A THEORETICAL INVESTIGATION OF OPTICAL ABSORPTION

BY DONOR IMPURITIES IN SILICON

by

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B.Sc., The University of British Columbia, 1960.

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF ARTS

in the Department

of

PHYSICS

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

September, 1961.

ABSTRACT

An investigation has been made into the possibility of observing optical transitions (in the 100-micron region) between the ground state of a donor impurity in silicon and the remaining five states of the $\{1s\}$ set introduced by Kohn and Luttinger. While such transitions are forbidden in the usual effective mass approximation, it is found that application of corrections to the effective-mass wave functions leads to an enhanced transition probability.

Under the assumption of a simple cubic lattice of impurities, the calculated absorption coefficient is of the order of 10 cm^{-1} at an impurity concentration of 1 x 10^{18} cm^{-3}, and falls off exponentially with decreasing impurity concentration. An upper limit is placed on the region in which the transition should be observable by the broadening of the 2s-2p impurity band. It is estimated that for concentrations greater than 5 x 10^{18} cm^{-3} the transition of interest will be obscured.

The calculated values of the absorption coefficient are probably only accurate to within one, or even two, orders of magnitude, because of the approximations involved. However, there would appear to be no firm theoretical reason why the $1s^{(0)} \rightarrow 1s^{(5)}$ transition should not be observed.

ACKNOWLEDGEMENT

The writer gratefully acknowledges the assistance and encouragement of Dr. Robert Barrie, who suggested the problem and supervised the writing of this thesis. Thanks are also due to Dr. J. Bichard and Dr. J.C. Giles of this department for several illuminating conversations, and for permission to use their unpublished experimental results.

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Introduction

The quantum-mechanical theory of crystalline solids depends, to a large extent, upon the consequences of the periodic arrangement of atoms in a crystal. It is the purpose of this thesis to discuss some of the effects of deviations from this periodicity.

To a first approximation, an electron in a pure elemental solid may be considered to move independently of other electrons through a rigid lattice of identical nuclei. In this adiabatic, one-electron approximation (Reitz, 1955), the only forces influencing the electron motion are those due to Coulomb interaction with the nuclei. The corresponding one-electron Schroedinger equation is:

$$\mathcal{H}_0 \varphi = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_p(\underline{r}) \right\} \varphi = \varepsilon \varphi \qquad (I:1)$$

where $V_p(\underline{r})$ is a potential function with the same periodicity as the crystal lattice, $\hbar$ is Planck's constant divided by 2π, and m is the mass of an electron. The Bloch theorem (Bloch, 1928; Wilson, 1953, p. 21) extended to three dimensions shows that the eigensolutions of equation (1) have the form:

$$\varphi_{n\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}} u_{n\underline{k}}(\underline{r}) \qquad (I:2)$$

where $u_{n\underline{k}}(\underline{r})$ has the same periodicity as $V_p(\underline{r})$. From this it may be shown (Wannier, 1959, Chapter 5) that the eigenvalue ε is a many-valued function $\varepsilon_n(\underline{k})$ of the electron wave-vector $\underline{k}$,

each subscript n labelling a different branch, or "energy band", of the function.[*] For uniqueness, the allowed values of $\underline{k}$ are confined to a region of momentum space known as the first Brillouin zone (Jones, 1960, p. 37).

The foregoing remarks apply to a completely periodic array of atoms. If this periodicity is disturbed slightly in some way, equation (1) must be replaced by:

$$\mathcal{H}\psi = \{\mathcal{H}_o + U\}\psi = E\psi \tag{I:3}$$

where U represents a perturbing potential due to the departure from strict periodicity.[**] Equation (3) has been studied with the aid of Wannier functions by several authors (Wannier, 1937; Koster and Slater, 1954 a and b; Slater, 1956). For the particular application to be studied in this thesis, however, a technique will be used which involves only the Bloch functions $\varphi_{n\underline{k}}(\underline{r})$ of the unperturbed lattice (Luttinger and Kohn, 1955, Appendix A; Kohn, 1957).

The specific problem to be considered is that in which one (or more) of the atoms in the lattice is replaced by an atom of a different type, referred to as a "substitutional impurity". Insofar as its atomic number permits, the impurity atom will take over the electronic bonds left unfilled by the removal of the original atom. Consequently, if the impurity

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[*] Note that the branches may be degenerate for some values of $\underline{k}$. (Wannier, 1959, p. 145.)

[**] It should be noted that for complete accuracy U must satisfy self-consistent field requirements.

nucleus has a smaller charge than the original nucleus, there will be a deficiency of electrons in the lattice due to a number of unfilled bonds; while if the impurity nucleus has a greater charge, there will be an electron excess. Impurities of the first type are known as "acceptors", while those of the second type are known as "donors".

For definiteness, consider the case of a donor impurity, such as phosphorus in silicon[*], whose atomic number is one greater than that of the lattice atoms. (An impurity of this type is said to be "monovalent".) The nature of the interaction of the impurity nucleus with the extra electron will depend on whether or not it is energetically favourable for the electron to occupy an orbit close to the nucleus. If such an orbit is favoured, what is known as a "deep" impurity state is produced, and the electron-nucleus interaction is highly complicated. However, in the case of a "shallow" impurity state, characterized by an orbit of large dimensions, only the excess charge on the impurity nucleus will be of importance in the interaction, and the impurity system will resemble a hydrogen-like atom imbedded in the lattice.

If it is assumed that the impurity in question is in a shallow state, the hydrogen-atom analogy mentioned in the last paragraph may be used to give a particular form to the perturbation U:

$$U(r) = -\frac{e^2}{\kappa r} \tag{I:4}$$

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[*] All numerical results in the present thesis will apply to this particular case.

(e is the electronic charge, and K is the static dielectric
constant of the host lattice). The use of the static
dielectric constant is justified by the fact that the orbital
frequency of the extra electron about the impurity nucleus is
sufficiently low to be neglected with respect to the orbital
frequencies of other electrons in the crystal. The concept
of polarization of the host material by means of relative
displacements of nuclei and electron shells will therefore
still be valid. It is this polarization which gives rise to
the static dielectric constant.

There is a major assumption implicit in the foregoing
argument — that of a spherically symmetric perturbing
potential. The true hamiltonian governing the motion of the
extra electron will have a symmetry determined by the physical
arrangement of the atoms surrounding the impurity nucleus. In
the case of phosphorus in silicon, for example, $U(\underline{r})$ must have
tetrahedral symmetry (denoted by T.S.), so that equation (3)
becomes:

$$\left\{ \mathcal{H}_o + U_{T.S.}(\underline{r}) \right\} \psi = E \psi$$

(I:5)

Group theory (Heine, 1960, Section 6) then shows that the wave
functions ψ belonging to each value of E in (5) must generate
an irreducible representation of the tetrahedral group T_d
(Eyring et al., 1944).

If the wave functions ψ are expanded in terms of the Bloch
functions of the unperturbed lattice as follows:[*]

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[*] See Chapter II for details of this derivation in the
approximation of a spherically symmetric perturbing potential.

$$\psi(\underline{r}) = \sum_m \int d\underline{k} \; D^{(m)}(\underline{k}) \; \varphi_{m\underline{k}}(\underline{r}) \tag{I:6}$$

(5) may be replaced by the equation:

$$\{\varepsilon_m(\underline{k}) - E\} D^{(m)}(\underline{k}) + \sum_{m'} \int d\underline{k}' \; D^{(m')}(\underline{k}') \langle m\underline{k} | U_{\text{T.S.}}(\underline{r}) | m'\underline{k}' \rangle = 0 \tag{I:7}$$

The Fourier transform of equation (7) is then:

$$\{\varepsilon_m(-i\underline{\nabla}) - E\} F^{(m)}(\underline{r})$$

$$+ \sum_{m'} \int d\underline{k}' \int d\underline{k} \; D^{(m')}(\underline{k}') e^{i\underline{k}\cdot\underline{r}} \langle m\underline{k} | U_{\text{T.S.}}(\underline{r}) | m'\underline{k}' \rangle = 0 \tag{I:8}$$

where $F^{(m)}(\underline{r})$ is the Fourier transform of $D^{(m)}(\underline{k})$.

Equation (8) may be simplified by neglecting interband terms, and by using a suitable approximation with regard to the "gentleness" (but not the symmetry) of $U_{\text{T.S.}}(\underline{r})$. The result of this simplification is:

$$\{\varepsilon_m(-i\underline{\nabla}) + U_{\text{T.S.}}(\underline{r})\} F^{(m)}(\underline{r}) = E F^{(m)}(\underline{r}) \tag{I:9}$$

Here again the wave functions corresponding to each E must generate an irreducible representation of the group T_d. It is obviously to be expected that replacing $U_{\text{T.S.}}(\underline{r})$ by a potential of higher symmetry would introduce additional degeneracies into the energy level scheme of (9).

After the solutions of (9) have been obtained, they may be Fourier transformed to give the $D^{(m)}(\underline{k})$, and hence the solutions of (5). Clearly any extra degeneracies caused by the use of an incorrect potential would be carried over into this case as well.

Unfortunately, because the exact form of $U_{T.S.}(\underline{r})$ is not known, the above method of solving equation (5) is not practicable. It is necessary to solve the problem using the spherically symmetric potential (4) as a first approximation. Corrections to this approximation may then be studied by the introduction of a tetrahedrally symmetric perturbation, or by some other less exact procedure.

It has been shown (Koster and Slater, 1954 b; Slater, 1952) that the energy eigenvalues of equation (3) are similar to those of equation (1), with the exception that allowed energy levels may now occur in the "forbidden" regions between the bands. For a shallow impurity state, these "split-off" levels are close to the parent band; hence it is to be expected that the wave functions corresponding to these levels are closely related to the Bloch functions at the band edge. If it is assumed that the band in question is of standard form (Wilson, 1953, p. 42), with its minimum in $\underline{k}$-space at $\underline{k} = 0$, then it may be shown (Kohn, 1957, Section 5a) that the equation:

$$\left\{ \mathcal{H}_0 - \frac{e^2}{\chi r} \right\} \psi = E \psi \qquad (I:10)$$

has solutions:

$$\psi^{(m)}(\underline{r}) = F^{(m)}(\underline{r}) \, \varphi_{m,0}(\underline{r}) \qquad (I:11)$$

where $F^{(m)}(\underline{r})$ is again the Fourier transform of the coefficient $D^{(m)}(\underline{k})$ defined by (6). $F^{(m)}(\underline{r})$ is a solution of the equation:

$$\left\{ \varepsilon_m(-i\nabla) - \frac{e^2}{\chi r} \right\} F^{(m)}(\underline{r}) = E \, F^{(m)}(\underline{r}) \qquad (I:12)$$

and the form of $\varepsilon_m(-i\nabla)$ is, to second order:

$$\varepsilon_m(-i\nabla) = \varepsilon_o^{(m)} - \frac{\hbar^2}{2} \left\{ \frac{1}{m_x} \frac{\partial^2}{\partial x^2} + \frac{1}{m_y} \frac{\partial^2}{\partial y^2} + \frac{1}{m_z} \frac{\partial^2}{\partial z^2} \right\} \qquad (\text{I}:13)$$

($\varepsilon_o^{(m)}$ is the energy at the bottom of the band, and m_x, m_y, and m_z are constants with the dimension of mass). Equation (13) may be solved approximately by setting $m_x = m_y = m_z = m^*$. In this case the functions $F^{(m)}(\underline{r})$ are simply modified hydrogen wave-functions, and the allowed values of $(E - \varepsilon_o^{(m)})$ form a hydrogen-like spectrum.

In the consideration of energy levels split off from the conduction band of silicon, allowance must be made for the fact that the band is not of standard form, but has six equivalent minima, at $(\pm k_o, 0, 0)$, $(0, \pm k_o, 0)$, and $(0, 0, \pm k_o)$ in the first Brillouin zone (Herman, 1954 and 1955). A tentative estimate of k_o has been made by Kohn (1957, Section 7c), who gives a value of 0.7 k_{max}. (k_{max} is the magnitude of $\underline{k}$ at the zone boundary in one of the six axial directions). Also, the conduction-band energy near one of these minima is given by an expression like: (Kohn and Luttinger, 1955a)

$$\varepsilon_c(\underline{k}) = \varepsilon_o + \frac{\hbar^2}{2m_1} (k_x - k_o)^2 + \frac{\hbar^2}{2m_2} (k_y^2 + k_z^2) \qquad (\text{I}:14)$$

using the minimum at $(k_o, 0, 0)$ as an example. The effective masses m_1 and m_2 are given by (R.N. Dexter, et al., 1954):

$$\begin{aligned} m_1 &= 0.98\,m \\ m_2 &= 0.19\,m \end{aligned} \qquad (\text{I}:15)$$

In the approximation of a spherically symmetric perturbing

potential, the solution of the many-minimum problem follows
along roughly the same lines as that for a single minimum.*
The problem is first solved for a single minimum at one of
the six equivalent positions listed above. Then it is argued
that by virtue of the spherical symmetry of the perturbing
potential, a similar solution would have been obtained if any
one of the other five minima had been used. It therefore
follows that if all six minima are present at the same time,
the single-minimum hydrogen-like levels will each acquire a
six-fold degeneracy in addition to its spin degeneracy.

If now a tetrahedrally symmetric perturbation is applied
to the hamiltonian of equation (10), in the case of many minima,
stationary perturbation theory (Schiff, 1955, p. 155) shows
that the zero-order wave functions for the six degenerate
states belonging to a particular energy level are given by
linear combinations of the six corresponding individual-minimum
wave functions. Group theory (Heine, 1960, p. 107) then
indicates what the correct linear combinations are. The purpose
of forming these combinations is to eliminate all non-zero
elements of the perturbation between degenerate states.

For the case of the conduction-band impurity levels of
phosphorus in silicon, it may be shown (Kohn, 1957, Section 5b)
that a tetrahedrally symmetric perturbation can only partially
remove the ground-state degeneracy caused by the spherical-
potential approximation — the maximum possible splitting is
into a non-degenerate level, a two-fold degenerate level, and

* See Chapter II.

a three-fold degenerate level. Experimental studies of the
hyperfine structure of the ground state (Fletcher et al.,
1954 a and b) indicate conclusively that the lowest of these
three levels is the one which is non-degenerate. As splitting
may occur, then, it should be profitable to examine the
possibility of radiation-induced transitions between the
ground state and the remaining five 1s states.

It will be shown that if the effective-mass wave functions
derived on the basis of a spherically symmetric perturbation
are used, the optical matrix elements for 1s-1s transitions
are very small compared with those for transitions between
other pairs of levels. Furthermore, they remain small even
after a correction has been applied to the non-degenerate ground
state wave function. Consequently, in the case of an isolated
phosphorus impurity in silicon, it should not be feasible to
observe the fine structure of the {1s} states experimentally.

If the impurity concentration is increased, however, the
selection rule governing the transitions of interest breaks
down. It may now be possible for an electron in the non-
degenerate ground state on one impurity atom to make the
transition to an excited 1s state on another such atom.
Unfortunately, treatment of this many-impurity problem is
complicated by the random distribution of impurities. It is
possible to approximate the actual situation, however, by
assuming that the impurity atoms form a regular lattice which
is superimposed on the lattice of the host crystal. In this
approximation the problem reduces to that of "solid hydrogen"

imbedded in a dielectric medium.*

The optical matrix elements for the many-impurity case also turn out to be very small if the spherical-potential effective-mass wave functions are used. However, using corrections to the effective mass theory based on those introduced by Kohn and Luttinger (1955 a), it will be shown that the matrix elements may be of a size which will permit observation of the transitions. The actual state of affairs depends upon the appropriateness of the corrected wave functions used. It is probable that the Kohn-Luttinger approach leads to results which are only good to within a factor of two or three. However, there would appear to be no firm theoretical reason why the fine structure of the {1s} states should not be observed.

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* See Chapter III.

CHAPTER II

The Theory of an Isolated Donor Impurity in Silicon.

A. Effective Mass Theorem for an Isolated Impurity.

Consider the problem of an isolated monovalent donor impurity in a crystal of silicon. Let the Schroedinger equation for the pure silicon lattice be:

$$\mathcal{H}_0 \, \varphi_{m\underline{k}}(\underline{r}) = \varepsilon_m(\underline{k}) \, \varphi_{m\underline{k}}(\underline{r}) \tag{II:1}$$

where:

$$\mathcal{H}_0 = -\frac{\hbar^2}{2m} \nabla^2 + V_p(\underline{r}) \tag{II:2}$$

and $V_p(\underline{r})$ is the periodic crystal potential. By the Bloch Theorem, the eigensolutions of (1) have the form:

$$\varphi_{m\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}} \, u_{m\underline{k}}(\underline{r}) \tag{II:3}$$

where:

$$u_{m\underline{k}}(\underline{r}) = u_{m\underline{k}}(\underline{r} + \underline{R}_s) \tag{II:4}$$

for any vector $\underline{R}_s$ of the pure silicon lattice. If the $u_{m\underline{k}}(\underline{r})$ satisfy the normalization:

$$\int_{unit\ cell} |u_{m\underline{k}}(\underline{r})|^2 \, d\underline{r} = \frac{\Omega}{(2\pi)^3} \tag{II:5}$$

where Ω is the volume of a unit cell of the silicon lattice, then the Bloch functions $\varphi_{m\underline{k}}(\underline{r})$ may be shown to form a complete

orthonormal set normalized over the whole crystal.

If the effect of introducing an impurity atom into the pure crystal is considered as a small perturbation, the Schroedinger equation for the isolated-impurity problem may be written:

$$\mathcal{H}\,\psi(\underline{r}) = E\,\psi(\underline{r}) \qquad (II:6)$$

where:

$$\mathcal{H} = \mathcal{H}_0 + U(\underline{r}) \qquad (II:7)$$

and $U(\underline{r})$ is the perturbing potential due to the extra charge on the impurity nucleus.[*] If the extra electron is assumed to move in a spherically symmetric potential, then at large distances from the impurity nucleus:

$$U(\underline{r}) \simeq -\frac{e^2}{K r} \qquad (II:8)$$

where e is the electronic charge, and K is the static dielectric constant of silicon.[**]

Since the $\varphi_{m\underline{k}}(\underline{r})$ form a complete set, the solutions of equation (6) may be written:

$$\psi(\underline{r}) = \sum_m \int d\underline{k}\; D^{(m)}(\underline{k})\; \varphi_{m\underline{k}}(\underline{r}) \qquad (II:9)$$

where the summation is over all the energy bands of equation (1)

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[*] For the purposes of this derivation, it will be assumed that shallow-state theory is applicable.

[**] See Chapter I for a more detailed discussion.

and the integration is over the first Brillouin zone of the silicon lattice. For simplicity it will be assumed that the wave functions belonging to energy levels split off from the conduction band of the unperturbed lattice, under a small perturbation $U(\underline{r})$, may be written in terms of conduction-band Bloch functions alone. Hence:

$$\psi(\underline{r}) \simeq \int d\underline{k} \, D(\underline{k}) \, \varphi_{c\underline{k}}(\underline{r}) \qquad (II:10)$$

where the integration is again over the first Brillouin zone, and the subscript c refers to the conduction band.

Substituting (10) into (6)[*], multiplying by the complex conjugate of $\varphi_{c\underline{k}'}(\underline{r})$, and integrating over the entire crystal leads to the equation:

$$\{ \varepsilon_c(\underline{k}) - E \} D(\underline{k}) + \int d\underline{k}' \, U(\underline{k},\underline{k}') D(\underline{k}') = 0 \qquad (II:11)$$

where:

$$U(\underline{k},\underline{k}') \equiv \int d\underline{r} \, \varphi_{c\underline{k}}^{*}(\underline{r}) \, U(\underline{r}) \, \varphi_{c\underline{k}'}(\underline{r}) = \langle c\underline{k}|U(\underline{r})|c\underline{k}'\rangle \qquad (II:12)$$

Now the conduction band of silicon has six equivalent minima in the first Brillouin zone, at $(\pm k_o,0,0)$, $(0,\pm k_o,0)$, and $(0,0,\pm k_o)$. If it is assumed that the coefficients $D(\underline{k})$ corresponding to $\underline{k}$ near different minima are very weakly coupled, the solutions of (11) may be written approximately:

$$D(\underline{k}) = \sum_{j=1}^{6} \alpha_j \, D_j(\underline{k}) \qquad (II:13)$$

where the $\{\alpha_j\}$ are numerical coefficients determined by the

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[*] The following argument is taken, in the main, from Luttinger and Kohn, 1955, Appendix A.

symmetry of the unperturbed lattice, and the summation is over the six conduction-band minima. Stationary perturbation theory (Schiff, 1955, p. 155) shows that there are six allowed linear combinations of the form (13); they will be distinguished by a superscript i:

$$D^i(\underline{k}) = \sum_j \alpha_j^i \, D_j(\underline{k}) \tag{II:14}$$

Following Kohn and Luttinger (1955 c) the coefficients required for the $\{1s\}$ set of solutions are:

$$\alpha_j^{(0)} = \tfrac{1}{\sqrt{6}}(1,1,1,1,1,1)$$

$$\alpha_j^{(1)} = \tfrac{1}{2}(1,1,-1,-1,0,0)$$

$$\alpha_j^{(2)} = \tfrac{1}{2}(1,1,0,0,-1,-1)$$

$$\alpha_j^{(3)} = \tfrac{1}{\sqrt{2}}(1,-1,0,0,0,0) \tag{II:15}$$

$$\alpha_j^{(4)} = \tfrac{1}{\sqrt{2}}(0,0,1,-1,0,0)$$

$$\alpha_j^{(5)} = \tfrac{1}{\sqrt{2}}(0,0,0,0,1,-1)$$

In the spherical-potential approximation, these six states all have the same energy.

For the $\{1s\}$ set, the coefficients $D_j(\underline{k})$ of (14) may be taken to satisfy:

$$\{\epsilon_c^j(\underline{k}) - E\} \, D_j(\underline{k}) + \int d\underline{k}' \, \mathcal{U}(\underline{k},\underline{k}') \, D_j(\underline{k}') = 0 \tag{II:16}$$

where $\epsilon_c^j(\underline{k})$ is a second-order expansion about $\underline{k}_j$ of the conduction-band energy $\epsilon_c(\underline{k})$:

$$\epsilon_c^j(\underline{k}) = \epsilon_0 + \sum_{\lambda,\mu} \eta_{\lambda\mu}^j (k_\lambda - k_{j_\lambda})(k_\mu - k_{j_\mu}) \tag{II:17}$$

Here:

$$\eta^{j}_{\lambda\mu} = \frac{\partial^2 \varepsilon_c(\underline{k})}{\partial k_\lambda \partial k_\mu}\bigg|_{\underline{k}=\underline{k}_j}$$

ε_o = energy at the conduction-band minimum.

Luttinger and Kohn (1955, Appendix A) show that provided $U(\underline{r})$ is a "gentle" potential,

$$\mathcal{U}(\underline{k},\underline{k}') \cong \frac{1}{(2\pi)^3}\int d\underline{r}\ U(\underline{r})\,e^{i(\underline{k}'-\underline{k})\cdot\underline{r}} \equiv \mathcal{U}(\underline{k}-\underline{k}'). \qquad (II:18)$$

so that (16) becomes:

$$\{\varepsilon^{j}_{c}(\underline{k}) - E\}\,D_j(\underline{k}) + \int d\underline{k}'\ \mathcal{U}(\underline{k}-\underline{k}')\,D_j(\underline{k}') = 0 \qquad (II:19)$$

Then, multiplying (19) by $e^{i(\underline{k}-\underline{k}_j)\cdot\underline{r}}$ and integrating over the first Brillouin zone:

$$\{\varepsilon_o + \sum_{\lambda\mu}\eta^{j}_{\lambda\mu}(\tfrac{1}{i}\nabla_\lambda\chi\tfrac{1}{i}\nabla_\mu) - E\}\int d\underline{k}\ D_j(\underline{k})\,e^{i(\underline{k}-\underline{k}_j)\cdot\underline{r}}$$

$$+ \frac{1}{(2\pi)^3}\int d\underline{k}\ e^{i(\underline{k}-\underline{k}_j)\cdot\underline{r}}\int d\underline{k}'\ D_j(\underline{k}')\int d\underline{r}'\ U(\underline{r}')\,e^{i(\underline{k}'-\underline{k})\cdot\underline{r}'} = 0 \qquad (II:20)$$

Hence to the approximation[*] that:

$$\int\limits_{\substack{\text{First Brillouin}\\ \text{Zone}}} d\underline{k}\ e^{i(\underline{r}-\underline{r}')\cdot\underline{k}} = (2\pi)^3\,\delta(\underline{r}-\underline{r}')$$

it follows that:

$$\{\sum_{\lambda\mu}\eta^{j}_{\lambda\mu}(\tfrac{1}{i}\nabla_\lambda\chi\tfrac{1}{i}\nabla_\mu) + U(\underline{r})\}\,F_j(\underline{r}) = (E-\varepsilon_o)\,F_j(\underline{r}) \qquad (II:21)$$

In this case, the function $F_j(\underline{r})$ must be defined as:

$$F_j(\underline{r}) = \int\limits_{\substack{\text{1ST Brillouin}\\ \text{Zone}}} d\underline{k}\ e^{i(\underline{k}-\underline{k}_j)\cdot\underline{r}}\,D_j(\underline{k}) \qquad (II:22)$$

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[*] For complete accuracy, this integration should be taken over all $\underline{k}$-space.

The required normalization of the $F_j(\underline{r})$ is:

$$\int d\underline{r}\, |F_j(\underline{r})|^2 = (2\pi)^3 \qquad\qquad (II:22')$$

where the integration is taken over the entire crystal.

This follows from the requirement that the $\psi(\underline{r})$ defined by (10) be normalized to unity over the entire crystal, since:

$$\int d\underline{r}\, |\psi(\underline{r})|^2 = \int d\underline{k} \int d\underline{k}'\, D^*(\underline{k})\, D(\underline{k}') \int d\underline{r}\, \varphi_{c\underline{k}}^*(\underline{r})\, \varphi_{c\underline{k}'}(\underline{r})$$

$$= \int d\underline{k}\, |D(\underline{k})|^2$$

while:

$$\int d\underline{r}\, |F(\underline{r})|^2 = \int d\underline{k} \int d\underline{k}'\, D^*(\underline{k})\, D(\underline{k}') \int d\underline{r}\, e^{-i(\underline{k}-k_j)\cdot\underline{r}}\, e^{i(\underline{k}'-k_j)\cdot\underline{r}}$$

$$= \int d\underline{k}\, (2\pi)^3\, |D(k)|^2 = (2\pi)^3 \int d\underline{r}\, |\psi(\underline{r})|^2 .$$

Substitution of (14) into (10) leads to the equation:

$$\psi_\ell^i(\underline{r}) = \sum_j \alpha_j^i \int d\underline{k}\, D_{j\ell}(\underline{k})\, \varphi_{c\underline{k}}(\underline{r}) \qquad\qquad (II:23)$$

$$\cong \sum_j \alpha_j^i\, F_{j\ell}(\underline{r})\, \varphi_{c k_j}(\underline{r}). \qquad\qquad (II:23')$$

where the subscript ℓ labels the eigenvalues of equation (21).

B. Optical Matrix Elements.

In the dipole approximation, the matrix elements of interest are:[*]

$$\langle i\ell | p_\sigma | i'\ell' \rangle \qquad \text{(II:24)}$$

where:

$$| i\ell \rangle \equiv \psi_\ell^i(r) \qquad \text{(II:25)}$$

It may be shown that:

$$p_\sigma = \sigma\text{-component of momentum} = \frac{m}{i\hbar}[x_\sigma, \mathcal{H}]_- \qquad \text{(II:26)}$$

where:

$$\mathcal{H} = \mathcal{H}_0 + U(r)$$

Hence the matrix elements (24) become:

$$\langle i\ell | p_\sigma | i'\ell' \rangle = \frac{m}{i\hbar} \langle i\ell | [x_\sigma, \mathcal{H}]_- | i'\ell' \rangle$$

$$= \frac{m}{i\hbar}(E_{\ell'}^{i'} - E_\ell^i)\langle i\ell | x_\sigma | i'\ell' \rangle \qquad \text{(II:27)}$$

Now by equation (10):

$$\langle i\ell | x_\sigma | i'\ell' \rangle = \sum_{jj'} \alpha_j^{i*} \alpha_{j'}^{i'} \int dk \int dk' \, D_{j\ell}^*(k) D_{j'\ell'}(k') \langle ck | x_\sigma | ck' \rangle \qquad \text{(II:28)}$$

$$\langle ck | x_\sigma | ck' \rangle \equiv \int dr \, x_\sigma \, e^{i(k'-k)\cdot r} u_{ck}^*(r) u_{ck'}(r)$$

$$= \frac{1}{i} \int \frac{\partial}{\partial k_\sigma'} \left\{ e^{i(k'-k)\cdot r} \right\} u_{ck}^*(r) u_{ck'}(r) \, dr$$

$$= \frac{1}{i} \frac{\partial}{\partial k_\sigma'} \langle ck | ck' \rangle - \frac{1}{i} \int dr \, e^{i(k'-k)\cdot r} u_{ck}^* \frac{\partial u_{ck'}}{\partial k_\sigma'} \qquad \text{(II:29)}$$

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[*] See Chapter IV.

$u_{c\underline{k}}^{*} \dfrac{\partial u_{c\underline{k}'}}{\partial k_{\sigma}'}$ has the periodicity of the unperturbed lattice,

so that:

$$u_{c\underline{k}}^{*} \frac{\partial u_{c\underline{k}'}}{\partial k_{\sigma}'} = \sum_{\underline{m}} B_{\underline{k}\underline{k}'\sigma}^{(\underline{m})} e^{i\underline{K}_{\underline{m}} \cdot \underline{r}} \tag{II:30}$$

where the summation is over the entire unperturbed reciprocal lattice, and:

$$B_{\underline{k}\underline{k}'\sigma}^{(\underline{m})} = \frac{1}{\Omega} \int_{\substack{unit \\ cell}} d\underline{r} \; e^{i\underline{K}_{\underline{m}} \cdot \underline{r}} \; u_{c\underline{k}}^{*} \frac{\partial u_{c\underline{k}'}}{\partial k_{\sigma}'} \tag{II:31}$$

Substituting (30) into (29):

$$\langle c\underline{k} | x_{\sigma} | c\underline{k}' \rangle = \frac{1}{i} \frac{\partial}{\partial k_{\sigma}'} \delta(\underline{k}' - \underline{k}) - \frac{1}{i} \sum_{\underline{m}} B_{\underline{k}\underline{k}'\sigma}^{(\underline{m})} \int d\underline{r} \; e^{i(\underline{k}' - \underline{k} - \underline{K}_{\underline{m}}) \cdot \underline{r}}$$

$$= \frac{1}{i} \frac{\partial}{\partial k_{\sigma}'} \delta(\underline{k}' - \underline{k}) - \frac{(2\pi)^3}{i} \sum_{\underline{m}} B_{\underline{k}\underline{k}'\sigma}^{(\underline{m})} \delta(\underline{k}' - \underline{k} - \underline{K}_{\underline{m}}) \tag{II:32}$$

Now $\underline{k}$ and $\underline{k}'$ both lie in the first Brillouin zone, by equation (10). Their difference can therefore never become as great as a non-zero vector of the reciprocal lattice. Hence the only non-zero contribution of the summation in (32) is for $\underline{K}_{\underline{m}} = 0$, so that:

$$\langle c\underline{k} | x_{\sigma} | c\underline{k}' \rangle = \frac{1}{i} \frac{\partial}{\partial k_{\sigma}'} \delta(\underline{k}' - \underline{k}) - \frac{(2\pi)^3}{i} B_{\underline{k}\underline{k}\sigma}^{(o)} \delta(\underline{k}' - \underline{k}) \tag{II:33}$$

Now:

$$B_{\underline{k}\underline{k}\sigma}^{(o)} = \frac{1}{\Omega} \int_{\substack{unit\ cell}} d\underline{r} \; u_{c\underline{k}}^{*} \frac{\partial u_{c\underline{k}}}{\partial k_{\sigma}} \tag{II:34}$$

Adams (1952) shows that if the phases of the $u_{c\underline{k}}(\underline{r})$ are properly chosen, the integral in (34) vanishes. It will be assumed that

this choice of phase has been made. Hence:

$$B^{(o)}_{\underline{k}\underline{k}\sigma} \equiv 0 \qquad (II:35)$$

Thus (33) becomes:

$$\begin{aligned}
\langle c\underline{k}|x_\sigma|c\underline{k}'\rangle &= \frac{1}{i}\frac{\partial}{\partial k_\sigma}\,\delta(\underline{k}'-\underline{k}) \\
&= \frac{1}{i}\frac{\partial}{\partial k_\sigma}\left\{\frac{1}{(2\pi)^3}\int d\underline{r}\, e^{i(\underline{k}'-\underline{k})\cdot\underline{r}}\right\} \\
&= \frac{1}{(2\pi)^3}\int x_\sigma\, e^{i(\underline{k}'-\underline{k})\cdot\underline{r}}\, d\underline{r} \qquad (II:36) \\
&= \frac{1}{(2\pi)^3}\langle\underline{k}|x_\sigma|\underline{k}'\rangle
\end{aligned}$$

where

$$|\underline{k}\rangle \equiv e^{i\underline{k}\cdot\underline{r}} \qquad (II:37)$$

Substituting (36) into (28):

$$\begin{aligned}
\langle i\ell|x_\sigma|i'\ell'\rangle &= \sum_{jj'}\alpha_j^{i\,*}\alpha_{j'}^{i'}\int d\underline{k}\int d\underline{k}'\, D_{j\ell}^*(\underline{k})D_{j'\ell'}(\underline{k}')\frac{1}{(2\pi)^3}\langle\underline{k}|x_\sigma|\underline{k}'\rangle \\
&= \frac{1}{(2\pi)^3}\sum_{jj'}\alpha_j^{i\,*}\alpha_{j'}^{i'}\langle j\ell|x_\sigma|j'\ell'\rangle \qquad (II:38)
\end{aligned}$$

where:

$$|j\ell\rangle \equiv F_{j\ell}(\underline{r})\,e^{i\underline{k}_j\cdot\underline{r}} \qquad (II:39)$$

The matrix elements $\langle j\ell|x_\sigma|j'\ell'\rangle$ may be written:

$$\langle j\ell|x_\sigma|j'\ell'\rangle = \int x_\sigma\, F_{j\ell}^*(\underline{r})\, F_{j'\ell'}(\underline{r})\, e^{i(\underline{k}_j-\underline{k}_j)\cdot\underline{r}}\, d\underline{r} \qquad (II:40)$$

For the transition to be considered, from the 1s ground state (characterized by $\alpha_j^{(o)}$) to another 1s state, the spherical-potential approximations to both $F_{j\ell}(\underline{r})$ and $F_{j'\ell'}(\underline{r})$ are even functions of x, y, and z. In this case (40) reduces to:

$$\langle j\ell | x_\sigma | j'\ell' \rangle = i \int x_\sigma F_{j1s}^*(\underline{r}) F_{j'1s}(\underline{r}) \sin(\underline{k}_{j'} - \underline{k}_j) \cdot \underline{r} \; d\underline{r} \qquad (II:41)$$

the real part of the expression having vanished because its
integrand is an odd function of x. Clearly if $j = j'$, the
matrix element (41) is identically zero. If $j \neq j'$, the matrix
element is not zero, but as the $F_{j\ell}(\underline{r})$ are slowly-varying
compared to the lattice spacing (Luttinger and Kohn, 1955,
Section III), it is reasonable to assume that the presence of
an oscillating term in the integrand will tend to make the
integral very small.

A more quantitative estimate of the non-zero matrix
elements may be obtained from consideration of the integrals:

$$\int d\underline{r} \; x_\sigma F_{j1s}^*(\underline{r}) F_{j'1s}(\underline{r}) \sin \underline{k}_j \cdot \underline{r} \; \cos \underline{k}_{j'} \cdot \underline{r} \qquad (II:42)$$

and

$$\int d\underline{r} \; x_\sigma F_{j1s}^*(\underline{r}) F_{j'1s}(\underline{r}) \sin \underline{k}_{j'} \cdot \underline{r} \; \cos \underline{k}_j \cdot \underline{r} \qquad (II:43)$$

If $j = j'$, both integrals are of the order of $5 \times 10^{-4} \alpha^*$,
where α^* is the approximate "Bohr radius" for the $F_{1s}(\underline{r})$. It
is to be expected that when $j \neq j'$ these integrals will have
even smaller values.[*] (41), which is equal to the difference
of (42) and (43), should therefore be negligible compared with
$1.9 \times 10^2 \alpha^*$, which is the value of the matrix element
$\langle j\ell | x_\sigma | j\ell' \rangle$ for the 1s $\rightarrow$ 2p$_0$ transition when spherical-
potential wave functions are used.

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[*] See (III:37) for examples which bear out this contention.

In Chapter III, corrections to the spherical-potential approximation will be considered. Anticipating the results, it may be stated here that, replacing the ground state wave function by its corrected value and using the estimation procedure of the last paragraph, values of less than $1 \times 10^{-3} \alpha^*$ are obtained for (41). As the $1s \rightarrow 2p_0$ matrix element is decreased by only a factor of two when the corrected functions are used, the $1s \rightarrow 1s$ matrix elements are again negligible by comparison. It is therefore unlikely that the fine structure of the $\{1s\}$ states will be experimentally observable when the impurities are too far apart to interact.

CHAPTER III

The Theory of Donor Impurities in Silicon
for Finite Impurity Concentrations.

A. Introduction.

The case in which there are many impurities present in a crystal lattice is difficult to treat because of the random nature of the impurity distribution.[*] If, however, the impurities are assumed to lie on a regular lattice within the crystal, the problem of their interaction may be attacked by means of the usual approximations of solid state physics. For simplicity, therefore, it will be assumed that the impurities lie on a simple cubic lattice, so that the problem of impurity-level broadening may be treated in the Bloch scheme.[**]

B. Tight-Binding (LCAO) Approximation.

1. The secular equation: Derivation.

The Schroedinger equation for the many-impurity problem is:

$$\mathcal{H}\, \psi_\kappa(\underline{r}) = E(\underline{\kappa})\psi_\kappa(\underline{r}) \qquad \text{(III:1)}$$

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[*] For the treatment of a one-dimensional lattice containing random impurities, see Lax and Phillips (1958).

[**] Conwell (1956) discusses the implications of the assumption of a regular impurity lattice. See also Baltensperger (1953).

where:

$$\mathcal{H} = \mathcal{H}_o + \mathcal{W}_p(\underline{r}) \tag{III:2}$$

and $\mathcal{W}_p(\underline{r})$ is a periodic potential with the periodicity of the impurity lattice. Following Slater and Koster (1954):

$$\mathcal{W}_p(\underline{r}) \cong \sum_{\underline{n}} U(\underline{r} - \underline{a}_n) \tag{III:3}$$

where the summation is over all sites $\underline{a}_n$ of the impurity lattice.

In the LCAO approximation, the wave functions $\Psi_{\underline{K}}(\underline{r})$ may be written:

$$\Psi_{\underline{K}}(\underline{r}) = \frac{1}{\sqrt{N}} \sum_{\ell,i} d_{i\ell} \sum_{\underline{n}} e^{i\underline{K}\cdot\underline{a}_n} \psi_\ell^i(\underline{r} - \underline{a}_n) \tag{III:4}$$

where N is the number of impurities present, and the summation over ℓ and i includes contributions from all eigenstates of the isolated-impurity problem. The energy:

$$E(\underline{K}) = \frac{\langle \underline{K} | \mathcal{H} | \underline{K} \rangle}{\langle \underline{K} | \underline{K} \rangle} \tag{III:5}$$

where:

$$| \underline{K} \rangle = \Psi_{\underline{K}}(\underline{r}) \tag{III:5'}$$

must then be minimized by the proper choice of the coefficients $d_{i\ell}$. Hence:

$$\frac{\partial E}{\partial d_{i'\ell'}} = \frac{1}{\langle \underline{K}|\underline{K}\rangle} \left\{ \frac{\partial}{\partial d_{i'\ell'}} \langle \underline{K} | \mathcal{H} | \underline{K} \rangle - E(\underline{K}) \frac{\partial}{\partial d_{i'\ell'}} \langle \underline{K}|\underline{K}\rangle \right\} = 0 \tag{III:6}$$

Now by equation (4) the matrix elements in (6) are:

$$\langle \underline{K} | \underline{K} \rangle = \frac{1}{N} \sum_{\ell\ell''} \sum_{ii''} d_{i\ell}^* d_{i''\ell''} \sum_{\underline{n},\underline{n}''} e^{i\underline{K}\cdot(\underline{a}_{n''} - \underline{a}_n)} \langle i\ell\underline{a}_n | i''\ell''\underline{a}_{n''} \rangle \tag{III:7}$$

and:

$$\langle \underline{K} | \mathcal{H} | \underline{K} \rangle = \frac{1}{N} \sum_{\ell\ell''} \sum_{ii''} d_{i\ell}^* d_{i''\ell''} \sum_{\underline{n}\,\underline{n}''} e^{i\underline{K}\cdot(\underline{a}_{\underline{n}''}-\underline{a}_{\underline{n}})} \langle i\ell \underline{a}_{\underline{n}} | \mathcal{H} | i''\ell'' \underline{a}_{\underline{n}''} \rangle \qquad (III:8)$$

where:

$$|i\ell \underline{a}_{\underline{n}}\rangle \equiv \psi_\ell^i(\underline{r}-\underline{a}_{\underline{n}}). \qquad (III:9)$$

Thus:

$$\frac{\partial}{\partial d_{i\ell'}} \langle \underline{K}|\underline{K}\rangle = \frac{1}{N} \sum_{\ell,i} d_{i\ell}^* \sum_{\underline{n},\underline{n}'} e^{i\underline{K}\cdot(\underline{a}_{\underline{n}'}-\underline{a}_{\underline{n}})} \langle i\ell \underline{a}_{\underline{n}} | i'\ell' \underline{a}_{\underline{n}'} \rangle$$

$$= \frac{1}{N} \sum_{\ell,i} d_{i\ell}^* \sum_{\underline{m},\underline{n}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}} \langle i\ell | i'\ell' \underline{a}_{\underline{m}}\rangle$$

$$= \sum_{\ell,i} d_{i\ell}^* \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}} \langle i\ell | i'\ell' \underline{a}_{\underline{m}}\rangle$$

$$\qquad (III:10)$$

(shifting the origin to $\underline{a}_{\underline{n}}$ and defining $\underline{a}_{\underline{m}} = \underline{a}_{\underline{n}'}-\underline{a}_{\underline{n}}$).

Similarly:

$$\frac{\partial}{\partial d_{i\ell'}} \langle \underline{K} | \mathcal{H} | \underline{K}'\rangle = \sum_{\ell,i} d_{i\ell}^* \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}} \langle i\ell | \mathcal{H} | i'\ell' \underline{a}_{\underline{m}}\rangle \qquad (III:11)$$

Substituting (10) and (11) into (6) leads to the equation:

$$\sum_{\ell,i} d_{i\ell}^* \left\{ \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}} \langle i\ell | \mathcal{H} | i'\ell' \underline{a}_{\underline{m}}\rangle - E(\underline{K}) \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}} \langle i\ell | i'\ell' \underline{a}_{\underline{m}}\rangle \right\} \qquad (III:12)$$
$$= 0$$

for each pair of values (i', ℓ'). Hence the secular determinant must vanish, giving:

$$\det_{\substack{i,\ell \\ i',\ell'}} \left\{ \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}} \langle i\ell | \mathcal{H} | i'\ell' \underline{a}_{\underline{m}}\rangle - E(\underline{K}) \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}} \langle i\ell | i'\ell' \underline{a}_{\underline{m}}\rangle \right\} = 0 \qquad (III:13)$$

Now by (2) and (3):

$$\langle i\ell | \mathcal{H} | i'\ell' \underline{a}_{\underline{m}}\rangle = \langle i\ell | \mathcal{H}_0 + \mathcal{W}_P(\underline{r}) | i'\ell' \underline{a}_{\underline{m}}\rangle$$

$$\langle i\ell | \mathcal{H} | i'\ell'\underline{a}_m \rangle = \langle i\ell | \mathcal{H}_o + U(\underline{r}-\underline{a}_m) | i'\ell'\underline{a}_m \rangle$$

$$+ \sum_{\underline{n} \neq \underline{m}} \langle i\ell | U(\underline{r}-\underline{a}_n) | i'\ell'\underline{a}_m \rangle$$

$$= E_\ell^{i'} \langle i\ell | i'\ell'\underline{a}_m \rangle + \sum_{\underline{n} \neq \underline{m}} \langle i\ell | U(\underline{r}-\underline{a}_n) | i'\ell'\underline{a}_m \rangle \qquad \text{(III:14)}$$

Then, substituting (14) into (13):

$$\det_{\substack{i,\ell \\ i',\ell'}} \Bigg\{ \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_m} \sum_{\underline{n} \neq \underline{m}} \langle i\ell | U(\underline{r}-\underline{a}_n) | i'\ell'\underline{a}_m \rangle$$

$$- [E(\underline{k}) - E_{\ell'}^{i'}] \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_m} \langle i\ell | i'\ell'\underline{a}_m \rangle \Bigg\} = 0 \qquad \text{(III:15)}$$

Using the expression (II:23) for $|i\ell\underline{a}_m\rangle$:

$$\langle i\ell | i'\ell'\underline{a}_m \rangle = \sum_{jj'} \alpha_j^{i*} \alpha_{j'}^{i'} \int d\underline{k} \int d\underline{k}' D_{j\ell}^*(\underline{k}) D_{j'\ell'}(\underline{k}') \langle c\underline{k} | c\underline{k}'\underline{a}_m \rangle$$

$$= \sum_{jj'} \alpha_j^{i*} \alpha_{j'}^{i'} \int d\underline{k} \int d\underline{k}' D_{j\ell}^*(\underline{k}) D_{j'\ell'}(\underline{k}') e^{-i\underline{k}'\cdot\underline{a}_m} \delta(\underline{k}-\underline{k}')$$

$$= \frac{1}{(2\pi)^3} \sum_{jj'} \alpha_j^{i*} \alpha_{j'}^{i'} \int d\underline{k} \int d\underline{k}' D_{j\ell}^*(\underline{k}) D_{j'\ell'}(\underline{k}') e^{-i\underline{k}'\cdot\underline{a}_m} \langle \underline{k} | \underline{k}' \rangle$$

$$= \frac{1}{(2\pi)^3} \sum_{jj'} \alpha_j^{i*} \alpha_{j'}^{i'} \int d\underline{k} \int d\underline{k}' D_{j\ell}^*(\underline{k}) D_{j'\ell'}(\underline{k}') \langle \underline{k} | \underline{k}'\underline{a}_m \rangle \qquad \text{(III:16)}$$

where: $$| \underline{k}\,\underline{a}_m \rangle \equiv e^{i\underline{k}\cdot(\underline{r}-\underline{a}_m)} \qquad \text{(III:17)}$$

Similarly:

$$\langle i\ell | U(\underline{r}-\underline{a}_n) | i'\ell'\underline{a}_m \rangle$$

$$= \sum_{jj'} \alpha_j^{i*} \alpha_{j'}^{i'} \int d\underline{k} \int d\underline{k}' D_{j\ell}^*(\underline{k}) D_{j'\ell'}(\underline{k}') e^{i\underline{k}\cdot\underline{a}_m} \langle c\underline{k} | U(\underline{r}-\underline{a}_n) | c\underline{k}' \rangle \qquad \text{(III:18)}$$

Now Luttinger and Kohn (1955, Appendix A) have shown that under the assumption that $U(\underline{r})$ is a "gentle" potential,

$$\langle c\underline{k} | U(\underline{r}) | c\underline{k}' \rangle \simeq \frac{1}{(2\pi)^3} \langle \underline{k} | U(\underline{r}) | \underline{k}' \rangle . \qquad \text{(III:19)}$$

Clearly $U(\underline{r} - \underline{a}_n)$ also satisfies the requirement of gentleness, so that (19) may be extended to give:

$$\langle c\underline{k} \mid U(\underline{r}-\underline{a}_n) \mid c\underline{k}'\rangle \;\cong\; \frac{1}{(2\pi)^3} \langle \underline{k} \mid U(\underline{r}-\underline{a}_n) \mid \underline{k}'\rangle \qquad (III{:}20)$$

Hence, substituting (20) into (18):

$$\langle i\ell \mid U(\underline{r}-\underline{a}_n) \mid i'\ell'\underline{a}_m \rangle$$

$$\cong \frac{1}{(2\pi)^3} \sum_{jj'} \alpha_j^{i*}\alpha_{j'}^{i'} \int d\underline{k} \int d\underline{k}' \, D_{j\ell}^*(\underline{k}) D_{j'\ell'}(\underline{k}') \langle \underline{k} \mid U(\underline{r}-\underline{a}_n) \mid \underline{k}'\underline{a}_m\rangle \qquad (III{:}21)$$

Then, making the substitution:

$$F_{j\ell}(\underline{r}) \equiv \int d\underline{k}\, D_{j\ell}(\underline{k})\, e^{i(\underline{k}-\underline{k}_j)\cdot\underline{r}} \qquad (III{:}22)$$

in (16) and (21), the following expressions are obtained:

$$\langle i\ell \mid i'\ell'\underline{a}_m\rangle \;=\; \frac{1}{(2\pi)^3} \sum_{jj'} \alpha_j^{i*}\alpha_{j'}^{i'} \langle j\ell \mid j'\ell'\underline{a}_m\rangle \qquad (III{:}23)$$

$$\langle i\ell \mid U(\underline{r}-\underline{a}_n) \mid i'\ell'\underline{a}_m\rangle \;=\; \frac{1}{(2\pi)^3} \sum_{jj'} \alpha_j^{i*}\alpha_{j'}^{i'} \langle j\ell \mid U(\underline{r}-\underline{a}_n) \mid j'\ell'\underline{a}_m\rangle \qquad (III{:}24)$$

where:

$$\mid j\ell\underline{a}_m\rangle \equiv F_{j\ell}(\underline{r}-\underline{a}_m)\, e^{i\underline{k}_j\cdot(\underline{r}-\underline{a}_m)} \qquad (III{:}25)$$

Finally, substituting (23) and (24) into (15), the secular equation becomes:

$$\det_{\substack{i,\ell \\ i',\ell'}} \left\{ \sum_m e^{i\underline{K}\cdot\underline{a}_m} \sum_{jj'} \alpha_j^{i*}\alpha_{j'}^{i'} \langle j\ell \mid \sum_{n\neq m} U(\underline{r}-\underline{a}_n) \mid j'\ell'\underline{a}_m\rangle \frac{1}{(2\pi)^3} \right. $$

$$\left. - \frac{1}{(2\pi)^3}[E(\underline{K}) - E_{\ell'}^{i'}] \sum_m e^{i\underline{K}\cdot\underline{a}_m} \sum_{jj'} \alpha_j^{i*}\alpha_{j'}^{i'} \langle j\ell \mid j'\ell'\underline{a}_m\rangle \right\} = 0 \qquad (III{:}26)$$

For the sake of simplicity, the range of ℓ in (26) is normally restricted to a small number of values, under the assumption that wave functions belonging to widely separated energy levels do not interact appreciably. For the problem

under consideration, ℓ will be taken as ls only. The five-fold degenerate[*] and the non-degenerate ls bands will then be considered separately in the light of equation (26).

For the five-fold degenerate ls band, the secular equation (26) is:

$$\det_{1 \leq i, i' \leq 5} \left\{ \frac{1}{(2\pi)^3} \sum_m e^{i K \cdot a_m} \sum_{jj'} \alpha_j^{i*} \alpha_{j'}^{i'} \langle j \, 1s | \sum_{n \neq m} U(r-a_n) | j' 1s \, a_m \rangle \right.$$
$$\left. - \frac{1}{(2\pi)^3} \left[E - E_{1s}^{(5)} \right] \sum_m e^{i K \cdot a_m} \sum_{jj'} \alpha_j^{i*} \alpha_{j'}^{i'} \langle j \, 1s | j' 1s \, a_m \rangle \right\} = 0 \qquad \text{(III:27)}$$

while for the non-degenerate ls band:

$$\frac{1}{(2\pi)^3} \sum_m e^{i K \cdot a_m} \sum_{jj'} \alpha_j^{o*} \alpha_{j'}^{o} \langle j \, 1s | \sum_{n \neq m} U(r-a_n) | j' 1s \, a_m \rangle$$
$$- \frac{1}{(2\pi)^3} \left[E - E_{1s}^{(0)} \right] \sum_m e^{i K \cdot a_m} \sum_{jj'} \alpha_j^{o*} \alpha_{j'}^{o} \langle j \, 1s | j' 1s \, a_m \rangle \qquad \text{(III:28)}$$
$$= 0$$

Equations (27) and (28) must now be solved.

2. Integrals involved in the secular equation.

It may be shown[**] that the coefficients $D_{j1s}(\underline{k})$ in (II:23) have the property that:[***]

$$D_{j1s}(\underline{k}) = D_{-j1s}^{*}(-\underline{k}) \qquad \text{(III:29)}$$

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[*]   In considering the exact solutions of the isolated-impurity problem, Kohn and Luttinger (1955 c) note that all ls states other than the non-degenerate ground state will have roughly the same energy. Thus, in spite of the fact that the exact solution will involve separate two-fold and three-fold degeneracies, the situation may be approximated by a single five-fold degeneracy. (See also Chapter I of this thesis).

[**] See Appendix A.

[***] The subscript "-j" in (29) denotes the coefficient associated with the conduction-band minimum at $-\underline{k}_j$.

Substitution of (29) into (22) leads immediately to the result that $F_{j1s}(\underline{r})$ is the complex conjugate of $F_{-j1s}(\underline{r})$. Hence if the phases of the $F_{j\ell}(\underline{r})$ are so chosen that $F_{j\ell}(0)$ is real and positive for all j, it follows that $F_{j1s}(\underline{r})$ and $F_{-j1s}(\underline{r})$ are equal. Therefore:

$$F_{j1s}(\underline{r})e^{i\underline{k}_j\cdot\underline{r}} + F_{j1s}(\underline{r})e^{-i\underline{k}_j\cdot\underline{r}} = |j\,1s\rangle + |-j1s\rangle = 2F_{j1s}(\underline{r})\cos\underline{k}_j\cdot\underline{r}$$

$$\text{(III:30)}$$

$$F_{j1s}(\underline{r})e^{i\underline{k}_j\cdot\underline{r}} - F_{j1s}(\underline{r})e^{-i\underline{k}_j\cdot\underline{r}} = |j\,1s\rangle - |-j\,1s\rangle = 2iF_{j1s}(\underline{r})\sin\underline{k}_j\cdot\underline{r}$$

Then, defining:

$$|i\,\underline{a}_m\rangle = \frac{1}{(2\pi)^{3/2}}\sum_j \alpha_j^i |j\,1s\,\underline{a}_m\rangle. \qquad \text{(III:31)}$$

and using the values of α_j^i given in (II:15), it follows that:

$$|0,\underline{a}_m\rangle = \frac{1}{(2\pi)^{3/2}}\sqrt{\frac{2}{3}}\left\{ F_1\cos\underline{k}_1\cdot(\underline{r}-\underline{a}_m) + F_3\cos\underline{k}_3\cdot(\underline{r}-\underline{a}_m) + F_5\cos\underline{k}_5\cdot(\underline{r}-\underline{a}_m)\right\}$$

$$|1,\underline{a}_m\rangle = \frac{1}{(2\pi)^{3/2}}\left\{ F_1\cos\underline{k}_1\cdot(\underline{r}-\underline{a}_m) - F_3\cos\underline{k}_3\cdot(\underline{r}-\underline{a}_m)\right\}$$

$$|2,\underline{a}_m\rangle = \frac{1}{(2\pi)^{3/2}}\left\{ F_1\cos\underline{k}_1\cdot(\underline{r}-\underline{a}_m) - F_5\cos\underline{k}_5\cdot(\underline{r}-\underline{a}_m)\right\}$$

$$\text{(III:32)}$$

$$|3,\underline{a}_m\rangle = \frac{i}{(2\pi)^{3/2}}\sqrt{2}\left\{ F_1\sin\underline{k}_1\cdot(\underline{r}-\underline{a}_m)\right\}$$

$$|4,\underline{a}_m\rangle = \frac{i}{(2\pi)^{3/2}}\sqrt{2}\left\{ F_3\sin\underline{k}_3\cdot(\underline{r}-\underline{a}_m)\right\}$$

$$|5,\underline{a}_m\rangle = \frac{i}{(2\pi)^{3/2}}\sqrt{2}\left\{ F_5\sin\underline{k}_5\cdot(\underline{r}-\underline{a}_m)\right\}$$

where the argument of F_j is $(\underline{r}-\underline{a}_m)$ in each case.

The integrals involved in evaluating $\langle i\,|\,i'\underline{a}_m\rangle$ are:

$$\frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \cos \underline{k}_j \cdot \underline{r} \, \cos \underline{k}_{j'} \cdot (\underline{r}-\underline{a}_m) \, d\underline{r}$$

$$= \alpha_{j'\underline{m}} \, I^\alpha_{jj'\underline{m}} + \beta_{j'\underline{m}} I^\beta_{jj'\underline{m}}$$

$$\frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \cos \underline{k}_j \cdot \underline{r} \, \sin \underline{k}_{j'} \cdot (\underline{r}-\underline{a}_m) \, d\underline{r}$$

$$= \alpha_{j'\underline{m}} \, I^\beta_{jj'\underline{m}} - \beta_{j'\underline{m}} I^\alpha_{jj'\underline{m}}.$$

$$\frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \sin \underline{k}_j \cdot \underline{r} \, \cos \underline{k}_{j'} \cdot (\underline{r}-\underline{a}_m) \, d\underline{r}$$

$$= \alpha_{j'm} \, I^{\beta'}_{jj'\underline{m}} + \beta_{j'm} I^\gamma_{jj'\underline{m}}$$

$$\frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \sin \underline{k}_j \cdot \underline{r} \, \sin \underline{k}_{j'} \cdot (\underline{r}-\underline{a}_m) \, d\underline{r}$$

$$= \alpha_{j'\underline{m}} \, I^\gamma_{jj'\underline{m}} - \beta_{j'\underline{m}} I^{\beta'}_{jj'\underline{m}} \qquad\qquad (III:33)$$

where:

$$\alpha_{j'\underline{m}} \equiv \cos \underline{k}_{j'} \cdot \underline{a}_m$$

$$(III:34)$$

$$\beta_{j'\underline{m}} \equiv \sin \underline{k}_{j'} \cdot \underline{a}_m$$

and:

$$I^\alpha_{jj'\underline{m}} = \frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \cos \underline{k}_j \cdot \underline{r} \, \cos \underline{k}_{j'} \cdot \underline{r} \, d\underline{r}$$

$$I^\beta_{jj'\underline{m}} = \frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \cos \underline{k}_j \cdot \underline{r} \, \sin \underline{k}_{j'} \cdot \underline{r} \, d\underline{r}$$

$$I^{\beta'}_{jj'\underline{m}} = \frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \sin \underline{k}_j \cdot \underline{r} \, \cos \underline{k}_{j'} \cdot \underline{r} \, d\underline{r} \qquad (III:35)$$

$$I^\gamma_{jj'\underline{m}} = \frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \sin \underline{k}_j \cdot \underline{r} \, \sin \underline{k}_{j'} \cdot \underline{r} \, d\underline{r}$$

Similarly, the integrals involved in evaluating $\langle i | U(\underline{r}-\underline{a}_n) | i'\underline{a}_m \rangle$ are combinations of integrals $U^\alpha_{jj'\underline{m}\,\underline{n}}$, $U^\beta_{jj'\underline{m}\,\underline{n}}$, $U^{\beta'}_{jj'\underline{m}\,\underline{n}}$, $U^\gamma_{jj'\underline{m}\,\underline{n}}$ of the form:

$$U^\alpha_{jj'\underline{m}\,\underline{n}} = \frac{1}{(2\pi)^3} \int F_j^*(\underline{r}) \, F_{j'}(\underline{r}-\underline{a}_m) \, U(\underline{r}-\underline{a}_n) \cos \underline{k}_j \cdot \underline{r} \, \cos \underline{k}_{j'} \cdot \underline{r} \, d\underline{r}$$

$$(III:36)$$

etc.

3. Evaluation of integrals.

The integrals of (35) and (36) may be shown to have the following approximate values (using the spherically symmetric potential (I:4) as an approximation to $U(\underline{r})$):

$$
\begin{cases}
I^{\alpha}_{jjo} = \frac{1}{2} + \frac{1}{4} \frac{1}{(1 + k_o^2 \beta^2)^2} \\[2mm]
I^{\alpha}_{jj'o} = \frac{1}{(1 + 2k_o^2 \beta^2)^2} \qquad [j \neq j'] \\[2mm]
I^{\alpha}_{jj\underline{m}} = \frac{1}{2} e^{-a_m/\beta} \left\{ \frac{1}{3} \left(\frac{a_m}{\beta}\right)^2 + \left(\frac{a_m}{\beta}\right) + 1 \right\} \\[2mm]
I^{\alpha}_{jj'\underline{m}} \ll I^{\alpha}_{jj\underline{m}} \quad \text{by analogy with the } \underline{m} = 0 \text{ case.}
\end{cases}
\qquad \text{(III:37)}
$$

$$
\begin{cases}
I^{\beta}_{jj'o} = I^{\beta'}_{jj'o} = 0 \qquad [\text{ All } j, j'] \\[2mm]
I^{\beta}_{jj\underline{m}} = I^{\beta'}_{jj\underline{m}} = 0 \\[2mm]
I^{\beta}_{jj'\underline{m}} \cong I^{\beta'}_{jj'\underline{m}} \cong 0 \quad \text{by analogy with the } \alpha\text{-integrals.}
\end{cases}
\qquad \text{(III:38)}
$$

$$
\begin{cases}
I^{\gamma}_{jjo} = 1 - I^{\alpha}_{jjo} \\[2mm]
I^{\gamma}_{jj'\underline{m}} \equiv 0 \qquad [j \neq j', \text{ all } \underline{m}]. \\[2mm]
I^{\gamma}_{jj\underline{m}} \cong I^{\alpha}_{jj\underline{m}}
\end{cases}
\qquad \text{(III:39)}
$$

$$
\begin{cases}
U^{\alpha}_{jjo} = -\frac{e^2}{\kappa a^4} \left\{ \frac{1}{2} + \frac{1}{2(1 + k_o^2 \beta^2)} \right\} \\[2mm]
U^{\alpha}_{jj'o} = -\frac{e^2}{\kappa a^4} \left\{ \frac{4}{9 + 4k_o^2 \beta^2} \right\} \qquad [j \neq j'] \\[2mm]
U^{\alpha}_{jj\underline{m}} = -\frac{e^2}{\kappa a^4} \left\{ \frac{1}{2} e^{-a_m/\beta} \left[1 + \frac{a_m}{\beta} \right] \right\} \\[2mm]
U^{\alpha}_{jj'\underline{m}} \ll U^{\alpha}_{jj\underline{m}} \quad \text{by analogy with the } \underline{m} = 0 \text{ case.}
\end{cases}
\qquad \text{(III:40)}
$$

$$\begin{cases} U^{\beta}_{jj'o} = U^{\beta'}_{jj'o} = 0 \qquad \text{[all } j, j'\text{]}. \\[2mm] U^{\beta}_{jj\underline{m}} \cong U^{\beta'}_{jj\underline{m}} \cong +\frac{e^2}{Ka^*}\left\{(5\times10^{-3})\left(\frac{a_m}{B}\right)^2 e^{-a_m/B} \sin k_o a_m\right\} \\[2mm] U^{\beta}_{jj'\underline{m}} \cong U^{\beta'}_{jj'\underline{m}} < U^{\beta}_{jj\underline{m}} \qquad \text{by analogy with the } \alpha\text{-integrals}. \end{cases}$$

(III:41)

$$\begin{cases} U^{\gamma}_{jjo} = -\frac{e^2}{Ka^*} - U^{\alpha}_{jjo} \\[2mm] U^{\gamma}_{jj'o} = U^{\gamma}_{jj'\underline{m}} \equiv 0 \qquad \text{[} j \neq j'\text{]} \\[2mm] U^{\gamma}_{jj\underline{m}} \cong U^{\alpha}_{jj\underline{m}} \end{cases}$$

(III:42)

Integrals $U_{jj'\underline{m}\,\underline{n}}$, for which $\underline{a}_n$ is neither equal to $\underline{a}_m$ nor zero, are difficult to evaluate. However, it is to be expected that they will be smaller than the two-centre integrals of (40, (41), and (42).[*] Consequently a two-centre approximation, in which these integrals are ignored, will be used.

In (37) to (42), the notation is as follows:

a_m = the magnitude of $\underline{a}_m$.

k_o = the magnitude of $\underline{k}j$.

e = the electronic charge.

(III:43)

K = the static dielectric constant of silicon.

A = the transverse "Bohr radius" for $F_{j1s}(\underline{r})$ in silicon.

B = the longitudinal "Bohr radius" for $F_{j1s}(\underline{r})$ in silicon.

a^* = an appropriate average of A and B.

(III:44)

The functional form of $F_{j1s}(\underline{r})$ used is that given by Kohn (1957,

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[*] See Slater and Koster, 1954, Section III.

equation 6.4):

$$F = \frac{(2\pi)^{3/2}}{(\pi A^2 B)^{1/2}} \exp\left\{ -\sqrt{\frac{x^2+y^2}{A^2} + \frac{z^2}{B^2}} \right\}$$ (III:45)

where the z-axis is taken in the direction of $\underline{k}_j$. For silicon, Kohn gives the values:

$$A = 25.0 \times 10^{-8} \text{ cm.}$$
$$B = 14.2 \times 10^{-8} \text{ cm.}$$ (III:46)

The necessity of using a^* arises from the occurrence of the term $1/r$ in the integrands of (40) to (42). Simplification of the exponential terms in these integrands leads to a complicated expression for the remaining r-dependence unless an average Bohr radius is used. From (46) it may be seen that the value of a^* will be approximately 20×10^{-8} cm. (Kohn, 1957, equation 5.10). Use of this value leads to:

$$\frac{e^2}{\kappa a^*} = 6.0 \times 10^{-2} \text{ eV.} \qquad [\text{for silicon}]$$ (III:47)

By Chapter I*, $k_o \simeq \frac{3\pi}{2d}$, where d is the silicon lattice spacing 5.42×10^{-8} cm.; and by (46) B is approximately equal to 2.5 d. Thus the value of $k_o B$ is approximately 12, so that:

$$\frac{1}{1 + k_o^2 B^2} \simeq \frac{1}{145} = 6.9 \times 10^{-3}$$

To a reasonable approximation, therefore, the integrals (37) to (42) may be taken as:

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* Jones (1960, p. 121) shows that the value of k_{max} is $\frac{2\pi}{d}$. Chapter I gives $k_o \simeq \frac{3}{4} k_{max}$.

$$\begin{cases} I^{\alpha}_{jjo} = I^{\gamma}_{jjo} = \tfrac{1}{2} \\ \text{all other } I\text{-integrals} = 0 \end{cases} \qquad (III:48)$$

$$\begin{cases} U^{\alpha}_{jjo} = U^{\gamma}_{jjo} = -\dfrac{e^2}{2Ka^*} \\ U^{\alpha}_{jj\underline{m}} = U^{\gamma}_{jj\underline{m}} = -\dfrac{e^2}{2Ka^*}\left\{1 + \dfrac{a_m}{B}\right\} e^{-a_m/B} \\ \text{all other } U\text{-integrals} = 0 \end{cases} \qquad (III:49)$$

If it is further assumed that:

$$U^{\alpha}_{jj\underline{m}} = U^{\gamma}_{jj\underline{m}} = 0 \qquad (III:50)$$

unless $\underline{a}_m$ is one of $(\pm a,0,0)$, $(0,\pm a,0)$, $(0,0,\pm a)$, or zero (where a is the impurity lattice spacing), then the secular equation (27) may be easily solved. (This assumption constitutes a nearest-neighbour approximation.)

4. Evaluation of matrix elements.

Using the results of (47), (48), and (49), the matrix elements of interest reduce to:

$$\langle o|o \rangle = 1$$

$$\begin{cases} \langle 1|1 \rangle = 1 \\ \langle 1|2 \rangle = \langle 2|1 \rangle = \tfrac{1}{2} \\ \langle 1|3 \rangle = \langle 1|4 \rangle = \langle 1|5 \rangle = 0 \end{cases} \qquad (III:51)$$

$$\begin{cases} \langle 2|2 \rangle = 1 \\ \langle 2|3 \rangle = \langle 2|4 \rangle = \langle 2|5 \rangle = 0 \end{cases}$$

$$\begin{cases} \langle 3|3 \rangle = \langle 4|4 \rangle = \langle 5|5 \rangle = 1 \\ \langle 3|4 \rangle = \langle 3|5 \rangle = \langle 4|5 \rangle = 0 \end{cases}$$

$$\langle 0|U|0\,\underline{a}_m\rangle \quad = \quad \tfrac{2}{3}\,U_{jjm}^{\alpha}\,\{2+\cos k_o a\}$$

$$\begin{cases}
\langle 1|U|1\,\underline{a}_m\rangle & = & U_{jjm}^{\alpha}\,\{\alpha_{1m} + \alpha_{3m}\} \\
\langle 1|U|2\,\underline{a}_m\rangle & = & \langle 2|U|1\,\underline{a}_m\rangle & = & U_{jjm}^{\alpha}\,\alpha_{1m} \\
\langle 1|U|i\,\underline{a}_m\rangle & = & 0 & [i = 3,4,5]
\end{cases}$$

$$\begin{cases}
\langle 2|U|2\,\underline{a}_m\rangle & = & U_{jjm}^{\alpha}\,\{\alpha_{1m} + \alpha_{5m}\} \\
\langle 2|U|i\,\underline{a}_m\rangle & = & 0 & [i = 3,4,5].
\end{cases}$$

$$\begin{cases}
\langle 3|U|3\,\underline{a}_m\rangle & = & 2\,U_{jjm}^{\alpha}\,\alpha_{1m} \\
\langle 4|U|4\,\underline{a}_m\rangle & = & 2\,U_{jjm}^{\alpha}\,\alpha_{3m} \\
\langle 5|U|5\,\underline{a}_m\rangle & = & 2\,U_{jjm}^{\alpha}\,\alpha_{5m} \\
\langle 3|U|4\,\underline{a}_m\rangle & = & \langle 3|U|5\,\underline{a}_m\rangle & = & \langle 4|U|5\,\underline{a}_m\rangle & = & 0.
\end{cases} \qquad \text{(III:52)}$$

Then, multiplying the matrix elements (52) by $e^{i\underline{K}\cdot\underline{a}_m}$, and summing over nearest neighbours:

$$\sum e^{i\underline{K}\cdot\underline{a}_m}\langle 0|U|0\,\underline{a}_m\rangle \quad = \quad \tfrac{4}{3}U\{2+\cos k_o a\}\{\cos K_x a + \cos K_y a + \cos K_z a\}$$

$$\sum e^{i\underline{K}\cdot\underline{a}_m}\langle 1|U|1\,\underline{a}_m\rangle \quad = \quad 2U\{(1+\cos k_o a)(\cos K_x a + \cos K_y a) + 2\cos K_z a\}$$

$$\sum e^{i\underline{K}\cdot\underline{a}_m}\langle 2|U|2\,\underline{a}_m\rangle \quad = \quad 2U\{(1+\cos k_o a)(\cos K_x a + \cos K_z a) + 2\cos K_y a\}$$

$$\sum e^{i\underline{K}\cdot\underline{a}_m}\langle 1|U|2\,\underline{a}_m\rangle \quad = \quad 2U\{\cos k_o a \cos K_x a + \cos K_y a + \cos K_z a\}$$

$$\sum e^{i\underline{K}\cdot\underline{a}_m}\langle 3|U|3\,\underline{a}_m\rangle \quad = \quad 4U\{\cos k_o a \cos K_x a + \cos K_y a + \cos K_z a\}$$

$$\sum e^{i\underline{K}\cdot\underline{a}_m}\langle 4|U|4\,\underline{a}_m\rangle \quad = \quad 4U\{\cos K_x a + \cos k_o a \cos K_y a + \cos K_z a\} \qquad \text{(III:53)}$$

$$\sum e^{i\underline{K}\cdot\underline{a}_m}\langle 5|U|5\,\underline{a}_m\rangle \quad = \quad 4U\{\cos K_x a + \cos K_y a + \cos k_o a \cos K_z a\}$$

all others = 0.

where:
$$U = U_{jj\underline{m}}^{\alpha} \quad \text{evaluated at } \underline{a}_m = (a,0,0). \qquad \text{(III:54)}.$$

5. The secular equation: Solution.

For brevity denote:

$$L = \cos k_o a \cos K_x a + \cos K_y a + \cos K_z a.$$
$$M = \cos K_x a + \cos k_o a \cos K_y a + \cos K_z a. \qquad \text{(III:55)}$$
$$N = \cos K_x a + \cos K_y a + \cos k_o a \cos K_z a.$$

$$\varepsilon = \frac{1}{2U} \left\{ E(\underline{K}) - E_{1s}^{(5)} \right\} \qquad \text{(III:56)}$$

Then, making use of the results of (51) and (53), equation (27) becomes:

$$\begin{vmatrix} (L+M)-\varepsilon & L-\varepsilon/2 & 0 & 0 & 0 \\ L-\varepsilon/2 & (L+N)-\varepsilon & 0 & 0 & 0 \\ 0 & 0 & 2L-\varepsilon & 0 & 0 \\ 0 & 0 & 0 & 2M-\varepsilon & 0 \\ 0 & 0 & 0 & 0 & 2N-\varepsilon \end{vmatrix}$$

$$= (2L-\varepsilon)(2M-\varepsilon)(2N-\varepsilon) \begin{vmatrix} (L+M)-\varepsilon & L-\varepsilon/2 \\ \\ L-\varepsilon/2 & (L+N)-\varepsilon \end{vmatrix}$$

$$= 0 \qquad \text{(III:57)}$$

The roots of equation (57) are:

$$\begin{cases} \varepsilon_1 = \frac{2}{3} \left\{ (L+M+N) + \sqrt{L^2+M^2+N^2-LM-LN-MN} \right\} \\ \varepsilon_2 = \frac{2}{3} \left\{ (L+M+N) - \sqrt{L^2+M^2+N^2-LM-LN-MN} \right\} \end{cases}$$

$$\qquad \text{(III:58)}$$

$$\begin{cases} \varepsilon_3 = 2L \\ \varepsilon_4 = 2M \\ \varepsilon_5 = 2N \end{cases}$$

Then, making use of these results in conjunction with the

requirement that $\Psi_{\underline{K}}(\underline{r})$ be normalized over the entire crystal, the corresponding d-coefficients may be obtained from equation (12):

$$\begin{cases} \varepsilon_1: & d_1, d_2 \neq 0. \quad \text{All others} = 0. \\ \varepsilon_2: & d_1, d_2 \neq 0. \quad \text{All others} = 0. \end{cases} \tag{III:59}$$

$$\begin{cases} \varepsilon_3: & d_3 = 1. \quad \text{All others} = 0. \\ \varepsilon_4: & d_4 = 1. \quad \text{All others} = 0. \\ \varepsilon_5: & d_5 = 1. \quad \text{All others} = 0. \end{cases} \tag{III:60}$$

In the isolated-impurity problem, as noted in Section B.1 of this chapter, group-theoretical considerations show that the five-fold degeneracy of the upper 1s state is only approximate. There are actually two sets of degenerate states: one ($\psi^{(1)}, \psi^{(2)}$) corresponding to the group E, and the other ($\psi^{(3)}, \psi^{(4)}, \psi^{(5)}$) corresponding to the group T_3 (Kohn and Luttinger, 1955 c). In the present approximation, therefore, the results of (59 and (60) indicate that the states corresponding to T_3 form bands independently of each other, while the states corresponding to E mix.

Substitution of (51) and (53) into equation (28) gives the energy for the non-degenerate 1s state in the spherical-potential effective-mass approximation as:

$$E - E_{1s}^{(o)} = \frac{4}{3} U \{2 + \cos k_o a\} \{\cos K_x a + \cos K_y a + \cos K_z a\} \tag{III:61}$$

For a simple comparison of the line broadenings described by (58) and (61), consider the case when $\cos k_o a = 1$. In this

instance, all the energies reduce to:

$$E - E_{1s} = 4U \{ \cos K_x a + \cos K_y a + \cos K_z a \} \tag{III:62}$$

The implication of (62) is that the degenerate and non-degenerate 1s levels broaden at approximately the same rate. Clearly this behaviour is due to the fact that spherical-potential wave functions were used throughout the calculation. However, it was assumed in the derivation of (27) and (28) that the non-degenerate and five-fold degenerate levels were sufficiently far apart to broaden independently. For this assumption to be valid, corrections to the spherical-potential approximation should have been taken into account.

As the corrected degenerate 1s levels are displaced relatively little from their spherical-potential values (Kohn and Luttinger, 1955 c), the results of (58) will be taken to apply in this case without alteration. The non-degenerate 1s level, on the other hand, is considerably lower in the exact formulation of the problem than it is in the spherical-potential approximation (Kohn and Luttinger, 1955 a and c). In this case, therefore, a corrected wave-function should have been used.[*] It is expected that if the correction were carried out in detail, the broadening of the non-degenerate level would be negligible for the impurity lattice spacings considered. This contention is based on the fact that the

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[*] See Section C.3 of this chapter.

correct $1s^{(0)}$ wave function would be much less extensive than its spherical-potential counterpart, so that $1s^{(0)}$ functions centered on neighbouring donor atoms would over-lap much less than the corresponding $1s^{(5)}$ functions.

6. Energy-band broadening.

Baltensperger (1953) has calculated the broadening of the 1s and 2s-2p bands of equation (1) assuming a single-minimum conduction band and using purely hydrogenic effective-mass wave functions. He finds that the lower edge of the 2p band is depressed:

$$\Delta E^{2p_0} = 0.15 \frac{e^2}{2\kappa a^*} \cong 5 \times 10^{-3} \, eV. \tag{III:63}$$

below the isolated-impurity level when $r_s = 3a^*$. Since:

$$r_s^3 \equiv \frac{3}{4\pi} a^3 \tag{III:64}$$

the corresponding value of the impurity lattice spacing is $a = 5a^*$. This spacing gives an impurity concentration, in silicon, of $1 \times 10^{18}/cm^3$.

At $a = 5a^*$, the results of (58) indicate that the upper edge of the five-fold degenerate 1s band is raised above the isolated-impurity level by at most:

$$\Delta E^{1s}_{max} = -12U \cong 1.3 \times 10^{-3} \, eV. \tag{III:65}$$

and at least:

$$\Delta E^{1s}_{min} = -4U \cong 0.3 \times 10^{-3} \, eV. \tag{III:66}$$

Using the values of the isolated-impurity level energies listed by Kohn and Luttinger (1955 c, Table VII), the separation of the $1s^{(5)}$ and $2p_0^{(6)}$ levels is:

$$\delta E_{isolated} = (3.2 \times 10^{-2} - 1.1 \times 10^{-2})ev. = 2.1 \times 10^{-2} ev. \quad (III:67)$$

By (63), (65), and (67), the separation at $a = 5a^*$ is at least:

$$\delta E_{4a^*} = (2.1 \times 10^{-2} - 0.5 \times 10^{-2} - 0.1 \times 10^{-2})ev. \\ = 1.5 \times 10^{-2} ev. \quad (III:68)$$

Hence at $a = 5a^*$, the separation has dropped to about two-thirds of its value in the isolated-impurity case.

Since Baltensperger's results are based on the cellular method, they are more applicable at small values of a than are the tight-binding results of (58). Using Baltensperger's figures as a rough guide, it is found that the 1s and 2s-2p bands overlap near $a = 3a^*$ (impurity concentration $4 \times 10^{18}/cm^3$). Hence any investigation of the $1s^{(0)} \longrightarrow 1s^{(5)}$ transition must be carried out for an impurity lattice spacing greater than $3a^*$, so that the line will not be obscured by that for the $1s \longrightarrow 2p_0$ transition.

C. Optical Matrix Elements.

1. Simplification of the matrix elements.

In the electric-dipole approximation, the optical matrix elements of interest are:[*]

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[*] See Chapter IV.

$$\langle S\underline{K}'|p_\sigma|0\underline{K}\rangle = \int \Psi_{\underline{K}'}^{(S)*} p_\sigma \Psi_{\underline{K}}^{(0)} d\underline{r}$$

$$= \frac{1}{N} \sum_{i=1}^{S} d_i^* \sum_{n'n} e^{i\underline{K}'\cdot \underline{a}_{n'}} e^{i\underline{K}\cdot \underline{a}_n} \langle i \, 1s \, \underline{a}_{n'}|p_\sigma|0 \, 1s \, \underline{a}_n\rangle$$

$$= \frac{m}{i\hbar} \frac{1}{N} \sum_{i=1}^{S} d_i^* \left\{ \sum_{n'n} e^{i\underline{K}'\cdot \underline{a}_{n'}} e^{i\underline{K}\cdot \underline{a}_n} \right.$$

$$\left. \langle i \, 1s \, \underline{a}_{n'}|[x_\sigma,\mathcal{H}]|0 \, 1s \, \underline{a}_n\rangle \right\}$$

$$\text{(III:69)}$$

making use of (II:26). Under the assumption that all

impurities are substitutional, so that each vector of the

impurity lattice is also a vector of the unperturbed lattice,

$$V_p(\underline{r}) = V_p(\underline{r}-\underline{a}_n)$$

so that:

$$\mathcal{H}|i\ell\underline{a}_n\rangle = E_\ell^i |i\ell\underline{a}_n\rangle \tag{III:70}$$

It then follows from (69) and (70) that:

$$\langle S\underline{K}'|p_\sigma|0\underline{K}\rangle = -\frac{m}{i\hbar}\left\{E_{1s}^{(S)}(\underline{K}') - E_{1s}^{(0)}(\underline{K})\right\}\frac{1}{N} \tag{III:71}$$

$$\times \sum_{i=1}^{S} d_i^* \sum_{nn'} e^{-i\underline{K}'\cdot\underline{a}_{n'}} e^{i\underline{K}\cdot\underline{a}_n} \langle i \, 1s \, \underline{a}_{n'}|x_\sigma|0 \, 1s \, \underline{a}_n\rangle$$

Now by a simple extension of the result of (II:36),

$$\langle i \, 1s \, \underline{a}_{n'}|x_\sigma|0 \, 1s \, \underline{a}_n\rangle = \langle i\underline{a}_{n'}|x_\sigma|0\underline{a}_n\rangle \tag{III:72}$$

Hence (71) may be written:

$$\langle 5\underline{K}'|p_\sigma|0\underline{K}\rangle = -\frac{m}{i\hbar}\left\{E^{(5)}_{1s}(\underline{K}') - E^{(0)}_{1s}(\underline{K})\right\}\frac{1}{N}$$

$$\times \sum_i d_i^* \sum_{\underline{n}'\underline{n}} e^{-i\underline{K}'\cdot\underline{a}_{\underline{n}'}} e^{i\underline{K}\cdot\underline{a}_{\underline{n}}} \langle i\underline{a}_{\underline{n}'}|x_\sigma|0\,\underline{a}_{\underline{n}}\rangle$$

$$= -\frac{m}{i\hbar}\left\{E^{(5)}_{1s}(\underline{K}') - E^{(0)}_{1s}(\underline{K})\right\}\frac{1}{N}$$

$$\times \sum_i d_i^* \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}} \langle i|x_\sigma|0\,\underline{a}_{\underline{m}}\rangle$$

$$\times \sum_{\underline{n}'} e^{i(\underline{K}-\underline{K}')\cdot\underline{a}_{\underline{n}'}} \qquad\qquad \text{(III:73)}$$

(shifting the origin to $\underline{a}_{\underline{n}'}$, and defining $\underline{a}_{\underline{m}} = \underline{a}_{\underline{n}} - \underline{a}_{\underline{n}'}$).

By (73), therefore:

$$\langle 5\underline{K}'|p_\sigma|0\underline{K}\rangle = -\frac{m}{i\hbar}E_{5,0}(\underline{K})\,\delta_{\underline{K},\underline{K}'}\sum_i d_i^* \sum_{\underline{m}} e^{i\underline{K}\cdot\underline{a}_{\underline{m}}}\langle i|x_\sigma|0\,\underline{a}_{\underline{m}}\rangle \quad \text{(III:74)}$$

where:

$$E_{5,0}(\underline{K}) = E^{(5)}_{1s}(\underline{K}) - E^{(0)}_{1s}(\underline{K}) \qquad\qquad \text{(III:75)}$$

and

$$\delta_{\underline{K},\underline{K}'} = \frac{1}{N}\sum_{\underline{n}'} e^{i(\underline{K}-\underline{K}')\cdot\underline{a}_{\underline{n}'}} \qquad\qquad \text{(III:75')}$$

$\delta_{\underline{K},\underline{K}'}$ is a Kronecker δ in three dimensions.[*] Its value is one whenever $\underline{K} = \underline{K}'$, and zero whenever $\underline{K} \neq \underline{K}'$.

2. Evaluation of integrals in the spherical-potential approximation.

The integrals involved in evaluating $\langle i|x_\sigma|0\,\underline{a}_{\underline{m}}\rangle$ (for $i = 1,2,3,4,5$) are similar to those defined in (35) and (36), and will be denoted by $X^{\alpha,\sigma}_{jj'\underline{m}}$, $X^{\beta,\sigma}_{jj'\underline{m}}$, $X^{\beta'\sigma}_{jj'\underline{m}}$, and $X^{\gamma\sigma}_{jj'\underline{m}}$. For example:

$$X^{\alpha\sigma}_{jj'\underline{m}} = \frac{1}{(2\pi)^3}\int x_\sigma\, F_j(\underline{r})\, F_{j'}(\underline{r}-\underline{a}_{\underline{m}})\,\cos\underline{k}_j\cdot\underline{r}\,\cos\underline{k}_{j'}\cdot\underline{r}\;d\underline{r} \qquad \text{(III:76)}$$

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[*] See Appendix B.

If spherical-potential effective-mass wave functions
are used for the evaluation of the integrals (76), it is
found that $X_{jj'\underline{m}}^{\alpha\sigma}$ and $X_{jj'\underline{m}}^{\gamma\sigma}$ vanish identically in almost all
cases of interest. Furthermore, the only non-zero integrals
of this type (certain of the $X_{jj'\underline{m}}^{\alpha\sigma}$ for which $j \neq j'$ and
$\underline{m} \neq 0$), as well as the integrals $X_{jj'\underline{m}}^{\beta\sigma}$ and $X_{jj'\underline{m}}^{\beta'\sigma}$, are
extremely small, being of the order of 1×10^{-6} B. Con-
sequently the matrix elements are very much smaller than
those for $1s \longrightarrow 2p$ transitions.[*]

As was pointed out in Chapter I, however, the assumption
of a spherically symmetric perturbing potential is incorrect.
It is therefore not a valid approximation to make use of the
procedure outlined in the last paragraph. Corrections to
the spherical-potential approximation must be considered.

3. Corrections to the spherical-potential approximation.

In Chapter I it was pointed out that the most appropriate
method of correcting the spherical-potential shallow-impurity
approximation would be to apply a tetrahedrally symmetric
perturbation to the hamiltonian of equation (II:7). This
perturbation would have to account for:

    i. Deviations from the approximation of large
       impurity-electron orbits.

    ii. Departures from spherical symmetry in general.
Unfortunately, the form of the required perturbing potential
is not known; it therefore becomes necessary to make use

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[*] See Chapter II, Section B.

of less exact techniques of correction.

Kohn and Luttinger (1955 a) have proposed such a technique. They argue that except in the immediate vicinity of the impurity nucleus, the spherical-potential approximation will be very nearly valid. Consequently, if the spherical-potential effective-mass equation is solved in an "exterior" region which excludes a small volume surrounding the donor atom, and the resulting wave function is joined to an exact solution of (II:6) in the "interior" region to determine the energy, an improved theory should result. In order to avoid the difficulties inherent in the second step of this procedure, Kohn and Luttinger have made use of the experimentally observed ground state ionization energy to determine the exterior wave function, and then have made a rough estimate of the solution for the interior region. They have found that their results are approximately consistent with the requirement that the two solutions join smoothly.

The experimental ionization of a phosphorus donor in silicon is (Morin et al., 1954)

$$E - \varepsilon_0 = -0.044 \text{ ev.} \tag{III:77}$$

Kohn and Luttinger (1955 a) show that if this value of $(E - \varepsilon_0)$ is substituted into the effective mass equation (II:27), the solution of the equation is:

$$F(x) = C \left\{ \frac{n}{2x} W_{n, \frac{1}{2}} \left(\frac{2x}{n} \right) \right\} \tag{III:78}$$

where:

$$x = r/a^*$$
$$n = 0.81$$
$$C = \text{normalization constant}$$
$$W = \text{the Whittaker function.}$$

(III:79)

The function (78) has the limiting behaviour:

$$F(x) = C e^{-x/n} \left\{ \frac{(1-n)}{2x} - (1-n)\ln 2x + 1 \right\} \qquad \text{as} \quad x \downarrow 0.$$

(III:80)

$$F(x) = C e^{-x/n} \left\{ \frac{2x}{n} \right\}^{n-1} \qquad \text{as} \quad x \uparrow \infty.$$

Thus $F(x)$ diverges near the origin. (This behaviour is due to the inapplicability of the potential $-\dfrac{e^2}{\kappa r}$ close to the donor nucleus.) Kohn and Luttinger therefore round off the solution within the Wigner-Seitz unit sphere of radius $0.08 a^*$ enclosing the impurity atom.

The following procedure was used to obtain a usable approximation to the function $F(x)$:

i. The approximations (80), divided by the normalization constant C, were plotted, and were found to be close together near $x = 4.5$. Accordingly, the two functions were joined at this value to give $F(x)/C$ approximately for all x.

ii. For large values of x the approximation to $F(x)/C$ given by (i) was found to be fitted very closely by the expression:

$$0.65 \exp (-1.25 \; x) \qquad \text{(III:81)}$$

iii. For small values of x, F(x)/C was assumed
to be approximately of the form:

$$0.65 \exp (-1.25 \; x) + p \exp (-qx) \qquad \text{(III:82)}$$

where q is greater than 1.25, so that the
second exponential decays more rapidly
than the first.

iv. The value of p was determined by requiring
the expression (82) to go to 2.30 at x = 0.
According to (i), this value is slightly
greater than the value of F(x)/C at the
Wigner-Seitz sphere boundary.)

v. The value of q was determined by requiring
that (82) have the same normalization as the
function plotted in (i). The result was:

$$F(x)/C = 0.65 \exp (-1.25 \; x) \qquad \text{(III:83)}$$
$$+ \; 1.65 \exp (-3.00 \; x)$$

(83) is compared graphically with the result
of (i) in Figure 1.

vi. The value of C was determined by integrating
the curve of (i) numerically, and requiring
that:

$$\int_{\text{all space}} |F(x)|^2 \; d\underline{r} = (2\pi)^3 \qquad \text{(III:84)}$$

The result was:

$$|C|^2 = (0.59)(2\pi)^3 \qquad \text{(III:85)}$$

vii. (85) was substituted into (83) to give for
the corrected ground state effective-mass
wave function the expression:

$$F^\circ(r) = (2\pi)^{3/2} \left\{ \frac{0.89}{\sqrt{\pi}(a^\circ)^{3/2}} e^{-1.25\, r/a^\circ} + \frac{2.24}{\sqrt{\pi}(a^\circ)^{3/2}} e^{-3\, r/a^\circ} \right\} \qquad \text{(III:86)}$$

viii. As a very rough check on the accuracy of (86)
with respect to energy, the radius for which
the radial probability distribution (Pauling
and Wilson, 1935) has its maximum was plotted
as a function of energy for the 1s, 2s, and 3s
states of a hydrogen-like atom (Figure 2).
The probability distribution maximum of (86)
was found to be consistent with an energy of
-0.044 ev. in this scheme.

If the requirements of tetrahedral symmetry are to be
satisfied[*], the effective mass wave functions used in
connection with the five-fold degenerate 1s states must be
different from those used with the non-degenerate ground state.
As the energy of the five-fold degenerate level is not known
accurately, however, the corrections to be used in this case
are difficult to determine. Kohn and Luttinger (1955 c) have

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[*] See Chapter I.

estimated that the level corresponds to an energy of about -0.032 ev. Using this value, and applying the procedure used above for the ground state, an approximate wave function similar to (86) should be obtained. As the energy used is so close to the effective-mass value (-0.029 ev.), it will be assumed that the correction is small enough for the effective-mass functions to be used without alteration. An estimate of the error introduced by this assumption will be made in conjunction with the evaluation of optical matrix elements.[*]

4. Evaluation of integrals in the corrected spherical-potential approximation.

Using the corrected wave functions introduced in the last section, the integrals (76) may be evaluated approximately.

$$X_{jj'm}^{\alpha\sigma} = \frac{1}{(2\pi)^3} \int x_\sigma F_j(r) F_{j'}^\circ(r-a_m) \cos^2 k_j \cdot r \, dr$$

Hence, if $m = 0$; or if $m \neq 0$, but a_m is perpendicular to the σ-axis,

$$X_{jjm}^{\alpha\sigma} = 0 \qquad\qquad (III:87)$$

since the integrand is an odd function. If a_m is parallel to the σ-axis, on the other hand,

$$X_{jjm}^{\alpha\sigma} = \frac{1}{(2\pi)^3} \cdot \frac{1}{2} \left\{ \int x_\sigma F_j(r) F_j^\circ(r-a_m) \, dr \right.$$
$$\left. + \int x_\sigma F_j(r) F_j^\circ(r-a_m) \cos 2k_j \cdot r \, dr \right\} \qquad (III:88)$$

---

[*] See Section C.4 of this chapter.

The second integral in (88) cannot be evaluated analytically. By the arguments of Chapter II, Section C, however, this integral should be small. Numerically, for $|\underline{a}_m| = 4\alpha^*$:

$$\frac{1}{(2\pi)^3} \int z\, F(\underline{r})\, F^\circ(\underline{r}-\underline{a}_m)\, d\underline{r} \;\cong\; -(2.57 \times 10^{-2})\,\alpha^* \qquad \text{(III:89)}$$

$$\frac{1}{(2\pi)^3} \int z\, F(\underline{r})\, F^\circ(\underline{r}-\underline{a}_m)\, \cos 2k_o z\, d\underline{r} \;\cong\; -(2.88 \times 10^{-3})\,\alpha^* \qquad \text{(III:90)}$$

Hence at this value of $|\underline{a}_m|$, the second integral is smaller than the first by approximately a factor of ten, and has the same sign.

It is also to be expected that integrals of the form:

$$\frac{1}{(2\pi)^3} \int x_{r'}\, F_j(\underline{r})\, F_j^\circ(\underline{r}-\underline{a}_m)\, \cos^2 \underline{k}_j \cdot \underline{r}\, d\underline{r} \qquad \text{(III:91)}$$

will differ in value from (88). However, this difference is clearly small; it vanishes altogether when the Bohr radii A and B are replaced by their average, α^*. Consequently, it will be assumed that all non-zero integrals of the form (91) are approximately equal to:

$$X_a^z = \frac{1}{(2\pi)^3} \cdot \frac{1}{2} \int z\, F(\underline{r})\, F^\circ(\underline{r}-\underline{a}_m)\, d\underline{r} \qquad (\underline{a}_m = [0,0,a])$$

$$= \frac{\alpha^*}{16}\left(\frac{a}{\alpha^*}\right)^4 \left\{ 0.89\left[A_3\left(1.13\frac{a}{\alpha^*}\right)B_1\left(0.13\frac{a}{\alpha^*}\right) - A_1\left(1.13\frac{a}{\alpha^*}\right)B_3\left(0.13\frac{a}{\alpha^*}\right)\right] \right.$$

$$\left. + 2.24\left[A_3\left(2\frac{a}{\alpha^*}\right)B_1\left(\frac{a}{\alpha^*}\right) - A_1\left(2\frac{a}{\alpha^*}\right)B_3\left(\frac{a}{\alpha^*}\right)\right] \right\} \qquad \text{(III:92)}$$

where:

$$A_s(\gamma) = \int_1^\infty \xi^s e^{-\gamma \xi} \, d\xi$$

$$B_t(\gamma) = \int_{-1}^1 \eta^t e^{-\gamma \eta} \, d\eta \qquad \text{(III:93)}$$

Values of these functions have been tabulated by Rosen (1931) for arguments greater than 1.5. For the values used here, see Figures 3a and 3b. X_a^Z is plotted as a function of a in Figure 4.

Other integrals of interest are:

$$X_{jjm}^{\beta\sigma} = X_{jjm}^{\beta'\sigma} = \frac{1}{(2\pi)^3} \int x_\sigma F_j(\underline{r}) F_j^0(\underline{r}-\underline{a}_m) \cos \underline{k}_j \cdot \underline{r} \, \sin \underline{k}_j \cdot \underline{r} \, d\underline{r}$$

$$= \frac{1}{(2\pi)^3} \cdot \frac{1}{2} \int x_\sigma F_j(\underline{r}) F_j^0(\underline{r}-\underline{a}_m) \sin 2\underline{k}_j \cdot \underline{r} \, d\underline{r} \qquad \text{(III:94)}$$

For $\underline{m} \neq 0$ the integrals (94) would be expected to have values of the same order of magnitude as those in (90). In any case, $X_{jjm}^{\beta\sigma}$ is less than or equal to $X_{jj0}^{\beta\sigma}$. The latter integral is non-zero and easy to evaluate. It is found that:

$$X_{jj0}^{\beta\sigma} \cong + (1.5 \times 10^{-3}) \, a^* \qquad \text{(III:95)}$$

Comparing this value with (89), it is seen that $X_{jjm}^{\beta\sigma}$ will be at least a factor of ten less than X_a^σ, though the two integrals will not necessarily have the same sign.

Finally,

$$X_{jjm}^{\gamma\sigma} = \frac{1}{(2\pi)^3} \int x_\sigma F_j(\underline{r}) F_j^0(\underline{r}-\underline{a}_m) \sin^2 \underline{k}_j \cdot \underline{r} \, d\underline{r}$$

$$= \frac{1}{(2\pi)^3} \cdot \frac{1}{2} \left\{ \int x_\sigma F_j(\underline{r}) F_j^0(\underline{r}-\underline{a}_m) \, d\underline{r} - \int x_\sigma F_j(\underline{r}) F_j^0(\underline{r}-\underline{a}_m) \cos 2\underline{k}_j \cdot \underline{r} \, d\underline{r} \right\}$$

Clearly, if $\underline{m} = 0$; or if $\underline{a}_m$ is perpendicular to the σ-axis,

$$X_{jjm}^{\gamma\sigma} = 0 \qquad \text{(III:96)}$$

If $\underline{m} \neq 0$ and $_m$ is parallel to the -axis,

$$X_{jjm}^{\gamma\gamma} \cong X_{jjm}^{\alpha\sigma} \cong X_{gm}^{\sigma} \qquad \text{(III:97)}$$

As in the development leading to (47) and (48), all integrals involving two different conduction-band minima (i.e. $j \neq j'$) will be neglected. By analogy with (36), it is expected that these integrals will be considerably smaller than those listed above.

As was pointed out in Section C.3, corrections should be applied to the effective-mass functions associated with the five-fold degenerate 1s level as well as to those associated with the ground state. Approximately, the corrected functions should have the same form as (86), namely:

$$\frac{(2\pi)^{3/2}}{\sqrt{\pi}(a^*)^{1/2}} \left\{ P e^{-Qr/a^*} + S e^{-Tr/a^*} \right\}$$

where the values of P, Q, S, and T are determined by the energy of the five-fold degenerate level. If these functions are used, corresponding corrections must be applied to the integrals in (87) to (97), all of which may be expressed in terms of X_a^z. The dependence of this quantity on the five-fold degenerate level energy is shown in Figure 5. Clearly the difference between values for $E_{1s}^{(5)} - \epsilon_o = -0.029$ ev. and $E_{1s}^{(5)} - \epsilon_o = -0.032$ ev. is sufficiently small for the use of

the 0.029 ev. energy to be a reasonable approximation.

5. Evaluation of the matrix elements.

The integrals in (87) to (97) may now be used to evaluate the matrix elements $\langle i | x_\sigma | 0 \underline{a}_m \rangle$, which may then be substituted into (75).

$$
\begin{cases}
\langle 1 | x_\sigma | 0 \, \underline{a}_m \rangle \cong \sqrt{2/3} \; (\alpha_{1m} - \alpha_{3m}) \, X^\sigma_{\underline{a}_m} \\
\langle 2 | x_\sigma | 0 \, \underline{a}_m \rangle \cong \sqrt{2/3} \; (\alpha_{1m} - \alpha_{5m}) \, X^\sigma_{\underline{a}_m}
\end{cases}
\tag{III:98}
$$

$$
\begin{cases}
\langle 3 | x_\sigma | 0 \, \underline{a}_m \rangle \cong - \frac{2i}{\sqrt{3}} \, \beta_{1m} \, X^\sigma_{\underline{a}_m} \\
\langle 4 | x_\sigma | 0 \, \underline{a}_m \rangle \cong - \frac{2i}{\sqrt{3}} \, \beta_{3m} \, X^\sigma_{\underline{a}_m} \\
\langle 5 | x_\sigma | 0 \, \underline{a}_m \rangle \cong - \frac{2i}{\sqrt{3}} \, \beta_{5m} \, X^\sigma_{\underline{a}_m}
\end{cases}
$$

$$\tag{III:99}$$

Substituting (98) and (99) into (75), restricting the summation to nearest neighbours, and noting that:

$$
\begin{aligned}
X^\sigma_{-\underline{a}_m} &= \frac{1}{(2\pi)^3} \int x_\sigma \, F(\underline{r}) \, \overset{\bullet}{F}(\underline{r}+\underline{a}_m) \, d\underline{r} \\
&= \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \; x_\sigma \, F(\underline{r}) \, \overset{\bullet}{F}(\underline{r}+\underline{a}_m) \\
&= - \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \; x_\sigma \, F(\underline{r}) \, F^\circ(\underline{r}-\underline{a}_m) \\
&= - X^\sigma_{\underline{a}_m}
\end{aligned}
\tag{III:100}
$$

it is found that:

$$\langle i\underline{K}'|p_\sigma|0\underline{K}\rangle = -\frac{m}{i\hbar} E_{5,0}(\underline{K})\, \delta_{KK'}$$

$$\times \left\{ 2d_1^*\sqrt{\tfrac{2}{3}} \left[(\cos k_0 a - i)(\sin\{K_x a\} X_1^\sigma - \sin\{K_y a\} X_3^\sigma) \right] \right.$$

$$+ 2d_2^*\sqrt{\tfrac{2}{3}} \left[(\cos k_0 a - i)(\sin\{K_x a\} X_1^\sigma - \sin\{K_z a\} X_5^\sigma) \right]$$

$$- d_3^* \frac{4i}{\sqrt{3}} \sin k_0 a\, \cos\{K_x a\}\, X_1^\sigma \qquad\qquad \text{(III:101)}$$

$$- d_4^* \frac{4i}{\sqrt{3}} \sin k_0 a\, \cos\{K_y a\}\, X_3^\sigma$$

$$\left. - d_5^* \frac{4i}{\sqrt{3}} \sin k_0 a\, \cos\{K_z a\}\, X_5^\sigma \right\}$$

For simplicity, consider:

$$\langle i\underline{K}'|p_z|0\underline{K}\rangle = -\frac{m}{i\hbar} E_{5,0}(\underline{K})\, \delta_{KK'}\, X_a^z$$

$$\times \left\{ 2d_2^*\sqrt{\tfrac{2}{3}} (1-\cos k_0 a) \sin K_z a \qquad\qquad \text{(III:102)} \right.$$

$$\left. - d_5^* \frac{4i}{\sqrt{3}} \sin k_0 a\, \cos K_z a \right\}$$

By (59) and (60), d_2 and d_5 are mutually exclusive. Hence only one of the bracketted terms in (102) will be non-zero. Expressions similar to (102) will arise for other choices of σ, the main difference being that d_2^* will be replaced by d_1^*, or by $-(d_1^* + d_2^*)$. Since d_1 and d_2 both depend on $\underline{K}$, and thus lead to cumbersome expressions, it will be assumed for simplicity that each of the coefficients involving these terms has a magnitude equal to one.

Hence, in the calculation of the absorption coefficient, two matrix elements are of importance:

$$\langle 2\underline{K}'|p_\sigma|0\underline{K}\rangle \cong -\frac{m}{i\hbar} 2\sqrt{\tfrac{2}{3}} (1-\cos k_0 a)\, E_{5,0}^{(2)}(\underline{K})\, \delta_{KK'}\, X_a^z \sin K_z a \qquad \text{(III:103)}$$

$$\langle 5\underline{K}'|p_\sigma|0\underline{K}\rangle \cong \frac{m}{\hbar} \frac{4}{\sqrt{3}} \sin k_0 a\, E_{5,0}^{(5)}(\underline{K})\, \delta_{KK'}\, X_a^z \cos K_z a. \qquad \text{(III:104)}$$

Both of these matrix elements vanish when $\cos k_o a = 1$,
but their sum is large when $\cos k_o a = 0$ or -1. Consequently
the combined effect of these matrix elements will be
relatively important, except in the neighbourhood of impurity
lattice spacings for which $k_o a$ is an even integral multiple
of π. (Clearly this behaviour will not be observable, since
in reality the impurity lattice spacing has only the
significance of an average distance between impurities —
the randomness of the impurity distribution removes effects
which are dependent upon the assumption of regularity.)

CHAPTER IV

Optical Absorption by Transitions between Impurity Bands in Phosphorus-doped Silicon.

A. Derivation of the Absorption Coefficient.

1. Transition probabilities.

In treating the phenomena of absorption and induced emission of electromagnetic radiation by atomic systems, the most commonly used approach is the semi-classical approximation. This approximation, in which the radiation field is treated classically and the atomic system is treated quantum-mechanically, leads to essentially correct results, and has the great advantage of simplicity over more accurate treatments involving quantization of the field. Consequently the semiclassical theory will be used in this thesis in obtaining an expression for the coefficient of absorption.

Consider an atomic system in state $|\ell\rangle$ upon which is incident a polarized beam of photons, of intensity $I(\omega)d\omega$ in the angular frequency range $(\omega, \omega + d\omega)$. Using first-order time-dependent perturbation theory, Schiff (1955, Chapter X, Section 35) has shown that the probability per unit time of a transition from $|\ell\rangle$ to another state $|u\rangle$, due to absorption of a photon from the incident beam, is:

$$P_{u,\ell} = \int_{-\infty}^{\infty} d\omega \; \frac{8\pi e^2}{m^2 c \omega^2} \; I(\omega) \; |M_{u\ell}(\gamma_\omega)|^2 \; \frac{\sin^2\{\tfrac{1}{2}(\omega_{u\ell} - \omega)t\}}{\{\omega_{u\ell} - \omega\}^2 \, t} \qquad (IV:1)$$

where:

e = electronic charge

m = electron mass

c = velocity of light

$\underline{\eta}\omega$ = photon wave-number vector, of magnitude $\frac{\omega}{c}$.

$$\omega_{u\ell} = \frac{|E_u - E_\ell|}{\hbar} \qquad \text{(where } E_u \text{ and } E_\ell \text{ are the energies of } |u\rangle \text{ and } |\ell\rangle \text{ respectively)} \qquad \text{(IV:2)}$$

$$M_{u\ell}(\underline{\eta}\omega) = \langle u | e^{i\underline{\eta}\omega\cdot\underline{r}} \nabla_\sigma | \ell \rangle \qquad\qquad \text{(IV:3)}$$

∇_σ = component of grad in the direction of

polarization.

Since the function

$$\frac{\sin^2\{\frac{1}{2}(\omega_{u\ell}-\omega)t\}}{\{\omega_{u\ell}-\omega\}^2 t}$$

is sharply peaked at $\omega = \omega_{u\ell}$, and:

$$\int_{-\infty}^{\infty} d\omega \; \frac{\sin^2\{\frac{1}{2}(\omega_{u\ell}-\omega)t\}}{\{\omega_{u\ell}-\omega\}^2 t} \;\; = \;\; \frac{\pi}{2}$$

equation (1) may be written approximately as:

$$P_{u\ell} = \int_{-\infty}^{\infty} d\omega \; \frac{4\pi^2 e^2}{m^2 c \omega^2} \; I(\omega) \, |M_{u\ell}(\underline{\eta}\omega_{u\ell})|^2 \; \delta(\omega_{u\ell}-\omega)$$

$$\equiv \int_{-\infty}^{\infty} d\omega \; P_{\omega;u\ell} \qquad\qquad \text{(IV:4)}$$

so that:

$$P_{\omega;u\ell} = \frac{4\pi^2 e^2}{m^2 c \omega^2} \; I(\omega) \, |M_{u\ell}(\underline{\eta}\omega_{u\ell})|^2 \; \delta(\omega_{u\ell}-\omega) \qquad\qquad \text{(IV:5)}$$

If $I(\omega)$ is approximately constant at the frequencies

considered, it may be replaced in (5) by $\overline{I}_\omega$, its average over unit frequency range at ω. $\mathcal{P}_{\omega;u\ell}$ then becomes the probability per unit time of a transition between $|\ell\rangle$ and $|u\rangle$ due to the absorption of a photon of frequency ω from a beam of intensity $\overline{I}_\omega$ per unit frequency range.

The intensity may also be written:

$$I(\omega)\,d\omega = n(\omega)\,\hbar\omega\,d\omega. \tag{IV:6}$$

where $n(\omega)\,d\omega$ is the number of photons in $(\omega,\ \omega + d\omega)$ crossing unit area per unit time. In terms of averages over unit frequency range:

$$\overline{I}_\omega = \overline{n}_\omega \hbar\omega \tag{IV:7}$$

where $\overline{n}_\omega$ is the number of photons crossing unit area per unit time per unit frequency range about ω. Then, substituting (7) into (5), the probability per unit time of a transition between $|\ell\rangle$ and $|u\rangle$ due to the absorption of a photon of frequency ω from an incident beam of $\overline{n}_\omega$ particles per unit area per unit time per unit frequency range about ω is found to be:

$$\mathcal{P}_{\omega;u\ell} = \frac{4\pi^2 e^2}{m^2 c\omega}\,\overline{n}_\omega\hbar\,|M_{u\ell}(\eta\omega_{u\ell})|^2\,\delta(\omega_{u\ell} - \omega). \tag{IV:8}$$

2. Specialization to a rigid lattice.

If the results of section 1 are applied to a crystalline array of atoms, the wave-vectors $|\ell\rangle$ and $|u\rangle$ will depend upon both the coordinates of the electrons within the individual

atoms, and the coordinates of the atoms themselves within the lattice. In this form solution of the problem presents formidable difficulties, since the lattice coordinates change as the atoms vibrate about their equilibrium positions. These difficulties may be reduced (D.L. Dexter, 1958, Chapter II, Section 5) by using the adiabatic approximation to partially separate the two types of coordinate dependence, and the Condon approximation to average over the dependence on the coordinates of the lattice. However, further simplification is to be desired.

Such simplification may be achieved by assuming that the lattice in question consists of a completely rigid array of atoms.[*] In this case, $|\ell\rangle$ and $|u\rangle$ refer solely to electronic states which may be denoted by $|\ell \underline{K}\rangle$ and $|u \underline{K}'\rangle$. The probability (8) then becomes:

$$P_{\omega; u\ell}(\bar{n}_\omega, \underline{K}, \underline{K}') = \frac{4\pi^2 e^2}{m^2 c} \frac{\hbar}{\omega} \bar{n}_\omega \, |M_{u\ell}(\underline{K}, \underline{K}', \underline{n}\omega_{\underline{K}'\underline{K}})|^2 \qquad \text{(IV:9)}$$
$$\delta(\omega_{\underline{K}'\underline{K}} - \omega)$$

where now:

$$M_{u\ell}(\underline{K}\,\underline{K}'\underline{n}\omega_{\underline{K}'\underline{K}}) = \langle u\underline{K}'| e^{i\underline{n}\omega_{\underline{K}'\underline{K}}\cdot\underline{r}} \nabla_\sigma | \ell \underline{K}\rangle \qquad \text{(IV:10)}$$

and:

$$\omega_{\underline{K}'\underline{K}} = \frac{1}{\hbar} \left| E_u(\underline{K}') - E_\ell(\underline{K}) \right| \qquad \text{(IV:11)}$$

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[*] In effect this approximation involves consideration of the crystal at the absolute zero of temperature, with all zero-point energies of vibrational states being ignored.

3. The coefficient of absorption.

In a cubic crystal of volume V, the number of electronic states whose $\underline{K}$-vector lies in the range $(\underline{K}, \underline{K} + d\underline{K})$ is (Dekker, 1957, p. 256):

$$\frac{V \, d\underline{K}}{(2\pi)^3}$$

considering one spin orientation only. Thus if $f_u(\underline{K}')$ denotes the Fermi distribution function for the energy band labelled by u, the total number of empty states of each spin in the range $(\underline{K}', \underline{K}' + d\underline{K}')$ in this band is:

$$\left[1 - f_u(\underline{K}')\right] \frac{V \, d\underline{K}'}{(2\pi)^3} \tag{IV:12}$$

It then follows from (9) and (12) that the probability per unit time of a transition from the state $|\ell\,\underline{K}\rangle$ into band u, due to the absorption of a photon of frequency ω from an incident beam of $\overline{n}_\omega$ particles per unit time per unit area per unit frequency range about ω is:

$$\mathcal{P}_{\omega;u\ell}(\overline{n}_\omega, \underline{K}) = \int \mathcal{P}_{\omega;u\ell}(\overline{n}_\omega, \underline{K}', \underline{K}) \left[1 - f_u(\underline{K}')\right] \frac{V \, d\underline{K}'}{(2\pi)^3} \tag{IV:13}$$

where the integration is over the first Brillouin zone. It is unnecessary to include both spin orientations, since the spin remains unaltered by the transition.

Consider a small cylindrical volume of the crystal, of cross-section A and length dx parallel to the incident photon beam. By an argument similar to that given above, the number of filled band-ℓ states of each spin in the range $(\underline{K}, \underline{K} + d\underline{K})$

in this small volume is:

$$f_{\ell}(\underline{K}) \frac{A\,dx\,d\underline{K}}{(2\pi)^3}$$

Each of these states may act as an "absorbing unit". Then, multiplying by two to account for both spin orientations, the total number of absorbing units in $(\underline{K}, \underline{K} + d\underline{K})$ in the volume Adx is:

$$2f_{\ell}(\underline{K}) \frac{A\,dx\,d\underline{K}}{(2\pi)^3} \qquad (IV:14)$$

Thus the probability per unit time of a transition from band ℓ into band u due to the absorption in volume Adx of a photon of angular frequency ω from an incident beam of $\bar{n}_\omega$ particles per unit time per unit area per unit frequency range about ω is:

$$\mathbb{P}_{\omega;u\ell}(\bar{n}_\omega)\,A\,dx = \int \mathscr{P}_{\omega;u\ell}(\bar{n}_\omega,\underline{K})\,2f_{\ell}(\underline{K})\,\frac{d\underline{K}}{(2\pi)^3}\,A\,dx \qquad (IV:15)$$

where the integration is again over the first Brillouin zone.

Equation (15) effectively gives the decrease per unit time of the number of photons in the beam due to absorption in Adx at the frequency of interest. The corresponding change in the mean energy flux W_ω ($= \bar{n}_\omega\,A\hbar\omega$) is:

$$dW_\omega = -\mathbb{P}_{\omega;u\ell}(\bar{n}_\omega)\,A\,dx\,\hbar\omega \qquad (IV:16)$$

Now the absorption coefficient $\mu_{u\ell}(\omega)$ is defined by the differential equation:

$$\frac{dW_\omega}{dx} = -\mu_{u\ell}(\omega)\,W_\omega \qquad (IV:17)$$

Hence, by (16) and (17):

$$\mu_{u\ell}(\omega) = \frac{\mathbb{P}_{\omega;u\ell}(\bar{n}_\omega)\,\hbar\omega}{\bar{n}_\omega\,\hbar\omega}$$

$$= \int d\underline{k} \int d\underline{k}' \; \frac{2V}{(2\pi)^6} \; \frac{f_\ell(\underline{k})[1-f_u(\underline{k}')]}{\bar{n}_\omega} \; \mathbb{P}_{\omega;u\ell}(\bar{n}_\omega \; \underline{k} \; \underline{k}') \qquad (IV:18)$$

$$= \frac{2V}{(2\pi)^4} \; \frac{e^2}{m^2 c} \; \frac{\hbar}{\omega} \int d\underline{k} \int d\underline{k}' \; f_\ell(\underline{k}) \; [1- f_u(\underline{k}')] \; |M_{u\ell}(\underline{k}\,\underline{k}'\,\underline{\eta}\,\omega_{\underline{k}'\underline{k}})|^2 \\ \cdot \delta(\omega_{\underline{k}'\underline{k}} - \omega)$$

where both integrations are over the first Brillouin zone.

4. Specialization to centres in a dielectric medium.

The result (18) applies to the interaction of radiation with a crystalline array of atoms imbedded in free space. If the array is now considered to be imbedded in a dielectric medium, several corrections must be applied (D.L. Dexter, 1958, Sections 2 and 4).

The first correction is concerned with modification of the magnitude of the radiation field. Schiff (1955, equations 35.11 and 35.14) shows that $\mathbb{P}_{\omega;u\ell}(\bar{n}_\omega, \underline{k}\underline{k}')$, and hence also the absorption coefficient, depends on ϵ_{eff}^2, where ϵ_{eff} is the magnitude of the field which acts at the atoms of the crystal. It was first pointed out by Lax (1952) that ϵ_{eff} is not in general equal to the average macroscopic field ϵ in the surrounding medium. Consequently, (18) must be multiplied by a factor $\{\epsilon_{eff}/\epsilon\}^2$.

The effective field ratio ϵ_{eff}/ϵ is difficult to evaluate accurately. For a very tight-binding approximation, in which overlap, exchange effects, and multipole interactions higher

than dipole-dipole may be neglected, D.L. Dexter (1956) derives the expression:

$$\frac{\epsilon_{eff}}{\epsilon} \simeq \frac{n^2 + 2}{3} \qquad\qquad \text{(IV:19)}$$

where n is the refractive index of the surrounding medium. However, for the case of diffuse centres such as impurities in germanium, Lax (1954) has shown that the effective field ratio must be taken as 1.

The second correction to be applied to (18) involves modification of photon energies and velocities by the dielectric medium. Essentially, (18) was derived by dividing the transition probability $\mathbb{P}_{\omega;u_\ell}(\bar{n}\omega)$ by the energy flux W_ω. In a dielectric medium (D.L. Dexter, 1956), W_ω is given by its free-space value multiplied by $\frac{K\nu}{c}$, where K is the static dielectric constant of the medium, and ν is the energy velocity c/n. For photon energies at which the medium is effectively transparent, K is approximately equal to n^2. Thus in these regions the multiplying factor may be replaced by $1/n$. (Dexter, 1958, Section 2 points out that multiplication by $1/n$ is still correct when the medium is not transparent. In this case n is the real part of the index of refraction.)

On applying the above corrections to (18), the absorption coefficient of interest for a rigid crystalline array imbedded in a dielectric medium of refractive index n is found to be:

$$\mu_{u\ell}(\omega) = \frac{1}{nc}\left(\frac{\epsilon_{eff}}{\epsilon}\right)^2 \frac{2V}{(2\pi)^4}\left(\frac{e}{m}\right)^2 \frac{\hbar}{\omega}\int d\underline{\kappa}\int d\underline{\kappa}' \ |M_{u\ell}(\underline{\kappa}'\underline{\kappa}\,\eta\omega_{\underline{s}'\underline{s}})|^2 \qquad \text{(IV:20)}$$
$$\cdot f_\ell(\underline{\kappa})\,[1-f_u(\underline{\kappa}')]\ \delta(\omega_{\underline{\kappa}'\underline{\kappa}} - \omega)$$

B. Evaluation of the Absorption Coefficient.

1. Simplifications and approximations.

As they stand, the integrations in (20) are intractable. Consequently, several approximations must be introduced, as follows:

i. Since the absorption process is to be considered only in the neighbourhood of the absolute zero of temperature, the Fermi functions $f_{\ell}(\underline{K})$ and $f_u(\underline{K}')$ assume a simple form. It is to be expected that when T is near 0, all the electrons will be in the ground-state band, labelled by ℓ. Hence:

$$f_u(\underline{K}') = 0 \qquad (IV:21)$$

The form of $f_{\ell}(\underline{K})$ when T is exactly zero must involve a discontinuity at the mid-point of the ℓ-band. This behaviour results from the fact that while there are as many impurity electrons in the crystal as there are impurity nuclei, spin-degeneracy ensures that there will be twice this number of electronic states available in the lowest impurity band. Thus when T = 0, only the lower half of band ℓ will be occupied.

As T increases slightly from zero, however, the discontinuity in the Fermi function $f_{\ell}(\underline{K})$ acquires a finite spread. For a very narrow band, such as the ℓ-band is expected to be,[*] this spread will

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[*] See Chapter III, Section 5.

probably equal or exceed the band width, so that the electrons will be distributed throughout the band. For simplification, it will therefore be assumed that in this case,

$$f_{\ell}(\underline{K}) = \frac{1}{2} \qquad \qquad \text{(IV:22)}$$

ii. By (3), the matrix elements $M_{u\ell}(\underline{K}'\underline{K}\,\eta\omega_{\underline{K}'\underline{K}})$ are:

$$M_{u\ell}(\underline{K}'\underline{K}\,\eta\omega_{\underline{K}'\underline{K}}) = \langle u\,\underline{K}'| e^{i\eta\omega_{\underline{K}'\underline{K}}\cdot r}\,\nabla_r | \ell\,\underline{K}\rangle$$

$$= \frac{i}{\hbar} \langle u\,\underline{K}'| e^{i\eta\omega_{\underline{K}'\underline{K}}\cdot r}\,\nabla_r | \ell\,\underline{K}\rangle \qquad \text{(IV:23)}$$

In the electric dipole approximation, it is assumed that the photon wave-number vector is of negligible magnitude, so that the exponential in (23) may be approximated by the first term in its expansion:

$$e^{i\eta\omega_{\underline{K}'\underline{K}}\cdot r} \cong 1 \qquad \qquad \text{(IV:24)}$$

Thus, in the cases of interest, the matrix elements are:

$$M_{s,0}(\underline{K}'\underline{K}) = \frac{i}{\hbar} \langle i\,\underline{K}'| p_\sigma | 0\,\underline{K}'\rangle \qquad \text{(IV:25)}$$

The expressions (25) may then be evaluated with the aid of equations (III:103) and (III:104).

iii. In order that the integrations in (20) may be carried out, the three-dimensional Kronecker δ, $\delta_{\underline{K},\underline{K}'}$, defined in (III:75') must be replaced by a Dirac

delta-function (Dirac, 1958, p. 58). It is shown

in Appendix B that with the correct normalization:

$$\left(\delta_{\underline{K}\,\underline{K}'}\right)^2 \;=\; \delta_{\underline{K}\,\underline{K}'} \;=\; \frac{(2\pi)^3}{V} \; \delta(\underline{K}-\underline{K}') \,. \qquad\qquad (IV:26)$$

where V is the volume of the impurity-lattice

"crystal".

iv. By (11), the function $\omega_{\underline{K},\underline{K}'}$ is defined to be:

$$\omega_{\underline{K}\,\underline{K}'} \;=\; \frac{1}{\hbar} \,\left| E_u(\underline{K}') - E_\ell(\underline{K}) \right|$$

Thus, in the cases of interest, the tight-binding

expressions (III:58) may be used for the energies

$E_u(\underline{K}')$. As stated in the discussion of (III:62),

the broadening of the lower band is expected to be

negligible, so that $E_\ell(\underline{K})$ may be set equal to the

isolated-impurity value of the ground-state energy.

Examination of (III:58) shows that the

expressions for the energy bands associated with

the group E are rather cumbersome. Consequently,

only the simpler expressions for the energies

associated with the group T_3 will be used in

explicit calculations.

2. The absorption coefficient for the $1s^{(o)} \rightarrow 1s^{(s)}$ transition.

Using the approximations outlined in the last section,

substitution of (III:104) into (25) leads to an expression

for the matrix element associated with the transition between

the ground state and the d_5 band.

$$M_{d_{5,0}}(\underline{K}'\underline{K} \, \underline{\eta}\omega_{\underline{K}'\underline{K}}) \cong \frac{im}{\hbar^2} \frac{4}{\sqrt{3}} \sin k_0 a \, X_a^z \, E_{5,0}^{(5)}(\underline{K}) \cos K_z a \, \delta_{\underline{K}\underline{K}'} \qquad \text{(IV:27)}$$

Hence:

$$|M_{d_{5,0}}(\underline{K}'\underline{K} \, \underline{\eta}\omega_{\underline{K}'\underline{K}})|^2 \cong \frac{m^2}{\hbar^4} \frac{16}{3} \sin^2 k_0 a \, (X_a^z)^2 \{E_{5,0}^{(5)}(\underline{K})\}^2 \cos^2 K_z a \, \delta_{\underline{K}\underline{K}'}$$

$$= \frac{m^2 V^{-1}}{\hbar^4} \frac{16}{3} \sin^2 k_0 a \, (X_a^z)^2 \{E_{5,0}^{(5)}(\underline{K})\}^2 \qquad \text{(IV:28)}$$
$$\cdot \cos^2 K_z a \, (2\pi)^3 \, \delta(\underline{K}-\underline{K}').$$

Then, substituting (28) into (20) and using the delta-function $\delta(\underline{K}' - \underline{K})$ to carry out the integration over $\underline{K}'$:

$$\mu_{d_{5,0}}(\omega) \cong \frac{1}{nc} \left\{ \frac{\epsilon_{eff}}{\epsilon} \right\}^2 \frac{16}{3(2\pi)} \left(\frac{e}{\hbar} \right)^2 (X_a^z)^2 \sin^2 k_0 a$$
$$\frac{1}{\omega} \int d\underline{K} \, \{E_{5,0}^{(5)}(\underline{K})\}^2 \cos^2 K_z a \, \delta\{E_{5,0}^{(5)}(\underline{K})-\hbar\omega\} \qquad \text{(IV:29)}$$

Clearly the absorption coefficient (29) vanishes whenever $\sin^2 k_0 a = 0$ and has its maximum value when $\cos k_0 a = 0$. For simplicity, intermediate cases will be ignored. Then, under the condition that $\cos k_0 a = 0$, (III:55), (III:56), and (III:58) show that:

$$E_{5,0}^{(5)}(\underline{K}) = -4|U| \{\cos K_x a + \cos K_y a\} + \Delta E_{5,0} \qquad \text{(IV:30)}$$

denoting:

$$\Delta E_{5,0} = \left[E_{1s}^{(5)} - E_{1s}^{(0)} \right]_{\substack{\text{isolated} \\ \text{impurities.}}} \qquad \text{(IV:31)}$$

Hence, substituting (30) into (29) and taking $\{E_{5,0}^{(5)}(\underline{K})\}^2$ outside the integral sign as $\hbar^2\omega^2$, by virtue of the delta-

function:

$$\mu_{ds,o}(\omega) \cong \frac{1}{nc}\left\{\frac{\epsilon_{eff}}{\epsilon}\right\}^2 \frac{16}{6\pi} (eX_a^z)^2 \frac{\omega}{4|U|} \int_{-\pi/a}^{\pi/a}dK_x \int_{-\pi/a}^{\pi/a}dK_y \int_{-\pi/a}^{\pi/a}dK_z \cos^2 K_z a$$
$$\cdot \delta\left\{\cos K_x a + \cos K_y a - \frac{(\Delta E_{s,o}-\hbar\omega)}{4|U|}\right\}$$

$$= \frac{1}{nc}\left\{\frac{\epsilon_{eff}}{\epsilon}\right\}^2 \frac{8}{3} \frac{(eX_a^z)^2}{a^3|U|} \omega \int_0^\pi dx \int_0^\pi dy\, \delta\left\{\cos x + \cos y - \frac{\Delta E_{s,o}-\hbar\omega}{4|U|}\right\} \quad (IV:32)$$

One of the integrations in (32) may be carried out immediately (Kahn, 1955, equations 3 and 4), by setting:

$$dx\, dy = \frac{d\mathcal{L}\, d(\cos x + \cos y)}{|\nabla(\cos x + \cos y)|} = \frac{d\mathcal{L}\, d(\cos x + \cos y)}{\sqrt{\sin^2 x + \sin^2 y}} \quad (IV:33)$$

where $d\mathcal{L}$ is a line element of constant (cos x + cos y).
Hence, defining:

$$\xi = \frac{\Delta E_{s,o} - \hbar\omega}{4|U|} \quad (IV:34)$$

the absorption coefficient (32) becomes:

$$\mu_{ds,o}(\omega) = \frac{1}{nc}\left\{\frac{\epsilon_{eff}}{\epsilon}\right\}^2 \frac{8}{3} \frac{(eX_a^z)^2}{a^3|U|} \omega \left[\int \frac{d\mathcal{L}}{\sqrt{\sin^2 x + \sin^2 y}}\right]_{\substack{\cos x + \cos y = \xi \\ 0 \le x,y \le \pi}} \quad (IV:35)$$

for ξ between +2 and -2.

In Appendix C the integration in (35) is carried out. The results are shown in Figure 6, where the integral:

$$\int \frac{d\mathcal{L}}{\sqrt{\sin^2 x + \sin^2 y}}\Bigg|_{\substack{\cos x + \cos y = \xi \\ 0 \le x,y \le \pi}} \quad (IV:36)$$

is plotted as a function of ξ . As may be seen from the graph, use of (36) leads to an expression for the absorption coefficient which is divergent at the centre of the band. However, it may be shown[*] that the divergence is sufficiently mild for the area under the absorption-coefficient curve to remain finite.

The divergent behaviour of (36) is a direct consequence of the tight-binding approximation, and may be modified by correcting the energy surfaces. (The tight-binding surfaces are shown schematically in Figure 7.) Jones (1960, pp. 44-46) shows that for a simple cubic lattice, such as that considered here, the surfaces of constant energy must intersect the planes $K_x = 0$, $K_y = 0$, $K_z = 0$, and the faces of the first Brillouin zone, at right angles. Clearly this requirement is not satisfied by the surfaces of Figure 7. The corrected surfaces are shown by Wilson (1953, p. 42, Figure II.10). In this case, the mid-point of the band will correspond to a surface whose cross-section is shown schematically in Figure 8, and the corresponding absorption coefficient will lie between infinity and the free-electron value obtained by approximating this surface by a right circular cylinder.[**]

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[*] See Appendix C.

[**] Free-electron energy surfaces are described by Dekker (1957, p. 262, Figure 10-10b). The free-electron absorption coefficient may be determined by setting (36) equal to its value at $\xi = 0$ for all values of ξ considered.

As the electrons in question should be described much more accurately by the tight-binding approximation than by the free-electron approximation, it is probable that the correct maximum of the absorption-coefficient curve may be obtained by rounding off the curve of Figure 6. If this is done, the maximum absorption coefficient may be written as a function of the impurity lattice spacing as follows:

$$\mu_{d_{5,0}(max)}(a) = \frac{1}{nc}\left\{\frac{\epsilon_{eff}}{\epsilon}\right\}^2 \frac{8}{3} 2K \frac{(x_a^2/a^*)^2 \, e^{a/a^*} \, g_{max}}{(a/a^*)^3 \left\{1 + a/a^*\right\}} \, \omega_{5,0}^{1s} \qquad \text{(IV:37)}$$

on substituting the expression (III:49) for U in (35). (g_{max} denotes the round-off value from Figure 6, while $\omega_{5,0}^{1s}$ denotes the frequency corresponding to the isolated-impurity energy gap between the $1s^{(o)}$ and $1s^{(5)}$ levels.)

In order to be able to make use of (37) to calculate the absorption coefficient, values must be determined for the index of refraction, n , and for the effective field ratio, ϵ_{eff}/ϵ . Since at the wave lengths of interest (about 100 microns), silicon is effectively transparent (Bichard and Giles), it should be a good approximation to write:[*]

$$n = \sqrt{K} \qquad \text{(IV:38)}$$

where K is the dielectric constant quoted by Kohn (1957, equation 5.8). To this approximation, the value of n is 3.46. Also, since centres in silicon are fairly diffuse, having a

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[*] See Section A.4 of this chapter.

Bohr radius of about half that in germanium (Kohn, 1957, equation 5.10), the effective field ratio should be approximately 1, according to the arguments of Lax (1952).[*]

The rounding-off of the tight-binding absorption coefficient carried out in (37) is a somewhat arbitrary procedure. While consistency might be obtained by cutting off the curve of Figure 6 at the resolution of the spectrometer used, such a method offers no guarantee of accuracy. In the calculations performed in this thesis, the cut-off value $\mathcal{G}_{max}$ will be taken as five.

Substituting the approximations of the last two paragraphs into (37), the expression for the absorption coefficient becomes:

$$\mu_{ds,0\,(max)}(a) = 27\sqrt{K}\,\frac{\omega_{s,0}^{15}}{c}\,\frac{\left(X_{a}^{2}/_{a^{*}}\right)^{2}e^{a/a^{*}}}{\left(a/_{a^{*}}\right)^{3}\left\{1+a/_{a^{*}}\right\}}$$

$$= (7.2 \times 10^{4})\,\frac{\left(X_{a}^{2}/_{a^{*}}\right)^{2}e^{a/a^{*}}}{\left(a/_{a^{*}}\right)^{3}\left\{1+a/_{a^{*}}\right\}}\quad cm^{-1} \qquad (IV:39)$$

values of this function are plotted in Figure 9.

C. Discussion of Results.

1. 1s → 2p$_0$ transition.

In Appendix D, the method used for the $1s^{(0)} \rightarrow 1s^{(5)}$ transition is extended to give an approximate expression for the $1s^{(0)} \rightarrow 2p_0^{(6)}$ absorption coefficient. As the latter transition has been observed experimentally (Bichard and Giles), it should be possible to use the results of this calculation as

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[*] See Section A.4 of this chapter.

a rough check on the method in general. In the Appendix it is shown that at concentrations for which the assumption of tight-binding should be a good approximation, the calculated absorption coefficient is in quite reasonable agreement with experiment. From this it would appear that there are no gross errors in the calculation, and that the method used might be expected to give a reasonable description of the $1s^{(0)} \rightarrow 1s^{(5)}$ transition.

2. $1s^{(0)} \rightarrow 1s^{(5)}$ transition.

The results plotted in Figure 9 indicate that at impurity concentrations of about 10^{18} per cm^3, the $1s^{(0)} \rightarrow 1s^{(5)}$ absorption coefficient is of the order of 10 cm^{-1}. As transitions with absorption coefficients in this range are observable by existing techniques (Bichard and Giles), the theory would appear to indicate that the fine structure of the 1s states will be identifiable. There are, however, several sources of error in the calculation which might tend to invalidate the results obtained.

The first possibility of major error lies in the choice of wave functions for the two 1s-states of interest. The Kohn-Luttinger approximation used in this part of the calculation may only be good to within a factor of two or three, for the matrix element. Also, as indicated in Figure 5, if the $1s^{(5)}$ level is depressed below its uncorrected effective-mass position, the matrix element for the transition will be reduced.

A second source of uncertainty in the calculation is the

assumption of a regular lattice of impurities. Clearly the random nature of the actual distribution will remove dependence on such quantities as $\cos k_o a$.[*] It is to be expected that this "smoothing-out" effect will be accompanied by an overall decrease in the magnitude of the absorption coefficient. This correction may be partially compensated, however, by the fact that more than one of the five degenerate 1s states are available for optical transitions in any given instance. Comparison of (III:103) and (III:104) indicates, for example, that the absorption coefficient (39) should be multiplied by a factor of three or four if the effect of transitions to the $d_1 - d_2$ bands is to be included.

There are several other points in the derivation at which corrections might be applied. In most cases the possible errors have already been discussed. One further alteration should be noted here, however: if the incident radiation is unpolarized, the absorption coefficient should be reduced to one-third of its value for a completely polarized beam, (D.L. Dexter, 1958).

There is no guarantee, therefore, that the results of Figure 9 are accurate to within less than one or two orders of magnitude. However, in view of the fact that results of the order of 10 cm^{-1} can be obtained, there would appear to be no firm theoretical reason for the $1s^{(0)} \rightarrow 1s^{(5)}$ transition to be unobservable.

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[*] See, for example, equations (III:103) and (III:104).

APPENDIX A

Properties of the Coefficients $D_j(\underline{k})$.

By equation (II:16) the coefficients $D_j(\underline{k})$ and $D_{-j}(\underline{k})$ satisfy:

$$\left\{ \varepsilon_c^j(\underline{k}) - E \right\} D_{j\ell}(\underline{k}) + \int \mathcal{U}(\underline{k},\underline{k}') D_{j\ell}(\underline{k}') \, d\underline{k}' = 0 \tag{A:1}$$

and:

$$\left\{ \varepsilon_c^{-j}(\underline{k}) - E \right\} D_{-j\ell}(\underline{k}) + \int \mathcal{U}(\underline{k},\underline{k}') D_{-j\ell}(\underline{k}') \, d\underline{k}' = 0 \tag{A:2}$$

respectively, where the subscript "$-j$" denotes the conduction band minimum associated with $-\underline{k}_j$. Now by (II:17):

$$\varepsilon_c^{-j}(\underline{k}) = \varepsilon_0 + \sum_{\lambda\mu} \eta_{\lambda\mu}^{-j} (k_\lambda + k_{j\lambda})(k_\mu + k_{j\mu}) \tag{A:3}$$

where:

$$\eta_{\lambda\mu}^{-j} = \left. \frac{\partial^2 \varepsilon_c(\underline{k})}{\partial k_\lambda \, \partial k_\mu} \right|_{\underline{k} = -\underline{k}_j}$$

$$= \left. \frac{\partial^2 \varepsilon_c(\underline{k})}{\partial(-k_\lambda)\partial(-k_\mu)} \right|_{\underline{k} = \underline{k}_j} \tag{A:4}$$

$$= \left. \frac{\partial^2 \varepsilon_c(\underline{k})}{\partial k_\lambda \, \partial k_\mu} \right|_{\underline{k} = \underline{k}_j} = \eta_{\lambda\mu}^{j}$$

Hence:

$$\varepsilon_c^{-j}(\underline{k}) = \varepsilon_0 + \sum_{\lambda\mu} (-1)^2 \eta_{\lambda\mu}^{j} (-k_\lambda - k_{j\lambda})(-k_\mu - k_{j\mu}) = \varepsilon_c^{j}(-\underline{k}) \tag{A:5}$$

Also, by (II:12):

$$\mathcal{U}(\underline{k},\underline{k}') = \int U(\underline{r}) \, \varphi_{c\underline{k}}^{*}(\underline{r}) \, \varphi_{c\underline{k}'}(\underline{r}) \, d\underline{r} \tag{A:6}$$

The periodic parts, $u_{c\underline{k}}(\underline{r})$, of the conduction-band Bloch functions may be shown (Jones, 1960, equation 2.25) to satisfy:

$$\nabla^2 u_{c\underline{k}}(\underline{r}) + 2i\underline{k}\cdot\underline{\nabla}\, u_{c\underline{k}}(\underline{r}) + \frac{2m}{\hbar^2}\left\{ \mathcal{E}_c(\underline{k}) - \frac{\hbar^2 k^2}{2m} - V_p(\underline{r})\right\} u_{c\underline{k}}(\underline{r}) = 0 \qquad (A:7)$$

Taking the complex conjugate of (7):

$$\nabla^2 u^*_{c\underline{k}} - 2i\underline{k}\cdot\underline{\nabla}\, u^*_{c\underline{k}} + \frac{2m}{\hbar^2}\left\{ \mathcal{E}_c(\underline{k}) - \frac{\hbar^2 k^2}{2m} - V_p(\underline{r})\right\} u^*_{c\underline{k}} = 0 \qquad (A:8)$$

By the symmetry of the crystal, $\mathcal{E}_c(\underline{k}) = \mathcal{E}_c(-\underline{k})$, so that (8) may be written:

$$\nabla^2 u^*_{c\underline{k}} - 2i\underline{k}\cdot\underline{\nabla}\, u^*_{c\underline{k}} + \frac{2m}{\hbar^2}\left\{ \mathcal{E}_c(-\underline{k}) - \frac{\hbar^2 (-k)^2}{2m} - V_p(\underline{r})\right\} u^*_{c\underline{k}} = 0 \qquad (A:9)$$

Hence, provided that the conduction band is non-degenerate:

$$u^*_{c\underline{k}}(\underline{r}) = u_{c-\underline{k}}(\underline{r}) \qquad (A:10)$$

and:

$$\varphi^*_{c\underline{k}} = \left(u_{c\underline{k}}\, e^{i\underline{k}\cdot\underline{r}}\right)^* = u_{c-\underline{k}}\, e^{-i\underline{k}\cdot\underline{r}} = \varphi_{c-\underline{k}} \qquad (A:11)$$

Therefore, substituting (11) into (6):

$$\begin{aligned}
\mathcal{U}^*(\underline{k},\underline{k}') &= \int U(\underline{r})\, \varphi_{c\underline{k}}(\underline{r})\, \varphi^*_{c\underline{k}'}(\underline{r})\; d\underline{r} \\[4pt]
&= \int U(\underline{r})\, \varphi^*_{c-\underline{k}}(\underline{r})\, \varphi_{c-\underline{k}'}(\underline{r})\; d\underline{r} \\[4pt]
&= \mathcal{U}(-\underline{k},-\underline{k}')
\end{aligned} \qquad (A:12)$$

From (2) it follows that:

$$\left\{\mathcal{E}_c^{-j}(-\underline{k}) - E\right\} D_{-j\ell}(-\underline{k}) + \int \mathcal{U}(-k,\underline{k}') D_{-j\ell}(\underline{k}') \, d\underline{k}' = 0 \tag{A:13}$$

Then, applying the results of (5) and (12) to (13):

$$\left\{\mathcal{E}_c^j(\underline{k}) - E\right\} D_{-j\ell}(-\underline{k}) + \int \mathcal{U}(-\underline{k},-\underline{k}') D_{-j\ell}(-\underline{k}') \, d\underline{k}' = 0$$

$$\left\{\mathcal{E}_c^j(\underline{k}) - E\right\} D_{-j\ell}(-\underline{k}) + \int \mathcal{U}^*(\underline{k},\underline{k}') D_{-j\ell}(-\underline{k}') \, d\underline{k}' = 0 \tag{A:14}$$

$$\left\{\mathcal{E}_c^j(\underline{k}) - E\right\} D_{-j\ell}^*(\underline{k}) + \int \mathcal{U}(\underline{k},\underline{k}') D_{-j\ell}^*(-\underline{k}') \, d\underline{k}' = 0$$

Thus, provided that the   th energy level of equation (1) is non-degenerate:

$$D_{j\ell}(\underline{k}) = D_{-j\ell}^*(-\underline{k}) \tag{A:15}$$

In the case of the 1s level the non-degeneracy condition is clearly satisfied, so that:

$$D_{j1s}(\underline{k}) = D_{-j1s}^*(-\underline{k}) \tag{A:16}$$

APPENDIX B

Properties of the Three-Dimensional Kronecker δ.

a. Equation (III:75') defines a function $\delta_{\underline{k},\underline{k}'}$ such that:

$$\delta_{\underline{k},\underline{k}'} = \frac{1}{N} \sum_{\underline{n}} e^{i(\underline{k}-\underline{k}')\cdot\underline{a}_{\underline{n}}} \tag{B:1}$$

where N is the number of atoms in a simple cubic "crystal", and the summation is over all lattice sites of this crystal. Expanding the scalar product occurring in the exponential term of (1), and making use of the cubic symmetry of the crystal being considered:

$$\delta_{\underline{k},\underline{k}'} = \frac{1}{N} \sum_{\underline{n}} e^{i\{(k_x-k_x')a_{n_x} + (k_y-k_y')a_{n_y} + (k_z-k_z')a_{n_z}\}}$$

$$= \left\{ \frac{1}{N^{1/3}} \sum_{n_x} e^{i(k_x-k_x')a_{n_x}} \right\}\left\{ \frac{1}{N^{1/3}} \sum_{n_y} e^{i(k_y-k_y')a_{n_y}} \right\} \tag{B:2}$$
$$\cdot \left\{ \frac{1}{N^{1/3}} \sum_{n_z} e^{i(k_z-k_z')\cdot a_{n_z}} \right\}$$

Now the allowed values of a_{n_x} are na, where a is the lattice spacing and n runs from 0 to $N^{1/3}-1$. Hence:

$$\frac{1}{N^{1/3}} \sum_{n_x} e^{i(k_x-k_x')a_{n_x}} = \frac{1}{N^{1/3}} \sum_{n=0}^{N^{1/3}-1} \left[e^{i(k_x-k_x')a} \right]^n$$

$$= \frac{1}{N^{1/3}} \sum_{n=0}^{N^{1/3}-1} A_{k_x k_x'}^n$$

$$= \frac{1}{N^{1/3}} \frac{A^{N^{1/3}} - 1}{A - 1} \tag{B:3}$$

(similarly for y and z.)

by the usual rules for summing a geometric series.

Now by the periodic boundary condition used to determine the allowed values of $\underline{K}$ in the first Brillouin zone (Jones, 1960, p. 36),

$$e^{iK_x N^{1/3} a} = 1 \tag{B:4}$$

for each allowed vector $\underline{K}$. By definition, $(\underline{k} - \underline{k}')$ is such a vector. Hence:

$$A_{k_x k_x'}^{N^{1/3}} = e^{i(k_x - k_x')N^{1/3}a} = 1 \tag{B:5}$$

Thus if $\underline{k} \neq \underline{k}'$:

$$\delta_{\underline{k}\underline{k}'} = \frac{1}{N}\left\{\frac{1-1}{A_{k_x k_x'}-1}\right\}\left\{\frac{1-1}{A_{k_y k_y'}-1}\right\}\left\{\frac{1-1}{A_{k_z k_z'}-1}\right\} = 0 \tag{B:6}$$

If, on the other hand, $\underline{k} = \underline{k}'$, then by (1):

$$\delta_{\underline{k}\underline{k}} = \frac{1}{N}\sum_{\underline{n}} e^{i(0)\cdot\underline{a}_n} = \frac{N}{N} = 1. \tag{B:7}$$

Hence, by (6) and (7):

$$\delta_{\underline{k}\underline{k}'} = \begin{cases} 0 & \text{if } \underline{k} \neq \underline{k}' \\ 1 & \text{if } \underline{k} = \underline{k}' \end{cases} \tag{B:8}$$

This behaviour is analogous to that of the usual one-dimensional Kronecker

b. The function $\delta_{\underline{k},\underline{k}'}$ may easily be approximated by a Dirac delta function, as follows:

$$\delta_{\underline{k}\underline{k}'} = \frac{1}{N} \sum_{\underline{n}} e^{-i(\underline{k}-\underline{k}')\cdot \underline{a}_n} = \frac{1}{N\Omega} \sum_{\underline{n}} e^{-i(\underline{k}-\underline{k}')\cdot \underline{a}_n} \Omega$$

$$\cong \frac{1}{V} \int d\underline{r}\, e^{i(\underline{k}'-\underline{k})\cdot \underline{a}_n}$$
$$\text{entire crystal}$$

$$= \frac{(2\pi)^3}{V} \delta(\underline{k}-\underline{k}') \tag{B:9}$$

where V is the volume of the crystal.

Clearly:

$$\left(\delta_{\underline{k}\underline{k}'}\right)^2 = \delta_{\underline{k},\underline{k}'} \tag{B:10}$$

Hence:

$$\left[\delta(\underline{k}-\underline{k}')\right]^2 = \frac{V^2}{(2\pi)^6} \left(\delta_{\underline{k}\underline{k}'}\right)^2$$

$$= \frac{V^2}{(2\pi)^6} \cdot \delta_{\underline{k}\underline{k}'}$$

$$= \frac{V}{(2\pi)^3} \delta(\underline{k}-\underline{k}') \tag{B:11}$$

The result (11) is used in Chapter IV in the calculation of absorption coefficients.

APPENDIX C

Evaluation of the Integral (IV:36).

In Chapter IV, the integral:

$$\int \frac{d\mathcal{L}}{\sqrt{\sin^2 x + \sin^2 y}} \Bigg|_{\substack{\cos x + \cos y = \zeta \\ 0 \leq x, y \leq \pi}} \tag{C:1}$$

occurred in connection with the calculation of the $1s^{(0)} \rightarrow 1s^{(5)}$ absorption coefficient in the tight-binding approximation. Lines typical of those over which the integration must be taken are sketched in Figure 7.

Now, by elementary calculus,

$$d\mathcal{L} = \sqrt{dx^2 + dy^2} \tag{C:2}$$

Along the line $(\cos x + \cos y) = \zeta$, dx and dy are related by:

$$dy = - \frac{\sin x}{\sin y} dx$$

$$= - \frac{\sin x \, dx}{\sqrt{1 - (\zeta - \cos x)^2}} \tag{C:3}$$

Therefore, by (2) and (3):

$$d\mathcal{L} = dx \left\{ \frac{\sin^2 x + \sin^2 y}{1 - (\zeta - \cos x)^2} \right\}^{1/2} \tag{C:4}$$

Hence the integrand in (1) becomes:

$$\frac{d\mathcal{L}}{\sqrt{\sin^2 x + \sin^2 y}} = \frac{dx}{\sqrt{1-(\xi-\cos x)^2}} \qquad (C:5)$$

with x varying between 0 and $\cos^{-1}(\xi-1)$ whenever ξ is greater than zero, and between $\cos^{-1}(\xi+1)$ and π whenever ξ is less than zero. By (5), the integral in (1) may thus be written:

$$\int_0^{\cos^{-1}(\xi-1)} \frac{dx}{\sqrt{1-(\xi-\cos x)^2}} \qquad [0 \leq \xi \leq 2] \qquad (C:6)$$

$$\int_{\cos^{-1}(\xi+1)}^{\pi} \frac{dx}{\sqrt{1-(\xi-\cos x)^2}} \qquad [-2 \leq \xi \leq 0] \qquad (C:6')$$

Changing the variable in (6) to:

$$\chi = \frac{\cos x - 1}{2-\xi} + 1 \qquad (C:7)$$

and defining:

$$\zeta = \frac{2\xi}{(2-\xi)^2} \qquad (C:8)$$

the integral (6) becomes:

$$\frac{2}{2-\xi} \int_0^{1/2} \frac{d\chi}{\sqrt{\chi(1-\chi)[\zeta + \chi(1-\chi)]}} \qquad (C:9)$$

Similarly, (6') becomes:

$$\frac{2}{2+\xi} \int_0^{1/2} \frac{dx}{\sqrt{x(1-x)[\zeta' + x(1-x)]}} \qquad \text{(C:9')}$$

where:

$$\zeta' = \frac{-2\xi}{(2+\xi)^2} \qquad \text{(C:10)}$$

Clearly, taking into account the allowed values of ξ in each case, integration of (9) and (9') will lead to a function which is symmetric about $\xi = 0$. Hence only (9) need be considered in detail.

In the limit as ξ approaches 2, ζ becomes large, and (9) may be approximated by:

$$\sqrt{\frac{2}{\xi}} \int_0^{1/2} \frac{dx}{\sqrt{x(1-x)}} = \frac{\pi}{\sqrt{2\xi}} \qquad \text{(C:11)}$$

Comparison of the values of $\xi x(1-x)$ and $[x(1-x)]^2$ in the range of x considered indicates that (11) will be a valid approximation for all ξ greater than 0.5.

When $\xi = 0$, (9) becomes:

$$\int_0^{1/2} \frac{dx}{x(1-x)} = -\left[\ln \frac{1-x}{x}\right]_0^{1/2} \qquad \text{(C:12)}$$

As this integral diverges, the limiting behaviour of (9) as ξ goes to zero must be examined in more detail.

The integral (9) may be rewritten as:

$$\frac{2}{2-\zeta} \int_0^{1/2} \frac{dX}{X(1-X)\sqrt{1 + \zeta/X(1-X)}} \tag{C:13}$$

Clearly, for values of X much less than ζ , the expression under the square root in (13) will be dominated by its second term, while for values of X much greater than ζ , the first term will dominate. Thus in the limit of small ζ , which corresponds to the limit of small ζ , (13) may be approximated by:

$$\frac{2}{2-\zeta} \left\{ \int_0^\zeta \frac{dX}{\sqrt{\zeta}\sqrt{X(1-X)}} + \int_\zeta^{1/2} \frac{dX}{X(1-X)\{1 + \zeta/2X(1-X)\}} \right\}$$

$$= \frac{2}{2-\zeta} \left\{ \frac{1}{\sqrt{\zeta}} \cos^{-1}(1-2\zeta) + \frac{2}{\sqrt{1+2\zeta}} \tanh^{-1} \frac{1-2\zeta}{\sqrt{1+2\zeta}} \right\} \tag{C:14}$$

$$= \sqrt{\frac{2}{\zeta}} \cos^{-1}\left\{1 - \frac{4\zeta}{(2-\zeta)^2}\right\} + \frac{4}{\sqrt{4+\zeta^2}} \tanh^{-1} \frac{\zeta^2 - 8\zeta + 4}{(2-\zeta)\sqrt{4+\zeta^2}}$$

$$\cong \sqrt{\frac{2}{\zeta}} \cos^{-1}\left\{1 - \frac{4\zeta}{(2-\zeta)^2}\right\} + 2 \tanh^{-1} \frac{2(1-2\zeta)}{2-\zeta}$$

Neglecting the first term, which goes to two as   goes to zero, (14) is seen to go to infinity as:

$$\lim_{\zeta \to 0} 2 \tanh^{-1} \frac{2(1-2\zeta)}{2-\zeta} \cong \lim_{\zeta \to 0} 2 \tanh^{-1}(1 - \tfrac{3}{2}\zeta)$$

$$\cong \lim_{\zeta \to 0} \ln \frac{2}{3\zeta} \tag{C:15}$$

As the natural logarithm of $2/3\zeta$ goes to infinity more slowly than any power of $2/3\zeta$, it is clear from (15) that the area under the absorption-coefficient curve will remain finite in spite of the divergence of (12).

Values of the integral (1) are plotted against ζ in Figure 6.

APPENDIX D

The Absorption Coefficient for the $1s \longrightarrow 2p_0$ Transition.

By a method completely analogous to that used for the $1s^{(0)} \longrightarrow 1s^{(5)}$ transition, an approximate expression may be derived for the absorption coefficient associated with the $1s^{(0)} \longrightarrow 2p_0^{(6)}$ transition.

Rather than carry out a complicated energy-band calculation for the broadening of the 2s-2p impurity band, a tight-binding expression will be assumed for the $2p_0$ energy, mixing with the other $n = 2$ states being ignored. The parameters in this tight-binding expression will then be determined from the results of Kohn and Luttinger (1955 c), and of Baltensperger (1953). The function so obtained is:

$$E_{2p_0}(\underline{K}) = E_{2p_0}^i - U' \{ \cos K_x a + \cos K_y a + \cos K_z a \}$$

$$(D:1)$$

where:

$E_{2p_0}^i$ = the isolated-impurity $2p_0$ energy, -1.1×10^{-2} ev.

U' = 1/6 of the 2p band-width given by

Baltensperger . $\hspace{3cm}$ (D:2)

In the case of high concentration, $E_{2p_0}^i$ must be modified according to Baltensperger's calculations.

Corrections to the effective mass theory will be ignored for the $2p_0$ wave functions, so that:

$$F_{2p_0}(\underline{r}) = \frac{(2\pi)^{3/2}}{\sqrt{\pi} \sqrt{32}} \frac{1}{(a^*)^{5/2}} z\, e^{-r/2a^*} \tag{D:3}$$

Using (3) and the corrected ground-state wave function (III:86), the integral:

$$X_a^{2p_0} = \frac{1}{(2\pi)^3} \int F_{2p_0}^*(\underline{r})\, z\, F_{1s}^0(\underline{r}-\underline{a}_m)\, d\underline{r} \tag{D:4}$$
$$\{a = |\underline{a}_m|\}$$

may be calculated. Rough values for this integral are shown in Figure 10.

By (1), (4), and (III:74), the optical matrix element of interest is, under the assumption that the six degenerate $2p_0$ levels broaden independently:

$$\langle \mathcal{I}_{2p_0}(\underline{K}') | p_\sigma | \mathcal{I}_{1s}^0(\underline{K}) \rangle = -\frac{m}{i\hbar} \delta_{\underline{K}\underline{K}'}\, E_{2p_0,1s}(\underline{K})$$
$$\cdot \left\{ X_0^{2p_0} + 2X_a^{2p_0}(\cos K_x a + \cos K_y a + \cos K_z a) \right\} \tag{D:5}$$

where:

$$E_{2p_0,1s}(\underline{K}) = E_{2p_0}(\underline{K}) - E_{1s}^{(0)}(\underline{K}) \tag{D:6}$$

By (5), (IV:20), and (IV:23), the absorption coefficient for the $1s^{(0)} \longrightarrow 2p_0^{(6)}$ transition is:

$$\mu_{1s,2p_0}(\omega) = \frac{6}{nc} \left\{ \frac{\epsilon_{eff}}{\epsilon} \right\}^2 \left(\frac{e}{m}\right)^2 \frac{V}{(2\pi)^4} \frac{1}{\omega} \int d\underline{K} \int d\underline{K}'\, |\langle \mathcal{I}_{2p_0}(\underline{K}') | p_\sigma | \mathcal{I}_{1s}^0(\underline{K}) \rangle|^2$$
$$\cdot \delta \left\{ E_{2p_0,1s}(\underline{K}) - \hbar\omega \right\}$$

$$= \frac{1}{nc} \left\{ \frac{\epsilon_{eff}}{\epsilon} \right\}^2 \frac{24 e^2}{\pi a^3 |U'|} \omega \left\{ X_0^{2p_0} + 2\eta X_a^{2p_0} \right\}^2 \tag{D:7}$$
$$\int_0^\pi\!\!\int\!\!\int dx\, dy\, dz\, \delta(\cos x + \cos y + \cos z - \eta)$$

where:

$$\eta = \frac{1}{|U'|}\left\{ E^i_{2P_0} - E^{(0)}_{1s} - \hbar\omega\right\} \tag{D:8}$$

and a factor 6 is included in (7) to account for the six-fold degeneracy of the $2p_0$ band. The expression (7) may be simplified by the procedure which led to equation (IV:25) for the $1s^{(0)} \longrightarrow 1s^{(5)}$ case. The result of this simplification is:

$$\mu_{1s,2p_0}(\omega) = \frac{1}{nc}\left\{\frac{\epsilon_{eff}}{\epsilon}\right\}^2 \frac{24\,e^2}{\pi a^3 |U'|}\,\omega\left\{ X^{2p_0}_0 + 2\eta X^{2p_0}_a\right\}\mathcal{J} \tag{D:9}$$

where:

$$\mathcal{J} = \int \frac{dS}{\sqrt{\sin^2 x + \sin^2 y + \sin^2 z}}\Bigg|_{\substack{\cos x + \cos y + \cos z = \eta \\ 0 \le x,y,z \le \pi}} \tag{D:10}$$

The integral (10) may be evaluated approximately by the methods of Appendix C. The element of surface area is:

$$dS = \left\{\frac{\sin^2 x + \sin^2 y + \sin^2 z}{1 - (\eta - \cos x - \cos y)^2}\right\}^{1/2} dx\,dy \tag{D:11}$$

Hence $\mathcal{J}$ reduces to:

$$\mathcal{J} = \int_0^{\cos^{-1}(\eta-2)} dx \int_0^{\cos^{-1}(\eta-1-\cos x)} \frac{dy}{\sqrt{1 - (\eta - \cos x - \cos y)^2}} \tag{D:12}$$

Whenever:

$$\eta - \cos x \cong 2 \tag{D:13}$$

the y-integral in (11) may be evaluated by means of (C:11):

$$\mathcal{J} \cong \int_0^{\cos^{-1}(\eta-2)} \frac{\pi\,dx}{\sqrt{2(\eta-\cos x)}} = \frac{\pi}{\sqrt{2(3-\eta)}} \int_0^1 \frac{dx}{\sqrt{\zeta-x}\,\sqrt{\zeta(1-x)-(1-x)^2}} \qquad (D:14)$$

where:

$$\zeta = \frac{2}{3-\eta} \qquad (D:15)$$

It may easily be seen that (12) corresponds to restriction of x, y, and z to values near the bottom of the band.

If ζ is assumed large, as it will be near the bottom of the band, the integral in (14) may be evaluated approximately. The final result is:

$$\mathcal{J} \cong \frac{\pi}{\sqrt{2(3-\eta)}} \int_0^1 \frac{dx}{\zeta(1-x)^{1/2}} = \frac{\pi}{\sqrt{2}}\sqrt{3-\eta}. \qquad (D:16)$$

The result (16) may also be obtained from direct consideration of the integral in (7). At the bottom of the band, when x, y, and z are near zero, the cosine terms in (7) may be expanded in a Taylor series about the origin:

$$\cos x + \cos y + \cos z \cong 3 - \tfrac{1}{2}r^2 \qquad (D:17)$$

Hence the integral becomes:

$$\mathcal{J} = \iiint_0^{\pi} \delta(\tfrac{r^2}{2}-(3-\eta))\,dx\,dy\,dz$$

$$= 2\int_0^{\pi/2}\sin\theta\,d\theta \int_0^{\pi/2} d\varphi \int_0^{\sqrt{3}\pi} r^2\,\delta(r^2-2[3-\eta])\,dr .$$

$$= \frac{\pi}{2}\int_0^{\sqrt{3}\pi} \sqrt{r^2}\,\delta(r^2-2[3-\eta])\,d(r^2) \qquad (D:18)$$

Using the delta function, (18) becomes:

$$\mathcal{I} \cong \frac{\pi}{\sqrt{2}} \sqrt{3-\eta}$$

(D:19)

which is the same as the result obtained in (16).

Near the centre of the band, the integral (9) is difficult to evaluate. Hence, as a first approximation, the expression obtained for the bottom of the band will be assumed to hold for all (x,y,z). The expression for the absorption coefficient at the centre of the band then becomes:

$$\mu_{1s,2p_0 (max)} (a) = \frac{1}{nc} \left\{ \frac{\epsilon_{eff}}{\epsilon} \right\}^2 \frac{24 e^2}{\pi a^3 |U'|} \omega \left\{ X_0^{2p_0} + 2\eta X_a^{2p_0} \right\}^2 \frac{\pi}{\sqrt{2}} \sqrt{3-\eta}$$

$$= \frac{12\sqrt{6}}{nc} \left\{ \frac{\epsilon_{eff}}{\epsilon} \right\}^2 \frac{e^2}{a^3} \omega \frac{(X_0^{2p_0})^2}{|U'|}$$

$$\cong (1.6 \times 10^{-30}) \frac{\omega}{a^3 |U'|} \left\{ X_0^{2p_0} \right\}^2 \frac{1}{(a^*)^2}$$

(D:20)

since $\eta = 0$ at the band centre. The absorption cross-section is then found by multiplying (20) by a^3 to obtain:

$$\sigma \cong (1.6 \times 10^{-30}) \frac{\omega}{|U'|} \left\{ X_0^{2p_0} / a^* \right\}^2$$

(D:21)

In Figure 11 the absorption cross-section (21) is plotted as a function of a/a^*. It may be seen from the graph that (21) is approximately constant between $a = 8a^*$ and $a = 14a^*$, with a value of about 3×10^{-15} cm^2. This value is in quite good agreement with the experimental results of Bichard and Giles, who obtain an absorption cross-section value between 2 and 4×10^{-15} cm^2.

The non-constancy of the calculated cross-section beyond

$a = 14\,a^*$ is probably due mainly to inaccuracies in the band-width $\delta U'$ as read from Baltensperger's graph. A contribution from the natural line-width should be included.

The close agreement between the observed and calculated cross-sections is probably fortuitous, since the use of the expression (16) for x,y, and z away from the origin is unjustified. It is expected that correction of this error would increase the absorption coefficient (20). However, this correction should be at least partially cancelled by taking into account the random distribution of the impurities.

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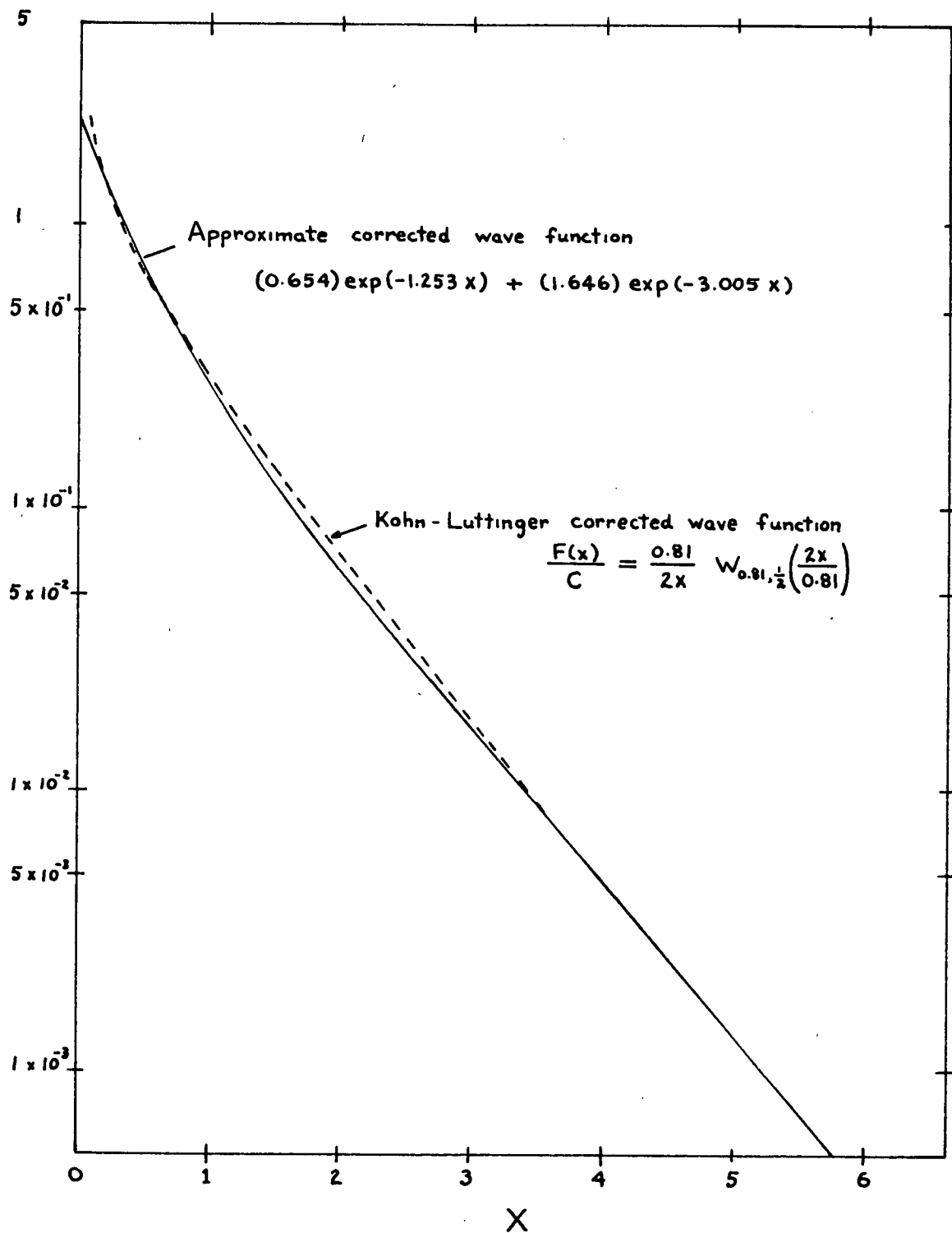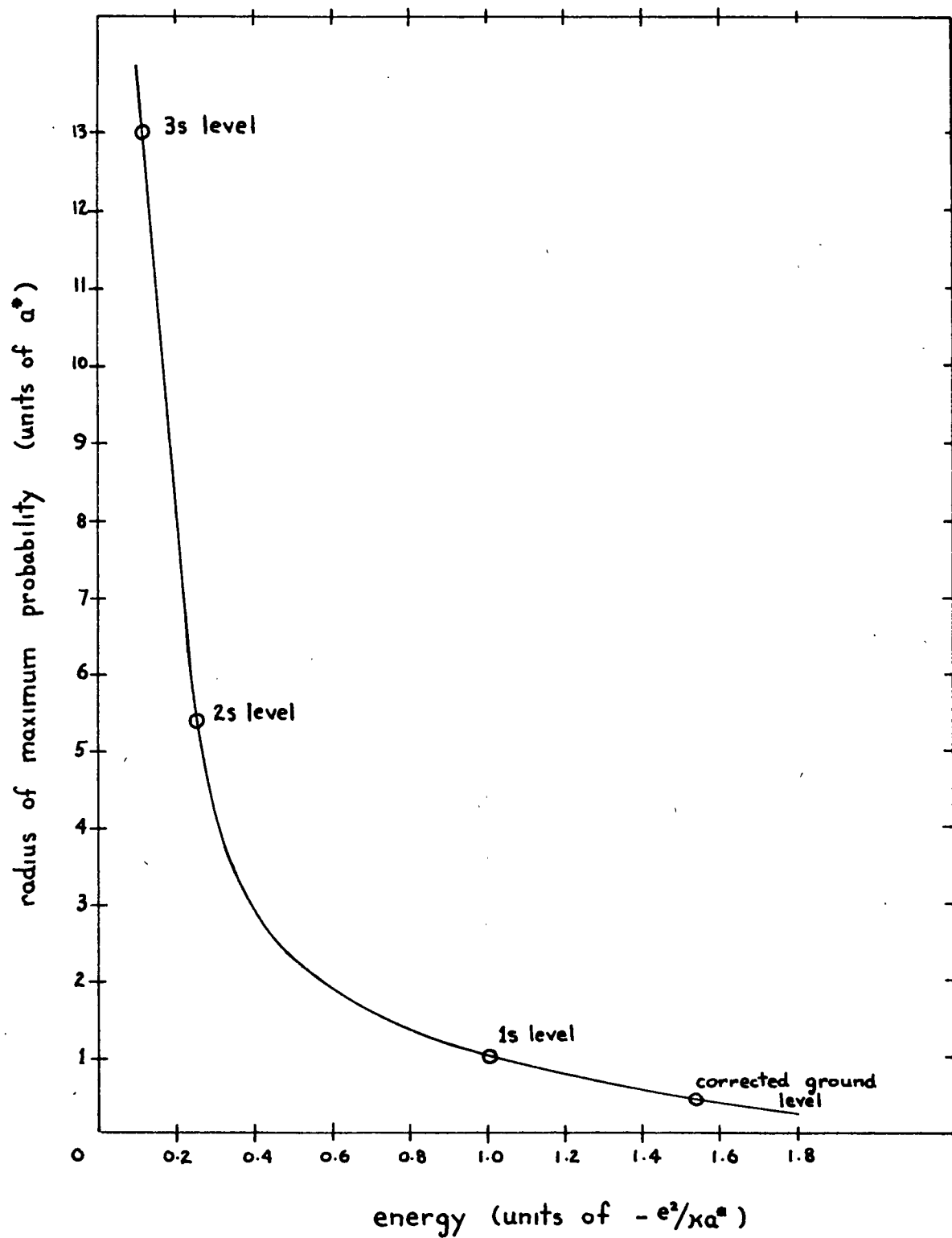
FIGURE 1

Corrected Ground-State Wave Function.
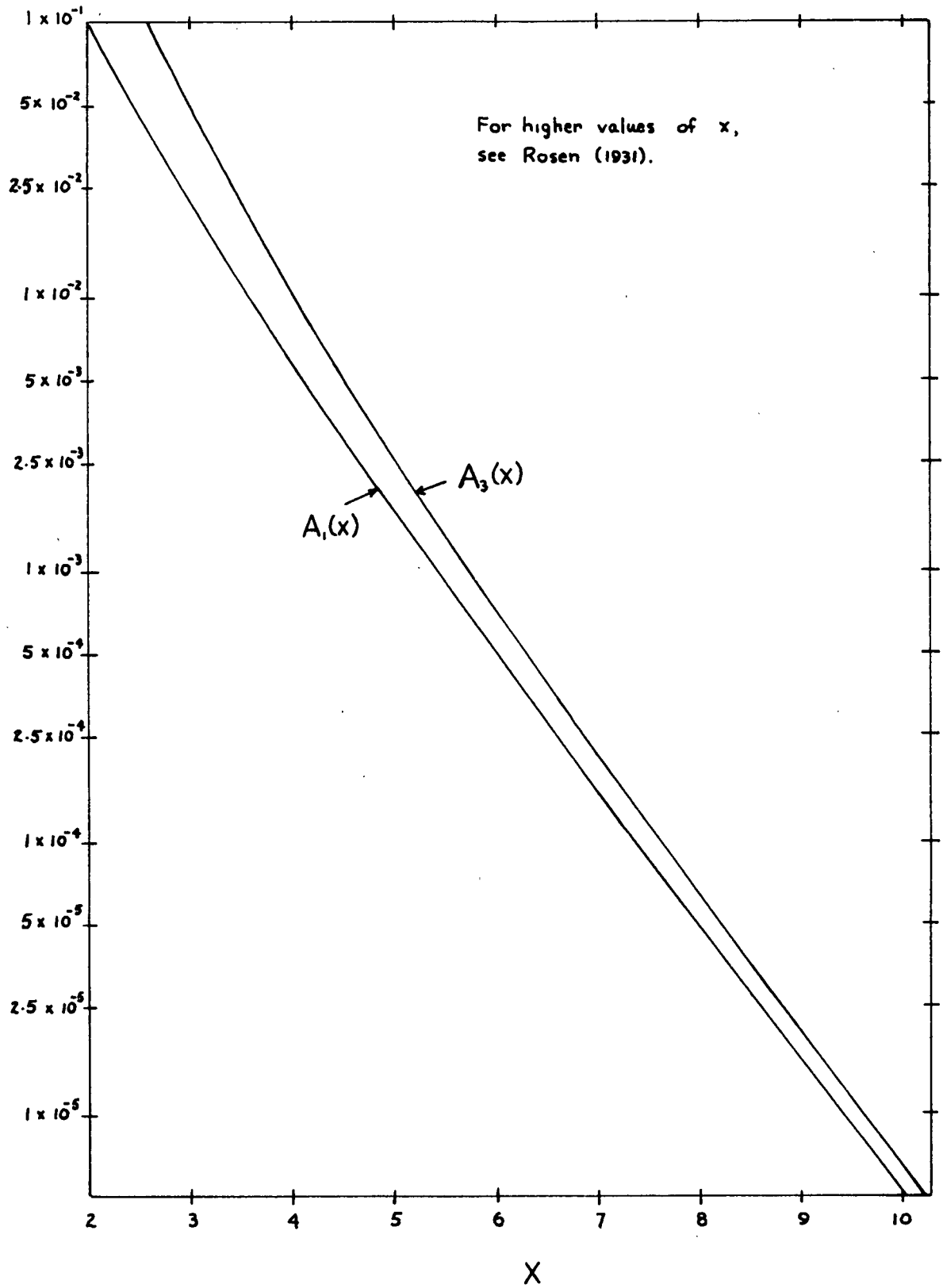
FIGURE 2

Location of Hydrogen-like Energy Levels.
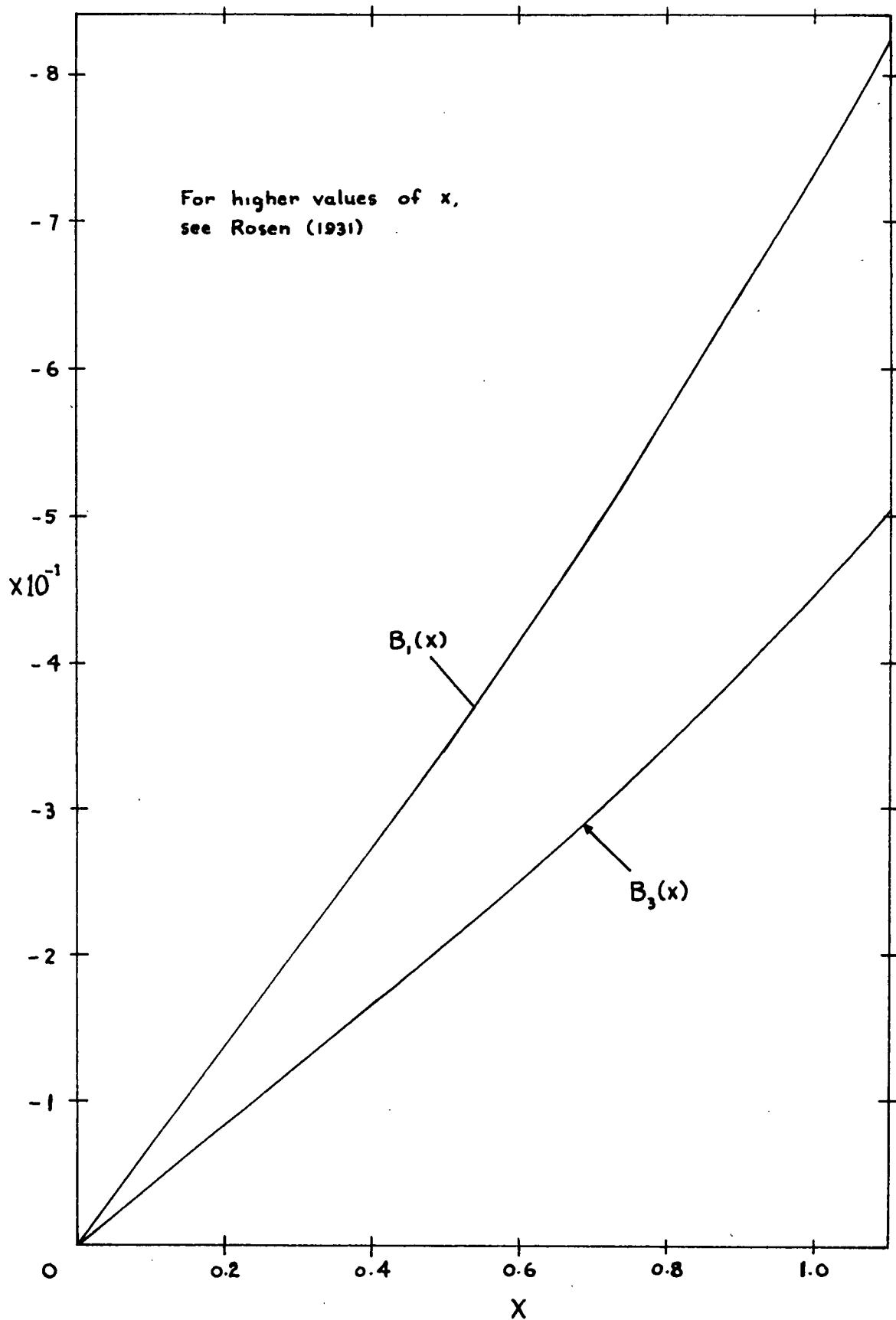
FIGURE 3a

Values of $A_1(x)$ and $A_3(x)$.

For higher values of x,
see Rosen (1931)

$\times 10^{-1}$

$B_1(x)$

$B_3(x)$

-8

-7

-6

-5

-4

-3

-2

-1

O   0.2   0.4   0.6   0.8   1.0

X

FIGURE 3b

Values of $B_1(x)$ and $B_3(x)$.

Y-axis label: $\dfrac{X_a^z}{a^*}$

Y-axis values (top to bottom): 6×10^{-2}, 4×10^{-2}, 2×10^{-2}, 1×10^{-2}, 7×10^{-3}, 5×10^{-3}

Annotation: approximate limits of error due to neglect of small integrals.

X-axis values: 3, 4, 5, 6, 7

$(4.6 \times 10^{18} cm^{-3})$ $(2.0 \times 10^{18} cm^{-3})$ $(1.0 \times 10^{18} cm^{-3})$ $(5.8 \times 10^{17} cm^{-3})$

a/a^*

(impurity concentrations in parentheses)
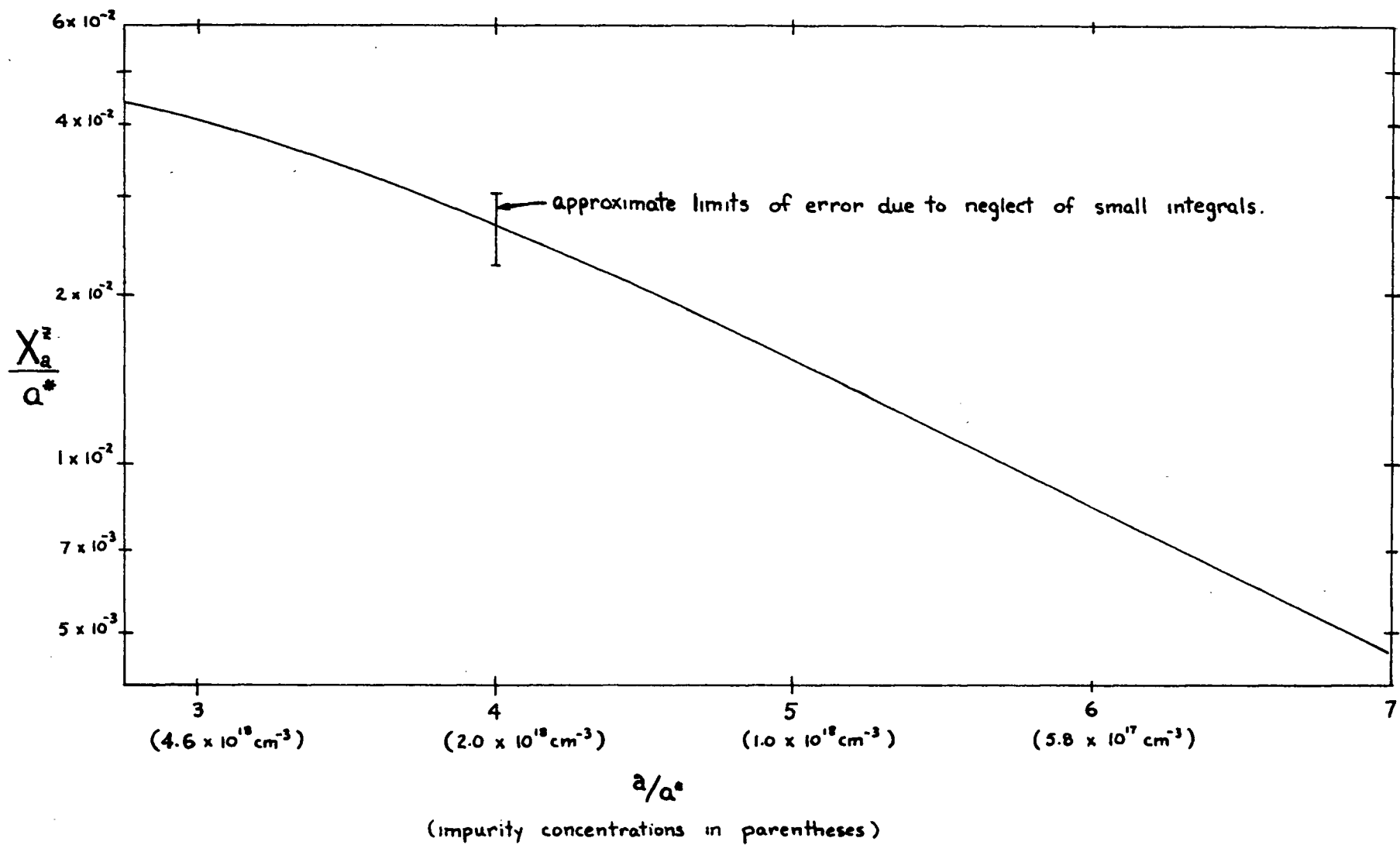
FIGURE 4

X_a^z as a Function of Impurity Lattice Spacing.
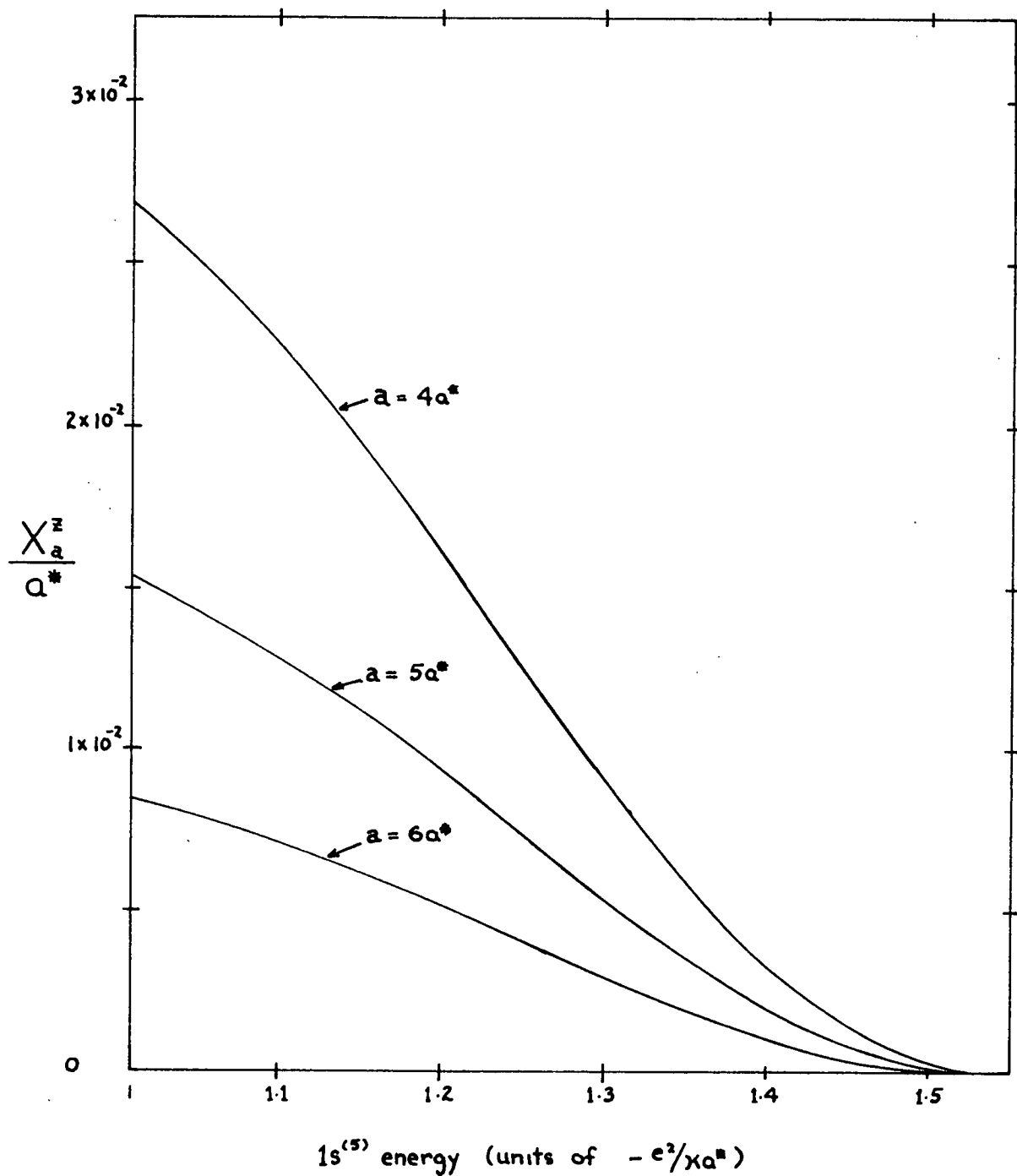
FIGURE 5

X_a^z as a Function of the Energy of the 1s$^{(5)}$ Level.

FIGURE 6

The Integral: $g(\xi) = \left[\displaystyle\int \frac{dx}{\sqrt{\sin^2 x + \sin^2 y}} \right]_{\substack{\cos x + \cos y = \xi \\ 0 \le x, y \le \pi}}$
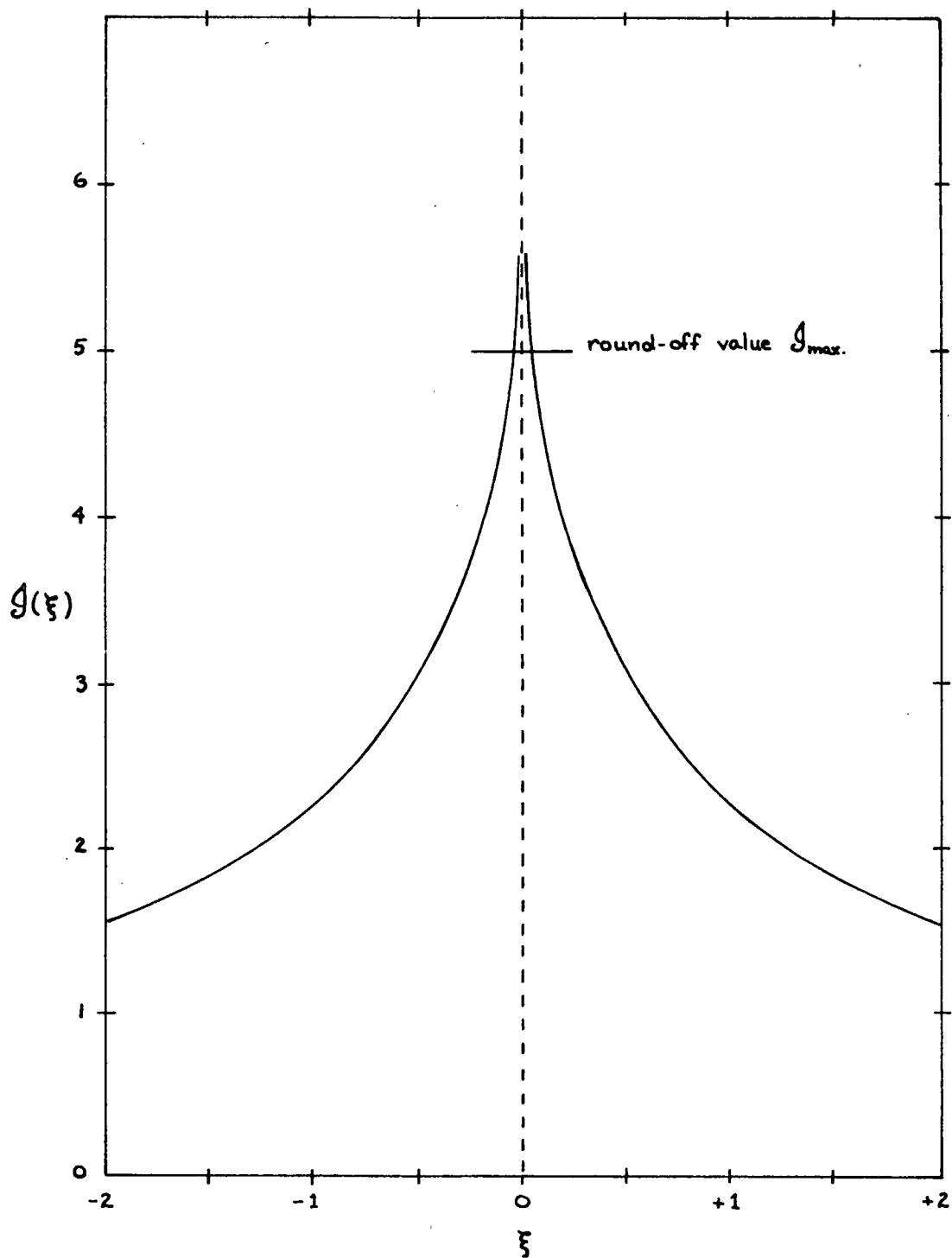
as a Function of ξ.

energy surfaces in the
first Brillouin zone.
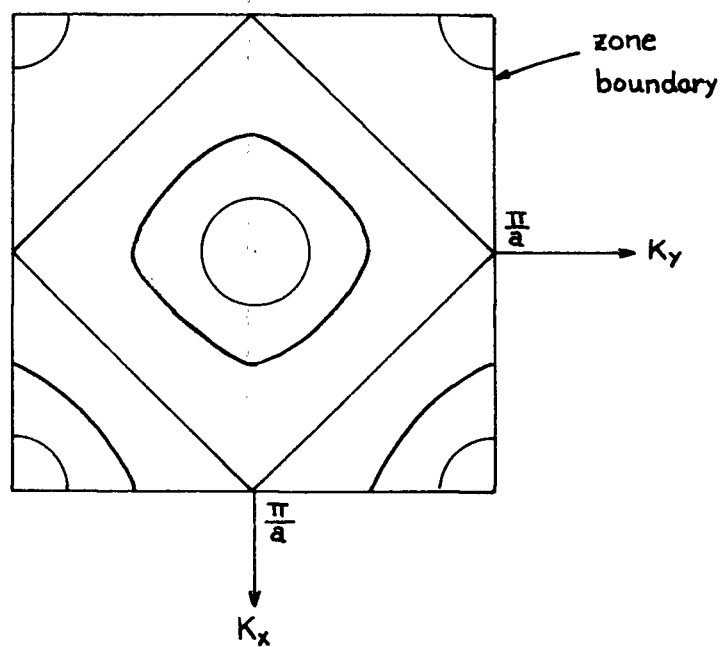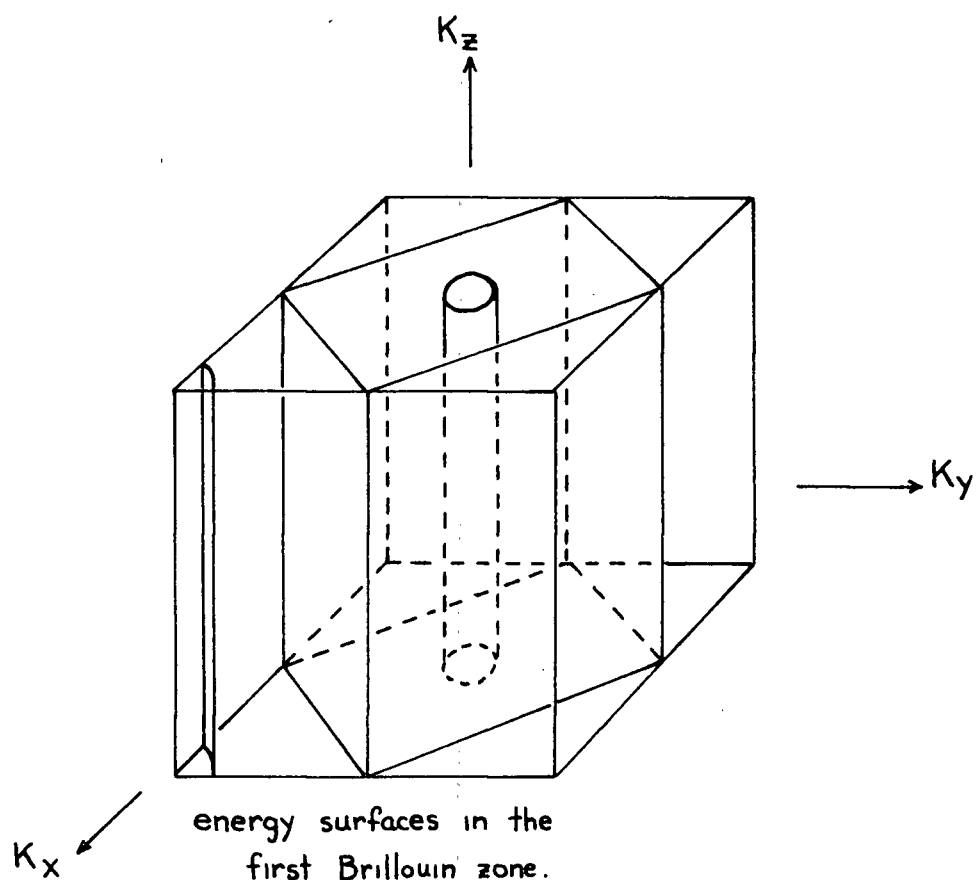
cross-section of energy surfaces

FIGURE 7

Tight-binding Energy Surfaces of (III:58) for cos $k_0a = 0$.

free-electron
surface

exact surface

tight-binding
surface
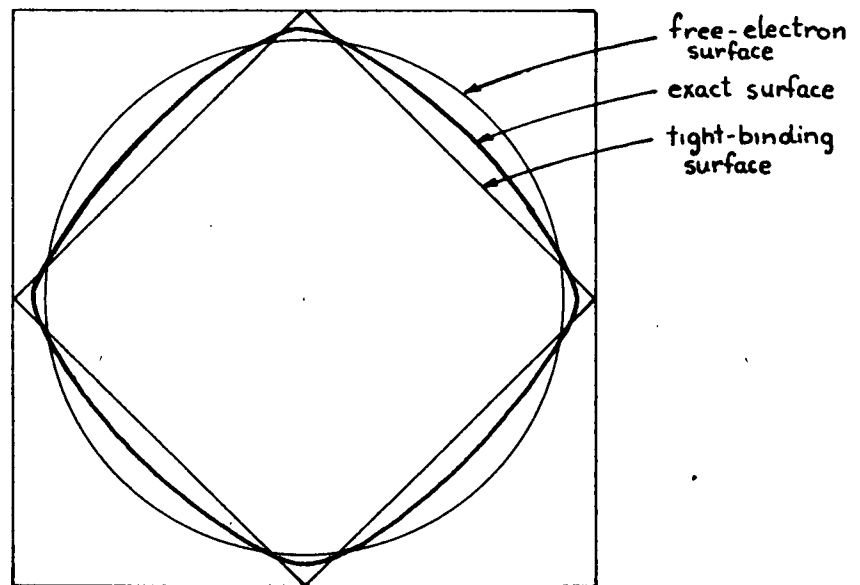
FIGURE 8

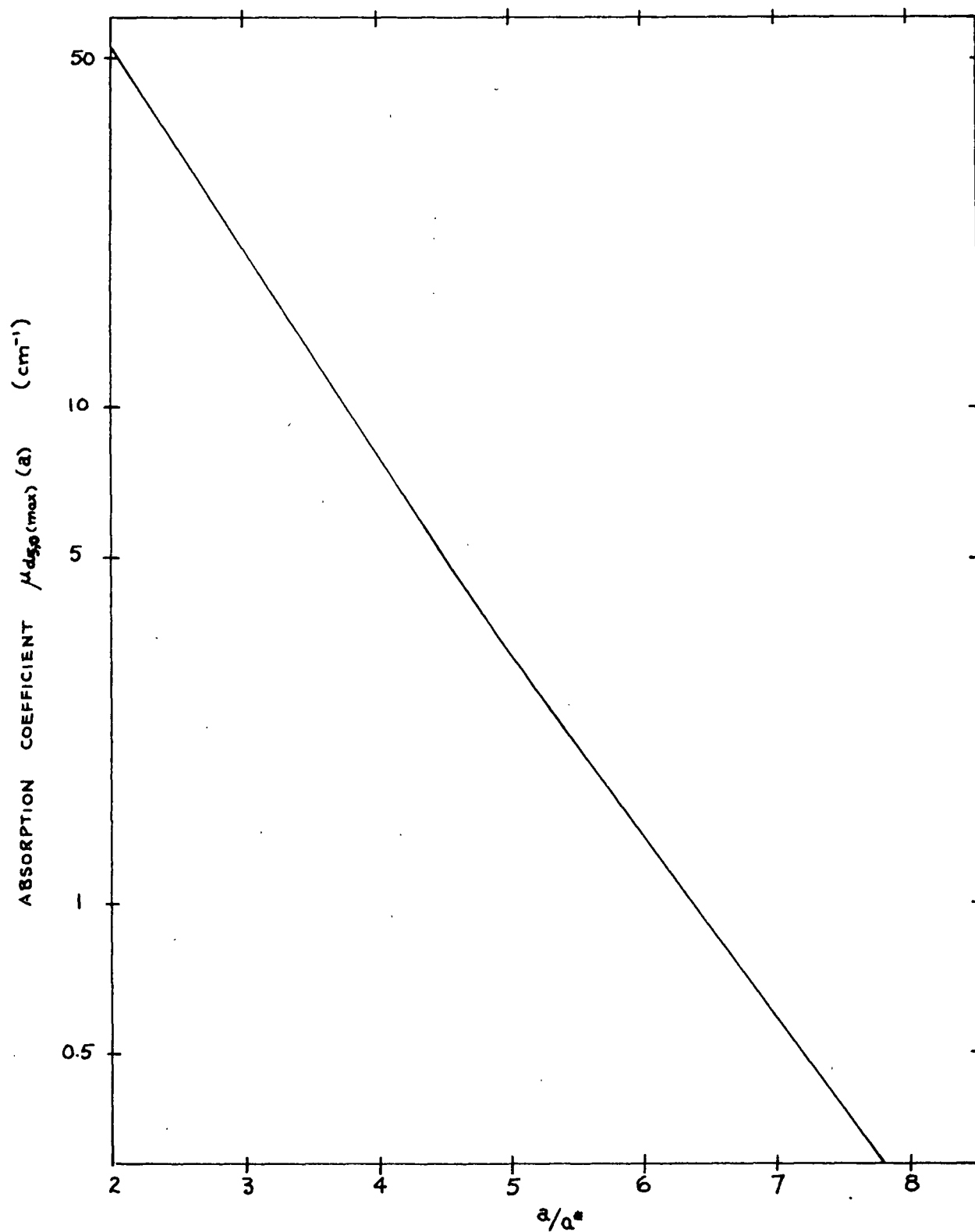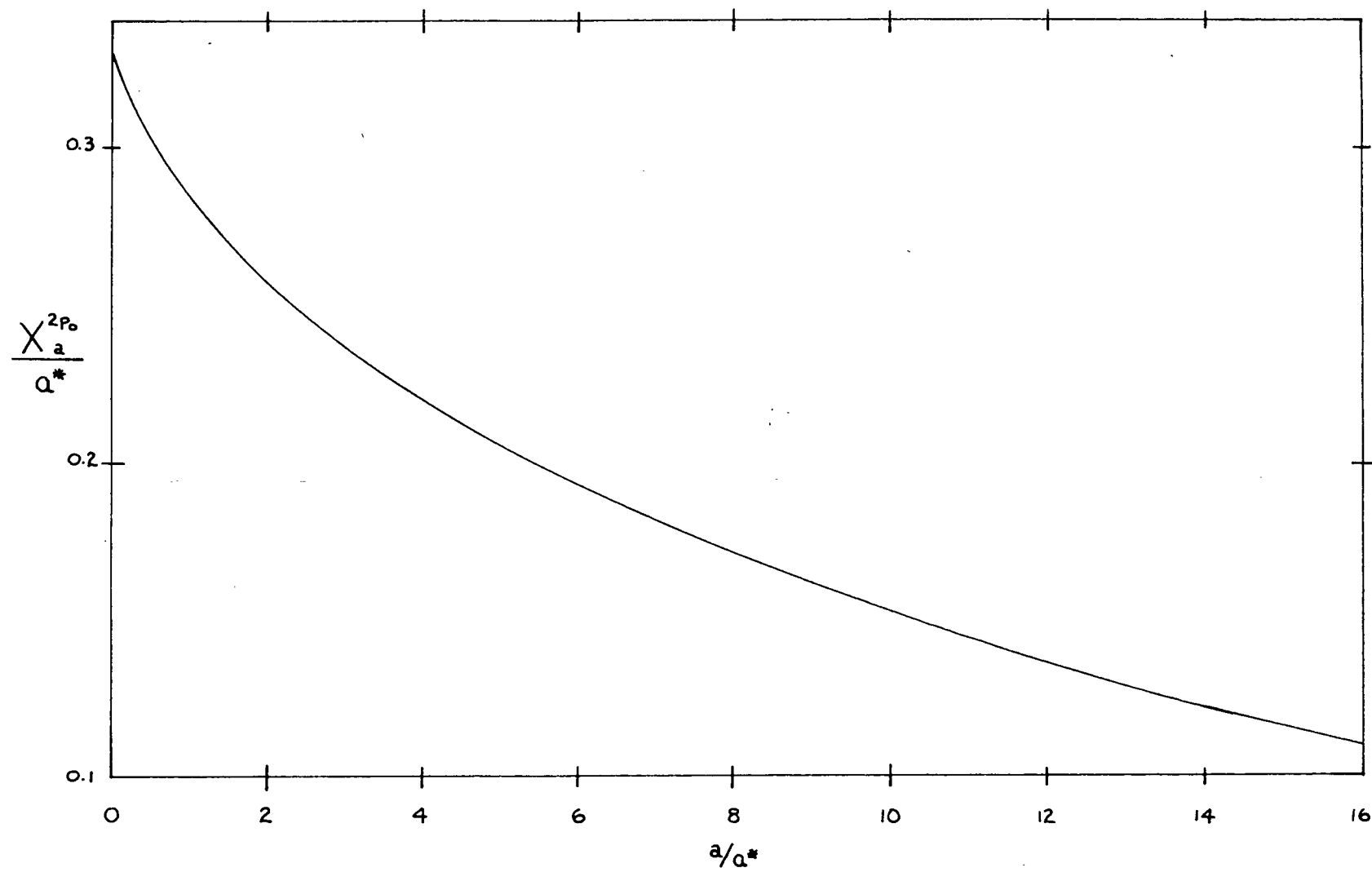Comparison of Corrected and Approximate

Energy Surfaces.

FIGURE 9

The $1s^{(0)} \longrightarrow 1s^{(5)}$ Absorption Coefficient as
a Function of Impurity Lattice Spacing.

FIGURE 10
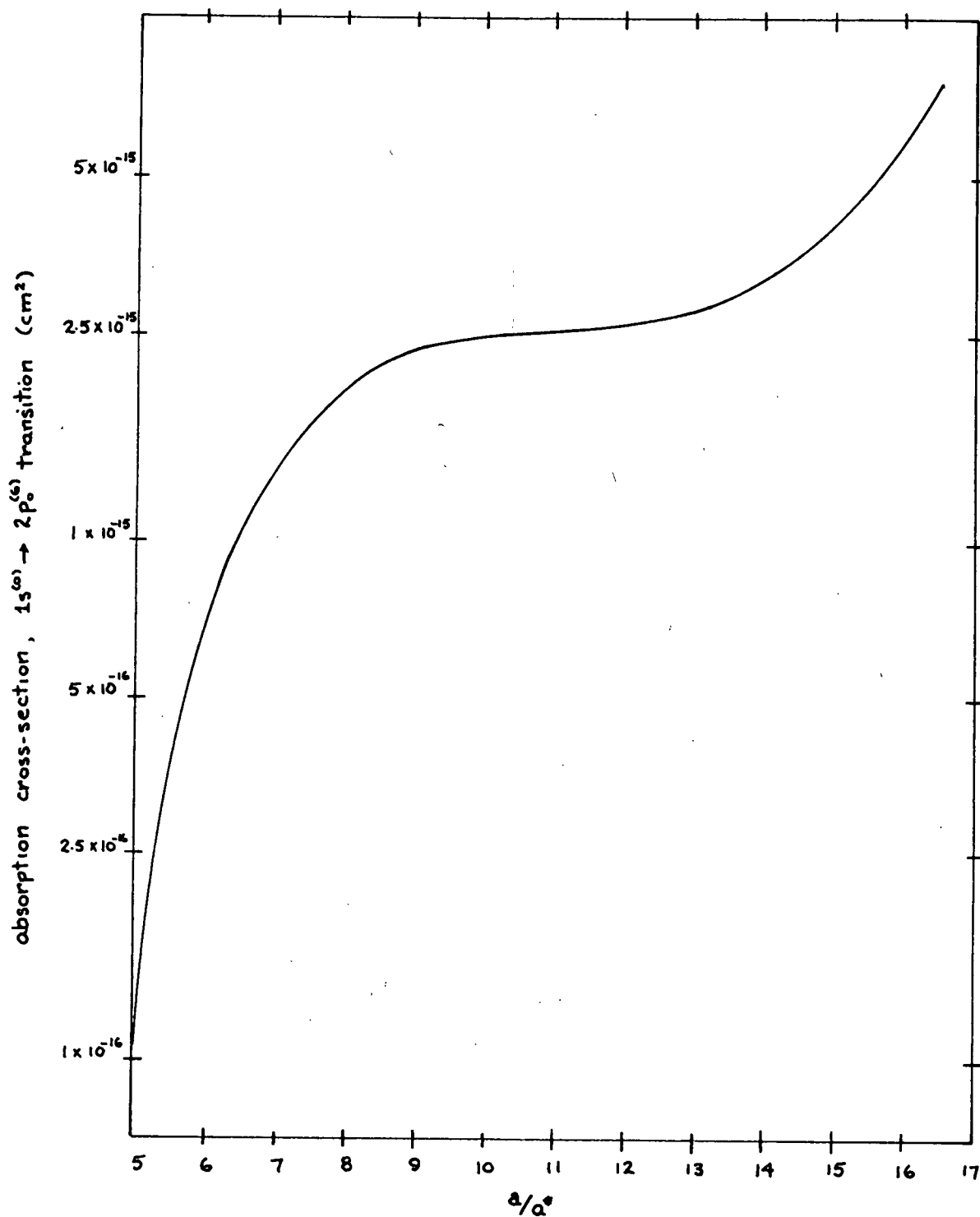
$X_a^{2p_0}$ as a Function of Impurity Lattice Spacing.

FIGURE 11

The Absorption Cross-Section for the
$1s^{(0)} \longrightarrow 2p_0^{(0)}$ Transition.