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Cellular Method for Wave Functions in Imperfect Metal Lattices

WALTER A. HARRISON
General Electric Research Laboratory, Schenectady, New York

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A general method is proposed for constructing conduction-band wave functions in nonperiodic monovalent metals and alloys. The method is a cellular approximation in which it is assumed that the lattice potential can be considered to be spherically symmetric within ellipsoidal cells centered on the individual ions. It is shown that the resulting wave functions are correct, within this approximation, to first order in a parameter which corresponds to the wave number in a perfect crystal. In the case of a strained metal in which the strains vary slowly in space the method takes a form analogous to the deformation-potential formalism, but contains a term which is first order in the derivatives of the strain.

The individual ionic potentials enter the procedure through parameters which are evaluated and tabulated for all of the alkali and noble metals. These parameters correspond to deformation-potential constants when that approximation is valid.

The general procedure is written in a form which is convenient for treating electron scattering, and the case of point defects is discussed. In particular, the influence of the lattice distortion on the scattering is considered in some detail.

The scattering of electrons by stacking faults is discussed, and some of the features of scattering by lattice vibrations in solid and liquid metals are considered.

I. INTRODUCTION

THE determination of electronic wave functions in nonperiodic structures has been most widely considered within the framework of scattering calculations. The customary procedure consists of considering a periodic structure in which a perturbation has been introduced. The particular approximation which is made in treating the scattering then depends upon the nature of the perturbation which is introduced. There has been no single method which is applicable, for example, both to slowly varying strains and to the presence of foreign atoms. In cases in which interference between two such effects is important, there has been considerable uncertainty in the results. Furthermore there have been no methods which are suitable for treating cases in which the deviation from periodicity is very large, such as it is in the immediate neighborhood of an interstitial atom, or as it is in a liquid metal. Thus it is desirable to have a single method for calculating wave functions in a wide variety of situations, and a method which is applicable when the periodicity is completely lost.

Two possible approaches to this problem come to mind: the wave function might be constructed in terms of localized functions which overlap to some extent; or the system might be divided into cells and functions determined in each cell could be matched on the cellular boundaries. Difficulty is encountered in pursuing the first method if atomic orbitals are used, since these are very poor approximations to the conduction-band wave functions in a metal. On the other hand, Wannier functions are not sufficiently well localized and sums of overlap terms do not converge well. Thus it would appear that a new set of localized functions would be needed if the problem were to be approached in this way. A cellular method would appear at first to be difficult because the matching of the wave function from cell to cell would seem formidable even if a suitable approach were found to construct the wave functions within each cell. It will turn out, however, that boundary conditions will arise in a natural way and will not be difficult to apply.

The wave functions in each cell will be determined by a generalization of the Wigner-Seitz cellular method[1] as extended by Bardeen[2] and by Hunter and Nabarro.[3] Since the functions will be determined only approximately in each cell, the matching from cell to cell will also be approximate.

Only a part of the physical problem will be treated in detail. We consider the problem of calculating the eigenstates of a given Hamiltonian which does not have the periodicity associated with a perfect lattice. There are terms in the Hamiltonian which are due careful consideration in the nonperiodic case; for example, the self-consistent screening problem should be treated in detail. Here a self-consistent potential will be introduced formally, and general features of the screening will be discussed, but the detailed form will be considered only in the Fermi-Thomas approximation. The effects of correlation will be included only in a crude manner by assuming that the electron in a cell sees an ionic rather than an atomic potential; thus all conduction-band electrons but the one under consideration are excluded from the atomic cell. The accuracy of the method as applied to a physical problem will, of course, depend upon the accuracy of the approximations used to treat these various effects.

II. DERIVATION OF THE METHOD

We wish to solve for the eigenstates of a Hamiltonian H appropriate to a nonperiodic structure; i.e., we seek solutions of the one-electron Schrödinger equation,

$$H\psi_i = E_i\psi_i.$$

It will be convenient to look briefly at the cellular solution for the periodic lattice first. We shall see that

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[1] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

[2] J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

[3] S. C. Hunter and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A220**, 542 (1953).

wave functions proposed by Bardeen diagonalize the assumed Hamiltonian to first order in wave number and are therefore solutions of the Schrödinger equation in that approximation. We shall then see how these solutions might be generalized to the nonperiodic case and show that these solutions diagonalize the nonperiodic Hamiltonian in the same approximation. This approach serves to motivate the choice of solutions for the nonperiodic case and to clarify the assumptions which are made. The validity of the method depends *only* upon the fact that the solutions we choose diagonalize the Hamiltonian.

1. Periodic Lattice

In a periodic lattice, wave functions may be written in the usual Bloch form $\psi_i = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r})$. Then $u_{\mathbf{k}}(\mathbf{r})$ can be constructed approximately according to the Wigner-Seitz cellular method[1] as extended by Bardeen.[2] Two major assumptions are made in this method.

(*a*) *Spherical approximation.*—It is assumed that the potential seen by an electron within an atomic cell is spherically symmetric and is appropriate to the ion in that cell. In addition, the atomic cells are approximated by spheres in the following way: from the fact that the functions $u_{\mathbf{k}}(\mathbf{r})$ must have the translational periodicity of the lattice, certain boundary conditions upon $u_{\mathbf{k}}(\mathbf{r})$ at the cell surfaces are obtained. In this method, the boundary conditions are applied at a spherical surface of volume equal to the cell volume rather than on the true cell surface. This assumption restricts us to spherical energy surfaces in the band.

(*b*) *Expansion in wave number.*—The wave functions are found to first order and the energy to second order in kr_s, where r_s is the radius of the atomic sphere. kr_s is equal to about two at the Fermi surface in monovalent metals. Thus it is not clear at once that this expansion is valid. We note, however, that in the empty-lattice limit; that is, as the ionic potential becomes small, $u_{\mathbf{k}}(\mathbf{r})$ becomes constant and our solutions are exact. Thus the expansion may be justified as an expansion from the free-electron limit or as the restriction to a single parabolic band. The expansion should be good in cases in which the band-edge wave function, $u_0(\mathbf{r})$, is flat over much of the cell. This assumption is particularly appropriate in the alkali metals.

The solutions given by Bardeen are of the form

$$\psi_{\mathbf{k}} = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} = [u_0(r) + v(r)i\mathbf{k}\cdot\mathbf{r}]e^{i\mathbf{k}\cdot\mathbf{r}}.$$

The boundary conditions on $u_{\mathbf{k}}$, which are applied on the sphere, are that the even term, $u_0(r)$, have vanishing normal derivative and that the odd term, $v(r)i\mathbf{k}\cdot\mathbf{r}$, vanish. These solutions diagonalize the Hamiltonian approximately:

$$(\psi_i, H\psi_j) = 0 \text{ to first order in } k \text{ for } i \neq j;$$
$$(\psi_i, H\psi_i) = E_i \text{ to second order in } k.$$

This procedure has been generalized by Hunter and Nabarro[3] to the case in which the atomic cells are approximated by ellipsoids. The appropriate boundary conditions are satisfied on the ellipsoid (to first order in the ellipticity) by constructing the even term in $u_{\mathbf{k}}$ from $u_0(r)$ and a d function and by constructing the odd term in $u_{\mathbf{k}}$ from $v(r)i\mathbf{k}\cdot\mathbf{r}$ and an f function. This does not introduce any new assumptions, but enables us to improve upon the spherical approximation in cases in which the cells are elongated or flattened.

We note that within the Bardeen approximation a more general eigenstate of the periodic crystal may be constructed by taking linear combinations of states of the same energy; i.e., states with wave number of the same magnitude. This is most conveniently done if $u_{\mathbf{k}}$ is rewritten in equivalent form by replacing $v(r)i\mathbf{k}\cdot\mathbf{r}$ by $v(r)\mathbf{r}\cdot\nabla$. We designate the new form of $u_{\mathbf{k}}$ by $\mathfrak{U}$. Then $\mathfrak{U}$ is formally independent of $\mathbf{k}$ and we may add degenerate states by simply adding the exponentials. The most general state of a particular energy has the form

$$\psi = \mathfrak{U}\varphi = [u_0(r) + v(r)\cdot\mathbf{r}\cdot\nabla]\varphi,$$

where φ satisfies $\nabla^2\varphi = -k^2\varphi$.

2. Nonperiodic Lattice

This suggests how the procedure may be generalized to nonperiodic lattices. The function $\mathfrak{U}$ may be constructed as a differential operator in the above way in each atomic cell. φ then will satisfy an appropriate differential equation within each cell such that the eigenstate energy is obtained in each cell. The major assumptions will be essentially the same as those for the periodic lattice:

(*a*) *Ellipsoidal approximation.*—The spherical approximation has been generalized to an ellipsoidal approximation without the necessity for further assumptions. However, in nonperiodic structures it may be more difficult to construct cells which are well approximated by ellipsoids than it is in periodic structures; thus the cellular approximation may be cruder in this case.

(*b*) *Expansion in wave number.*—The expansion in wave number becomes an assumption that φ be slowly varying in each cell in the sense that $\exp(i\mathbf{k}\cdot\mathbf{r})$ was assumed to be slowly varying in the Bardeen approximation. This assumption may become more questionable in the case of nonperiodic structures[4] since, in the case of a strong perturbation, the energy of an electron may be profoundly modified and fairly rapid variations in φ may be required. In the case of an impurity, for example, the Fermi energy of an electron in the solute metal may lie very far from the Wigner-Seitz energy corresponding to the impurity metal. In such a case the use of band-edge wave functions in the impurity cell would be very crude. Thus the validity of this

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[4] The author is indebted to Dr. Melvin Lax for pointing this difficulty out to him.

assumption must be tested in each region of the crystal for the conditions which are appropriate there.

It should also be pointed out that in Bardeen's calculations the properties studied depend on *all* of the electrons in the band, whereas scattering depends on only those electrons at the *top* of the filled region of the band. Thus in metals in which the band becomes nonparabolic at large wave numbers, the validity of the expansion in wave number is not so well justified in scattering problems as it is in the problems treated by Bardeen.

One further question arises immediately. In the periodic case boundary conditions upon $u_{\mathbf{k}}$ at the cell surfaces arose from symmetry conditions which do not apply to the nonperiodic case. It is not clear that these boundary conditions remain appropriate now. This reflects the fact that there is no longer a unique way to separate the wave function into factors. It will be most convenient to apply the same cellular boundary conditions to $u_{\mathbf{k}}$, which fixes the way the separation is done, and then to determine what boundary conditions this places on the function φ. These conditions on φ will become clear when we require that the functions diagonalize the Hamiltonian. It will be noted then that these conditions are consistent with the requirement that φ be slowly varying *within* the cells.

Thus if we can verify that the functions $\mathfrak{U}\varphi$ satisfy the conditions

$$(\mathfrak{U}\varphi_i,H\mathfrak{U}\varphi_j)=0 \text{ to first order in } \nabla\varphi \text{ for } i\neq j, \tag{1}$$

$$(\mathfrak{U}\varphi_i,H\mathfrak{U}\varphi_i)=E_i \text{ to second order in } \nabla\varphi, \tag{2}$$

we will have shown that these functions are solutions of the nonperiodic Hamiltonian in essentially the same approximation that the functions given by Bardeen are solutions of the periodic Hamiltonian.

We will now write down the proposed solutions explicitly and show that they do in fact diagonalize the Hamiltonian. The generalization of $u_{\mathbf{k}}$ as given in the ellipsoidal approximation to a differential operator $\mathfrak{U}$ proceeds in the same way that it does in the spherical approximation. We obtain our proposed solutions directly from the expressions given by Hunter and Nabarro:

$$\psi=\mathfrak{U}\varphi=(U+\chi g_2)\varphi-(U+\chi g_2)\mathbf{r}\cdot\nabla\varphi+g_1P_\varphi+g_3F_\varphi. \tag{3}$$

U, g_1, g_2, and g_3 are spherically symmetric functions satisfying the s-, p-, d-, and f-radial Schrödinger equations:

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}g_l+V_Ig_l+\frac{\hbar^2}{2m}\frac{l(l+l)}{r^2}g_l=\epsilon_0g_l. \tag{4}$$

ϵ_0 is chosen by the Wigner-Seitz condition; i.e., it is the energy of the s function satisfying the boundary condition

$$\left.\frac{\partial U(r)}{\partial r}\right|_{r_\Delta}=0. \tag{5}$$

r_Δ is the radius of a sphere of volume equal to the cell volume. The subscript Δ indicates that r_Δ depends upon the dilatation of the cell in question.

P_φ, χ, and F_φ are p-, d-, and f-angular functions, respectively, to first order in the derivatives of φ and to first order in the shear strains (or in the ellipticity). Thus the boundary conditions are to be satisfied only to first order in the ellipticity of the cell. Coordinate axes may be taken along the principal axes of the ellipsoid, and principal strains ϵ_1, ϵ_2, and ϵ_3 may be defined. Thus the ellipsoid is given to first order in ϵ_i by

$$\frac{x_1^2}{1+2\epsilon_1}+\frac{x_2^2}{1+2\epsilon_2}+\frac{x_3^2}{1+2\epsilon_3}=r_\Delta^2. \tag{6}$$

The angular functions are written down.

$$P_\varphi=\frac{\mathbf{r}\cdot\nabla\varphi}{r}+\frac{2\lambda r_\Delta}{5}\sum_{l=1}^{3}\frac{x_l}{r}(\epsilon_l-\tfrac{1}{3}\Delta)\frac{\partial\varphi}{\partial x_l}; \tag{7}$$

$$\chi=\sum_{l=1}^{3}(\epsilon_l-\tfrac{1}{3}\Delta)\frac{x_l^2}{r^2}; \tag{8}$$

$$F_\varphi=\lambda r_\Delta\frac{\mathbf{r}\cdot\nabla\varphi}{r}\sum_{l=1}^{3}(\epsilon_l-\tfrac{1}{3}\Delta)\frac{x_l^2}{r^2} -\frac{2\lambda r_\Delta}{5}\sum_{l=1}^{3}(\epsilon_l-\tfrac{1}{3}\Delta)\frac{x_l}{r}\frac{\partial\varphi}{\partial x_l}. \tag{9}$$

The dilatation Δ is given by $\Delta=\epsilon_1+\epsilon_2+\epsilon_3$. The parameter λ is given by

$$\lambda r_\Delta=\left(1-r\frac{g_1'}{g_1}+r\frac{g_2}{g_1}\right)_{r_\Delta}. \tag{10}$$

The boundary conditions, which are the same as those used by Hunter and Nabarro, are the following:

(a) The normal derivative of the zero-order [in derivatives of φ] solution, $(\partial/\partial n)(U+\chi g_2)$, is to vanish on the ellipsoid to first order in the shear strains.

(b) The magnitude of the first-order [in derivatives of φ] term in ψ, $-(\mathbf{r}\cdot\nabla\varphi)(U+\chi g_2)+g_1P_\varphi+g_3F_\varphi$, is to vanish on the ellipsoid, to first order in the shear strains.

That these conditions are satisfied by ψ may be verified using Eqs. (5) through (10), provided that the normalization of the p, d, and f terms is determined from the following relations:

$$g_1(r_\Delta)=g_3(r_\Delta)=r_\Delta U(r_\Delta), \tag{11}$$

$$\left.\frac{\partial g_2}{\partial r}\right|_{r_\Delta}=-r_\Delta\left.\frac{\partial^2U}{\partial r^2}\right|_{r_\Delta}. \tag{12}$$

The normalization of the s term remains at our disposal.

(*a*) *Diagonal Elements of the Hamiltonian*

It is now possible to construct the diagonal elements of the Hamiltonian with respect to any function $\mathfrak{U}\varphi$. The diagonal element (2) may be written

$$(\mathfrak{U}\varphi, H\mathfrak{U}\varphi)=\int(\mathfrak{U}\varphi)^*H\mathfrak{U}\varphi d\tau. \tag{13}$$

The integration is to be performed over the entire crystal. The Hamiltonian is assumed to have the form

$$H=(-\hbar^2/2m)\nabla^2+V_I+V_S. \tag{14}$$

V_I is the ionic potential, which is spherically symmetric in each cell. V_S is any slowly varying potential which may occur. In particular, it will include a self-consistent screening potential. We assume that V_S varies sufficiently slowly over the cell that it may be considered constant in each cell.

It will be convenient first to consider the integral (13) performed over a single unit cell, keeping only terms to second order in the derivatives of φ and to first order in the shear strains. The calculation, which is somewhat long, yields a result analogous to that obtained by Hunter and Nabarro:

$$(\mathfrak{U}\varphi, H\mathfrak{U}\varphi)_C=\left[\epsilon_0(\Delta)-\frac{\hbar^2}{2m}\alpha(\Delta)\frac{\nabla^2\varphi}{\varphi}-\frac{\hbar^2\beta(\Delta)}{2m\varphi}\right.$$
$$\left.\times\sum_{l=1}^{3}(\epsilon_l-\tfrac{1}{3}\Delta)\frac{\partial^2\varphi}{\partial x_l^2}+V_S\right](\mathfrak{U}\varphi,\mathfrak{U}\varphi)_C. \tag{15}$$

$\epsilon_0(\Delta)$ is found from the Wigner-Seitz condition. $\alpha(\Delta)$ and $\beta(\Delta)$ are given for any atomic cell by

$$\alpha(\Delta)\int_C U^2d\tau=-\frac{4\pi}{3}r_\Delta{}^3U^2(r_\Delta)$$
$$+\frac{8\pi}{3}\int_0^{r_\Delta}(2g_1Ur+r^2Ug_1')dr; \tag{16}$$

$$\beta(\Delta)\int_C U^2d\tau=\frac{16\pi}{15}r_\Delta{}^3U(r_\Delta)\left(\frac{g_1(r_\Delta)}{r_\Delta}-g_1'(r_\Delta)\right)$$
$$+\frac{16\pi}{15}\left[\int_0^{r_\Delta}(r^2g_1'-rg_1)g_2dr-\lambda r_\Delta\int_0^{r_\Delta}r^2g_1U'dr\right]. \tag{17}$$

β is the quantity m/m_3 defined by Hunter and Nabarro.

It is seen that if φ satisfies the equation

$$\left[\epsilon_0(\Delta)-\frac{\hbar^2}{2m}\alpha(\Delta)\nabla^2-\frac{\hbar^2}{2m}\beta(\Delta)\right.$$
$$\left.\times\sum_l(\epsilon_l-\tfrac{1}{3}\Delta)\frac{\partial^2}{\partial x_l^2}+V_s\right]\varphi=E\varphi \tag{18}$$

within the cell, (15) may be written

$$(\mathfrak{U}\varphi, H\mathfrak{U}\varphi)_C=E(\mathfrak{U}\varphi,\mathfrak{U}\varphi)_C. \tag{19}$$

Then if E is the same in every cell, Eq. (19) may be summed over all cells and, subject to the normalization of $\mathfrak{U}\varphi$ in the entire crystal, we obtain for each function φ satisfying (18) in every cell, the Eq. (2).

(*b*) *Off-Diagonal Elements of the Hamiltonian*

It can be seen by letting H operate on $\mathfrak{U}\varphi_j$ as given in (3), that to first order in $\nabla\varphi$ in any cell, $H\mathfrak{U}\varphi_j=E_j\mathfrak{U}\varphi_j$, where E_j is determined from (18). The matrix element (1) becomes

$$(\mathfrak{U}\varphi_i, H\mathfrak{U}\varphi_j)=E_j\int(\mathfrak{U}\varphi_i)^*\mathfrak{U}\varphi_jd\tau$$

to first order in $\nabla\varphi$. Thus to verify that the off-diagonal matrix elements vanish, we need simply to show that the functions $\mathfrak{U}\varphi_i$ are orthogonal to first order in $\nabla\varphi$. Using the form of $\mathfrak{U}\varphi$ from (3), we see that to first order in $\nabla\varphi$ and to first order in the ellipticities,

$$\int(\mathfrak{U}\varphi_i)^*\mathfrak{U}\varphi_jd\tau=\int\frac{U^2(r_\Delta)}{\gamma}\varphi_i{}^*\varphi_jd\tau, \tag{20}$$

where γ is the parameter defined by Bardeen,

$$\gamma=\frac{4\pi}{3}r_\Delta{}^3U^2(r_\Delta)\bigg/\int_C U^2(r)d\tau. \tag{21}$$

Values of $U(r_\Delta)$ and of γ are to be defined for each cell. Within each cell the φ_i satisfy Eq. (18),[5] which may be rewritten as $H'\varphi_i=E_i\varphi_i$. Since both H' and E_i are real, we may use this to rewrite the integral in (20).

$$\int\frac{U^2(r_\Delta)}{\gamma}\varphi_i{}^*\varphi_jd\tau=\frac{1}{E_i-E_j}$$
$$\times\int\frac{U^2(r_\Delta)}{\gamma}[\varphi_jH'\varphi_i{}^*-\varphi_i{}^*H'\varphi_j]d\tau. \tag{22}$$

Thus the matrix elements connecting nondegenerate states vanish if

$$\int\frac{U^2(r_\Delta)}{\gamma}\varphi_jH'\varphi_i{}^*d\tau=\int\frac{U^2(r_\Delta)}{\gamma}\varphi_i{}^*H'\varphi_jd\tau. \tag{23}$$

Matrix elements connecting degenerate states can be made to vanish by taking suitable linear combinations.

H' may be inserted in (23) and terms on the left-hand side which contain derivatives may be integrated by parts twice in each atomic cell. The left-hand side is found to be equal to the integral on the right plus surface integrals which are to be added for all atomic

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[5] Up to this point we have been concerned with the evaluation of the integral in the individual cells, which we have discussed to first order in $\nabla\varphi$. The fact that (20) will vanish depends upon the variation of the φ_i over the entire crystal, so we must now use the precise prescription by which we will determine the φ_i.

cells. These may be written

$$\sum_C -\frac{\hbar^2}{2m}U^2(r_\Delta)\sum_l\left[\frac{\alpha}{\gamma}+\frac{\beta}{\gamma}(\epsilon_l-\tfrac{1}{3}\Delta)\right] \int_C\left[\varphi_j\frac{\partial\varphi_i^*}{\partial x_l}-\varphi_i^*\frac{\partial\varphi_j}{\partial x_l}\right]dS_l.$$

dS_l is the component of the surface element (treated as a vector) along the x_l direction. We now select boundary conditions such that the integration over each portion of surface is exactly canceled by the integration over the same portion but performed in the adjacent cell. This will be achieved if $U(r_\Delta)$ is taken the same in every cell, if φ is continuous across cell boundaries, and if

$$\sum_l\left[\frac{\alpha}{\gamma}+\frac{\beta}{\gamma}(\epsilon_l-\tfrac{1}{3}\Delta)\right]n_l\frac{\partial\varphi}{\partial x_l}$$

is also continuous across cell boundaries. n_l is the component of a unit normal to the surface along the x_l direction. This may be more conveniently written in a coordinate system with one axis (the x_i axis) normal to the matching surface. Thus the quantity

$$\sum_j\left[\frac{\alpha}{\gamma}\delta_{ij}+\frac{\beta}{\gamma}(\epsilon_{ij}-\tfrac{1}{3}\Delta\delta_{ij})\right]\frac{\partial\varphi}{\partial x_j} \tag{24}$$

is to be continuous across the matching surface.

The details of the matching procedure remain obscure. It is seen, however, that if the state of strain in adjacent cells is the same (the case treated by Bardeen and by Hunter and Nabarro), φ is matched smoothly. Furthermore, if adjacent cells differ in size, but not in shape, a discontinuity in $\partial\varphi/\partial x_i$ is introduced which just cancels the change in the normal derivative of $\mathfrak{U}$ at the cell surfaces.

Thus the method which has been proposed generates functions $\mathfrak{U}\varphi_i$ which diagonalize the assumed Hamiltonian to first order in the generalized electronic wave number, and is therefore a first-order method for constructing wave functions in a nonperiodic lattice. The method consists of solving for a function φ according to Eq. (18) in all regions of uniform strain (such regions may be single atomic cells) and matching at surfaces between regions of different strain or composition according to specified rules. Because only a limited set of functions are included, the diagonalization is not complete; that is, a one-band approximation has been made.

3. Deformation-Potential Approximation

A further approximation may be made in cases in which the strain is slowly varying; that is, a deformation-potential method. Then an added curvature of φ appears in the cells, rather than discontinuities in the slope at the cell surfaces.

In order to see how to do this, we rewrite the quantity (24) as $\sum_j\kappa_{ij}\partial\varphi/\partial x_j$. Since φ is to be continuous across the boundary, $\partial\varphi/\partial x_j$ for $j\neq i$ is also continuous. Thus the matching of the quantity (24) simply introduces a change in the normal derivative given by $\kappa_{ii}\delta(\partial\varphi/\partial x_i) = -\sum_j\delta\kappa_{ij}\partial\varphi/\partial x_j$ to first order in the change in κ_{ij}. To first order in the derivatives of κ_{ij} and to second order in the derivatives of φ, it is equivalent to spread this change in $\partial\varphi/\partial x_i$ over a region of length equal to the interatomic distance; i.e., to add a curvature given by

$$\kappa_{ii}\partial^2\varphi/\partial x_i^2=-\textstyle\sum_j(\partial\kappa_{ij}/\partial x_i)(\partial\varphi/\partial x_j).$$

Thus Eq. (18) may be modified to include the effect of the matching approximately. We obtain

$$(\epsilon_0+V_S)\varphi-\frac{\hbar^2\gamma}{2m}\sum_{i,j}\frac{\partial}{\partial x_i} \times\left[\left(\frac{\alpha}{\gamma}\delta_{ij}+\frac{\beta}{\gamma}(\epsilon_{ij}-\tfrac{1}{3}\Delta\delta_{ij})\right)\frac{\partial\varphi}{\partial x_j}\right]=E\varphi. \tag{25}$$

Here ϵ_0, V_S, γ, α, β, and ϵ_{ij} are to be considered to be slowly varying functions and φ and $\nabla\varphi$ are everywhere continuous. This is analogous to the form obtained by Hunter and Nabarro, but contains the extra term which is first order in the derivatives of φ and of the parameters α, γ, β, and ϵ_{ij}. It may be verified that this term makes the operator in (25) Hermitian. Hunter and Nabarro noted that their perturbing operator was not Hermitian and that their symmetrization procedure was not unique.

III. PERTURBING OPERATOR

In order to treat a scattering problem, it is convenient to construct a perturbing operator; that is, to cast (18) into the form of a simple free-electron Schrödinger equation with an operator playing the role of a perturbing potential.

Let α_0 and ϵ_{00} be the values of α and ϵ_0 appropriate to the normal material ($\Delta=0$). Then if k_0 is the magnitude of the wave vector to be associated with an electron outside of the region of a scattering center, the energy may be written $E=\epsilon_{00}+\alpha_0\hbar^2k_0^2/2m$. Equation (18) may be rewritten

$$\frac{-\hbar^2}{2m}\nabla^2\varphi+(H_D+H_E+H_S)\varphi=\frac{\hbar^2}{2m}k_0^2\varphi; \tag{26}$$

where

$$H_D=\frac{\epsilon_0-\epsilon_{00}}{\alpha}+\frac{\hbar^2k_0^2}{2m}\left(1-\frac{\alpha_0}{\alpha}\right), \tag{27}$$

$$H_E=\frac{-\hbar^2\beta}{2m\alpha}\sum_l(\epsilon_l-\tfrac{1}{3}\Delta)\frac{\partial^2}{\partial x_l^2}, \tag{28}$$

$$H_S=V_S/\alpha. \tag{29}$$

It is seen that φ satisfies a free-electron Schrödinger equation in each cell with perturbing operators which are determined from (27), (28), and (29). Boundary conditions are to be applied at cellular surfaces such that φ and the quantity (24) are continuous.

In order to determine the operators (27) and (28), once the atomic cells are specified, it is necessary to know ϵ_0, α, and β as a function of the cell size for the monovalent metal in question. The parameter γ is also needed in order to perform the matching. All of these parameters depend upon the ion-core potential and are obtainable by the quantum-defect method or by direct integration of the Hartree field. These calculations have been made for all of the alkali and noble metals and are described in the appendix. Using these calculated parameters, the quantities entering the perturbing operator and the matching conditions were determined and tabulated in Table I.

H_D is a simple scalar which vanishes in the normal material and which depends upon the electron energy. It is written, for the Fermi energy, to second order in the dilatation in the following dimensionless form:

$$(mr_s^2/\hbar^2)H_D=E_1\Delta+E_2\Delta^2+O(\Delta^3).$$

Here r_s is the radius of an atomic sphere in the normal material for the metal in question. E_1 and E_2 are given for the various metals in Table I. In treating impurities, an additional term in H_D arises due to the difference in ϵ_{00} and α_0 in the two metals. This term may be calculated directly from (27) using parameters discussed in the appendix.

α/γ, which enters the matching condition, is written to second order in the dilatation in the form

$$\alpha/\gamma=A_0+A_1\Delta+A_2\Delta^2+O(\Delta^3).$$

A_0, A_1, and A_2 are given in Table I.

Finally, β is calculated for $\Delta=0$. Though it would be surprising if any of these values were in error by as much as 0.1, the *percent* error in the smallest values might be rather large. The fact that the values are generally small (with the exception of gold) and the fact that they tend to increase with increasing atomic number (with the exception of lithium) seems established. This is in marked contrast to the results of Hunter and Nabarro, who obtained a value $\beta=m/m_3=-1.116$ for copper by using a square-well approximation to the ion-core potential.

IV. SCATTERING BY POINT DEFECTS

The scattering center will be considered to be spherically symmetric in the case of point defects. That is, the cell of the vacancy, interstitial, or impurity is a sphere surrounding the defect. The nearest neighbors, then, lie in a spherical *shell* surrounding this, and having volume equal to the sum of the volumes of the near-neighbor cells. Similarly, spherical shells may be constructed for the more distant neighbors. Since H_D and H_S are scalars, it is a consistent approximation to treat them as spherically symmetric and constant in a shell consisting of equivalent atoms; the forms (27) and (29) are unchanged. H_E, on the other hand, is a tensor and simply writing its spacial dependence as spherically symmetric automatically introduces a variation over the shell. Thus H_E must be treated by a deformation-potential approximation within each cell.

TABLE I. Interaction constants for monovalent metals.

	E_1	E_2	A_0	A_1	A_2	β
Li	1.28	−0.61	0.678	0.411	−0.281	0.191
Na	0.68	0.14	1.000	0.210	−0.056	−0.006
K	0.81	0.42	1.020	0.215	−0.101	0.069
Rb	0.89	−0.21	1.051	0.253	−0.047	0.080
Cs	0.80	0.68	1.097	0.199	+0.037	0.272
Cu	1.57	−1.34	0.994	0.277	−0.147	0.087
Ag	1.65	−0.81	1.051	0.326	−0.103	0.260
Au	1.82	−0.93	1.247	0.343	−0.072	0.720

1. Spherical Approximation

We consider the deformation potential as applied to a single shell. The quantities ϵ_0, V_S, α, γ, and β do not vary within the shell since only H_E is to be considered in the deformation-potential approximation. The Eq. (25) is written down for a Cartesian coordinate system centered on the defect and all terms are evaluated on an axis (the x_1 axis). For spherically symmetric strains $\epsilon_{11}-\frac{1}{3}\Delta=-2(\epsilon_{22}-\frac{1}{3}\Delta)=-2(\epsilon_{33}-\frac{1}{3}\Delta)$ on this axis and the only nonvanishing first derivatives of these strains are the derivatives with respect to x_1. On this axis $\epsilon_{12}=\epsilon_{23}=\epsilon_{31}=0$, but $\partial\epsilon_{12}/\partial x_2=\partial\epsilon_{31}/\partial x_3=3(\epsilon_{11}-\frac{1}{3}\Delta)/2x_1$; the other derivatives vanish. The resulting deformation-potential equation is rewritten in the form (26) and we obtain

$$H_E=\frac{-\hbar^2\beta}{2m\alpha}\left[\epsilon_r\left(\frac{\partial^2}{\partial x_1^2}-\frac{1}{2}\frac{\partial^2}{\partial x_2^2}-\frac{1}{2}\frac{\partial^2}{\partial x_3^2}\right)+\left(\frac{\partial\epsilon_r}{\partial x_1}+3\frac{\epsilon_r}{x_1}\right)\frac{\partial}{\partial x_1}\right]_{x_2=x_3=0}, \tag{30}$$

where $\epsilon_r=\epsilon_{11}-\frac{1}{3}\Delta$ is a general function of r. The derivatives with respect to the x_i may be written in terms of derivatives with respect to the spherical coordinates and if the angular dependence of φ is written as a spherical harmonic (as will be done later), we obtain finally

$$H_E=\frac{-\hbar^2}{2m}\frac{\beta}{\alpha}\left[\epsilon_r\frac{\partial^2}{\partial r^2}+2\frac{\epsilon_r}{r}\frac{\partial}{\partial r}+\frac{\epsilon_r l(l+1)}{2r^2}+\frac{\partial\epsilon_r}{\partial r}\frac{\partial}{\partial r}\right]. \tag{31}$$

We may now treat ϵ_r as a slowly varying function of r, continuing use of the deformation potential, or we might set it constant in each shell and apply suitable boundary conditions at the shell surfaces in the spirit of the cellular method. We will proceed with the latter point of view, but will note that the term in $\partial\epsilon_r/\partial r$ (which vanishes in the cellular method) must be retained when the deformation-potential approximation is used for the radial dependence.

Now that the operators have been written in spherically symmetric form we may separate the wave equation by writing $\varphi(\mathbf{r})=\varphi_l(r)Y_l^m(\theta,\phi)$, where the $Y_l^m(\theta,\phi)$ are spherical harmonics. An equation for the radial part, $\varphi_l(r)$, may then be obtained from (26):

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\varphi_l-\frac{2m}{\hbar^2}(H_D+H_E+H_S)\varphi_l-\frac{l(l+1)}{r^2}\varphi_l=-k_0^2\varphi_l. \quad (32)$$

H_D and H_S are given by (27) and (29), respectively, and H_E is given by (31) (with $\partial\epsilon_r/\partial r=0$).

The matching function (24) may be written

$$\left(\frac{\alpha}{\gamma}+\frac{\beta}{\gamma}\epsilon_r\right)\frac{\partial\varphi}{\partial r},$$

and the matching conditions become

$$\left.\frac{\partial\varphi}{\partial r}\right|^+=R\left.\frac{\partial\varphi}{\partial r}\right|^-,\quad \varphi|^+=\varphi|^-. \quad (33)$$

Here the plus signs represent values just outside of a shell surface and the minus signs represent values just inside. R is the ratio of $\alpha/\gamma+\beta\epsilon_r/\gamma$ defined inside the surface to that defined outside.

It should be verified at this point that (23) is satisfied by the operator represented by (32) in conjunction with the boundary conditions (33), and thus that this mixture of cellular and deformation-potential methods is consistent. Note that in doing this one must multiply Eq. (32) by α in order to get it in a form in which the operator H' is explicitly independent of φ_l. As it stands H_D depends upon φ_l through k_0^2.

(*a*) *Asymptotic Behavior*

Radial wave functions will be found in accordance with Eq. (32), with boundary conditions (33) being applied on the shell surfaces. At large distances the radial wave functions approach the form[6]

$$\varphi_l\rightarrow\sin(kr+\delta_l-\tfrac{1}{2}l\pi)/r,$$

where l denumerates the angular momentum of the states, and the δ_l are phase shifts which are to be found and which will determine the scattering.

Since the scattering is described entirely in terms of the asymptotic forms, and since in this single-band spherical model the asymptotic forms are identical to the free-electron forms, we may carry over the free-electron formula for the scattering area; i.e., the scattering area is given by[7]

$$A=(4\pi/k_0^2)\textstyle\sum_l(l+1)\sin^2(\delta_l-\delta_{l+1}).$$

Furthermore, the incremental resistivity per atomic percent of scattering centers may be written in terms of the scattering area and we have

$$\Delta\rho=(4\pi\hbar/100e^2k_0)\textstyle\sum_l(l+1)\sin^2(\delta_l-\delta_{l+1}).$$

The value of the coefficient preceding the sum is 3.8 microhm centimeters per atomic percent for copper.

(*b*) *Born Approximation*

An approximate formula for the phase shifts may be obtained using the Born approximation.[8] The partial integration must be performed separately in each shell since the final wave function has discontinuous derivatives at the shell surfaces. This yields extra terms and the final result is

$$\delta_l=\sum_j\frac{(1-R_j)(k_0r_j)^2}{2}\frac{1}{k_0}\left.\frac{\partial j_l^2(k_0r)}{\partial r}\right|_{r_j}-\frac{2mk_0}{\hbar^2}\int_0^\infty r^2j_l(k_0r)(H_D+H_E+H_S)j_l(k_0r)dr. \quad (34)$$

The index j denumerates the shell surfaces. R_j is the parameter entering (33) defined for the jth shell surface. The $j_l(k_0r)$ are spherical Bessel functions.

Use of the Born approximation simplifies the calculations somewhat and the errors introduced are not large, as long as the phase shifts are small. This simplification will be made in calculating the contribution of H_E since the phase shifts arising from this term are small. The phase shifts arising from H_D may be quite large, on the other hand, and this contribution will be determined by solving (32) exactly with the calculated H_D.

Next, the three terms in the perturbing operator will be considered individually. The effect of H_D will be discussed in terms of impurity scattering, since in many such cases, the other terms may be neglected.

2. Monovalent Impurities

If the effects of strain and of screening are neglected, the atomic sphere associated with a substitutional impurity atom is simply the atomic sphere of the substitutional site in the normal material and the perturbing operator is simply H_D. H_D is a scalar which may be determined for the impurity atom as described in Sec. III, and which vanishes in the remainder of the crystal. The matching parameter R in Eq. (33) becomes simply the ratio of α/γ defined inside the surface to that

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[6] See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 104.

[7] This form was derived by L. M. Roth [thesis, Radcliffe College, 1956 (unpublished)] directly from a relation given by K. Huang [Proc. Phys. Soc. (London) **60**, 161 (1948)].

[8] Reference 6, p. 164.

outside. The general solutions of the Eq. (32) in the impurity cell and in the normal material are[6]

$$C_0 j_l(\bar{k}r),$$

and

$$C_1[\cos\delta_l j_l(k_0 r)-\sin\delta_l n_l(k_0 r)],$$

respectively. The j_l and n_l are spherical Bessel functions. Only solutions which are regular at $r=0$ have been included in the impurity cell. $\bar{k}$ is to be determined from the equation

$$\hbar^2\bar{k}^2/2m+H_D=\hbar^2k_0^2/2m.$$

If the interior and exterior solutions are matched on the cell surface according to (33) the following expression for δ_l is obtained:

$$\tan\delta_l=\frac{xj_l^2(x)\left[\dfrac{xj_l'(x)}{j_l(x)}-R\dfrac{\bar{x}j_l'(\bar{x})}{j_l(\bar{x})}\right]}{1+xj_l(x)n_l(x)\left[\dfrac{xj_l'(x)}{j_l(x)}-R\dfrac{\bar{x}j_l'(\bar{x})}{j_l(\bar{x})}\right]},$$

where $\bar{x}=\bar{k}r_s$, $x=kr_s$, and R is the ratio of α/γ in the impurity cell to that outside.

This is precisely the form found by Roth.[9] The results obtained by applying this to the noble metal alloys were in fair agreement with experiment (within 30%) except for the case of Cu in Ag and Ag in Cu, in which cases the results were too small. The discrepancy in these two cases can presumably be explained by the inclusion of the effect of elastic strain. The method showed a considerable improvement over the Mott[10] square-well method.

3. Effects of Shear

Since, as was mentioned in Sec. III, the interaction of the electrons with shear is generally quite small, it is reasonable to treat the effects of shear in the Born approximation. It will also be convenient to make a deformation-potential approximation, which should be satisfactory for obtaining a range of magnitude. We will calculate the phase shifts associated with the strain field surrounding a point imperfection such as a vacancy, an interstitial, or an impurity.

The displacements of neighbors to a point imperfection fall off as $1/r^2$ at large distances; i.e., in the elastic range. These displacements may be conveniently written as $\mathbf{u}_L=A(a^3/r^3)\mathbf{r}$, where a is the lattice distance (a unit cube edge.) This corresponds to $\epsilon_r=-2Aa^3/r^3$. It is clear, on the other hand, that the shear strain to be associated with the central cell is zero; thus we assume $\epsilon_r=0$ for $r<r_s$, and $\epsilon_r=-2Aa^3/r^3$ for $r>r_s$. Because there is a discontinuity in ϵ_r at $r=r_s$, the matching term associated with that surface must be retained. The remainder of the crystal is to be treated in the deformation-potential approximation. We may now substitute (31) into (34), retaining only terms which depend upon the shear strains. $1-R$ is determined to first order in ϵ_r. We obtain finally

$$\delta_l=-\frac{2A(ka)^3}{\alpha}\beta\left\{\frac{1}{2x}\frac{\partial}{\partial x}j_l^2\bigg|_{x_s}+\int_{x_s}^{\infty}j_l\left[\frac{1}{x}\frac{\partial^2 j_l}{\partial x^2}-\frac{1}{x^2}\frac{\partial j_l}{\partial x}+\frac{l(l+1)}{2x^3}j_l\right]dx\right\}. \quad (35)$$

Here kr has been replaced by x and kr_s by x_s. The calculation of the δ_l is facilitated by using the following recursion relation which may be derived from (35) using the properties of the j_l:

$$\delta_l=\frac{l-1}{l+1}\delta_{l-1}+\frac{A(ka)^3}{2\alpha}\frac{\beta}{l+1}\left[(l+1)^2\frac{j_l^2}{x^2}+\frac{(l-1)^2}{x^2}j_{l-1}^2+2\left(j_l^2-4l\frac{j_l j_{l-1}}{x}+j_{l-1}^2\right)\right]_{x_s}.$$

The resulting phase shifts are given by $\delta_0=+0.2135$, $\delta_1=+0.0436$, $\delta_2=-0.0012$, $\delta_3=-0.0007$, $\delta_4=-0.0001$, for a close-packed metal, where each is to be multiplied by $A(ka)^3\beta/\alpha$ for the particular case in question.

We may expect the shear strains to be largest in the case of an interstitial atom. For interstitials in copper, Huntington[11] has calculated A to be about 0.04. We may insert the other parameters for copper and determine a resistivity per interstitial arising from this effect alone. We obtain $\Delta\rho=0.021$ microhm-cm per atomic percent. This is quite small, and we may conclude that, at least in copper, this effect will be unimportant unless the phase shifts arising from the other terms in the perturbing operator are quite small.

4. Effects of Screening

Use of the ionic potentials in each cell may not be sufficient for determining the wave functions in a nonperiodic structure since charges may tend to accumulate in the region of a disturbance. These would give rise to long-range Coulomb fields unless they were properly screened. For this reason a self-consistent screening potential V_S was introduced in formulating the method. We shall now consider some general features of the screening of a spherically symmetric center. We shall first determine the accumulation of conduction electrons in the region, and then shall consider the entire center.

(a) Conduction Electrons

Friedel[12] has shown that number of electrons in a free-electron gas which are accumulated in the region

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[9] L. M. Roth, thesis, Radcliffe College, 1956 (unpublished). Portions have been published: Bull. Am. Phys. Soc. Ser. II, **2**, 58 (1957); Bull. Am. Phys. Soc. Ser. II, **2**, 214 (1957).

[10] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

[11] H. B. Huntington, Phys. Rev. **91**, 1092 (1953); Acta Met. **2**, 554 (1954).

[12] J. Friedel, Phil. Mag. **43**, 153 (1952), see Appendix.

of a spherically symmetric perturbation may be written in terms of the phase shifts evaluated at the Fermi surface according to the following formula:

$$n=(2/\pi)\sum_l (2l+1)\delta_l.$$

A parallel proof may be made for the case of a conduction band in the framework of the approximations which have been made here.

Equation (32) may be rewritten by multiplying through by α, writing out the operators explicitly, and rearranging terms. We find that within each shell, φ_l satisfies the equation

$$[\alpha+\beta\epsilon_r]\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi_l}{\partial r}\right)-\frac{2m}{\hbar^2}(\epsilon_0-\epsilon_{00}+V_S)\varphi_l -\left[\alpha-\beta\frac{\epsilon_r}{2}\right]\frac{l(l+1)}{r^2}\varphi_l=-\alpha_0k_0^2\varphi_l. \quad (36)$$

Similarly we may write down (36) for a different function φ_l' with a different parameter k_0'. This equation is multiplied by φ_l^*, the complex conjugate of Eq. (36) is multiplied by φ_l' and the two are subtracted.

$$\left[\alpha+\beta\epsilon_r\right]\left[\frac{\varphi_l'}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi_l^*}{\partial r}\right)-\frac{\varphi_l^*}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi_l'}{\partial r}\right)\right] =-\alpha_0(k_0^2-k_0'^2)\varphi_l^*\varphi_l'.$$

This is divided by γ and integrated over a large volume.

$$4\pi\int_0^M\left[\frac{\alpha}{\gamma}+\frac{\beta}{\gamma}\epsilon_r\right]\left[\varphi_l'\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi_l^*}{\partial r}\right)-\varphi_l^*\frac{\partial}{\partial r}(r^2\varphi_l')\right]dr =-\alpha_0(k_0^2-k_0'^2)\int_0^M\frac{\varphi_l^*\varphi_l'd\tau}{\gamma}.$$

Within each shell we integrate the left-hand side by parts.

$$4\pi\left[\frac{\alpha}{\gamma}+\beta\frac{\epsilon_r}{\gamma}\right]\left[r^2\varphi_l'\frac{\partial\varphi_l^*}{\partial r}-r^2\varphi_l^*\frac{\partial\varphi_l'}{\partial r}\right]\Bigg|_0^{r_i^-}\Bigg|_{r_i^+}^{M} =-\alpha_0(k_0^2-k_0'^2)\int\frac{\varphi_l^*\varphi_l'}{\gamma}d\tau.$$

The expression on the left is to be evaluated at $r=0$, at r equal to a large radius M, and at all shell surfaces. However, by virtue of the boundary conditions (33), terms evaluated at the inside of each shell surface just cancel those at the outside. The $r=0$ term vanishes also, so we are left with only the value at the upper limit. We now let k_0' approach k_0. To first order in $k_0'-k_0$, we obtain

$$\frac{2\pi}{k_0\gamma_0}\left[r^2\frac{\partial\varphi_l}{\partial k}\frac{\partial\varphi_l^*}{\partial r}-r^2\varphi_l^*\frac{\partial^2\varphi_l}{\partial k\partial r}\right]_{r=M}=\int\frac{\varphi_l^*\varphi_l}{\gamma}d\tau. \quad (37)$$

Let the radius of the crystal be M'. Thus $M'\gg M\gg r_s$. The asymptotic form for the normalized functions φ_l is given by

$$\varphi_l\rightarrow\left(\frac{\gamma_0}{2\pi M'}\right)^{\frac{1}{2}}\frac{\sin(kr+\delta_l-\frac{1}{2}l\pi)}{r}.$$

[Note the form of the normalizing integral (20) with $U(r_s)$ the same in every cell.] This may be substituted in the left-hand side of (37). We obtain

$$\frac{1}{M'}\left[M+\frac{\partial\delta_l}{\partial k}-\frac{1}{2k}\sin 2(kM+\delta_l-\tfrac{1}{2}l\pi)\right]=\int_0^M\frac{\varphi_l^*\varphi_l}{\gamma}d\tau.$$

The integral on the right gives the fraction of the electron which lies within the radius M. The corresponding equation in the absence of the perturbation is subtracted from this and the expressions are summed over all occupied states. The right-hand side becomes the total number of extra electrons in the region. The left becomes a sum over l of an integral over k. [The number of states of angular momentum quantum number l between k and $k+dk$ is $2(2l+1)M'dk/\pi$.] The oscillating term is dropped and we obtain

$$n=(2/\pi)\sum_l(2l+1)\delta_l. \quad (38)$$

The Friedel sum rule retains the same form within the framework of the approximations made here.

(*b*) *Entire Center*

In order to consider the screening problem, we again construct a large sphere surrounding the imperfection site. Unless the total charge enclosed in this sphere vanishes, the imperfection has not been properly screened. We construct the scattering center step-by-step to determine the total charge.

Before the imperfection is introduced the total ionic charge exactly cancels the total charge of the conduction electrons within the sphere. If a vacancy, an interstitial, or a polyvalent ion is introduced at the imperfection site without distortion of the other ions or the conduction electrons, an integral number of electronic charges, Q_I, are added. For vacancies $Q_I=-e$, for interstitials $Q_I=+e$.

If now, the lattice is allowed to relax, the ionic displacements at large distances are radial and may be written $u_L=Aa^3/r^2$, where r is the radial distance to the ion in question. Thus the total ionic charge displaced *inward* across the sphere is given by $Q_I'=-4\pi M^2(Aa^3/M^2)e/\Omega=-4\pi Aa^3e/\Omega$, where Ω is the atomic volume. Upon using Huntington's[13] values for A, this gives $Q_I'=+0.44e$ for vacancies in copper and $Q_I'=-2.0e$ for interstitials. Clearly this is an important term in the ionic charge of an imperfection. Blatt[14] has analyzed the implications of this term on the resistivity of dilute

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[13] Vacancies: H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942); interstitials: reference 11.

[14] F. J. Blatt, Phys. Rev. **108**, 285 (1957) and (to be published).

alloys of the noble metals, and has found that it gives rise to a dependence of the resistivity of the alloy upon the location of the solute atom in the periodic table.

The displacement of the conduction electrons due to the scattering operator H_D+H_E may be found using the Friedel sum rule, (38), where the phase shifts are calculated from H_D+H_E. We call this contribution Q_C.

Finally, there is a displacement of the conduction electrons by the unknown screening potential V_S; this contribution is written Q_S. The requirement that the total charge vanish $(Q_I+Q_I'+Q_C+Q_S=0)$ in conjunction with (38) gives a normalization condition upon V_S. In order to determine the form of V_S, the distribution of the charge $Q_I+Q_I'+Q_C$ must be known, whereas the calculation just described gives only the total charge.

As a first approximation we might assume that the excess charge is distributed in proportion to the excess ionic charge density as defined in each cell by $e(\delta Z-\Delta)/[\Omega(1+\Delta)]$. Here δZ is the difference between the ionic charge in the cell and that in the normal monovalent metal; Δ is the dilatation; and Ω is an atomic cell volume. Then in the Fermi-Thomas approximation, the screening potential in each shell may be written

$$V_S=\frac{4\pi e}{q^2}\rho_0+A\frac{e^{-qr}}{qr}+B\frac{e^{qr}}{qr},$$

where ρ_0 is the excess charge density in the shell. A and B are to be evaluated in each shell such that V_S and ∇V_S are everywhere continuous and V_S vanishes at infinity. The screening parameter q is defined by[15]

$$q^2=4me^2k/\pi\hbar^2\alpha.$$

For normal copper this gives $qr_s=2.58$. It may be noted that V_S may not be slowly varying within each shell as assumed in Sec. II. However, it is not rapidly varying in the sense that the ionic potential is, and this approximation may be suitable when V_S does not make a large contribution to the resistivity.

V. OTHER SOURCES OF SCATTERING

1. Dislocations

The method is directly applicable to nonspherical centers, such as dislocations. The major difficulty in treating dislocations, however, is the lack of knowledge of the details of the core. Once a suitable model of the core is available, it will be possible to treat the scattering using the cellular method. A deformation potential method is suitable only for treating the strain field, and it appears that this is an unimportant contribution to the scattering.[16] In the case of screw dislocations in particular, the contribution of the strain to the scattering in copper would be reduced by a factor of about 170 from that calculated by Hunter and Nabarro[3] if the value of β of Table I were used rather than the value determined by the square-well method.

2. Stacking Faults

There has recently been interest in the scattering by a stacking fault. Two pieces of evidence have been proposed[17] as indicating that this scattering is appreciable: first, it has not been possible to understand the increase in resistivity due to cold work in terms of the calculated resistivities to be associated with dislocations; second, a calculation of the scattering by stacking faults by Seeger[17] yielded a reflectivity of the order of one half. The experimental evidence appears inconclusive since there has not been a satisfactory treatment of the scattering by the core, and since this contribution to the scattering may be expected to be of the right order of magnitude to produce agreement.[16] The reflectivity calculation appears to be questionable inasmuch as the lattice potential was treated as a first-order perturbation in the scattering calculation; but to obtain a first-order matrix element, one must use wave functions which are of zero order in the lattice potential; i.e., free-electron functions. Since free-electron functions give a vanishing matrix element for scattering, a consistent first-order procedure gives vanishing reflectivity. The second-order perturbation procedure has not been done, and it is not evident that it will give a nonvanishing result.

Both Δ and ϵ_l vanish for all cells in the neighborhood of the stacking fault, so none of the parameters entering the determination of φ nor the matching of φ change; hence, the cellular method yields vanishing reflectivity. This simply means that any scattering by a stacking fault must come from terms in the wave function of lower symmetry than those considered here. It is concluded that the reflectivity should be very small.

3. Lattice Vibrations

For the case of scattering by long-wavelength phonons, the assumptions leading to Eq. (25) are justified and use of the deformation-potential formalism is suitable. Furthermore, it is reasonable to treat this effect in the Born approximation. A complete analysis has not been made, but a few features of the method are apparent and will be discussed briefly.

(a) *Long-Wavelength Longitudinal Phonons*

In the limit of long-wavelength phonons, we may neglect terms containing the derivatives of the strain. Thus the deformation-potential Eq. (25) becomes identical to (18) and the interaction may be discussed in terms of the perturbing operators of Eq. (26).

Neglecting, for the moment, the effect of H_E, we note that H_D+H_S is a scalar interaction. In the long-wavelength limit the net potential must be such as to

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[15] This form was given by L. M. Roth, reference 9.

[16] W. A. Harrison, J. Phys. Chem. Solids (to be published).

[17] A. Seeger, Can. J. Phys. 34, 1219 (1956).

bring about screening of the ionic charge accumulated in regions of compression. If H_D+H_S is calculated in the Fermi-Thomas approximation to first order in the dilatation, it is found that $H_D+H_S=2E_F\Delta/3$, where $E_F=\hbar^2k_0^2/2m$. Thus the interaction is independent of H_D in this approximation.

H_E, on the other hand, does not shift the average energy of the conduction electrons at any point, and therefore does not affect the screening. The ionic displacements associated with a longitudinal phonon may be written $\mathbf{u}_L=(\boldsymbol{\sigma}/\sigma)\exp(i\boldsymbol{\sigma}\cdot\mathbf{r})$. It is seen that $\epsilon_{11}=\Delta$; $\epsilon_{22}=\epsilon_{33}=0$, where the x_1 axis is taken along $\boldsymbol{\sigma}$. Thus H_E becomes $(\hbar^2\beta/2m\alpha)(\Delta/3)(2k_1^2-k_2^2-k_3^2)$. This may be written $-\beta E_F\Delta/3\alpha$ in the case of small-angle scattering where $\boldsymbol{\sigma}$ is perpendicular to $\mathbf{k}$. The total interaction becomes simply $H_D+H_E+H_S=\frac{2}{3}[1-\frac{1}{2}(\beta/\alpha)]E_F\Delta$. It is seen that the interaction with shear reduces the small-angle scattering by longitudinal phonons. We may expect the interaction to be correspondingly enhanced in the case of umklapp process. However, owing to the smallness of β (see Table I), this effect would be relatively unimportant except in the case of gold.

(b) *Long-Wavelength Transverse Phonons*

The ionic displacements associated with a transverse phonon may be written $\mathbf{u}_L=\boldsymbol{\tau}\exp(i\boldsymbol{\sigma}\cdot\mathbf{r})$, where $\boldsymbol{\tau}$ is perpendicular to $\boldsymbol{\sigma}$. If we take the x_1 axis along $\boldsymbol{\sigma}$, and the x_2 axis along $\boldsymbol{\tau}$, we see that only ϵ_{12} is nonvanishing. Thus the only perturbing term contains a factor of $\epsilon_{12}k_1k_2$. In the limit of small-angle scattering $k_1=0$, so this term does not contribute. In umklapp processes, on the other hand, this term will not necessarily vanish.

(c) *Short-Wavelength Phonons*

It is appropriate to consider short-wavelength phonons in terms of a cellular method. However, difficulty is encountered in constructing cells. A reasonable picture would consist of having the cells unchanged and moving the ions off center. In the cellular method as developed here cells were always centered upon the ion. The procedure could presumably be readily generalized to include such a distortion, but that has not been done.

(d) *Liquid Metals*

It may be remarked that this analysis would not change appreciably in a treatment of small-angle scattering in liquid metals. The method is not sensitive to the detailed symmetry of the cells, so one need only determine the atomic cell volume from the density and construct the phonons in the liquid metal. This is consistent with the known properties of the noble metals, which do not change volume greatly upon melting: the change in resistivity can be very well understood solely on the basis of the change in phonon energies.[18]

VI. CONCLUSIONS

A cellular method has been proposed for constructing one-electron wave functions for a nonperiodic monovalent metal. The factor which corresponds to the exponential in the periodic case must satisfy a particular differential equation in each cell, as well as specific matching conditions at all cell surfaces. The potential seen by the electrons was assumed to be spherically symmetric within ellipsoidal cells centered on the metal ions and the ellipticity of these cells was treated as small. It was shown that the proposed functions are in fact solutions of the corresponding Hamiltonian to first order in the electronic wave number (as generalized to nonperiodic structures).

The form which this method takes in the case that the strains are slowly varying was also written down. It was seen that there is a term which depends upon the spacial variation of the strains which does not occur in the deformation potential of Hunter and Nabarro, and that this term is necessary if the Hamiltonian is to be Hermitian.

The procedure for constructing the wave functions depends upon the lattice ions through certain parameters which are obtainable from the quantum defect method or from integration of the Hartree field. These parameters were calculated for the alkali metals and the noble metals. These constants become the deformation-potential constants in the deformation-potential approximation.

The cellular method was used to construct wave functions in crystals containing a single point imperfection and thereby to determine the scattering. It was found that in the absence of shear strains and of screening effects, the method reduces to that of Roth[9] for treating monovalent impurities in monovalent metals.

It was found that shear strains associated with point imperfections are usually unimportant since the parameter which determines the coupling of the electrons with the shear strains is small in all of the metals considered except gold.

The screening problem was considered in general terms. It was seen that the ionic charge to be associated with a point imperfection depends upon the deformation of the lattice, as well as upon the point imperfection itself. It was also seen that the Friedel sum rule for determining the excess electronic charge to be associated with the singularity remains valid within the framework of the approximations of this calculation.

It was indicated that application of this method to stacking faults yields a vanishing reflectivity. This result was discussed briefly in relation to considerations of this problem which have been made previously.

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[18] A. N. Gerritsen, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 178.

The method was not applied to the scattering by lattice vibrations in detail, but several limiting cases which give some insight into the problem were discussed. It was pointed out that a generalization of the method would probably be necessary if the scattering by short-wavelength phonons were to be treated properly. It was also mentioned that if the scattering of electrons in liquid metals is treated by this method using a simple model for the liquid, the results are qualitatively correct.

Calculations by this method of the resistivity of vacancies and interstitials in copper are currently in progress. Preliminary results indicate that the resistivity due to a vacancy is of the order of 0.8 microhm centimeter per atomic percent and that the resistivity due to an interstitial is somewhat smaller.

VII. ACKNOWLEDGMENTS

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APPENDIX

The parameters ϵ_0, α, γ, and β must be determined for the metal under consideration if the perturbing operator is to be found explicitly. The ϵ_0, α, and γ are identical in this treatment to the same parameters defined by Bardeen.[2] The parameter γ is given by (21). Bardeen showed that α, which is given here by Eq. (16), may be expressed in terms of the logarithmic derivative of the p function: $\alpha=\gamma(\Delta)\beta_1(\Delta)$, where $\beta_1(\Delta)=r_\Delta g_1'(r_\Delta)/g_1(r_\Delta)$. These parameters have been calculated for three values of atomic sphere radius for the alkali metals by Brooks[19] and for the noble metals by Kambe.[20] We obtain values for intermediate atomic cell sizes by quadratic interpolation with respect to dilatation.

The parameter β is given by Eq. (17). The first term in the expression for β arises from an integration over the cell surface. This term was apparently omitted by Hunter and Nabarro.[3] In addition, a transcription error occurred in the first integral term and the g_2 factor did not appear in their paper.

Equation (17) may be written in terms of the logarithmic derivatives of g_1 and g_2 by performing operations similar to those used by Bardeen in calculating α. We obtain

$$\beta=\frac{2\gamma}{5}\left[1-\beta_1{}^2+r_\Delta{}^2\frac{U''}{U}\left(\frac{2\beta_1}{\beta_2}-1\right)\right],$$

where $\beta_2=r_\Delta g_2'(r_\Delta)/g_2(r_\Delta)$.

We shall neglect the variation of β with Δ and evaluate it for $\Delta=0$. Since the boundary conditions are satisfied only to first order in the shear strains, it is consistent to neglect this variation which corresponds to terms of the order $\epsilon_{ij}\Delta$.

γ and β_1 are obtained from the interpolated values of γ and α found above. Hunter and Nabarro have shown that $\gamma r^2U''/U=(2mr^3/3\hbar^2)\partial\epsilon_0/\partial r$, which we may calculate from the interpolation of ϵ_0. Thus only the logarithmic derivatives of the d functions are needed.

Ham[21] has calculated the logarithmic derivatives of the d functions for the alkali metals at the band-edge energy and at the observed lattice spacing by using the quantum-defect method. Ham points out that the interpolation is considerably less reliable when applied to the d function than it is when applied to the s and p functions. Absolute errors in β are about equal to the corresponding fractional errors in β_2, i.e., $\delta(\beta)\approx\delta\beta_2/\beta_2$. The estimated possible errors, $\delta\beta_2/\beta_2$, for K, Rb, and Cs were less than 0.06. Errors for Li and Na should be even smaller.

It seemed advisable to estimate β_2 for the noble metals by integration of the Hartree field since the extrapolation required in the quantum-defect method is quite unreliable in these cases. The tabulated Hartree fields[22] for the noble metal ions were corrected for the removal of a single d electron and the addition of a conduction electron distributed uniformly over the atomic cells. The resulting field was integrated numerically for the band-edge energy, ϵ_0, to obtain the logarithmic derivative of the d function. It is difficult to estimate the error entailed in this approach, but an error of greater than ten percent would seem surprising.

The values of β determined from these various parameters appear in Table I.

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[19] H. Brooks, Phys. Rev. **91**, 1027 (1953), and unpublished work which is given by F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 185.

[20] K. Kambe, Phys. Rev. **99**, 419 (1955).

[21] The author is indebted to Dr. Ham for supplying him with the results of these calculations, which have not been published.

[22] Hartree calculations for Cu^+, Ag^+, and Au^+ have been made by D. R. Hartree, Proc. Roy. Soc. (London) **A141**, 282 (1933); M. M. Black, Mem. Proc. Manchester Lit. and Phil. Soc. **79**, 29 (1935); and Douglas, Hartree, and Runciman, Proc. Cambridge Phil. Soc. **51**, 486 (1955), respectively.