THE DISTRIBUTION FUNCTION FOR

IMPURITY STATES IN SEMICONDUCTORS

by

CHEUK YIN CHEUNG

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THE DISTRIBUTION FUNCTIONS FOR
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ABSTRACT

For a monovalent donor impurity in a semiconductor, the number of electrons that can be bound to an impurity site is either zero or one. The one bound electron can have either direction of spin. For the discussion of the occupancy of such bound states, one does not apply the usual Fermi-Dirac statistics. A new derivation of the electron distribution function is presented in terms of creation and annihilation operators and the appropriate projection operators for the case of no interaction with the phonons. With the use of double-time temperature-dependent Green's Functions, the electron and phonon distribution functions are derived when there is interaction between the bound electron and phonons.

Under certain circumstances, one can speak of a quasi-particle spectrum and the distribution functions have the same form as the interaction-free case but with renormalized energies, which are temperature dependent. The temperature dependence of the distribution functions is then two-fold; one, the usual statistical dependence, the other due to the temperature dependence of the energies themselves. The latter quantity requires detailed knowledge of the wave-function, the interaction potential, and energy spectrum of the donor impurity. An application is made to phosphorus donors in silicon. The shifts in the energy levels are found to be small. The agreement with experiment is not completely satisfactory.

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Robert Barrie

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CHAPTER I : INTRODUCTION

In a valence semiconductor, such as silicon or germanium, the electronic structure is such that at absolute zero temperature, the entire valence band is filled while the conduction band, which is separated from the valence band by a forbidden energy gap of about 1 ev, is completely empty. No electrical conduction can be observed when the crystal is subjected to an applied electric field. At high enough temperature, however, an electron can be thermally excited into the conduction band from the valence band where a hole is consequently left behind. When this happens, an electric current would be produced with the application of an electric field.

If a substitutional atom of a group V element is introduced into the crystal, four of the five outer electrons are engaged in bonding the impurity atom to the crystal lattice. The excess electron is, at low temperature, bound to the impurity atom via a Coulomb-like potential. The eigenstates of this electron in the rigid lattice can be obtained by solving a hydrogen-like Schroedinger equation with two modifications (Kohn and Luttinger 1955). The scalar mass of the electron is replaced by an effective mass tensor whose particular form depends on the details of the band structure. Also the potential $-e/r$ is replaced by a weaker field $-e/\varepsilon r$ where ε is the dielectric constant of the host lattice. One expects therefore a whole spectrum of excited states as well as the ground state, corresponding to the spectrum of the hydrogen atom. That such excited states exist is well confirmed by optical absorption experiments (Burstein, Bell, Davisson and Lax 1953, Hrostowski and Kaiser 1957, Bichard and Giles 1962). These donor states, as

they are called, are localized at the impurity site and they lie in the forbidden energy gap just below the conduction band. An electron occupying one of these states can be excited into the conduction band with a small expenditure of energy ($\sim 1/10$ of the width of the energy gap). Hence, at all but the highest temperature, it is these electrons donated by impurities that dominate the electrical properties of semiconductors.

If the substitutional atom had been a Group III element, then " acceptor " levels would have been produced just above the valence band. An electron near the top of the valence band can be excited thermally into these levels (hence, acceptor levels). A hole would have been left behind in the valence band and is responsible for electrical conduction.

These shallow impurity states (donor and acceptor) have been discussed extensively in a review article by Kohn (1957).

In discussing physical properties of impure semi-conductors, it is of interest to know the occupation probabilities of these impure levels at any given temperature T. The usual Fermi-Dirac distribution which describes the electron distribution in the conduction band is not applicable to the impurity states. This is due to the fact that only one electron can be bound to any one impurity site even though other electrons may be available for binding. The correct expression for the electron distribution function for these

impurity states has been obtained by many authors in many ways.[*]

It is the purpose of this thesis to present a new approach, based on the use of creation and annihilation operators, projection operators, and double-time temperature-dependent Green's Functions which are the appropiate generalization of the concept of correlation functions (Zubarov 1960). This approach enables one to take account of the effect of electron-phonon interaction in a natural manner.

In Chapter II, the system of interest will be discussed in more detail and the required projection operators will be introduced. The general procedure for obtaining the electron distribution function via the Green's Function method will be outlined. The case of no interaction between electron and phonons will be treated as a trivial example to obtain the already well-known result. Finally, the effect of electron-phonon interaction is discussed in detail. The phonon distribution function is only briefly discussed since the treatment parallels that for the electron distribution function.

In Chapter III, we discuss the correction to the

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[*] Elementary combinatorial analysis, Wilson (1953); Minimizing the free energy, Mott and Gurney (1948) and Landsberg (1952); Absolute activity, Guggenheim (1952); Mass action law, Rose (1957). See also Shifrin(1944) and Weinreich (1965) for the inclusion of excited states.

effective-mass approximation due to electron-phonon interaction, and the temperature dependence in the shifts of the energy levels. The theory is applied to phosphorus donors in silicon for which experimental results are availble (Aggarwal and Ramdas 1965, White and Bichard 1966).

The final chapter will be a summary of results and conclusions.

CHAPTER II : DISTRIBUTION FUNCTIONS

1. Model System and the Hamiltonian

The donor impurity is considered as a system capable
of losing its bound electron to the surrounding medium in which
case the electron is ejected into the conduction band, i.e. the
impurity is ionized. Conversely, an electron can be captured
by the ionized impurity into some bound state to form a neutral
atom. In other words, we have a system consisting of impurity
sites in thermal equilibrium at temperature T with a particle
reservoir. We shall consider the concentration of impurities
to be sufficiently small that one can consider just a single
impurity embedded in the host crystal lattice.

For such a system, we write the following Hamiltonian
(Nishikawa and Barrie 1963):

$$(2.1) \qquad H = H_e + H_{ph} + H_{e-ph},$$

$$(2.2a) \qquad H_e = \sum_\lambda \sum_s E_\lambda \, a^\dagger_{\lambda s} a_{\lambda s},$$

$$(2.2b) \qquad H_{ph} = \sum_{\vec{q}} \omega_{\vec{q}} \, b^\dagger_{\vec{q}} b_{\vec{q}},$$

$$(2.2c) \qquad H_{e-ph} = \sum_\lambda \sum_{\lambda'} \sum_{\vec{q}} \sum_s (V_{\lambda\lambda'\vec{q}s} b_{\vec{q}} + V^*_{\lambda\lambda'\vec{q}s} b^\dagger_{\vec{q}}) \, a^\dagger_{\lambda s} a_{\lambda's}.$$

The first term H_e is the Hamiltonian of the bound
electron in the rigid lattice fixed at the equilibrium position
that the lattice would have in the absence of the electron. $a^\dagger_{\lambda s}$
and $a_{\lambda s}$ are the creation and annihilation operators for an elec-
tron in the impurity state specified by the energy E_λ and

and spin s. The second term H_{ph} is the Hamiltonian for the lattice vibrational modes centred about the above-mentioned equilibrium position. $b_{\vec{q}}^{+}$ and $b_{\vec{q}}$ are the corresponding creation and annihilation operators for a phonon of energy $\omega_{\vec{q}}$ and wave-number vector $\vec{q}$.

These operators satisfy the usual anti-commutation and commutation relations:

$$\left[a_{\lambda s}, a_{\chi s'} \right]_{+} = \left[a_{\lambda s}^{\dagger}, a_{\chi' s'}^{\dagger} \right]_{+} = 0,$$

$$\left[a_{\lambda s}, a_{\chi s'}^{\dagger} \right]_{+} = \delta_{\lambda \lambda'} \delta_{ss'},$$

(2.3)

$$\left[b_{\vec{q}}, b_{\vec{q}'} \right]_{-} = \left[b_{\vec{q}}^{\dagger}, b_{\vec{q}'}^{\dagger} \right]_{-} = 0,$$

$$\left[b_{\vec{q}}, b_{\vec{q}'}^{\dagger} \right]_{-} = \delta_{\vec{q}\vec{q}'},$$

$$\left[a_{\lambda s}, b_{\vec{q}} \right]_{-} = \left[a_{\lambda s}^{\dagger}, b_{\vec{q}} \right]_{-} = \left[a_{\lambda s}, b_{\vec{q}}^{\dagger} \right]_{-} = \left[a_{\lambda s}^{\dagger}, b_{\vec{q}}^{\dagger} \right]_{-} = 0,$$

where $\left[A, B \right]_{\pm} = A B \pm B A$.

The last term H_{e-ph} is the electron-phonon interaction arising as a result of the deviations of the lattice ions from their equilibrium positions. The coupling constant $\mathcal{K}$ characterizing the strength of the interaction is here assumed to be small. In the absence of any external perturbation, the electron-phonon interaction provides the only mechanism in inducing electronic transitions. Due to this finite life-time of the electron in any one state against decaying into other states, each of the energy levels is broadened in accordance with the uncertainty relation.

The matrix elements of the interaction potential, $V_{\lambda\lambda'\vec{q}s}$, will be assumed non-vanishing over a wide range of $\omega_{\vec{q}}$ and that any summation involving them is convergent. In the form of (2.2c), the interaction potential is taken to be spin-independent.

In order to calculate thermodynamic properties of a system specified by the Hamiltonian (2.1), we need to specify the statistical ensemble. In the absence of the restriction that only zero or one electron can be bound to the impurity site, we would use the grand canonical ensemble with the density operator given by

$$(2.4) \qquad \rho = \frac{e^{-\beta(H - \mu\hat{N})}}{\text{Tr}\left\{ e^{-\beta(H-\mu\hat{N})} \right\}} \; , \qquad \beta = 1/kT.$$

where μ is the chemical potential and $\hat{N}$ is the number operator of the electrons. To use (2.4) for the system we are interested in, we must confine ourselves to the 0- and 1-electron subspace when computing the trace. This restriction presents no difficulty in the absence of electron-phonon interaction. When electron-phonon interaction is present, one must take account of this restriction explicitly. This we will do in the next section by the introduction of the appropiate projection operators.

2. Projection Operators, Density Matrix and Thermal Averages

Projection operators P_0 and P_1 are defined as follows[*]:

$$P_0|u\rangle = \begin{cases} |u\rangle & \text{if } |u\rangle \text{ is a state with \underline{no} bound electron,} \\ 0 & \text{otherwise,} \end{cases}$$

(2.5)

$$P_1|u\rangle = \begin{cases} |u\rangle & \text{if } |u\rangle \text{ is a state with \underline{one} bound electron,} \\ 0 & \text{otherwise.} \end{cases}$$

It follows that

(2.6)
$$a_{\lambda s} P_0 = P_0 a^+_{\lambda s} = 0,$$

(2.7)
$$P_0 a_{\lambda s} = a_{\lambda s} P_1 \;;\; a^+_{\lambda s} P_0 = P_1 a^+_{\lambda s},$$

(2.8)
$$P_0 P_1 = P_1 P_0 = 0.$$

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[*] In the absence of the electron-phonon interaction, the projection operators can be defined explicitly in terms of the creation and annihilation operators as in the following:

$$P_0 = \prod_{\lambda s} (1 - a^+_{\lambda s} a_{\lambda s}),$$

$$P_1 = \sum_{\lambda s} \prod_{\substack{\lambda' s' \\ (\neq \lambda s)}} (1 - a^+_{\lambda' s'} a_{\lambda' s'}) a^+_{\lambda s} a_{\lambda s}.$$

The last property shows that P_0 and P_1 are orthogonal. Hence the sum

$$(2.9) \qquad P = P_0 + P_1$$

is also a projection operator. From (2.6) and (2.7), we obtain

$$(2.10) \qquad \left[a^+_{\lambda s} a_{\lambda' s'} \, , \, P \right]_- = 0,$$

$$(2.11) \qquad a_{\lambda s} a_{\lambda' s'} \, P = P \, a^+_{\lambda s} a^+_{\lambda' s'} = 0.^*$$

It now remains to define the density matrix appropriate for our present system with the use of the projection operators.

We note first of all that in the absence of the restriction of only one or zero bound electron, the

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* In the papers by Zubarev (1960) and Nishikawa and Barrie (1963), the restriction to a one-electron system is incorrectly stated. Their statements are not consistent with the anticommutation relations. Compare footnote in paper by Barrie and Rystephanick (1966). Their restriction leads to the following contradiction: $(\lambda \neq \lambda')$, $\langle a^+_\lambda a_\lambda \rangle =$

$$\left\langle (a^+_\lambda a_{\lambda'} + a_{\lambda'} a^+_\lambda) \, a^+_\lambda a_\lambda \right\rangle = \left\langle a^+_\lambda a_\lambda a_\lambda \, e^{-\beta H} a_{\lambda'} \, e^{\beta H} \right\rangle = 0.$$

thermodynamical average of an operator A over the grand

canonical ensemble is given by

$$(2.12) \qquad \langle A \rangle = \frac{\sum_j' \langle j|A|j \rangle \, e^{-\beta(E_j-\mu N_j)}}{\sum_j e^{-\beta(E_j-\mu N_j)}} = \text{Tr} \left\{ \rho \, A \right\}.$$

Here, $|j\rangle$ represents a state of the system with energy E_j

and number of electrons N_j. The summation is over all

states of the system with all possible values of N.

If we impose the restriction that only zero or one

electron can be bound to the impurity site, the summation

must be confined to those states in which $N_j = 0$ or 1. With

(2.5) and (2.9), we can then write the thermal average of A as

$$(2.13) \qquad \langle A \rangle_P = \frac{\sum_j \langle j|P A P|j \rangle \, e^{-\beta(E_j-\mu N_j)}}{\sum_j \langle j|P|j \rangle \, e^{-\beta(E_j-\mu N_j)}},$$

where the subscript P denotes that the summation is over

the restricted set of states. We can rewrite (2.13) as

$$\langle A \rangle_P = \frac{\sum_j \langle j| e^{-\beta(H-\mu N)} PAP|j \rangle}{\sum_j \langle j| e^{-\beta(H-\mu N)} P|j \rangle} = \frac{\text{Tr}\left\{ P e^{-\beta(H-\mu N)} PA \right\}}{\text{Tr}\left\{ e^{-\beta(H-\mu N)} P \right\}}$$

$$(2.14)$$

$$= \text{Tr} \left\{ \tilde{\rho} \, A \right\}.$$

The final step is obtained by defining

$$(2.15) \qquad \tilde{\rho} = \frac{P e^{-\beta(H-\mu N)} P}{\text{Tr}\left\{ e^{-\beta(H-\mu N)} P \right\}} = \frac{P \rho P}{\text{Te}\left\{ \rho P \right\}},$$

which is the appropriate density matrix for the description of our physical system. Furthermore, since P commutes with $\wp$ because of (2.10), we can write

(2.16)
$$\tilde{\wp} = \frac{\wp P}{Tr\{\wp P\}}$$

and

(2.17)
$$\langle A \rangle_P = \frac{\langle P\,A \rangle}{\langle P \rangle}$$

Our particular interest here is in the calculation of the occupation probabilities for impurity states and phonon modes, namely

(2.18)
$$\tilde{n}_{\lambda s} = \langle a^+_{\lambda s} a_{\lambda s} \rangle_P = \langle A^+_{\lambda s} a_{\lambda s} \rangle,$$

(2.19)
$$\tilde{\mathcal{V}}_{\vec{q}} = \langle b^+_{\vec{q}} b_{\vec{q}} \rangle_P = \langle B^+_{\vec{q}} b_{\vec{q}} \rangle,$$

where we have defined

(2.20)
$$A^+_{\lambda s} = \frac{P a^+_{\lambda s}}{\langle P \rangle},$$

(2.21)
$$B^+_{\vec{q}} = \frac{P b^+_{\vec{q}}}{\langle P \rangle}.$$

The quantities $\tilde{n}_{\lambda s}$ and $\tilde{\mathcal{V}}_{q}$ will be calculated by the Green's Function method. An outline of the technique will be presented in the following section.

3. Green's Function Method

For any two operators A and B, the Green's Function $\langle\!\langle A\,|\,B\rangle\!\rangle_E$ is defined as

(2.21)

$$\langle\!\langle A\,|\,B\rangle\!\rangle_E = \begin{cases} \dfrac{i}{2\pi}\displaystyle\int_{-\infty}^{0} dt\; e^{iEt}\langle\,[A(t),\,B]_\gamma\,\rangle & \text{Im } E < 0 \\[4mm] \dfrac{-i}{2\pi}\displaystyle\int_{0}^{\infty} dt\; e^{iEt}\langle\,[A(t),\,B]_\gamma\,\rangle & \text{Im } E > 0 \end{cases}$$

where $[A,\,B]_\gamma = A\,B - \gamma\,B\,A,\quad \gamma = \pm 1,$

$$A(t) = e^{it\mathcal{H}}\,A\,e^{-it\mathcal{H}}, \qquad \mathcal{H} = H - \mu\,\hat{N}.$$

The Green's Function satisfies the following equation:

(2.22) $\qquad E\langle\!\langle A\,|\,B\rangle\!\rangle_E = \dfrac{1}{2\pi}\langle\,[A,\,B]_\gamma\,\rangle + \langle\!\langle\,[A,\,\mathcal{H}]_{-}\,|\,B\rangle\!\rangle_E.$

As defined in (2.21), $\langle\!\langle A\,|\,B\rangle\!\rangle_E$ is a two-branch analytic function with a branch cut along the real axis. The discontinuity across the real axis is related to the thermal average of the product BA by the following identity (Zubarev 1960):

(2.23) $\qquad \langle BA\rangle = \lim_{\eta\to 0^+} i\int_{-\infty}^{\infty} d\omega\; \dfrac{\langle\!\langle A|B\rangle\!\rangle_{\omega+i\eta} - \langle\!\langle A|B\rangle\!\rangle_{\omega-i\eta}}{e^{\beta\omega} - \gamma}$

To calculate $\tilde{n}_{\lambda s}$, we choose $A = a_{\lambda s}$, $B = A^{\dagger}_{\lambda s}$ and $\gamma = -1$. To calculate $\tilde{\nu}_{\vec{q}}$, we choose $A = b_{\vec{q}}$, $B = B^{\dagger}_{\vec{q}}$ and $\gamma = +1$. The problem now is to solve equation (2.22).

As a trivial example, we first treat the case where $\mathcal{K} = 0$, and discuss in detail only the electron distribution function , obtaining results that are already in the literature.

The equation for the Green's Function is

$$(2.24) \qquad E \langle\!\langle a_{\lambda s} | A^{\dagger}_{\lambda s} \rangle\!\rangle_E = \frac{1}{2\pi} \langle [a_{\lambda s}, A^{\dagger}_{\lambda s}]_+ \rangle_0 + \langle\!\langle [a_{\lambda s}, \mathcal{H}_0]_- | A^{\dagger}_{\lambda s} \rangle\!\rangle_E$$

where $\mathcal{H}_0 = \sum_{\lambda s} T_{\lambda} a^{\dagger}_{\lambda s} a_{\lambda s} + \sum_{\vec{q}} \omega_{\vec{q}} b^{\dagger}_{\vec{q}} b_{\vec{q}}$, $T_{\lambda} = E_{\lambda} - \mu$ and $\langle \ldots \rangle_0$ means that $\mathcal{H}_0$ is used in the thermal average. Now

$$[a_{\lambda s}, \mathcal{H}_0]_- = T_{\lambda} a_{\lambda s}$$

and

$$\langle [a_{\lambda s}, A^{\dagger}_{\lambda s}]_+ \rangle_0 = \tilde{n}^{0}_{\lambda s} + \langle P_0 \rangle_0 / \langle P \rangle_0$$

so that the solution to (2.24) that is compatible with the required analyticity of the Green's Function is

$$(2.25) \qquad \langle\!\langle a_{\lambda s} | A^{\dagger}_{\lambda s} \rangle\!\rangle_E = \frac{1}{2\pi} \frac{\left(\tilde{n}^{0}_{\lambda s} + \langle P_0 \rangle_0 / \langle P \rangle_0 \right)}{E - T_{\lambda}}.$$

Using the identity

$$(2.26) \qquad \lim_{\eta \to 0^+} \frac{1}{x \pm i\eta} = \wp \left(\frac{1}{x}\right) \mp i\pi \delta(x),$$

where $\wp$ denotes the Cauchy principal value, the discontinuity

across the real axis is

(2.27) $\lim\limits_{\eta \to 0^+} \left\{ \ll a_{\lambda s} | A_{\lambda s}^\dagger \gg_{\omega+i\eta} - \ll a_{\lambda s} | A_{\lambda s}^\dagger \gg_{\omega-i\eta} \right\} = -i \left(\tilde{n}_{\lambda s}^0 + \langle P_0 \rangle_0 / \langle P \rangle_0 \right) \delta(\omega - T_\lambda)$

Because of the δ-function, the integration in (2.23) is trivial. The result is

(2.28) $\tilde{n}_{\lambda s}^0 = \dfrac{\tilde{n}_{\lambda s}^0 + \langle P_0 \rangle_0 / \langle P \rangle_0}{e^{\beta T_\lambda} + 1}$,

which can be rewritten as

(2.29) $\tilde{n}_{\lambda s}^0 = \left(\langle P_0 \rangle_0 / \langle P \rangle_0 \right) e^{-\beta T_\lambda}$

Now $\langle P_0 \rangle_0 / \langle P \rangle_0 = \left(1 + \sum\limits_{\lambda s} e^{-\beta T_\lambda} \right)^{-1}$, where the sum is over <u>states.</u> The final result is then

(2.30) $\tilde{n}_{\lambda s}^0 = \dfrac{e^{-\beta T_\lambda}}{1 + \sum\limits_{\lambda s} e^{-\beta T_\lambda}} = \dfrac{e^{-\beta(E_\lambda - \mu)}}{1 + \sum\limits_{\lambda s} e^{-\beta(E_\lambda - \mu)}}$

which agrees with that of Shifrin (1944).

In the limit that there is only one value of E_λ and that the only degeneracy is due to spin of 1/2, then

(2.31) $\tilde{n}_\lambda^0 = \sum\limits_s \tilde{n}_{\lambda s}^0 = \dfrac{1}{\frac{1}{2} e^{\beta T_\lambda} + 1}$,

a result that can be obtained by an elementary combinatorial treatment (Wilson 1953).

For the phonons, the procedure follows as before. The result is

$$(2.32) \qquad \widetilde{\nu}_{\vec{q}}^{\,0} = \frac{1}{e^{\beta \omega_{\vec{q}}} - 1} = \nu_{\vec{q}}^{\,0}$$

i.e. the phonon distribution function is unaffected by the presence of the projection operators , which is indeed not surprising.

4. Effect of Electron-Phonon Interaction

(i) Electron Distribution Function

In section 3, we have seen that solution to the equation of motion is exact in the absence of electron-phonon interaction. We shall now include the effect of the electron-phonon interaction and will see presently that we no longer obtain an exact solution.

We shall study the Green's Function $\langle\langle a_{\lambda s} | A^{\dagger}_{\lambda's'} \rangle\rangle_E$ for which the equation is

$$(2.33) \qquad E \langle\langle a_{\lambda s} | A^{\dagger}_{\lambda's'} \rangle\rangle_E = \frac{1}{2\pi} \langle [a_{\lambda s}, A^{\dagger}_{\lambda's'}]_+ \rangle + \langle\langle [a_{\lambda s}, \mathcal{H}]_- | A^{\dagger}_{\lambda's'} \rangle\rangle_E$$

where $\mathcal{H} = \mathcal{H}_0 + H_{e-ph}$. This becomes

$$(2.34) \qquad (E - T_{\lambda}) \langle\langle a_{\lambda s} | A^{\dagger}_{\lambda's'} \rangle\rangle_E = \frac{1}{2\pi} \langle [a_{\lambda s}, A^{\dagger}_{\lambda's'}]_+ \rangle$$
$$+ \kappa \sum_{\nu \vec{q}} \left\{ V_{\lambda\nu\vec{q}s} \langle\langle b_{\vec{q}} a_{\nu s} | A^{\dagger}_{\lambda's'} \rangle\rangle_E + V^*_{\nu\lambda\vec{q}s} \langle\langle b^{\dagger}_{\vec{q}} a_{\nu s} | A^{\dagger}_{\lambda's'} \rangle\rangle_E \right\}$$

Therefore, the presence of electron-phonon interaction has introduced into the equation for $\langle\langle a_{\lambda s} | A^{\dagger}_{\lambda's'} \rangle\rangle_E$ some higher order Green's Functions, namely $\langle\langle b_{\vec{q}} a_{\nu s} | A^{\dagger}_{\lambda's'} \rangle\rangle_E$ and $\langle\langle b^{\dagger}_{\vec{q}} a_{\nu s} | A^{\dagger}_{\lambda's'} \rangle\rangle_E$. The equations satisfied by these higher order Green's Functions can be obtained similarly from (2.22) with the appropiate substitutions of A and B;

$$(E - T_\nu - \omega_{\vec{q}}) \ll b_{\vec{q}} a_{\nu s} | A^\dagger_{\chi' s'} \gg_E$$

$$(2.35)$$
$$= \frac{1}{2\pi} \langle [b_{\vec{q}} a_{\nu s}, A^\dagger_{\chi' s'}]_+ \rangle + \varkappa \sum_{r r' \sigma} V^*_{r' r \sigma} \ll a_{\nu s} a^\dagger_{r \sigma} a_{r' \sigma} | A^\dagger_{\chi' s'} \gg_E$$

$$+ \varkappa \sum_{\mu \vec{q}'} \left\{ V_{r \mu \vec{q}' s} \ll b_{\vec{q}'} b_{\vec{q}} a_{\mu s} | A^\dagger_{\chi' s'} \gg_E + V^*_{\mu \nu \vec{q}' s} \ll b^\dagger_{\vec{q}'} b_{\vec{q}} a_{\mu s} | A^\dagger_{\chi' s'} \gg_E \right\}$$

$$(E - T_\nu + \omega_{\vec{q}}) \ll b^\dagger_{\vec{q}} a_{\nu s} | A^\dagger_{\chi' s'} \gg_E$$

$$(2.36)$$
$$= \frac{1}{2\pi} \langle [b^\dagger_{\vec{q}} a_{\nu s}, A^\dagger_{\chi' s'}]_+ \rangle - \varkappa \sum_{r r' \sigma} V_{r r' \sigma} \ll a_{\nu s} a^\dagger_{r \sigma} a_{r' \sigma} | A^\dagger_{\chi' s'} \gg_E$$

$$+ \varkappa \sum_{\mu \vec{q}'} \left\{ V_{\nu \mu \vec{q}' s} \ll b_{\vec{q}'} b^\dagger_{\vec{q}} a_{\mu s} | A^\dagger_{\chi' s'} \gg_E + V^*_{r \nu \vec{q}' s} \ll b^\dagger_{\vec{q}'} b^\dagger_{\vec{q}} a_{\mu s} | A^\dagger_{\chi' s'} \gg_E \right\}.$$

Using (2.3) and (2.11), it can be shown that

$$(2.37) \qquad \ll a_{\nu s} a^\dagger_{\mu \sigma} a_{\mu' \sigma'} | A^\dagger_{\chi' s'} \gg_E = \delta_{\nu \mu} \delta_{s \sigma} \ll a_{\mu' \sigma'} | A^\dagger_{\chi' s'} \gg_E.$$

The thermal averages appearing on the right hand sides of (2.34), (2.35) and (2.36) can be written as

$$(2.38) \qquad \langle [a_{\lambda s}, A^\dagger_{\chi' s'}]_+ \rangle = \langle A^\dagger_{\chi' s'} a_{\lambda s} \rangle + \delta_{\lambda \chi} \delta_{s s'} (\langle P_0 \rangle / \langle P \rangle),$$

$$(2.39) \qquad \langle [b_{\vec{q}} a_{\nu s}, A^\dagger_{\chi' s'}]_+ \rangle = \langle b_{\vec{q}} A^\dagger_{\chi' s'} a_{\nu s} \rangle + \delta_{\chi \nu} \delta_{s s'} (\langle b_q P_0 \rangle / \langle P \rangle),$$

$$(2.40) \qquad \langle [b^\dagger_{\vec{q}} a_{\nu s}, A^\dagger_{\chi' s'}]_+ \rangle = \langle b^\dagger_{\vec{q}} A^\dagger_{\chi' s'} a_{\nu s} \rangle + \delta_{\chi \nu} \delta_{s s'} (\langle b^\dagger_q P_0 \rangle / \langle P \rangle),$$

where use has been made of the properties of P (eqs. (2.6)to (2.9)). Furthermore, it can be shown by expanding $e^{-\beta \mathcal{H}}$ in powers of $\mathcal{K}$ that

(2.41) $$\langle b_{\vec{q}} \, P_o \rangle = \langle b_{\vec{q}}^{\dagger} \, P_o \rangle = 0.$$

So far the equations are exact. We can see, however, that still higher order Green's Functions are appearing on the right hand sides of (2.35) and (2.36), and their equations of motions can similarly be found. In this fashion, one obtains an infinite hierachy of coupled equations. Instead of doing this, we shall decouple the chain after equations (2.35) and (2.36). The decoupling is similar to that used by Nishikawa and Barrie (1963) for the two-particle Green's Function and can be justified in the same manner(Appendix II). We merely quote the results here:

$$\langle\langle b_{\vec{q}}^{\dagger} b_{\vec{q}} a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E = \nu_{\vec{q}} \langle\langle a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E + O\left(\frac{\mathcal{K}^2}{\mathcal{N}}\right)$$

$$\langle\langle b_{\vec{q}'}^{\dagger} b_{\vec{q}} a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E = O\left(\frac{\mathcal{K}^2}{\mathcal{N}}\right)\langle\langle a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E, \qquad (\vec{q} \neq \vec{q}')$$

(2.42) $$\langle\langle b_{\vec{q}} b_{\vec{q}'} a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E = O\left(\frac{\mathcal{K}^2}{\mathcal{N}}\right)\langle\langle a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E,$$

$$\langle\langle b_{\vec{q}}^{\dagger} b_{\vec{q}'}^{\dagger} a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E = O\left(\frac{\mathcal{K}^2}{\mathcal{N}}\right)\langle\langle a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E,$$

$$\langle\langle a_{\mu s} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E = \delta_{\mu \lambda'} \delta_{s s'} \langle\langle a_{\lambda' s'} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E + O(\mathcal{K}) \langle\langle a_{\mu s} | A_{\mu s}^{\dagger} \rangle\rangle_E$$
$$+ O(\mathcal{K}^2) \langle\langle a_{\lambda' s'} | A_{\lambda' s'}^{\dagger} \rangle\rangle_E,$$

where $\mathcal{N}$ is the number of phonon states for which $V_{\mu\mu'\vec{q}s} \neq 0$, and $\nu_{\vec{q}} = (e^{\beta\omega\vec{q}} - 1)^{-1}$. When (2.37)-(2.42) are substituted into (2.35) and (2.36), we have a closed set of equations. We are interested in the case $\lambda,s = \lambda',s'$ in which case the equations are

$$(2.43) \quad (E - T_\lambda) \langle\!\langle a_{\lambda s} | A^\dagger_{\lambda s} \rangle\!\rangle_E = \frac{1}{2\pi} \left\{ \tilde{n}_{\lambda s} + \frac{\langle P_0 \rangle}{\langle P \rangle} \right\}$$

$$+ \varkappa \sum_{\nu\vec{q}} \left\{ V_{\lambda\nu\vec{q}s} \langle\!\langle b_{\vec{q}} a_{\nu s} | A^\dagger_{\lambda s} \rangle\!\rangle_E + V^*_{\nu\lambda\vec{q}s} \langle\!\langle b^\dagger_{\vec{q}} a_{\nu s} | A^\dagger_{\lambda s} \rangle\!\rangle_E \right\}$$

$$(2.44) \quad (E - T_\nu - \omega_{\vec{q}}) \langle\!\langle b_{\vec{q}} a_{\nu s} | A^\dagger_{\lambda s} \rangle\!\rangle_E = \frac{1}{2\pi} \langle b_{\vec{q}} A^\dagger_{\lambda s} a_{\nu s} \rangle$$

$$+ \varkappa V^*_{\lambda\nu\vec{q}s} (1 + \nu_{\vec{q}}) \langle\!\langle a_{\lambda s} | A^\dagger_{\lambda s} \rangle\!\rangle_E$$

$$(2/45) \quad (E - T_\nu + \omega_{\vec{q}}) \langle\!\langle b^\dagger_{\vec{q}} a_{\nu s} | A^\dagger_{\lambda s} \rangle\!\rangle_E = \frac{1}{2\pi} \langle b^\dagger_{\vec{q}} A^\dagger_{\lambda s} a_{\nu s} \rangle$$

$$+ \varkappa V_{\nu\lambda\vec{q}s} \, \nu_{\vec{q}} \langle\!\langle a_{\lambda s} | A^\dagger_{\lambda s} \rangle\!\rangle_E .$$

These can now be solved for $\langle\!\langle a_{\lambda s} | A^\dagger_{\lambda s} \rangle\!\rangle_E$, yielding

$$(2.46) \quad \langle\!\langle a_{\lambda s} | A^\dagger_{\lambda s} \rangle\!\rangle_E = \frac{1}{2\pi} \frac{\left(\tilde{n}_{\lambda s} + \langle P_0 \rangle / \langle P \rangle \right) \left(1 + \varkappa^2 N_{\lambda s}(E) \right)}{E - T_\lambda - \varkappa^2 L_{\lambda s}(E)}$$

with

$$(2.47) \quad L_{\lambda s}(E) = \sum_{\nu\vec{q}} |V_{\lambda\nu\vec{q}s}|^2 \left\{ \frac{1 + \nu_{\vec{q}}}{E - T_\nu - \omega_{\vec{q}}} + \frac{\nu_{\vec{q}}}{E - T_\nu + \omega_{\vec{q}}} \right\}$$

$$(2.48) \qquad \varkappa N_{\lambda s}(E) = \frac{1}{\tilde{n}_{\lambda s} + \langle P_0 \rangle / \langle P \rangle} \sum_{\nu \vec{q}} \oplus \left\{ \frac{V_{\lambda \nu \vec{q} s} \langle b_{\vec{q}} A_{\lambda s}^\dagger a_{\nu s} \rangle}{E - T_\nu - \omega_{\vec{q}}} + \frac{V_{\nu \lambda \vec{q} s}^* \langle b_{\vec{q}}^\dagger A_{\lambda s}^\dagger a_{\nu s} \rangle}{E - T_\nu + \omega_{\vec{q}}} \right\}$$

We now write (cf. Nishikawa and Barrie 1963)

$$(2.49) \qquad \langle\!\langle a_{\lambda s} | A_{\lambda s}^\dagger \rangle\!\rangle_E = \frac{1}{2\pi} \frac{\tilde{n}_{\lambda s} + (\langle P_0 \rangle / \langle P \rangle)}{E - T_\lambda - \varkappa^2 M_{\lambda s}(E)}$$

where

$$(2.50) \qquad M_{\lambda s}(E) = L_{\lambda s}(E) + (E - T_\lambda) N_{\lambda s}(E).$$

Our aim has been to determine the poles of the Green's Function correct to order $\varkappa^2$ and this has now been done. Therefore in evaluating

$$\frac{\langle b_{\vec{q}} A_{\lambda s}^\dagger a_{\nu s} \rangle}{\tilde{n}_{\lambda s} + (\langle P_0 \rangle / \langle P \rangle)} \qquad \text{and} \qquad \frac{\langle b_{\vec{q}}^\dagger A_{\lambda s}^\dagger a_{\nu s} \rangle}{\tilde{n}_{\lambda s} + (\langle P_0 \rangle / \langle P \rangle)}$$

in (2,48), we need only to retain terms up to $O(\varkappa)$ (Appendix III).

Using the relation (2.26) and

$$(2.51) \qquad \lim_{\eta \to 0^+} \frac{\omega - x \pm i\eta}{\omega - y \pm i\eta} = \left[1 + (y-x) \mathcal{P}\left(\frac{1}{\omega - y}\right) \right] \mp i\pi (y-x) \delta(\omega - y)$$

we can write

$$(2.52) \qquad \lim_{\eta \to 0^+} M_{\lambda s}(\omega \pm i\eta) = \Delta_{\lambda s}(\omega) \mp i\gamma_{\lambda s}(\omega),$$

where

$$
\Delta_{\lambda s}(\omega) = \mathcal{P} \sum_{\nu \vec{q}} |V_{\lambda \nu \vec{q}s}|^2 \left\{ \frac{1 + \nu_{\vec{q}}}{\omega - T_\nu - \omega_{\vec{q}}} + \frac{\nu_{\vec{q}}}{\omega - T_\nu + \omega_{\vec{q}}} \right.
$$

(2.53)

$$
+ (\omega - T_\lambda) \left[\frac{n^0_{\lambda s}(1 - e^{\beta(T_\lambda - T_\nu - \omega_{\vec{q}})})}{T_\lambda - T_\nu - \omega_{\vec{q}}} \frac{1 + \nu_{\vec{q}}}{\omega - T_\nu - \omega_{\vec{q}}} \right.
$$

$$
\left. \left. + \frac{n^0_{\lambda s}(1 - e^{\beta(T_\lambda - T_\nu + \omega_{\vec{q}})})}{T_\lambda - T_\nu + \omega_{\vec{q}}} \frac{\nu_{\vec{q}}}{\omega - T_\nu + \omega_{\vec{q}}} \right] \right\}
$$

and

$$
\gamma_{\lambda s}(\omega) = \pi \sum_{\nu \vec{q}} |V_{\lambda \nu \vec{q}s}|^2 \left\{ (1 + \nu_{\vec{q}}) \delta(\omega - T_\nu - \omega_{\vec{q}}) + \nu_{\vec{q}} \delta(\omega - T_\nu + \omega_{\vec{q}}) \right.
$$

(2.54)

$$
+ (\omega - T_\lambda) \left[\frac{n^0_{\lambda s}(1 - e^{\beta(T_\lambda - T_\nu - \omega_{\vec{q}})})}{T_\lambda - T_\nu - \omega_{\vec{q}}} (1 + \nu_{\vec{q}}) \delta(\omega - T_\nu - \omega_{\vec{q}}) \right.
$$

$$
\left. \left. + \frac{n^0_{\lambda s}(1 - e^{\beta(T_\lambda - T_\nu + \omega_{\vec{q}})})}{T_\lambda - T_\nu + \omega_{\vec{q}}} \nu_{\vec{q}} \delta(\omega - T_\nu + \omega_{\vec{q}}) \right] \right\}
$$

$$
= \pi \sum_{\nu \vec{q}} |V_{\lambda \nu \vec{q}s}|^2 \left\{ \frac{e^{-\beta(T_\nu + \omega_{\vec{q}})} + 1}{e^{-\beta T_\lambda} + 1} (1 + \nu_{\vec{q}}) \delta(\omega - T_\nu - \omega_{\vec{q}}) \right.
$$

$$
\left. + \frac{e^{-\beta(T_\nu - \omega_{\vec{q}})} + 1}{e^{-\beta T_\lambda} + 1} \nu_{\vec{q}} \delta(\omega - T_\nu + \omega_{\vec{q}}) \right\}.
$$

In the above expressions, the results of Appendix III have been substituted.

The discontinuity of the Green's Function can be shown to be

(2.55)

$$
\lim_{\eta \to \delta^+} \left(\langle\!\langle a_{\lambda s} | A^\dagger_{\lambda s} \rangle\!\rangle_{\omega + i\eta} - \langle\!\langle a_{\lambda s} | A^\dagger_{\lambda s} \rangle\!\rangle_{\omega - i\eta} \right)
$$

$$
= \frac{\tilde{n}_{\lambda s} + \langle P_0 \rangle / \langle P \rangle}{\pi i} \frac{\varkappa^2 \gamma_{\lambda s}(\omega)}{[\omega - T_\lambda - \varkappa^2 \Delta_{\lambda s}(\omega)]^2 + \varkappa^4 \gamma^2_{\lambda s}(\omega)}
$$

which is no longer a well-defined δ-function as was the case
when electron-phonon interaction is absent. It has in fact a
quasi-Lorentzian form with frequency-dependent shift $\Delta_{\lambda s}(\omega)$
and width $\gamma_{\lambda s}(\omega)$. The factor ($\tilde{n}_{\lambda s} + \langle P_0 \rangle / \langle P \rangle$) is a
renormalization factor for the Green's Function due to the
presence of prjection operators.

The required correlation function can now be obtained
by using (2.23):

$$(2.56) \qquad \langle A^{\dagger}_{\lambda s} a_{\lambda s} \rangle \equiv \tilde{n}_{\lambda s} = (\tilde{n}_{\lambda s} + \langle P_0 \rangle / \langle P \rangle) \, \mathcal{J}_{\lambda s},$$

where

$$(2.57) \qquad \mathcal{J}_{\lambda s} = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \; \frac{\varkappa^2 \gamma_{\lambda s}(\omega) \left[e^{\beta \omega} + 1 \right]^{-1}}{\left[\omega - T_{\lambda} - \varkappa^2 \Delta_{\lambda s}(\omega) \right]^2 + \varkappa^4 \gamma^2_{\lambda s}(\omega)} .$$

The final result is, by rearranging (2.56)

$$(2.58) \qquad \tilde{n}_{\lambda s} = (\langle P_0 \rangle / \langle P \rangle) \, \frac{\mathcal{J}_{\lambda s}}{1 - \mathcal{J}_{\lambda s}}$$

If $\varkappa^2 \gamma_{\lambda s}(\omega)$ is small compared with T_{λ}, then the quasi-
Lorentzian function has a steep maximum at some value $\tilde{T}_{\lambda s}$,
which is given by the zero of $\omega - T_{\lambda} - \Delta_{\lambda s}(\omega)$, i.e.

$$(2.59) \qquad \tilde{T}_{\lambda s} = T_{\lambda} + \varkappa^2 \Delta_{\lambda s}(\tilde{T}_{\lambda s}).$$

If, in addition, we have $\varkappa^2 \Delta_{\lambda s}(\omega)$ and $\varkappa^2 \gamma_{\lambda s}(\omega)$ being slowly-
varying functions in the vicinity of $\tilde{T}_{\lambda s}$, then we can replace

them by $\varkappa^2 \Delta_{\lambda s}(\widetilde{T}_{\lambda s})$ and $\varkappa^2 \gamma_{\lambda s}(\widetilde{T}_{\lambda s})$. Since $\varkappa^2 \gamma_{\lambda s}(\widetilde{T}_{\lambda s})$ is small, the Lorentzian function

$$\frac{\varkappa^2 \gamma_{\lambda s}(\widetilde{T}_{\lambda s})}{\left[\omega - T_{\lambda} - \varkappa^2 \Delta_{\lambda s}(\widetilde{T}_{\lambda s})\right]^2 + \varkappa^4 \gamma_{\lambda s}^2(\widetilde{T}_{\lambda s})}$$

is replaced by a δ-function, $\delta(\omega - \widetilde{T}_{\lambda s})$.

Thus

$$(2.60) \qquad \mathcal{J}_{\lambda s} = \frac{1}{e^{\beta \widetilde{T}_{\lambda s}} + 1} .$$

Since $(\langle P_0 \rangle / \langle P \rangle)$ can be interpreted as the probability that the impurity electron is not in any of the bound states, then we must have the relation that

$$(2.61) \qquad \sum_{\lambda s} \widetilde{n}_{\lambda s} + \left(\langle P_0 \rangle / \langle P \rangle\right) = 1.$$

It then follows from (2.58) and (2.60) that

$$(2.62) \qquad \widetilde{n}_{\lambda s} = \frac{e^{-\beta \widetilde{T}_{\lambda s}}}{1 + \sum_{\lambda s} e^{-\beta \widetilde{T}_{\lambda s}}} .$$

The above result has the same form as $\widetilde{n}_{\lambda s}^0$, except that T_{λ} is now replaced by the quasi-particle energy $\widetilde{T}_{\lambda s}$, which is temperature-dependent through the term $\varkappa^2 \Delta_{\lambda s}(\widetilde{T}_{\lambda s})$. This temperature-dependence will be the subject matter of Chapter III, where we make an application to the case of phosphorus

donors in silicon.

Actually, the integral $\mathcal{G}_{\lambda s}$ in (2.60) should have been

(2.63)
$$\mathcal{G}_{\lambda s} = \frac{1}{e^{\beta \widetilde{T}_{\lambda s}} + 1} \; (1 + \varkappa^2 \varphi_{\lambda s}),$$

where the contribution $\varkappa^2 \varphi_{\lambda s}$ comes from the wings of the integrand, from the next term in the expansion of $\varkappa^2 \gamma_{\lambda s}(\omega)$ and $\varkappa^2 \Delta_{\lambda s}(\omega)$ about the peak and from the fact that near the peak, we have a Lorentzian line shape rather than a δ-function. This will be dealt with in the following subsection.

(ii) Calculation of $x^2 \varphi_{\lambda s}$

With the definition

(2.64)
$$A_{\lambda s}(\omega) = \frac{1}{\pi} \frac{x^2 \gamma_{\lambda s}(\omega)}{\left[\omega - T_\lambda - x^2 \Delta_{\lambda s}(\omega)\right]^2 + x^4 \gamma_{\lambda s}^2(\omega)},$$

we write (2.57) as

(2.65)
$$\mathcal{G}_{\lambda s} = \int_{-\infty}^{\infty} d\omega \; A_{\lambda s}(\omega) \; (e^{\beta\omega} + 1)^{-1}.$$

and look at the behavior of $A_{\lambda s}(\omega)$ more carefully.

For values of ω near $\widetilde{T}_{\lambda s}$ as given by (2.59), we can expand $\left[\omega - T_\lambda - x^2 \Delta_{\lambda s}(\omega)\right]$ and $x^2 \gamma_{\lambda s}(\omega)$ about $\widetilde{T}_{\lambda s}$, obtaining

(2.66)
$$A_{\lambda s}(\omega) \longrightarrow A_{\lambda s}(\omega)^{\text{peak}} = \frac{Z_{\lambda s}}{\pi} \frac{x^2 \gamma_{\lambda s}(\widetilde{T}_{\lambda s}) Z_{\lambda s}}{(\omega - \widetilde{T}_{\lambda s})^2 + x^4 \gamma_{\lambda s}^2(\widetilde{T}_{\lambda s}) Z_{\lambda s}}$$

where

(2.67)
$$Z_{\lambda s} = \left[1 - x^2 \frac{\partial \Delta_{\lambda s}(\omega)}{\partial \omega}\bigg|_{\widetilde{T}_{\lambda s}} \right]^{-1}$$

$$\simeq 1 + x^2 \frac{\partial \Delta_{\lambda s}}{\partial \omega}\bigg|_{T_\lambda}$$

Hence, near the peak, $A_{\lambda s}(\omega)$ has a Lorentzian shape with $Z_{\lambda s}$ as an amplitude factor. Up to order x^2, one can replace $x^2 \gamma_{\lambda s}(\widetilde{T}_{\lambda s}) Z_{\lambda s}$ by $x^2 \gamma_{\lambda s}(T_\lambda)$ and (2.59) by $\widetilde{T}_{\lambda s} = T_\lambda + x^2 \Delta_{\lambda s}(T_\lambda)$.

It is then obvious that $\kappa^2 \Delta_{\lambda s}(T_\lambda)$ is a shift in the impurity state (λ,s) from the unperturbed value $T_{\lambda s}$, while $2\kappa^2 \gamma_{\lambda s}(T_\lambda)$ is the width at half maximum of the resonance peak. The latter quantity is simply related to the life-time of an electron in the impurity state (λ,s) by

$$(2.68) \qquad \frac{1}{\tau_{\lambda s}} = 2\kappa^2 \gamma_{\lambda s}(T_\lambda)$$

where τ denotes the life-time.

Away from the peak, however, the function $A_{\lambda s}(\omega)$ is simply approximated by

$$(2.69) \qquad A_{\lambda s}(\omega) \longrightarrow A_{\lambda s}(\omega)^{wing} = \frac{1}{\pi} \frac{\kappa^2 \gamma_{\lambda s}(\omega)}{(\omega - T_\lambda)^2}$$

While we cannot perform an exact integration of (2.69), we can proceed as in the following[*]:

$$\mathcal{G}_{\lambda s} = \int_{peak} d\omega\, A_{\lambda s}(\omega)\, (e^{\beta \omega} + 1)^{-1} + \int_{wing} d\omega\, A_{\lambda s}(\omega)\, (e^{\beta \omega} + 1)^{-1}$$

$$(2.70)$$
$$= \int d\omega\, A_{\lambda s}(\omega)^{peak}(e^{\beta \omega} + 1)^{-1}$$
$$+ \int d\omega\, A_{\lambda s}(\omega)^{wing}(e^{\beta \omega} + 1)^{-1}.$$

---

[*] The approximation of splitting the integral into an integration over the peak region and another over the wings gives the correct result for the normalization of $A_{\lambda s}(\omega)$. The normalization is derived in Appendix IV.

The integration over the wings can be done readily using (2.54). The result is

$$\kappa^2 \sum_{\nu \vec{q}} |V_{\lambda \nu \vec{q} s}|^2 \frac{1}{e^{\beta T_\lambda} + 1} \left\{ \frac{1 + \nu_{\vec{q}}}{(T_\lambda - T_\nu - \omega_{\vec{q}})^2} \frac{e^{-\beta(T_\nu + \omega_{\vec{q}})} + 1}{e^{\beta(T_\nu + \omega_{\vec{q}})} + 1} + \frac{\nu_{\vec{q}}}{(T_\lambda - T_\nu + \omega_{\vec{q}})^2} \frac{e^{-\beta(T_\nu - \omega_{\vec{q}})} + 1}{e^{\beta(T_\nu - \omega_{\vec{q}})} + 1} \right\}.$$

(2.71)

Hence, the contribution to $\kappa^2 \psi_{\lambda s}$ due to the wing regions is

$$\kappa^2 \sum_{\nu \vec{q}} |V_{\lambda \nu \vec{q} s}|^2 \frac{e^{\beta T_\lambda} + 1}{e^{\beta T_\lambda} + 1} \left\{ \frac{1 + \nu_{\vec{q}}}{(T_\lambda - T_\nu - \omega_{\vec{q}})^2} \frac{e^{-\beta(T_\nu + \omega_{\vec{q}})} + 1}{e^{\beta(T_\nu + \omega_{\vec{q}})} + 1} + \frac{\nu_{\vec{q}}}{(T_\lambda - T_\nu + \omega_{\vec{q}})^2} \frac{e^{-\beta(T_\nu - \omega_{\vec{q}})} + 1}{e^{\beta(T_\nu - \omega_{\vec{q}})} + 1} \right\}.$$

(2.72)

We now consider the integration over the peak region, viz.

$$\int d\omega \; A_{\lambda s}(\omega)^{\text{peak}} (e^{\beta \omega} + 1)^{-1}.$$

If $\kappa^2 \gamma_{\lambda s}$ is sufficiently small and $(e^{\beta \omega} + 1)^{-1}$ is slowly-varying over the peak region, and if one makes the replacement $A_{\lambda s}(\omega)^{\text{peak}} \longrightarrow Z_{\lambda s} \delta(\omega - \widetilde{T}_{\lambda s})$, the integral is clearly equal to

(2.73)
$$Z_{\lambda s} (e^{\beta \widetilde{T}_{\lambda s}} + 1)^{-1} = \left(1 + \kappa^2 \frac{\partial \Delta_{\lambda s}}{\partial \omega} \Big|_{T_\lambda} \right) (e^{\beta \widetilde{T}_{\lambda s}} + 1)^{-1}.$$

It is evident from (2.73) that the coefficient, $\kappa^2 \frac{\partial \Delta_{\lambda s}}{\partial \omega} \Big|_{T_\lambda}$, is one of the terms included in $\kappa^2 \psi_{\lambda s}$, due to the gradient of $\kappa^2 \Delta_{\lambda s}^{(\omega)}$ at the peak. Its magnitude can be very small irrespective of the smallness of κ. The extreme case is when

$\kappa^2 \triangle_{\lambda s}(\omega)$ is independent of ω, then the gradient is zero. In general, the explicit expression can be obtained from (2.53):

$$(2.74) \qquad \kappa^2 \frac{\partial \triangle_{\lambda s}}{\partial \omega}\bigg|_{T_\lambda} = -\kappa^2 \sum_{\nu \vec{q}} |V_{\lambda \nu qs}|^2 \Bigg\{ \frac{1 + \nu_{\vec{q}}}{(T_\lambda - T_\nu - W_{\vec{q}})^2} \frac{e^{-\beta(T_\nu + W_{\vec{q}})} + 1}{e^{-\beta T_\lambda} + 1} + \frac{\nu_{\vec{q}}}{(T_\lambda - T_\nu + W_{\vec{q}})^2} \frac{e^{-\beta(T_\nu - W_{\vec{q}})} + 1}{e^{-\beta T_\lambda} + 1} \Bigg\}$$

which can be seen to be always less than zero.

Instead of making the δ-function approximation, let us now consider the correction due to the finite width near the peak. First of all, we note that the fractional change of the function $f(\omega) = (e^{\beta \omega} + 1)^{-1}$ over the width of the line is given by

$$(2.75) \qquad \begin{aligned} \frac{\delta f}{f} &= \frac{f(\tilde{T}_{\lambda s} + \kappa^2 \gamma_{\lambda s}) - f(\tilde{T}_{\lambda s} - \kappa^2 \gamma_{\lambda s})}{f(\tilde{T}_{\lambda s})} \\ &\simeq 2 \kappa^2 \gamma_{\lambda s} \frac{1}{f(\tilde{T}_{\lambda s})} \frac{\partial f}{\partial \omega}\bigg|_{\tilde{T}_{\lambda s}} \\ &= -\frac{\kappa^2 \gamma_{\lambda s}}{kT} \frac{e^{\beta \tilde{T}_{\lambda s}} + 1}{1 + \cosh \beta \tilde{T}_{\lambda s}} \end{aligned}$$

so that

(a) for $kT \gg |\tilde{T}_{\lambda s}|$ $\quad |\frac{\delta f}{f}| \sim \kappa^2 \gamma_{\lambda s}/kT \ll \kappa^2 \gamma_{\lambda s}/|\tilde{T}_{\lambda s}| \ll 1$,

(b) for $kT \sim |\tilde{T}_{\lambda s}|$ $\quad |\frac{\delta f}{f}| \sim \kappa^2 \gamma_{\lambda s}/kT \sim \kappa^2 \gamma_{\lambda s}/|\tilde{T}_{\lambda s}| \ll 1$,

(c) for $kT \ll |\tilde{T}_{\lambda s}|$ $\quad |\frac{\delta f}{f}| \ll (\kappa^2 \gamma_{\lambda s}/|\tilde{T}_{\lambda s}|)(kT/|\tilde{T}_{\lambda s}|) \ll 1$.

Therefore, as long as $\kappa^2 \gamma_{\lambda s} \ll |\tilde{T}_{\lambda s}|$, the slowly-varying assumption of $f(\omega)$ over the peak region should be a good

approximation for all temperatures.

As a demonstration of the type of expression that appears in $x^2 \mathcal{P}_{\lambda s}$ as a result of the finite width, we carry out the following calculation using a Boltzmann factor. That is, we assume that $\beta \widetilde{T}_{\lambda s} \gg 1$, a condition that will restrict us to state (λ, s) lying above the chemical potential. Then, the the integral we need to do is

$$(2.76) \qquad \mathcal{G}_{\lambda s} = \int_{T_{\lambda s} - x^2 \gamma_{\lambda s}}^{\infty} \frac{d\omega}{\pi} \, e^{-\beta \omega} \, \frac{x^2 \gamma_{\lambda s}}{(\omega - \widetilde{T}_{\lambda s})^2 + x^4 \gamma_{\lambda s}^2} \; ; \; \beta \widetilde{T}_{\lambda s} \gg 1,$$

where the upper limit is taken to infinity, since the exponantial factor will assure the rapid falling off of the integrand for values of ω away from the peak.

Changing the variable of integration to $x = \beta(\omega - \widetilde{T}_{\lambda s})$ and splitting the integral

$$\int_{-x^2 \gamma_{\lambda s}/kT}^{\infty} dx \longrightarrow \int_{0}^{\infty} dx \quad + \quad \int_{-x^2 \gamma_{\lambda s}/kT}^{0} dx$$

we obtain from (2.76)

$$(2.77) \qquad \mathcal{G}_{\lambda s} = e^{-\beta \widetilde{T}_{\lambda s}} \left\{ 1 + \left[-1 + \frac{1}{\pi} \left(C_i \frac{x^2 \gamma_{\lambda s}}{kT} \sin \frac{x^2 \gamma_{\lambda s}}{kT} - S_i \frac{x^2 \gamma_{\lambda s}}{kT} \cos \frac{x^2 \gamma_{\lambda s}}{kT} \right) \right. \right.$$
$$\left. \left. + \int_{0}^{x^2 \gamma_{\lambda s}/kT} dx \, \frac{(x^2 \gamma_{\lambda s}/kT) e^{x}}{x^2 + (x^2 \gamma_{\lambda s}/kT)^2} \right] \right\}$$

where Ci y and Si y are the cosine and sine integrals, and the formula[*]

$$(2.78) \qquad \int_{a}^{\infty} dx \; \frac{e^{-\mu x}}{x^2 + a^2} = \frac{1}{a} \left[Ci(a\mu)\sin(a\mu) - Si(a\mu)\cos(a\mu) \right]$$
$$(\mu > 0)$$

has been used.

The quantity within the $[\;]$-bracket in (2.77) is therefore the correction due to the finite line width. As $(\varkappa^2 \gamma_{\lambda s}/kT) \rightarrow 0$, we have $[\;] \rightarrow 0$, which should be the case.

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[*] See for example Gradshteyn and Ryzhik (1965)

(iii) Phonon Distribution Function

The phonon distribution function can be obtained following the same procedure as for the electron distribution function.

The relevant Green's Function is $\langle\langle b_{\vec{q}} | B_{\vec{q}}^{\dagger} \rangle\rangle_E$ with $\gamma = +1$. The equation of motion for $\langle\langle b_{\vec{q}} | B_{\vec{q}}^{\dagger} \rangle\rangle_E$ is

$$(2.79) \qquad (E - \omega_{\vec{q}})\langle\langle b_{\vec{q}} | B_{\vec{q}}^{\dagger} \rangle\rangle_E = \frac{1}{2\pi} + \varkappa \sum_{\mu\mu's} V^*_{\mu\mu qs} \langle\langle a^{\dagger}_{\mu s} a_{\mu's} | B_{\vec{q}'}^{\dagger} \rangle\rangle_E.$$

where the higher order Green's Function $\langle\langle a^{\dagger}_{\mu s} a_{\mu's} B_{\vec{q}'}^{\dagger} \rangle\rangle_E$ satisfy the equation,

$$(2.80) \qquad \left(E - T_{\mu'} + T_{\mu}\right)\langle\langle a^{\dagger}_{\mu s} a_{\mu's} | B_{\vec{q}'}^{\dagger} \rangle\rangle_E$$

$$= \varkappa \sum_{\eta\vec{\zeta}} \left\{ V_{\mu'\eta\vec{\zeta}s}\langle\langle b_{\vec{\zeta}} a^{\dagger}_{\mu s} a_{\eta s} | B_{\vec{q}'}^{\dagger} \rangle\rangle_E + V^*_{\eta\mu'\vec{\zeta}s}\langle\langle b^{\dagger}_{\vec{\zeta}} a^{\dagger}_{\mu s} a_{\eta s} | B_{\vec{q}'}^{\dagger} \rangle\rangle_E \right.$$

$$\left. - V_{\eta\mu\vec{\zeta}s}\langle\langle b_{\vec{\zeta}} a^{\dagger}_{\eta s} a_{\mu's} | B_{\vec{q}'}^{\dagger} \rangle\rangle_E - V^*_{\mu\eta\vec{\zeta}s}\langle\langle b^{\dagger}_{\vec{\zeta}} a^{\dagger}_{\eta s} a_{\mu's} | B_{\vec{q}'}^{\dagger} \rangle\rangle_E \right\}$$

The decoupling is now carried out at this equation with the following order estimation:

$$(2.81) \qquad \langle\langle b_{\vec{\zeta}} a^{\dagger}_{\mu s} a_{\eta s} | B_{\vec{q}'}^{\dagger} \rangle\rangle_E = \delta_{\nu\eta}\, \delta_{\vec{\zeta}\vec{q}'}\, \tilde{n}^{\circ}_{\nu s} \langle\langle b_{\vec{q}} | B_{\vec{q}}^{\dagger} \rangle\rangle_E + O(\varkappa),$$

$$\langle\langle b^{\dagger}_{\vec{\zeta}} a^{\dagger}_{\nu s} a_{\eta s} | B_{\vec{q}'}^{\dagger} \rangle\rangle_E = O(\varkappa^2).$$

This leads to

(2.82)
$$\langle\langle b_{\vec{q}}|B^{+}_{\vec{q}}\rangle\rangle_E = \frac{1}{2\pi}\;\frac{1}{E - W_{\vec{q}} - \varkappa^2 M_{\vec{q}}(E)}$$

where

(2.83)
$$M_{\vec{q}}(E) = \sum_{\nu\nu's}|V_{\nu\nu'qs}|^2\frac{\tilde{n}^0_{\nu s} - \tilde{n}^0_{\nu's}}{E - T_{\nu'} + T_{\nu}}$$

Writing $M_q(\omega \pm i\eta) = \Delta_{\vec{q}}(\omega) \mp i\gamma_{\vec{q}}(\omega)$, where

(2.84)
$$\Delta_{\vec{q}}(\omega) = \sum_{\nu\nu's}|V_{\nu\nu'\vec{q}s}|^2\,(\tilde{n}^0_{\nu s} - \tilde{n}^0_{\nu's})\,\wp\left(\frac{1}{\omega - T_{\nu'} + T_{\nu}}\right)$$

(2.85)
$$\gamma_{\vec{q}}(\omega) = \sum_{\nu\nu's}|V_{\nu\nu'\vec{q}s}|^2\,(\tilde{n}^0_{\nu s} - \tilde{n}^0_{\nu's})\,\delta(\omega - T_{\nu'} + T_{\nu})$$

we finally arrive at

(2.86)
$$\tilde{\nu}_{\vec{q}} = \frac{1}{\pi}\int_{-\infty}^{\infty}d\omega\;\frac{\varkappa^2\gamma_{\vec{q}}(\omega)(e^{\beta\omega} - 1)^{-1}}{[\omega - \omega_{\vec{q}} - \varkappa^2\Delta_{\vec{q}}(\omega)]^2 + \varkappa^4\gamma^2_{\vec{q}}(\omega)}$$

$$\simeq \frac{1}{e^{\beta\tilde{\omega}_{\vec{q}}} - 1}$$

with $\tilde{\omega}_{\vec{q}} = \omega_{\vec{q}} + \varkappa^2\Delta_{\vec{q}}(\omega_{\vec{q}})$.

CHAPTER III: ENERGY-LEVEL SHIFTS

1. <u>General Remarks</u>

From the treatment of the one-particle Green's Functions in the previous chapter, we have shown that the electron-phonon interaction introduces a complex shift in the unperturbed energy spectrum. In the limit that the imaginary part of the shift is small, one obtains a quasi-particle energy spectrum. Take for instance an electronic state $\lambda^{\S}$. The energy level of this state is shifted and broadened by amounts $\kappa^2 \Delta_\lambda(T_\lambda)$ and $2\kappa^2 \gamma_\lambda(T_\lambda)$ respectively (see remarks after eq.(2.67)). These quantities can be obtained readily from (2.53) and (2.54):

$$(3.1) \quad \Delta_\lambda(T_\lambda) = \sum_\mu \sum_{\vec{q}\sigma} |V_{\lambda\mu\vec{q}\sigma}|^2 \, \mathcal{P} \left\{ \frac{1 + \nu_{\vec{q}\sigma}}{T_\lambda - T_\mu - \hbar\omega_{\vec{q}\sigma}} + \frac{\nu_{\vec{q}\sigma}}{T_\lambda - T_\mu + \hbar\omega_{\vec{q}\sigma}} \right\}$$

$$(3.2) \quad 2\gamma_\lambda(T_\lambda) = 2\pi \sum_{\substack{\mu \\ (\neq\lambda)}} \sum_{\vec{q}\sigma} |V_{\lambda\mu\vec{q}\sigma}|^2 \left\{ (1 + \nu_{\vec{q}\sigma}) \, \delta(T_\lambda - T_\mu - \hbar\omega_{\vec{q}\sigma}) + \nu_{\vec{q}\sigma} \, \delta(T_\lambda - T_\mu + \hbar\omega_{\vec{q}\sigma}) \right\}$$

In these expressions, we have displayed the polarization of the phonon mode by σ. In (3.2), we have also used the relation that

$$(3.3) \quad \sum_{\vec{q}\sigma} |V_{\lambda\mu q\sigma}|^2 \, \delta(\omega_{\vec{q}\sigma}) = 0,$$

which follows from the fact that the density of phonon states

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$\S$ From here on, we include the spin index s in λ.

vanishes at $\omega_{\vec{q}\sigma} = 0$. Thus, the only contribution to the width comes from non-diagonal matrix elements.

By comparision with the shift and width of the optical absorption line between two states α and β as obtained by Nishikawa and Barrie (1963), we make the following identifications[*]:

$$(3.4) \qquad \triangle_{\alpha\beta}^{NB}(T_\beta - T_\alpha) = \triangle_\beta(T_\beta) - \triangle_\alpha(T_\alpha),$$

$$(3.5) \qquad \gamma_{\alpha\beta}^{NB}(T_\beta - T_\alpha) = \gamma_\beta(T_\beta) + \gamma_\alpha(T_\alpha).$$

We have used NB to label the corresponding quantities of Nshikawa and Barrie.

At this stage, let us summarize what will be done in this chapter. The problem is to calculate the effect of the electron-phonon interaction on the energy spectrum of an impurity[‡]. The basic formula is

$$(3.6a) \qquad \widetilde{T}_\lambda = T_\lambda + \varkappa^2 \triangle_\lambda(T_\lambda).$$

We write this as

$$(3.6b) \qquad \widetilde{T}_\lambda = T_\lambda + \sum_{\lambda'} S_{\lambda\lambda'} + \sum_{\lambda'} \triangle_{\lambda\lambda'} ,$$

---

[*] One could have made the Nishikawa-Barrie expressions as starting point and then defined the single-level shift and width by (3.4)and(3.5). ~~However, the restriction to one-electron system was not taken care of properly in their paper; see footnote on p. 9.~~

[‡] The widths have been discussed by Barrie and Nishikawa (1963).

where

(3.7)
$$S_{\lambda\lambda'} = \sum_{\vec{q}\sigma} \frac{-|V_{\lambda\lambda'\vec{q}\sigma}|^2}{T_\lambda - T_{\lambda'} - \hbar\omega_{\vec{q}\sigma}}$$

(3.8)
$$\triangle_{\lambda\lambda'} = \sum_{\vec{q}\sigma} |V_{\lambda\lambda'\vec{q}\sigma}|^2 \, \nu_{\vec{q}\sigma} \left\{ \frac{1}{T_\lambda - T_{\lambda'} - \hbar\omega_{\vec{q}\sigma}} + \frac{1}{T_\lambda - T_{\lambda'} + \hbar\omega_{\vec{q}\sigma}} \right\}.$$

$S_{\lambda\lambda'}$ is a temperature-independent contribution to the shift arising from the zero-point vibrations of the lattice. This represents a correction to the standard calculation of the spectrum which assumes a rigid lattice. This standard calculation is basically a purely quantum mechanical calculation; our treatment has included statistical aspects and $S_{\lambda\lambda'}$ is the correction at zero temperature. $\triangle_{\lambda\lambda'}$ contains the temperature-dependence of the energy level. The two subscripts $(\lambda\lambda')$ then refer to the shift of the λth level due to mixing with the λ'th.

As can be seen above, the basic steps are to calculate matrix elements $V_{\lambda\lambda'\vec{q}\sigma}$ and then to carry out the appropiate summations over $\vec{q}, \sigma$. §2 of this chapter deals with the calculation of the matrix elements on the assumption that the electron-phonon interaction is the deformation potential interaction with long wave-length acoustic phonons; the electronic wave functions are those appropiate to a many-valley semiconductor.

§3 of this chapter deals with the summations over $\vec{q}, \sigma$.

Finally, §4 contains the numerical estimations and comparision with experiment for phosphorus donors in silicon.

2. Calculation of Matrix Elements

(i) General Expression

Before we can calculate the various matrix elements $V_{\lambda\lambda'\vec{q}\sigma}$, we need to know the wave-function of the impurity electron and the form of the interaction potential.

According to Kohn and Luttinger (1955), the wave-function for the impurity electron can be written as

$$(3.9) \qquad \overline{\Psi}_{\lambda(\mu)}(\vec{r}) = \sum_{j} a^{(j)}_{\lambda(\mu)} \, \psi^{(j)}_{\lambda}(\vec{r}),$$

where the summation over j, in the case of silicon, is summing over the six equivalent minima (valleys) in the conduction band. The function $\psi^{(j)}_{\lambda}(\vec{r})$ is a superposition of Bloch states at and about the jth minimum, i.e.

$$(3.10) \qquad \psi^{(j)}_{\lambda}(\vec{r}) = \int \frac{d\vec{k}}{(2\pi)^3} \, A^{(j)}_{\lambda}(\vec{k}) \, \varphi_{\vec{k}}(\vec{r}) \quad ; \quad \varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$

where $A^{(j)}_{\lambda}(\vec{k})$ satisfies the relation

$$(3.11) \qquad A^{(j)}_{\lambda}(\vec{k}) = 0 \qquad \text{for} \quad \left| \vec{k} - \vec{k}_j \right| \gg 1/a*$$

with $a*$ being the effective Bohr radius. Since $1/a*$ is small compared with the length of a reciprocal lattice vector ($\overline{k}/k_{BZ} \simeq 0.04$, $\overline{k} = 1/a*$), $\psi^{(j)}_{\lambda}(\vec{r})$ can be approximated by the product of $\varphi_{\vec{k}_j}(r)$, the Bloch function at the jth minimum, and an envelope function

$$(3.12) \qquad F_\lambda^{(j)}(\vec{r}) = \int \frac{d\vec{k}}{(2\pi)^3} A_\lambda^{(j)}(\vec{r}) \; e^{i(\vec{k} - \vec{k}_j) \cdot \vec{r}}.$$

This latter function is a solution to an effective-mass equation with the z_j-axis defined in the direction of the jth minimum from the origin. The label λ designates the different approximate λ eigenstates of this equation; for example

$$F_{"1s"}^{(j)}(\vec{r}) = \frac{1}{(\pi a^2 b)^{1/2}} \; e^{-\rho_j}$$

$$(3.13) \qquad F_{"2s"}^{(j)}(\vec{r}) = \frac{1}{(32\pi a^2 b)^{1/2}} \; (2 - \rho_j) \, e^{-\rho_j/2}$$

$$F_{"2p_o"}^{(j)}(\vec{r}) = \frac{1}{(32\pi a^2 b)^{1/2}} \; \frac{z_j}{b} \, e^{-\rho_j/2}, \text{ etc.,}$$

where

$$(3.14) \qquad \rho_j = \sqrt{\frac{x_j^2 + y_j^2}{a^2} + \frac{z_j^2}{b^2}}$$

and a, b are respectively the transverse and longitudinal Bohr radii.

The $\alpha_{\lambda(\mu)}^{(j)}$ in (3.9) are numerical coefficients that can be determined by elementary group theory so that the total wave-function $\overline{\Psi}_{\lambda(\mu)}(r)$ has the required tetrahedral

symmetry about the impurity site. For simplicity in notation, we have used a single label μ to denote the irreducible representation and the row within the representation according to which the wave-function $\Psi_{\lambda(\mu)}$ transforms. The particular set of $\alpha_{\lambda(\mu)}^{(j)}$ for the "1s"-state is given in Kohn and Luttinger's paper[*]:

	μ	$\alpha_{\lambda(\mu)}^{(j)}$	irred. repr[n].
	1	$1/\sqrt{6}\,\{1,\ 1,\ 1,\ 1,\ 1,\ 1\}$	A_1
	2	$1/\sqrt{12}\,\{1,\ 1,\ 1,\ 1,-2,-2\}$	E
(3.15)	3	$1/2\,\{-1,-1,\ 1,\ 1,\ 0,\ 0\}$	E
	4	$1/\sqrt{2}\,\{1,-1,\ 0,\ 0,\ 0,\ 0\}$	T_1
	5	$1/\sqrt{2}\,\{0,\ 0,\ 1,-1,\ 0,\ 0\}$	T_1
	6	$1/\sqrt{2}\,\{0,\ 0,\ 0,\ 0,\ 1,-1\}$	T_1

In accordance with the classification of impurity states according to irreducible representations given also in Kohn and Luttinger's paper, one can show that (3.15) also apply to the "2s"-, "2p₀"-states. Therefore, for our purposes, we can write $\alpha_{\mu}^{(j)}$ instead of $\alpha_{\lambda(\mu)}^{(j)}$.

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[*] The two rows belonging to the E-representation are actually different from those of Kohn and Luttinger. They are here chosen such that they are orthogonal (see relation (3.27) on p. 44)

The interaction between the impurity electron and the acoustic modes of the lattice vibrations, which is the interaction with which we shall be concerned, was first discussed by Bardeen and Shockley (1950) from the deformation potential point of view. In order to take account of the many-valley nature of the conduction band, the generalized theory of Herring and Vogt (1956) will be used in the present treatment. According to these authors, the shift in energy in the jth valley due to deformation brought about by elastic waves is

$$(3.16) \qquad \Xi_d \left(\epsilon_{x_j x_j} + \epsilon_{y_j y_j} \right) + \left(\Xi_d + \Xi_u \right) \epsilon_{z_j z_j}$$

where $\epsilon_{x_j x_j}$, $\epsilon_{y_j y_j}$ and $\epsilon_{z_j z_j}$ are elements of the strain tensor; Ξ_d and Ξ_u are phenomenological constants. In the present case, the strain is brought about by lattice vibrations. Writing the displacement of the lattice at the point $\vec{r}$ in terms of normal modes as usual, we have

$$(3.17) \qquad \vec{u}(\vec{r}) = \sum_{\vec{q}\sigma} \sqrt{\frac{\hbar}{2\rho V \omega_{\vec{q}\sigma}}} \left[\vec{e}_\sigma(\vec{q})\, b_{\vec{q}\sigma}\, e^{i\vec{q}\cdot\vec{r}} + \vec{e}_\sigma^*(\vec{q})\, b_{\vec{q}\sigma}^+\, e^{-i\vec{q}\cdot\vec{r}} \right]$$

where $\vec{e}_\sigma(\vec{q})$, $e_\sigma^*(\vec{q})$ are polarization vectors satisfying the relation

$$(3.18) \qquad \vec{e}_\sigma(\vec{q}) = \vec{e}_\sigma^*(-\vec{q}) , \qquad \sigma = 1 \text{ (longitudinal)} \\ 2, 3 \text{ (transverse)}.$$

ρ and V are respectively the density and volume of the crystal.

Since the interaction Hamiltonian is given by

$$(3.19) \qquad H_{e-ph} = -\vec{u}(\vec{r}) \cdot \vec{\nabla} \, V(\vec{r})_{periodic}.$$

then we can calculate the matrix element for the interaction term using (3.9)-(3.19)[‡], and find for $_\varkappa V_{\lambda(\mu)\lambda'(\mu')\vec{q}\sigma}$ the following expression;

$$(3.20) \qquad _\varkappa V_{\lambda(\mu)\lambda'(\mu')\vec{q}\sigma} = i \sqrt{\frac{\hbar}{2\rho V \omega_{\vec{q}\sigma}}} \sum_j \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} \; \Theta_{\lambda\lambda'}^{(j)}(\vec{q})$$
$$\times \left[\vec{e}_\sigma(\vec{q}) \cdot (\Xi_d \vec{1} + \Xi_u \vec{U}^{(j)}) \cdot \vec{q} \right],$$

where $\vec{1}$ is the unit matrix and

$$(3.21) \qquad \vec{U} = \begin{vmatrix} 0 & & \\ & 0 & \\ & & 1 \end{vmatrix} \quad ; \quad \vec{U}^{(j)} = \vec{U}^{(-j)},$$

$$(3.22) \qquad (\Xi_d \vec{1} + \Xi_u \vec{U}^{(j)}) = \frac{\hbar^2}{m\Omega} \int_{cell} d\vec{r} \, (\vec{\nabla} u^*_{\vec{k}_j})(\vec{\nabla} u_{\vec{k}_j});$$

(Ω = volume of unit cell)

$$(3.23) \qquad \Theta_{\lambda\lambda'}^{(j)}(\vec{q}) = \int d\vec{r} \, F_\lambda^{(j)*}(\vec{r}) \, F_{\lambda'}^{(j)}(\vec{r}) \, e^{i\vec{q}\cdot\vec{r}}.$$

In writing down (3.20), we have also neglected intervalley contributions for reasons to be discussed later.

[‡] See for example Hesagawa (1960).

The function $\Theta_{\lambda\lambda'}^{(j)}(\vec{q})$ can be calculated using the envelope functions of (3.13)[‡]. The results for $\lambda, \lambda' = 1s, 2s,$ and $2p_0$ are given in Table I.

Using the relation

$$\vec{e}_1(\vec{q}) = \frac{\vec{q}}{q} = \text{polarization of longitudinal phonons;}$$

$$(q = |\vec{q}|)$$

we write (3.20) as

$$(3.24) \qquad \varkappa V_{\lambda(\mu)\lambda'(\mu')\vec{q}\sigma} = i\sqrt{\frac{\hbar q^2}{2\rho V \omega_{\vec{q}\sigma}}} \sum_j \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} \Theta_{\lambda\lambda'}^{(j)}(\vec{q})$$
$$\times \left[\vec{e}_\sigma(\vec{q}) \cdot (\Xi_d \vec{1} + \Xi_u \vec{U}^{(j)}) \cdot \vec{e}_1(\vec{q}) \right]$$

Since $\vec{e}_\sigma(\vec{q}) \cdot \vec{e}_1(\vec{q}) = \delta_{\sigma,1}$, one can see that in the absence of uniaxial stress Ξ_u, there can be no interaction involving transverse phonons.

To proceed further, we make the following approximation:

$$(3.25) \qquad a^2(q_{x_j}^2 + q_{y_j}^2) + b^2 q_{z_j}^2 \longrightarrow (a^* q)^2,$$

i.e., we replace the ellipsoidal energy surface by a spherical one. a^* is the effective Bohr radius. Making this approximation at this stage does not lose any essential feature; the

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[‡] Because of the anisotropy of ρ_j, we transform to a new coordinate system $S'(x'=x, y'=y, z'=(a/b)z)$ and then use the method of calculation of Nishikawa (1962).

TABLE I: Table of $\Theta_{\lambda\lambda'}^{(j)}(\vec{q})$ for $\lambda, \lambda' = $ 1s, 2s, and 2p$_o$. Notations used:

$$\chi_j = \sqrt{a^2(q_{x_j}^2 + q_{y_j}^2) + b^2 q_{z_j}^2}$$

θ_j = angle between $\vec{q}$ and z_j-axis.

	1s	2s	2p$_o$
1s	$\dfrac{1}{\left(1+\frac{\chi_j^2}{4}\right)^2}$	$\dfrac{2^{5/2}(2/3)^6 \chi_j^2}{\left(1+\frac{4}{9}\chi_j^2\right)^3}$	$i\,\dfrac{2^{15/2}}{3^5}\dfrac{\chi_j}{\left(1+\frac{4}{9}\chi_j^2\right)^3}\cos\theta_j$
2s		$\dfrac{1-3\chi_j^2+2\chi_j^4}{\left(1+\chi_j^2\right)^4}$	$i\,3\,\dfrac{\chi_j(1-\chi_j^2)}{\left(1+\chi_j^2\right)^4}\cos\theta_j$
2p$_o$			$\dfrac{1+\chi_j^2-6\chi_j^2\cos^2\theta_j}{\left(1+\chi_j^2\right)^4}$

important information about the non-spherical nature of the energy surface has already been contained in the $\alpha_\mu^{(j)}$. In using Table I then, we shall replace χ_j by $\chi = a^*q$.

(ii) <u>Mixing Among s-States ($\lambda, \lambda' = 1s, 2s.$)</u>

We write $\Theta_{\lambda\lambda'}^{(j)}(\vec{q}) \rightarrow f_{\lambda\lambda'}(\chi)$ according to the approximation (3.25). Then (3.24) becomes

$$(3.26) \qquad \varkappa^V\lambda(\mu)\chi(\mu')\vec{q}\sigma = i \sqrt{\frac{\hbar q^2}{2\rho V\omega_{q\sigma}}} f_{\lambda\lambda'}(\chi) \left[\Xi_d \delta_{\sigma,1} \delta_{\mu\mu'} \right.$$
$$\left. + \Xi_u \vec{e}(\vec{q}) \cdot D_{\mu\mu'}^{(o)} \vec{e}_1(\vec{q}) \right]$$

where we have used the orthogonality relation

$$(3.27) \qquad \sum_j \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} = \delta_{\mu\mu'}$$

and have defined

$$(3.28) \qquad D_{\mu\mu'}^{(o)} = \sum_j \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} \vec{U}^{(j)}.$$

It follows from the fact that $\vec{U}^{(j)}$ is symmetric under interchange of (j) and (-j) (i.e., $\vec{U}^{(j)}$ is the same tensor for a pair of opposite ellipsoids), we obtain

$$(3.29) \qquad D_{\mu\mu'}^{(o)} = 0 \qquad \text{if} \qquad \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} = - \alpha_\mu^{(-j)} \alpha_{\mu'}^{(-j)}.$$

It is apparent from (3.26) and the auxiliary condition that

(a) the Ξ_d-component of the deformation potential invovles

only longitudinal phonons, which is indeed a general

result (see remarks after (3.24)) and that mixing between any any pair of s-like states is possible only if $\alpha_{\mu}^{(j)}$ for both states come from the same row of the same irreducible representation.

(b) the $\overline{\Xi}_u$-component in general involves both longitudinal and transverse phonons, and the relation (3.29) rules out mixing of a triplet (μ = 4, 5, 6) with a doublet (μ = 2, 3) or with a singlet (μ = 1).

The complete results for $D_{\mu\mu'}^{(o)}$ is given in Table II.

To find $\vec{e}_r(\vec{q}) \cdot D_{\mu\mu'}^{(o)} \cdot \vec{e}_1(\vec{q})$, we choose the following set of polarization vectors:

$$\vec{e}_1(\vec{q}) = \vec{1}_x \sin\theta \cos\phi + \vec{1}_y \sin\theta \sin\phi + \vec{1}_z \cos\theta$$

(3.30) $$\vec{e}_2(\vec{q}) = \vec{1}_x \cos\theta \cos\phi + \vec{1}_y \cos\theta \sin\phi - \vec{1}_z \sin\theta$$

$$\vec{e}_3(\vec{q}) = -\vec{1}_x \sin\phi + \vec{1}_y \cos\phi$$

where $\vec{1}_x$, $\vec{1}_y$, and $\vec{1}_z$ are unit vectors along the x-, y-, and z-axis respectively; the co-ordinate system is chosen such that $x = x_3$, $y = y_3$, $z = z_3$ (see Fig.1)

Fig. 1
Labelling of the six
energy minima of the
conduction band.
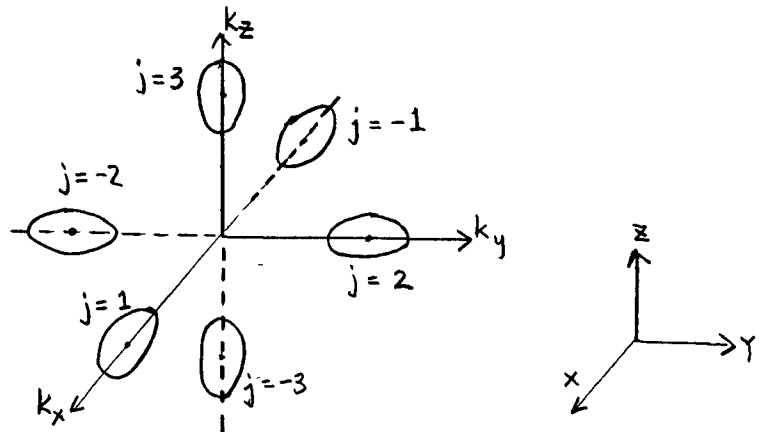
In Table III, we list the results for $\vec{e}_\sigma(\vec{q}) \cdot D^{(o)}_{\mu\mu'} \cdot \vec{e}_1(\vec{q})$. It is now a simple matter to obtain the expression in bracket in (2.26), viz.

$$(3.31) \qquad \left\{ \Xi_d \, \delta_{\sigma,1} \delta_{\mu\mu'} + \Xi_u \, \vec{e}_\sigma(\vec{q}) \cdot D^{(o)}_{\mu\mu'} \cdot \vec{e}_1(\vec{q}) \right\}$$

which is then given in Table IV.

TABLE II : Table of $D_{\mu\mu'}^{(o)} = \sum_j \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} \vec{U}^{(j)}$

μ' \ μ	1	2	3	4	5	6
1	$\frac{1}{3}\begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix}$					
2	$\frac{1}{3\sqrt{2}}\begin{vmatrix} 1 \\ 1 \\ -2 \end{vmatrix}$	$\frac{1}{6}\begin{vmatrix} 1 \\ 1 \\ 4 \end{vmatrix}$				
3	$\frac{1}{\sqrt{6}}\begin{vmatrix} -1 \\ 1 \\ 0 \end{vmatrix}$	$\frac{1}{2\sqrt{3}}\begin{vmatrix} -1 \\ 1 \\ 0 \end{vmatrix}$	$\frac{1}{2}\begin{vmatrix} 1 \\ 1 \\ 0 \end{vmatrix}$			
4	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\begin{vmatrix} 1 \\ 0 \\ 0 \end{vmatrix}$		
5	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\begin{vmatrix} 0 \\ 1 \\ 0 \end{vmatrix}$	
6	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\begin{vmatrix} 0 \\ 0 \\ 1 \end{vmatrix}$

TABLE III : Table of $e_\sigma(\vec{q}).D_{\mu\mu'}^{(0)}.\vec{e}_1(\vec{q})$.
The three entries in each block correspond to the three polarization in the order $\sigma = \begin{Bmatrix} 1 \\ 2 \\ 3 \end{Bmatrix}$.

μ \ μ'	1	2	3	4	5	6
1	$\frac{1}{3}$ 0 0					
2	$\frac{1}{3\sqrt{2}}(\sin^2\theta - 2\cos^2\theta)$ $\frac{1}{\sqrt{2}}\sin\theta\cos\theta$ 0	$\frac{1}{6}(3\cos^2\theta + 1)$ $\frac{-1}{2}\sin\theta\cos\theta$ 0				
3	$\frac{-1}{\sqrt{6}}\sin^2\theta\cos 2\phi$ $\frac{-1}{\sqrt{2}}\sin\theta\cos\theta\cos 2\phi$ $\frac{1}{\sqrt{6}}\sin\theta\sin 2\phi$	$\frac{-1}{2\sqrt{3}}\sin^2\theta\cos 2\phi$ $\frac{-1}{2\sqrt{3}}\sin\theta\cos\theta\cos 2\phi$ $\frac{1}{2\sqrt{3}}\sin\theta\sin 2\phi$	$\frac{1}{2}\sin^2\theta$ $\frac{1}{2}\sin\theta\cos\theta$ 0			
4	0	0	0	$\sin^2\theta\cos^2\phi$ $\sin\theta\cos\theta\cos^2\phi$ $\frac{-1}{2}\sin\theta\sin 2\phi$		
5	0	0	0	0	$\sin^2\theta\sin^2\phi$ $\sin\theta\cos\theta\sin^2\phi$ $\frac{1}{2}\sin\theta\sin 2\phi$	
6	0	0	0	0	0	$\cos^2\theta$ $-\sin\theta\cos\theta$ 0

TABLE IV : Table of $\left\{\left\{(o)\right\}\right\}.$

$$= \left\{ \Xi_d\,\delta_{\tau,1}\,\delta_{\mu\mu'} + \Xi_u\,\vec{e}_\tau(\vec{q}).D(o)_{\mu\mu'}.\vec{e}_1(\vec{q}) \right\}.$$

	1	2	3	4	5	6
1	$\left(\Xi_d + \dfrac{\Xi_u}{3}\right)$ 0 0					
2	$\dfrac{\Xi_u}{3\sqrt{2}}(\sin^2\theta - 2\cos^2\theta)$ $\dfrac{\Xi_u}{\sqrt{2}}\sin\theta\cos\theta$ 0	$\Xi_d + \dfrac{\Xi_u}{6}(3\cos^2\theta+1)$ $-\dfrac{\Xi_u}{2}\sin\theta\cos\theta$ 0				
3	$-\dfrac{\Xi_u}{\sqrt{6}}\sin^2\theta\cos 2\phi$ $-\dfrac{\Xi_u}{\sqrt{6}}\sin\theta\cos\theta\cos 2\phi$ $\dfrac{\Xi_u}{\sqrt{6}}\sin\theta\sin 2\phi$	$-\dfrac{\Xi_u}{2\sqrt{3}}\sin^2\theta\cos 2\phi$ $-\dfrac{\Xi_u}{2\sqrt{3}}\sin\theta\cos\theta\cos 2\phi$ $\dfrac{\Xi_u}{2\sqrt{3}}\sin\theta\sin 2\phi$	$\Xi_d + \dfrac{\Xi_u}{2}\sin^2\theta$ $\dfrac{\Xi_u}{2}\sin\theta\cos\theta$ 0			
4	0	0	0	$\Xi_d + \Xi_u\sin^2\theta\cos^2\phi$ $\Xi_u\sin\theta\cos\theta\cos^2\phi$ $-\dfrac{\Xi_u}{2}\sin\theta\sin 2\phi$		
5	0	0	0	0	$\Xi_d + \Xi_u\sin^2\theta\sin^2\phi$ $\Xi_u\sin\theta\cos\theta\sin^2\phi$ $\dfrac{\Xi_u}{2}\sin\theta\sin 2\phi$	
6	0	0	0		0	$\Xi_d + \Xi_u\cos^2\theta$ $-\Xi_u\sin\theta\cos\theta$ 0
$\mu'\diagdown\mu$	1	2	3	4	5	6

(iii) <u>Mixing of 2p$_0$-states with 1s- and 2s-states</u>

From Table I, we find that $\Theta^{(j)}_{\lambda\lambda'}(\vec{q})$ is of the form

$$g_{\lambda\lambda'}(\chi) \cos \theta_j$$

after the approximation $\chi_j \to \chi$ has been performed. Hence, (3.24) becomes

$$(3.32) \quad \chi V_{\lambda(\mu)\lambda'(\mu')\vec{q}\sigma} = i\sqrt{\frac{\hbar q^2}{2\rho V \omega_{\vec{q}\sigma}}} \, g_{\lambda\lambda'}(\chi) \left[\Xi_d \delta_{\sigma,1} \sum_j \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} \cos\theta_j \right.$$
$$\left. + \Xi_u \, \vec{e}_\sigma(\vec{q}) . D^{(1)}_{\mu\mu'} . \vec{e}_1(\vec{q}) \right]$$

where we have defined

$$(3.33) \quad D^{(1)}_{\mu\mu'} = \sum_j \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} \vec{U}^{(j)} \cos \theta_j.$$

Since $\cos \theta_j = - \cos \theta_{-j}$, it follows that

$$(3.34) \quad \chi V_{\lambda(\mu)\lambda'(\mu')\vec{q}\sigma} = 0 \quad \text{if} \quad \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} = \alpha^{(-j)}_\mu \alpha^{(-j)}_{\mu'}.$$

In analogy to (ii), we tabulate the following quantities (Tables V to VII);

$$(3.35) \quad \sum_j \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} \cos \theta_j,$$

$$(3.36) \quad \vec{e}_\sigma(\vec{q}) . D^{(1)}_{\mu\mu'} . \vec{e}_1(\vec{q})$$

$$(3.37) \quad \left\{ \Xi_d \delta_{\sigma,1} \sum_j \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} \cos \theta_j + \Xi_u \, \vec{e}_\sigma(\vec{q}) . D^{(1)}_{\mu\mu'} . \vec{e}_1(\vec{q}) \right\}.$$

TABLE V : Table of $\sum_j \alpha_\mu^{(j)} \alpha_{\mu}^{(j)} \cos\theta_j$.

μ \ μ'	1	2	3	4	5	6
1	○					
2	○	○				
3	○	○	○			
4	$\frac{1}{\sqrt{3}}\sin\theta\cos\phi$	$\frac{1}{\sqrt{6}}\sin\theta\cos\phi$	$\frac{-1}{\sqrt{2}}\sin\theta\cos\phi$	○		
5	$\frac{1}{\sqrt{3}}\sin\theta\sin\phi$	$\frac{1}{\sqrt{6}}\sin\theta\sin\phi$	$\frac{1}{\sqrt{2}}\sin\theta\cos\phi$	○	○	
6	$\frac{1}{\sqrt{3}}\cos\theta$	$-\sqrt{\frac{2}{3}}\cos\theta$	○	○	○	○

TABLE VI : Table of $\vec{e}_\sigma(\vec{q}) . D^{(J)}_{\mu\mu'} . \vec{e}_1(\vec{q})$.

μ \ μ'	1	2	3	4	5	6
1	○					
2	○	○				
3	○	○	○			
4	$\frac{1}{\sqrt3}\sin^3\theta\cos^3\phi$ $\frac{1}{\sqrt3}\sin^2\theta\cos\theta\cos^3\phi$ $\frac{1}{\sqrt3}\sin^2\theta\sin\phi\cos^2\phi$	$\frac{1}{\sqrt6}\sin^3\theta\cos^3\phi$ $\frac{1}{\sqrt6}\sin^2\theta\cos\theta\cos^3\phi$ $\frac{1}{\sqrt6}\sin^2\theta\sin\phi\cos^2\phi$	$\frac{1}{\sqrt2}\sin^3\theta\cos^3\phi$ $\frac{1}{\sqrt2}\sin^2\theta\cos\theta\cos^3\phi$ $\frac{1}{\sqrt2}\sin^2\theta\sin\phi\cos^2\phi$	○		
5	$\frac{1}{\sqrt3}\sin^2\theta\sin^3\phi$ $\frac{1}{\sqrt3}\sin\theta\cos\theta\sin^3\phi$ $\frac{1}{\sqrt3}\sin^2\theta\sin\phi\cos\phi$	$\frac{1}{\sqrt6}\sin^3\theta\sin^3\phi$ $\frac{1}{\sqrt6}\sin^2\theta\cos\theta\sin^3\phi$ $\frac{1}{\sqrt6}\sin^2\theta\sin\phi\cos\phi$	$\frac{1}{\sqrt2}\sin^3\theta\sin^3\phi$ $\frac{1}{\sqrt2}\sin^2\theta\cos\theta\sin^3\phi$ $\frac{1}{\sqrt2}\sin^2\theta\sin\phi\cos\phi$	○	○	
6	$\frac{1}{\sqrt3}\cos^3\theta$ $\frac{1}{\sqrt3}\sin\theta\cos^2\theta$	$\sqrt{\frac{2}{3}}\cos^3\theta$ $\sqrt{\frac{2}{3}}\sin\theta\cos^2\theta$	○		○	○

TABLE VII : Table of $\{\ \}_{(ij)}$

$$= \left\{ \Xi_d\, \delta_{\sigma,1} \sum_j a_{-\mu}^{(j)} a_{-\mu'}^{(j)} \cos\theta_j \right.$$
$$\left. + \ \Xi_u\, \vec{e}_\sigma(\vec{q}) \cdot D_{\mu\mu'}^{(1)} \cdot \vec{e}_1(\vec{q}) \right\}_{(ij)}.$$

μ' \ μ	1	2	3	4	5	6
1	◯					
2	◯	◯				
3	◯	◯	◯			
4	$-\frac{\Xi_d}{\sqrt{3}}\sin\theta\cos\phi$ $+\frac{\Xi_u}{\sqrt{3}}\sin^3\theta\cos^3\phi$ $-\frac{\Xi_u}{\sqrt{3}}\sin^2\theta\sin\phi\cos^2\phi$	$\frac{\Xi_d}{\sqrt{6}}\sin\theta\cos\phi$ $+\frac{\Xi_u}{\sqrt{6}}\sin^3\theta\sin^3\phi$ $-\frac{\Xi_u}{\sqrt{6}}\sin^2\theta\sin\phi\cos^2\phi$	$-\frac{\Xi_d}{\sqrt{2}}\sin\theta\cos\phi$ $-\frac{\Xi_u}{\sqrt{2}}\sin^3\theta\cos^3\phi$ $-\frac{\Xi_u}{\sqrt{2}}\sin^2\theta\cos\theta\cos^3\phi$ $-\frac{\Xi_u}{\sqrt{2}}\sin^2\theta\sin\phi\cos^2\phi$	◯		
5	$\frac{\Xi_d}{\sqrt{3}}\sin\theta\sin\phi$ $+\frac{\Xi_u}{\sqrt{3}}\sin^3\theta\sin^3\phi$ $-\frac{\Xi_u}{\sqrt{3}}\sin^2\theta\sin\phi\cos^2\phi$	$\frac{\Xi_d}{\sqrt{6}}\sin\theta\sin\phi$ $+\frac{\Xi_u}{\sqrt{6}}\sin^3\theta\cos\theta\sin^3\phi$ $-\frac{\Xi_u}{\sqrt{6}}\sin^2\theta\sin\phi\cos\phi$	$\frac{\Xi_d}{\sqrt{2}}\sin\theta\sin\phi$ $+\frac{\Xi_u}{\sqrt{2}}\sin^3\theta\sin^3\phi$ $+\frac{\Xi_u}{\sqrt{6}}\sin^2\theta\cos\theta\sin^2\phi$ $-\frac{\Xi_u}{\sqrt{6}}\sin^2\theta\sin^2\phi\cos\phi$	◯	◯	
6	◯	$-\sqrt{\frac{2}{3}}\Xi_d\cos\theta - \sqrt{\frac{2}{3}}\Xi_u\cos^3\theta$ $+\sqrt{\frac{3}{2}}\Xi_u\sin^2\theta\cos\theta$	◯	◯	◯	◯

(iv) <u>Mixing among $2p_o$-states</u>

For this case (cf. Table I and (3.25)),

$$\Theta^{(j)}_{2p_o,2p_o}(\vec{q}) \longrightarrow h(\chi) - \tilde{h}(\chi)\cos^2\theta_j,$$

where

(3.38)
$$h(\chi) = \frac{1}{(1+\chi^2)^3}$$

(3.39)
$$\tilde{h}(\chi) = \frac{6\chi^2}{(1+\chi^2)^4}.$$

The matrix element is therefore given by

(3.40)
$$\varkappa V_{2p_o(\mu),2p_o(\mu'),\vec{q},\sigma} = i\sqrt{\frac{\hbar q^2}{2\rho V \omega_{\vec{q}\sigma}}} \sum_j \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} \left\{ h(\chi) - \tilde{h}(\chi)\cos^2\theta_j \right\}$$
$$\times \left\{ \Xi_d \delta_{\sigma,1} + \Xi_u \vec{e}_\sigma(\vec{q}) \cdot \vec{U} \cdot \vec{e}_1^{(j)}(\vec{q}) \right\}.$$

It can be seen that

(3.41)
$$\varkappa V_{2p_o(\mu),2p_o(\mu'),\vec{q},\sigma} = 0 \quad \text{if} \quad \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} = -\alpha^{(-j)}_\mu \alpha^{(-j)}_{\mu'}.$$

Eq.(3.40) can be rewritten as

(3.42)
$$\varkappa V_{2p_o(\mu),2p_o(\mu'),\vec{q},\sigma} = i\sqrt{\frac{\hbar q^2}{2\rho V \omega_{\vec{q}\sigma}}} \left[h(\chi)\{\}_{(0)} - \tilde{h}(\chi)\{\}_{(2)} \right],$$

where $\left\{\right\}_{(0)}$ is given by (3.31), and

(3.43)
$$\{\}_{(2)} = \left\{ \Xi_d \delta_{\sigma,1} \sum_j \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} \cos^2\theta_j + \Xi_u \vec{e}_\sigma(\vec{q}) \cdot \vec{D}^{(2)}_{\mu\mu'} \cdot \vec{e}_1(\vec{q}) \right\}$$

where $D_{\mu\mu}^{(2)}$ is defined by

$$(3.44) \qquad D_{\mu\mu'}^{(2)} = \sum_j \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} \vec{U}^{(j)} \cos^2\theta_j.$$

In Tables VIII and IX, we tabulate

$$(3.45) \qquad \sum_j \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} \cos^2\theta_j,$$

$$(3.46) \qquad \vec{e}_\sigma(\vec{q}) \cdot D_{\mu\mu'}^{(j)} \cdot \vec{e}_1(\vec{q})$$

from which one can readily evaluate $\left\{ \ \right\}_{(2)}$ in (3.43).

TABLE VIII : Table of $\sum_j \alpha_\mu^{(j)} \alpha_{\mu'}^{(j)} \cos^2\theta_j$.

$\mu' \backslash \mu$ ... μ	1	2	3	4	5	6
1	$\frac{1}{3}$					
2	$\frac{1}{\sqrt{18}}(\sin^2\theta - 2\cos^2\theta)$	$\frac{1}{6}(1+\cos^2\theta)$				
3	$\frac{-1}{\sqrt{6}}\sin^2\theta\cos 2\phi$	$\frac{-1}{\sqrt{12}}\sin^2\theta\cos 2\phi$	$\frac{1}{2}\sin^2\theta$			
4	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\sin^2\theta\cos^2\phi$		
5	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\sin^2\theta\sin^2\phi$	
6	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\cos^2\theta$

TABLE IX : Table of $\vec{e}_\sigma(\vec{q}) . D^{(2)}_{\mu'\mu} . \vec{e}_1(\vec{q})$.

$\mu'\backslash\mu$	1	2	3
1	$\frac{1}{3}[\sin^4\theta(\cos^4\phi+\sin^4\phi)+\cos^4\theta]$ $\frac{1}{3}\sin\theta\cos\theta[\sin^2\theta(\cos^4\phi+\sin^4\phi)-\cos^2\theta]$ $-\frac{1}{6}\sin^3\theta\sin2\phi\cos2\phi$	$\frac{1}{6}[\sin^4\theta(\cos^4\phi+\sin^4\phi)+4\cos^4\theta]$ $\frac{1}{6}\sin\theta\cos\theta[\sin^2\theta(\cos^4\phi+\sin^4\phi)-4\cos^2\theta]$ $-\frac{1}{12}\sin^3\theta\sin2\phi\cos2\phi$	$\frac{1}{2}\sin^4\theta(\cos^4\phi+\sin^4\phi)$ $\frac{1}{2}\sin^3\theta\cos\theta(\cos^4\phi+\sin^4\phi)$ $-\frac{1}{4}\sin^3\theta\sin2\phi\cos2\phi$
2	$\frac{1}{\sqrt{18}}[\sin^4\theta(\cos^4\phi+\sin^4\phi)-2\cos^4\theta]$ $\frac{1}{\sqrt{18}}\sin\theta\cos\theta[\sin^2\theta(\cos^4\phi+\sin^4\phi)+2\cos^2\theta]$ $-\frac{1}{2\sqrt{18}}\sin^3\theta\sin2\phi\cos2\phi$	$-\frac{1}{\sqrt{12}}\sin^4\theta(\cos^4\phi-\sin^4\phi)$ $-\frac{1}{\sqrt{12}}\sin^3\theta\cos\theta(\cos^4\phi+\sin^4\phi)$ $\frac{1}{2\sqrt{12}}\sin^3\theta\sin2\phi$	
3	$-\frac{1}{\sqrt{6}}\sin^4\theta(\cos^4\phi-\sin^4\phi)$ $-\frac{1}{\sqrt{6}}\sin^3\theta\cos\theta(\cos^4\phi-\sin^4\phi)$ $\frac{1}{2\sqrt{6}}\sin^3\theta\sin2\phi$		
4	0	0	0
5	0	0	0
6	0	0	0

←

continued
from
last page

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μ / μ'	4	5	6
4	$\sin^4\theta \cos^4\phi$ $\sin^3\theta \cos\theta \cos^4\phi$ $-\sin^3\theta \sin\phi \cos^3\phi$		
5	◯	$\sin^4\theta \sin^4\phi$ $\sin^3\theta \cos\theta \sin^4\phi$ $\sin^3\theta \sin^3\phi \cos\phi$	
6	◯	◯	$\cos^4\theta$ $-\sin\theta \cos^3\theta$ ◯

(3) Expressions for Shifts

As a summary of the results of the last section, we list here the following expressions:

$$(3.47) \qquad \chi^V_{ns(\mu),n's(\mu'),\vec{q},\sigma} = i \sqrt{\frac{\hbar q^2}{2\rho V \omega_{\vec{q}\sigma}}} \; f_{ns,n's}(\chi) \left\{ \begin{array}{c} \\ \end{array} \right\}_{(0)},$$

$$(3.48) \qquad \chi^V_{ns(\mu),2p_0(\mu'),\vec{q},\sigma} = i \sqrt{\frac{\hbar q^2}{2\rho V \omega_{\vec{q}\sigma}}} \; g_{ns,2p_0}(\chi) \left\{ \begin{array}{c} \\ \end{array} \right\}_{(1)},$$

$$(3.49) \qquad \chi^V_{2p_0(\mu),2p_0(\mu'),\vec{q},\sigma} = i \sqrt{\frac{\hbar q^2}{2\rho V \omega_{\vec{q}\sigma}}} \left[h_{2p_0,2p_0}(\chi) \left\{ \begin{array}{c} \\ \end{array} \right\}_{(0)} - \tilde{h}_{2p_0,2p_0}(\chi) \left\{ \begin{array}{c} \\ \end{array} \right\}_{(2)} \right],$$

where $ns = 1s$ or $2s$; $\left\{ \begin{array}{c} \\ \end{array} \right\}_{(0)}$ and $\left\{ \begin{array}{c} \\ \end{array} \right\}_{(1)}$ are given by Tables IV and VII, and $\left\{ \begin{array}{c} \\ \end{array} \right\}_{(2)}$ is readily obtainable from Tables VIII and IX.

The remaining task is to substitute these expressions into (3.7) and (3.8), and rewriting these latter equations in such a way that numerical values can be obtained readily.

To begin with, we note that the phonon spectrum for long wave-length acoustic phonons is given by the dispersion relation

$$(3.50) \qquad \omega_{\vec{q}\sigma} = v_\sigma q \qquad , \quad (q = |\vec{q}|)$$

where v_σ is the velocity of sound with polarization mode given by σ. Our reason for considering only the long wave-length

acoustic phonons is as follows.

We have assumed that the electron-phonon interaction is weak and that the interaction is effective over a wide range of phonon energies. For any given phonon dispersion, the latter assumption can be justified if the electron-phonon interaction is sufficiently small. In the case of silicon, the strength of the interaction is such that the two assumptions are justified only for the long wave-length acoustic phonons (Lax and Burstein, 1955). Consequently, contributions due to optical phonons and intervalley processes are not taken into account. In any case, the energy difference between impurity states is small compared with the Debye energy so that, in the temperature range we are interested in, these latter contributions can indeed be neglected.

It is also to be assumed here that the density of phonon states is unaffected by the presence of the impurity so that the replacement

$$(3.51) \qquad \sum_{\vec{q}} \rightarrow \frac{V}{(2\pi)^3} \int_0^\infty q^2 dq \int d\Omega \quad ; \quad \int d\Omega \equiv \text{integration over angle variables}$$

can be made. The upper limit is extended to infinity in view of the fact that the phonon energies of importance are much less than the Debye energy.

With the above specifications, we can then write

$$(3.52) \quad \sum_{\vec{q}} \frac{\kappa^2 |V_{\lambda(\mu)\lambda'(\mu')\vec{q}\sigma}|^2}{T_{\lambda(\mu)} - T_{\lambda'(\mu')} \pm \hbar\omega_{\vec{q}\sigma}} \mathcal{F}(\omega_{\vec{q}\sigma})$$

$$= \frac{1}{4\pi^2} \left(\frac{\hbar v_\sigma}{a^*}\right) \frac{\overline{\{\}^2_{\lambda(\mu)\lambda'(\mu')}}}{\rho v_\sigma^3 a^{*2} \hbar} \int_0^\infty dx \frac{x^3 |f_{\lambda\lambda'}(x)|^2}{\frac{T_{\lambda(\mu)} - T_{\lambda'(\mu')}}{\hbar v_\sigma/a^*} \pm x} \mathcal{F}\left(\frac{v_\sigma}{a^*} x\right)$$

where $\mathcal{F}(\omega_{\vec{q}\sigma})$ is some function of $\omega_{\vec{q}\sigma}$, and $\overline{A(\vec{q})}$ is defined by

$$(3.53) \quad \overline{A(\vec{q})} = \frac{1}{4\pi} \int d\Omega \, A(\vec{q}).$$

The quantity $\overline{\{\}^2}$ can be obtained from the results of the

last section. See Tables X and XI for the tabulations of

$\overline{\{\}^2_{ns(\mu),n's(\mu')}} \left(\equiv \overline{\{\}^2_{(0)}}\right)$ and $\overline{\{\}^2_{ns(\mu),2p_0(\mu')}} \left(\equiv \overline{\{\}^2_{(1)}}\right)$.

In particular, the quantity $S_{\lambda\lambda'}$ as defined in (3.7)
now becomes

$$(3.54) \quad S_{\lambda(\mu)\lambda'(\mu')} = \sum_{\vec{q}\sigma} \frac{\kappa^2 |V_{\lambda(\mu)\lambda'(\mu')\vec{q}\sigma}|^2}{T_{\lambda(\mu)} - T_{\lambda'(\mu')} - \hbar\omega_{\vec{q}\sigma}}$$

$$= \sum_\sigma \frac{1}{4\pi^2} \left(\frac{\hbar v_\sigma}{a^*}\right) \frac{\overline{\{\}^2_{\lambda(\mu)\lambda'(\mu')}}}{\rho v_\sigma^3 a^{*2} \hbar} \int_0^\infty dx \frac{x^3 |f_{\lambda\lambda'}(x)|^2}{\frac{T_{\lambda(\mu)} - T_{\lambda'(\mu')}}{\hbar v_\sigma/a^*} - x},$$

which, depending on the relative positions of $\lambda(\mu)$ and $\lambda'(\mu')$,

can be classified as in the following:

(a) $T_{\lambda(\mu)} = T_{\lambda'(\mu')}$ and $\lambda(\mu) = \lambda'(\mu')$

(3.55)

$$S_{\lambda(\mu)\lambda'(\mu')} \longrightarrow S_{\lambda(\mu)\lambda(\mu)} = -\sum_\sigma \frac{1}{4\pi^2}\left(\frac{\hbar U_\sigma}{a^*}\right)\frac{\overline{\{\}^2_{\lambda(\mu)\lambda(\mu)}}}{\rho U_\sigma^3 a^{*2}\hbar}\int_0^\infty dx\ x^2\left|f_{\lambda\lambda}(x)\right|^2$$

(b) $T_{\lambda(\mu)} = T_{\lambda'(\mu')}$ but $\lambda(\mu) \neq \lambda'(\mu')$

(3.56)

$$S_{\lambda(\mu)\lambda'(\mu')} = -\sum_\sigma \frac{1}{4\pi^2}\left(\frac{\hbar U_\sigma}{a^*}\right)\frac{\overline{\{\}^2_{\lambda(\mu)\lambda'(\mu')}}}{\rho U_\sigma^3 a^{*2}\hbar}\int_0^\infty dx\ x^2\left|f_{\lambda\lambda}(x)\right|^2$$

(c) $T_{\lambda(\mu)} \neq T_{\lambda'(\mu')}$

(3.57)

$$S_{\lambda(\mu)\lambda'(\mu')} = \pm\sum_\sigma \frac{1}{4\pi^2}\left(\frac{\hbar U_\sigma}{a^*}\right)\frac{\overline{\{\}^2_{\lambda(\mu)\lambda'(\mu')}}}{\rho U_\sigma^3 a^{*2}\hbar}\int_0^\infty dx\ \frac{x^3\left|f_{\lambda\lambda'}(x)\right|^2}{\frac{\left|T_{\lambda(\mu)}-T_{\lambda'(\mu')}\right|}{\hbar U_\sigma/a^*} \mp x};$$

$$\left[\text{upper sign for } T_{\lambda(\mu)} > T_{\lambda'(\mu')}\right.$$
$$\left.\text{lower sign for } T_{\lambda(\mu)} < T_{\lambda'(\mu')}\right].$$

The temperature-dependent part of the shift, however, involves electronic states that are separated by a non-zero energy difference. In this case , $\Delta_{\lambda\lambda'}$ of (3.8) becomes

(3.58)

$$\Delta_{\lambda(\mu)\lambda'(\mu')} = \sum_{\vec{q}\sigma} \frac{x^2\left|V_{\lambda(\mu)\lambda'(\mu')\vec{q}\sigma}\right|^2}{e^{\beta\hbar\omega_{\vec{q}\sigma}}-1}\left\{\frac{1}{T_{\lambda(\mu)}-T_{\lambda'(\mu')}-\hbar\omega_{\vec{q}\sigma}} + \frac{1}{T_{\lambda(\mu)}-T_{\lambda'(\mu')}+\hbar\omega_{\vec{q}\sigma}}\right\}$$

$$= \pm \sum_\sigma \frac{1}{4\pi^2} \left(\frac{\hbar U_\sigma}{a^*}\right) \frac{\overline{\{\}^2_{\lambda(\mu)\lambda'(\mu')}}}{\rho V_\sigma^3 a^{*2} \hbar} \int_0^\infty d\chi \; \frac{\chi^3 \left|f_{\chi\chi'}(\chi)\right|^2}{e^{\beta \frac{\hbar U_\sigma}{a^*}\chi} - 1}$$

$$\times \left\{ \frac{1}{\frac{\left|\overline{T}_{\lambda(\mu)} - \overline{T}_{\lambda'(\mu')}\right|}{\hbar U_\sigma / a^*} - \chi} + \frac{1}{\frac{\left|\overline{T}_{\lambda(\mu)} - \overline{T}_{\lambda'(\mu')}\right|}{\hbar U_\sigma / a^*} + \chi} \right\};$$

where the upper sign is used when $T_{\lambda(\mu)} > T_{\lambda'(\mu')}$, the lower sign when $T_{\lambda(\mu)} < T_{\lambda'(\mu')}$.

With the expressions given in (3.55)-(3.58), we are therefore ready to make a numerical estimation of the shift of the level $T_{\lambda(\mu)}$ due to a state $\lambda'(\mu')$. This will be done in the following section.

TABLE X : Table of $\overline{\left\{\ \right\}}^2_{(o)}$;

$$\left\{\ \right\}_{(o)} = \left\{\Xi_d\, \delta_{\sigma,1}\delta_{\mu\mu'} + \Xi_u\, \vec{e}_\sigma(\vec{q}).D^{(o)}_{\mu\mu'}.\vec{e}_1(\vec{q})\right\}$$

μ \ μ'	1	2	3	4	5	6
1	$\left(\Xi_d + \frac{\Xi_u}{3}\right)^2$ 0 0					
2	$\frac{2}{45}\Xi_u^2$ $\frac{1}{15}\Xi_u^2$ 0	$\left(\Xi_d^2 + \frac{2}{3}\Xi_u\Xi_d + \frac{2}{15}\Xi_u^2\right)$ $\frac{1}{30}\Xi_u^2$ 0				
3	$\frac{2}{45}\Xi_u^2$ $\frac{1}{90}\Xi_u^2$ $\frac{1}{18}\Xi_u^2$	$\frac{1}{45}\Xi_u^2$ $\frac{1}{180}\Xi_u^2$ $\frac{1}{36}\Xi_u^2$	$\left(\Xi_d^2 + \frac{2}{3}\Xi_u\Xi_d + \frac{2}{15}\Xi_u^2\right)$ $\frac{1}{30}\Xi_u^2$ 0			
4	◯	◯	◯	$\Xi_d^2 + \frac{2}{3}\Xi_u\Xi_d + \frac{\Xi_u^2}{5}$ $\frac{1}{20}\Xi_u^2$ $\frac{1}{12}\Xi_u^2$		
5	◯	◯	◯	◯	$\Xi_d^2 + \frac{2}{3}\Xi_u\Xi_d + \frac{1}{5}\Xi_u^2$ $\frac{1}{20}\Xi_u^2$ $\frac{1}{12}\Xi_u^2$	
6	◯	◯	◯	◯	◯	$\Xi_d^2 + \frac{2}{3}\Xi_u\Xi_d + \frac{1}{5}\Xi_u^2$ $\frac{2}{15}\Xi_u^2$ 0

TABLE XI : Table of $\overline{\{\}^2_{(j)}}$;

$$\{\}_{(j)} = \left\{ \Xi_d \, \delta_{j,1} \sum_j \alpha^{(j)}_\mu \alpha^{(j)}_{\mu'} \cos\theta_j + \Xi_u \, \vec{e}_\sigma(\vec{q}) . D^{(1)}_{\mu\mu'} . \vec{e}_1(\vec{q}) \right\}$$

μ \ μ'	1	2	3	4	5	6
1	◯					
2	◯	◯				
3	◯	◯	◯			
4	$\frac{1}{9}\left(\Xi_d^2 + \frac{6}{5}\Xi_u\Xi_d + \frac{3}{7}\Xi_u^2\right)$ $\frac{1}{126}\Xi_u^2$ $\frac{1}{90}\Xi_u^2$	$\frac{1}{18}\left(\Xi_d^2 + \frac{6}{5}\Xi_u\Xi_d + \frac{3}{7}\Xi_u^2\right)$ $\frac{1}{252}\Xi_u^2$ $\frac{1}{180}\Xi_u^2$	$\frac{1}{6}\left(\Xi_d^2 + \frac{6}{5}\Xi_u\Xi_d + \frac{3}{7}\Xi_u^2\right)$ $\frac{1}{84}\Xi_u^2$ $\frac{1}{60}\Xi_u^2$	◯		
5	$\frac{1}{9}\left(\Xi_d^2 + \frac{6}{5}\Xi_u\Xi_d + \frac{3}{7}\Xi_u^2\right)$ $\frac{1}{126}\Xi_u^2$ $\frac{1}{90}\Xi_u^2$	$\frac{1}{18}\left(\Xi_d^2 + \frac{6}{5}\Xi_u\Xi_d + \frac{3}{7}\Xi_u^2\right)$ $\frac{1}{252}\Xi_u^2$ $\frac{1}{180}\Xi_u^2$	$\frac{1}{6}\left(\Xi_d^2 + \frac{6}{5}\Xi_u\Xi_d + \frac{3}{7}\Xi_u^2\right)$ $\frac{1}{84}\Xi_u^2$ $\frac{1}{60}\Xi_u^2$	◯	◯	
6	$\frac{1}{9}\left(\Xi_d^2 + \frac{6}{5}\Xi_u\Xi_d + \frac{3}{7}\Xi_u^2\right)$ $\frac{2}{105}\Xi_u^2$ ◯	$\frac{2}{9}\left(\Xi_d^2 + \frac{6}{5}\Xi_u\Xi_d + \frac{3}{7}\Xi_u^2\right)$ $\frac{4}{105}\Xi_u^2$ ◯	◯	◯	◯	◯

(4) Numerical Results

For numerical calculation, we adopt the following set of data for phosphorus donors in silicon:

(3.59)

$$\rho = 2.33 \text{ gm/cm}^3$$

$$a^* = 20.0 \text{ Å}$$

$$v_\ell = 9.33 \times 10^5 \text{ cm/sec}^\ddagger = v_1$$

$$v_t = 5.37 \times 10^5 \text{ cm/sec}^\ddagger = v_2 = v_3$$

$$\Xi_u = 11 \text{ ev.}^\#$$

$$\Xi_d = 10 \text{ ev.}$$

$$E_{1s(A_1)} = -45.31 \text{ mev.}^{\S \dagger} \qquad E_{2s(A_1)} = -10.8 \text{ mev.}^{\S}$$

$$E_{1s(T_1)} = -33.69 \text{ mev.}^{\S} \qquad E_{2s(T_1)} = -8.4 \text{ mev.}^{\S}$$

$$E_{1s(E)} = -32.36 \text{ mev.}^{\S} \qquad E_{2s(E)} = -8.1 \text{ mev.}^{\S}$$

$$E_{2p_o} = -11.1 \text{ mev.}^{\S \dagger}$$

For calculations involving expressions like (3.35) and (3.36), the integrals can be evaluated exactly using

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‡ Hasegawa (1960).

Wilson and Feher (1961)

† Bichard and Giles (1962)

§ Aggarwal and Ramdas (1965)

§ Calculations by quantum defect method (Kohn and Luttinger, 1955)

tables of integrals[‡]. Integrals appearing in (3.57) and (3.58) are evaluated by graphical methods, a discussion of which is given in Appendix V.

We note also that the ground state energy $E_{1s(A_1)}$ is considerably less than the effective-mass value (-0.029 ev.). We therefore take into account this valley-orbit splitting, as it is called in literature, and redefine the effective Bohr radius for the ground state in the manner of Kohn (1957) by

$$(3.60) \qquad b^* = a^* \sqrt{E_{eff.}/E_{obs}} \, ,$$

where $E_{eff.} = -0.029$ ev., $E_{obs.} = -0.045$ ev., yielding a value of 16 Å for b^*. With this modification, the envelope function for the ground state is taken to be

$$(3.61) \qquad F_{1s(A_1)} = \frac{1}{(\pi b^{*3})^{1/2}} \, e^{-r/b^*} \, .$$

Some typical contributions to the shift of $1s(A_1)$ at $T=0°K$ is given in the following table:

TABLE XII : Typical contributions to $S_{1s(A_1),\chi'(\mu')}$, in units of ev.

$\chi'(\mu')$	longitudinal	transverse
1s(A₁)	$- 7.15 \times 10^{-4}$	0
1s(E)	$- 0.8 \times 10^{-5}$	$- 2.8 \times 10^{-5}$
1s(T₁)	0	0
2s(A₁)	$- 1.4 \times 10^{-5}$	0
2s(E)	$\sim 0.0 \times 10^{-5}$	$- 0.3 \times 10^{-5}$
2s(T₁)	0	0
2p₀(A₁)	0	0
2p₀(E)	0	0
2p₀(T₁)	$- 0.7 \times 10^{-5}$	$\sim 0.0 \times 10^{-5}$

Thus, the estimated shift for $1s(A_1)$ at $T = 0°K$ is 0.77 mev. with $\sim 90\%$ coming from the diagonal matrix element involving longitudinal phonons. The corresponding quantities for $1s(E)$ and $1s(T_1)$ are $- 0.42$ mev. and -0.48 mev. respectively. These shifts are $< 2\%$ of the respective activation energies.

The shift for the $2p_0$ is of even smaller magnitude. Take for instance $2p_0(6)$, we obtain for $S_{2p_0(6),2p_0(6)}$ the value of $- 0.01$ mev., with transverse phonons contributing $\sim 20\%$.

The temperature-dependent part of the shift, on the other hand, has contributions only from mixing of states with non-vanishing energy separation. Some typical contributions to the $1s(A_1)$-state at $T = 30°K$ and $60°K$ are shown in Table XIII.

TABLE XIII: Typical contributions to $\triangle_{1s(A_1),\chi(\mu')}$ at $T=30°K$ and $60°K$.

$\chi(\mu')$	T	longitudinal	transverse
1s(E)	30°K	-0.4×10^{-5} ev.	-3.1×10^{-5} ev.
	60°K	-1.7×10^{-5} ev.	-8.9×10^{-5} ev.
2s(A$_1$)	30°K	-0.3×10^{-5} ev.	0
	60°K	-1.3×10^{-5} ev.	0

The results of $\sum_{\chi(\mu')} \triangle_{\lambda(\mu),\chi(\mu')}$ for the various $\lambda(\mu)$ of interest are now listed in the following:

$\lambda(\mu)$	30°K	60°K
1s(A$_1$)	-0.038 mev.	-0.119 mev.
1s(E)	+0.013 mev.	+0.035 mev.
1s(T$_1$)	-0.004 mev.	-0.014 mev.
2p$_0$(A$_1$) 2p$_0$(E)	-0.008 mev.	-0.020 mev.
2p$_0$(T$_1$)	$\gtrsim$ -0.008 mev.	$\gtrsim$ -0.020 mev.

which can be represented schematically as in Fig.2.

Comparision with experiment is given in Table XIV.

Fig. 2. Schematic diagram for energy-level
shifts.

The spacings are not drawn to scale.
The arrow indicates the direction of shift as
temperature is increased from 0°K and the number
is the magnitude of shift in units of mev.

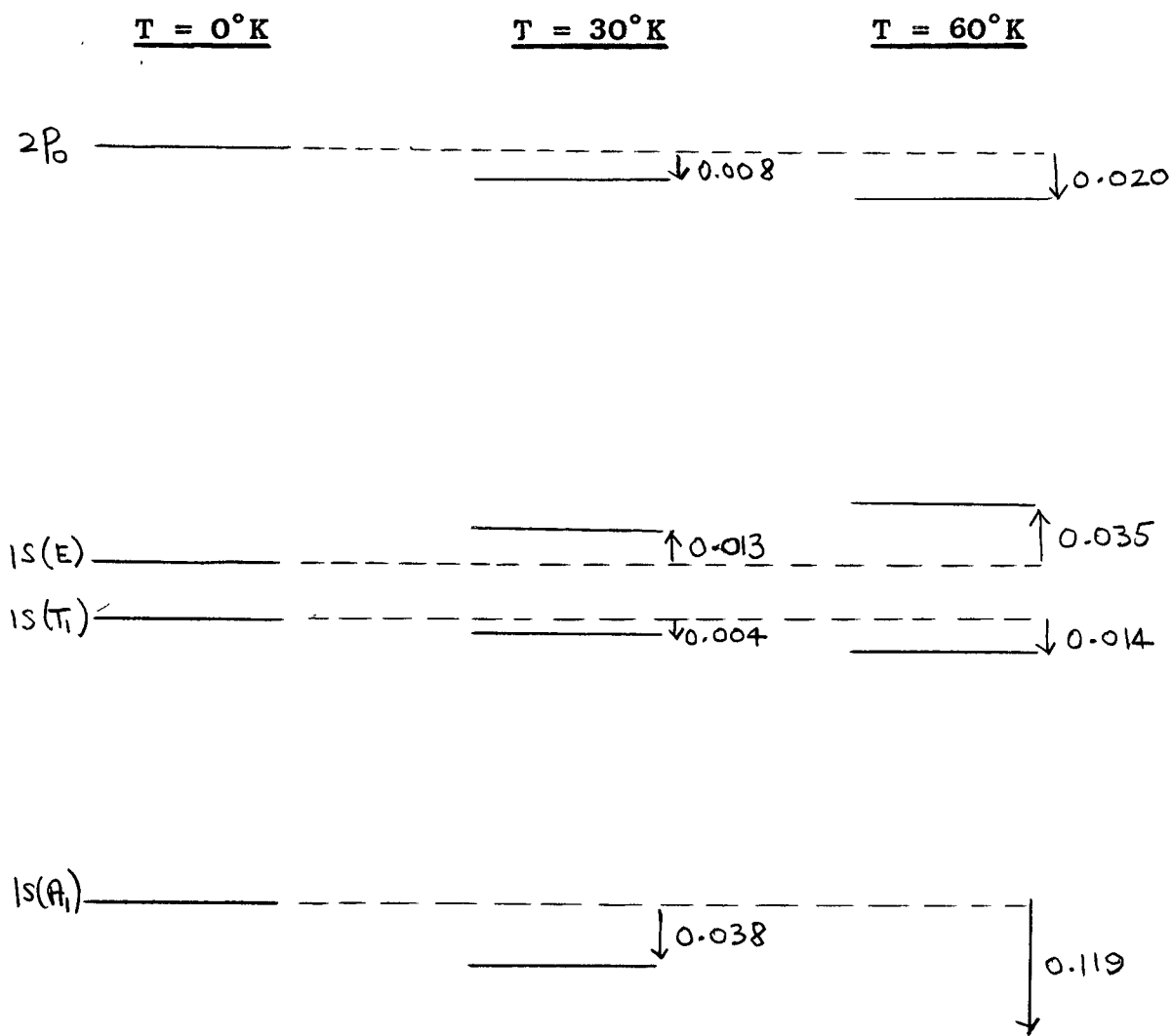| $T = 0°K$	$T = 30°K$	$T = 60°K$

$2P_0$ ———— $\downarrow 0.008$ $\downarrow 0.020$

$1S(E)$ ———— $\uparrow 0.013$ $\uparrow 0.035$

$1S(T_1)$ ———— $\downarrow 0.004$ $\downarrow 0.014$

$1S(A_1)$ ———— $\downarrow 0.038$ 0.119

TABLE XIV :Comparision with Experiment.
In units of mev.

1s()	THØRECTICAL		EXPERIMENTAL		
	Shift of 1s()→2p line at T rel. to shift at 0°K	Shift of 1s()→2p line at 60°K rel. to shift at 30°K	Transition energy 1s()→2p$_o$	Shift of 1s()→2p$_o$ line at T rel. to shift at 4.2°K	Shift of 1s()→2p$_o$ line at T$_u$ rel. to shift at T$_\ell$
1s(A₁)	0.03 (30°K) 0.10 (60°K)	+ 0.07		0.025±0.006 * (32.5°K) 0.102±0.025 * (60°K)	+ 0.08
1s(T₁)	-0.00(4) (30°K) -0.00(6) (60°K)	- 0.00(2)	22.44±0.04 § (30°K) 22.38±0.04 § (59°K)		- 0.06
1s(E)	-0.02 (30°K) -0.05(5) (60°K)	- 0.03(5)	21.11±0.04 § (30°K) 21.01±0.04 § (59°K)		- 0.10

* Bichard and white (1966)

§ Aggarwal and Ramdas (1965)

T_u= 60°K, T_ℓ =32.5°K for first entry;
T_u= 59°K, T_ℓ= 30°K for the other two entries.

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CHAPTER IV : SUMMARY AND DISCUSSIONS

The effect of the electron-phonon interaction on the electron distribution function for shallow impurity states has been discussed within the framework of the Green's Function method. The specific problem considered is one in which the set of localized states at any one impurity site cannot contain more than one electron. The formalism developed can be extended to treat other classes of problem. As an example, another interesting situation in semiconductors is one in which there is one bound state which contains possibly one or two electrons, but not less than one (Wilson, 1953). For no interaction, Wilson's result is obtained by using the projection operator $P_1 + P_2$, where P_2 projects onto the two-electron subspace, and then using one value of E_λ.

Our formalism applies also to holes in acceptor impurity states.

The problem remains to determine the chemical potential μ when one has a concentration N_d of impurities in a semiconductor. For this purpose, one has to take into account the detailed nature of the conduction band states and calculate also the electron distribution function for such states. Then, μ is determined from the relation $\sum_{\lambda s} \widetilde{n}_{\lambda s} + \sum_{\vec{k}s} \widetilde{n}_{\vec{k}s} = N_d$ (compare with eq.(2.61)).

In the limit that the damping can be neglected, one obtains for the electron distribution function an expression

similar to that of the interaction-free case, but with re-normalized energies (compare eqs. (2.30) and (2.62)). These renormalized energies are in general temperature-dependent.

A numerical calculation has been made to obtain the relative shift of these renormalized energies and the unperturbed energies for a few states in the case of phosphorus donors in silicon. The results can be summarized as follows.

The shift at zero temperature represents a correction to the unperturbed energy spectrum due to the zero-point vibrations of the lattice. This correction is small compared with the activation energy ($\lesssim 2\%$) and is essentially a negative quantity. The dominant contributions come from the state mixing with itself, involving primarily the longitudinal mode. The transverse modes are important in some mixing of different states, but then its magnitude is $\lesssim 10\%$ of the afore-mentioned contribution.

In contradistinction to the shift at $T = 0$, the temperature dependence of the shift is due entirely to mixing of states whose energy levels are separated by a definite amount. The numerical results show that the mixing between $1s(A_1)$ and $1s(E)$ states predominantly determine the temperature dependence in the shifts of the same two levels. Also, the mixing is most favorable for the exchange of transverse phonons. The $1s(T_1)$-states, on the other hand, do not mix with the $1s(A_1)$ nor with the $1s(E)$ through the electron-phonon interaction. Therefore, one would expect, as was borne

out by numerical calculations, that the temperature-dependent shift of $1s(T_1)$ would have a smaller magnitude; the shift comes mostly from mixing with the 2s and $2p_o$ states, so that a larger energy denominator is involved and the matrix element involves two different envelope functions.

Comparision of the theoretical results with experiment is not completely satisfactory. The shift of the $1s(A_1) \rightarrow 2p_o$ optical absorption line observed by Bichard and White (1966) agrees reasonably well with the relative shift of $1s(A_1)$ and $2p_o$ at $30°K$ and $60°K$. The same comparision between the excited 1s states and the $2p_o$ shows poor agreement with the $1s(E) \rightarrow 2p_o$, $1s(T_1) \rightarrow 2p_o$ transition lines of Aggarwal and Ramdas (1965). However, if one only considers the relative displacement of the two excited 1s levels from each other from $30°K$ to $60°K$, the theoretical value is 0.03 mev. as compared with the experimental value of 0.04 mev.. Also, the drifting apart of the two levels when the temperature is increased from $30°K$ to $60°K$ is consistent with the ordering of $1s(E)$ lying above $1s(T_1)$ in the energy scheme of Aggarwal and Ramdas.

In our calculations, we have taken into account only the mixing among 1s, 2s and $2p_o$ states. The number of all higher states are numerous and closely spaced so that their effect on $2p_o$ and 1s states cannot be simulated. All that can be said is that these higher states would tend to depress the states considered. It is reasonable to expect, however, that such an effect would be more strongly felt by $2p_o$ than

by 1s, since the latter is so much further away than $2p_o$ is from the higher states. If $2p_o$ were depressed by 0.06 mev. from $30°K$ to $60°K$ by these higher states, with no depression of 1s from them, then agreement with experiment would be obtained for both the $1s(E) \rightarrow 2p_o$ and $1s(T_1) \rightarrow 2p_o$ transitions.

As a concluding remark, we mention a few factors that might affect the numerical results. First is the lack of knowledge of the exact wave function for the ground state whose orbit is small. The effective Bohr radius appears in our calculation as a factor of $(1/a*)^3$, so that a certain percentage change in the value of a* would induce a tripled percentage change in the entire factor. Secondly, the exact positions of the 2s-states in the energy spectrum is not known. The values given in (3.59) are determined from the spectrum of the 1s-states by the quantum defect method (Kohn and Luttinger 1955). One would have liked to be able to extract this information from the half-width measurements of the spectral lines $1s \rightarrow 2p_o$. However, such measurements are at present not reliable due to instrumental broadening and dislocation (Bichard and White 1966).

APPENDIX I ‡

ORDER ESTIMATION OF EQUATION (2.34)

For an order estimation of eq. (2.34), it suffices to consider just the term

$$(A.I.1) \qquad \varkappa \sum_{\vec{q}} V_{\lambda \nu \vec{q} s} \langle\!\langle b_{\vec{q}} a_{\nu s} \mid A^+_{\lambda' s'} \rangle\!\rangle_E$$

since the other term is obviously of the same order. We write the equation of motion for $\langle\!\langle b_{\vec{q}} a_{\nu s} \mid A^+_{\lambda' s'} \rangle\!\rangle_E$ as

$$(A.I.2) \qquad (E - T_\nu - \omega_{\vec{q}}) \langle\!\langle b_{\vec{q}} a_{\nu s} \mid A^+_{\lambda' s'} \rangle\!\rangle_E = O(\varkappa) \cdot const.$$

$$+ \varkappa V^*_{\lambda \nu s} \langle\!\langle a_{\lambda s} \mid A^+_{\lambda' s'} \rangle\!\rangle_E + \ldots$$

It is only necessary to consider $\varkappa V^*_{\lambda \nu s} \langle\!\langle a_{\lambda s} \mid A^+_{\lambda' s'} \rangle\!\rangle_E$ since the other terms will not change the order of magnitude on the R.H.S. of (A.I.2) near the singularity of $\langle\!\langle a_{\lambda s} \mid A^+_{\lambda' s'} \rangle\!\rangle_E$.

Let us look at the region of E where

$$(A.I.3) \qquad \langle\!\langle a_{\lambda s} \mid A^+_{\lambda' s'} \rangle\!\rangle_E = O(\varkappa^{-g})$$

where g is assumed to be zero or positive. We now write

---

‡In this and the following appendix, the treatment follows closely that of Nishikawa and Barrie (1963).

(A.I.4)
$$\sum_{\vec{q}} = \sum_{\alpha \geqslant 0} \sum_{\vec{q}}^{\alpha}$$

where $\sum_{\vec{q}}'^{a}$ denotes summation of $\vec{q}$ over those values of $\vec{q}$ such that

(A.I.5)
$$(E - T_{\nu} - \omega_{\vec{q}}) = O(\varkappa^{\alpha}).$$

Therefore for the values of $\vec{q}$ such that (A.I.5) is satisfied, we have

(A.I.6)
$$\langle\langle b_{\vec{q}} a_{\nu s} | A_{\lambda s}^{+} \rangle\rangle_{E} = O(\varkappa^{1-g-a}).$$

On the other hand, the number of phonon states for which (A.I.5) is satisfied is of $O(\varkappa^{\alpha})$. Hence

(A.I.7)
$$\varkappa \sum_{\vec{q}}^{\alpha} V_{\lambda\nu\vec{q}s} \langle\langle b_{\vec{q}} a_{\nu s} | A_{\lambda s}^{+} \rangle\rangle_{E} = O(\varkappa^{1+a+(1-g-a)})$$
$$= O(\varkappa^{2}) \langle\langle a_{\lambda s} | A_{\lambda s}^{+} \rangle\rangle_{E}$$

a result that is independent of a. Then, as long as $\sum_{\alpha \geqslant 0}$ is convergent, which is true since the number of phonon states is finite, we obtain

(A.I.8)
$$\varkappa \sum_{\vec{q}} V_{\lambda\nu\vec{q}s} \langle\langle b_{\vec{q}} a_{\nu s} | A_{\lambda s}^{+} \rangle\rangle_{E} = O(\varkappa^{2}) \langle\langle a_{\lambda s} | A_{\lambda s}^{+} \rangle\rangle_{E}.$$

APPENDIX II

PROOF OF (2.42)

This appendix is divided into two parts. The first is concerned with an estimation in $\mathcal{N}$ whereas the second part is with an estimation in $\mathcal{K}$.

(i) Order Estimation in $\mathcal{N}$.

We are required to prove

(A.II.1)
$$\langle\langle b_{\vec{q}}^{+} b_{\vec{q}'} a_{\mu s} \mid A_{\lambda s'}^{+} \rangle\rangle_{E} = \delta_{\vec{q}\vec{q}'} \, \mathcal{V}_{\vec{q}} \langle\langle a_{\mu s} \mid A_{\lambda s'}^{+} \rangle\rangle_{E} + O\left(\frac{1}{\mathcal{N}}\right)$$

(A.II.2)
$$\langle\langle b_{\vec{q}} b_{\vec{q}'} a_{\mu s} \mid A_{\lambda s'}^{+} \rangle\rangle_{E} = O\left(\frac{1}{\mathcal{N}}\right)$$

(A.II.3)
$$\langle\langle b_{\vec{q}}^{+} b_{\vec{q}'}^{+} a_{\mu s} \mid A_{\lambda s'}^{+} \rangle\rangle_{E} = O\left(\frac{1}{\mathcal{N}}\right)$$

Using the relation[*]

(A.II.4)
$$\langle\langle A \mid B \rangle\rangle_{E} = \frac{1}{4\pi^{2}} \int_{-\infty}^{\infty} d\omega \, \frac{e^{\beta\omega} - 1}{E - \omega \pm i\eta} \int_{-\infty}^{\infty} dt \, \langle BA(t) \rangle e^{iEt},$$

the problem is reduced to an order estimation in $\mathcal{N}$ of the correlation functions; namely

(A.II.5)
$$\langle e^{-it\mathcal{H}} A_{\lambda s'}^{+} e^{it\mathcal{H}} b_{\vec{q}}^{+} b_{\vec{q}'} a_{\mu s} \rangle = \delta_{\vec{q}\vec{q}'} \, \mathcal{V}_{\vec{q}} \langle e^{-it\mathcal{H}} A_{\lambda s'}^{+} e^{it\mathcal{H}} a_{\mu s} \rangle$$
$$+ O\left(\frac{1}{\mathcal{N}}\right)$$

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[*] See Zubarov (1960)

(A.II.6) $\qquad \langle e^{-it\mathcal{H}} A^+_{X's'} e^{it\mathcal{H}} b_{\vec{q}} b_{\vec{q}'} a_{\mu s} \rangle = O(\frac{1}{\sqrt{N}}),$

(A.II.7) $\qquad \langle e^{-it\mathcal{H}} A^+_{X's'} e^{it\mathcal{H}} b^+_{\vec{q}} b^+_{\vec{q}'} a_{\mu s} \rangle = O(\frac{1}{\sqrt{N}}).$

The procedure is here demonstrated by considering only (A.II.5). The others can be proved in the same manner. Let us then write

$\qquad$ L.H.S. of (A.II.5)

(A.II.8)
$$= Q^{-1} Tr \left\{ e^{-\beta\mathcal{H}} e^{-it\mathcal{H}} A^+_{X's'} e^{it\mathcal{H}} b^+_{\vec{q}} b_{\vec{q}'} a_{\mu s} \right\}$$

$$= \frac{Q_0}{Q} e^{-it\overline{T}_{X'}} \left\{ Q_0^{-1} Tr [e^{-\beta\mathcal{H}_0} F] \right\}$$

where $\quad Q = Tr \left\{ e^{-\beta\mathcal{H}} \right\}$, $Q_0 = Tr \left\{ e^{-\beta\mathcal{H}_0} \right\} \quad$ and

(A.II.9) $\quad F = \left\{ e^{\beta\mathcal{H}_0} e^{-\beta\mathcal{H}} e^{-it\mathcal{H}} e^{it\mathcal{H}_0} A^+_{X's'} e^{-it\mathcal{H}_0} e^{it\mathcal{H}} b^+_{\vec{q}} b_{\vec{q}'} a_{\mu s} \right\}.$

If we use the formula

(A.II.10)
$$e^{\beta\mathcal{H}_0} e^{-\beta\mathcal{H}} = \sum_{n=0}^{\infty} (-1)^n \int_{\beta > u_1 > \cdots > u_n > 0} du_1 \cdots du_n \, H_{ep}(u_1) \cdots H_{ep}(u_n)$$

$$e^{-it\mathcal{H}_0} e^{it\mathcal{H}} = \sum_{n=0}^{\infty} i^n \int_{t > u_1 > \cdots > u_n > 0} du_1 \cdots du_n \, H_{ep}(-iu_1) \cdots H_{ep}(-iu_n)$$

$$e^{-it\mathcal{H}} e^{it\mathcal{H}_0} = \sum_{n=0}^{\infty} (-i)^n \int_{t > u_1 > \cdots > u_n > 0} du_1 \cdots du_n \, H_{ep}(-iu_n) \cdots H_{ep}(-iu_1)$$

with $H_{ep}(u) = e^{u\mathcal{H}_0} H_{ep} e^{-u\mathcal{H}_0}$, then F can be written as a

sum of products of creation and annihilation operators. This enables us to use the contraction theorem of Bloch and Dominicis (1958) on the expression in $\{\ \}$-bracket in (A.II.8). We now distinguish two groups of terms in the summation of all possible contractions taken among the creation and annihilation operators. We have on the one hand terms that contain a contraction of $b_{\vec{q}}^{+} b_{\vec{q}'}$ appearing explicitly in F. The sum of these terms is

$$(A.II.11) \qquad \overline{b_{\vec{q}}^{+} b_{\vec{q}'}}\ Q_0^{-1}\ \text{Tr}\left\{ e^{-\beta \mathcal{H}}\ e^{-it\mathcal{H}}\ e^{it\mathcal{H}_0}\ A_{\chi's}^{+}\ e^{-it\mathcal{H}_0}\ e^{it\mathcal{H}}\ a_{\mu s} \right\},$$

where $\overline{b_{\vec{q}}^{+} b_{\vec{q}'}}$ is defined as the contraction of $b_{\vec{q}}^{+}$ with $b_{\vec{q}}$ given by

$$(A.II.12) \qquad \overline{b_{\vec{q}}^{+} b_{\vec{q}'}} = Q_0^{-1}\ \text{Tr}\left\{ e^{-\beta \mathcal{H}_0}\ b_{\vec{q}}^{+} b_{\vec{q}'} \right\} = \delta_{\vec{q}\vec{q}'}\ \nu_{\vec{q}}.$$

On the other hand, we have terms in which each of the phonon operators appearing explicitly in F is contracted with one phonon operator in the expansion of the exponantials. This will introduce a factor of the form $\varkappa^2 V_{\alpha\alpha\vec{q}} V_{\beta\beta\vec{q}'}^{*}$ which is of order $1/\mathcal{N}$. Combining this result and (A.II.11), we have

$$(A.II.13) \qquad Q_0^{-1}\ \text{Tr}\left[e^{-\beta \mathcal{H}_0} F \right]$$
$$= \delta_{\vec{q}\vec{q}'}\ \nu_{\vec{q}}\ Q_0^{-1}\ \text{Tr}\left\{ e^{-\beta \mathcal{H}}\ e^{-it\mathcal{H}}\ e^{it\mathcal{H}_0}\ A_{\chi's}^{+}\ e^{-it\mathcal{H}_0}\ e^{it\mathcal{H}}\ a_{\mu s} \right\} + O(\tfrac{1}{\mathcal{N}}),$$

and so from (A.II.8),

(A.II.14)   L.H.S. of (A.II.5) $= \delta_{qq'} \, \nu_{\vec{q}}^{-1} \, Q^{-1} \, T_r \left\{ e^{-\beta \mathcal{H}} e^{-it\mathcal{H}} A_{\chi's'}^{+} e^{it\mathcal{H}} a_{\mu s} \right\}$

$$+ \, O\left(\frac{1}{\mathcal{N}}\right)$$

$$= \text{R.H.S. of (A.II.5)}$$

(ii) <u>Order Estimation in $\mathcal{K}$</u>.

From the discussion of (i), it follows that

(A.II.15) $\left\langle e^{-it\mathcal{H}} A_{\chi's'}^{+} e^{it\mathcal{H}} b_{\vec{q}}^{+} b_{\vec{q}'} a_{\mu s} \right\rangle = O(\mathcal{K}^2)$ for $\vec{q} \neq \vec{q}'$

since each $V_{\lambda\lambda'\vec{q}}$ or $V_{\lambda\lambda'\vec{q}}^{*}$ is accompanied by a factor $\mathcal{K}$.
Therefore, for values of E that are not near the singularities
of the Green's Function $\left\langle\!\left\langle b_{\vec{q}}^{+} b_{\vec{q}'} a_{\mu s} \,\middle|\, A_{\chi's'}^{+} \right\rangle\!\right\rangle_{E}$, we have

(A.II.16) $\left\langle\!\left\langle b_{\vec{q}}^{+} b_{\vec{q}'} a_{\mu s} \,\middle|\, A_{\chi's'}^{+} \right\rangle\!\right\rangle_{E} = O(\mathcal{K}^2)$ $(\vec{q} \neq \vec{q}')$.

Near the singularities, the situation is different.
We proceed by writing down the equation of motion for the
Green's Function, viz.

$$(E - T_\mu - \omega_{\vec{q}'} + \omega_{\vec{q}}) \left\langle\!\left\langle b_{\vec{q}}^{+} b_{\vec{q}'} a_{\mu s} \,\middle|\, A_{\chi's'}^{+} \right\rangle\!\right\rangle_{E} = \frac{1}{2\pi} \left\langle \left[b_{\vec{q}}^{+} b_{\vec{q}'} a_{\mu s}, A_{\chi's'}^{+} \right]_{+} \right\rangle$$

$$- \mathcal{K} \sum_{\nu} \left\{ V_{\mu\nu\vec{q}s} \left\langle\!\left\langle b_{\vec{q}'} a_{\nu s} \,\middle|\, A_{\chi's'}^{+} \right\rangle\!\right\rangle_{E} - V_{\nu\mu\vec{q}'s}^{*} \left\langle\!\left\langle b_{\vec{q}}^{+} a_{\nu s} \,\middle|\, A_{\chi's'}^{+} \right\rangle\!\right\rangle_{E} \right\}$$

(A.II.17)

$$+ \mathcal{K} \sum_{\substack{\nu \\ \vec{3}}} \left\{ V_{\mu\nu\vec{3}s} \left\langle\!\left\langle b_{\vec{3}}^{+} b_{\vec{q}}^{+} b_{\vec{q}'} a_{\nu s} \,\middle|\, A_{\chi's'}^{+} \right\rangle\!\right\rangle_{E} + V_{\nu\mu\vec{3}s}^{*} \left\langle\!\left\langle b_{\vec{3}}^{+} b_{\vec{q}}^{+} b_{\vec{q}'} a_{\nu s} \,\middle|\, A_{\chi's'}^{+} \right\rangle\!\right\rangle_{E} \right\}.$$

The possible singularities of $\langle\langle b_{\vec{q}}^{\dagger} b_{\vec{q}'} a_{\mu s} | A_{\chi s'}^{+} \rangle\rangle_{E}$ occur at $E = T_{\mu} - \omega_{\vec{q}'} + \omega_{\vec{q}}$ and at the singularities of the Green's Functions on the R.H.S. of (A.II.17). The first singularity is obviously $\vec{q}$- and $\vec{q}'$-dependent so that it can be ignored as it becomes unimportant after summing over $\vec{q}$ and $\vec{q}'$. To find the singularities of the Green's Functions on the R.H.S. of (A.II.17), we have to write down their equations of motion. For $\langle\langle b_{\vec{q}'} a_{\nu s} | A_{\chi s'}^{+} \rangle\rangle_{E}$ and $\langle\langle b_{\vec{q}}^{+} a_{\nu s} | A_{\chi s'}^{+} \rangle\rangle_{E}$, the equations are given by (2.35) and (2.36). We note that the singularities of these Green's Functions that are $\vec{q}$- and $\vec{q}'$-independent occur at the same values of E as those of $\langle\langle a_{\mu's} | A_{\chi''s'}^{+} \rangle\rangle_{E}^{\ddagger}$. Out of these singularities, the one that contributes to the lowest order in $\varkappa$ is that of $\langle\langle a_{\chi's'} | A_{\chi''s'}^{+} \rangle\rangle_{E}$. Therefore, $\langle\langle b_{\vec{q}'} a_{\nu s} | A_{\chi s'}^{+} \rangle\rangle_{E}$ and $\langle\langle b_{\vec{q}}^{+} a_{\nu s} | A_{\chi s'}^{+} \rangle\rangle_{E}$ are of order $\varkappa \langle\langle a_{\chi's'} | A_{\chi''s'}^{+} \rangle\rangle_{E}$ so that the first term on the R.H.S. of (A.II.17) is of order $\varkappa^2 \langle\langle a_{\chi's'} | A_{\chi''s'}^{+} \rangle\rangle_{E}$. The same is true for terms with $\vec{\zeta} = \vec{q}$ or $\vec{q}'$ in the second sum. The other terms can be shown to be of order $\varkappa^2 \langle\langle a_{\chi's'} | A_{\chi''s'}^{+} \rangle\rangle_{E}$ by an order estimation similar to that used in Appendix I.

Thus, we have shown that $\langle\langle b_{\vec{q}}^{\dagger} b_{\vec{q}'} a_{\mu s} | A_{\chi s'}^{+} \rangle\rangle_{E}$ is of order $\varkappa^2 \langle\langle a_{\chi's'} | A_{\chi''s'}^{+} \rangle\rangle_{E}$ near the singularity of $\langle\langle a_{\chi's'} | A_{\chi''s'}^{+} \rangle\rangle_{E}$ and is of higher order near other singularities.

$\ddagger$ Since $\langle\langle a_{\nu s} a_{\mu \sigma}^{\dagger} a_{\mu'\sigma'} | A_{\chi's'}^{+} \rangle\rangle_{E} = \delta_{\nu\mu} \delta_{s\sigma} \langle\langle a_{\mu's'} | A_{\chi's'}^{\dagger} \rangle\rangle_{E}$.

APPENDIX III

EXPLICIT EXPRESSIONS FOR

$$\frac{\langle b_{\vec{q}} A_{\lambda s}^{\dagger} a_{\nu s}\rangle}{\langle A_{\lambda s}^{\dagger} a_{\lambda s}\rangle + \frac{\langle P_0\rangle}{\langle P\rangle}} \quad \text{AND} \quad \frac{\langle b_{\vec{q}}^{\dagger} A_{\lambda s}^{\dagger} a_{\mu s}\rangle}{\langle A_{\lambda s}^{\dagger} a_{\lambda s}\rangle + \frac{\langle P_0\rangle}{\langle P\rangle}}.$$

Let us just look at the first thermal average in detail; the treatment for the other follows in exactly the same manner.

From (2.44) and (2.49), we obtain

$$(A.III.1) \quad \langle\langle b_{\vec{q}} a_{\nu s}| A_{\lambda s}^{\dagger}\rangle\rangle_E = \frac{1}{2\pi}\left\{ \frac{\langle b_{\vec{q}} A_{\lambda s}^{\dagger} a_{\nu s}\rangle}{E - T_{\nu} - w_{\vec{q}}} + \frac{\kappa(1 + \nu_{\vec{q}}) V_{\lambda\nu\vec{q}s}^{*}}{E - T_{\nu} - w_{\vec{q}}} \frac{\langle A_{\lambda s}^{\dagger} a_{\lambda s}\rangle + \frac{\langle P_0\rangle}{\langle P\rangle}}{E - T_{\lambda} - \kappa^2 M_{\lambda s}(E)} \right\}.$$

Also, from (2.23) by choosing $A = b_{\vec{q}} a_{\nu s}$, $B = A_{\lambda s}^{+}$ and $\gamma = -1$, we have

$$(A.III.2) \quad \langle A_{\lambda s}^{\dagger} b_{\vec{q}} a_{\nu s}\rangle = i \int_{-\infty}^{\infty} d\omega \lim_{\eta \to 0^+} \frac{\left\{\langle\langle b_{\vec{q}} a_{\nu s}| A_{\lambda s}^{\dagger}\rangle\rangle_{\omega + i\eta} - \langle\langle b_{\vec{q}} a_{\nu s}| A_{\lambda s}^{\dagger}\rangle\rangle_{\omega - i\eta}\right\}}{e^{\beta\omega} + 1}.$$

Since we are interested in the singularity of $\langle\langle b_{\vec{q}} a_{\nu s}| A_{\lambda s}^{+}\rangle\rangle_E$, we can ignore $\kappa^2 M_{\lambda s}(E)$ in (A.III.1). Then, the discontinuity of $\langle\langle b_{\vec{q}} a_{\nu s}| A_{\lambda s}^{+}\rangle\rangle_E$ across the real axis is given by

$$(A.III.3)$$
$$\langle\langle b_{\vec{q}} a_{\nu s}| A_{\lambda s}^{\dagger}\rangle\rangle_{\omega + i\eta} - \langle\langle b_{\vec{q}} a_{\nu s}| A_{\lambda s}^{\dagger}\rangle\rangle_{\omega - i\eta}$$
$$= \frac{1}{2\pi}\left\{ \langle b_{\vec{q}} A_{\lambda s}^{\dagger} a_{\nu s}\rangle \delta(\omega - T_{\nu} - w_{\vec{q}}) + \frac{\kappa(1 + \nu_{\vec{q}}) V_{\lambda\nu\vec{q}s}^{*}(\langle A_{\lambda s}^{\dagger} a_{\lambda s}\rangle + \frac{\langle P_0\rangle}{\langle P\rangle})}{(T_{\lambda} - T_{\nu} - w_{\vec{q}})} \right.$$
$$\left. \times \left[\delta(\omega - T_{\lambda}) - \delta(\omega - T_{\nu} - w_{\vec{q}}) \right] \right\}.$$

Substituting (A.III.3) into (A.III.2), we get

(A.III.4) $\quad \langle A^{\dagger}_{\lambda s} b_{\vec{q}} a_{\nu s} \rangle = \dfrac{\langle A^{\dagger}_{\lambda s} b_{\vec{q}} a_{\nu s} \rangle}{e^{\beta(T_{\nu}+\omega_{\vec{q}})}+1}$

$\quad + \dfrac{\varkappa \langle 1+\nu_{\vec{q}} \rangle V^{*}_{\lambda \nu \vec{q} s} \left(\langle A^{\dagger}_{\lambda s} a_{\nu s} \rangle + \frac{\langle P_0 \rangle}{\langle P \rangle} \right)}{(T_{\lambda}-T_{\nu}-\omega_{\vec{q}})} \left[\dfrac{1}{e^{\beta T_{\lambda}}+1} - \dfrac{1}{e^{\beta(T_{\nu}+\omega_{\vec{q}})}+1} \right]$.

After rearranging, (A.III.4) becomes

(A.III.5) $\quad \langle A^{\dagger}_{\lambda s} b_{\vec{q}} a_{\nu s} \rangle = \varkappa \dfrac{(1+\nu_{\vec{q}}) V^{*}_{\lambda \nu \vec{q} s}}{(T_{\lambda}-T_{\nu}-\omega_{\vec{q}})} \dfrac{\left(\langle A^{\dagger}_{\lambda s} a_{\nu s} \rangle + \frac{\langle P_0 \rangle}{\langle P \rangle} \right)}{e^{\beta T_{\lambda}}+1} \left(1 - e^{\beta(T_{\lambda}-T_{\nu}-\omega_{\vec{q}})} \right)$

so that

(A.III.6) $\quad \dfrac{\langle A^{\dagger}_{\lambda s} b_{\vec{q}} a_{\nu s} \rangle}{\langle A^{\dagger}_{\lambda s} a_{\nu s} \rangle + \frac{\langle P_0 \rangle}{\langle P \rangle}} = \varkappa \dfrac{(1+\nu_{\vec{q}}) V^{*}_{\lambda \nu \vec{q} s}}{(T_{\lambda}-T_{\nu}-\omega_{\vec{q}})} \dfrac{1 - e^{\beta(T_{\lambda}-T_{\nu}-\omega_{\vec{q}})}}{e^{\beta T_{\lambda}}+1}$.

By the same procedure, it can be shown that

(A.III.7) $\quad \dfrac{\langle A^{\dagger}_{\lambda s} b^{\dagger}_{\vec{q}} a_{\nu s} \rangle}{\langle A^{\dagger}_{\lambda s} a_{\nu s} \rangle + \frac{\langle P_0 \rangle}{\langle P \rangle}} = \dfrac{\varkappa \nu_{\vec{q}} V_{\nu \lambda \vec{q} s}}{(T_{\lambda}-T_{\nu}+\omega_{\vec{q}})} \dfrac{1 - e^{\beta(T_{\lambda}-T_{\nu}+\omega_{\vec{q}})}}{e^{\beta T_{\lambda}}+1}$.

One also arrives at the same results by using the expansion in (A.II.10).

APPENDIX IV

SUM RULE

It is the purpose of this appendix to prove the following sum rule:

$$(A.IV.1) \quad i \int_{-\infty}^{\infty} d\omega \lim_{\eta \to 0^+} \left\{ \langle\langle a_{\lambda s} | A^{\dagger}_{\lambda s} \rangle\rangle_{\omega+i\eta} - \langle\langle a_{\lambda s} | A^{\dagger}_{\lambda s} \rangle\rangle_{\omega-i\eta} \right\} = \tilde{n}_{\lambda s} + \frac{\langle P_0 \rangle}{\langle P \rangle}$$

It is in fact just as easy to work in the general case for any two operators A and B, and then deduce (A.IV.1) as a special case.

We start with the relation[‡]

$$(A.IV.2) \quad \langle B(0) A(t) \rangle = i \int_{-\infty}^{\infty} d\omega \; e^{-i\omega t} \frac{\lim_{\eta \to 0^+} \left\{ \langle\langle A|B \rangle\rangle_{\omega+i\eta} - \langle\langle A|B \rangle\rangle_{\omega-i\eta} \right\}}{e^{\beta\omega} - \gamma}$$

with $\gamma = -1$, if A and B are electron operators;

$\gamma = +1$, if A and B are phonon operators.

Since the trace is invariant under cyclic permutation of operators, it follows that

$$(A.IV.3) \quad \langle A(t) B(0) \rangle = \langle B(0) A(t+i\beta) \rangle$$

$$= i \int_{-\infty}^{\infty} d\omega \; e^{\beta\omega} e^{-i\omega t} \frac{\lim_{\eta \to 0^+} \left\{ \langle\langle A|B \rangle\rangle_{\omega+i\eta} - \langle\langle A|B \rangle\rangle_{\omega-i\eta} \right\}}{e^{\beta\omega} - \gamma}$$

[‡] See Zubarov (196o); eq.(2.23) is obtained from (A.IV.2) by setting t = 0.

Combining (A.IV.2) and (A.IV.3), we see that

(A.IV.4)
$$\langle A(t) B(0) \rangle - \gamma \langle B(0) A(t) \rangle$$

$$= i \int_{-\infty}^{\infty} d\omega \, e^{-i\omega t} \lim_{\eta \to 0^+} \left\{ \langle\!\langle A|B \rangle\!\rangle_{\omega+i\eta} - \langle\!\langle A|B \rangle\!\rangle_{\omega-i\eta} \right\}.$$

Putting t = 0 and rearranging, the sum rule is then given by

(A.IV.5)
$$i \int_{-\infty}^{\infty} d\omega \lim_{\eta \to 0^+} \left\{ \langle\!\langle A|B \rangle\!\rangle_{\omega+i\eta} - \langle\!\langle A|B \rangle\!\rangle_{\omega-i\eta} \right\} = \langle [A,B]_\gamma \rangle.$$

In particular, if we choose $A = a_{\lambda s}$, $B = A_{\lambda s}^+$, $\gamma = +1$, we
arrive at (A.IV.1).

As a final remark, we mention that in the absence
of the projection operator, the R.H.S. of (A.IV.1) would
have been unity.

APPENDIX V

DISCUSSION ON THE METHOD OF CALCULATION

We present in this appendix a brief discussion on the method of numerical integration used.

The integrals that we were concerned with are of the form

(A.V.1) $$I = I^{(+)} + I^{(-)}$$

with

(A.V.2) $$I^{(\pm)} = \int_0^\infty d\chi \, \frac{F(\chi)}{\xi \pm \chi}$$

where

(A.V.3) $$F(\chi) \longrightarrow \begin{cases} |f_{\lambda\lambda'}(\chi)|^2 & , \quad T = 0 \\[2ex] \dfrac{|f_{\lambda\lambda'}(\chi)|^2}{\beta e^{\frac{\hbar\sqrt{\sigma}}{\alpha^*}\chi} - 1} & , \quad T \neq 0 \end{cases}$$

(A.V.4) $$\xi \longrightarrow \frac{|\Delta E_{\lambda\lambda'}|}{\hbar\sqrt{\sigma}/\alpha^*} \quad ; \quad |\Delta E_{\lambda\lambda'}| = |T_\lambda - T_{\lambda'}|.$$

The typical plot of $F(\chi)$ is given in Fig.3. The functions $\dfrac{1}{\xi \pm \chi}$ are plotted in Fig.4 for an arbitrary value of ξ.
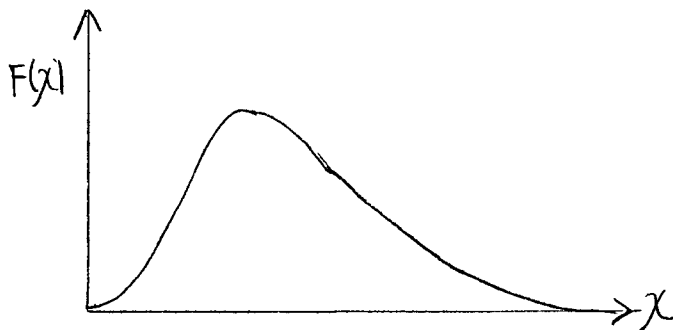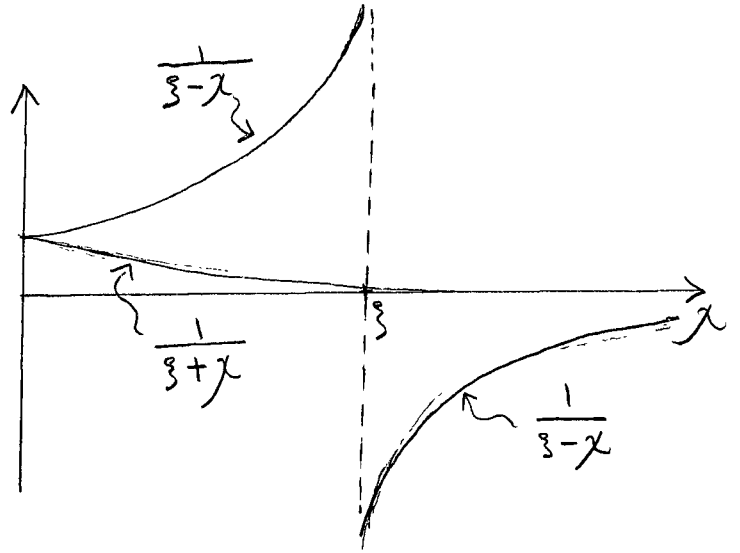

Fig. 3.

Typical plot of $F(\chi)$.

Fig. 4.

Plot of $\dfrac{1}{\xi \pm \chi}$.

Since $\dfrac{1}{\xi + \chi}$ is a well-behaved function, there is no problem in carrying out the numerical integration of $I^{(+)}$. As for $\dfrac{1}{\xi - \chi}$, on the other hand, the function behaves critically on either side of ξ . If ξ is large enough (i.e., far from where $F(\chi)$ is appreciable), we again encounter no difficulty in evaluating $I^{(-)}$. Otherwise, the asymtotic behaviour of $\dfrac{1}{\xi - \chi}$ may become important.

Let us consider in particular the case $\lambda \to 2s(T_1)$, $\lambda' \to 2p_0$. The plots of the corresponding $F(\chi)$ and $F(\chi)/(\xi - \chi)$ are given in Fig.5. We see from these plots that the pronounced nature of $\dfrac{1}{\xi - \chi}$ appears only in a narrow region of χ and that the area under these portions of the curve is indeed small compared with the rest. It is expected also that whatever error is introduced into the area for $\chi < \xi$ should be partially cancelled by that for $\chi > \xi$.

For the impurity states considered in the main text, the variation of $F(\chi)$ and the placement of energy levels are such that the above is already and extreme situa-

tion in that the value of ζ is closest to the dominant regions of $F(\chi)$. Therefore, other numerical integrated results are at least as good as the above example.

However, since there is no experimental evidence as to the positions of the 2s-states, it is worthwhile to consider the situation in which ζ is even closer or perhaps within the dominant regions of $F(\chi)$. The integrand may therefore look like the following:
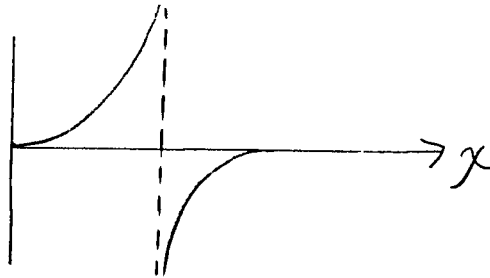
When this happens, the straight-forward numerical integration may give very poor accuracy, since we have here the difference of two large areas. To improve on the accuracy, one can proceed as follows:

(i) Write the Cauchy principal value in the representation

$$\wp\left(\frac{1}{\zeta-\chi}\right) = \lim_{\eta\to 0^+} \frac{(\zeta-\chi)}{(\zeta-\chi)^2 + \eta^2}$$

so that

$$I^{(-)} = \lim_{\eta\to 0^+} \int_0^\infty d\chi \, F(\chi) \frac{(\zeta-\chi)}{(\zeta-\chi)^2 + \eta^2} = \lim_{\eta\to 0^+} I_\eta^{(-)}$$

(ii) Carry out the numerical integration of $I_\eta^{(-)}$ for some small values of η.

(iii) Plot the values of $I_\eta^{(-)}$ as a function of η. Then, the value of $I^{(-)}$ is obtained by extrapolating $I_\eta^{(-)}$ to $\eta=0$.
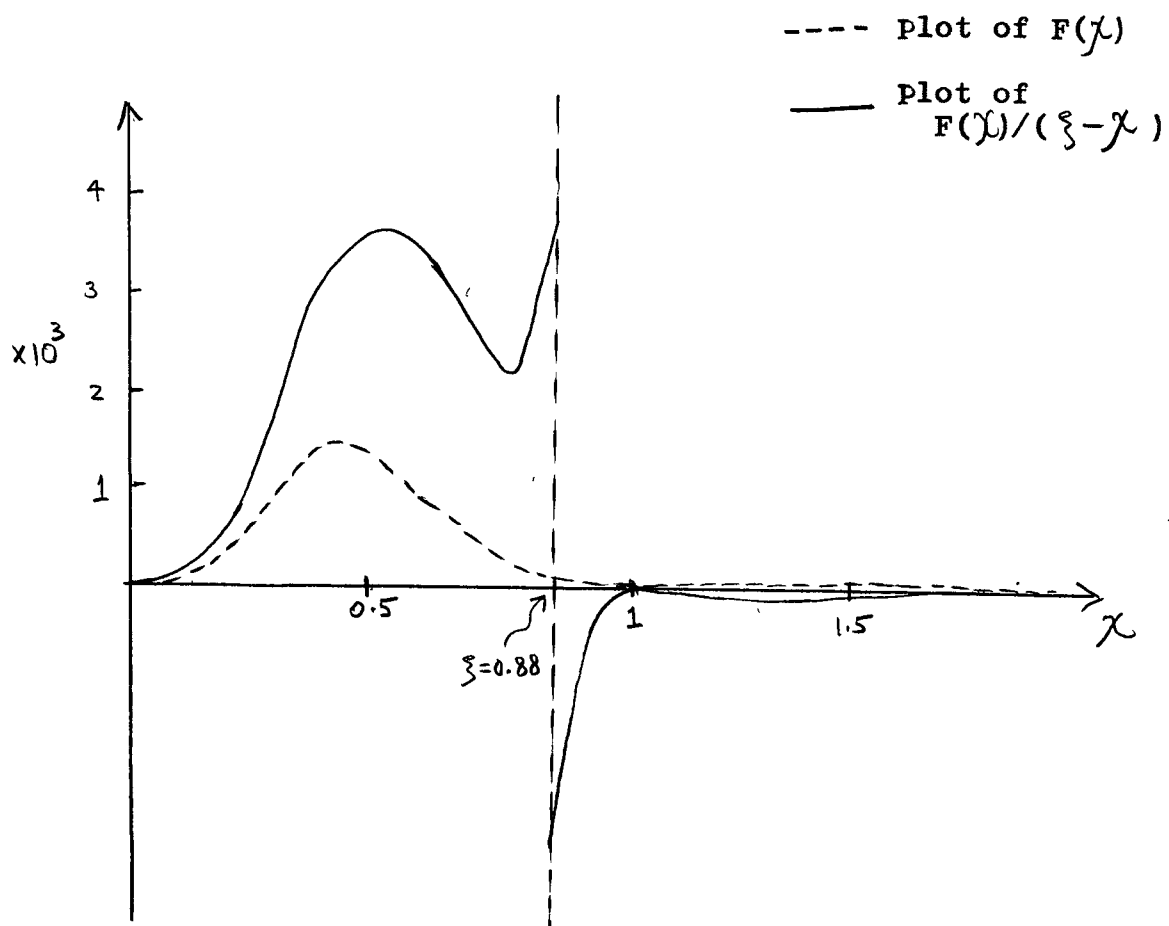
Fig. 5.

Plots of $F(\chi)$ and $F(\chi)/(\xi-\chi)$.

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