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An Investigation of Impurity Centers in Semiconductors of Variable Composition

Part I: General Theory and Some Applications

O.H. von Roos

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Wright-Patterson Air Force Base, Ohio
Through an Agreement with
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Abstract

A theory of deep point defects imbedded in otherwise perfect semiconductor crystals is developed with the aid of pseudopotentials. The dominant short-range forces engendered by the impurity will be sufficiently weakened in all cases where the cancellation theorem of the pseudopotential formalism is operative. Thus, effective-mass-like equations exhibiting local effective potentials derived from nonlocal pseudopotentials are shown to be valid for a large class of defects. A two-band secular determinant for the energy eigen-values of deep defects will also be derived from the set of integral equations which corresponds to the set of differential equations of the effective-mass type. Subsequently, the theory in its simplest form, will be applied to the system $Al_xGa_{1-x}As$:Se. It is shown that the one-electron donor level of Se within the forbidden gap of $Al_xGa_{1-x}As$ as a function of the AlAs mole fraction x reaches its maximum of about 300 meV (as measured from the conduction band edge) at the cross-over from the direct to the indirect band-gap at $x = 0.44$ in agreement with recent experiments.

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1. Introduction. One of the outstanding problems in modern day solid state physics continues to be the determination of the properties of "deep" impurities in otherwise perfect semiconductor crystals. By "deep" point impurities we mean either substitutional or interstitial foreign atoms embedded in the host lattice or just the absence of a lattice atom, a vacancy, with the proviso that the defect is capable of binding either one or more electrons or one or more holes in various energy states which are lying deep inside the band-gap. This distinguishes deep impurities from donors and acceptors, also known as shallow impurities, their energy levels being situated very close to a band edge. Whereas for some time now, the theoretical understanding of shallow levels has reached a quite satisfactory state based on the hydrogen mode, the difficulties encountered in the study of deep impurities largely stem from the existence of a relatively strong and rather short-range potential which valence electrons experience in the vicinity of the impurity. This is particularly true for isoelectronic impurities since there exists no Coulomb tail in this case, the potential being entirely confined to the central cell. The major difficulty presents itself in the fact that the extremely short-range nature of the interaction potential with its concomitant abundance of high Fourier components in wave vector or crystal momentum space prevents the applicability of effective-mass theory used so successfully in dealing with shallow levels (donors and acceptors). Much progress has been achieved however during the last decade concerning the deep-impurity problem. Here is not the place to review past achievements in the theoretical understanding of deep impurities nor do we want to discuss in any detail the importance of deep impurities as recombination centers governing the lifetime of electron-

hole pairs, a quantity so important for semiconductor device technology. Suffice it to cite recent review articles on the subject of both the theoretical understanding, or lack thereof, and the importance for device technology.[1] The reader will also find a plethora of references on the subject in the literature cited.[1]

As we have mentioned earlier, it is the strong, short-range potential engendered by an impurity which constitutes one of the main difficulties in solving successfully the impurity problem. This situation may be ameliorated by the use of a pseudopotential formalism, and the aim of this report is to give an account of a theory of deep impurities encompassing such a formalism. To be sure, there have appeared in the literature a number of accounts on the application of pseudopotentials to the impurity problem.[3][22][34] The reason for the idea to employ pseudopotentials in the kind of problems we are discussing here lies in their very nature.[4] Pseudopotentials and pseudo wave functions define a mathematical transformation of the original Schrodinger equation which, while leaving invariant the eigen-values of the energy, modify the wave function and the potential in a certain desirable manner. By orthogonalizing wave functions belonging to higher quantum states (valence bands) to the tightly bound inner electron shells (core states), this transformation achieves a weakening of the original potential in the inner core, precisely where the original potential, as seen by an outer electron, is strongest. This so-called cancellation theorem has, as a consequence, the agreeable feature to concomitantly weaken the high Fourier components in a crystal momentum expansion of the perturbed impurity wave function, thus making it possible to use effective-mass theory in cases where hitherto it was thought to

be inapplicable. The pioneering work of Pantelides[3)22)] bears ample witness to the truth of this conjecture.

In this report, we again tackle the problem of deep impurities with the aid of the pseudopotential formalism. In contradistinction to previous work[3)22)], we stay in the Wannier representation throughout. The advantages are twofold. Firstly, it is easier to ascertain the validity of - always inevitable - approximations made during the course of the derivation, and secondly, it will turn out that the equations governing the envelope functions peculiar to the impurity problem become local partial differential equations in contrast to the nonlocal equations derived previously.[3)]

Section 2 of this report concerns itself with pseudo-Wannier functions of the perfect crystal which form the basis for an expansion of the impurity wave function. Although pseudo wave functions and pseudopotentials are not unique generally, we confine ourselves to the use of the Austin form of the pseudo-potential[6)], in which case there exists a unique one-to-one correspondence between ordinary (true) wave functions and pseudo wave functions. The pseudo-Wannier functions will turn out to be less localized than the ordinary Wannier functions, and to what degree this might be detrimental will be discussed. In section 3, effective-mass type equations for the motion of electrons in the presence of a point impurity will be derived. The role of screening of the bare electron-ion potential mediated by electron-electron interactions will also be discussed. The main part of section 4 deals with the derivation of a secular determinant for the energy eigen-values from the set of integral equations, corresponding to the differential equations found in section 3, by a method first introduced by Bassani et al.[39)] Because of the use of pseudo-potentials, the number of bands to be considered in setting up the

secular determinant may be limited to but a few. In section 5 finally, the theory developed in section 4 will be applied to the system $A\ell_xGa_{1-x}As:Se$. Since selenium is a donor substituting for arsenic, an occupied level fairly close to the conduction band will be present so that the theory in its simplest form, taking into account only the conduction band with its various equivalent and non-equivalent minima without intervalley mixing, seems to be adequate to compute the donor energy level as a function of x, the mole fraction of AlAs in the compound under consideration. It is found, in agreement with experiment, that the magnitude of the energy level exhibits a maximum of ∿300 meV at $x = 0.44$, i.e. at the cross-over from the direct to the indirect band edge. The calculations reported here, have been performed by means of a variational principle and constitute one of the few cases in which computational labor could be held to a minimum.

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2. Preliminaries

Before we embark on the general theory of imperfections, let us review briefly the pseudo-potential formalism as it applies to a perfect crystal.

Let the Hamiltonian of the perfect crystal be

$$H = T + V \quad , \tag{1}$$

where T signifies the kinetic energy and V the periodic potential energy with the property

$$V(\underset{\sim}{r} + \underset{\sim}{R}_\alpha) = V(\underset{\sim}{r}) \quad . \tag{2}$$

Here $\underset{\sim}{R}_\alpha = \sum_j n_j^{(\alpha)} \underset{\sim}{a}_j$, a Bravais lattice vector, is defined by the arbitrary integers $n_j^{(\alpha)}$ and the primitive vectors $\underset{\sim}{a}_j$ of the unit cell. For crystals consisting of a single kind of atom, for instance silicon, we have

$$V = \sum_\alpha v(\underset{\sim}{r} - \underset{\sim}{R}_\alpha) \quad , \tag{3}$$

where the sum runs over all sites $\underset{\sim}{R}_\alpha$ within the periodicity volume V, and $v(\underset{\sim}{r})$ signifies the potential energy of an individual ion located at the site $\underset{\sim}{R}_\alpha$. For crystals containing more than one kind of ion within the unit cell, for instance GaAs, we may write

$$V = \sum_\alpha \sum_j v_j\left(\underset{\sim}{r} - \underset{\sim}{R}_\alpha - \underset{\sim}{b}_j\right) \quad . \tag{4}$$

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In this case, the additional sum runs over the various ions j located at positions $\underset{\sim}{b}_j$ within the unit cell defined by the lattice vector $\underset{\sim}{R}_\alpha$. With the definition

$$v(\underset{\sim}{r} - \underset{\sim}{R}_\alpha) = \sum_j v_j\left(\underset{\sim}{r} - \underset{\sim}{R}_\alpha - \underset{\sim}{b}_j\right) \quad , \tag{5}$$

eqs. (3) and (4) become identical, and no mention need be made of the complication arising from having more than one species of ions within the unit cell, at least as far as the development of the general theory is concerned.

Schrödinger's equation now reads

$$(T + V)\psi_{n\underset{\sim}{k}} = E_n(\underset{\sim}{k})\psi_{n\underset{\sim}{k}} \quad . \tag{6}$$

The Bloch functions,

$$\psi_{n\underset{\sim}{k}} = e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} u_{n\underset{\sim}{k}}(\underset{\sim}{r}) \quad , \tag{7}$$

therefore possess the energy eigen-values $E_n(\underset{\sim}{k})$, with k the crystal wave vector and n the band index in customary fashion. The quantity $u_{n\underset{\sim}{k}}$ is periodic in $\underset{\sim}{R}_\alpha$ and therefore satisfies an equation identical to eq. (2). It is to be stressed that we imply the Hartree-Fock one-electron approximation when writing eq. (6)[2]. The potential V is therefore by necessity non-local.[2] But these complications do not concern us here, since we assume that the unperturbed crystal eigen-values, $E_n(\underset{\sim}{k})$, are given, known functions of their parameters.

For reasons which will become apparent later, we will transcribe eq. (6) into the pseudo-potential formalism in the Wannier representation (similar calculations

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have been performed by Pantelides[3]). The reason for "pseudizing" the potential (3) are amply described in ref. 4. Here we can only give a very brief outline. Suppose we separate the eigen-functions, $\psi_{n\underset{\sim}{k}}$, into those belonging to the core states, $\psi_{c\underset{\sim}{k}}$, and those belonging to the valence and conduction bands, $\psi_{v\underset{\sim}{k}}$[5]. The inner core electrons are usually strongly localized at the atomic sites whereas the outer valence electrons form broad bands and are therefore delocalized to a greater or lesser extent. To each wave function, $\psi_{v\underset{\sim}{k}}$, satisfying eq. (6), we now associate *uniquely* a pseudo wave function $\phi_{v\underset{\sim}{k}}$ satisfying

$$(T + V)\phi_{v\underset{\sim}{k}} - \sum_{c} \psi_{c\underset{\sim}{k}} \langle\psi_{c\underset{\sim}{k}}|V|\phi_{v\underset{\sim}{k}}\rangle = E_v(\underset{\sim}{k})\phi_{v\underset{\sim}{k}} \quad . \tag{8}$$

The eigen-value, $E_v(\underset{\sim}{k})$, of eq. (8) is *identical* with the corresponding one for $\psi_{v\underset{\sim}{k}}$ corresponding to eq. (6). Furthermore, the connection between ϕ_v and ψ_v is given by

$$\phi_{v\underset{\sim}{k}} = \psi_{v\underset{\sim}{k}} + \sum_{c} \beta_{cv}(\underset{\sim}{k})\psi_{c\underset{\sim}{k}} \quad , \tag{9}$$

where the coefficients, $\beta_{cv}(\underset{\sim}{k})$, satisfy

$$\left(E_c(\underset{\sim}{k}) - E_v(\underset{\sim}{k})\right)\beta_{cv}(\underset{\sim}{k}) - \sum_{c'} \langle\psi_{c\underset{\sim}{k}}|V|\psi_{c'\underset{\sim}{k}}\rangle\beta_{c'v}(\underset{\sim}{k}) = \langle\psi_{c\underset{\sim}{k}}|V|\psi_{v\underset{\sim}{k}}\rangle \quad . \tag{10}$$

We have used the familiar Dirac notation throughout. As can be seen from eq. (8), we have used the Austin form for the pseudo potential.[6] From eq. (9), it follows that

$$\beta_{cv}(\underset{\sim}{k}) = \langle\psi_{c\underset{\sim}{k}}|\phi_{v\underset{\sim}{k}}\rangle \quad , \tag{11}$$

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because $\psi_{c\underset{\sim}{k}}$ and $\psi_{v\underset{\sim}{k}}$ are orthogonal. Sometimes the argument is turned around by writing

$$\psi_{v\underset{\sim}{k}} = \phi_{v\underset{\sim}{k}} - \sum_{c} \langle\psi_{c\underset{\sim}{k}}|\phi_{v\underset{\sim}{k}}\rangle\psi_{c\underset{\sim}{k}} \quad , \tag{12}$$

which shows that with *any* choice of $\phi_{v\underset{\sim}{k}}$, the wave function $\psi_{v\underset{\sim}{k}}$ is made orthogonal to the core states $\psi_{c\underset{\sim}{k}}$ by construction. This is important for practical calculations where convergence of a secular determinant toward a valence band energy eigen-value rather than toward a core state is desired or where a variational principle is desired to "home in" on a valence band energy rather than on a core state energy, the latter being several keV below the valence-band energies. As an added bonus, the convergence of the secular determinant in a plane-wave expansion, using simple plane waves to represent the wave functions $\phi_{v\underset{\sim}{k}}$, becomes much more rapid when using the device of eq. (12). Known by the name of the orthogonalized plane-wave method (OPW method) in this case, it had been proposed by Herring long before pseudopotentials became fashionable.[7)8)]

As seen from eq. (8), the pseudopotential is nonlocal[9)], but we will see later that, nevertheless, the impurity problem formulated here within the pseudopotential approach will give rise to a *local* effective potential. The true advantage of the Austin pseudopotential employed here consists of the validity of the cancellation theorem.[3)] This theorem states that the pseudopotential of eq. (8), which we may rewrite concisely as[11)]

$$V_A = V - \sum_{c,\underset{\sim}{k}'} \psi_{c\underset{\sim}{k}'}\langle\psi_{ck'}|V \tag{13}$$

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is considerably weaker in the core regions than the original potential V which is rather strong there.[12] This is of paramount importance for the impurity problem, as clearly realized some time ago.[3)14)34)] But before going into this matter, let us transcribe eqs. (8) and (10) into the Wannier representation.

The Wannier functions are defined by

$$w_n(\alpha) = N^{-1/2} \sum_{\underset{\sim}{k}} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} \psi_{n\underset{\sim}{k}} \quad , \tag{14a}$$

with the inverse transformation being

$$\psi_{n\underset{\sim}{k}} = N^{-1/2} \sum_{\alpha} e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} w_n(\alpha) \quad . \tag{14b}$$

The normalization adopted here is the following: $\langle \psi_{n\underset{\sim}{k}} | \psi_{n'\underset{\sim}{k}'} \rangle = \delta_{nn'}\delta_{\underset{\sim}{k}|\underset{\sim}{k}'}$, $\sum_{\underset{\sim}{k}} e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} = N\delta_{\alpha|0}$, $\sum_{\alpha} e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} = N \sum_{n} \delta_{\underset{\sim}{k}|\underset{\sim}{K}_n}$, where N is the number of unit cells in the quantization volume V, $\underset{\sim}{K}_n$ is a reciprocal lattice vector and sums over $\underset{\sim}{k}$ only extend over the first Brillouin zone.[10] Also, for a potential as given by eq. (4), the expression (14b), for instance, becomes

$\psi_{n\underset{\sim}{k}} = N^{-1/2} \sum_{\alpha} e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} \sum_{j} w_n^{(j)}(\underset{\sim}{r} - \underset{\sim}{R}_\alpha - \underset{\sim}{b}_j)$. For simplicity of notation, we write $w_n(\alpha) = w_n(\underset{\sim}{r} - \underset{\sim}{R}_\alpha) = \sum_{j} w_n^{(j)}(\underset{\sim}{r} - \underset{\sim}{R}_\alpha - \underset{\sim}{b}_j)$.

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Analogous to eqs. (14), the Wannier pseudofunctions may be introduced via

$$W_v(\alpha) = N^{-1/2} \sum_k e^{-ik\cdot R_\alpha} \phi_{vk} \tag{15a}$$

and

$$\phi_{vk} = N^{-1/2} \sum_\alpha e^{ik\cdot R_\alpha} W_v(\alpha) \quad . \tag{15b}$$

Note that the band index n of eqs. (14) encompasses all possibilities (core and valence states) whereas the band index v in eqs. (15) is reserved to valence states only.

Introducing now the Fourier transform of the coefficients, $\beta_{cv}(k)$, defined in eq. (10) as

$$\beta_{cv}(\alpha) = N^{-1} \sum_k \beta_{cv}(k) e^{-ik\cdot R_\alpha} \tag{16a}$$

with the inverse

$$\beta_{cv}(k) = \sum_\gamma \beta_{cv}(\gamma) e^{ik\cdot R_\gamma} \quad , \tag{16b}$$

we obtain from eqs. (9) and (15) the connection between the pseudo-Wannier functions W and the regular Wannier functions w[16], namely the relationship

$$W_v(\alpha) = w_v(\alpha) + \sum_{c,\gamma} \beta_{cv}(\alpha - \gamma) w_c(\gamma) \quad . \tag{17}$$

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Since the Wannier functions, $w_\nu(\alpha)$, are localized about their respective atomic sites,[17] we notice that the pseudo Wannier functions, $W_\nu(\alpha)$, are localized about all sites as the sum over γ in eq. (17) reveals. However, this is accomplished with varying success depending on the magnitude of the coefficients $\beta_{c\nu}(\alpha - \gamma)$ as a function of γ for fixed α. In order to transcribe eqs. (8) and (10) into the Wannier representation, we will employ the following device. Because the potential V is periodic (eq. (1)), we have in general that

$$\langle v_{n'k'}|V|v_{nk}\rangle = \delta_{k'k}\langle v_{n'k}|V|v_{nk}\rangle \quad . \tag{18}$$

This is the reason why, in eq. (8), the sum over the core states only extends over the band index c, keeping k fixed. We now relax this requirement. Equations (8) and (9) then go over into

$$(T + V)\phi_{\nu k} = \sum_{ck'} v_{ck'}\langle v_{ck'}|V|\phi_{\nu k}\rangle = E_\nu(k)\phi_{\nu k} \tag{19}$$

and

$$\phi_{\nu k} = v_{\nu k} + \sum_{ck'} \beta_{c\nu}(k,k')v_{ck'} \quad . \tag{20}$$

Equation (10) becomes analogously

$$\left(E_c(k') - E_\nu(k)\right)\beta_{c\nu}(k,k') = \sum_{c''k''} \langle v_{ck'}|V|v_{c''k''}\rangle\beta_{c''\nu}(k,k'') - \langle v_{ck'}|V|v_{\nu k}\rangle \quad . \tag{21}$$

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Equations (19) and (21) are, of course, equivalent to eqs. (8) to (10) provided that eq. (18) is used.[19] Now the transformation into the Wannier representation with the aid of eqs. (14) and (15) becomes easy. But first let us define the Fourier transforms of the band energies, $E_n(\underset{\sim}{k})$[17][18], as

$$\mathscr{E}_n(\alpha) = N^{-1} \sum_{\underset{\sim}{k}} E_n(\underset{\sim}{k}) e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} \tag{22a}$$

concomitantly with

$$E_n(\underset{\sim}{k}) = \sum_{\alpha} \mathscr{E}_n(\alpha) e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} \quad . \tag{22b}$$

Introducing the Fourier coefficient,

$$\tilde{\beta}_{cv}(\alpha,\gamma) = N^{-1} \sum_{\underset{\sim}{k},\underset{\sim}{k}'} \beta_{cv}(\underset{\sim}{k},\underset{\sim}{k}') e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha + i\underset{\sim}{k}'\cdot\underset{\sim}{R}_\gamma} \quad , \tag{23}$$

we obtain from eq. (21), after some algebra,

$$\sum_{\delta} \left[\mathscr{E}_c(\delta - \gamma)\tilde{\beta}_{cv}(\alpha,\delta) - \mathscr{E}_v(\alpha - \delta)\, \tilde{\beta}_{cv}(\delta,\gamma) \right] - \sum_{c',\delta} \langle w_c(\gamma)|V|w_{c'}(\delta)\rangle\, \tilde{\beta}_{c'v}(\alpha,\delta) =$$

$$\langle w_c(\gamma)|V|w_v(\alpha)\rangle \, . \tag{24}$$

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If we now restrict ourselves to the symmetry of eq. (18), $\tilde{\beta}_{cv}(\alpha,\beta)$ becomes only a function of the difference $(\alpha-\beta)$. In this case, eq. (23) goes over into eq. (16a), and equation (24) becomes

$$\sum_{\delta}\left(\mathscr{E}_c(\delta) - \mathscr{E}_v(\delta)\right)\tilde{\beta}_{cv}(\alpha - \gamma - \delta) - \sum_{c'\delta'} \langle w_c(\gamma)|V|w_{c'}(\delta)\rangle\tilde{\beta}_{c'v}(\alpha - \delta) = \langle w_c(\gamma)|V|w_v(\alpha)\rangle \cdot \tag{25}$$

It is eq. (25) which is the counterpart of eq. (10) in the Wannier representation. A direct transformation of eq. (10) with the aid of eqs. (14) would have met with difficulties. This is why we first relaxed the symmetry condition of eq. (18) and imposed it after the transformation had been performed.

The transformation of eq. (19) into the Wannier representation follows along the same lines and is given by

$$(T + V)W_v(\alpha) - \sum_{c,\gamma} w_c(\gamma)\langle w_c(\gamma)|V|W_v(\alpha)\rangle = \sum_{\gamma}\mathscr{E}_v(\gamma - \alpha)W_v(\gamma) \quad . \tag{26}$$

Before we go to the heart of the matter, the impurity problem, let us investigate the meaning of eq. (17). The pseudo-Wannier function, eq. (17), evidently is localized about all sites, as already mentioned. The coefficients, $\tilde{\beta}_{cv}$, which determine the localization about centers other than the main site α, obey eq. (25). Now, in order to deal with impurities, particularly deep centers with their strong localized potentials, one wishes to employ wave functions which are themselves localized so that a perturbation scheme of one type or another may converge rapidly (it is hoped). At the same time "pseudizing" the potential weakens its central core, so that high Fourier components in k-space become small,

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and approximations patterned after the effective-mass approximation may become acceptable even for deep centers (bound energy states deep in the forbidden gap between valence and conduction bands). But at the same time, the pseudo wave function of eq. (17) becomes somewhat delocalized. How much delocalization takes place is governed by the coefficients $\tilde{\beta}_{cv}$. Because of the strong localization of the core Wannier functions $w_c(\gamma)$, we have

$$\langle w_c(\gamma)|V|w_{c'}(\alpha)\rangle \approx V_{cc'}\delta_{\gamma\alpha} \tag{27}$$

to a very good approximation. Putting $\alpha - \gamma = \zeta$[20] and

$$\langle w_c(\gamma)|V|w_v(\alpha)\rangle = V_{cv}(\zeta) \tag{28}$$

as well as

$$\mathscr{E}_c(\gamma) - \mathscr{E}_v(\gamma) = \Delta_{cv}\mathscr{E}(\gamma) \quad , \tag{29}$$

equation (25) goes over into

$$\sum_{\gamma} \Delta_{cv}\mathscr{E}(\gamma)\tilde{\beta}_{cv}(\zeta - \gamma) - \sum_{c'} V_{cc'}\tilde{\beta}_{c'v}(\zeta) = V_{cv}(\zeta) \quad . \tag{30}$$

Although it is difficult to solve eq. (30) exactly, it is quite easy to see, at least qualitatively, that the dependence of $\tilde{\beta}_{cv}(\zeta)$ on ζ, the distance between any two lattice sites, is governed by $V_{cv}(\zeta)$. For if we put the RHS of eq. (30) equal to zero, the only solutions for the coefficients $\tilde{\beta}$ are $\tilde{\beta}_{cv}(\zeta) \equiv 0$, since the determinant of the coefficients of the ensuing linear equation for the quantities $\tilde{\beta}_{cv}(\zeta)$ does not vanish in general.[21] Introducing the potential matrix element $V_{cv}(\zeta)$, we see that $\tilde{\beta}_{cv}(\zeta)$ will become proportional to $V_{cv}(\zeta)$ and in higher order,

will become a function of $V_{cv}V_{c'v}$, etc. But from the definition $V_{cv}(\zeta)$ of eq. (28), we note that, due to the strong localization of the core state $w_c(\gamma)$, the matrix element $V_{cv}(\zeta)$ will exponentially decay with increasing ζ. Therefore, the delocalization inherent in eq. (17) is rather weak and may be ignored in many applications.

3. The Point Impurity Problem

Suppose now that the perfect crystal contemplated in the previous section contains an isolated impurity. This impurity may be a substitutional or interstitial atom or it may be a vacancy. Whatever it is, it will give rise to an additional potential energy which we denote by U. Rather detailed analyses of the structure of U have been presented by several authors, particularly for Si.[3)22)23)] It is fairly straightforward to generalize this analysis to other semiconductors. But we will treat U for the time being as a given function of all its relevant parameters, in particular its spatial coordinates. In order that no confusion arises, let us introduce the following notation. All unperturbed quantities ($U = 0$) will be annotated with a superscript zero. Therefore the periodic potential V of the previous section now becomes V^0, the Wannier function $w_n(\alpha)$ becomes $w_n^0(\alpha)$, the new quantities remain unprimed, etc. Also, since the implantation of a foreign atom (or removal of a lattice atom) will alter the equilibrium positions of at least the adjacent atoms from $\underset{\sim}{R}_\alpha$ to $\underset{\sim}{R}'_\alpha$ say, we denote this fact by a primed Greek letter. A core function $w_c^0(\alpha)$ of the unperturbed lattice now becomes $w_c^0(\alpha')$, for instance. We assume that the imperfection is located at $\alpha = 0$ ($\underset{\sim}{R}_\alpha = 0$) or, for an interstitial atom, in the immediate neighborhood of $\alpha = 0$. Incidentally, the collection of quantum numbers c for the core states differs in general for foreign atoms from those of the host atom except of course for isocoric atoms. This fact must be duly taken into account, but we will not mention it explicitly in the ensuing formalism.[24)]

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With $H^0 = T + V^0$, Schrödinger's equation in the "pseudized" version for the system-perfect lattice-plus-impurity - reads now, in analogy to eq. (26),

$$(H^0 + U)\psi - \sum_{c,\gamma'} w_c(\gamma')\langle w_c(\gamma')|V^0 + U|\psi\rangle = E\psi \quad , \tag{31}$$

where the sum runs over all core states and all sites γ'. We propose to solve eq. (31) with the following ansatz:

$$\psi = \sum_{v,\alpha} F_v(\alpha) W_v^0(\alpha) \quad . \tag{32}$$

We note that the sum extends only over valence (and conduction) bands, and the positions α are taken as those of the unperturbed crystal. This latter fact does not constitute an approximation, since the envelope functions F_v will depend parametrically on the α'. The pseudo-Wannier functions W_v^0 do not form a complete set unlike the ordinary Wannier functions, w_n^0. Had we expanded ψ into the complete set w_n^0, we would have had to include core states $n = c$ in the expansion *even in the limit $U = 0$*, since for $U = 0$, eq. (31) goes over into eq. (8) (or eq. (19)). In this case, any of the W_v^0 themselves become solutions of eq. (31), and according to eq. (17), even then core states are present. In other words, there would be no hope to confine an expansion of ψ into regular Wannier functions w_n^0 to include only a few valence bands, since even in 0th order, ψ would already contain a sizable amount of core levels. The ansatz (32) truly represents an approximation in anticipation of the need for only a few terms in the sum over the bands. From the orthonormality of the Wannier functions[17], we have

$$\langle w_n^0(\alpha)|w_{n'}^0(\beta)\rangle = \delta_{nn'}\delta_{\alpha\beta} \tag{33}$$

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and from eq. (17), it follows that

$$\langle w_v^0(\alpha)|W_{v'}^0(\beta)\rangle = \delta_{vv'}\delta_{\alpha\beta} \quad . \tag{34}$$

Multiplying eq. (31) by $\langle w_v^0(\alpha)|$, using eqs. (22) and the well-known relation[18)]

$$\langle w_v^0(\alpha)|H^0|w_{v'}^0(\beta)\rangle = \delta_{vv'}\mathscr{E}_v(\beta - \alpha) \quad , \tag{35}$$

we obtain a set of equations for the envelope functions $F_v(\alpha)$:

$$\sum_\beta \mathscr{E}_v(\beta - \alpha)F_v(\beta) + \sum_{v',\beta} \langle w_v^0(\alpha)|U|W_v^0(\beta)\rangle F_{v'}(\beta) - \sum_{v',c',\beta\gamma} \langle w_v^0(\alpha)|w_c(\gamma')\rangle$$

$$\times \langle w_c(\gamma')|V^0 + U|W_{v'}^0(\beta)\rangle F_{v'}(\beta) = EF_v(\alpha) \quad . \tag{36}$$

Since the core states are well localized, we make the further approximations

$$\langle w_v^0(\alpha)|w_c(\gamma')\rangle \approx \delta_{\alpha\gamma'}\langle w_v^0(\alpha)|w_c(\alpha')\rangle \tag{37a}$$

and

$$\langle w_c(\gamma')|V^0 + U|W_{v'}^0(\beta)\rangle \approx \delta_{\beta\gamma'}\langle w_c(\beta')|V^0 + U|W_{v'}^0(\beta)\rangle \quad . \tag{37b}$$

The meaning of these approximations is given in the following. The equilibrium positions $\underset{\sim}{R}_\alpha$ of the host lattice are slightly displaced to $\underset{\sim}{R}'_\alpha = \underset{\sim}{R}_\alpha + \delta\underset{\sim}{R}_\alpha$ due to the perturbation U. Owing to the strong localization of the core states about their respective sites and also to a lesser degree the localization of the Wannier functions for valence bands around their own sites, the matrix elements (37) are expected to be largest when the sites almost coincide. We presuppose that $\delta R_\alpha/R_\alpha \ll 1$, so that there is no intermixing of sites.

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Next we consider the matrix element,

$$M_{\alpha\beta} = \langle w_v^0(\alpha)|U|W_{v'}^0(\beta)\rangle \quad . \tag{38}$$

Away from the impurity (we remember that the impurity is located at $\alpha = 0$ ($R_\alpha = 0$)) the potential U is smooth, so we may approximate[18] we have

$$M_{\alpha\beta} \approx \delta_{\alpha\beta} U(\alpha) \quad . \tag{39}$$

In the vicinity of the impurity where U varies rather strongly, this approximation is not allowed and the matrix element must remain as it is. Equation (39) tells us that the second sum over β on the LHS of eq. (36) reduces to a single term if α is sufficiently far away from 0 (the position of the impurity).

Finally, with the well-known expression

$$\sum_\beta \mathscr{E}_v(\beta - \alpha) F_v(\beta) = E_v(-i\nabla_\alpha) F_v(\alpha) \quad , \tag{40}$$

(which follows from eqs. (22) together with[17)18)] ,

$$e^{\underset{\sim}{R}_\gamma \cdot \nabla_\alpha} F(\gamma) = F(\gamma + \alpha) \quad , \tag{41}$$

where ∇_α signifies the gradient with respect to α (or $\underset{\sim}{R}_\alpha$)) we obtain the following set of equations for the envelope functions F_v from eq. (36):

$$E_v(-i\nabla_\alpha) F_v(\alpha) + \sum_{v'} \langle w_v^0(\alpha)| \left\{ U - \sum_c |w_c(\alpha')\rangle\langle w_c(\alpha')| V^0 + U \right\} |W_{v'}^0(\alpha)\rangle F_{v'}(\alpha) = E F_v(\alpha) \quad . \tag{42}$$

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Before eq. (42) can be put to use, the potential U must be specified. But first, some general properties of eqs. (42) which are independent of the precise form of U may be pointed out. If α (or $\underset{\sim}{R}_\alpha$) is considered a continuous variable, as is customary,[17)18)] eqs. (42) constitute a set of *local* partial differential equations, although the underlying theory is essentially nonlocal. For an isocoric impurity, we have

$$w_c(\alpha') \approx w_c^0(\alpha) \tag{43}$$

for all α, even in the neighborhood of the impurity cell, and eqs. (42) go over into

$$E_v(-i\nabla_\alpha)F_v(\alpha) + \sum_{v'} \langle w_v^0(\alpha)|U|W_{v'}^0(\alpha)\rangle F_{v'}(\alpha) = EF_v(\alpha) \quad , \tag{44}$$

owing to the orthogonality of the valence functions w_v with the core states w_c. Furthermore, far enough from the impurity when α becomes equal to α', the core states w_c also become equal to w_c^0, and again eqs. (44) become valid. This is true whether the impurity core states are isocoric with the host core states or not. Therefore, the pseudopotential of the interaction matrix element in eq. (42) becomes effective only within the central cell of the impurity center and will effectively considerably weaken the interaction potential U precisely there where it is strongest. This is another manifestation of the cancellation theorem.[4)] Similar findings have also been reported by Pantelides.[3)14)]

The interaction potential energy U consists of a number of terms. Signifying the interaction of the valence electrons with the rest of the system and with each other, it consists of the bare interaction with the nuclei and all the core

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states U_b, together with the *self-consistent* electron-electron interaction.[25] In the one-electron approximation in which an electron satisfies the Schrödinger equation, the analog of the "pseudized" version of eq. (31) is

$$(H^0 + U)\psi = E\psi \quad , \quad U = U_b + U_s \tag{45}$$

in which the potential U is given by the sum of the bare (or external) potential U_b and a polarization or screening potential U_s. This latter potential can be thought of as being due to the readjustment of the electron configuration which existed prior to the application of the external potential U_b into a new configuration. In the simplest case, the Hartree approximation, U_s, is given by

$$U_s = e^2 \int d^3r' |\underset{\sim}{r} - \underset{\sim}{r}'|^{-1} \left(|\psi(\underset{\sim}{r}')|^2 - |\psi^0(\underset{\sim}{r}')|^2 \right) \quad , \tag{46}$$

where ψ is the solution of eq. (45) and ψ^0 signifies the solution of eq. (45) with $U_b = 0$. The solution of the non-linear system of eqs. (45), (46) constitutes what is generally known as the self-consistent solution and the potential $U=U_b+U_s$ as the self-consistent potential. The derivation just sketched, when followed through in detail, taking due account of the occupancy of all quantum states[26], results for each Fourier component of the bare potential U_b, in a correspondingly screened potential

$$U(\underset{\sim}{q}) = U_b(\underset{\sim}{q})/\varepsilon(\underset{\sim}{q}) \quad . \tag{47}$$

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The Fourier transform of $U_b(r)$ is defined by $U_b(\underset{\sim}{q}) = V^{-1}\int d^3v U_b(\underset{\sim}{r})e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}}$ with the inverse $U_b(\underset{\sim}{r}) = \sum_{\underset{\sim}{q}} U_b(\underset{\sim}{q})e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}$ where the sum over $\underset{\sim}{q}$ extends over all of $\underset{\sim}{q}$ space, not just the 1st Brillouin zone. The choice of discrete values for $\underset{\sim}{q}$ is consistent with the normalization imposed by the use of a periodic quantization volume V throughout this work.

A particularly simple expression for the dielectric constant ε is obtained if a) eqs. (45) and (46) are solved in 1st order perturbation theory (linearization), and b) if Umklapp processes are neglected.[27] It is given by

$$\varepsilon(\underset{\sim}{q}) = 1 - \frac{4\pi e^2}{Vq^2}\sum_{\underset{\sim}{k}v,v'}\left|\langle\psi_{v'\underset{\sim}{k}}|e^{-\underset{\sim}{q}\cdot\underset{\sim}{r}}|\psi_{v\underset{\sim}{k}+\underset{\sim}{q}}\rangle\right|^2\frac{F_v(\underset{\sim}{k}+\underset{\sim}{q}) - F_{v'}(\underset{\sim}{k})}{E_v(\underset{\sim}{k}+\underset{\sim}{q}) - E_{v'}(\underset{\sim}{k})} \quad . \qquad (48)$$

In eq. (48), the quantities $F_v(k)$ are the occupation numbers (1 or 0) of the unperturbed quantum states v, $\underset{\sim}{k}$ and the $E_v(\underset{\sim}{k})$ are the usual valence and conduction band energies. The neglect of Umklapp or central field corrections seems to be justified if the bands involved are sufficiently broad. Explicit calculations[28] have shown that Umklapp contributions are indeed small in most cases of interest.[29] Underlying expression (48) for the dielectric constant is yet another approximation to all those already made. It is the assumption that the polarizability of the core states may also be neglected. This is expressed by the fact that the summations in eq. (48) extend over valence bands only. But this neglect is justified since the core states are tightly bound and therefore much less susceptible to the influence from the outer electrons. To summarize, the dielectric constant given by eq. (48) has been obtained under the stated

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approximations by solving the self-consistent eqs. (45) and (46). Equations (48), being based on the Hartree approximation, by necessity ignores exchange and correlation contributions [25], but these contributions give rise to small effects[30] which we ignore.

One more remark is in order. The analysis for the screening of the bare potential U_b outlined above is based on eq. (45) which is the analog of eq. (31) but does not contain the pseudopotential included in eq. (31). The pseudo-part of the potential becomes significant only within the central cell at the locations of the lattice and impurity sites owing to the presence of the core states $w_c(\alpha')$. It is precisely in these regions near the ionic sites where Unklapp, as far as the dielectric constant is concerned, becomes important. But we have seen that Umklapp is negligible for the broad valence bands we are considering here. Therefore, as long as we are justified in using expression (48) for the dielectric constant, we do not have to screen the bare potential U_b at all as far as its appearance inside the nonlocal pseudo-part of the total potential is concerned. We may therefore write for the total potential

$$\tilde{V}_{vv'}(\alpha') = \langle w_v^0(\alpha)| \left\{ \tilde{U} - \sum_c |w_c(\alpha')\rangle \langle w_c(\alpha')| V^0 + U_b \right\} |W_{v'}^0(\alpha)\rangle \quad , \qquad (49)$$

where

$$\tilde{U} = \sum_{\underset{\sim}{q}} \frac{U_b(\underset{\sim}{q})}{\varepsilon(\underset{\sim}{q})} e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}} \qquad (50)$$

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is the screened bare potential with ϵ given by eq. (48). Equations (42) for the envelope functions $F_v(\alpha)$ now become

$$E_v(-iV_\alpha)F_v(\alpha) + \sum_{v'} \tilde{V}_{vv'}(\alpha')F_{v'}(\alpha) = EF_v(\alpha) \ . \tag{51}$$

Equations (49) to (51) form the basis of our further investigations. Inasmuch as the dielectric screening, eq. (48), follows from *linear* response theory, the potential $\tilde{V}$ must be considered to be weak. But this is true for most applications. The potential within the inner core is weak because of the cancellation theorem, and far away from the impurity $\tilde{V}$, becomes just

$$\lim_{R=\infty} \tilde{V} \approx \frac{e^2 Z}{\epsilon(0)R} \delta_{vv'} \tag{52}$$

with the net atomic number, Z, and the static dielectric constant, $\epsilon(0)$. Then for small enough Z, the total potential $\tilde{V}$ is indeed weak.[31)]

4. Methods of Solution

There exist essentially two methods to solve eqs. (51) for the envelope function $F_v(\alpha)$ and the associated energy eigenvalues. The first method consists of considering eqs. (51) as differential equations in the now continuous variable α (or $\underset{\sim}{R}_\alpha$ $\underset{\sim}{R}$) and expanding the operator of the band energy $E_v(-iV_\alpha)$ in a power series in $-iV_\alpha$ about an energy extremum and breaking off this series usually after the quadratic term. This is called the effective mass approximation (EMA) and an excellent review of it is given by Stoneham.[32)] Complications arise when the bands are degenerate, which is usually true for the valence bands just below the conduction band in semiconductors of group IV and III-V compounds.[32)33)] The EMA is valid only for shallow states (donors or acceptors) when a one-band

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approximation suffices. However, it is also valid for many *deep* levels provided that the band gap is indirect, as shown in ref. 2 and 13. For semiconductors with a direct band gap, the one-band approximation is almost certainly incorrect for deep levels even though the effective interaction (49) has been considerably diminished in the central impurity cell by the pseudopotential device. An attempt along these lines taking several bands into account has been made some time ago.[34] But in this work, the Kleinman-Phillips version of the pseudopotential[6] was used and the sum over the core states, the analog of our eq. (31), included also valence states, and no screening was taken into consideration. That theory is therefore difficult to compare with eqs. (51). Before we leave a discussion of the EMA, we like to point out one simple approach which is applicable to eqs. (51) when they collapse into a single equation (one-band approximation). We have seen in the last section, that the potential $\tilde{V}_{vv'}(R)$ becomes a slowly varying function of R (see for instance eq. (52)) for large distances from the impurity, whereas near the impurity the pseudopart of the potential avoids much of the variation of the original potential. For a single donor-like impurity, as an example, we may therefore approximate the potential for the ground state (S-state) by

$$\tilde{V}(R) = \begin{cases} -e^2/\varepsilon(0)R & \text{for } R > R_0 \\ -\mathscr{A} & \text{for } R < R_0 \end{cases} \tag{53}$$

where $\mathscr{A}$ is a suitably adjusted constant.[35] The equation for the envelope function $F_c(r)$ (the subscript c indicates that the level to be determined

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splits off the conduction band), assuming a scalar effective mass m^* for simplicity, becomes

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2 + V(R)\right) F_c(R) = (E - E_c)\, F_c(R) \tag{54}$$

E_c is the energy of the edge of the conduction band and $V(R)$ is given by eq. (53). The boundary conditions, i.e., F_c goes to zero at infinity and F_c stays finite at zero together with the continuity of the logarithmic derivative at $R = R_0$, determine the eigen-value for E once α and R_0 are known. The potential (53) constitutes a model potential, and as such has been introduced, albeit in a somewhat different context, long ago.[36] Usually, the constants R and α are determined from experimental data. If we can adopt a "muffin-tin" model, then the choice of R is somewhat arbitrary[37] and may be fixed once and for all. If α is determined using the experimentally known ground state energy, all excited states and their energies can be computed using the same constant α. This follows from eq. (49) and is quite a distinction from the usual model potential for unperturbed crystals where for each angular momentum ℓ, a new constant α_ℓ has to be determined.[36]

For deep levels in direct-band-gap semiconductors, the one-band EMA constitutes at best a poor approximation. We are looking, therefore, for an alternative way of solving eqs. (51). Now, if the energy eigen-values of the impurity are expected to lie in mid-band-gap, then not only do the conduction and valence bands contribute, but also considerable parts in k-space of the band energies

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$E_v(k)$ are involved. To take full advantage of the situation, a Fourier transformation of eqs. (51) is indicated. Therefore, defining

$$F_v(\alpha) = F_v(\underset{\sim}{R}_\alpha) = N^{-1/2} \sum_k f_v(\underset{\sim}{k}) e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} \quad , \tag{55a}$$

$$f_v(k) = N^{-1/2} \sum_\alpha F_v(\underset{\sim}{R}_\alpha) e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} \tag{55b}$$

as well as[38)]

$$\tilde{V}_{vv'}(\underset{\sim}{k}) = N^{-1} \sum_\alpha \tilde{V}_{vv'}(\underset{\sim}{R}_\alpha) e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}_\alpha} \quad , \tag{56}$$

we obtain from eqs. (51),

$$\left[E - E_v(\underset{\sim}{k})\right] f_v(\underset{\sim}{k}) = \sum_{v',\underset{\sim}{k}'} \tilde{V}_{vv'}(\underset{\sim}{k} - \underset{\sim}{k}') f_{v'}(\underset{\sim}{k}') \quad . \tag{57}$$

The summations over $\underset{\sim}{k}$ or $\underset{\sim}{k}'$ in the above equations only extend over the 1st Brillouin zone. The integral equations (57) are equivalent to eqs. (51). Before going any further, we allow the quantization volume V to become infinite. In this case, we are dealing with continuous variables, both in $\underset{\sim}{k}$ as well as in $\underset{\sim}{R}$ space The transcription follows the usual rules:

$$\sum_{\underset{\sim}{k}} \cdots \to \frac{V}{(2\pi)^3} \int d^3k \ \cdots \ ; \quad \sum_\alpha \cdots \to v^{-1} \int d^3R \ \cdots \quad , \tag{58a}$$

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where

$$v = \underset{\sim}{a}_1 \cdot (\underset{\sim}{a}_2 \times \underset{\sim}{a}_3) \tag{58b}$$

is the volume of a unit cell with the primitive lattice vectors $\underset{\sim}{a}_1$, $\underset{\sim}{a}_2$ and $\underset{\sim}{a}_3$. We also have $V = Nv$. The Kronecker δ symbols go over into their respective Dirac δ-functions

$$\delta_{\underset{\sim}{k}|\underset{\sim}{k}'} = \frac{(2\pi)^3}{V}\,\delta(\underset{\sim}{k} - \underset{\sim}{k}') \qquad \delta_{\alpha\beta} = v\,\delta(\underset{\sim}{R} - \underset{\sim}{R}') \quad . \tag{58c}$$

Equation (56) now becomes

$$\tilde{V}_{vv'}(\underset{\sim}{k}) = V^{-1}\int d^3R\,\tilde{V}_{vv'}(R)\,e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}} \quad . \tag{59}$$

The integral equations (57) are solved readily if the kernel $\tilde{V}(\underset{\sim}{k} - \underset{\sim}{k}')$ may be written as a product $V_1(\underset{\sim}{k})V_2(\underset{\sim}{k}')$. This can be achieved by using a complete set of normalized functions such that[39)]

$$\delta(\underset{\sim}{R} - \underset{\sim}{R}') = \sum_m g_m^*(\underset{\sim}{R})\,g_m(\underset{\sim}{R}') \quad . \tag{60}$$

We now define the new quantities

$$\int d^3R\,g_m(\underset{\sim}{R})\left[\tilde{V}_{vv'}(R)\right]^{1/2} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}} = \mathscr{T}^m_{vv'}(\underset{\sim}{k}) \tag{61a}$$

and

$$\int d^3R\,g_m^*(\underset{\sim}{R})\left[V_{vv'}(R)\right]^{1/2} e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}} = \bar{\mathscr{T}}^m_{vv'}(\underset{\sim}{k}) \quad . \tag{61b}$$

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It is to be noted that $\overline{\mathscr{F}}$ is not the complex conjugate to $\mathscr{F}$ because the potential $\tilde{V}$ may become negative or positive as a function of R depending on position. This is so because, for instance, a totally attractive true potential (negative for all R) will acquire positive parts for small R due to "pseudizing."[4] We also have assumed the interaction potential $\tilde{V}_{vv'}(R)$ to be centrally symmetric. From eqs. (57), (59), (60) and (61), it follows that

$$\left[E - E_v(\underset{\sim}{k})\right] f_v(\underset{\sim}{k}) = \sum_{v',m} \mathscr{F}^m_{vv'}(\underset{\sim}{k}) \frac{1}{(2\pi)^3} \int \overline{\mathscr{F}}^m_{vv'}(\underset{\sim}{k}') \, f_{v'}(\underset{\sim}{k}') \, d^3k' \quad . \tag{62}$$

Introducing the quantities

$$G^{\ell m}_{v_1 v|vv'} = (2\pi)^{-3} \int d^3k \; \overline{\mathscr{F}}^{\ell}_{v_1 v}(\underset{\sim}{k}) \; \mathscr{F}^m_{vv}(\underset{\sim}{k}) \left[E - E_v(\underset{\sim}{k})\right]^{-1} \tag{63a}$$

and

$$A^m_{vv'} = (2\pi)^{-3} \int d^3k \; \overline{\mathscr{F}}^m_{vv'}(\underset{\sim}{k}) f_{v'}(\underset{\sim}{k}) \quad , \tag{63b}$$

we obtain the linear set of equations

$$A^{\ell}_{v_1 v} = \sum_{v',m} G^{\ell m}_{v_1|vv} \; A^m_{vv'} \quad . \tag{64}$$

We now consider only two bands, assuming that the energy eigen-values within the band gap between the conduction band and the valence band are mainly determined by these two bands. We ignore the complications introduced by degeneracy of several valence bands. Designating the conduction band by v = 1 and the valence

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band by $v = 2$, we obtain four equations (they are still matrix equations in the space generated by the g_m) which may be written in matrix notation

$$\left.\begin{aligned} A_{11} &= G_{11|11}\, A_{11} + G_{11|12}\, A_{12} \quad , \quad & A_{12} &= G_{12|21}\, A_{21} + G_{12|22}\, A_{22} \\ A_{21} &= G_{21|11}\, A_{11} + G_{21|12}\, A_{12} \quad , \quad & A_{22} &= G_{22|21}\, A_{21} + G_{22|22}\, A_{22} \end{aligned}\right\} . \tag{65}$$

The determinant of the coefficients of this linear system must vanish, and it is this condition which determines the possible energy values within the band gap. With the help of the defining equations (59) and (63a), we also have:

$$\left(G_{ij/jl}\, G_{jl/lk}\right)^{ln} = \sum_m G^{lm}_{ij/jl}\, G^{mn}_{jl/lk}$$

$$= \frac{V}{(2\pi)^6} \int d^3k\, d^3k' \, \frac{\mathscr{F}^{l}_{ij}(\underset{\sim}{k})\, \mathscr{F}^{n}_{lk}(\underset{\sim}{k}')}{\left(E - E_j(\underset{\sim}{k})\right)\left(E - E_l(\underset{\sim}{k}')\right)}\, \tilde{V}_{jl}(\underset{\sim}{k}' - \underset{\sim}{k}) = \mathscr{G}^{ln}_{ij/lk} \quad . \tag{66}$$

After some manipulations, eqs. (65) may now be reduced to (again in matrix notation)

$$\left(G_{11|11} + G_{11|12}\, \mathscr{B}_1^{-1}\, \mathscr{G}_{12|11} - 1\right) A_{11} + G_{11|12}\, \mathscr{B}_1^{-1}\, G_{12|22}\, A_{22} = 0 \tag{67a}$$

and

$$G_{22|21}\, \mathscr{B}_2^{-1}\, G_{21|11}\, A_{11} + \left(G_{22|22} + G_{22|21}\, \mathscr{B}_2^{-1}\, \mathscr{G}_{21|22} - 1\right) A_{22} = 0 \quad . \tag{67b}$$

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Here we have introduced the inverse matrices $\mathscr{B}_1$ and $\mathscr{B}_2$ defined by:

$$\mathscr{B}_1 = 1 - \mathscr{G}_{12|12} \tag{68a}$$

and

$$\mathscr{B}_2 = 1 - \mathscr{G}_{21|21} \quad . \tag{68b}$$

Eliminating A_{11} from eq. (67b) gives

$$A_{11} = G^{-1}_{21|11} \left\{ \mathscr{G}_{21|22} + \mathscr{B}_2 \, G^{-1}_{22|21} \left(G_{22|22} - 1 \right) \right\} A_{22} \ , \tag{69}$$

so that inserting this into eq. (67a), it is seen that the energy eigen-values of the impurities are determined from the condition

$$\mathrm{DET} \left\{ \left(G_{11|11} - 1 + G_{11|12} \, \mathscr{B}_1^{-1} \, \mathscr{G}_{12|11} \right) G^{-1}_{21|11} \left(\mathscr{G}_{21|22} + \mathscr{B}_2 \, G^{-1}_{22|21} (G_{22|22} - 1) \right) + G_{11|12} \, \mathscr{B}_1^{-1} \, G_{12|22} \right\} \quad 0 \, . \tag{70}$$

Here the symbol DET signifies a determinant in the matrix space generated by the functions g_m introduced via eq. (60). Since the functions $g_m(\underset{\sim}{R})$ are largely arbitrary, a judicious choice may reduce the dimension of the (infinite) determinant of eq. (70) to a manageable size. In principle then, it is possible to compute the energy eigen-values of a point impurity, be it a substitutional or interstitial impurity or even a vacancy, with the aid of eq. (70) provided that the underlying band structure of the host crystal and the potential energy of the defect are known and provided that a number of approximations made in the course of this analysis are justified. It is perhaps worthwhile in concluding this work to point out the various approximations which led to the basic equations (49)

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through (51) and also to the determinantal eq. (70). The underlying, unperturbed crystal structure has been formulated in the one-electron approximation. This in itself does not constitute a limitation, since it is not necessarily predicated on the use of a single Slater determinant as it is in the Hartree-Fock approximation. Correlations may well have been taken into account. We left this question largely open, assuming that the unperturbed crystal properties (its wave functions and energy bands) are sufficiently well known in order to attack successfully the point impurity problem. The approximations made during the course of this work may be discussed in their order of appearance. First, we expanded the wave function ψ of the system - crystal + impurity - in pseudowave functions ϕ_v belonging only to valence and conduction bands, ignoring the core states. But the pseudo-functions contain an admixture of core states in a natural way. As far as only valence states are concerned, they form a complete, albeit non-orthogonal set since there is a one-to-one correspondence, barring accidental degeneracy, between $\psi^0_{v\underset{\sim}{k}}$ and $\phi^0_{v\underset{\sim}{k}}$. Furthermore, the pseudopotential weakens the strength of the true potential, as we have seen, so that high Fourier components and therefore admixtures of core states in the expansion (32) tend to be de-emphasized. Next, the approximations eqs. (37a) and (37b) diagonalize the corresponding matrix elements. While this constitutes an excellent approximation as far as eq. (37a) is concerned, it is less so for eq. (37b). The culprit here appears to be the pseudo-Wannier function, W^0_v, which is less localized than its counterpart, w^0_v. But we have seen from eq. 30 and the discussion following it, that the delocalization is not severe, and so the approximation of eq. (37b) is still quite justified. Another approximation which has not really been used, however, at least as far as the general formulation culminating in eqs. (49) to (51) is concerned, appears via eq. (39). It is self-evident, and it is certainly true

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far away from the impurity. The last covey of approximations to be discussed here briefly (since it has been done extensively in section 2) concerns itself with the screening of the bare potential or the influence of many-body electron-electron interactions on the one-electron Hamiltonian. The most severe limitation in this case consisted in using linear response theory, the bare potential being screened by means of a dielectric constant as in eq. (47). But this implies that the potential $U_b(R)$ is to be considered weak in the sense of first order perturbation theory. While this is justified in most cases of interest for large R, first-order perturbation theory will simply not do for small R. However by means of "pseudizing", the true potential had been weakened for small R to such an extent that first-order theory became viable throughout the whole range of R. The neglect of Umklapp (central field corrections), core polarizations, exchange and correlation corrections to the dielectric constant and the neglect of the screening of the pseudo-part (the nonlocal part) of the pseudopotential constitute additional approximations. They have been discussed in section 2 and their effects found to be small in many cases of interest.

Finally, turning to the derivation of eq. (70), two additional approximations have been introduced. Confining the expansion (eq. 32) to two bands only, constitutes one, and to assume the potential $\tilde{V}$ to be centrally symmetric constitutes the other approximation. While the first approximation is certainly valid if the bands considered are broad, so that there exists a large energy separation between the valence bands and all the lower bands, the second approximation implies an averaging over angular variables, a procedure often used in the literature.

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5. Donor Energy Level for Se in $A\ell_xGa_{1-x}As$.

In this section we like to apply some of the theory developed in the previous sections to a simple system. Selenium with the electronic structure [A] $3d^{10}4s^24p^4$, when substituted for arsenic with the electronic structure [A] $3d^{10}4s^24p^3$ in the crystalline compound $A\ell_xGa_{1-x}As$ will evidently behave as a donor since it contributes one more 4p electron to the lattice. It is known experimentally that in pure GaAs ($x = 0$), Se does indeed exhibit a donor level at 6 meV below the conduction band edge.[40] Recently, the position of this donor level within the band gap of the compound $A\ell_xGa_{1-x}As$ as a function of x has been determined experimentally.[41] With the aid of eq. (57) we shall now try to determine this donor level theoretically. In order to be able to do so, we must know the underlying band structure, $E_v(\underset{\sim}{k})$, and the interaction potential, $\tilde{V}_{vv'}$. Since we are dealing with donor states, the drastic simplification of ignoring all valence bands may be made. Furthermore, the conduction band of $A\ell_xGa_{1-x}As$ possesses one minimum at the Γ point ($\underset{\sim}{k} = 0$) and six equivalent minima at X $\Big((100), (\bar{1}00) \ldots (00\bar{1})\Big)$. The relative position of these minima with respect to each other as well as their effective masses are a function of x, the mole fraction of $A\ell As$ in GaAs. Before we go into the details of the calculations, let us write eq. (57) again for the convenience of the reader, dropping the band index now that we are dealing only with the conduction band:

$$\Big(E(\underset{\sim}{k}) - E\Big)f(\underset{\sim}{k}) + \sum_{k'} \tilde{V}(\underset{\sim}{k} - \underset{\sim}{k}')f(\underset{\sim}{k}') = 0 \ . \tag{71}$$

Let us assume with Twose[42] that we may write for $f(\underset{\sim}{k})$,

$$f(\underset{\sim}{k}) = \phi_j(\underset{\sim}{k} - \underset{\sim}{k}_j) \ , \tag{72}$$

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which is large *only* in the vicinity of a band extremum, such that

$$E(\underset{\sim}{k})f(\underset{\sim}{k}) = \left[E(\underset{\sim}{k}_j) + (\hbar^2/2)\sum_{\alpha,\beta} m^{-1}_{j\alpha\beta}(k - k_j)_\alpha(k - k_j)_\beta\right]\phi_j(\underset{\sim}{k} - \underset{\sim}{k}_j) \tag{73}$$

with sufficient accuracy. Here we have assumed a number of minima located at the positions $\underset{\sim}{k}_j$ and have performed a Taylor series expansion about $\underset{\sim}{k} = \underset{\sim}{k}_j$ retaining only the first two terms. Evidently

$$\left.\frac{\partial^2 E(\underset{\sim}{k})}{\partial k_\alpha \partial k_\beta}\right|_{\underset{\sim}{k}=\underset{\sim}{k}_j} = \frac{\hbar^2}{2m_{j\alpha\beta}} \tag{74}$$

defines the effective mass tensor, $m_{\alpha\beta}$, in the usual way (α,β indicate Cartesian components). In the neighborhood of $\underset{\sim}{k} = \underset{\sim}{k}_j$, eq. (71) now becomes

$$\left[E(\underset{\sim}{k}_j) - E + (\hbar^2/2)\sum_{\alpha,\beta} m^{-1}_{j\alpha\beta}(\underset{\sim}{k} - \underset{\sim}{k}_j)_\alpha(\underset{\sim}{k} - \underset{\sim}{k}_j)_\beta\right]\phi_j(\underset{\sim}{k} - \underset{\sim}{k}_j)$$

$$+\sum_{\underset{\sim}{k}'\ell} \tilde{V}(\underset{\sim}{k} - \underset{\sim}{k}')\,\phi_\ell(\underset{\sim}{k}' - \underset{\sim}{k}_\ell) = 0 \tag{75}$$

Multiplying eq. (75) by $e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}$ and summing over all $\underset{\sim}{k}$ yields

$$\sum_{\ell,\underset{\sim}{k}} e^{i\underset{\sim}{k}_\ell\cdot\underset{\sim}{r}}\left\{\left[E(k_\ell) - (\hbar^2/2)\sum_{\alpha,\beta} m^{-1}_{j\alpha\beta}\,\partial^2/\partial x_\alpha\partial x_\beta\right]\phi_\ell(\underset{\sim}{k} - \underset{\sim}{k}_\ell)e^{i(\underset{\sim}{k}-\underset{\sim}{k}_\ell)\cdot\underset{\sim}{r}}\right.$$

$$\left.+\sum_{k'} V(k - k')e^{i(\underset{\sim}{k}-\underset{\sim}{k}')\cdot r}\phi_\ell(\underset{\sim}{k}' - \underset{\sim}{k}_\ell)e^{i(\underset{\sim}{k}' - \underset{\sim}{k}_\ell)\cdot r}\right\} = 0 \tag{76}$$

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By analogy to eqs. (55a) and (56), we define

$$F_\ell(\underset{\sim}{r}) = N^{-1/2} \sum_{\underset{\sim}{k}} \phi_\ell(\underset{\sim}{k} - \underset{\sim}{k}_\ell) e^{i(\underset{\sim}{k}-\underset{\sim}{k}_\ell)\cdot \underset{\sim}{r}} \tag{77a}$$

and

$$\tilde{V} = \sum_{\underset{\sim}{k}} V(\underset{\sim}{k}) e^{i(\underset{\sim}{k}-\underset{\sim}{k}')\cdot \underset{\sim}{r}} \quad . \tag{77b}$$

If we also define

$$H_\ell = E(\underset{\sim}{k}_\ell) - (\hbar^2/2) \sum_{\alpha,\beta} m_{j\alpha\beta}^{-1} \partial^2/\partial x_\alpha \partial x_\beta + \tilde{V}(r) \quad , \tag{78}$$

we may write eq. (76) in the compact form

$$\sum_j e^{i\underset{\sim}{k}_j \cdot r} (H_j - E) F_j(\underset{\sim}{r}) = 0 \quad . \tag{79}$$

The physical significance of the functions F_j may be seen if we retrace the steps which lead from eq. (32) to eq. (77a). Since ϕ_j is large only in the vicinity of $\underset{\sim}{k}_j$, we may write

$$F(\underset{\sim}{k}) = \sum_j \phi_j(\underset{\sim}{k} - \underset{\sim}{k}_j) \tag{80}$$

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Then using eqs. (80), (77a) and (32) we find

$$\psi = \sum_{\ell} F_{\ell}(\underset{\sim}{r})\phi^{0}_{c\underset{\sim}{k}_{\ell}} \tag{81}$$

where $\phi^{0}_{c\underset{\sim}{k}_{\ell}}$ are the pseudo Bloch functions associated with the conduction band minima located at $\underset{\sim}{k} = \underset{\sim}{k}_{\ell}$, and the wave function ψ of eq. (81) is an approximate solution of eq. (31). It follows now from both eqs. (79) and (81) that the energy can be expressed by

$$E = \frac{\sum_{j,\ell} \langle F_j | e^{i(\underset{\sim}{k}_{\ell}-\underset{\sim}{k}_j)\cdot \underset{\sim}{r}} H_{\ell} | F_{\ell} \rangle}{\sum_{j,\ell} \langle F_j | e^{i(\underset{\sim}{k}_{\ell}-\underset{\sim}{k}_j)\cdot \underset{\sim}{r}} | F_{\ell} \rangle} \tag{82}$$

an expression which lends itself nicely to a variational calculation. But before we go ahead and do this, we must delve into the significance of eq. (79). Equation (79) constitutes *one* equation for apparently *many* functions F_j. Now, if we are dealing with a crystal like Si for instance, where only equivalent minima (6 in this case) exist, then all functions F_j are equal by symmetry except for certain coefficients depending on the particular point group symmetry involved. But these factors are known from group theory, and therefore eq. (79) is sufficient for a solution of the eigen-value problem. However in cases of non-equivalent minima, the argument fails and eq. (79) is not sufficient for finding a unique solution. Equation (79) has been derived from eq. (75) essentially by summing over *all* $\underset{\sim}{k}$. But if the summation over $\underset{\sim}{k}$ is restricted to a subzone centered about each minimum at $\underset{\sim}{k}_j$, we obtain a set of equations, one for each F_j.

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This device has been used by Bassani et al.[23] But this method leads also to non-local potentials in configuration space and gives significant simplifications only for potentials which are very strongly localized in momentum space. It would be therefore best to work with eq. (75), which is really a set of equations, one for each ϕ_j, rather than with eq. (79), which constitutes only one equation for all F_j. However we can avoid this complication if we use eq. (82) as a variational principle in which the function F_j belonging to non-equivalent minima are varied independently. Consequently, we set

$$F_0 = (\pi a^3)^{-1/2} \, e^{-r/a} \tag{83a}$$

and for j = 1 to 6

$$F_j = \alpha_j (\pi b^3)^{-1/2} \, e^{-r/b} \tag{83b}$$

representing the envelope functions belonging to the minimum at Γ (83a) and the six equivalent minima at X (83b) of the conduction band of the $A\ell_x Ga_{1-x}As$. a and b constitute two independent variational parameters. The coefficients α_j are assigned the value $1/\sqrt{6}$ for the ground state (the A_1 representation of the group T_d[43]). As model for the band structure, we take a simplified version of eq. (78). For the sole minimum at Γ, we put

$$H_0 = -\frac{\hbar^2}{2m_0} \nabla^2 + \tilde{V}(\underset{\sim}{r}) \tag{84a}$$

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and for the six equivalent minima at (k,0,0) (-k,0,0) (0,k,0) (0,-k,0) (0,0,k) and (0,0,-k) we put

$$H_j = H_1 = \frac{\hbar^2}{2m_1} \nabla^2 + \mathscr{E}_c + \tilde{V}(\underset{\sim}{r}) . \tag{84b}$$

The zero of energy is measured from the position of the Γ minimum. For the potential $\tilde{V}$, we use the semi-empirical expression (53). All quantities, the effective masses m_0 and m_1, $\mathscr{E}_c$, the energy difference between direct and indirect band minima, k, the magnitude of the wave vector connecting the direct with any of the indirect minima, $\mathscr{A}$, the strength of the attractive effective potential well and finally the static dielectric constant ε(0) are functions of x. Values for the effective masses m_0 and m_1 and for the static dielectric constant ε(0) have been used as reported by Hauser et al.[44]. Values for $\mathscr{E}_c$ have been computed using band gap versus composition expressions culled from the same report. Continuing with the calculations, we insert eqs. (83) into eq. (82) and perform the indicated integrations. After some tedious but straightforward algebra we obtain for E:

$$E = D^{-1}\left\{N_1 + N_2 + N_3 + N_4 + N_5 + N_6 + N_7\right\}, \tag{85}$$

where with

$$c = ab/(a + b),$$

$$D = 2 + 16\sqrt{6}\left[c/(a + b)\right]^{3/2}(1 + k^2c^2)^{-2} + (1 + k^2b^2)^{-2} + 16(2 + k^2b^2)^{-2}, \tag{86a}$$

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$$N_1 = \frac{\hbar^2}{2m_0a^2} + \frac{\hbar^2}{2m_1b^2} + \mathcal{E}_c, \tag{86b}$$

$$N_2 = 2\sqrt{6}\,\frac{\hbar^2}{ab}\left[\frac{2c}{1+k^2c^2}\left(\frac{1}{m_0a}+\frac{1}{m_1b}\right) - \frac{c^2}{(1+k^2c^2)^2}\left(\frac{1}{m_0a^2}+\frac{1}{m_1b^2}\right)\right]$$

$$+ \frac{\hbar^2}{2m_1b^2}\left[\frac{1+2k^2b^2}{(1+k^2b^2)^2} + 16\,\frac{1+k^2b^2}{(2+k^2b^2)^2}\right]$$

$$+ \mathcal{E}_c\left[(1+k^2b^2)^{-2} + 16(2+k^2b^2)^{-2} + 8\sqrt{6}\,[c/(a+b)]^{3/2}(1+k^2c^2)^{-2}\right], \tag{86c}$$

$$N_3 = -e\mathcal{E}\left[1 - \left(1 + 2\,\frac{R}{a} + 2\,\frac{R^2}{a^2}\right)e^{-2R/a}\right] - \frac{e^2}{\varepsilon a}\left(1 + 2\,\frac{R}{a}\right)e^{-2R/a}, \tag{86d}$$

$$N_4 = -\sqrt{6}\;8(ab)^{-3/2}\left\{\frac{e^2}{\varepsilon}\,c^2(1+k^2c^2)^{-1}\left(\frac{\sin kR}{kc} + \cos kR\right)e^{-R/c}\right.$$

$$+ e\mathcal{E}c^3(1+k^2c^2)^{-2}\left(2 - \left[\left(\frac{1}{kc} - kc\right)\sin kR + \cos kR\right]e^{-R/c}\right)$$

$$\left. - e\mathcal{E}Rc^2\,\frac{e^{-R/c}}{1+k^2c^2}\left(\frac{\sin kR}{kc} + \cos kR\right)\right\}, \tag{86e}$$

$$N_5 = -e\mathcal{E}\,1\left[-\left(1 + 2\,\frac{R}{b} + 2\,\frac{R^2}{b^2}\right)e^{-2R/b}\right] - \frac{e^2}{\varepsilon b}\left(1 + 2\,\frac{R}{b}\right)e^{-2R/b}, \tag{86f}$$

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$$N_6 = -\frac{e^2}{\mathcal{E}b}(1 + k^2b^2)^{-1}\left(\frac{\sin kR}{kb} + \cos kR\right) - \mathcal{A}(1 + k^2b^2)^{-2}\left(1 + \left[2\cos 2kR + \frac{1}{2}\left(\frac{1}{kb} - kb\right)\sin 2kR\right]e^{-2R/b}\right) + \mathcal{A}\frac{R}{b}(1 + k^2b^2)^{-1}\left(\frac{\sin kR}{kb} + \cos 2kR\right)e^{-2R/b}, \tag{86g}$$

$$N_7 = -\frac{8e^2}{\mathcal{E}b}(2 + k^2b^2)^{-1}\left(\frac{\sin\sqrt{2}kR}{kb} + \cos\sqrt{2}kR\right)e^{-2R/b}$$
$$- 4\mathcal{A}(2 + k^2b^2)^{-2}\left(4 - \sqrt{2}\left[4\cos\sqrt{2}kR + \left(\frac{2}{kb} - kb\right)\sin\sqrt{2}kb\right]e^{-2R/b}\right)$$
$$+ 8\mathcal{A}\frac{R}{b}(2 + k^2b^2)^{-1}\left(\sqrt{2}\,\frac{\sin\sqrt{2}kR}{kb} + \cos\sqrt{2}kR\right)e^{-2R/b} \tag{86h}$$

The task now becomes formidable. Given the quantities R, ϵ, k, e^2 (the square of the electronic charge) and $\mathcal{A}$, one must determine the variational parameters a and b via the equations

$$\frac{\partial E}{\partial a} = \frac{\partial E}{\partial b} = 0 \tag{87}$$

using of course, all expressions (86) in the defining equation (85) for E. After having solved the transcendental eqs. (87) for a and b, the energy E finally is computed via eq. (85). However, a and b signify the extent of the electron cloud for an electron bound to the impurity and, for shallow states, this extent is large, covering many lattice sites. The magnitude of k is of the order of a reciprocal lattice vector. Therefore it is expected that the product ka or kb is large compared to unity. If this is true, a drastic simplification arises since most of the terms of eqs. (86) become negligibly small. The neglect of the

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terms containing ka or kb is tantamount to the neglect of intervalley mixing. Neglecting then intervalley mixing, the equation for the energy becomes

$$E = \frac{1}{2}\ \mathscr{E}_c + \frac{\hbar^2}{4m_0 a^2} + \frac{\hbar^2}{4m_1 b^2} + \frac{1}{2}\ (N_3 + N_5) \tag{88}$$

where N_3 and N_5 are given by eqs. (86d) and (86f), respectively. If we measure all lengths in units of the Bohr radius $a_H = 0.529\text{Å}$ and energies in units of the Rydberg $R_H = 13.6054$ eV, and if we introduce the quantities

$$R = \alpha a_H, \quad m_0 = \gamma_0 m_e, \quad m_1 = \gamma_1 m_e, \quad y_0 = 2R/a, \quad y_1 = 2R/b \tag{89}$$

where m_e is the mass of a free electron, the variational eqs. (87) become simply

$$y_j\ e^{y_j} = \gamma_j \left[\alpha^2 (\mathscr{A}/R_H) y_j^2 + (2\alpha/\epsilon)\left(1 + y_j - y_j^2\right)\right], \qquad j = 0 \text{ or } 1\ . \tag{90}$$

The energy E becomes, with the aid of eqs. (90),

$$E = \frac{1}{2}\ \mathscr{E}_c - \mathscr{A} + \frac{1}{2}\ \mathscr{A} \sum_{j=0}^{1} \left(1 + y_j + \frac{1}{2}\ y_j^2 + \frac{1}{4}\ y_j^3\right) e^{-y_j}$$

$$- (R_H/4\epsilon\alpha) \sum_{j=0}^{1} \left(y_j + y_j^2 + y_j^3\right) e^{-y_j}\ . \tag{91}$$

For any given values of the parameters γ_j, α, ϵ and $\mathscr{A}$, eqs. (90) possess a unique set of solutions y_j. Once these solutions are found, the energy level E can be

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computed via eq. (91). It is interesting to note that if ε is made formally infinite, eqs. (90) become

$$e^{y_j} = \left(\gamma_j \alpha^2 \mathscr{A}/R_H\right) y_j \tag{92}$$

Letting $\varepsilon \to \infty$ is tantamount to setting the Coulomb tail of the potential (53) equal to zero, and such a potential is representative of an isoelectronic impurity. But eqs. (92) only permit a solution (a bound state) if

$$\gamma_j \alpha^2 \mathscr{A}/R_H \geq e = 2.7183 \ , \tag{93}$$

and this inequality is almost identical to the well-known criterion for the onset of bound states derived from the one-band, one-site model for impurity energy levels by Koster and Slater.[45] That theory leads to the expression

$$1 = -\mathscr{A} N^{-1} \sum_{\underset{\sim}{k}} \left(E - E_c(\underset{\sim}{k})\right)^{-1} \tag{94}$$

for the energy level of an isoelectronic impurity. If we now replace $E_c(\underset{\sim}{k})$, rather boldly, by the expression $h^2k^2/2\gamma m_e$ and replace the 1st Brillouin zone by a sphere of radius $R = \alpha a_H$, it can be shown that eq. (94) allows for a solution or energy level below the edge of the conduction band if the strength of the potential well $\mathscr{A}$ satisfies the following inequality:

$$\gamma \alpha^2 \mathscr{A}/R_H \geq \pi = 3.1416 \tag{95}$$

However eqs. (90), valid for donor-like impurities with Z = 1 always possess a solution, or in other words, a bound state within the energy gap always exists.

Returning to the calculation of the energy eigen-value based on eqs. (90) and (91), it is necessary to obtain values for α and $\mathscr{A}$. Remembering that $\alpha = R/a_H$ and choosing for the cut-off radius R of the Coulomb potential (53) the covalent radius of Se, we find that $\alpha = 2.19$. The last parameter to be determined is the strength of the attractive potential well $\mathscr{A}$ of eq. (53). A first-principle calculation via the defining eqs. (49) and (50) for the potential being a rather complicated undertaking, we choose to adopt a semi-empirical approach. Consequently, we put

$$\mathscr{A} = x\mathscr{A}_{A\ell As} + (1 - x)\mathscr{A}_{GaAs} \tag{96}$$

and determined the values of the effective potential for pure AℓAs, $\mathscr{A}_{A\ell As}$, and for pure GaAs, $\mathscr{A}_{GaAs}$, by means of the *known* energy values $E \approx 6$ meV in these two cases. In other words, taking the values for all relevant parameters like effective masses, etc., corresponding to either GaAs or AℓAs, we determined $\mathscr{A}$ by means of eqs. (90) and (91) in such a manner that the energy E came out to have the experimentally determined value of 6 meV. In this manner we obtained

$$\mathscr{A}_{A\ell As} = 0.91\ R_H; \quad \mathscr{A}_{GaAs} = 1.05\ R_H \tag{97}$$

Using these values and eq. (96) as well as the values of all the other parameters as culled from ref. 44, we computed the energy eigen-value as a function of x. The results are plotted in fig. 1. Also plotted (as a dashed curve) is an average over experimentally determined values of the same quantity.[41] Considering the enormous simplicity of our theory, the overall agreement is rather good. The sharp maximum at the cross-over between direct and indirect band gap, experimentally 321 meV, is calculated as 316 meV. On the other hand the agreement is

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rather poor in the "wings", that is to say for either small values of x ($x < 0.25$) or for large values of x ($x > 0.8$). Here deviations of the computed values for the energy from the actual values are pronounced. One reason for this is due to the neglect of intervalley mixing. Another reason is due to the neglect of higher order terms in the expansion (eq. 73) of the energy $E_c(\underset{\sim}{k})$. This becomes clear when we look at the magnitude of the variational parameters a and b. It turns out that a varies betwen 207 (at $x = 0$) and 83 (at $x = 1$) Bohr radii and is thus comfortably large. This implies that the Fourier transform (eq. 72) is sufficiently peaked at $\underset{\sim}{k}_j = 0$ so that higher order terms in a Taylor series expansion about 0 may be neglected and eq. (73) is justified and at the same time, a mixing of this valley at $\underset{\sim}{k} = 0$ with the other six valleys at $\underset{\sim}{k}_j$ ($j = 1 \cdots 6$) contribute negligibly to the energy. However b turned out to be much smaller than a. In fact, b varies between 2.68 (for $x = 0$) and 2.35 (for $x = 1$) Bohr radii. In this case, the Fourier transform (72) becomes fairly delocalized, and eq. (73) constitutes a poor approximation. Also the product $k\,b$, where k is the magnitude of the distance (in k-space) between the central valley at the Γ point and any of the six equivalent minima at X, now becomes small enough, so that intervalley mixing cannot be neglected. These shortcomings must be eliminated before an adequate theoretical understanding of the donor level of Se in $A\ell_x Ga_{1-x}As$ becomes possible.

For the sequel to this report, it is planned to investigate these topics further.

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2) J. R. Reitz, Solid State Physics, Vol. 1, 1-95, Academic Press 1955.

3) S. T. Pantelides, Theory of Point Imperfection States in Semiconductors, Doctoral Thesis, University of Illinois, Urbana, Ill. 1973.

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5) As an example, consider gallium. Its electronic configuration is $[A]3d^{10}4s^{2}4p$. The inner electrons of the argon shells $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}$ and the ten 3d electrons may be designated as core states (there are altogether 28 of those states per atom) whereas the 3 outer electrons $4s^{2}4p$, the valence electrons, participate in the formation of valence bands.

6) B. J. Austin, V. Heine and L. J. Sham, Phys. Rev. 127, 276-282 (1962).

7) C. Herring, Phys. Rev. 57, 1169 (1940).

8) For a discussion of the OPW method see for instance J. M. Ziman, Solid State Physics, Vol. 26, 1-101, chapter 3, Academic Press 1971.

9) Although the original potential V is also nonlocal due to the exchange terms[1)10)], it is frequently possible to replace this nonlocality by an effective local potential, the Slater exchange potential.[13)]

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10) C. Kittel, Quantum Theory of Solids, John Wiley & Sons, 1963, chapter 5.

11) The definition of V_A given by eq. (13) is

$$V_A\phi = V\phi - \sum_{c\underset{\sim}{k}} \psi_{c\underset{\sim}{k}}(\underset{\sim}{r}) \int d^3r' \psi^*_{c\underset{\sim}{k}}(\underset{\sim}{r}')V(\underset{\sim}{r}')\phi(r') \quad ,$$

which clearly shows its nonlocal character.

12) Further detailed discussions and critiques of the pseudopotential approach may be found in chapter 3 of ref. 8.

13) F. Herman and S. Skillman, Atomic Structure Calculations, Prentice Hall, 1963.

14) S. T. Pantelides and C. T. Sah, Phys. Rev. B10, 638-658 (1974).

15) J. Callaway, Energy Band Theory, Academic Press, 1964, Appendix 2.

16) The notation $w(\gamma)$, $\tilde{\beta}(\alpha - \gamma)$ is short for $w(\underset{\sim}{r} - \underset{\sim}{R}_\gamma)$ and $\tilde{\beta}(\underset{\sim}{R}_\alpha - \underset{\sim}{R}_\gamma)$, etc.

17) J. M. Ziman, Principles of the Theory of Solids, Cambridge, at the University Press, 1965, p. 148 f.f.

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19) Imposing eq. (8) on eq. (21) yields eq. (10), provided that $\beta_{cv}(\underset{\sim}{k},\underset{\sim}{k}') = \beta_{cv}(\underset{\sim}{k})\delta_{\underset{\sim}{k}|\underset{\sim}{k}'}$.

20) We remind the reader that α-γ is short for $\underset{\sim}{R}_\alpha - \underset{\sim}{R}_\gamma$, the difference of lattice vectors at sites α and γ.

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21) Setting $V_{cv}(\zeta)$ identically equal to zero differs from putting *all* matrix elements of the potential V equal to zero in eq. (30). The latter case corresponds to "undoing the pseudizing" by reverting from eq. (8) back to eq. (6), and so obviously all coefficients $\tilde{\beta}$ must be zero.

22) S. T. Pantelides and C. T. Sah, Phys. Rev. B10, 621-637 (1974).

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24) The separation of core states into those of the host atoms and foreign atoms has been discussed by Glodeanu; see A. Glodeanu, Rev. Roum. Phys. 14, 139 (1969).

25) For a detailed discussion of all these various interactions, in particular various approximation schemes geared to the impurity problem, see the review article by Bassani et al., pages 1116-1128 of ref. 14. For a more general review, see also L. Hedin and S. Lundquist, Solid State Physics 23, 1-181 (1969).

26) We remember that in the Hartree approximation, $\psi = \psi_{n_1}(1)\psi_{n_2}(2) \cdots$ consists of a product of single particle wave-functions, and U_s becomes

$$U_s = e^2 \int d^3r' |\underset{\sim}{r} - \underset{\sim}{r}'|^{-1} \sum_{n_i}^{0c} \left(|\psi_{n_i}(\underset{\sim}{r}')|^2 - |\psi^0_{n_i}(\underset{\sim}{r}')|^2 \right)$$ where the sum runs over all occupied quantum states n_i.

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37) R_0 must be larger than the core radii but small enough in order that its corresponding sphere does not intersect neighboring spheres.

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38) The interaction potential (49) depends, among other things, also on $\underset{\sim}{R}'_\alpha = \underset{\sim}{R}_\alpha + \delta\underset{\sim}{R}_\alpha$, the displaced nuclear positions. But inasmuch as the displacements $\delta\underset{\sim}{R}_\alpha$ are functions of R which are known in principle, the whole expression (49) ultimately becomes a function of $\underset{\sim}{R}_\alpha$.

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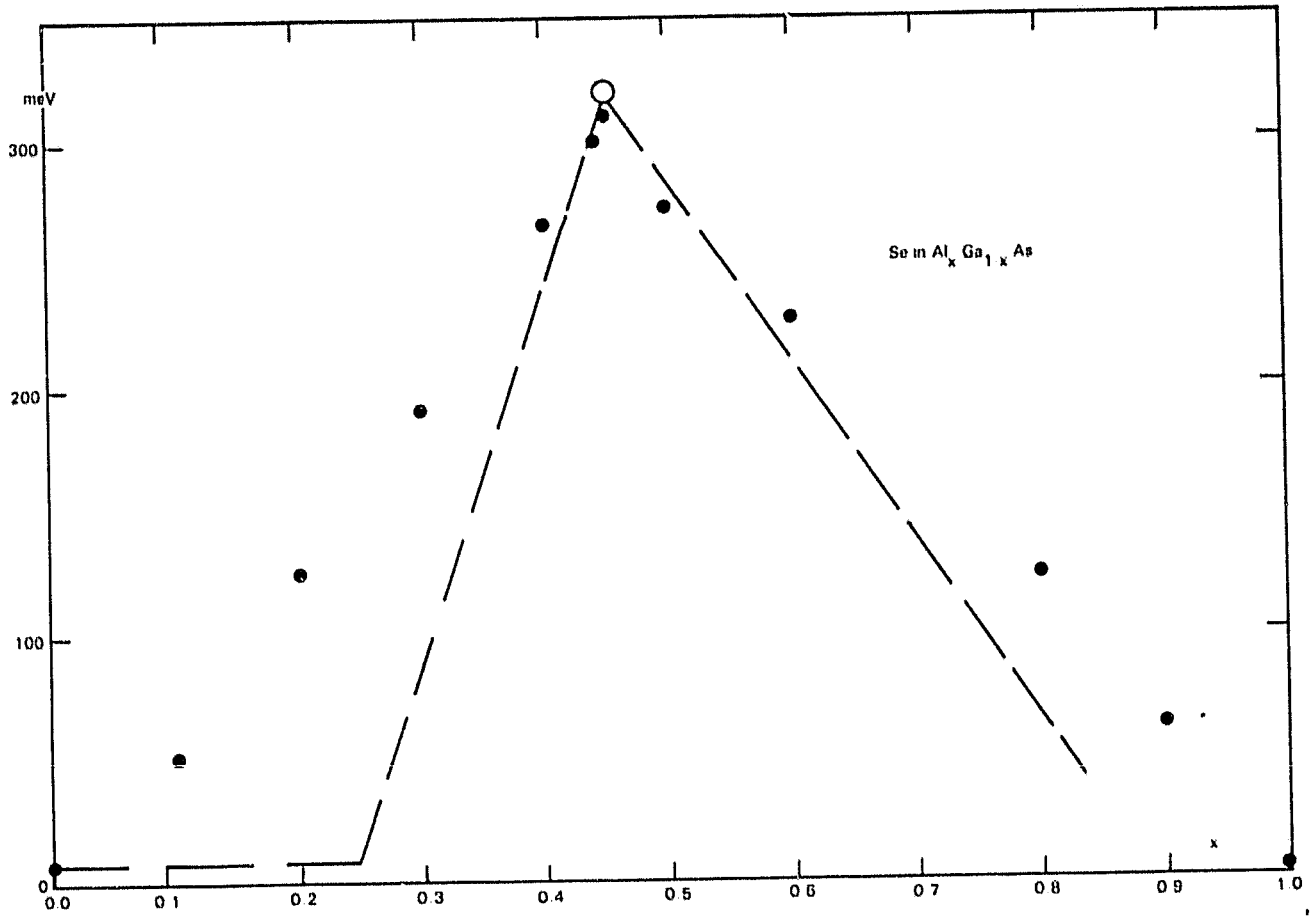

Fig. 1. Comparison of computed (dots) and experimental (dashed lines) values of the donor level of Se in $Al_x Ga_{1-x} As$ as a function of x. The dashed lines are averages over several measurements[24].