Effects of Resonant Phonon Interactions on Shapes of Impurity Absorption Lines*

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A study is made of the interaction of an electron bound to an impurity center in a semiconductor with the phonon field of the material. In particular we study the shift and shape of optical absorption lines of donor impurities in semiconductors when the excitation energy lies close to the energy of an optical phonon branch of the vibrational spectrum of the crystal. The results exhibit a variety of phenomena. The optical absorption lines may be split or broadened either symmetrically or asymmetrically. The different possibilities depend primarily on the dispersion of the phonon bands in the vicinity of the electronic excitation energy. If the phonon energy is approximately independent of the wave number, a splitting of the line arises. Particular emphasis is given to the case of bismuth donors in silicon interacting with transverse optical phonons.

I. INTRODUCTION

In a recent publication Onton *et al.*[1] have reported, among other experimental results, a remarkable broadening of an excitation line of bismuth donor in silicon. They find that the optical transition lines from the ground state of Bi in Si $[1s(A_1)]$[2] to the excited states $2p_\pm$, $3p_0$, $3p_\pm$ are sharp. However, the $1s(A_1) \rightarrow 2p_0$ transition line is anomalously broad and asymmetric. The energy of this excitation is 59.51 meV. The authors of Ref. 1 attribute this broadening to an interaction between the electron excitation and transverse optical modes TO $\langle 100 \rangle$ of Si which have energies around 58.7 ± 1.2 meV at the Brillouin zone edge. They also notice that the $1s(A_1) \rightarrow 2p_\pm$ transition has an energy of 64.57 meV, which is very close to the Raman energy of Si, 64.8 meV. However, this line is not anomalously broad.

That the $1s(A_1) \rightarrow 2p_0$ line is broadened by the resonant interaction of the bound electron with an optical mode is demonstrated by the behavior of this line when the material is subjected to uniaxial strain. By applying a uniaxial stress along either a $\langle 100 \rangle$ or a $\langle 110 \rangle$ crystallographic direction,[3] the lines $1s(A_1) \rightarrow np$ split into two components called $np(\pm)$, where the $\pm$ refer to the high-energy and the low-energy components, respectively. Figure 1 of Ref. 1 shows the excitation spectra of Bi donors in Si. It is seen that under uniaxial compression along $\langle 110 \rangle$ the $2p_0(+)$ component is much sharper than the $2p_0(-)$ component, both being sharper than the zero stress line. The sharpening of the $2p_0(\pm)$ lines arises because the energy shifts are sufficiently large to take these excitation lines out of resonance with the strongly coupled optical modes; the $2p_0(+)$ line is sharper than the $2p_0(-)$ line because the former is shifted twice as much from the zero stress position as compared to the latter, which apparently takes it farther out of resonance. The pronounced resonance effect is clearly seen in Fig. 2 of Ref. 1. Onton *et al.*[1] also draw attention to the anomalous width of line 2 of the gallium acceptor in silicon[4]; for this case, the energy of the transition is indeed close to the Raman energy of silicon. These results appear to suggest strongly that the nature of the impurity wave functions determine the nature of the phonons involved in the resonant broadening. It is indeed interesting that such a pronounced electron-phonon interaction occurs even in a covalent crystal like Si, given the resonance conditions. The recent experimental findings of Dickey and Larsen[5] and of Summers *et al.*[6] are further examples of line broadening under resonant conditions. The effect of uniaxial stress on line 1 of tellurium donors in aluminum antimonide[7] is yet another example of a similar phenomenon.

The object of the present paper is to discuss a theory of the phenomenon described in Ref. 1 with special reference to bismuth donors in silicon.

Section II deals first with the general theory of the broadening of an optical absorption line due to the interaction of the electronic system with a phonon field. We then discuss the particular problem under consideration and analyze the different forms which the line shape can take.

II. THEORY

A. General Formulation

We are concerned here with an optical transition from the electronic ground state of an impurity to some excited state whose excitation energy ϵ (we shall take units such that $\hbar = 1$) is approximately equal to the energy of the phonons that are most strongly coupled to this electronic transition.

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Thus we first consider a simple model in which we calculate the transition rate from the initial state to each of the "exact" eigenstates in the space spanned by the unperturbed states (of an excited impurity and a de-excited impurity plus any phonon).[8] We denote the states by

$$\begin{aligned} |u\rangle &\equiv \text{impurity excited, no phonons and no photons,} \\ |\mathbf{q}\mu\rangle &\equiv \text{impurity in the ground state, one phonon in state } \mathbf{q}\mu \text{ and no photons.} \end{aligned} \tag{1}$$

We enumerate all lattice modes by the labels $\mathbf{q}$ and μ, where $\mathbf{q}$ is the wave vector of the phonon and μ the particular branch to which it belongs. If the crystal contains N primitive cells and z_0 atoms per primitive cell there are $3z_0N$ phonon modes. Thus the label μ indicates whether the phonons are longitudinal or transverse, optical or acoustical. We assume that the Hamiltonian can be decomposed into a diagonal and a nondiagonal part

$$H=H_0+H_1 \tag{2}$$

in the representation given by Eq. (1). We will have

$$\begin{aligned} &H_0|u\rangle=\epsilon|u\rangle, \qquad H_0|\mathbf{q}\mu\rangle=\omega_{q\mu}|\mathbf{q}\mu\rangle, \\ &H_1|u\rangle=\sum_{q\mu}\beta_{q\mu}|\mathbf{q}\mu\rangle, \quad H_1|\mathbf{q}\mu\rangle=\beta^*_{q\mu}|u\rangle. \end{aligned} \tag{3}$$

H_1 is the electron-phonon interaction in the concrete example that we analyze later.

Thus H is represented by a $(3z_0N+1)\times(3z_0N+1)$ matrix whose diagonal components are ϵ and $\omega_{q\mu}$ for all $\mathbf{q}\mu$. The nondiagonal matrix elements are $\langle\mathbf{q}\mu|H_1|u\rangle=\beta_{q\mu}$, $\langle u|H_1|\mathbf{q}\mu\rangle=\beta^*_{q\mu}$ while all other matrix elements vanish.

The rate at which photons of energy ν are absorbed is *proportional* to

$$P(\nu)=2\pi\sum_{\lambda}|\langle u|\lambda\rangle|^2\delta(\nu-E_\lambda), \tag{4}$$

where the $|\lambda\rangle$ are the exact eigenstates of H with eigenvalues E_λ. Using the well-known relation

$$\delta(\nu-E_\lambda)=-(1/\pi)\,\mathrm{Im}(\nu-E_\lambda+i\eta)^{-1}, \tag{5}$$

where η is a positive infinitesimal, we have

$$\begin{aligned} P(\nu)&=-2\,\mathrm{Im}\sum_{\lambda}\langle u|\lambda\rangle(\nu-E_\lambda+i\eta)^{-1}\langle\lambda|u\rangle \\ &=-2\,\mathrm{Im}\langle u|(\nu-H+i\eta)^{-1}|u\rangle. \end{aligned} \tag{6}$$

[8] A simpler model for this broadening was developed concurrently with the present work by Harris and Prohofsky, Phys. Rev. **170**, 749 (1968). In their model, the transition is coupled to only one phonon mode, which in turn is mixed with all other phonon modes by a constant matrix element. This model also gives a line broadening with structure. Since the model corresponds to a particular and rather unrealistic specialization of the model presented here, the structure should not be considered so comparable with experiment. The Harris and Prohofsky model is discussed in some detail in Appendix A. Some necessary mathematical results are derived in Appendix B.

If we define

$$|\chi_\nu\rangle=(\nu-H+i\eta)^{-1}|u\rangle \tag{7}$$

and expand in our subspace

$$|\chi_\nu\rangle=B(\nu)|u\rangle+\sum_{q\mu}D_{q\mu}(\nu)|\mathbf{q}\mu\rangle, \tag{8}$$

then

$$P(\nu)=-2\,\mathrm{Im}B(\nu). \tag{9}$$

To obtain $B(\nu)$ we combine Eqs. (7) and (8), obtaining the set of linear equations

$$(\nu-\epsilon+i\eta)B(\nu)-\sum_{q\mu}\beta^*_{q\mu}D_{q\mu}(\nu)=1, \tag{10}$$

$$-\beta_{q\mu}B(\nu)+(\nu-\omega_{q\mu}+i\eta)D_{q\mu}(\nu)=0. \tag{11}$$

These equations are simply solved:

$$D_{q\mu}(\nu)=[\beta_{q\mu}/(\nu-\omega_{q\mu}+i\eta)]B(\nu) \tag{12}$$

and

$$B(\nu)=\left[\nu-\epsilon+i\eta-\sum_{q\mu}\frac{|\beta_{q\mu}|^2}{\nu-\omega_{q\mu}+i\eta}\right]^{-1}. \tag{13}$$

In the limit in which N approaches infinity, the summation over q can be replaced by an integral. We define

$$\rho(\omega)|\beta(\omega)|^2=\sum_{\mu}\frac{\Omega}{(2\pi)^3}\int\frac{dS_\mu|\beta_{q\mu}|^2}{|\nabla_q\omega_{q\mu}|}, \tag{14}$$

where Ω is the volume of the crystal and the integral over dS_μ is to be taken over the surface in q space for which $\omega_{q\mu}=\omega$. It might appear at first sight that $\rho(\omega)|\beta(\omega)|^2$ is proportional to the volume of the crystal. However, we shall see that $\beta_{q\mu}$ is proportional to $\Omega^{-1/2}$ so that $|\beta(\omega)|^2\rho(\omega)$ is independent of Ω; $\rho(\omega)$ is the density of phonon states of energy ω. The quantity $|\beta(\omega)|^2$ is thus the average of $|\beta_{q\mu}|^2$ over all phonon modes having energy ω. We can now rewrite Eq. (13) as follows:

$$B(\nu)=\left\{\nu-\epsilon-\mathcal{P}\int\frac{|\beta(\omega)|^2\rho(\omega)d\omega}{\nu-\omega}+i[\eta+\pi|\beta(\nu)|^2\rho(\nu)]\right\}^{-1}. \tag{15}$$

Thus, for ν such that $\beta(\nu)\neq 0$,

$$P(\nu)=2\pi|\beta(\nu)|^2\rho(\nu)\Big/\left\{\left[\nu-\epsilon-\mathcal{P}\int\frac{|\beta(\omega)|^2\rho(\omega)d\omega}{\nu-\omega}\right]^2+[\pi|\beta(\nu)|^2\rho(\nu)]^2\right\}. \tag{16}$$

Here $\mathcal{P}$ before an integral signifies that the principal value of the integral is to be taken.

B. Inclusion of the Natural Width

We have assumed that the only states to which $|u\rangle$ is connected by the Hamiltonian are the states $|\mathbf{q}\mu\rangle$. To include the natural width, we must also allow $|u\rangle$ to decay to states with the impurity in its ground state and a photon $\mathbf{p}$ present, states which we denote by $|\mathbf{p}\rangle$. If $\nu_p=c|\mathbf{p}|$ is the energy of such a photon, the Hamiltonian has the following structure:

$$\langle\mathbf{p}|H|\mathbf{p}\rangle=\nu_p,\quad \langle u|H|u\rangle=\epsilon,\quad \langle\mathbf{q}\mu|H|\mathbf{q}\mu\rangle=\omega_{q\mu},$$
$$\langle\mathbf{q}\mu|H|u\rangle=\beta_{q\mu},\quad \langle\mathbf{p}|H|u\rangle=\gamma_p. \tag{17}$$

Notice that we have not specified the photon polarizations explicitly but they are to be considered as implicit in all sums over $\mathbf{p}$. Equation (8) must now be replaced by

$$|\chi_\nu\rangle=\sum_p A_p(\nu)|\mathbf{p}\rangle+B(\nu)|u\rangle+\sum_{q\mu} D_{q\mu}(\nu)|\mathbf{q}\mu\rangle. \tag{18}$$

The system of Eqs. (10) and (11) is now enlarged to

$$(\nu-\nu_p+i\eta)A_p(\nu)-\gamma_pB(\nu)=0, \tag{19}$$

$$-\sum_p \gamma_p^*A_p(\nu)+(\nu-\epsilon+i\eta)B(\nu)-\sum_{q\mu}\beta^*_{q\mu}D_{q\mu}(\nu)=1, \tag{20}$$

and

$$-\beta_{q\mu}B(\nu)+(\nu-\omega_{q\mu}+i\eta)D_{q\mu}(\nu)=0. \tag{21}$$

From Eq. (19)

$$A_p(\nu)=[\gamma_p/(\nu-\nu_p+i\eta)]B(\nu), \tag{22}$$

so that Eq. (20) becomes

$$(\nu-\tilde{\epsilon}+i\eta)B(\nu)-\sum_{q\mu}\beta^*_{q\mu}(\nu)D_{q\mu}(\nu)=1, \tag{23}$$

where

$$\tilde{\epsilon}=\epsilon+\mathcal{P}\sum_p\frac{|\gamma_p|^2}{\nu-\nu_p}-i\pi\sum_p|\gamma_p|^2\delta(\nu-\nu_p) \tag{24}$$

is an effective complex energy for the excited state. Thus the natural width is included in our original calculation if, in Eq. (15), we replace ϵ by $\tilde{\epsilon}$, the energy of $|u\rangle$ when the real and imaginary parts of the self-energy due to interaction with the electromagnetic field are included.

C. Electron-Phonon Interaction

We now turn to the calculation of $\beta_{q\mu}$ for the particular problem that we have in mind. We consider a donor impurity in Si. Let $\mathbf{k}_j(j=\pm1,\pm2,\pm3)$ be the positions in $\mathbf{k}$ space where the minima of the conduction band of Si occur. These minima are located at $\mathbf{k}_{\pm1}=(\pm k_0,0,0)$, $\mathbf{k}_{\pm2}=(0,\pm k_0,0)$, and $\mathbf{k}_{\pm3}=(0,0,\pm k_0)$, where k_0 is 0.82 of the wave number from the center of the fundamental Brillouin zone (FBZ) to its boundary along the [100] direction. Within the framework of the effective mass approximation,[2] the wave functions for the stationary states of the donor electron are of the form $F_j(\mathbf{r})\varphi_j(\mathbf{r})$, where

$$\varphi_j(\mathbf{r})=\exp(i\mathbf{k}_j\cdot\mathbf{r})u_j(\mathbf{r}) \tag{25}$$

is the Bloch function for a conduction electron at $\mathbf{k}_j$ in the FBZ and $F_j(\mathbf{r})$ is an envelope function satisfying the equation

$$[E_j(-i\nabla)-e^2/\kappa_0 r]F_j(\mathbf{r})=EF_j(\mathbf{r}). \tag{26}$$

Here κ_0 is the static dielectric constant of Si and $E_j(\mathbf{k})$ is the energy eigenvalue of a conduction electron near the minimum at $\mathbf{k}_j$. If we take the minimum at $(0,0,k_0)$, we have

$$E(\mathbf{k})=(k_x^2+k_y^2)/2m_t+(k_z-k_0)^2/2m_l, \tag{27}$$

for values of $\mathbf{k}$ in the vicinity of $\mathbf{k}_3$. The Cartesian axes are parallel to the cubic axes of the crystal. The longitudinal and transverse effective masses are $m_l=0.98$ and $m_t=0.19$ in units of the free-electron mass.[9] Using the trial wave function[10]

$$F^{(0)}(\mathbf{r})=(\pi a^2b)^{-1/2}\exp\{-[(x^2+y^2)/a^2+z^2/b^2]^{1/2}\}, \tag{28}$$

a minimum of the expectation value of the Hamiltonian in Eq. (26) is obtained by setting $a=25\times10^{-8}$ cm and $b=14.2\times10^{-8}$ cm. We mention this fact only to remind the reader that, despite the large anisotropy of the effective masses, a and b differ by much less. From now on we shall take $a=b$ in order to simplify our calculations. We also remind the reader that the ground state is sixfold degenerate within the framework of the effective mass approximation. However, this degeneracy is split by the crystal potential into a single A_1, a doublet E, and a triplet T_1. The symmetry-adapted wave functions corresponding to these states can be found in Ref. 2. In this paper we shall only need the state $1s(A_1)$ given by

$$\Psi_0(\mathbf{r})=(1/\sqrt{6})\sum_j F_j^{(0)}(\mathbf{r})\varphi_j(\mathbf{r}). \tag{29}$$

The excited states are also degenerate and are, in principle, split by the crystal potential. However, since these wave functions extend over many lattice constants their energy is not substantially altered by the central core potential and can then be regarded as degenerate. This is indeed supported by experiments. The excited state $2p_0$ will be taken to be

$$F^{(2p)}(\mathbf{r})=[z/4a^2(2\pi a)^{1/2}]\exp(-r/2a), \tag{30}$$

where we have already set $a=b$ as before.

We must now consider the matrix elements of the electron-phonon interaction involving transitions between the ground state $1s(A_1)$ to a state $2p_0$ with absorption of a phonon.

Let $\mathbf{n}$ be the lattice points and $\boldsymbol{\rho}$ be the vectors from the origin of a primitive cell to the different atoms in the

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cell. For Si $\mathbf{n}$ is the set of translation vectors of a face-centered-cubic lattice and $\boldsymbol{\varrho}=(0,0,0)$ or $a_L(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, where a_L is the lattice constant. The equilibrium positions of the atoms are $\mathbf{n}+\boldsymbol{\varrho}$ while their actual positions will be designated by $\mathbf{R}_{n\rho}=\mathbf{n}+\boldsymbol{\varrho}+\mathbf{u}_{n\rho}$. The vectors $\mathbf{u}_{n\rho}$ are simply the displacements of the atoms from their equilibrium positions.

The Hamiltonian of the crystal with one electron in the conduction band is

$$H=p^2/2m+V(\mathbf{r},\{\mathbf{n}+\boldsymbol{\varrho}+\mathbf{u}_{n\rho}\})+\sum_{q\mu}\omega_{q\mu}a^\dagger_{q\mu}a_{q\mu}$$

$$\approx H_0+\sum_{n\rho}\mathbf{u}_{n\rho}\cdot(\partial V/\partial\mathbf{u}_{n\rho})_{\{u_{n\rho}\}=0}, \quad (31)$$

where

$$H_0=p^2/2m+V(\mathbf{r},\{\mathbf{n}+\boldsymbol{\varrho}\})+\sum_{q\mu}\omega_{q\mu}a^\dagger_{q\mu}a_{q\mu}. \quad (32)$$

Here $a^\dagger_{q\mu}(a_{q\mu})$ is a creation (destruction) operator of a phonon in state $\mathbf{q}\mu$ and $V(\mathbf{r},\{\mathbf{n}+\boldsymbol{\varrho}+\mathbf{u}_{n\rho}\})$ is the potential energy of an electron in the deformed lattice. In the second line of Eq. (31) we have expanded this potential and neglected terms containing the displacements $\mathbf{u}_{n\rho}$ to orders higher than the first.

We notice that $(\partial V/\partial\mathbf{u}_{n\rho})_{\{u_{n\rho}\}=0}$ is a function of the position vector $\mathbf{r}$ of the electron. It is easy to convince oneself from symmetry considerations that

$$(\partial V/\partial\mathbf{u}_{n\rho})_{\{u_{n\rho}\}=0}=\mathbf{C}_\rho(\mathbf{r}-\mathbf{n}) \quad (33)$$

depends on $\mathbf{r}-\mathbf{n}$ only. Also, it is clear that $\mathbf{C}_\rho(\mathbf{r}-\mathbf{n})$ is significantly different from zero only if $\mathbf{r}$ is in the vicinity of $\mathbf{n}$. This is because $-\mathbf{C}_\rho(\mathbf{r}-\mathbf{n})$ is the force acting on the atom at $\mathbf{n}\boldsymbol{\varrho}$ due to an electron at $\mathbf{r}$, or equivalently the negative of the force on an electron at $\mathbf{r}$ due to the atom at $\mathbf{n}\boldsymbol{\varrho}$. Thus the electron-phonon interaction can be written as

$$H_1=\sum_{n\rho}\mathbf{u}_{n\rho}\cdot\mathbf{C}_\rho(\mathbf{r}-\mathbf{n}). \quad (34)$$

The displacement $\mathbf{u}_{n\rho}$ can be expanded in terms of creation and destruction operators for phonons as follows:

$$\mathbf{u}_{n\rho}=\sum_{q\mu}\mathbf{e}_{\rho q\mu}(2\delta_0\Omega\omega_{q\mu})^{-1/2}(a_{q\mu}+a^\dagger_{-q\mu})\exp(i\mathbf{q}\cdot\mathbf{n}), \quad (35)$$

where $\mathbf{e}_{\rho q\mu}$ is a unit polarization vector, δ_0 the mass density of the crystal, Ω its volume, $\mathbf{q}$ the wave vector of the phonon, μ its polarization and character (i.e., acoustic or optical), and $\omega_{q\mu}$ the frequency of that mode.

Since the six $2p_0$ states are degenerate we consider transitions from $|\mathbf{q}\mu\rangle\equiv|1s(A_1);\mathbf{q}\mu\rangle$ [in which the electron is in state (29) and there is one phonon present in the state $\mathbf{q}\mu$] to $|u_i\rangle\equiv|2p_0,i;0\rangle$ [where the electron is in $F_i^{(2p_0)}(\mathbf{r})\varphi_i(\mathbf{r})$ and there is no phonon present]. The matrix element is

$$\langle u_i|H_1|\mathbf{q}\mu\rangle=\sum_{n\rho}(2\delta_0\Omega\omega_{q\mu})^{-1/2}$$

$$\times e^{i\mathbf{q}\cdot\mathbf{n}}\mathbf{e}_{\rho q\mu}\cdot\int\Psi_i^{(2p_0)*}(\mathbf{r})\mathbf{C}_\rho(\mathbf{r}-\mathbf{n})\Psi_0(\mathbf{r})d\mathbf{r}. \quad (36)$$

We now let

$$\sum_\rho\mathbf{e}_{\rho q\mu}\cdot\mathbf{C}_\rho(\mathbf{r}-\mathbf{n})=\mathcal{U}_{q\mu}(\mathbf{r}-\mathbf{n}). \quad (37)$$

Then

$$\langle u_i|H_1|\mathbf{q}\mu\rangle=\sum_{\mathbf{n}}(12\delta_0\Omega\omega_{q\mu})^{-1/2}e^{i\mathbf{q}\cdot\mathbf{n}}$$

$$\times\sum_j\int d\mathbf{r}\,F_i^{(2p_0)}(\mathbf{r})\varphi_i^*(\mathbf{r})\mathcal{U}_{q\mu}(\mathbf{r}-\mathbf{n})F_j^{(0)}(\mathbf{r})\varphi_j(\mathbf{r}).$$

Now $F_i^{(2p_0)}(\mathbf{r})$ and $F_j^{(0)}(\mathbf{r})$ vary slowly with $\mathbf{r}$ as compared with $\mathcal{U}_{q\mu}(\mathbf{r}-\mathbf{n})$ because the latter is significantly different from zero in the vicinity of $\mathbf{r}-\mathbf{n}=0$ while the former wave functions extend over many primitive cells. Thus we write

$$\langle u_i|H_1|\mathbf{q}\mu\rangle\approx(12\delta_0\Omega\omega_{q\mu})^{-1/2}\sum_n\sum_j F_i^{(2p_0)*}(\mathbf{n})F_j^{(0)}(\mathbf{n})$$

$$\times\exp[i(\mathbf{k}_j-\mathbf{k}_i+\mathbf{q})\cdot\mathbf{n}]\int d\mathbf{r}\;\varphi_i^*(\mathbf{r})\mathcal{U}_{q\mu}(\mathbf{r})\varphi_j(\mathbf{r}). \quad (38)$$

Here we have used

$$\int d\mathbf{r}\;\varphi_i^*(\mathbf{r})\mathcal{U}_{q\mu}(\mathbf{r}-\mathbf{n})\varphi_j(\mathbf{r})=\exp[i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{n}]$$

$$\times\int d\mathbf{r}\;\varphi_i^*(\mathbf{r})\mathcal{U}_{q\mu}(\mathbf{r})\varphi_j(\mathbf{r}),$$

which follows from Bloch's theorem. We can now rewrite Eq. (38) in the form

$$\langle u_i|H_1|\mathbf{q}\mu\rangle=(12\delta_0\Omega\omega_{q\mu})^{-1/2}\sum_j\int d\mathbf{r}\;\varphi_i^*(\mathbf{r})\mathcal{U}_{q\mu}(\mathbf{r})\varphi_j(\mathbf{r})$$

$$\times\sum_{\mathbf{n}}F_i^{(2p_0)*}(\mathbf{n})F_j^{(0)}(\mathbf{n})\exp(i\mathbf{Q}_{ij}\cdot\mathbf{n}), \quad (39)$$

where

$$\mathbf{Q}_{ij}=\mathbf{k}_j-\mathbf{k}_i+\mathbf{q}. \quad (40)$$

We can approximate the sum over $\mathbf{n}$ in Eq. (39) as follows:

$$\sum_{\mathbf{n}}F_i^{(2p_0)*}(\mathbf{n})F_j^{(0)}(\mathbf{n})e^{i\mathbf{Q}\cdot\mathbf{n}}$$

$$\approx\Omega_0^{-1}\int d\mathbf{r}\,F_i^{(2p_0)*}(\mathbf{r})F_j^{(0)}(\mathbf{r})e^{i\mathbf{Q}\cdot\mathbf{r}},$$

where Ω_0 is the volume of the primitive cell. The integral can be estimated using Eqs. (28) and (30), where, in the

former, we set $a=b$. We find that

$$\sum F_i^{(2p_0)*}(\mathbf{n})F_j^{(0)}(\mathbf{n})e^{i\mathbf{Q}\cdot\mathbf{n}}\approx\frac{6\sqrt{2}iQ}{a^5\Omega_0(Q^2+\kappa^2)^3}\cos(\mathbf{Q},\mathbf{k}_i), \quad (41)$$

where

$$\kappa=3/2a, \quad (42)$$

and $\cos(\mathbf{Q},\mathbf{k}_i)$ is the cosine of the angle formed by the vectors $\mathbf{Q}$ and $\mathbf{k}_i$. We see from Eqs. (41) and (40) that the selection rule $\mathbf{k}_j-\mathbf{k}_i+\mathbf{q}=0$ for the matrix elements, which one would expect from the naive consideration that a donor electron, because of its extended wave function, behaves approximately like a Bloch function, is not correct. In fact we can write for transitions to $|u_i\rangle=|2p_0,i;\,0\rangle$ the following matrix element:

$$\beta_{q\mu}=\langle u_i|H_1|\mathbf{q}\mu\rangle^*=\sum_j A_{ij}^{q\mu}\frac{Q_{ij}}{(\kappa^2+Q_{ij}^2)^3}\cos(\mathbf{Q}_{ij},\mathbf{k}_i), \quad (43)$$

where

$$A_{ij}^{q\mu}=-i(6/\delta_0\Omega\omega_{q\mu})^{1/2}(a^5\Omega_0)^{-1}\times\int d\mathbf{r}\;\varphi_i(\mathbf{r})\mathcal{U}_{q\mu}(\mathbf{r})\varphi_j^*(\mathbf{r}). \quad (44)$$

Thus, when the selection rule $\mathbf{k}_j-\mathbf{k}_i+\mathbf{q}=0$ is strictly satisfied, $\beta_{q\mu}=0$. For Q_{ij} small, $\beta_{q\mu}\neq0$, but because $\beta_{q\mu}$ decreases very rapidly when $Q_{ij}a>1$ it is appreciably different from zero only for small values of $|\mathbf{Q}_{ij}|$. Thus, in a sense, the selection rule mentioned above is not entirely inaccurate.

According to Lax and Hopfield,[11] transitions between one valley and the opposite one ($\mathbf{k}_3\rightarrow\mathbf{k}_{-3}$) occur only with a longitudinal acoustic phonon (LA) of symmetry Δ_1. Transitions between adjacent valleys occur either with a LA phonon or a TO phonon of symmetry Σ_1. Because of energy considerations the last case is the only one of ultimate interest to us. This explains why the $2p_0$ line is anomalously broad while $2p_\pm$ is not, as mentioned in the introduction.

D. Calculating the Self-Energy Function

We return now to a detailed consideration of the actual line shape. According to Eq. (16),

$$P(\nu)=\frac{\Gamma_\beta(\nu)}{\{\nu-\epsilon-\Sigma_\beta(\nu)\}^2+\{\frac{1}{2}\Gamma_\beta(\nu)\}^2}, \quad (45)$$

where

$$\tfrac{1}{2}\Gamma_\beta(\nu)=\pi\sum_{q\mu}|\beta_{q\mu}|^2\delta(\nu-\omega_{q\mu}) \quad (46)$$

and

$$\Sigma_\beta(\nu)=\frac{1}{2\pi}\mathcal{P}\int\frac{\Gamma_\beta(\epsilon')}{\nu-\epsilon'}d\epsilon' \quad (47)$$

are the imaginary and real parts of the self-energy function

$$\Sigma_\beta(\nu)+\tfrac{1}{2}i\Gamma_\beta(\nu)=\sum_{q\mu}\frac{|\beta_{q\mu}|^2}{\nu-\omega_{q\mu}-i\eta}. \quad (48)$$

We have neglected the natural line width, which we assume to be small compared with all values of $\Gamma_\beta(\nu)$ of interest.

Of fundamental interest, we see, is the line-width function $\Gamma_\beta(\nu)$. This function has contributions from decay processes via phonons connecting all pairs of conduction band valleys. The dominant contributions to $\Gamma_\beta(\nu)$ will be from phonons having $\mathbf{q}$'s for which

$$\mathbf{Q}_{ij}(\mathbf{q})=\mathbf{q}-\mathbf{k}_{ij}\equiv\mathbf{q}-(\mathbf{k}_i-\mathbf{k}_j) \quad (49)$$

is small and $\mathbf{q}$ may be outside the fundamental Brillouin zone. In this latter case the phonon frequency $\omega_{q\mu}$ is defined by periodically extending $\omega_{q\mu}$ from the FBZ.

Using Eqs. (43) and (44) we must calculate

$$|\beta_{q\mu}|^2=\sum_{jj'}\frac{A_{ij}^{q\mu}A_{ij'}^{q\mu*}Q_{ij}Q_{ij'}\cos(\mathbf{Q}_{ij},\mathbf{k}_i)\cos(\mathbf{Q}_{ij'},\mathbf{k}_i)}{(\kappa^2+Q_{ij}^2)^3(\kappa^2+Q_{ij'}^2)^3}. \quad (50)$$

Terms in the sum for which $j\neq j'$ will be negligible because at least one of Q_{ij} and $Q_{ij'}$ will be large. Thus

$$|\beta_{q\mu}|^2=\sum_j\frac{|A_{ij}^{q\mu}|^2Q_{ij}^2\cos^2(\mathbf{Q}_{ij},\mathbf{k}_i)}{(\kappa^2+Q_{ij}^2)^6}. \quad (51)$$

In evaluating

$$\Gamma_\beta(\nu)=2\pi\sum_{q\mu}|\beta_{q\mu}|^2\delta(\nu-\omega_{q\mu}), \quad (52)$$

the contributions from $\mathbf{k}_{ij}=0,\mathbf{k}_{ij}$ along [101], [011], [$\bar{1}$01], [0$\bar{1}$1] and $\mathbf{k}_{ij}$ along [100] will occur at well-separated energies, so we can compute them one at a time.

Now the dependence of $|A_{ij}^{q\mu}|^2$ on $\mathbf{q}$ is not known, in general. For some branches, it vanishes for $\mathbf{q}$ along certain symmetry directions. We shall neglect any branch and pair of valleys for which $A_{ij}^{k_{ij}\mu}=0$. If $|A_{ij}^{k_{ij}\mu}|^2\neq0$ we may expand in Q_{ij}. The dominant term in $\Gamma_\beta(\nu)$ will come from $|A_{ij}^{k_{ij}\mu}|^2$, and we ignore corrections.

Also, we shall only be interested in modes for which $\nu\approx\epsilon$.

Let us then discuss the three different cases in turn.

Case I. $\mathbf{k}_{ij}=0$ $(j=i)$. For the μth band we must evaluate an integral of the form

$$I_\mu^{(1)}(\nu)=\int d\mathbf{Q}\frac{Q_z^2}{(\kappa^2+Q^2)^6}\delta(\nu-\omega_{q\mu}), \quad (53)$$

where we have taken the z axis in the $\mathbf{k}_i$ direction. If $\nu\approx\epsilon$, we must consider only optical modes for which we shall assume $\omega_{q\mu}$ to have the form

$$\omega_{q\mu}=\omega_{q=0,\mu}-M_\mu Q^2. \quad (54)$$

[11] M. Lax and J. J. Hopfield, Phys. Rev. 124, 115 (1961).

Let us call the frequency of the phonon $q_{ij,\mu}$ for this case $\omega_{1,\mu}$:

$$\omega_{1,\mu}\equiv\omega_{q=0,\mu}. \tag{55}$$

We find then that

$$I_\mu^{(1)}(\nu)=\tfrac{2}{3}\pi M_\mu^{7/2}\frac{(\omega_{1,\mu}-\nu)^{3/2}}{(M_\mu\kappa^2+\omega_{1,\mu}-\nu)^6}, \quad \text{if} \quad \nu<\omega_{1,\mu}$$
$$=0, \quad \text{if} \quad \nu>\omega_{1,\mu}. \tag{56}$$

Case II. $\mathbf{k}_{ij}$ *along* [101], [011], [$\bar{1}$01], [0$\bar{1}$1] (*i.e.*, $j\neq\pm i$). It is obvious that the contributions from these four directions are the same. We consider $\mathbf{k}_i$ along [001], $\mathbf{k}_j$ along [0$\bar{1}$0] so that $\mathbf{k}_i-\mathbf{k}_j$ is along [011].

We see from Fig. 1 that $\mathbf{k}_{ij}$ lies outside the fundamental Brillouin zone, because $\lambda>\frac{3}{4}$, where the valleys lie at $\lambda k_{\max}(\lambda\approx0.82)$ and $k_{\max}$ is the distance to the zone boundary in the [100] direction. In fact, it lies on the square face of the zone boundary between the primitive cells in $\mathbf{k}$ space centered at (1,1,1) and (−1, 1, 1) in $\mathbf{k}$ space. We take $\mathbf{k}_{ij}$ as a polar axis and introduce three unit vectors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$ in this coordinate system, as shown in Fig. 2. Then we have

$$\mathbf{Q}=Q\cos\theta\mathbf{u}_3+Q\sin\theta(\cos\varphi\mathbf{u}_1+\sin\varphi\mathbf{u}_2),$$
$$\hat{z}=(\sqrt{\tfrac{1}{2}})(\mathbf{u}_1+\mathbf{u}_3),$$
$$Q_z=\mathbf{Q}\cdot\hat{z}=Q(\cos\theta+\sin\theta\cos\varphi)/\sqrt{2}.$$

Also, in the neighborhood of $\mathbf{k}_{ij}$, we can expand $\omega_{q\mu}$:

$$\omega_{q\mu}=\omega_{k_{ij},\mu}+\mathbf{Q}_{ij}\cdot(\nabla\omega_{q\mu})_{q=k_{ij}}+\cdots. \tag{57}$$

We call the resonant frequency of case II

$$\omega_{2,\mu}\equiv\omega_{k_{ij},\mu}. \tag{58}$$

Furthermore, by symmetry, we can see from Fig. 1 that $(\nabla\omega_{q\mu})_{k_{ij}}$ is along $\mathbf{k}_{ij}$. Let

$$\nabla\omega_{q,\mu}=s_{2,\mu}\mathbf{u}_3, \tag{59}$$

where $s_{2,\mu}$ can be $\gtrless0$.

Then we must evaluate

$$I_\mu^{(2)}(\nu)=\int d\mathbf{Q}\frac{Q^2}{(\kappa^2+Q^2)^6}\cos^2(\mathbf{Q},\mathbf{k})\delta(\nu-\omega_{q\mu})$$
$$=\int d\mathbf{Q}\tfrac{1}{2}Q^2\frac{(\sin\theta\cos\varphi+\cos\theta)^2}{(\kappa^2+Q^2)^6}$$
$$\times\delta(\nu-\omega_{2,\mu}-Qs_{2,\mu}\cos\theta). \tag{60}$$

We obtain

$$I_\mu^{(2)}(\nu)=\frac{|s_{2,\mu}|^7}{80}\frac{9(\nu-\omega_{2,\mu})^2+s_{2,\mu}{}^2\kappa^2}{[(\nu-\omega_{2,\mu})^2+(s_{2,\mu}\kappa)^2]^5}. \tag{61}$$

Case III. $\mathbf{k}_{ij}$ *along* [001]. We note again that $\mathbf{k}_{ij}$ is not in the FBZ. This time it is within one of the neighboring primitive cells in $\mathbf{k}$ space, and is equivalent to $\mathbf{k}_{ij}=2(1-\lambda)k_{\max}\hat{z}$ in the FBZ.

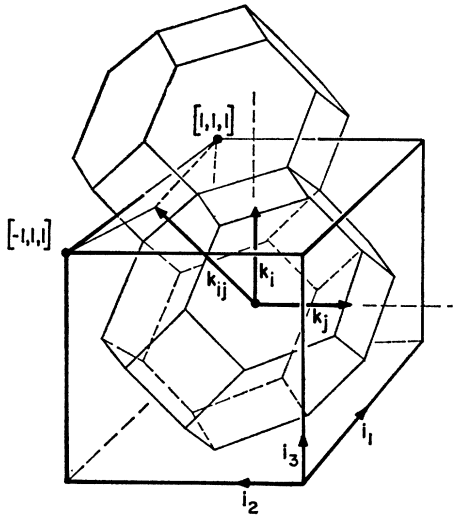


FIG. 1. Two cells in $\mathbf{k}$ space showing that, in case II, $\mathbf{k}_{ij}$ lies outside the fundamental Brillouin zone.

Now we can take the polar axis along [001] so that

$$Q^2\cos^2(\mathbf{Q},\hat{z})=Q^2\cos^2\theta.$$

If we make the linear expansion of $\omega_{q\mu}$,

$$\omega_{q\mu}=\omega_{3,\mu}-s_{3,\mu}Q\cos\theta, \tag{62}$$

then we find that

$$I_\mu^{(3)}(\nu)=\frac{\pi|s_{3,\mu}|^7}{5}\frac{(\nu-\omega_{3,\mu})^2}{[(\nu-\omega_{3,\mu})^2+(s_{3,\mu}\kappa)^2]^5}. \tag{63}$$

This is in error when

$$(\nu-\omega_{3,\mu})^2\lesssim(s_{3\mu}\kappa)^2(\kappa/q_{ij})$$

(we assume $\kappa/q_{ij}\ll1$) because of the inadequacy of Eq. (62). The form of $I_\mu^{(3)}(\nu)$ is more accurately determined near ω_μ if we replace Eq. (62) by

$$\omega_{q\mu}=\omega_{3,\mu}-s_{3,\mu}(|\mathbf{q}|-|\mathbf{q}_{ij}|). \tag{64}$$

Then, when $\nu\rightarrow\omega_{3,\mu}$, we obtain

$$I_\mu^{(3)}(\nu)=(\pi|s_{3,\mu}|^7/120)[(s_{3,\mu}q_{ij})^2(s_{3,\mu}\kappa)^3]^{-1}, \tag{65}$$

which is small but not zero.

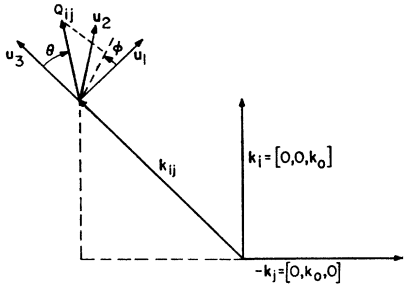


FIG. 2. Coordinate system $\mathbf{u}_1$, $\mathbf{u}_2$, $\mathbf{u}_3$ to describe $\mathbf{Q}_{ij}$ in case II.

In the three cases we observe that $\Gamma_\beta(\nu)$ has a local minimum at $\omega_{1,\mu}$, $\omega_{2,\mu}$, or $\omega_{3,\mu}$, respectively, and goes to zero again rapidly away from the minimum. In the first case $\Gamma_\beta(\nu)$ is zero for all $\nu>\omega_{1,\mu}$ as well. In the second and third cases, $\Gamma_\beta(\nu)$ is an even function about this central minimum. We now turn to a qualitative discussion of the expected absorption line shape to be observed if ϵ is near one of these three frequencies.

E. Qualitative Discussion

We wish to discuss the energy dependence of $P(\nu)$ as given by

$$P(\nu)=\frac{\Gamma_\beta(\nu)}{[\nu-\epsilon-\Sigma_\beta(\nu)]^2+[\frac{1}{2}\Gamma_\beta(\nu)]^2}, \tag{66}$$

where

$$\Gamma_\beta(\nu)=2\pi\sum_{q\mu}|\beta_{q\mu}|^2\delta(\nu-\omega_{q\mu})=2\pi|\beta(\nu)|^2\rho(\nu) \tag{67}$$

and

$$\Sigma_\beta(\nu)=\frac{1}{2\pi}\mathcal{P}\int\frac{\Gamma_\beta(\epsilon')}{\nu-\epsilon'}d\epsilon' \tag{68}$$

and we have neglected the natural linewidth Γ_γ (and, of course, η). We assume $\Gamma_\beta(\nu)$ to be localized around some frequency ω_0, to have a value Γ_0 at ω_0, and a half-width δ defined in some reasonable way [like $\Gamma_\beta(\omega_0+\delta)=\frac{1}{2}\Gamma_0$].

The exact character of the absorption curve, for a given form of $\Gamma_\beta(\nu)$, depends on three parameters: Γ_0, δ, and

$$\Delta=\epsilon-\omega_0. \tag{69}$$

To put this dependence into its most explicit form, we express $\Gamma_\beta(\nu)$ in terms of a function $g(x)$ centered at the origin and having unit peak height and unit half-width:

$$g(x)=\Gamma_\beta(\omega_0+x\delta)/\Gamma_0, \tag{70}$$

so that

$$\Gamma_\beta(\nu)=\Gamma_0 g[(\nu-\omega_0)/\delta]. \tag{71}$$

Then $g(0)=1$ and $g(1)=\frac{1}{2}$.

Similarly, the real part of the self-energy function $\Sigma_\beta(\nu)$ can be expressed in terms of a function $\sigma(x)$ defined by

$$\sigma(x)=\frac{1}{\pi}\mathcal{P}\int\frac{g(x')}{x-x'}dx', \tag{72}$$

so that

$$\Sigma_\beta(\nu)=\tfrac{1}{2}\Gamma_0\sigma[(\nu-\omega_0)/\delta]. \tag{73}$$

In case I, because $\Gamma_\beta(\omega_{1,\mu})=0$, we take ω_0 to be some frequency $<\omega_{1,\mu}$. In case III, $\Gamma_\beta(\omega_{3,\mu})=0$ unless we use

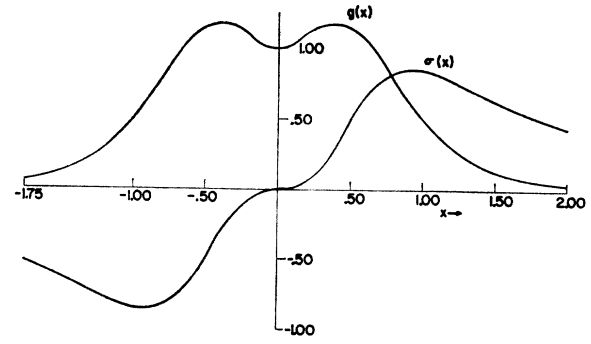
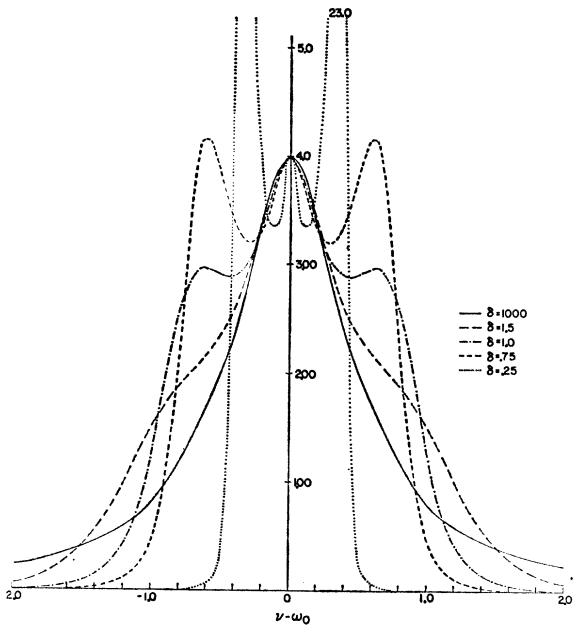
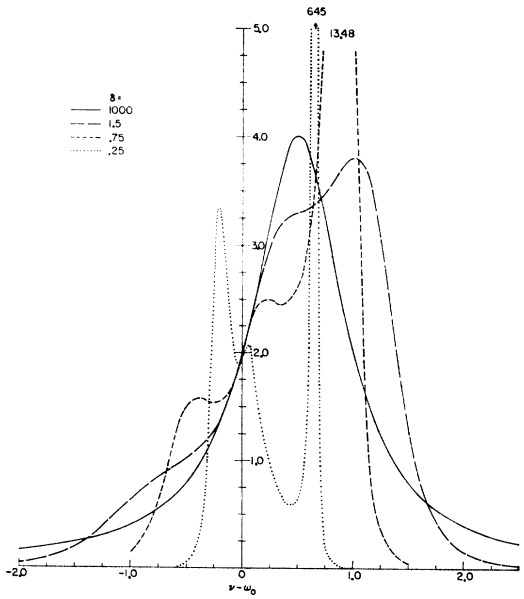


FIG. 3. Graphs of the functions $g(x)$ and $\sigma(x)$.



(a)



(b)

FIG. 4. Absorption line shape for various values of δ when in resonance [$\Delta=0$, Fig. 4(a)] and off resonance [$\Delta=0.5$, Fig. 4(b)]. Energy units, $\Gamma_0=1$.

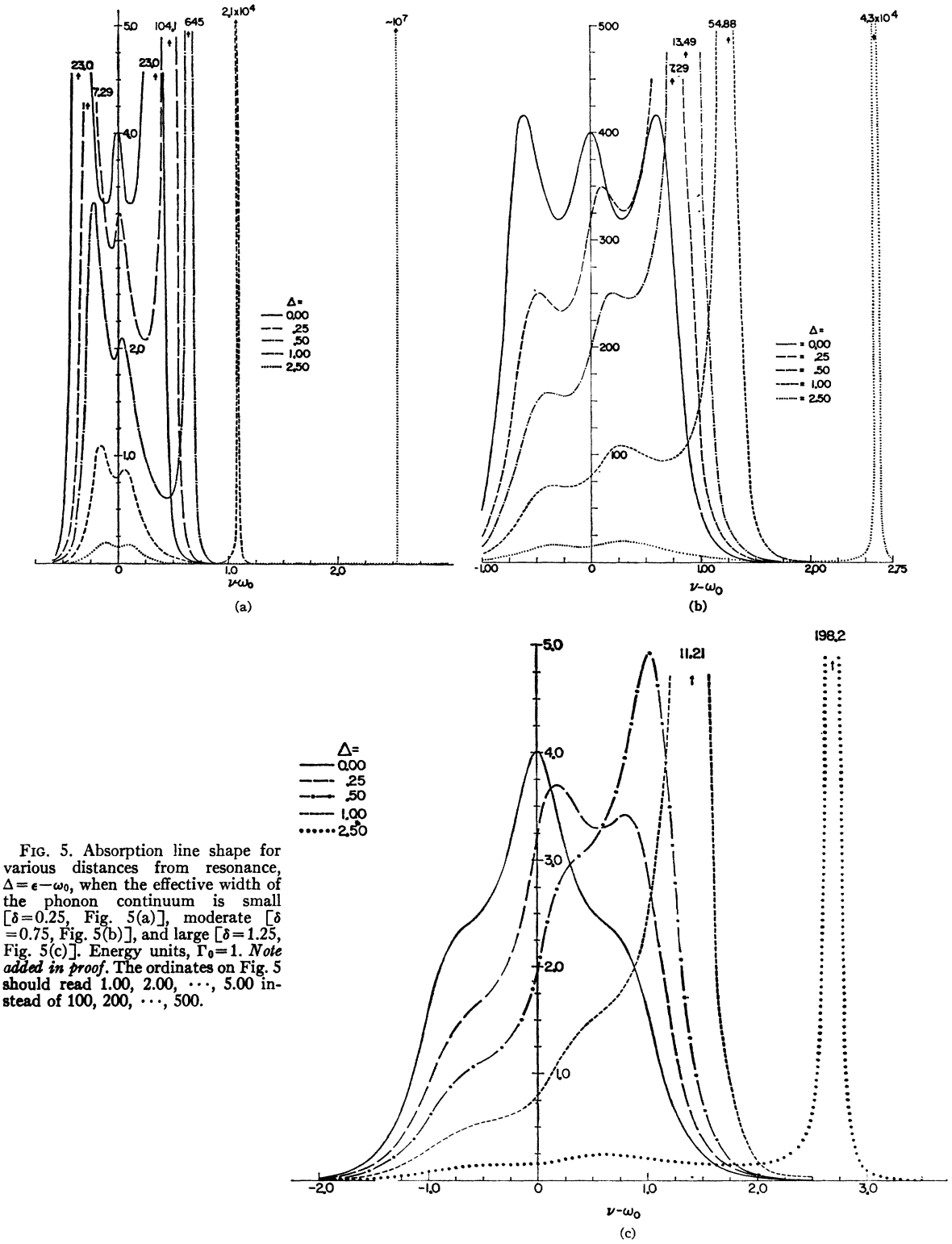


FIG. 5. Absorption line shape for various distances from resonance, $\Delta=\epsilon-\omega_0$, when the effective width of the phonon continuum is small [$\delta=0.25$, Fig. 5(a)], moderate [$\delta=0.75$, Fig. 5(b)], and large [$\delta=1.25$, Fig. 5(c)]. Energy units, $\Gamma_0=1$. *Note added in proof.* The ordinates on Fig. 5 should read 1.00, 2.00, ···, 5.00 instead of 100, 200, ···, 500.

the more accurate form implied by (64). $g(x)$ is an even function about $x=0$, whichever form we use. In case II, we take $\omega_0=\omega_{2,\mu}$ and $g(x)$ is again even. Because of the particular form of $g(x)$, $\sigma(x)$ is not only odd but also $\sigma'(0)=0$. For this case $g(x)$ and $\sigma(x)$ are shown in Fig. 3.

We can now express $P(\nu)$ in terms of the functions $g(x)$

and $\sigma(x)$:

$$P(\nu)=\frac{4}{\Gamma_0}\frac{g(x)}{[[(2\delta/\Gamma_0)(x-\Delta/\delta)-\sigma(x)]^2+[g(x)]^2]}, \quad (74)$$

where

$$x=(\nu-\omega_0)/\delta. \quad (75)$$

Although there are three independent parameters all having the dimensions of energy, variations of these parameters for which Γ_0/δ and Δ/δ remain constant produce changes in $P(\nu)$ that amount only to scale changes of P and ν. In the calculations displayed in Figs. 4 and 5, we have fixed Γ_0 and varied independently δ (or δ/Γ_0) and Δ [or $(\Delta/\delta)/(\Gamma_0/\delta)$].

As an aid in discussing the qualitative behavior of $P(\nu)$ for arbitrary $g(x)$, we should recall from Eq. (4) [or its analog in terms of the exact eigenstates of (17), in the event the natural width of $|u\rangle$ is included] that

$$\int P(\nu)d\nu=2\pi\sum_{\lambda}|\langle u|\lambda\rangle|^2=2\pi. \quad (76)$$

Thus, whatever the function $g(x)$ and the values of the parameters Δ, Γ_0, and δ, the total area under $P(\nu)$ is just 2π.

From the form (73), the qualitative behavior of $P(\nu)$ can now be discussed for various values of Δ, Γ_0, and δ. We restrict our discussion to case II.

Characteristics of case II. The line shape $P(\nu)$ for case II is plotted for different values of δ and Δ in Figs. 4 and 5. Before considering limiting cases and detailed behavior, we can make some general remarks about these line shapes.

(a) If $\Delta=0$, the line is symmetric; otherwise, it is not and the bigger peak occurs at a higher (lower) energy when ϵ is greater (less) than ω_0.

(b) If $\Gamma_\beta(\nu)$ is a slowly varying function near ϵ, because either δ or Δ is large, then $P(\nu)$ will be close to a Lorentzian line of width $\Gamma_\beta(\epsilon)$.

(c) In general, the line is neither symmetric nor Lorentzian. It can have one or two prominent peaks and possibly a third one if $\Gamma_\beta(\nu)$ has a sufficiently pronounced minimum at ω_0.

In order to understand the dependence of line shape on δ and Δ, we have calculated $P(\nu)$ for many points on the "$\delta-\Delta$ plane," especially along the lines $\Delta=0$ and 0.5 and $\delta=0.25$, 0.75, and 1.25 as shown schematically in Fig. 6. It is useful first to comment on the various limiting cases and then to make more detailed observations.

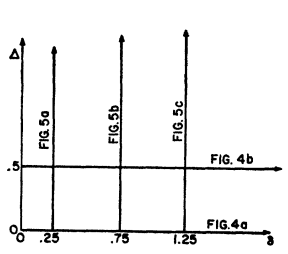


FIG. 6. Schematic diagram showing the ranges of δ and Δ in Figs. 4(a) and 4(b) and 5(a)–5(c).

$\delta\to\infty$. As seen in Figs. 4(a) and 4(b) and anticipated above, the absorption line approaches a pure Lorentzian around ϵ with linewidth Γ_0 for all Δ. This is because the linewidth function $\Gamma_\beta(\nu)$ is then essentially constant near ϵ.

$\delta\to 0$. If $\Delta\neq 0$ [Fig. 4(b)], $P(\nu)$ becomes an extremely sharp line at ϵ. If $\Delta=0$ [Fig. 4(a)], $P(\nu)$ becomes two very sharp lines at $\epsilon\pm[(1/2\pi)\int\Gamma_\beta(\epsilon)d\epsilon]^{1/2}$ which stay apart if $\Gamma_0\delta$ is held constant but which merge if Γ_0 is held constant. This special case, with $\Gamma_0\delta=$const, was treated by Sander.[12] The electronic state $|u\rangle$ forces discrete states to split off both above and below the cluster of continuum states around ω_0, each being composed about 50% of $|u\rangle$.

$\Delta\to\infty$ [Figs. 5(a)–5(c)]. When Δ is sufficiently large that the absorption line near ϵ and the width function $\Gamma_\beta(\nu)$ have well-separated peaks, then $\Gamma_\beta(\nu)$ is essentially constant in the neighborhood of ϵ, whatever the size of δ. The absorption line near ϵ is a Lorentzian with a width $\simeq\Gamma_\beta(\epsilon)$. The line is centered about an energy $\epsilon-\Sigma_\beta(\epsilon)$, i.e., it is displaced slightly from ϵ in a direction away from ω_0 by the small self-energy function $\Sigma_\beta(\epsilon)$. There will also be a very small (and possibly broad) absorption peak around ω_0 essentially proportional to $\Gamma_\beta(\epsilon)$. This "peak" will have a height $\alpha\Gamma_0/\Delta^2$, a half-width δ, and so an area $\Gamma_0\delta/\Delta^2$, which is assumed to be very small.

$\Delta=0$ [Fig. 4(a)]. The line in this case is symmetric. For small δ, in addition to the two peaks mentioned above (as $\delta\to 0$), there is also a small central peak arising from the central minimum in $\Gamma_\beta(\nu)$. In order that $\int\Gamma_\beta(\epsilon)d\epsilon$ remain constant, Γ_0 must tend to ∞ if $\delta\to 0$. But the central peak height is proportional to $1/\Gamma_0$, so in this limit it disappears. As δ increases, the central peak remains while the big side peaks move out, are broadened, and become smaller. Finally the side peaks disappear, leaving only a central Lorentzian.

If Δ is small but different from zero [Fig. 4(b)], then, for small δ, the three peaks seen for $\Delta=0$ are still present although the one nearest to ϵ is larger and the others are smaller. As δ increases, the side peaks decrease in magnitude the central peak increases and merges with the dominant side peak. Eventually only this central peak remains, becoming a Lorentzian centered at ϵ.

We also observe that, even for large Δ, if δ is large enough there is never more than one noticeable peak, whatever the value of Δ, although the shape may be far from Lorentzian.

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[12] L. Sander, Phys. Letters **27A**, 355 (1968).

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APPENDIX A

In a recent paper,[8] Harris and Prohofsky have considered a similar model in which the impurity can decay, emitting a phonon into only one special mode which we shall call k_0, which in turn can be scattered into any mode of a continuum $k_1, k_2, \cdots, k_N$. We designate the frequency of the mode k_n by Ω_n. Thus, neglecting natural widths, this model, slightly generalized, is described by the Hamiltonian

$$H=\begin{pmatrix} \epsilon & \beta^* & 0 & \cdots & 0 \\ \beta & \Omega_0 & \lambda_1^* & \cdots & \lambda_N^* \\ 0 & \lambda_1 & \Omega_1 & \cdots & 0 \\ \vdots & & & & \\ 0 & \lambda_N & 0 & & \Omega_N \end{pmatrix}, \tag{A1}$$

in the representation $|u\rangle, |k_0\rangle, \cdots, |k_N\rangle$. The trivial generalization has been to let λ_n depend on n. We note that $\lambda_n=0(N^{-1/2})$.

It is immediately clear that this model is equivalent to a special case of that described by Eq. (3) if we make a one-to-one correspondence between the states $|q\mu\rangle$ and the eigenstates $|\alpha\rangle$ of the $(N+1)\times(N+1)$ matrix in the lower right corner of (A1). To see this we write

$$|\alpha\rangle=\varphi_{\alpha 0}|k_0\rangle+\sum_{n=1}^{N}\varphi_{\alpha n}|k_n\rangle. \tag{A2}$$

Then, the eigenvalue equation

$$H|\alpha\rangle=\omega_\alpha|\alpha\rangle \tag{A3}$$

is equivalent to the set of algebraic equations

$$\Omega_0\varphi_{\alpha 0}+\sum_{n=1}^{N}\lambda_n^*\varphi_{\alpha n}=\omega_\alpha\varphi_{\alpha 0}, \tag{A4}$$

$$\lambda_n\varphi_{\alpha 0}+\Omega_n\varphi_{\alpha n}=\omega_\alpha\varphi_{\alpha n}. \tag{A5}$$

These equations are readily solved to yield

$$\omega_\alpha=\Omega_0+\sum_{n=1}^{N}\frac{|\lambda_n|^2}{\omega_\alpha-\Omega_n}, \tag{A6}$$

while the normalization of the eigenvectors gives

$$|\varphi_{\alpha 0}|^2=\left[1+\sum_{n=1}^{N}\frac{|\lambda_n|^2}{(\omega_\alpha-\Omega_n)^2}\right]^{-1}. \tag{A7}$$

Whatever the value of Ω_0, if the Ω_n $(n=1, 2, \cdots, N)$ form a quasi-continuum, there are N-1 quasicontinuum energies ω_α, one lying between every consecutive pair of Ω_n, Ω_{n+1}. There are also two discrete energies ω_0 and ω_N lying below the continuum and above the continuum, respectively.

In the new representation $|u\rangle$, and $\{|\alpha\rangle\}$, the Hamiltonian has the same form as that in Eq. (3), with

$$\beta_\alpha=\langle\alpha|H|u\rangle=\beta\varphi_{\alpha 0} \tag{A8}$$

for all α. Thus

$$\beta_\alpha=\beta\left[1+\sum_{n=1}^{N}\frac{|\lambda_n|^2}{(\omega_\alpha-\Omega_n)^2}\right]^{-1/2}. \tag{A9}$$

Now for a finite box and no degeneracies, the energies Ω_n are split by $O(N^{-1})$. It is shown in Appendix B that as N approaches infinity, if ω_α lies between Ω_m and Ω_{m+1}, then

$$\sum_n\frac{|\lambda_n|^2}{(\omega_\alpha-\Omega_n)}\to\mathcal{P}\int d\Omega\,\rho(\Omega)\frac{|\lambda(\Omega)|^2}{\omega_\alpha-\Omega}+\pi|\lambda(\omega_\alpha)|^2\rho(\omega_\alpha)\cot\delta_\alpha, \tag{A10}$$

where

$$\delta_\alpha=\pi\left(\frac{\omega_\alpha-\Omega_m}{\Omega_{m+1}-\Omega_m}\right), \quad m\geq 1. \tag{A11}$$

$\rho(\Omega)$ is the density of phonon energies at Ω, and $|\lambda(\Omega)|^2$ is the average of $|\lambda(\Omega_n)|^2$ over all modes with energies lying in a small neighborhood of Ω. The phase shift δ_α is determined by inserting Eq. (A10) into the eigenvalue equation (A6) to give

$$\omega_\alpha-\Omega_0-\mathcal{P}\int d\Omega\,\rho(\Omega)\frac{|\lambda(\Omega)|^2}{\omega_\alpha-\Omega}=\pi|\lambda(\omega_\alpha)|^2\rho(\omega_\alpha)\cot\delta_\alpha, \tag{A12}$$

where now ω_α can be replaced by Ω_n everywhere except in δ_α.

It is also shown in Appendix B that

$$\sum_n\frac{|\lambda_n|^2}{(\omega_\alpha-\Omega_n)^2}=[\pi\rho(\omega_\alpha)\lambda(\omega_\alpha)]^2(1+\cos^2\delta_\alpha)+O(1)$$
$$=\frac{[\omega_\alpha-\Omega_0-\mathcal{P}\int d\Omega\,\rho(\Omega)|\lambda(\Omega)|^2/(\omega_\alpha-\Omega)]^2+[\pi\rho(\omega_\alpha)|\lambda(\omega_\alpha)|^2]^2}{|\lambda(\omega_\alpha)|^2}+O(1),$$
if ω_α is in the continuum
$$=\int d\Omega\rho(\Omega)|\lambda(\Omega)|^2(\omega_\alpha-\Omega)^{-2}+O(1), \quad \text{if } \omega_\alpha \text{ is discrete.} \tag{A13}$$

For the case considered in Ref. 8, as $N\to\infty$,

$$|\beta_\alpha|^2=|\beta|^2\frac{|\lambda(\omega_\alpha)|^2}{[\omega_\alpha-\Omega_0-\mathcal{P}\int d\Omega\,\rho(\Omega)|\lambda(\Omega)|^2/(\omega_\alpha-\Omega)]^2+[\pi\rho(\omega_\alpha)|\lambda(\omega_\alpha)|^2]^2}. \tag{A14}$$

Since the vectors $(\beta,0,0,\cdots,0)$ and $(\beta_0,\beta_1,\cdots,\beta_N)$ are related by an orthogonal transformation, they must have the same norm: $|\beta|^2=\sum_\alpha|\beta_\alpha|^2$. That this is so is seen explicitly in the limit $\lambda\to 0$, when

$$\beta_\alpha\underset{\lambda\to 0}{\longrightarrow}\beta\delta(\omega_\alpha-\Omega_0). \tag{A15}$$

Thus the model of Ref. 8 is equivalent to assuming that the electronic transition is coupled to all phonon modes but with a coupling strength dependent only on energy and having essentially a Lorentzian shape [neglecting the energy dependence of $\lambda(\Omega)$ and $\rho(\Omega)$ and the line shift $\int d\Omega\,\rho|\lambda|^2(\omega-\Omega)^{-1}$] around an energy Ω_0.

To complete the rederivation of the result of Ref. 8 for optical absorption under the assumption (A14), we return to Eq. (13). To include the natural linewidth, we make the replacement

$$\epsilon\to\epsilon-\tfrac{1}{2}i\Gamma_\gamma. \tag{A16}$$

We must evaluate

$$\sum_{\alpha=0}^{N}\frac{|\beta_\alpha|^2}{\nu-\omega_\alpha+i\eta}=|\beta|^2\sum_\alpha\frac{1}{\pi\rho(\omega_\alpha)}\frac{\tfrac{1}{2}\Gamma_\lambda(\omega_\alpha)}{[\omega_\alpha-\Omega_0+\tfrac{1}{2}i\Gamma_\lambda(\omega_\alpha)][\omega_\alpha-\Omega_0-\tfrac{1}{2}i\Gamma_\lambda(\omega_\alpha)](\nu-\omega_\alpha+i\eta)}, \tag{A17}$$

where we have introduced $\Gamma_\lambda(\omega)=2\pi\rho(\omega)|\lambda(\omega)|^2$ and have neglected the line shift

$$\int d\Omega\rho(\Omega)|\lambda(\Omega)|^2/(\nu-\Omega).$$

When $N\to\infty$ we may convert the sum to an integral. The dominant contribution comes from ω_α near Ω_0 or ϵ. If these are close together we may replace $\Gamma_\lambda(\omega_\alpha)$ by its value in this range, which we call Γ_λ. If these regions are also sufficiently removed from the minimum and maximum frequencies among the ω_α, we may also extend the integration (which goes from $\omega_{\min}$ to $\omega_{\max}$) to the entire infinite interval $(-\infty,\infty)$. Then we obtain, by a simple contour integration,

$$B(\nu)=[\nu-\epsilon+\tfrac{1}{2}i\Gamma_\gamma-|\beta|^2/(\nu-\Omega_0+\tfrac{1}{2}i\Gamma_\lambda)]^{-1}. \tag{A18}$$

Thus

$$P=-2\,\mathrm{Im}B=\frac{\Gamma_\lambda|\beta|^2+\Gamma_\gamma[(\nu-\omega_0)^2+\tfrac{1}{4}\Gamma_\lambda^2]}{[(\nu-\epsilon)(\nu-\Omega_0)-|\beta|^2-\tfrac{1}{4}\Gamma_\gamma\Gamma_\lambda]^2+[(\nu-\epsilon)\tfrac{1}{2}\Gamma_\lambda+(\nu-\Omega_0)\tfrac{1}{2}\Gamma_\gamma]^2}. \tag{A19}$$

Except for a spurious factor $\frac{1}{2}\Gamma_\gamma$, Harris and Prohofsky's Eq. (3.20) agrees with (A19). When $\Gamma_\gamma\to 0$,

$$P\to\frac{\Gamma_\lambda|\beta|^2}{[(\nu-\epsilon)(\nu-\Omega_0)-|\beta|^2]^2+(\tfrac{1}{2}\Gamma_\lambda)^2(\nu-\epsilon)^2}. \tag{A20}$$

APPENDIX B

Consider a set of coupling constants $\{\lambda_n\}$ and energies $\{\Omega_n\}$ which are quasicontinuous functions of the integer n as it ranges over $1,\cdots,N$. We assume that as $n\to\infty$

$$\lambda_n\to(1/\sqrt{N})\lambda(n/N) \tag{B1}$$

and

$$\Omega_n\to\Omega(n/N), \tag{B2}$$

where $\lambda(x)$ and $\Omega(x)$ are continuous functions and the ordering is so chosen that $\Omega(x)$ is monotonic. We wish to calculate

$$S_1(\omega)=\sum_{n=1}^{N}\frac{|\lambda_n|^2}{\omega-\Omega_n} \tag{B3}$$

and

$$S_2(\omega)=\sum_{n=1}^{N}\frac{|\lambda_n|^2}{(\omega-\Omega_n)^2} \tag{B4}$$

as $N\to\infty$, where ω lies within the range of the Ω_n's. If ω lies outside this range, then the sums go directly to the integrals

$$\int dx\frac{|\lambda(x)|^2}{[\omega-\Omega(x)]^{1,2}}$$

and there is no problem.

Suppose ω lies between Ω_m and Ω_{m+1}:

$$\omega=\Omega_m+\delta_m(\Omega_{m+1}-\Omega_m)\equiv\Omega_m+\delta_m\Delta_m, \tag{B5}$$

i.e., δ_m is the fractional displacement of ω from Ω_m toward Ω_{m+1}. Then

$$S_1(x)=\sum_{n=1}^{N}\frac{|\lambda_n|^2}{\Omega_m+\frac{1}{2}\Delta_m-\Omega_n}$$
$$+\sum_{n=1}^{N}|\lambda_n|^2\frac{(\frac{1}{2}-\delta_m)\Delta_m}{(\Omega_n-\Omega_m-\delta_m\Delta_m)(\Omega_n-\Omega_m-\frac{1}{2}\Delta_m)}. \quad \text{(B6)}$$

When $N\to\infty$, the first sum can be replaced by the principal value integral

$$\mathcal{P}\int dx\frac{|\lambda(x)|^2}{\omega-\Omega(x)}.$$

The second sum is rapidly converging with the dominant contribution coming from $\Omega_n\simeq\Omega_m$. When $N\to\infty$ we can replace $|\lambda_n|^2$ by $|\lambda_m|^2\simeq(1/N)|\lambda(m/N)|^2$ and approximate $\Omega_n-\Omega_m$ by $(n-m)\Delta_m\to[(n-m)/N]\times\Omega'(m/N)$, and extend the range of summation to $(-\infty,\infty)$. Using the relation

$$\sum_{l=-\infty}^{\infty}\frac{a-b}{(l-a)(l-b)}=\pi(\cot\pi b-\cot\pi a) \quad \text{(B7)}$$

and setting $a=\frac{1}{2}$, $b=\delta_m\to\delta(m/N)$, we obtain

$$S_1(\omega)\underset{N\to\infty}{\to}\mathcal{P}\int\frac{|\lambda(\Omega)|^2}{\omega-\Omega}\rho(\Omega)d\Omega$$
$$+\pi|\lambda(\omega)|^2\rho(\omega)\cot\pi\delta(\omega), \quad \text{(B8)}$$

where $\rho(\omega)$ is defined by

$$\rho(\omega)=\frac{1}{\Omega'(x)}\Big|_{\Omega(x)=\omega}. \quad \text{(B9)}$$

Similarly, to evaluate $S_2(\omega)$, we use the fact that

$$\sum_{l=-\infty}^{\infty}\frac{1}{(l-b)^2}=\left(\frac{\pi}{\sin\pi b}\right)^2=\pi^2(1+\cot^2\pi b) \quad \text{(B10)}$$

obtained from (B7) by letting $a\to b$, and obtain

$$S_2(\omega)=\sum_n\frac{|\lambda_n|^2}{(\Omega_n-\Omega_m-\delta_m\Delta_m)^2}\simeq\frac{|\lambda(\omega)|^2}{N\Delta_m{}^2}\sum\frac{1}{(l-\delta_m)^2}$$
$$=N[\pi\lambda(\omega)\rho(\omega)]^2[1+\cot^2\pi\delta(\omega)], \quad \text{(B11)}$$

i.e., if ω is in the range of Ω_n's, then $S_2(\omega)$, but not $S_1(\omega)$ is of order N.

The assumptions (B1) and (B2) are consistent with the interactions encountered in Appendix A if the modes are those of a one-dimensional lattice or of just one representation of the point group of the lattice *cum* impurity for a three-dimensional lattice, because we assume that, when $N\to\infty$, percentage variations in λ_n and Ω_n of the same order occur over the same range of n. In general this is not true. In three dimensions, λ_n can vary appreciably when n changes by $O(N^{2/3})$ while, if the labelling is chosen to make the Ω_n's vary monotonically, Ω_n changes appreciably only when n changes by $0(N)$. This is the case, for example, if the n's refer to different $\mathbf{k}$ vectors and enumerate all the $\mathbf{k}$'s on one surface of essentially constant energy before going to the next surface.

Ultimately these difficulties are more formal than real. One way out is to assume that the Ω_n's will divide into many $[0(N^{1/3})]$ degenerate sets while the λ_n's vary as n runs through each set. If one assumes such strict degeneracies, then one must first sum over all n in each degenerate set and then sum over the different sets. If there are $\mathfrak{N}(\omega)=0(N^{2/3})$ modes in the set with $\Omega_n=\omega$, then $|\lambda_n|^2\to(1/N)|\lambda(\omega)|^2\mathfrak{N}(\omega)$, where $|\lambda(\omega)|^2$ is the average over the $\mathfrak{N}(\omega)$ modes. The different sets can now be indexed with n. Formulas (B8) and (B11) are still valid if by $\rho(\omega)$ one now understands $\mathfrak{N}(\omega)/\Omega'(x)|_{\Omega(x)=\omega}$, the *total* density of modes per unit range of ω.