PHYSICAL REVIEW VOLUME 186, NUMBER 3 15 OCTOBER 1969

Some Properties of Phonon Thermal-Conductivity Resonances*

MILES V. KLEIN†
Sandia Laboratories, Albuquerque, New Mexico 87115 and University of Illinois, Urbana, Illinois 61801
(Received 28 March 1969)

A unified treatment is given of impurity-induced phonon scattering resonances in thermal conductivity. A mean scattering rate may be defined within the relaxation-time approximation which has a nearly common Lorentzian form for all resonances occurring at a given frequency, except that the width may vary. The peak mean scattering rate is nearly independent of everything about the impurity except the resonance frequency and the degeneracy of the resonance mode. Three impurity types are discussed in detail and compared: (a) a substitutional impurity with no internal degrees of freedom, (b) an impurity with an internal harmonic-oscillator degree of freedom, and (c) an impurity with an internal degree of freedom having just two energy levels. The dominant role of resonance widths in determining thermal-conductivity dips is emphasized, and additional line-shape effects are discussed.

I. INTRODUCTION

THE purpose of this paper is to derive and discuss expressions for the rate of scattering of phonons by three different types of resonant systems: (a) a substitutional harmonic point defect, (b) a substitutional harmonic oscillator, and (c) a substitutional 2-level atom (2-level tunneling system or spin system). In cases (b) and (c), the coupling to the lattice will be assumed to be bilinear in oscillator and lattice coordinates. The phonon scattering rates are intended to be used in calculations of the lattice thermal conductivity in a manner to be described shortly.

We shall show that in the vicinity of a resonance all three systems have similar behavior. For cases (a) and (b), the mean scattering rate resonance obeys a "peak theorem," Eq. (2.10), which can be generalized slightly [Eq. (2.17)] to include the effects of anharmonic broadening, etc. For the 2-level atom of case (c), there is an explicit generalization given by Eq. (4.30). The peak theorem says roughly that all resonances occurring at a given frequency have the same peak mean scattering rate. It then follows that different resonances can only be distinguished by their widths. As we shall see, the width and resonance frequency cannot be independently varied in case (a), whereas they can be so varied in cases (b) and (c).

In order to obtain results in analytic form, we shall be forced to assume that the coupling to the lattice involves only one configurational coordinate X, which we do not further specify. These results may then be applied to specific impurity systems, where the dominant coordinate X has been determined experimentally or theoretically from a more basic theory.

The model 2-level atom considered here may be considered as a prototype of more complicated multilevel tunneling systems such as those of Li^+, CN^-, or OH^- in alkali halides.[1–3] In the latter case, there are also higher energy levels (the 30-cm^{-1} or non-Devonshire levels) of unknown character, perhaps oscillatorlike, perhaps more like tunneling levels which produce strong thermal conductivity resonances. These non-Devonshire levels are also infrared-active. With these facts as motivation, in this paper we derive an expression [Eq. (4.21)] for models (b) and (c) connecting the phonon scattering rate with the optical (or microwave) absorption coefficient.

For completeness, we also discuss a combination of model (b) with (a) or (c) with (a), i.e., a substitutional harmonic oscillator or 2-level atom coupled to harmonically perturbed phonons.

The phonon scattering rate will be used to calculate the thermal conductivity in the following way, which is not completely rigorous, but which seems to work fairly well in practice. For a cubic crystal, the conductivity is assumed to be given by

$$\kappa(T)=\frac{1}{3}\int_0^{\omega(\max)} C(\omega)v^2(\omega)\tau(\omega)\rho_0(\omega)d\omega. \qquad (1.1)$$

Here $C(\omega)$ is the phonon specific heat per unit volume per unit frequency, $v^2(\omega)$ is the mean of the group velocity squared for phonons of frequency ω, $\tau(\omega)$ is the mean time between collisions that destroy the heat current for all phonons of frequency ω, and $\rho_0(\omega)$ is the total density of states normalized to unity:

$$\int_0^{\omega(\max)} \rho_0(\omega)d\omega=1. \qquad (1.2)$$

To obtain τ, we assume that we may add mean scatter-

---

* Work supported by the U. S. Atomic Energy Commission, and by the Advanced Research Projects Agency under Contract No. SD-131.

† Permanent address: Department of Physics, University of Illinois, Urbana, Ill. 61801.

[1] G. Lombardo and R. O. Pohl, Phys. Rev. Letters **15**, 291 (1965); A. Lakatos and H. S. Sack, Solid State Commun. **4**, 315 (1966); N. Byer and H. S. Sack, J. Phys. Chem. Solids **29**, 677 (1968); M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. **153**, 1009 (1967); F. C. Baumann, J. P. Harrison, R. O. Pohl, and W. D. Seward, *ibid.* **159**, 691 (1967); J. P. Harrison, P. P. Peressini, and R. O. Pohl, *ibid.* **171**, 1037 (1968).

[2] V. Naranamurti, Phys. Rev. Letters **13**, 693 (1964); W. D. Seward and V. Naranamurti, Phys. Rev. **148**, 463 (1966); J. P. Harrison, P. P. Peressini, and R. O. Pohl, *ibid.* **167**, 856 (1968).

[3] For extensive references on OH^-, see F. Lüty, J. Phys. (Paris) **28**, Suppl. C4, 120 (1967); B. M. Wedding and M. V. Klein, Phys. Rev. **177**, 1274 (1969).

ing rates:

$$\tau^{-1}(\omega)=\langle\tau^{-1}\rangle_0(\omega)+\langle\tau^{-1}\rangle_i(\omega)\,. \qquad (1.3)$$

The first term represents the mean scattering rate for phonons of frequency ω in the perfect crystal; the second term represents the extra scattering due to impurities. In what follows, we speak only of the impurity-induced scattering rate $\langle\tau^{-1}\rangle_i(\omega)$ and drop the subscript i.

II. SUBSTITUTIONAL POINT DEFECT

The impurities are assumed to be identical and randomly distributed with fractional concentration $p\ll 1$. The perfect crystal dynamical matrix will be denoted by $\mathbf{A}$, the perfect crystal mass matrix by $\mathbf{M}$. The defect matrix for a single impurity will be denoted by $\boldsymbol{\gamma}_l$. The perfect-crystal Green's-function matrix is $\mathbf{G}=(\mathbf{A}-\omega^2\mathbf{I})^{-1}$; in the defect space where $\boldsymbol{\gamma}_l$ is nonzero, $\mathbf{G}$ will have a projection denoted by $\mathbf{g}(\omega)$. The single impurity t matrix is then given by

$$\mathbf{t}(\omega)=\boldsymbol{\gamma}_l(\mathbf{I}+\mathbf{g}(\omega)\boldsymbol{\gamma}_l)^{-1}. \qquad (2.1)$$

The perturbed Green's-function matrix is given by

$$\mathbf{G}=(\mathbf{A}+\boldsymbol{\gamma}_l-\omega^2\mathbf{I})^{-1}=\mathbf{G}-\mathbf{G}\mathbf{t}\mathbf{G}\,. \qquad (2.2)$$

Here ω may be complex. One can easily see that $\mathbf{G}$, $\mathbf{g}$, and $\mathbf{t}$ are even functions of ω. For this reason they are often written as $\mathbf{G}(\omega^2)$, etc. The applications of these functions require only positive values of ω. Hence, setting $\omega=\omega_{\text{real}}+i\epsilon$ with $\epsilon=0^+$ is equivalent to setting $\omega^2=\omega_{\text{real}}{}^2+i\epsilon$.

In this paper, we choose ω as the independent variable rather than ω^2, because ω occurs as the variable in the thermodynamic Green's-function treatment to be given below.

Let $|q)$ represent a normalized phonon eigenvector, with q standing both for wave vector and polarization index. ω_q is the corresponding frequency. Then the scattering rate for phonon q is[4,5]

$$\tau_q{}^{-1}=-\omega_q{}^{-1}pN\,\mathrm{Im}(q|\mathbf{t}(\omega_q+i\epsilon)|q)\,. \qquad (2.3)$$

Here N is the total number of unit cells in the crystal. This equation is valid for all three cases (a), (b), and (c) mentioned above, if $\mathbf{t}$ is defined appropriately. The mean scattering rate for phonons of frequency $\omega_q=\omega$ is given by

$$\langle\tau^{-1}\rangle(\omega)=\sum_q \tau_q{}^{-1}\delta(\omega_q-\omega)\Big/\sum_q \delta(\omega_q-\omega)\,.$$

The denominator is given by

$$\sum_q \delta(\omega_q-\omega)=3rN\rho_0(\omega)\,, \qquad (2.4)$$

where r is the number of atoms per unit cell ($3rN$ is the total number of phonon states), and $\rho_0(\omega)$ is the normalized density of states. We then obtain[6]

$$\langle\tau^{-1}\rangle=[-2p/3r\pi\rho_0(\omega)]\times\mathrm{Tr}\{[\mathrm{Im}\mathbf{t}(\omega+i\epsilon)][\mathrm{Im}\mathbf{g}(\omega+i\epsilon)]\}\,. \qquad (2.5)$$

The part of $\mathbf{G}$ outside the defect space does not enter into the trace in Eq. (2.5).

For low-frequency resonances, $\mathrm{Im}\mathbf{g}$ is much less than $\mathrm{Re}\mathbf{g}$. In this case, the eigenvalues μ_{a0} and eigenvectors f_a (not necessarily normalized) of the non-Hermitian matrix $\mathrm{Re}\mathbf{g}\boldsymbol{\gamma}_l$ are of use. First-order perturbation theory says that the f_a are approximate eigenvectors of $\mathbf{g}\boldsymbol{\lambda}_l$ with eigenvalues

$$\mu_{a0}+i\mu_{ai}\,,$$

where

$$\mu_{ai}=\tilde{f}_a\boldsymbol{\gamma}_l\,\mathrm{Im}\mathbf{g}\boldsymbol{\gamma}_l f_a/\tilde{f}_a\boldsymbol{\gamma}_l f_a\,. \qquad (2.6)$$

One can then derive the approximate result[5]

$$\mathrm{Im}\mathbf{t}=-\boldsymbol{\gamma}_l\sum_a \frac{\mu_{ai}}{[(1+\mu_{a0})^2+\mu_{ai}{}^2]}\frac{f_a\tilde{f}_a}{\tilde{f}_a\boldsymbol{\gamma}_l f_a}\boldsymbol{\gamma}_l\,. \qquad (2.7)$$

Thus

$$\langle\tau^{-1}\rangle(\omega)=\frac{2p}{3r\pi\rho_0(\omega)}\sum_a\frac{\mu_{ai}{}^2}{(1+\mu_{a0})^2+\mu_{ai}{}^2}\,. \qquad (2.8)$$

Now assume that all $\mu_{ai}\ll 1$ and that of all the μ_{a0} only one, μ_{b0} is near resonance $(1+\mu_{b0}\approx 0)$, the others having absolute values much less than 1. Let d be the degeneracy of μ_{b0}, then Eq. (2.8) becomes

$$\langle\tau^{-1}\rangle(\omega)\approx\frac{2pd}{3r\pi\rho_0(\omega)}\frac{\mu_{bi}{}^2}{(1+\mu_{b0})^2+\mu_{bi}{}^2}\,. \qquad (2.9)$$

μ_{bi} and μ_{b0} are still functions of ω.

At resonance, we have $\omega=\omega_r$ and

$$1+\mu_{b0}(\omega_r)=0\,.$$

Thus

$$\langle\tau^{-1}\rangle(\omega_r)=2pd/3r\pi\rho_0(\omega_r)\,. \qquad (2.10)$$

Equation (2.10) constitutes a peak theorem for phonon scattering resonances. For convenience, we repeat the definitions of the parameters occurring here: $\langle\tau^{-1}(\omega)\rangle$ is the mean defect-induced scattering rate for all phonons having $\omega_q=\omega$. In Eq. (2.10), we evaluate it at the resonance peak. p is the fractional impurity concentration, d is the degeneracy of the resonance (e.g., in a crystal with 0_h symmetry, d is 3 for a T_{1u} resonance, d is 2 for an E_g resonance, and d is 1 for an A_{1g} resonance), r is the number of atoms per unit cell, and $\rho_0(\omega)$ is the normalized phonon density of states.

The remarkable feature of Eq. (2.10) is that no specific properties of the resonant system appear in it, apart from the degeneracy and the resonant frequency ω_r. Thus all d-fold degenerate resonances at $\omega=\omega_r$ in a given host lattice should have the same peak mean scat-

---

[4] M. V. Klein, Phys. Rev. **141**, 716 (1966).

[5] M. V. Klein, in *Physics of Color Centers*, edited by W. B. Fowler (Academic Press Inc., New York, 1968), Chap. 7.

[6] This result was erroneously given in Ref. 5 (Eq. 7.73′) with a missing factor of $(3rN)^{-1}$.

tering rate. Such resonances may have different widths or shapes, however. The Lorentzian shape is obtained through approximations valid when ω is close to ω_r:

$$\mu_{bi}(\omega)\approx\mu_{bi}(\omega_r)\,,$$
$$1+\mu_{b0}(\omega)\approx 0+(d\mu_{b0}/d\omega^2)_r(\omega^2-\omega_r^2)\,.$$

Then the widths are given by

$$\omega_r\Delta\omega\approx\Delta_{1/2}\omega^2\equiv\Gamma=\mu_{bi}(\omega_r)/(d\mu_{b0}/d\omega^2)_r\,. \qquad (2.11)$$

Here $\Delta\omega$ is the full width at half-maximum when $\langle\tau^{-1}\rangle$ is considered to be a function of ω, and $\Delta_{1/2}\omega^2$ is the half-width at half-maximum when $\langle\tau^{-1}\rangle$ is considered to be a function of ω^2. The Lorentzian approximation to (2.9) is

$$\langle\tau^{-1}\rangle(\omega^2)=\frac{2pd}{3r\pi\rho_0(\omega_r)}\frac{\Gamma^2}{(\omega^2-\omega_r^2)^2+\Gamma^2}\,. \qquad (2.12)$$

Often the eigenvector v_b corresponds to a mixture of several configurations in the defect space that have the same symmetry. If there is only one such configuration, denoted symbolically by X, then we may write $v_b=|X)$. The defect space is essentially one-dimensional, and we have

$$\boldsymbol{\gamma}_l=\gamma_l|X)(X|\,,\quad \mathbf{g}=g|X)(X|\,,\quad \mathbf{t}=t|X)(X|\,,$$

with

$$g=\sum_q X_q^2(\omega_q^2-\omega^2)^{-1}\,, \qquad (2.13\text{a})$$

and

$$t=\gamma_l(1+g\gamma_l)^{-1}\,, \qquad (2.13\text{b})$$

all scalars. Then

$$\mu_{b0}=\gamma_l\,\mathrm{Re}g,\quad \mu_{bi}=\gamma_l\,\mathrm{Im}g\,.$$

The resonance condition is simply

$$1+\gamma_l\,\mathrm{Re}g(\omega_r)=0\,,$$

and for a frequency-independent γ_l the width becomes

$$\Gamma=\mathrm{Im}g(\omega_r)/[(d/d\omega^2)\,\mathrm{Re}g]_r\,. \qquad (2.13\text{c})$$

The only unknown parameter in Eq. (2.12) or (2.13) is the width. If a good fit of experimental conductivity data is obtained with these expressions, the resulting numerical value of Γ should agree with the width determined by other means, e.g., far infrared absorption measurements.

The width Γ is due to radiative decay of the resonance mode into a propagating phonon mode. If other lifetime broadening mechanisms are also operative, for example, anharmonic decays of the resonance mode into two or more propagating phonons, then the linewidth is $\Gamma'>\Gamma$, and (2.12) becomes

$$\langle\tau^{-1}\rangle(\omega^2)=\frac{2pd}{3r\pi\rho_0(\omega)}\frac{\Gamma\Gamma'}{(\omega^2-\omega_r^2)^2+\Gamma'^2}\,. \qquad (2.14)$$

Only one factor of Γ in the numerator is changed to Γ'. The other factor comes from the Im$\mathbf{g}$ part of $\mathrm{Tr}[\mathrm{Im}\mathbf{g}\,\mathrm{Im}\mathbf{t}]$ and is a result of the averaging process leading to Eq. (2.8). The peak theorem is then changed to

$$\langle\tau^{-1}\rangle(\omega_r^2)=\frac{2pd}{3r\pi\rho_0(\omega_r)}\frac{\Gamma}{\Gamma'}\,, \qquad (2.15)$$

and this may be temperature-dependent, e.g., for Γ' resulting from multiphonon decays.

A still more general situation may involve a resonance with a temperature-dependent strength $S(T)$, defined so that $S(0)=1$. Equation (2.14) would then be written

$$\langle\tau^{-1}\rangle(\omega^2,T)=\frac{2pd}{3r\pi\rho_0(\omega_r)}\frac{\Gamma\Gamma'(T)S(T)}{(\omega^2-\omega_r^2)^2+[\Gamma'(T)]^2}\,. \qquad (2.16)$$

The peak theorem then becomes

$$\langle\tau^{-1}\rangle(\omega_r^2,T)=\frac{2pd}{3\pi r\rho_0(\omega_r)}\frac{\Gamma S(T)}{\Gamma'(T)}\,. \qquad (2.17)$$

The role of τ in the thermal-conductivity integral [Eq. (1.1)] is such that the conductivity is determined by the shape of $\langle\tau^{-1}\rangle$ in the wings away from resonance. For substitutional point defects, all low-frequency resonances have $\Gamma\ll\omega_r^2$, and even for very anharmonic resonances, we also have $\Gamma'\ll\omega_r^2$. Then the conductivity integral is insensitive to the presence of Γ'^2 in the denominator, i.e., one might just as easily use the expression

$$\langle\tau^{-1}\rangle(\omega^2,T)=\frac{2pd}{3\pi r\rho_0(\omega_r)}\frac{\Gamma\Gamma'(T)S(T)}{(\omega^2-\omega_r^2)^2}\,. \qquad (2.18)$$

Equation (2.18) holds not too far from resonance. To make it more generally valid, we should replace $\rho_0(\omega_r)$ by $\rho_0(\omega)$ and let Γ and Γ' have the frequency dependency of $\mu_{\mathrm{b}i}(\omega)$.

The strength of the thermal-conductivity dip that signals the resonance is thus determined by the product $p\Gamma\Gamma'(T)S(T)$. When comparing resonance phonon scattering data in different samples, one should keep in mind that not only the concentration p, but also the width Γ' may be different, if different broadening mechanisms are present in the various samples.

III. HARMONIC-OSCILLATOR IMPURITY

Initially we assume the simplest possible case and later indicate how some of the assumptions may be relaxed. We assume that the impurity atom has an internal degree of freedom which acts as a harmonic oscillator[7,8] with reduced coordinate x [reduced coordinate $=(\text{mass})^{1/2}\times(\text{physical displacement})$], momentum p, and frequency ω_0, when the lattice atoms are

---

[7] M. Wagner, Phys. Rev. **133**, A750 (1964).

[8] D. L. Huber and J. H. Van Vleck, Rev. Mod. Phys. **38**, 187 (1966).

at rest. The oscillator Hamiltonian is then

$$H_0=\tfrac{1}{2}p^2+\tfrac{1}{2}\omega_0{}^2x^2. \tag{3.1}$$

The reduced lattice coordinates and momenta will be denoted by v_q and p_q. They will be assumed real for simplicity. Then phonon Hamiltonian is then

$$H_l=\tfrac{1}{2}\sum_q (p_q{}^2+\omega_q{}^2v_q{}^2). \tag{3.2}$$

The coupling between the phonons and the local oscillator will be assumed to be bilinear:

$$H'=\lambda x\sum_q X_qv_q, \tag{3.3}$$

where for simplicity, the X_q are assumed real and normalized to unity:

$$\sum_q X_q{}^2=1. \tag{3.4}$$

Under the assumption of an $e^{i\omega t}$ time dependence, the equations of motion for this system with the Hamiltonian $H=H_0+H+H'$ yield for the oscillator coordinate the equation

$$(\omega_0{}^2-\omega^2)x=-\lambda\sum_{q'} X_{q'}v_{q'}, \tag{3.5}$$

and for the qth lattice coordinate

$$(\omega_q{}^2-\omega^2)v_q=-\lambda X_qx. \tag{3.6}$$

When (3.5) is inserted in (3.6), one obtains

$$\begin{aligned}(\omega_q{}^2-\omega^2)v_q&=\lambda^2/(\omega_0{}^2-\omega^2)\sum_{q'} X_qX_{q'}v_{q'}\\ &\equiv-\sum_{q'}\Gamma_{qq'}{}^0v_{q'}.\end{aligned} \tag{3.7}$$

This equation has the same form as those involved in case (a) for a substitutional point defect. One need only to identify a defect matrix $\boldsymbol{\gamma}_0$ with elements

$$(q|\boldsymbol{\gamma}_0|q')=\Gamma_{qq'}{}^0.$$

Then we may write

$$\boldsymbol{\gamma}_0=\gamma_0|X)(X|, \tag{3.8a}$$

with

$$\gamma_0=-\lambda^2(\omega_0{}^2-\omega^2)^{-1} \tag{3.8b}$$

and

$$(X|q)=(q|X)=X_q. \tag{3.8c}$$

The defect space is one-dimensional and spanned by the vector $|X)$. The reduced Green's-function matrix $\mathbf{g}$ may be written

$$\mathbf{g}=g|X)(X|, \tag{3.9}$$

where g is a scalar given by Eq. (2.13a).

The t matrix then takes the form

$$\mathbf{t}=t|X)(X|, \tag{3.10a}$$

where the scalar t is given by

$$t=\gamma_0(1+g\gamma_0)^{-1}=-\lambda^2/(\omega_0{}^2-\omega^2-\lambda^2g). \tag{3.10b}$$

A. Some Generalizations

If v_q and X_q are complex, replace $X_q{}^2$ by $|X_q|^2$ in (3.9b). If x represents one component x^i of a degenerate oscillator with degeneracy d coupled to a superposition $\sum_q X_q{}^iv_q$ of phonon states having the same symmetry as x^i, then H' becomes

$$H'=\sum_{i,q}\lambda x^iX_q{}^iv_q, \tag{3.11}$$

and

$$\mathbf{t}=t\sum_i |X^i)(X^i|, \tag{3.12}$$

with t still given by Eq. (3.10b). Explicit use of these different coordinates x^i, X^i will not be made, except at the end of derivations where a factor of d will sometimes be added.

B. Polarizability

If the local oscillator has charge e^* and is infrared-active, then there will be an induced dipole moment $p=e^*x/\sqrt{m}$ in response to an applied field $Ee^{+i\omega t}$. For an uncoupled oscillator ($H'=0$) with infinitesimal damping, the polarizability is given by

$$\alpha_0(\omega)=p/Ee^{i\omega t}=e^{*2}/m[\omega_0{}^2-(\omega+i\epsilon)^2]. \tag{3.13a}$$

With $H'\neq0$, we add a term $e^*Ee^{i\omega t}/\sqrt{m}$ to the right-hand side of Eq. (3.5) and solve it together with Eq. (3.6), with the result

$$\alpha(\omega)=e^{*2}/m[\omega_0{}^2-\omega^2-\lambda^2g(\omega+i\epsilon)]. \tag{3.13b}$$

The factors $\sqrt{m}$ are necessary, because x is a reduced coordinate.

Note that in passing from γ to t or from α_0 to α, we simply replace $\omega_0{}^2$ by the expression

$$\Sigma(\omega+i\epsilon)=\omega_0{}^2-\lambda^2g(\omega+i\epsilon). \tag{3.14}$$

C. Phonon Scattering Rate

Using the result

$$\mathrm{Im}t(\omega+i\epsilon)=-\lambda^4/[(\omega_0{}^2-\omega^2-\lambda^2\,\mathrm{Re}g)^2+(\lambda^2\,\mathrm{Im}g)^2]$$

and the result

$$\mathrm{Tr}[\mathrm{Im}\mathbf{g}\;\mathrm{Im}\mathbf{t}]=d\;\mathrm{Im}g\;\mathrm{Im}t,$$

where d is the degeneracy of the oscillator and of the coordinate X to which it is coupled, we find that Eq. (2.8) becomes

$$\langle\tau^{-1}\rangle(\omega)=\frac{2pd}{3r\pi\rho_0(\omega)}\frac{(\lambda^2\,\mathrm{Im}g)^2}{(\omega_0{}^2-\omega^2-\lambda^2\,\mathrm{Re}g)^2+(\lambda^2\,\mathrm{Im}g)^2}. \tag{3.15}$$

The resonance is shifted from $\omega^2=\omega_0{}^2$ to

$$\omega^2=\omega_r{}^2=\omega_0{}^2-\lambda^2\,\mathrm{Re}g(\omega_r+i\epsilon). \tag{3.16}$$

At low frequencies this amounts to a decrease in frequency, since $\mathrm{Re}g(0)$ is positive. At resonance we again recover the peak theorem [Eq. (2.10)]. If we expand about $\omega^2=\omega_r^2$, we again obtain a Lorentzian resonance as in Eq. (2.12), but with

$$\omega_r\Delta\omega\approx\Delta_{1/2}\omega^2=\Gamma=\frac{\lambda^2\operatorname{Im}g(\omega_r+i\epsilon)}{1+\lambda^2[(d/d\omega^2)\operatorname{Re}g]_r}\approx\lambda^2\operatorname{Im}g(\omega_r+i\epsilon). \quad (3.17)$$

Some numerical estimates have suggested that even with coupling constants λ strong enough to cause a marked shift of the resonance frequency away from ω_0, it is nevertheless true that

$$|\lambda^2(d\operatorname{Re}g/d\omega^2)_r|\ll 1.$$

Thus the last approximate equality in Eq. (3.17) is likely to be accurate. This means that λ has a very strong influence on the resonance width, whereas it has a relatively weaker influence on the resonance frequency, except for cases of very strong coupling. This state of affairs is different from that in case (a). There the defect matrix $\boldsymbol{\gamma}_l$ plays the role of a coupling constant, especially in the simple case where $\boldsymbol{\gamma}_l=\gamma_l|X)(X|$, and it exerts a dominant influence on the resonance frequency via the equation

$$1+\gamma_l\operatorname{Re}g(\omega_r)=0.$$

But once ω_r is determined, there is no explicit functional dependence of the width on γ_l since

$$\Gamma=\operatorname{Im}g(\omega_r)/[(d/d\omega^2)\operatorname{Re}g]_r.$$

At low frequencies, this expression gives very small values for Γ.

These considerations suggest that a broad resonance, especially one at low frequencies, is unlikely to be a type-(a) resonance. On the other hand, type-(b) resonances [and type-(c) resonances] can exist at arbitrary frequencies and have arbitrary widths.

One should use Eq. (3.15) rather than the Lorentzian approximation. This is especially true above resonance, since $\operatorname{Im}g(\omega)$ will have a strong ω dependence in many cases, e.g., $\sim\omega^3$ for a breathing configuration, and will exhibit structure at the Van Hove singularities. In fact, for large ω the second term in the denominator may dominate above resonance, and we obtain

$$\langle\tau^{-1}\rangle(\omega)\sim 2pd/3r\pi\rho_0(\omega). \quad (3.18)$$

Since $\rho_0(\omega)\sim\omega^2$, this drops off more slowly than the ω^{-4} dependence of Eq. (2.12) far above resonance.

D. Coupling of Harmonic Oscillator to Perturbed Phonons

The atom that has the internal degree of freedom, being an impurity, is likely to introduce an additional perturbation

$$\boldsymbol{\gamma}_l=\Delta\mathbf{A}-\mathbf{M}^{-1/2}\Delta\mathbf{M}\mathbf{M}^{-1/2}\omega^2$$

into the lattice, even if the internal oscillator coordinate x could be neglected. The total perturbation matrix is

$$\boldsymbol{\gamma}=\boldsymbol{\gamma}_l+\boldsymbol{\gamma}_0,\quad \boldsymbol{\gamma}_0=\gamma_0|X)(X|,$$
$$\gamma_0=-\lambda^2|X)(X|/(\omega_0^2-\omega^2),$$

and the t matrix is still

$$\mathbf{t}=\boldsymbol{\gamma}(\mathbf{1}+\mathbf{g}\boldsymbol{\gamma})^{-1}.$$

For simplicity, we further *assume* that $\boldsymbol{\gamma}_l$ couples only to the same configuration X that the internal degree of freedom couples to. Thus $\boldsymbol{\gamma}_l$ takes the form

$$\boldsymbol{\gamma}_l=|X)(X|\gamma_l. \quad (3.19a)$$

The total defect matrix is then

$$\boldsymbol{\gamma}=|X)(X|(\gamma_l+\gamma_0). \quad (3.19b)$$

This gives

$$t=\frac{\gamma_l}{1+g\gamma_l}+\frac{\gamma_0}{(1+g\gamma_l)^2[1+g(1+g\gamma_l)^{-1}\gamma_0]}. \quad (3.20)$$

The resonance condition is now

$$\omega_r^2=\omega_0^2-\lambda^2\operatorname{Re}g(\omega_r)/[1+\gamma_l\operatorname{Re}g(\omega_r)], \quad (3.21)$$

and the peak theorem [Eq. (2.9)] still holds. The width is now given by

$$\Gamma=\Delta_{1/2}\omega^2=\left|\frac{[(\omega_0^2-\omega_r^2)\gamma_l-\lambda^2]\operatorname{Im}g(\omega_r+i\epsilon)}{[(\omega_0^2-\omega_r^2)\gamma_l-\lambda^2](d\operatorname{Re}g/d\omega^2)_r-[1+\gamma_l\operatorname{Im}g(\omega_r+i\epsilon)]}\right|. \quad (3.22)$$

To see how the presence of γ_l affects the polarizability, we return to Eq. (3.6), which gives

$$\sum_{q'}[\delta_{qq'}(\omega_q^2-\omega^2)+\gamma_lX_qX_{q'}]v_{q'}=-\lambda X_qx. \quad (3.23)$$

The unperturbed Green's-function matrix

$$\mathbf{G}(\omega)=(\mathbf{A}-\omega^2\mathbf{I})^{-1}$$

gives the following result in phonon space:

$$(q|\mathbf{G}^{-1}(\omega)|q')=\delta_{qq'}(\omega_q^2-\omega^2).$$

Define a Green's-function matrix $\mathbf{G}_l$ that obeys the equation

$$\mathbf{G}_l^{-1}=\mathbf{G}^{-1}+\boldsymbol{\gamma}_l. \quad (3.24a)$$

It is readily shown that

$$\mathbf{G}_l=\mathbf{G}(\mathbf{1}+\boldsymbol{\gamma}_l\mathbf{G})^{-1}=(\mathbf{1}+\mathbf{G}\boldsymbol{\gamma}_l)^{-1}\mathbf{G}, \quad (3.24b)$$

and that the projection of $\mathbf{G}_l$ onto our simple defect space is

$$g_l=(X|\mathbf{G}_l|X)=g(1+g\gamma_l)^{-1}. \quad (3.24c)$$

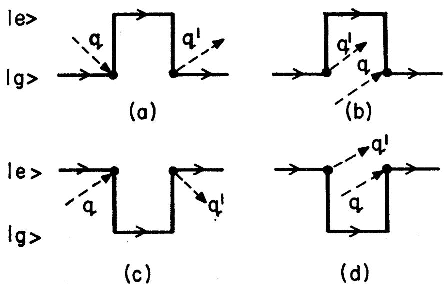

FIG. 1. Four scattering events that contribute in lowest order to phonon scattering by a two-level atom.

Equation (3.23) then becomes

$$\sum_{q'} (q|\mathbf{G}_l^{-1}(\omega+i\epsilon)|q')v_{q'} = -\lambda X_q x$$

and has the solution

$$v_{q'} = -\lambda x \sum_q (q'|\mathbf{G}_l(\omega+i\epsilon)|q)X_q = -\lambda x(q'|\mathbf{G}_l(\omega+i\epsilon)|X).$$

The polarizability then becomes

$$\alpha(\omega) = e^{*2}/m[\omega_0^2-\omega^2-\lambda^2 g_l(\omega+i\epsilon)], \quad (3.25a)$$

or

$$\alpha = e^{*2}/m[\omega_0^2-\omega^2-\lambda^2 g(1+\gamma_l g)^{-1}]. \quad (3.25b)$$

The last equality follows from (3.24c).

The appearance of g_l in Eq. (3.25a) is easy to understand—the oscillator is coupled to a perturbed lattice; hence the quantity

$$\Sigma = \omega_0^2 - \lambda^2 g_l.$$

contains the perturbed Green's function g_l.

IV. TWO-LEVEL IMPURITY ATOM

Suppose the impurity atom has an internal degree of freedom with dynamical coordinate x and with just two energy levels having unperturbed eigenstates $|g\rangle$ and $|e\rangle$ with respective energy levels $-\frac{1}{2}\hbar\omega_0$ and $\frac{1}{2}\hbar\omega_0$. Select the phases of $|e\rangle$ and $|g\rangle$ so that the matrix element $a=\langle g|x|e\rangle$ is real and let

$$a^2 = f(\hbar/2\omega_0) \quad (4.1)$$

define the oscillator strength f.

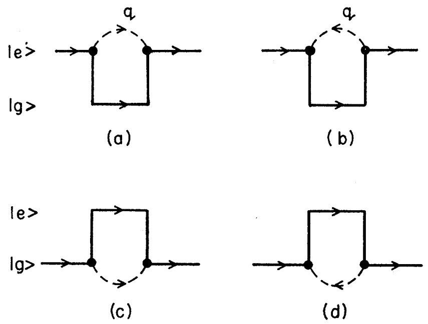

FIG. 2. Four lowest-order contributions to the self-energy of ground and excited states of a two-level atom.

The Hamiltonian is then

$$H = H_2 + H_l + H', \quad (4.2)$$

where H_l and H' are still given by Eqs. (3.2) and (3.3);

$$H_l = \tfrac{1}{2}\sum_q (p_q^2+\omega_q^2 v_q^2), \quad H' = \lambda \sum_q X_q v_q x,$$

and with

$$H_2 = -\tfrac{1}{2}\hbar\omega_0|g\rangle\langle g| + \tfrac{1}{2}\hbar\omega_0|e\rangle\langle e|. \quad (4.3)$$

A. Perturbation Treatment

Before attempting a more complete treatment, we shall first discuss some results of second-order pertubation theory. We calculate the amplitude $A_{q'q}$ for the scattering of a phonon q into q'; i.e., for an event which changes the phonon occupation numbers from n_q and $n_{q'}$ to n_q-1 and $n_{q'}+1$. We must consider the four processes shown in Fig. 1. In process 1(a), the atom starts in its ground state, absorbs phonon q, is virtually excited to the upper level, and then returns to the ground state emitting phonon q'. In process 1(b), the atom emits q' while going from $|g\rangle$ to $|e\rangle$ and absorbs q' while returning. Processes 1(c) and (d) describe the analogous events for the atom initially in state $|e\rangle$.

Let P_g and P_e denote the probability that ground and excited states are occupied. Second-order perturbation theory then gives for each contribution to $A_{q'q}$ an expression of the form

$$\lambda^2 X_q X_{q'} P[(n_{q'}+1)n_q]^{1/2}(a^2/\hbar D)[\hbar/2(\omega_q\omega_{q'})^{1/2}], \quad (4.4)$$

where

$$\begin{aligned} D &= \omega_q-\omega_0, P=P_g && \text{for } 1(a)\\ &-\omega_{q'}-\omega_0, P=P_g && \text{for } 1(b)\\ &\omega_0+\omega_q, P=P_e && \text{for } 1(c)\\ &\omega_0-\omega_{q'}, P=P_e && \text{for } 1(d). \end{aligned}$$

Here n_q and $n_{q'}$ are the numbers of phons in states q and q'. If we assume elastic scattering by setting $\omega_{q'}=\omega_q$, we obtain

$$A_{q'q} = -\lambda^2 X_q X_{q'}[(n_{q'}+1)n_q]^{1/2} \times[2\omega_0 a^2/\hbar(\omega_0^2-\omega_q^2)](P_g-P_e).$$

If the atom is in thermal equilibrium, then

$$P_g - P_e = \tanh(\beta\hbar\omega_0/2), \quad \beta=(kT)^{-1}.$$

We also use Eq. (4.1) and find

$$A_{q'q} = -\lambda^2 f \tanh(\beta\hbar\omega_0/2)X_{q'}X_q \times\{[(n_{q'}+1)n_q]^{1/2}/(\omega_0^2-\omega_q^2)\}(\hbar/2\omega_q\omega_{q'}).$$

This is the same amplitude that would be obtained in first order if the perturbation were

$$H_{\text{eff}}'=\tfrac{1}{2}\sum_{qq'}\Gamma_{qq'}{}^{\text{eff}}v_q v_{q'}\,,$$

with

$$\Gamma_{qq'}{}^{\text{eff}}=-\lambda^2 f\tanh(\beta\hbar\omega_0/2)X_q X_{q'}/(\omega_0{}^2-\omega_q{}^2)\,. \quad (4.5)$$

Equation (4.5) may be improved by replacing ω_0 by the result of a calculation in second-order perturbation theory of the energy levels of the atom. The processes to be considered are shown in Fig. 2. From Fig. 2(a) we obtain

$$\Delta_a E_e=\left\langle\sum_q \frac{\langle n_q,e|H'|(n_q+1),g\rangle\langle(n_q+1),g|H'|n_q,e\rangle}{\hbar(\omega_q-\omega_0)}\right\rangle$$

$$=\sum_q \frac{(\hbar/2\omega_q)\lambda^2 X_q{}^2 a^2\langle n_q+1\rangle}{\hbar(\omega_q-\omega_0)}\,.$$

From Fig. 2(b)

$$\Delta_b E_e=\sum_q \frac{\hbar}{2\omega_q}\frac{\lambda^2 X_q{}^2 a^2\langle n_q\rangle}{\hbar(-\omega_q-\omega_0)}\,.$$

Thus

$$\Delta E_e=\Delta_a E_e+\Delta_b E_e=\lambda^2 a^2\sum \frac{X_q{}^2[-\omega_q-\omega_0(2\langle n_q\rangle+1)]}{(\omega_q{}^2-\omega_0{}^2)2\omega_q}\,.$$

The proper second-order energies are complex and are obtained by giving ω_0 a small imaginary part $\omega_0\to\omega_0+i\epsilon$ or $\omega_0{}^2\to\omega_0{}^2+i\epsilon$.

In a similar manner, we obtain

$$\Delta E_g=\Delta_c E_g+\Delta_d E_g$$

$$=\frac{\hbar^2\lambda^2 a^2}{\hbar}\sum_q \frac{X_q{}^2[-\omega_q+\omega_0(2\langle n_q\rangle+1)]}{(\omega_q{}^2-\omega_0{}^2-i\epsilon)2\omega_q}\,.$$

Thus

$$E_e-E_g=\hbar\omega_0+\Delta E_e-\Delta E_g$$

$$=\hbar\omega_0-\hbar\lambda^2\left(\frac{2a^2\omega_0}{\hbar}\right)\sum_q \frac{X_q{}^2(2\langle n_q\rangle+1)}{(\omega_q{}^2-\omega_0{}^2-i\epsilon)2\omega_q}\,.$$

The new transition frequency $\bar{\omega}_0=(E_g-E_e)/\hbar$ is given by

$$\bar{\omega}_0=\omega_0-\lambda^2 f\sum_q \frac{X_q{}^2(2\langle n_q\rangle+1)}{(\omega_q{}^2-\omega_0{}^2-i\epsilon)2\omega_q}\,,$$

or approximately

$$\bar{\omega}_0{}^2=\omega_0{}^2-\lambda^2 f\sum_q \frac{X_q{}^2(2\langle n_q\rangle+1)\omega_0}{(\omega_q{}^2-\omega_0{}^2-i\epsilon)\omega_q}\,. \quad (4.6)$$

Equation (4.6) is an approximation to the more exact self-energy term $\Sigma(\omega,T)$ that we shall derive below. Note that Eq. (4.6) is obtained from Eq. (3.14) by replacing g by a more complicated temperature-dependent function. When we replace $\omega_0{}^2$ in (4.5) by $\bar{\omega}_0{}^2$ as given by (4.6), we obtain an approximation to the t matrix for this problem, $t_{qq'}=tX_q X_q'$, with

$$t\approx-\lambda^2 f\tanh(\beta\hbar\omega_0/2)/D,$$

$$D=\omega_0{}^2-\omega_q{}^2-\lambda^2 f\omega_0\sum_{q''}X_{q''}{}^2(2\langle n_{q''}\rangle+1)$$

$$\times[(\omega_{q''}{}^2-\omega_0{}^2)\omega_{q''}]^{-1}\,. \quad (4.7)$$

B. Thermodynamic Green's-Function Treatment

Our approach will be similar to that of Huber and Van Vleck[8] and will use Zubarev's[9] double-time thermodynamic Green's functions.

The advanced and retarded functions will be denoted by subscripts a and r, and for Heisenberg operators A and B, they are defined as follows:

$$\langle\langle A(t);B(t')\rangle\rangle_a$$
$$=+i\theta(t'-t)\langle A(t)B(t')-B(t')A(t)\rangle\,, \quad (4.8\text{a})$$

$$\langle\langle A(t);B(t')\rangle\rangle_r$$
$$=-i\theta(t-t')\langle A(t)B(t')-B(t')A(t)\rangle\,, \quad (4.8\text{b})$$

where the thermal expectation value for an operator L is defined by

$$\langle L\rangle=\text{Tr}(e^{-\beta H}L)/\text{Tr}e^{-\beta H}\,. \quad (4.9)$$

These Green's functions have a spectral representation

$$\langle\langle A;B\rangle\rangle_{a,r}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle A(t);B(0)\rangle\rangle_{a,r}e^{i\omega t}dt\,. \quad (4.10\text{a})$$

One can show that the function defined by

$$\langle\langle A;B\rangle\rangle(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle A(t);B(0)\rangle\rangle_r e^{i\omega t}\,,$$
$$\text{for}\quad \text{Im}\omega>0 \quad (4.10\text{b})$$

$$\langle\langle A;B\rangle\rangle(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle A(t);B(0)\rangle\rangle_a e^{i\omega t}\,,$$
$$\text{for}\quad \text{Im}\omega<0 \quad (4.10\text{c})$$

is an analytic function of ω except on the real axis, where there is a cut and where it equals

$$\langle\langle A;B\rangle\rangle_{r,a}(\omega),\quad \text{for}\quad \omega=\omega_{\text{real}}\pm i\epsilon\,.$$

For a system with Hamiltonian H, the equations of motion for $\langle\langle A;B\rangle\rangle$ are

$$\omega\langle\langle A;B\rangle\rangle(\omega)=(2\pi)^{-1}\langle[A(0),B(0)]\rangle$$
$$+\hbar^{-1}\langle\langle[A,H];B\rangle\rangle(\omega)\,, \quad (4.11\text{a})$$

$$\omega\langle\langle A;B\rangle\rangle(\omega)=(2\pi)^{-1}\langle[A(0),B(0)]\rangle$$
$$-\hbar^{-1}\langle\langle A;[B,H]\rangle\rangle(\omega)\,. \quad (4.11\text{b})$$

Here $[r,s]=rs-sr$ denotes the commutator. One can

---

[9] D. N. Zubarev, Usp. Fiz. Nauk. **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

readily show that

$$\langle\langle A;B\rangle\rangle(\omega)=\langle\langle B;A\rangle\rangle(-\omega). \tag{4.11c}$$

These new Green's functions enable us to calculate the quantities of interest. For instance, under the influence of an applied electric field $Ee^{i\omega t}$, there results a complex atomic polarizability given by

$$\begin{aligned}\alpha(\omega)&=-(2\pi/\hbar)(e^{*2}/m)\langle\langle x;x\rangle\rangle(\omega+i\epsilon)\\&=-(2\pi/\hbar)(e^{*2}/m)\langle\langle x;x\rangle\rangle_r(\omega)(\omega\text{ real}).\end{aligned} \tag{4.12}$$

In the lattice there is a corresponding mechanical susceptibility

$$\begin{aligned}\mathfrak{G}_{LL'}&\equiv-(2\pi/\hbar)\langle\langle v_L;v_{L'}\rangle\rangle(\omega+i\epsilon)\\&=-(2\pi/\hbar)\langle\langle v_L;v_{L'}\rangle\rangle_r(\omega),\end{aligned} \tag{4.13a}$$

which gives the displacement at site L when a unit alternating force $e^{i\omega t}$ is applied at site L'. Equation (4.13a) defines a matrix $\mathfrak{G}$, which is an analytic function of ω except on the real axis. In the representation of unperturbed phonons we have

$$(q|\mathfrak{G}(\omega)|q')=-(2\pi/\hbar)\langle\langle v_q;v_{q'}\rangle\rangle(\omega). \tag{4.13b}$$

When the phonons are completely unperturbed ($H'=0$), one can show that

$$(q|\mathfrak{G}(\omega)|q')=\delta_{qq'}(\omega_q^2-\omega^2)^{-1}\quad\text{(see Appendix A)}.$$

Then $\mathfrak{G}$ is the unperturbed Green's-function matrix $\mathbf{G}=(\mathbf{A}-\omega^2\mathbf{I})^{-1}$.

We must calculate the Green's functions $\langle\langle x;x\rangle\rangle(\omega)$ and $\langle\langle v_q;v_{q'}\rangle\rangle(\omega)$. For convenience, we summarize the Hamiltonian

$$H=H_2+H_l+H', \tag{4.3}$$

where

$$H_2=-\tfrac{1}{2}\hbar\omega_0[|g\rangle\langle g|-|e\rangle\langle e|]\equiv-\tfrac{1}{2}\hbar\omega_0\eta \tag{4.14a}$$

defines the operator η, which obeys the identity

$$\eta^2=1. \tag{4.14b}$$

In addition,

$$H_l=\tfrac{1}{2}\sum_q(p_q^2+\omega_q^2v_q^2) \tag{3.2}$$

and

$$H'=\lambda x\sum_q X_qv_q. \tag{3.3}$$

We may write an explicit representation for the operators x and p:

$$x=a[|g\rangle\langle e|+|e\rangle\langle g|], \tag{4.15a}$$

with

$$x^2=a^2=\hbar f/2\omega_0 \tag{4.15b}$$

and

$$\begin{aligned}p=(i\hbar)^{-1}[x,H]&=(i\hbar)^{-1}[x,H_2]\\&=-i\omega_0a[|g\rangle\langle e|-|e\rangle\langle g|],\end{aligned} \tag{4.16a}$$

and with

$$p^2=\omega_0^2a^2=\tfrac{1}{2}\hbar\omega_0f. \tag{4.16b}$$

The operators η, x, and p are closely related to the Pauli operators σ_z, σ_x, and σ_y for the spin-$\frac{1}{2}$ system. H_2 then represents the Zeeman energy and H' the off-diagonal spin-phonon coupling. With these analogies our problem is the same as that considered by Huber and Van Vleck, with two differences—their perturbation H' included a term coupling η to the phonon coordinates v_q, and they did not treat the phonon scattering side of the problem.

C. Some Results

There is an exact relationship between $\langle\langle v_q;v_{q'}\rangle\rangle(\omega)$ and $\langle\langle x;x\rangle\rangle(\omega)$ which is derived in Appendix A:

$$\begin{aligned}\langle\langle v_q;v_{q'}\rangle\rangle(\omega)=&\frac{-\hbar}{2\pi}\frac{\delta_{qq'}}{(\omega_q^2-\omega^2)}\\&+\lambda^2\frac{X_q}{\omega_q^2-\omega^2}\langle\langle x;x\rangle\rangle(\omega)\frac{X_{q'}}{\omega_{q'}^2-\omega^2}.\end{aligned} \tag{4.17}$$

This is a general result that holds for any atomic Hamiltonian H_2; it depends only on the forms assumed for H' and H_l. Since Eq. (4.11c) says that $\langle\langle x;x\rangle\rangle(\omega)$ is an even function of ω, Eq. (4.17) says that $\langle\langle v_q;v_{q'}\rangle\rangle(\omega)$ is also.

When (4.17) is used in Eq. (4.13b), one finds that the Green's-function matrix $\mathfrak{G}(\omega)$ obeys the equation

$$\mathfrak{G}(\omega)=\mathbf{G}(\omega)-\mathbf{G}(\omega)\mathbf{t}(\omega)\mathbf{G}(\omega), \tag{4.18a}$$

with

$$\mathbf{t}(\omega)=|X)(X|t(\omega), \tag{4.18b}$$

$$t(\omega)=2\pi\lambda^2\langle\langle x;x\rangle\rangle(\omega)/\hbar. \tag{4.18c}$$

Thus $t(\omega)$ may be related to the polarizability by

$$t(\omega)=-(\lambda^2m/e^{*2})\alpha(\omega). \tag{4.19}$$

If a dilute solution of the 2-level atoms is imbedded in a medium with a refractive index $n(\omega)$, assumed real, and if the Lorentz local field correction applies, then one readily derives the following expression for the absorption coefficient (in cm^{-1}):

$$K(\omega)=(4\pi\omega p/cv_0)[(n^2+2)^2/9n]\,\text{Im}\alpha(\omega+i\epsilon). \tag{4.20}$$

Here c is the velocity of light and v_0 the volume of a unit cell. When Eqs. (1.7), (4.19), and (4.10) are combined, the result is

$$\langle\tau^{-1}\rangle(\omega)=\frac{3dmcv_0}{2\pi^2r\omega e^{*2}}\left[\frac{9n}{(n^2+2)^2}\right]\lambda^2\frac{\text{Im}g(\omega+i\epsilon)}{\rho_0(\omega)}K(\omega). \tag{4.21}$$

In favorable circumstances, one may be able to use this expression with experimental absorption data directly in the conductivity integral. Note that λ in Eq. (4.21) is the coupling constant in H' and not the wavelength.

In Appendix B an approximate result is derived for $\langle\langle x;\, x\rangle\rangle(\omega)$:

$$\frac{m\alpha(\omega)}{e^{*2}}=-\frac{2\pi}{\hbar}\langle\langle x;\, x\rangle\rangle(\omega)=\frac{f\langle\eta\rangle}{\omega^2-\omega_0{}^2+\lambda^2(\omega/\omega_0)g_T(\omega)}. \tag{4.22a}$$

Here $\langle\eta\rangle$ is given by Eq. (4.14a):

$$\langle\eta\rangle=\langle[|g\rangle\langle g|-|e\rangle\langle e|]\rangle\approx\tanh(\beta\hbar\omega_0/2), \tag{4.22b}$$

and the oscillator strength f by Eqs. (4.1) and (4.2):

$$f=2\omega_0|\langle g|x|e\rangle|^2/\hbar. \tag{4.22c}$$

The Green's function $g_T(\omega)$ appearing in (4.22a) is

$$g_T(\omega)=\sum_q\frac{\omega X_q{}^2\coth(\beta\hbar\omega_q/2)}{\omega_q(\omega_q{}^2-\omega^2)}. \tag{4.22d}$$

Separating imaginary and real parts gives (for ω positive)

$$\begin{aligned}\mathrm{Im}g_T(\omega+i\epsilon)&=\coth(\beta\hbar\omega/2)\pi\sum_q X_q{}^2\delta(\omega_q{}^2-\omega^2)\\&=\coth(\beta\hbar\omega/2)\ \mathrm{Im}g(\omega+i\epsilon)\end{aligned} \tag{4.23a}$$

and

$$\mathrm{Re}g_T(\omega+i\epsilon)=2\pi\omega P\int_0^\infty\frac{\mathrm{Im}g_T(\omega')d\omega'}{\omega'^2-\omega^2}. \tag{4.23b}$$

Here the symbol P denotes the principal value. Equation (4.23b) should be contrasted with the result

$$\mathrm{Re}g(\omega+i\epsilon)=2\pi P\int_0^\infty\frac{\omega'\ \mathrm{Im}g(\omega')}{\omega'^2-\omega^2}d\omega'. \tag{4.23c}$$

Note that $g_T(0)=0$, whereas

$$g(0)=2\pi\int_0^\infty\omega^{-1}\ \mathrm{Im}g(\omega)d\omega\neq 0.$$

Thus for the 2-level atom,

$$\Sigma(\omega,T)\longrightarrow\omega_0{}^2$$

as $\omega\longrightarrow 0$, whereas for the harmonic-oscillator impurity, Eq. (3.14) gives

$$\Sigma(0)=\omega_0{}^2-\lambda^2 g(0)<\omega_0{}^2.$$

The resonance condition obtained from Eq. (4.22a) is

$$\omega_r{}^2=\omega_0{}^2-\lambda^2(\omega_r/\omega_0)f\ \mathrm{Re}g_T(\omega_r). \tag{4.24}$$

For small ω_r, this will be close to ω_0, since $\mathrm{Re}g_T$ will be very small. It is then a good approximation to use the unperturbed value of $\langle\eta\rangle$:

$$\langle\eta\rangle_0=\tanh(\beta\hbar\omega_0/2).$$

At higher frequencies, if ω_r is noticeably different from ω_0, it is better to use

$$\langle\eta\rangle\approx\tanh(\beta\hbar\omega_r/2). \tag{4.25a}$$

An experiment would give ω_r as the resonance frequency; ω_0 would not be directly measurable. An experimental value f_e for the oscillator strength would be obtained by setting

$$|\langle g|x|e\rangle|^2=\hbar f_e/2\omega_r. \tag{4.25b}$$

One should then put $f=f_e(\omega_0/\omega_r)$ into Eqs. (4.22a) and (4.24):

$$\frac{m\alpha(\omega)}{e^{*2}}=\frac{-2\pi}{\hbar}\langle\langle x;\, x\rangle\rangle(\omega+i\epsilon)=\frac{\omega_0 f_e\langle\eta\rangle/\omega_r}{\omega^2-\omega_0{}^2+\lambda^2 f_e(\omega/\omega_r)g_T(\omega+i\epsilon)}, \tag{4.26a}$$

$$\omega_r{}^2=\omega_0{}^2-\lambda^2 f_e\ \mathrm{Re}g_T(\omega_r). \tag{4.26b}$$

The width of the resonance is given by

$$\begin{aligned}\omega_r\Delta\omega\approx\Delta_{1/2}\omega^2=\Gamma&=\frac{\lambda^2 f_e\ \mathrm{Im}g_T(\omega_r+i\epsilon)}{1+\lambda^2 f_e(d/d\omega^2\ \mathrm{Re}g_T)_r}\\&\approx\lambda^2 f_e\ \mathrm{Im}g(\omega_r+i\epsilon)\ \coth(\beta\hbar\omega_r/2).\end{aligned} \tag{4.27a}$$

Note that Eq. (4.27a) may be written

$$\begin{aligned}\Gamma(T)&=\Gamma(0)\ \coth(\beta\hbar\omega_r/2),\\\Gamma(0)&=\lambda^2 f_e\ \mathrm{Im}g(\omega_r+i\epsilon),\end{aligned} \tag{4.27b}$$

or

$$\Gamma(T)=f_e\ \coth(\beta\hbar\omega_r/2)\Gamma_{\mathrm{osc}}, \tag{4.27c}$$

where

$$\Gamma_{\mathrm{osc}}=\lambda^2\ \mathrm{Im}g(\omega_r+i\epsilon)$$

is the width of the equivalent harmonic-oscillator impurity level.

The strength S of the resonance may be identified with the ratio of the area $A(T)$ under the resonance part of the absorption curve to its value at $T=0$:

$$S(T)=A(T)/A(0)=\langle\eta\rangle=\tan(\beta\hbar\omega_r/2). \tag{4.28}$$

The mean phonon scattering rate is

$$\langle\tau^{-1}\rangle(\omega)=\frac{2pd\lambda^4 f_e{}^2(\omega_0\omega/\omega_r{}^2)(\mathrm{Im}g)^2\ \coth(\beta\hbar\omega/2)\ \tanh(\beta\hbar\omega_r/2)}{3r\pi\rho_0(\omega)\{[\omega^2-\omega_0{}^2+\lambda^2 f_e(\omega/\omega_r)\ \mathrm{Re}g_T]^2+[\lambda^2 f_e(\omega/\omega_r)\ \coth(\beta\hbar\omega/2)\ \mathrm{Im}g]^2\}}. \tag{4.29}$$

At resonance, we obtain a new peak theorem,

$$\langle\tau^{-1}\rangle(\omega_r)=[2pd/3r\pi\rho(\omega_r)](\omega_0/\omega_r)[\tanh(\beta\hbar\omega_r/2)]^2. \tag{4.30}$$

Except for the appearance of the ratio (ω_0/ω_r), which is likely to be close to unity, this result was foreseen in Eq. (2.17).

The new peak theorem differs only moderately from the peak theorem Eq. (2.9) for harmonic oscillator and/or substitutional impurities. It may be difficult to distinguish them in practical situations.

The optical-absorption coefficient may be obtained by combining Eqs. (4.21) and (4.29). Equations (4.29) and (3.15) share a property that may be very important when used in (4.21) to determine the absorption. The functions $\operatorname{Im}g(\omega+i\epsilon)$, $\operatorname{Re}g(\omega)$, and $\operatorname{Re}g_T(\omega)$ will have discontinuities in slope at the frequencies of those Van Hove singularities that couple to the configuration X. If the resonance frequency ω_r is close to one or more of these singular frequencies, there will be structure in the absorption curve. Such a structure is, of course, not included in the Lorentzian approximation or in the expression derived from the perturbation theory result for t [Eq. (4.7)].

D. Coupling of a Two-Level Atom to Perturbed Phonons

With a nonzero perturbation γ_l assumed of the form $\gamma_l|X)(X|$ in the lattice due to changes in force constants and/or mass, we have to modify the above results. The modifications are very similar to those for a harmonic oscillator coupled to perturbed phonons.

In Appendix C, it is shown that $\langle\langle x;x\rangle\rangle$ is changed by replacing $g_T(\omega)$ by $g_T(\omega)[1+\gamma_l g(\omega)]^{-1}$. Thus

$$\frac{m\alpha(\omega+i\epsilon)}{e^{*2}}=\frac{-2\pi}{\hbar}\langle\langle x;x\rangle\rangle(\omega+i\epsilon)$$

$$=\frac{\omega_0 f_e\langle\eta\rangle/\omega_r}{\omega^2-\omega_0{}^2+\lambda^2 f_e(\omega/\omega_r)g_T(1+\gamma_l g)^{-1}}. \qquad (4.31)$$

It is also shown in Appendix C that the scalar part of the t matrix is now given by

$$t=t_l+(\hbar/2\pi)[\lambda^2\langle\langle x;x\rangle\rangle/(1+g\gamma_l)^2], \qquad (4.32)$$

with

$$t_l=\gamma_l(1+g\gamma_l)^{-1}$$

and $\langle\langle x;x\rangle\rangle$ given by Eq. (4.31). Equation (4.32) is the exact analog for this problem of Eq. (3.20c). Explicit expressions for $\langle\tau^{-1}\rangle(\omega,T)$ and Γ are readily derived, but they are complicated and will not be given here. The peak theorem is also complicated, but it tends to Eq. (2.9) when the first term in (4.32) dominates and to (4.30) when the second term in (4.32) dominates.

V. APPLICATIONS TO EXPERIMENTS

An application of the results of this paper has been made to fit thermal-conductivity data on OH^- in alkali halides and will be published separately.[10]

One can look back at previous calculations of phonon scattering rates to see if they obey the peak theorem. A good example is $NaCl:Ag^+$.[11] In Ref. 11, a nearest-neighbor central force model was applied, with the force constant adjusted to give an infrared-active resonance at the observed 53-cm^{-1} frequency. $\langle\tau^{-1}\rangle(\omega)$ was then calculated on a computer using Eq. (1.8). The numerical result may be shown to agree quite well with the peak theorem. A recent detailed far infrared study of this system has shown that noncentral-force-constant changes, rather than central-force-constant changes, have the major role.[12] The width of the resulting calculated infrared resonance is not changed, but its oscillator strength is. The considerations of the present paper show that the behavior of $\langle\tau^{-1}\rangle(\omega)$ in the vicinity of the resonance would still be the same if it were machine calculated using the new force-constant models. The only differences would come away from the peak, where the Lorentzian approximation might break down. Thus unless the resonance tails really have a strong effect, the new calculation would not give better agreement with the experimental data than the old calculation did. The old discrepancies between theory and experiment, seen in Ref. 11, would not be due to inadequacies in the defect model, but rather to the incorrectness of Eqs. (1.1) and (1.2) at relatively high frequencies and/or to an inadequate treatment of 3-phonon processes.

In Ref. 12, data are presented showing an infrared resonance in $NaCl:F^-$ at 59.5 cm^{-1} with a width of less than 2 cm^{-1}. At 80°K the peak shifts to 64 cm^{-1}, and the width grows to 14 cm^{-1}. Thus at temperatures where a thermal-conductivity dip would appear (20–70°K), the F^- and Ag^+ resonances would have roughly the same position and shape. The considerations of the present paper then predict that thermal-conductivity-resonances dips should be qualitatively and quantatively similar, and the data in Ref. 11 show that they are.

When we apply the ideas of this paper to $NaCl:Li^+$, we learn something new about this system. There is a far infrared resonance at 44.5 cm^{-1} having widths of 5 cm^{-1} at 7°K and 17 cm^{-1} at 80°K.[12] Infrared absorption curves calculated using various theoretical models could give a peak in the right place, but the infrared oscillator strength was overestimated by factors of 20 to 300. One explanation was that not all the Li ions in the crystal were participating in this resonance; another was that the effective charge associated with the defect was anomalously low. If the second explanation were correct, the thermal-conductivity dip for a given concentration of Li^+ should be greater than that for the same concentration of Ag^+ because of the greater high-temperature width and lower frequency of the Li^+ resonance. Instead, the experimental-conductivity data

---

[10] R. L. Rosenbaum, C. K. Chau, and M. V. Klein, following paper, Phys. Rev. **186**, 852 (1969).

[11] R. F. Caldwell and M. V. Klein, Phys. Rev. **158**, 851 (1967).

[12] H. F. MacDonald, M. V. Klein, and T. P. Martin, Phys. Rev. **177**, 1292(1969).

show a weaker Li^+ depression for a given concentration by a factor of about 6. This proves rather convincingly that not all the Li^+ is active in producing the resonance.

ACKNOWLEDGMENTS

The author wishes to thank D. Cowan for useful discussions, D. K. Brice for a critical reading of the manuscript, and F. L. Vook for the opportunity to work on this paper while at Sandia Laboratories.

APPENDIX A

It is desired to derive Eq. (4.17). Starting with Eqs. (4.3), (4.14a), (3.2), (3.3), (4.15a), (4.15b), and (4.16a), (4.16b) [summarized above Eq. (4.17)], the following commutation relations may be derived:

$$[x,H]=i\hbar p\,, \tag{A1}$$

$$[p,H]=-i\hbar\omega_0{}^2x-i\hbar f\lambda\sum_q X_q v_q\eta\,, \tag{A2}$$

$$[x,p]=i\hbar f\eta\,, \tag{A3}$$

$$[\eta,x]=2ip/\omega_0\,, \tag{A4}$$

$$[\eta,p]=-2i\omega_0 x\,, \tag{A5}$$

$$[v_q,p_{q'}]=i\hbar\delta_{qq'}\,, \tag{A6}$$

$$[v_q,H]=i\hbar p_q\,, \tag{A7}$$

$$[p_q,H]=-i\hbar\omega_q{}^2v_q-i\hbar\lambda X_q x\,, \tag{A8}$$

$$[\eta,H]=2i\lambda\sum_q X_q v_q p/\omega_0\,. \tag{A9}$$

We begin by applying Eq. (4.11a) to $\langle\langle v_q;\, v_{q'}\rangle\rangle$. With the aid of Eq. (A7), we find

$$\langle\langle v_q;\, v_{q'}\rangle\rangle=i\langle\langle p_q;\, v_{q'}\rangle\rangle/\omega\,.$$

We apply Eq. (4.11a) again and use Eqs. (A6) and (A8) to obtain

$$\langle\langle v_q;\, v_{q'}\rangle\rangle=\frac{-\hbar\delta_{qq'}}{2\pi(\omega_q{}^2-\omega^2)}-\frac{\lambda X_q}{\omega_q{}^2-\omega^2}\langle\langle x;\, v_{q'}\rangle\rangle\,. \tag{A10}$$

Now apply Eq. (4.11b) twice to $\langle\langle x;\, v_{q'}\rangle\rangle$,

$$\langle\langle x;\, v_{q'}\rangle\rangle=[-\lambda X_{q'}/(\omega_{q'}{}^2-\omega^2)]\langle\langle x;\, x\rangle\rangle\,. \tag{A11}$$

Equations (A10) and (A11) together give Eq. (4.17).

APPENDIX B

In this Appendix, we derive Eqs. (4.22). We start by applying Eq. (4.11a) twice to $\langle\langle x;\, x\rangle\rangle$ and using Eqs. (A1)-(A3):

$$\langle\langle x;\, x\rangle\rangle=\frac{f\hbar\langle\eta\rangle}{2\pi(\omega^2-\omega_0{}^2)}+\frac{\lambda f}{\omega^2-\omega_0{}^2}\sum_q X_q\langle\langle v_q\eta;\, x\rangle\rangle\,. \tag{B1}$$

At this point we have a choice of operating on $v_q\eta$ or on x in $\langle\langle v_q\eta;\, x\rangle\rangle$. The result, Eq. (4.22), will be the same. Apply Eq. (4.11a) to $\langle\langle v_q\eta;\, x\rangle\rangle$:

$$\langle\langle v_q\eta;\, x\rangle\rangle=\frac{1}{2\pi\omega}\langle v_q[\eta,x]\rangle+\frac{2i\lambda}{\hbar\omega\omega_0}\sum_{q'} X_{q'}\langle\langle v_q v_{q'} p;\, x\rangle\rangle+\frac{i}{\omega}\langle\langle p_q\eta;\, x\rangle\rangle\,. \tag{B2}$$

When Eq. (4.11a) is applied to $\langle\langle p_q\eta;\, x\rangle\rangle$ in Eq. (B2), we obtain

$$\langle\langle p_q\eta;\, x\rangle\rangle=\frac{1}{2\pi\omega}\langle p_q[\eta,x]\rangle+\frac{2i\lambda}{\hbar\omega\omega_0}\sum_{q'} X_{q'}\langle\langle p_q v_{q'} p;\, x\rangle\rangle-i\lambda X_q\langle\langle x\eta;\, x\rangle\rangle/\omega-i\omega_q{}^2\langle\langle v_q\eta;\, x\rangle\rangle/\omega\,.$$

Thus

$$(\omega^2-\omega_q{}^2)\langle\langle v_q\eta;\, x\rangle\rangle=(\omega/2\pi)\langle v_q[\eta,x]\rangle+(i/2\pi)\langle p_q[\eta,x]\rangle+\frac{2\lambda}{\hbar\omega_0}\sum_{q'} X_{q'}\langle\langle(i\omega v_q-p_q)v_{q'}p;\, x\rangle\rangle+\lambda X_q\langle\langle x\eta;\, x\rangle\rangle\,. \tag{B3}$$

Consider the factor $\langle\langle x\eta;\, x\rangle\rangle$ appearing in the last term in Eq. (B3). By applying Eq. (4.11a) twice, we find

$$\langle\langle x\eta;\, x\rangle\rangle=\frac{[\omega\langle x\eta x-xx\eta\rangle+i\langle p\eta x-xp\eta\rangle]}{2\pi(\omega^2-\omega_0{}^2)}-\frac{\lambda f\omega/\omega_0}{\omega^2-\omega_0{}^2}\Sigma\,, \tag{B4}$$

where Σ is the sum appearing in Eq. (B1):

$$\Sigma=\sum_q X_q\langle\langle v_q\eta;\, x\rangle\rangle\,. \tag{B5}$$

Use of Eq. (A4) gives

$$\langle x\eta x-xx\eta\rangle=2i\langle xp\rangle/\omega_0\,. \tag{B6}$$

Differentiating (4.15b) gives

$$0=dx^2/dt=xp+px\,.$$

Hence, by Eq. (A3),

$$xp=\tfrac{1}{2}(xp-px)+\tfrac{1}{2}(xp+px)=\tfrac{1}{2}i\hbar f\eta\,. \tag{B7}$$

Then (B6) becomes

$$\langle x\eta x-xx\eta\rangle=-\hbar f\langle\eta\rangle/\omega_0\,. \tag{B8}$$

Now consider

$$\begin{aligned}p\eta x-xp\eta&=(p\eta x-px\eta)+(px\eta-xp\eta)\\&=2ip^2/\omega_0-i\hbar f\eta^2=0\end{aligned} \tag{B9}$$

by Eqs. (4.14b) and (4.16b). Equation (B4) then becomes

$$\langle\langle x\eta;\, x\rangle\rangle=-\frac{\hbar f\langle\eta\rangle\omega}{2\pi\omega_0(\omega^2-\omega_0{}^2)}-\frac{\lambda f\omega/\omega_0}{\omega^2-\omega_0{}^2}\Sigma\,. \tag{B10}$$

This result is exact.

With the aid of Eq. (A4), the first two terms in Eq. (B3) become

$$(i/\pi\omega_0)\langle(\omega v_q+ip_q)p\rangle\equiv -F_qX_q\lambda\hbar/2\pi. \qquad \text{(B11)}$$

This will be further evaluated below.

The third term in Eq. (B3) involves a fourth-order Green's function. We evaluate it approximately by replacing the products $v_qv_{q'}$ and $p_qv_{q'}$ by their expectation values

$$\langle v_qv_{q'}\rangle=\tfrac{1}{2}\delta_{qq'}(\hbar/\omega_q)\coth(\beta\hbar\omega_q/2) \qquad \text{(B12)}$$

and

$$\langle p_qv_{q'}\rangle=-\tfrac{1}{2}i\hbar\delta_{qq'}. \qquad \text{(B13)}$$

Equation (B12) is approximate, but holds exactly for the unperturbed phonons ($H'=0$). Equation (B13) is exact:

$$\begin{aligned}\langle p_qv_{q'}\rangle&=\tfrac{1}{2}\langle p_qv_{q'}-v_{q'}p_q\rangle+\tfrac{1}{2}\langle p_qv_{q'}+v_{q'}p_q\rangle\\&=\tfrac{1}{2}i\hbar\delta_{qq'}+\tfrac{1}{2}(d/dt)\langle v_qv_{q'}\rangle=-\tfrac{1}{2}i\hbar\delta_{qq'}+0.\end{aligned}$$

This approximation gives

$$\begin{aligned}&\langle\langle(i\omega v_q-p_q)v_qv_{q'}p;\,x\rangle\rangle\\&\quad\cong[(i\omega\hbar/2\omega_q)\coth(\beta\hbar\omega_q/2)+\tfrac{1}{2}i\hbar]\langle\langle p;\,x\rangle\rangle\\&\quad=\tfrac{1}{2}\hbar\omega[(\omega/\omega_q)\coth(\beta\hbar\omega_q/2)+1]\langle\langle x;\,x\rangle\rangle. \qquad \text{(B14)}\end{aligned}$$

Equation (B3) then becomes

$$\begin{aligned}&(\omega^2-\omega_q^2)\langle\langle v_q\eta;\,x\rangle\rangle\\&=-\lambda\frac{F_qX_q}{2\pi}\hbar+\frac{\lambda\omega}{\omega_0}X_q\left[\frac{\omega}{\omega_q}\coth(\beta\hbar\omega_q/2)+1\right]\langle\langle x;\,x\rangle\rangle\\&\qquad-\frac{\hbar\lambda f\langle\eta\rangle\omega X_q}{2\pi\omega_0(\omega^2-\omega_0^2)}-\frac{\lambda^2f(\omega/\omega_0)}{\omega^2-\omega_0^2}X_q\Sigma. \qquad \text{(B15)}\end{aligned}$$

Thus the quantity $\Sigma=\sum_q X_q\langle\langle v_q\eta;\,x\rangle\rangle$ obeys the equation

$$\begin{aligned}\Sigma=\frac{\lambda\hbar}{2\pi}g_1-\frac{\lambda\omega}{\omega_0}g_T\langle\langle x;\,x\rangle\rangle+\frac{\hbar f\langle\eta\rangle\omega}{2\pi\omega_0(\omega^2-\omega_0^2)}g\\+\frac{\lambda^2f(\omega/\omega_0)}{\omega^2-\omega_0^2}g\Sigma, \qquad \text{(B16)}\end{aligned}$$

with

$$g_1=\sum_q\frac{X_q^2F_q}{\omega_q^2-\omega_0^2}. \qquad \text{(B17)}$$

g_T is defined by Eq. (4.22d) and g is given by (2.12a). Equation (B16) when solved for Σ gives, for the second term in Eq. (B1),

$$\frac{\lambda f\Sigma}{\omega^2-\omega_0^2}=\frac{\dfrac{\lambda^2fg_1\hbar}{2\pi}-\dfrac{\lambda^2f\omega}{\omega_0}(g_T+g)\langle\langle x;\,x\rangle\rangle+\dfrac{\hbar\lambda^2f^2\langle\eta\rangle\omega}{2\pi\omega_0(\omega^2-\omega_0^2)}}{\omega^2-\omega_0^2-\lambda^2(\omega/\omega_0)fg}.$$

The resulting equation may be solved for $\langle\langle x;\,x\rangle\rangle$:

$$\begin{aligned}\langle\langle x;\,x\rangle\rangle=\frac{f\hbar\langle\eta\rangle/(2\pi)}{\omega^2-\omega_0^2+\lambda^2(\omega/\omega_0)fg_T}\\+\frac{\lambda^2fg_1\hbar/(2\pi)}{\omega^2-\omega_0^2+\lambda^2(\omega/\omega_0)fg_T}. \qquad \text{(B18)}\end{aligned}$$

We shall not use the second term in Eq. (B18), but for the record we shall derive an expression for g_1 by evaluating the left-hand side of (B11). By applying the equations of motion to the equation

$$(d/dt)\langle p_qx\rangle=0,$$

one obtains the result

$$\langle p_qx\rangle=-\langle v_qp\rangle. \qquad \text{(B19)}$$

Next consider

$$\begin{aligned}0=(d/dt)\langle p_qp\rangle=-\omega_q^2\langle v_qp\rangle-\omega_0^2\langle v_qx\rangle\\+f\lambda\sum_{q'}X_{q'}\langle p_qv_{q'}\eta\rangle+\lambda X_q\langle xp\rangle. \qquad \text{(B20)}\end{aligned}$$

The third term is already first order in λ. We therefore evaluate it using the unperturbed expectation value

$$\langle p_qv_{q'}\eta\rangle=\langle p_qv_{q'}\rangle\langle\eta\rangle=-\tfrac{1}{2}i\hbar\langle\eta\rangle\delta_{qq'}.$$

Use of Equations (B7) and (B18) in (B19) gives

$$\langle v_qp\rangle=0. \qquad \text{(B21)}$$

For $\langle p_qp\rangle$, consider the equations

$$\begin{aligned}0&=d\langle p_qx\rangle/dt=\langle p_qp\rangle-\omega_q^2\langle v_qx\rangle-\lambda X_q\hbar f/(2\omega_0),\\0&=d\langle v_qp\rangle/dt=\langle p_qp\rangle-\omega_0^2\langle v_qx\rangle-f\lambda\textstyle\sum_{q'}X_{q'}\langle v_{q'}v_q\eta\rangle.\end{aligned}$$

We make the approximation

$$\langle v_{q'}v_q\eta\rangle=\langle v_{q'}v_q\rangle\langle\eta\rangle=\tfrac{1}{2}\langle\eta\rangle(\hbar/\omega_q)\delta_{qq'}\coth(\beta\hbar\omega_q/2)$$

and solve for $\langle p_qp\rangle$:

$$\begin{aligned}\langle p_qp\rangle=[\lambda X_q\hbar f\langle\eta\rangle/2(\omega_q^2-\omega_0^2)]\\\times[\omega_q\coth(\beta\hbar\omega_q/2)-\omega_0\langle\eta\rangle^{-1}].\end{aligned}$$

This gives

$$F_q=[f\langle\eta\rangle/\omega_0(\omega_q^2-\omega_0^2)][\omega_q\coth(\beta\hbar\omega_q/2)-\omega_0\langle\eta\rangle^{-1}]$$

and

$$g_1=\frac{f\langle\eta\rangle}{\omega_0}\times\sum_q\frac{X_q^2[\omega_q\coth(\beta\hbar\omega_q/2)-\omega_0\coth(\beta\hbar\omega_0/2)]}{(\omega_q^2-\omega_0^2)(\omega_q^2-\omega^2)}. \qquad \text{(B22)}$$

We neglect the second term in Eq. (B18) because it is second order in λ and because it might greatly complicate the analysis of this problem. It may be that a consistent treatment that includes this term should also use a more exact expression than (B12) in the third term of Eq. (B3). The decoupling procedure represented by Eq. (B14) neglects multiple phonon effects, which appear to be very difficult to handle, but which might be important in the strong coupling limit.

APPENDIX C

Here Eqs. (4.31) and (4.32) will be justified. In the presence of a lattice perturbation matrix $\boldsymbol{\gamma}_l=\gamma_l|X)(X|$ everywhere in our derivation of $\langle\langle x;x\rangle\rangle$, we should replace an equation of the form

$$(\omega^2-\omega_q^2)f_q=j_q,$$

by

$$\sum_{q'}(\mathbf{G}^{-1}+\boldsymbol{\gamma}_l)_{qq'}f_{q'}=j_q.$$

The solution changes from $f_q=(\omega^2-\omega_q^2)j_q$ to

$$f_{q'}=\sum_q(\mathbf{G}^{-1}+\boldsymbol{\gamma}_l)_{q'q}{}^{-1}j_q. \tag{C1}$$

When this is done in Eq. (B11), which is then solved for $\langle\langle v_{q'}\eta;x\rangle\rangle$, we obtain

$$\langle\langle v_q\eta;x\rangle\rangle=\sum_{q'}(\mathbf{G}^{-1}+\boldsymbol{\gamma}_l)_{qq'}{}^{-1}R_{q'},$$

where $R_{q'}$ represents the right-hand side of Eq. (B11). The resulting expression for Σ is simply the old expression with different Green's functions. In particular, any Green's function of the form

$$\sum_q\frac{X_q{}^2N_q}{\omega_q{}^2-\omega^2}$$

becomes

$$\begin{aligned}\sum_{qq'}X_qN_q(\mathbf{G}^{-1}+\boldsymbol{\gamma}_l)_{qq'}X_{q'}&=\sum_{qq'}X_qN_q[\mathbf{G}^{-1}(\mathbf{I}+\boldsymbol{\gamma}_l\mathbf{G})^{-1}]_{qq'}X_{q'}\\&=\sum_{qq'}\frac{X_qN_q}{\omega_q{}^2-\omega^2}[(\mathbf{I}+\boldsymbol{\gamma}_l\mathbf{G})^{-1}]_{qq'}X_{q'}\\&=\sum_q\frac{X_q{}^2N_q}{(\omega_q{}^2-\omega^2)(1+\gamma_lg)}.\end{aligned} \tag{C2}$$

This last result follows from an expansion

$$(\mathbf{I}+\boldsymbol{\gamma}_l\mathbf{G})^{-1}=\mathbf{I}-\boldsymbol{\gamma}_l\mathbf{G}+\boldsymbol{\gamma}_l\mathbf{G}\boldsymbol{\gamma}_l\mathbf{G}-\cdots.$$

For example, consider the second term

$$\begin{aligned}-\sum_{q'}(\boldsymbol{\gamma}_l\mathbf{G})_{qq'}X_{q'}&=-\gamma_l\sum_{q'q''}X_qX_{q''}G_{q''q'}X_{q'}\\&=-\gamma_lX_q\sum_{q'}\frac{X_{q'}{}^2}{\omega_{q'}{}^2-\omega^2}=-\gamma_lgX_q.\end{aligned}$$

This is the second term of an expansion of $N_q(1+\gamma_lg)^{-1}$. Use of Eq. (C2) transforms Eq. (4.26a) into (4.31).

When the changes indicated by Eq. (C1) are made in Eqs. (A10) and (A11), we obtain

$$\begin{aligned}&\langle\langle v_q,v_{q'}\rangle\rangle\\&=-(\hbar/2\pi)\sum_p[(\mathbf{G}^{-1}+\boldsymbol{\gamma}_l)^{-1}]_{qp}\delta_{pq'}\\&\quad+\lambda^2\sum_{pp'}[(\mathbf{G}^{-1}+\boldsymbol{\gamma}_l)^{-1}]_{qp}\\&\quad\times X_p[(\mathbf{G}^{-1}+\boldsymbol{\gamma}_l)^{-1}]_{q'p'}X_{p'}\langle\langle x;x\rangle\rangle\\&=-(\hbar/2\pi)(\mathbf{G}-\mathbf{G}\mathbf{t}_l\mathbf{G})_{qq'}\\&\quad-\frac{\lambda^2X_qX_{q'}(-\hbar/2\pi)[\langle\langle x;x\rangle\rangle(2\pi/\hbar)]}{(\omega_q{}^2-\omega^2)(\omega_{q'}{}^2-\omega^2)(1+g\gamma_l)^2}.\end{aligned}$$

Thus the matrix $\mathfrak{G}$ has elements

$$\begin{aligned}\mathfrak{G}_{qq'}&=-2\pi\langle\langle v_q;v_{q'}\rangle\rangle/\hbar=G_{qq'}-(\mathbf{G}\mathbf{t}_l\mathbf{G})_{qq'}\\&\quad-\left[\mathbf{G}\frac{\lambda^2|X)(X|}{(1+g\gamma_l)^2}\langle\langle x;x\rangle\rangle\frac{2\pi}{\hbar}\mathbf{G}\right]_{qq'}=(\mathbf{G}-\mathbf{G}\mathbf{t}\mathbf{G})_{qq'},\end{aligned}$$

with $\mathbf{t}-|X)(X|t$ and t given by Eq. (4.32). Of course, $\langle\langle x;x\rangle\rangle$ will also contain new Green's functions as described by Eq. (C2) and will be given by Eq. (4.31).