

and the double-brackets notation

$$\langle\langle X\rangle\rangle=\langle X\rangle/\langle aa^\dagger\rangle \tag{4.14}$$

has been introduced for convenience to make $\langle\langle aa^\dagger\rangle\rangle=1$. With this notation we immediately observe the following rules:

$$\langle\langle X\mathbf{P}Y\rangle\rangle=\langle\langle Xa^\dagger\rangle\rangle\langle\langle aY\rangle\rangle, \tag{4.15}$$

$$\langle\langle aLX\rangle\rangle=-\langle\langle(La)X\rangle\rangle, \tag{4.16}$$

which we have used in obtaining Eq. (4.13). It is important to note that the operators $\mathbf{P}$ and L operate on everything which follows them unless otherwise specified, as in the case of the first L on the right-hand side of Eqs. (4.13) and (4.16), which acts only on a as denoted by the parentheses.

5. EVALUATION OF KERNEL $K(t)$ AND FUNCTION g TO $O(\lambda^2)$

As stated earlier, we are interested in evaluating the correlation function $G(t)$ in the weak-coupling limit. In the following we shall calculate the kernel $K(t)$ and the function g up to $O(\lambda^2)$, which for $K(t)$ is indeed the first nonvanishing term as usual.

Kernel $K(t)$

We shall first calculate $(La^\dagger)$ and (La) in the kernel. For this purpose it is convenient to write the Liouville operator in the form

$$LX=L^0X+\lambda L'X=(1/\hbar)[H^0,X]+(\lambda/\hbar)[H',X], \tag{5.1}$$

where H^0 and H' are defined by Eqs. (2.4) and (2.7) and L^0, L' are the respective Liouville operators. Since H^0 describes the unperturbed motion of harmonic oscillators, we immediately have

$$L^0a^\dagger=\omega_Ia^\dagger,\quad L^0a=-\omega_Ia. \tag{5.2}$$

Substituting Eqs. (5.1) and (5.2) into Eq. (4.13), we can eliminate L^0 from L contained in the parentheses to obtain

$$K(t)=-\lambda^2\langle\langle(L'a)e^{i(1-P)Lt}(1-\mathbf{P})(L'a^\dagger)\rangle\rangle, \tag{5.3}$$

where the following identities for an arbitrary X are used:

$$X(1-\mathbf{P})a^\dagger=0,\quad \langle\langle a(1-\mathbf{P})X\rangle\rangle=0.$$

Since we are interested in $K(t)$ to $O(\lambda^2)$, and λ^2 appears in front of the double brackets, we need to calculate the double brackets only up to the zeroth order in λ. Thus we may replace L, $\mathbf{P}$ and $\langle\langle\cdots\rangle\rangle$ by the respective zeroth-order quantities to obtain

$$K(t)=-\lambda^2\langle\langle(L'a)e^{i(1-\mathbf{P}^0)L^0t}(1-\mathbf{P}^0)(L'a^\dagger)\rangle\rangle^0 + O(\lambda^2), \tag{5.4}$$

where $\mathbf{P}^0$ and $\langle\langle\cdots\rangle\rangle^0$ are defined by

$$\mathbf{P}^0X=a^\dagger\langle\langle aX\rangle\rangle^0=a^\dagger\,\mathrm{Tr}(e^{-\beta H^0}aX)/\mathrm{Tr}(e^{-\beta H^0}aa^\dagger). \tag{5.5}$$

Next the formidable operator $\mathbf{P}^0$ in the exponential on the right-hand side of Eq. (5.4) is eliminated by using the fact that the operators L^0 and $\mathbf{P}^0$ commute, i.e., $L^0\mathbf{P}^0X=\mathbf{P}^0L^0X$, since both sides are equal for an arbitrary operator X. We see this directly from the relations

$$L^0\mathbf{P}^0X=L^0a^\dagger\langle\langle aX\rangle\rangle^0=\omega_Ia^\dagger\langle\langle aX\rangle\rangle^0=\omega_I\mathbf{P}^0X,$$

$$\mathbf{P}^0L^0X=a^\dagger\langle\langle aL^0X\rangle\rangle^0=-a^\dagger\langle\langle(L^0a)X\rangle\rangle^0=\omega_I\mathbf{P}^0X,$$

where we have used Eq. (5.2). Accordingly, the exponential appearing in Eq. (5.4) can be factorized to give

$$e^{i(1-\mathbf{P}^0)L^0t}(1-\mathbf{P}^0)X=e^{iL^0t}(1-\mathbf{P}^0)X, \tag{5.6}$$

where besides the fact that L^0 and $\mathbf{P}^0$ commute we have used the identity $\mathbf{P}^0(1-\mathbf{P}^0)=0$. Thus we obtain for

$K(t)$ the form

$$K(t)=-\lambda^2\langle\langle(L'a)e^{iL^0t}(1-\mathbf{P}^0)(L'a^\dagger)\rangle\rangle^0+O(\lambda^3). \quad (5.7)$$

For further simplification it is necessary to use the linear-coupling assumption [Eq. (2.7)] which gives a specific form for L' defined by Eq. (5.1). In this case we have

$$L'a^\dagger=\Gamma/\hbar, \quad L'a=-\Gamma/\hbar, \quad (5.8)$$

where we have used the commutator relations for a and $a^\dagger$, and accordingly we have

$$\mathbf{P}^0L'a^\dagger=a^\dagger\langle\langle a\rangle\rangle^0\langle\langle\Gamma\rangle\rangle^0/\hbar=0. \quad (5.9)$$

Here we have used the fact that the matrix a has diagonal elements which are all zero. Substitution of Eqs. (5.8) and (5.9) into Eq. (5.7) along with the definition of L^0 yields

$$K(t)=(\lambda/\hbar)^2\langle\langle\Gamma\Gamma(t)\rangle\rangle^0+O(\lambda^3). \quad (5.10)$$

Thus for the linear-coupling approximation the kernel in the lowest order becomes simply the autocorrelation function of Γ, a function of bath variables only, averaged over the unperturbed equilibrium ensemble.

Function *g*

We shall not calculate the function g up to the $O(\lambda^2)$. For this purpose we write g given by Eq. (4.12) in a more convenient form,

$$g=\omega_I+\lambda\langle\langle aL'a^\dagger\rangle\rangle=\omega_I+(\lambda/\hbar)\langle\langle a\Gamma\rangle\rangle, \quad (5.11)$$

where we have used Eqs. (4.12), (5.2), and (5.8). First we shall write the explicit form for $\langle\langle a\Gamma\rangle\rangle$:

$$\langle\langle a\Gamma\rangle\rangle=\mathrm{Tr}(e^{-\beta H}a\Gamma)/\langle aa^\dagger\rangle \quad (5.12)$$

and the well-known expansion formula for $e^{-\beta H}$:

$$e^{-\beta H}=e^{-\beta H^0}\left(1+\frac{i\lambda}{\hbar}\int_0^{i\hbar\beta}H'(-t)dt\right)+O(\lambda^2), \quad (5.13)$$

where here we may give the explicit expression for $H'(-t)$:

$$\begin{aligned}H'(-t)&=e^{-iH^0t/\hbar}(a+a^\dagger)\Gamma e^{iH^0t/\hbar}\\&=(a^\dagger e^{-i\omega_It}+ae^{i\omega_It})\Gamma(-t). \quad (5.14)\end{aligned}$$

Substituting Eqs. (5.12)–(5.14) into Eq. (5.11) and using the relation

$$\langle a^\dagger a\rangle/\langle aa^\dagger\rangle=e^{-\beta\hbar\omega_I}+O(\lambda^2)$$

and the fact that $\langle a^2\rangle^0=0$, $\langle a\rangle^0=0$, which are true since both a^2 and a are matrices whose diagonal matrix element are all zero, we have

$$g=\omega_I+i(\lambda/\hbar)^2S(\omega_I)+O(\lambda^3), \quad (5.15)$$

where the function $S(\omega_I)$, defined by

$$S(\omega_I)=\int_0^{i\hbar\beta}\langle\Gamma\Gamma(t)\rangle^0e^{i\omega_It}dt, \quad (5.16)$$

satisfies the following useful symmetry relation:

$$S(\omega_I)=e^{-\beta\hbar\omega_I}S(-\omega_I), \quad (5.17)$$

which can be easily proven by changing integral variable from t to $i\hbar\beta-t$ and using the cyclic invariance of the trace.

For later use it is more convenient to switch the integration in $S(\omega_I)$ from the imaginary time axis to the real time axis by using Cauchy's integral theorem and the fact that the correlation function $\langle\Gamma\Gamma(t)\rangle^0$ is analytic in the domain $0\leq\mathrm{Im}t\leq\hbar\beta$ of the complex t plane. Then

$$S(\omega)=\int_0^\infty\langle\Gamma\Gamma(t)\rangle^0e^{i\omega t}dt-\int_{i\hbar\beta+0}^{i\hbar\beta+\infty}\langle\Gamma\Gamma(t)\rangle^0e^{i\omega t}dt$$

since the contribution from the path at infinity is zero under the usual assumption[1] $\lim_{t\to\infty}\langle\Gamma\Gamma(t)\rangle^0=0$. Straightforward calculation along with the use of the symmetry relation given in Eq. (5.17) yields the desired form,

$$S(\omega)=e^{-\beta\hbar\omega}\int_0^\infty\langle\Gamma\Gamma(t)\rangle^0e^{-i\omega t}dt-\int_0^\infty\langle\Gamma(t)\Gamma\rangle^0e^{-i\omega t}dt. \quad (5.18)$$

6. SOLUTION OF INTEGRO-DIFFERENTIAL EQUATION FOR *G*(*t*)

We shall first solve the differential equation for $G(t)$, Eq. (4.11), in the Van Hove weak-coupling limit[7] which is chosen for its elegance and easy application to our problem. Later we shall justify its validity by direct calculation.

To begin with we shall introduce a function $F(x)$ defined by

$$F(x)=e^{-igt}G(t), \quad x=\lambda^2t, \quad (6.1)$$

where the variable x is introduced to take the Van Hove limit, i.e., $\lambda\to0$, $t\to\infty$, and x kept constant. Then, in terms of F, Eq. (4.11) may be written as

$$\frac{dF(x)}{dx}=-\int_0^{x/\lambda^2}\left\{\frac{K(t')}{\lambda^2}\right\}e^{-igt'}F(x-\lambda^2t')dt'. \quad (6.2)$$

Since $\{K(t)/\lambda^2\}$ is of $O(1)$ from Eq. (5.10) and $g=\omega_I+O(\lambda^2)$ from Eq. (5.15), the Van Hove limit of this equation yields

$$dF(x)/dx=-\{\hat{K}(\omega_I)/\lambda^2\}F(x), \quad (6.3)$$

where $\hat{K}(\omega_I)$ is the half-interval Fourier transform of the kernel $K(t)$,

$$\hat{K}(\omega_I)=\int_0^\infty K(t)e^{-i\omega_It}dt. \quad (6.4)$$

We can write the solution immediately,

$$F(x)=e^{-\{\hat{K}(\omega_I)/\lambda2\}x}F(0), \quad (6.5)$$

or using Eq. (6.1) we have for $G(t)$,

$$G(t)=e^{\{ig-\hat{K}(\omega_I)\}t}G(0). \tag{6.6}$$

Accordingly, the half-interval Fourier transform of $G(t)$ is

$$\hat{G}(\omega)=G(0)/[i(\omega-g)+\hat{K}(\omega_I)]. \tag{6.7}$$

The validity of this result based on the Van Hove limit can be verified in the following manner. We take the Fourier transform of Eq. (4.11) directly to obtain the exact result

$$\hat{G}(\omega)=G(0)/[i(\omega-g)+\hat{K}(\omega)]. \tag{6.8}$$

Comparison of Eqs. (6.7) and (6.8) shows that the sole difference lies in the argument of the function $\hat{K}(\omega)$. If this function is a slowly varying function of ω in the neighborhood of ω_I, so that we can write

$$\hat{K}(\omega)=\hat{K}(\omega_I)+O(\omega-\omega_I),$$

then the first term in the expansion gives the result of the Van Hove limit. Because of the basic assumption of separating the impurity mode from the rest which is valid only near the band center, the Van Hove limit seems as good as the last expression.

Substituting the explicit forms for $\hat{K}(\omega_I)$ and g given by Eqs. (5.10) and (5.15), we immediately obtain

$$\hat{G}(\omega)=G(0)/[i(\omega-\omega_I)+\gamma(\omega_I)], \tag{6.9}$$

where in going from the double- to single-brackets form for $K(t)$ we used the relation $\langle aa^\dagger\rangle^0=(1-e^{-\beta\hbar\omega_I})^{-1}$. The function $\gamma(\omega_I)$ is the half-interval Fourier transform of the ensemble average of the commutator $[\Gamma,\Gamma(t)]$ with respect to the unperturbed bath,

$$\gamma(\omega_I)=\left(\frac{1}{\hbar}\right)^2\int_0^\infty\langle[\Gamma,\Gamma(t)]\rangle^0e^{-i\omega_It}dt, \tag{6.10}$$

where now we have set $\lambda=1$.

The main result of our method, which clearly shows all the approximations involved in the derivation, is embodied in this simple and interesting form for $\gamma(\omega_I)$.

Based on the zeroth-order Hartree approximation, Lax[8] has obtained a similar expression as that given above; however, his method does not seem to define the approximation involved in his derivation. Thus his supposition of the validity of the expression for the case of high external field does not seem to prevail[9] since the present calculation shows that one probably needs the linear approximation in the sense of the Kubo LRT.

In order to express the final results for the absorption coefficient in its simplest form we shall define the real and imaginary parts of $\gamma(\omega)$ by

$$\gamma(\omega)=\gamma_1(\omega)-i\gamma_2(\omega). \tag{6.11}$$

Then by definition from Eq. (6.10) we have

$$\gamma_1(\omega)=\left(\frac{1}{i\hbar^2}\right)\int_0^\infty\langle[\Gamma,\Gamma(t)]\rangle^0\sin\omega t\,dt$$

and

$$\gamma_2(\omega)=\left(\frac{i}{\hbar^2}\right)\int_0^\infty\langle[\Gamma,\Gamma(t)]\rangle^0\cos\omega t\,dt. \tag{6.12}$$

Obviously the functions γ_1 and γ_2 satisfy the following symmetry relations:

$$\gamma_1(-\omega)=-\gamma_1(\omega),\quad\gamma_2(-\omega)=\gamma_2(\omega) \tag{6.13}$$

and the Kramers-Kronig relations[12,13]

$$\gamma_1(\omega)=-\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\gamma_2(\omega')}{\omega-\omega'}d\omega'. \tag{6.14}$$

One simple way to see this last relation may be to introduce the expression for $\gamma(\omega)$ given in Eq. (6.10) in the matrix representation which diagonalizes the Hamiltonian H_B for the bath and then to use the properties of the Dirac delta function.

We may now write the absorption coefficient $a_{xx}(\omega)$ in its final form:

$$\alpha_{xx}(\omega)=[8\pi\omega/c\eta(\omega)]C\gamma_1(\omega_I)\{[(\omega-\omega_I+\gamma_2)^2+\gamma_1^2]^{-1}+[(\omega+\omega_I+\gamma_2)^2+\gamma_1^2]^{-1}\} \tag{6.15}$$

$$\cong[8\pi\omega/c\eta(\omega)]C\gamma_1(\omega_I)\times[(\omega-\omega_I+\gamma_2)^2+\gamma_1^2]^{-1}, \tag{6.16}$$

where we have substituted Eq. (6.9) for the Fourier transform $\hat{G}(\omega)$ into Eq. (3.9), used the definition of α_{xx} given by Eq. (3.1), and evaluated the coefficient of $\psi(\omega)$ at ω_I. In going from Eq. (6.9) to Eq. (6.10) we have as usual neglected the second term as small compared to the first to give finally a Lorentzian line shape for the absorption band when the frequency ω is located near the impurity frequency ω_I.

7. DISCUSSION

Recently, Berne *et al.*[14] have derived an exact integrodifferential equation for classical correlation functions in general. Their working equation is essentially identical to ours in the classical limit. Rice has made the interesting ansatz that the kernel in his equation is exponential form. We note that our results confirm Rice's ansatz and in addition provide an explicit expression for the kernel in terms of the correlation function $\langle[\Gamma,\Gamma(t)]\rangle^0$; however, the present result is valid for the classical or quantum domain and for any temperature in the long-time and weak-coupling limits.

Finally, it would seem that the present method is also suitable for the discussion of other impurity absorption

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[12] H. A. Kramers, Att. Cong. Intern. Fis. Como **2**, 545 (1927).

[13] R. de L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926).

[14] B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. **45**, 1086 (1966).

phenomena associated with lasers,[15] neutron scattering in liquids,[16] and thermal conductivity.[17] At least the correlation functions which appear in the various linear-response theories are formally similar in structure to those which appear in this paper. In fact the strong formal resemblance between our width and shift functions with the linear response formula for the thermal conductivity itself suggests the eventual possibility of correlating the optical properties to such other transport properties as thermal conductivity for impurity systems.

APPENDIX

We shall show that the present integral forms for the width and shift [Eq. (6.12)] are equivalent to those of Maradudin's if we take the form for Γ expressed in terms of the bath phonon normal coordinates given by Eq. (2.9). We outline the method only for those terms which arise from two- and three-phonon processes, namely, $\Gamma^{(2)}$ and $\Gamma^{(3)}$. From Eq. (2.9) the Heisenberg operator $\Gamma^{(2)}(t)$ can be written as

$$\Gamma^{(2)}(t)=3\sum_{rs}{}'\,\Phi_{Irs}Q_r(t)Q_s(t). \tag{A1}$$

We then have for the correlation function

$$\langle[\Gamma^{(2)},\Gamma^{(2)}(t)]\rangle^0=9\sum_{rs}{}'\sum_{r's'}{}'\,I_{rs}\Phi_{r's'} \times\langle[Q_rQ_s,Q_{r'}(t)Q_{s'}(t)]\rangle^0. \tag{A2}$$

By straightforward calculation of the commutators on the right-hand side of Eq. (A2) we can express them in terms of the following two quantities:

$$[Q_r,Q_r(t)]=e^{i\omega_rt}-e^{-i\omega_rt},$$
$$\langle Q_rQ_r(t)\rangle^0=(n_r+1)e^{i\omega_rt}+n_re^{-i\omega_rt},$$

where $n_r=(e^{\beta\hbar\omega_r}-1)^{-1}$. Thus we obtain

$$\langle[\Gamma^{(2)}\Gamma^{(2)}(t)]\rangle^0 =18\sum_{rs}{}'\,\Phi_{rs}{}^2\{(n_r+n_s+1)[e^{i(\omega_r+\omega_s)t}-e^{-i(\omega_r+\omega_s)t}] +2(n_r-n_s)e^{-i(\omega_r-\omega_s)t}\}. \tag{A3}$$

We note that the cross terms from Eq. (A1) have been removed since, as is readily verified, their contribution to the ensemble average is zero. We take the half-interval Fourier transform of the correlation function according to Eq. (6.10) to arrive at the following result for $\gamma^{(2)}(\omega_I)$ which describes two-phonon processes:

$$\begin{aligned}\gamma^{(2)}(\omega_I)&=\frac{1}{\hbar^2}\int_0^\infty e^{-i\omega_It}\langle[\Gamma^{(2)},\Gamma^{(2)}(t)]\rangle^0dt\\&=\frac{18}{\hbar^2}\sum_{rs}{}'\,\Phi_{Irs}{}^2\{(n_r+n_s+1)[\theta(\omega_I-\omega_r-\omega_s)\\&\quad-\theta(\omega_I+\omega_r+\omega_s)]+2(n_r-n_s)\theta(\omega_I+\omega_r-\omega_s)\},\end{aligned} \tag{A4}$$

where

$$\theta(\omega)=\int_0^\infty e^{-i\omega t-\epsilon t}dt=\pi\delta(\omega)-iP(1/\omega). \tag{A5}$$

As usual $\delta(\omega)$ and $P(1/\omega)$ denote Dirac's delta function and the principal part, respectively. Obviously the real part of $\gamma^{(2)}(\omega_I)$ describes the width and the imaginary part describes the shift.

When two phonon processes do not contribute to the band shape due to the condition $2\omega_{\text{max}}<\omega_I$, then we must consider three-phonon processes and accordingly the function

$$\Gamma^{(3)}(t)=4\sum_{rsp}{}'\,\Phi_{Irsp}Q_r(t)Q_s(t)Q_p(t). \tag{A6}$$

A similar calculation as that presented above for the two-phonon processes along with the use of Wick's theorem[18] gives, for the function $\gamma^{(3)}(\omega_I)$ defined by

$$\gamma^{(3)}(\omega_I)=(1/\hbar^2)\int_0^\infty e^{-i\omega_It}\langle[\Gamma^{(3)},\Gamma^{(3)}(t)]\rangle^0dt, \tag{A7}$$

the following result for three-phonon processes:

$$\begin{aligned}\gamma^{(3)}(\omega_I)=\frac{96}{\hbar^2}\sum_{rsp}{}'\,\Phi_{Irsp}{}^2\{&[(n_r+1)(n_s+1)(n_p+1)-n_rn_sn_p]\\&\times[\theta(\omega_I-\omega_r-\omega_s-\omega_p)-\theta(\omega_I+\omega_r+\omega_s+\omega_p)]\\&+3[n_r(n_s+1)(n_p+1)-(n_r+1)n_sn_p]\\&\times[\theta(\omega_I+\omega_r-\omega_s-\omega_p)-\theta(\omega_I-\omega_r+\omega_s+\omega_p)]\},\end{aligned} \tag{A8}$$

where the terms corresponding to one-phonon processes are neglected.

In summary, the results presented above which are valid for $\omega\approx\omega_I$ are in essential agreement with those of Maradudin at this frequency except for the two small frequency-independent quartic terms which he included in his shift expression.[5]

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[15] I. R. Senitzky, Phys. Rev. **119**, 670 (1960).

[16] L. Glass and S. A. Rice, Phys. Rev. **165**, 186 (1968).

[17] R. A. Cowley, Advan. Phys. **12**, 421 (1963).

[18] G. C. Wick, Phys. Rev. **80**, 268 (1950); C. Bloch and C. de Dominicis, Nucl. Phys. **7**, 459 (1958).