that in a superconducting rod carrying a current in a longitudinal magnetic field, a solenoidal current configuration is set up when the metal is in the intermediate state. The collapse of this solenoid when the metal goes normal is thought to be the cause of a sharp paramagnetic peak observed in the magnetic moment. A visual examination of the field changes at the end of such a rod when the rod is driven normal could provide some useful data. In particular, the results should have a bearing on the question of whether the paramagnetic effect is indeed a fundamental property of the superconducting state or due to a peculiar current configuration dependent on geometry.

Another application not involving superconductivity might be found in studies of ferromagnetic domains and the motion of the domain walls in alternating fields.

PHYSICAL REVIEW VOLUME 105, NUMBER 1 JANUARY 1, 1957

Calculation of the Band Structure of "Complex" Crystals

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(Received August 13, 1956)

A method for studying the band structure of "complex" crystals (i.e., crystals having more than one atom per unit cell) is developed. This method is a generalization of one proposed independently and arrived at by different approaches by Korringa and Kohn and Rostoker for the study of the band structure of "simple" crystals. The general approach leads to a promising method when the crystalline potential can reasonably be approximated by a potential which is spherically symmetric within nonoverlapping spheres about the lattice sites and is constant elsewhere. Important virtues of the method are its expected accuracy and the fact that the largest part of the labor involved is in the computation of certain "structure constants" which are applicable to all crystals with the same crystallographic structure.

I. INTRODUCTION

OF basic importance to the theoretical study of the solid state is the knowledge of the nature of the electronic energy bands in a perfect crystal. Consequently, a great deal of effort has been put into devising various techniques for solving the Schrödinger equation with a periodic potential, and in applying these techniques to particular crystals. The problem of determining the band structure of "complex"[1] crystals has presented a particularly formidable computational problem.

This note will be concerned with the problem of determining the band structure of "complex" crystals. In view of the rather great amount of work encountered in carrying out a calculation for these crystals, it is highly desirable to establish a method that is at once accurate and that does not involve an excessive amount of computational labor. A means of accomplishing the latter aim would be a method in which a large part of the computation is independent of the potential and hence is applicable to all crystals with the same structure. In this way the labor involved in studying the band structure of each individual crystal, or of a particular crystal with each of a number of assumed potentials, is considerably reduced.

For the case of a "simple" lattice, such a method has been developed independently by Korringa[2] and Kohn and Rostoker.[3,*] Korringa approached the problem by considering the scattering of the electron wave by all the atoms in the crystal using an analysis analogous to that employed by Ewald in his study of the diffraction of x-rays by crystals. Kohn and Rostoker, on the other hand, proceeded by establishing a variational principle based on the integral equation for the electron wave function. Both approaches lead to practical results when the crystalline potential can be approximated by a potential which is spherically symmetric within nonoverlapping spheres (henceforth called "atomic" spheres) centered at the lattice sites and constant elsewhere.

The virtues of the method make it apparent that it would be highly desirable to have a method of the type described for the study of "complex" lattices. It is felt that there are many such crystals, particularly those having two atoms per unit cell, for which the abovementioned approximating potential would be appropriate. The difference between the actual crystalline potential and a judiciously chosen approximating potential could then be handled by perturbation theory. With this in mind, we have generalized both the Korringa and Kohn-Rostoker approaches so that the schemes would encompass the more general class of crystals which contain an arbitrary finite number of atoms per unit cell.

The general approach has several important virtues. It has the advantage of the cellular method in that the approximate solutions one works with are solutions of

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[1] In the following, we shall use the term "complex" crystal (or structure) to mean a crystal with more than one atom per unit cell. Similarly, the adjective "simple" will imply one atom per unit cell.

[2] J. Korringa, Physica 13, 392 (1947).

[3] W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).

[*] P. M. Morse, Proc. Natl. Acad. Sci. U. S. 42, 276 (1956).

the Schrödinger equation. On the other hand, it obviates the difficulties involved in that method associated with satisfying boundary conditions. In the present method the boundary conditions are incorporated in the general formulation of the problem. Because of the satisfactory manner in which the boundary conditions are handled and the fact that the solutions within the "atomic" sphere are accurate, the method promises to be rapidly convergent. Finally, there is the important advantage mentioned previously. The greater part of the computations involved is in the evaluation of certain "structure constants" which are the same for all crystals forming with the same structure. The evaluation of these constants can readily be performed on currently available digital computers.

In Sec. II we develop the method for "complex" crystals in a manner paralleling that used by Kohn and Rostoker. This approach has some mathematical advantages over the scattering approach. For one thing, we see that the error in the energy is of the second order in the error in the wave function. The new structure constants appearing as a result of there being more than one atom per unit cell are studied in Appendix A where explicit expressions for their evaluation are given. In Appendix B, we give a derivation along the lines of Korringa's work.

II. GENERAL FORMULATION OF THE METHOD

In this section we shall follow closely the approach of Kohn and Rostoker, but shall reduce the discussion of points in common with their treatment as much as we feel coherency permits. For the elaboration of some of these points the reader is referred to their paper.

To define our "complex" crystal we use the lattice translation vectors, $\mathbf{r}_n$, given by

$$\mathbf{r}_n = n_1\boldsymbol{\tau}_1 + n_2\boldsymbol{\tau}_2 + n_3\boldsymbol{\tau}_3, \quad (n_i = 0, \pm 1, \pm 2, \cdots), \tag{1}$$

where $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, and $\boldsymbol{\tau}_3$ are the primitive translational vectors of the lattice, and the basis vectors $\mathbf{a}_1, \mathbf{a}_2, \cdots, \mathbf{a}_m$ which locate the centers of the m atoms in the unit cell.

We are seeking solutions of the Schrödinger equation

$$[-\Delta + V(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{2}$$

with the periodic potential

$$V(\mathbf{r}+\mathbf{r}_n) = V(\mathbf{r}), \tag{3}$$

which satisfy the Block condition, that is,

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{r}_n) = e^{i\mathbf{k}\cdot\mathbf{r}_n}\psi_{\mathbf{k}}(\mathbf{r}). \tag{4}$$

Equation (2) with condition (4) on the wave function can be formulated as the integral equation

$$\psi(\mathbf{r}) = \int_\tau G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')d\mathbf{r}', \tag{5}$$

where the integral extends over a unit cell with volume τ. The Green's function, $G(\mathbf{r},\mathbf{r}')$, satisfies

$$(\Delta + E)G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \tag{6}$$

and has the property that

$$G(\mathbf{r}+\mathbf{r}_n, \mathbf{r}') = e^{i\mathbf{k}\cdot\mathbf{r}_n}G(\mathbf{r},\mathbf{r}'). \tag{7}$$

The Green's function can be constructed from the plane wave solutions of the homogeneous equation corresponding to (6). The explicit expression found in this way is

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{\tau}\sum_{\mathbf{K}_n}\frac{\exp\{i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{r}-\mathbf{r}')\}}{(\mathbf{K}_n+\mathbf{k})^2 - E}, \tag{8}$$

where the $\mathbf{K}_n$ are the lattice vectors in reciprocal space, i.e., are defined by

$$\mathbf{K}_{n'}\cdot\boldsymbol{\tau}_i = 2\pi n, \quad n = \text{an integer} \quad (i = 1,2,3). \tag{9}$$

Expressions equivalent to (9) are

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{4\pi}\sum_{\mathbf{r}_n} e^{i\mathbf{k}\cdot\mathbf{r}_n}\frac{\exp\{i\kappa|\mathbf{r}-\mathbf{r}'-\mathbf{r}_n|\}}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_n|} \tag{10}$$

$$= -\frac{1}{4\pi}\sum_{\mathbf{r}_n} e^{i\mathbf{k}\cdot\mathbf{r}_n}\frac{\cos\{i\kappa|\mathbf{r}-\mathbf{r}'-\mathbf{r}_n|\}}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_n|} \tag{11}$$

with

$$\begin{aligned} \kappa &= \sqrt{E} && \text{for} \quad E>0 \\ &= i\sqrt{(-E)} && \text{for} \quad E<0. \end{aligned}$$

The function G has the usual Hermiticity property,

$$G(\mathbf{r},\mathbf{r}') = G^*(\mathbf{r}',\mathbf{r}), \tag{12}$$

as is evident from (11).

The variational principle set up by Kohn and Rostoker which is equivalent to (5) is

$$\delta\Lambda = 0,$$

with

$$\Lambda = \int_\tau \psi^*(\mathbf{r})V(\mathbf{r})d\mathbf{r} \times\left[\psi(\mathbf{r}) - \int_\tau G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')\right]d\mathbf{r}'. \tag{13}$$

This variational principle, particularly with the use of the Rayleigh-Ritz technique, is a very powerful tool. Unfortunately, however, the integrals involved are, in general, very difficult to evaluate. But as mentioned in Sec. I, practical results are obtained if the potential $V(\mathbf{r})$ is taken to be

$$V(\mathbf{r}) = \begin{cases} V^{(i)}(|\mathbf{r}-\mathbf{r}_n-\mathbf{a}_i|) & \text{for} \quad |\mathbf{r}-\mathbf{r}_n-\mathbf{a}_i| \leq R_i \\ V_0 = \text{constant} & \text{elsewhere}, \end{cases} \tag{14}$$

where R_i is the radius of the "atomic" sphere about the ith atom in the unit cell and where the various $V^{(i)}(r)$

can be different within the nonoverlapping "atomic" spheres. By choosing the zero of the energy scale so that $V_0=0$, the nonvanishing contributions to Λ are restricted to regions within the "atomic" spheres.

Because of the spherical symmetry of the potential within the "atomic" spheres, the wave function can be expanded in terms of (normalized) spherical harmonics as

$$\psi(\mathbf{r})=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{lm}{}^{(j)}\mathcal{R}_l{}^{(j)}(|\mathbf{r}-\mathbf{a}_j|)Y_{lm}(\mathbf{r}-\mathbf{a}_j), \qquad |\mathbf{r}-\mathbf{a}_j|\leq R_j, \tag{15}$$

where $Y_{lm}(\mathbf{x})$ represents a spherical harmonic of the spherical polar angles of $\mathbf{x}$ and $\mathcal{R}_l{}^{(j)}(r)$ is the solution of

$$\left[-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}+\frac{l(l+1)}{r^2}+V^{(j)}(r)-E\right]\mathcal{R}_l{}^{(j)}(r)=0, \tag{16}$$

which is finite at the origin. While the infinite sum (15) represents an exact solution, it cannot, of course, be used as a trial function in a practical application. However, it suggests that the finite sum

$$\sum_{l=0}^{l_{\max}}\sum_{m=-l} C_{lm}{}^{(j)}\mathcal{R}_l{}^{(j)}(|\mathbf{r}-\mathbf{a}_j|)Y_{lm}(\mathbf{r}-\mathbf{a}_j), \qquad |\mathbf{r}-\mathbf{a}_j|\leq R_j, \tag{17}$$

which is also a solution to the Schrödinger equation, be used as the trial function.

With this wave function it is possible to further simplify the expression for Λ. By utilizing the fact that (17) is a solution to (2) to eliminate the potential, and Green's theorem to convert the volume integrals to surface integrals, Λ can be shown to equal

$$\Lambda=\lim_{\epsilon\to 0}\Lambda_\epsilon,$$

$$\begin{aligned}\Lambda_\epsilon=&\left\{\int_{S_1(R_1-2\epsilon)}ds\left[\psi^*(\mathbf{r})\frac{\partial}{\partial n}-\frac{\partial}{\partial n}\psi^*(\mathbf{r})\right]\right.\\&\left.+\int_{S_2(R_2-\epsilon)}ds[\;]+\cdots+\int_{S_m(R_m-2\epsilon)}ds[\;]\right\},\\&\times\left\{\int_{S_1(R_1-\epsilon)}ds'\left[G(\mathbf{r},\mathbf{r}')\frac{\partial}{\partial n'}\psi(\mathbf{r}')-\psi(\mathbf{r}')\frac{\partial}{\partial n'}G(\mathbf{r},\mathbf{r}')\right]\right.\\&\left.+\int_{S_2(R_2-\epsilon)}ds'[\;]+\cdots+\int_{S_m(R_m-\epsilon)}ds'[\;]\right\},\end{aligned} \tag{18}$$

where $\partial/\partial n$ represents the derivative normal to the surface and where the ϵ's are introduced so as to avoid difficulties arising from the singularity in the Green's function. The notation $S_i(R_i-\epsilon)$ signifies the spherical surface of radius $R_i-\epsilon$ about the ith atom in the unit cell.

The terms in (18) arising from products of integrals over surfaces centered about the same nucleus can be handled exactly as was done by Kohn and Rostoker. That is, the Green's function is expanded in spherical harmonics for $r<r'<R_j$ as

$$\begin{aligned}G(\mathbf{r},\mathbf{r}')=&\sum_{l,m}\sum_{l',m'}\\&\times[A_{lm;l'm'}{}^{(j,j)}j_l(\kappa r)j_{l'}(\kappa r')+\delta_{ll'}\delta_{mm'}j_l(\kappa r)n_l(\kappa r')]\\&\times Y_{lm}(\mathbf{r})Y_{l'm'}(\mathbf{r}'),\end{aligned} \tag{19}$$

where $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions,[4] respectively. Then by carrying out the surface integrals with the use of the orthonormality of $Y_{l,m}$, the contribution of a typical term "diagonal" in the centers is found to be

$$\begin{aligned}&\sum_{l,m}\sum_{l',m'} C_{lm}{}^{(j)*}C_{l'm'}{}^{(j)}[j_l{}'\mathcal{R}_l{}^{(j)}-j_l\mathcal{R}_l{}^{(j)\prime}]\\&\quad\times\{A_{lm;l'm'}{}^{(j,j)}[j_{l'}\mathcal{R}_{l'}{}^{(j)\prime}-j_{l'}{}'\mathcal{R}_{l'}{}^{(j)}]\\&\quad+\kappa\delta_{ll'}\delta_{mm'}[n_{l'}\mathcal{R}_{l'}{}^{(j)\prime}-n_{l'}{}'\mathcal{R}_{l'}{}^{(j)}]\}|_{r=R_j},\end{aligned} \tag{20}$$

in which

$$\mathcal{R}_l{}^{(j)\prime}\equiv\frac{d}{dr}\mathcal{R}_l{}^{(j)}(r), \quad j_l{}'\equiv\frac{d}{dr}j_l(\kappa r), \text{ etc.} \tag{21}$$

The terms involving products of surface integrals over different spheres (terms to be called "off diagonal" in the centers) are slightly more troublesome because the natural coordinate systems for $\mathbf{r}$ and $\mathbf{r}'$ have their origins at different points. It is clear, however, that if the Green's function were to be expanded about the appropriate centers for $\mathbf{r}$ and $\mathbf{r}'$, the integrals could be readily evaluated. For convenience we define $\mathbf{r}_j$ to be the position vector with respect to the jth nucleus in the unit cell, i.e.,

$$\mathbf{r}_j=\mathbf{r}-\mathbf{a}_j. \tag{22}$$

We also define the Green's function $\mathcal{G}^{(j,j')}(\mathbf{r}_j,\mathbf{r}_{j'}{}')$ by

$$\mathcal{G}^{(j,j')}(\mathbf{r}_j,\mathbf{r}_{j'}{}')=G(\mathbf{r},\mathbf{r}')=G(\mathbf{r}_j-\mathbf{r}_{j'}{}'-(\mathbf{a}_{j'}-\mathbf{a}_j)). \tag{23}$$

Because of the assumption that the spheres do not touch, the Green's function is never singular for $\mathbf{r}$ in one sphere and $\mathbf{r}'$ in another. For these values of the arguments, $\mathcal{G}^{(j,j')}(\mathbf{r}_j,\mathbf{r}_{j'}{}')$ must then satisfy the homogeneous equation related to (6) in both $\mathbf{r}_j$ and $\mathbf{r}_{j'}{}'$, and since it must be finite about both origins, it must be expansible in the series

$$\mathcal{G}^{(j,j')}(\mathbf{r}_j,\mathbf{r}_{j'}{}')=\sum_{l,m}\sum_{l'm'} A_{lm;l'm'}{}^{(j,j')}j_l(\kappa r_j)j_{l'}(\kappa r_{j'}{}')\times Y_{lm}(\mathbf{r}_j)Y_{l'm'}{}^*(\mathbf{r}_{j'}{}') \tag{24}$$

for

$$(r_j+r_{j'}{}')<|\mathbf{a}_j-\mathbf{a}_i|.$$

The contribution to Λ of the term with $\mathbf{r}$ centered about the jth nucleus and $\mathbf{r}'$ centered about the j'th nucleus

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[4] See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), first edition, p. 77.

can then be shown to be

$$\sum_{l,m}\sum_{l'm'} A_{lm;l'm'}{}^{(j,j')}C_{lm}{}^{(j)*}C_{l'm'}{}^{(j')} \times[j_l'\mathcal{R}_l{}^{(j)}-j_l\mathcal{R}_l{}^{(j)\prime}]|_{r=R_j} \times[j_{l'}\mathcal{R}_{l'}{}^{(j')\prime}-j_{l'}'\mathcal{R}_{l'}{}^{(j')}]|_{r=R_{j'}}. \tag{25}$$

The quantity Λ, which is the sum of all the "diagonal" terms (20), and all the "off-diagonal" terms (25) is

$$\sum_{j,j'}\sum_{l',m}\sum_{l',m'} C_{lm}{}^{(j)*}C_{l'm'}{}^{(j')} \times\{A_{lm;l'm'}{}^{(j,j')}[j_l'\mathcal{R}_l{}^{(j)}-j_l\mathcal{R}_l{}^{(j)\prime}]|_{r=R_j} \times[j_{l'}\mathcal{R}_{l'}{}^{(j')\prime}-j_{l'}'\mathcal{R}_{l'}{}^{(j')}]|_{r=R_{j'}} +\kappa\delta_{ll'}\delta_{mm'}\delta_{jj'}[j_l'\mathcal{R}_l{}^{(j)}-j_l\mathcal{R}_l{}^{(j)\prime}] \times[n_{l'}\mathcal{R}_{l'}{}^{(j)\prime}-n_{l'}'\mathcal{R}_{l'}{}^{(j)}]|_{r=R_j}\}. \tag{26}$$

By taking the variation of Λ with respect to the variational coefficients and setting it equal to zero, we obtain the equations for the variational coefficients:

$$\sum_{l',m',j'}\{A_{lm,l'm'}{}^{(j,j')}[j_{l'}\mathcal{R}_{l'}{}^{(j')\prime}-j_{l'}'\mathcal{R}_{l'}{}^{(j')}]|_{r=R_i} +\kappa\delta_{ll'}\delta_{mm'}\delta_{jj'}[n_{l'}\mathcal{R}_{l'}{}^{(j)\prime}-n_{l'}'\mathcal{R}_{l'}{}^{(j)}]|_{r=R_j}\} \times C_{l'm'}{}^{(j')}=0. \tag{27}$$

In order that the solutions of (27) be nontrivial, the determinant of the coefficients must be equal to zero. If we divide each column by $[j_{l'}\mathcal{R}_{l'}{}^{(j')\prime}-\mathcal{R}_{l'}{}^{(j')}j_{l'}']|_{r=R_{j'}}$, we obtain for the secular equation

$$\det\left\{A_{lm;l'm'}{}^{(j,j')}+\kappa\delta_{ll'}\delta_{mm'}\delta_{jj'}\left[\frac{n_l'-n_lL_l{}^{(j)}}{j_l'-j_lL_l{}^{(j)}}\right]\Bigg|_{r=R_j}\right\}=0, \tag{28}$$

where $L_l{}^{(j)}$ is the logarithmic derivative of $\mathcal{R}_l(r)$ at $r=R_j$ which is defined by

$$L_l{}^{(j)}=\left[\frac{d}{dr}\mathcal{R}_l{}^{(j)}(r)\right]\Big/\mathcal{R}_l{}^{(j)}(r). \tag{29}$$

Since the structure coefficients are functions of $\mathbf{k}$ and the energy (or κ), Eq. (28) determines the functional relationship between E and $\mathbf{k}$. It is to be noted that (28) is very similar in form to the corresponding result of Kohn and Rostoker although it applies to more general lattices.

The structure constants $A_{lm;l'm'}{}^{(j,j)}$, which are "diagonal" in the centers, are identical to the Kohn-Rostoker $A_{lm;l'm'}$ for a "simple" crystal with the same translational symmetry. On the other hand, the structure constants "off diagonal" in the centers, $A_{lm;l'm'}{}^{(j,j')}$ $(j'\neq j)$, are different. These quantities will be discussed in Appendix A where we shall derive explicit expressions for their evaluation and shall obtain certain useful relationships satisfied by them and related quantities.

The secular equation (28), while being valid for all $\mathbf{k}$ vectors including those with special symmetry (those $\mathbf{k}$ vectors invariant under some of the operations of the group of symmetry operations), can be considerably simplified at the symmetry points. For this purpose, instead of expanding the wave function in terms of spherical harmonics, it is most advantageous to expand in terms of functions forming a basis for an irreducible representation of the group of the wave vector.[5] A wave function belonging to sth irreducible representation could then be expanded about the jth center as

$$\psi^s=\sum_{l,\nu}^{l_{\max}} C_{l\nu}{}^{(j)s}\mathcal{R}_l{}^{(j)}(r_j)L_{l\nu}{}^s(\mathbf{r}_j), \tag{30}$$

where

$$L_{l\nu}{}^s(\mathbf{r})=\textstyle\sum_m\alpha_{lm;\nu}{}^{(j)s}Y_{lm}(\mathbf{r}) \tag{31}$$

and will contain, in general, fewer terms than (17). It should be noted here that if the wave function expanded about the jth nucleus belongs to the irreducible representation S, the wave function expanded about the j'th nucleus will belong to the irreducible representation S' which is closely related but not necessarily identical to the irreducible representation S. The secular equation that obtains from the use of expansion (30) is

$$\det\left\{B_{l\nu;l'\nu'}{}^{(j,j')}+\kappa\delta_{ll'}\delta_{\nu\nu'}\delta_{jj'}\left[\frac{n_l'-n_lL_l{}^{(j)}}{j_l'-j_lL_l{}^{(j)}}\right]\Bigg|_{r=R_j}\right\}=0, \tag{32}$$

where the new structure constants are given by

$$B_{l\nu;l'\nu'}{}^{(j,j')} =\textstyle\sum_{m,m'}\alpha_{lm;\nu}{}^{(j)s*}A_{lm;l'm'}{}^{(j,j')}\alpha_{l'm';\nu'}{}^{(j')s'}. \tag{33}$$

The corresponding equations for the wave functions at a symmetry point are

$$\sum_{l',\nu',j'}\{B_{l\nu;l'\nu'}{}^{(j,j')}[j_{l'}\mathcal{R}_{l'}{}^{(j')\prime}-j_l'\mathcal{R}_{l'}{}^{(j')}]|_{r=R_i} +\kappa\delta_{ll'}\delta_{\nu\nu'}\delta_{jj'}[n_l\mathcal{R}_l{}^{(j)\prime}-n_l'\mathcal{R}_l{}^{(j)}]|_{r=R_j}\} \times C_{l'\nu'}{}^{(j')}=0. \tag{34}$$

III. DISCUSSION

The secular equations, (28) and (32), and the related equations for the wave functions, (27) and (34), bear a close resemblance to those of Kohn and Rostoker. Much of their discussion of the method is, of course, applicable here. Thus, because of the particular variational procedure, we expect the method to lead to accurate results. As in other variational procedures, the method ensures that the error in $E(\mathbf{k})$ will be of the

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[5] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947); D. G. Bell, Revs. Modern Phys. **26**, 311 (1954).

second order of the error in the trial function; but it also has the advantage of being based on the integral equation for ψ. Such variational procedures tend to result in greater accuracy than those based on the differential equation. Also, the present method has the advantage over certain other methods (e.g., the orthogonalized plane-wave method) that difficulties associated with the lack of orthogonality of the trial functions to the true core states[6] do not arise. Finally, since the trial function is needed inside the "atomic" spheres only and not in the whole unit cell, relatively few terms in the spherical harmonic decomposition of ψ should be sufficient to obtain accurate energies and wave functions.

The present equations differ from the corresponding ones for a "simple" structure in that they comprise a larger system of equations because of the lower symmetry of the "complex" structure. For example, let us assume that the secular equation for the "simple" case is the determinant of an $N\times N$ matrix for a general point in the Brillouin zone. Then, assuming that the same $l_{\max}$ is used in all expansions, the secular equation for the "complex" case will be the determinant of an $mN\times mN$ matrix, where m is the number of atoms in the unit cell. In addition, the present equations contain the new structure constants $A_{lm;l'm'}{}^{(j,j')}(j'\neq j)$, which are "off diagonal" in the centers. The significance of these is most easily understood when the problem is thought of in terms of the scattering picture as is done in Appendix B. From this point of view, the constants $A_{lm;l'm'}{}^{(j,j)}$ relate the wave "incident" on one of the atoms of the sublattice $\mathbf{r}_n+\mathbf{a}_j$ to the sum of the waves scattered from all other atoms of the same sublattice. The constants $A_{lm;l'm'}{}^{(j,j')}(j'\neq j)$, on the other hand, relate the contribution to the "incident" wave from the sum of the waves scattered from all atoms of the sublattice $\mathbf{r}_n+\mathbf{a}_{j'}$. The separation of the two sublattices is $\mathbf{a}_j-\mathbf{a}_{j'}$ which, of course, is not a translation vector, $\mathbf{r}_n$, of the lattice. We might then expect that for each momentum component of the electron wave there will be an additional phase factor of $\exp\{i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{a}_j-\mathbf{a}_{j'})\}$ in the "off-diagonal" terms. In the detailed analysis of Appendix A we show, in fact, that except for a term arising from the singular part of the Green's function, the phase factors are the only differences between the "off-diagonal" and the "diagonal" structure constants.

Of central importance to the applicability of the method is the question of the appropriateness of the approximating potential, (14), to particular crystals. If a potential satisfying the condition (14) represents a reasonable zero-order approximation, the method appears to be very satisfactory. In examining the question of applicability, we must remember that at the present stage of our knowledge we are more or less forced to resort to the use of atomic potentials in order to construct a crystalline potential. Atomic potentials are, of course, spherically symmetric, but in a crystalline array of these potentials there will be some overlap of atomic potentials about neighboring sites which destroys strict spherical symmetry at the outer regions of the "atomic" spheres. However, owing to the symmetrical arrangement of the neighbors about any lattice point, these deviations will to a fair degree be canceled. For example, if we expand the nonspherically symmetric part of the potential in spherical harmonics, we find that the first nonvanishing term is the $l=4$ term for the rock salt and diamond structures and the $l=3$ term for the zinc blende structure. It would thus seem that the deviations from spherical symmetry inside the "atomic" spheres will be small. In the regions exterior to the "atomic" spheres, where the approximating potential is taken to be constant, there may be points where the relative deviation of the actual potential from the constant potential (i.e., the difference divided by the actual potential) is not small. However, at these points the potential and its deviation from the approximating potential (which equals the potential as the zero of the energy scale is chosen so that $V_0=0$) are small. One can then see on the basis of perturbation theory that, in general, only relatively small errors in the energy and in the wave function should arise from the use of (14). It thus appears likely that the approximating potential could be used satisfactorily in many cases. The deviations from a judiciously chosen approximating potential can then be taken into account by perturbation theory. For a more quantitative and definitive investigation of the effect of deviations from the assumed potential, it will be necessary to await the completion of the detailed band structure calculations now in progress.

The feasibility of using this method is determined largely by the feasibility of the computation of the structure constants. From the expressions for the "off-diagonal" structure constants (Appendix A), it can be seen that they are only slightly more difficult to compute than the structure constants for "simple" lattices. Thus, from the experience with the computation of the structure constants for the "simple" body-centered cubic structures,[7] it appears that the computations for the "complex" cases should present no serious difficulties.

A program for the study of a few types of structures with two atoms per unit cell by the present method has been initiated. The first crystals we hope to investigate are those having the zinc blende structure (e.g., Ge, ZnS, InSb). We then intend to study a few crystals which form with the rock salt structure (e.g., NaCl).

The author wishes to thank Professor Walter Kohn for discussions.

APPENDIX A

As indicated in Sec. II, the "diagonal" structure constants are identical with those for a "simple" lattice

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[6] J. Callaway, Phys. Rev. 97, 933 (1955).

[7] F. S. Ham and J. Snyder (private communication).

with the same translational symmetry; thus, it is only necessary for us to discuss the "off-diagonal" structure constants, $A_{lm;l'm'}{}^{(j,j')}$. One important property of these coefficients results from the Hermiticity, (12), of the Green's function. From the definition of $\mathcal{G}^{(j,j')}$, (23), we find that

$$\mathcal{G}^{(j,j')}(\mathbf{r}_j,\mathbf{r}_{j'}{}')=\mathcal{G}^{(j',j)*}(\mathbf{r}_{j'}{}',\mathbf{r}_j), \tag{A-1}$$

and from a subsequent expansion of both sides of (A-1) by (24) we can verify that

$$A_{lm;l'm'}{}^{(j,j')}=A_{l'm';lm}{}^{(j',j)*}. \tag{A-2}$$

An explicit expression for the Green's function $\mathcal{G}^{(j,j')}$ is easily obtained from (8) and (22), and is

$$\mathcal{G}^{(j,j')}(\mathbf{r}_j,\mathbf{r}_{j'}{}')=\frac{-1}{\tau}\sum_{\mathbf{K}_n}\times\frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{a}_j-\mathbf{a}_{j'})]\exp[i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{r}_j-\mathbf{r}_{j'}{}')]}{(\mathbf{K}_n+\mathbf{k})^2-E}. \tag{A-3}$$

To arrive at an expansion of the form (24), the two plane wave functions of each term of the sum are expanded according to the well-known formula

$$e^{i\mathbf{k}\cdot\mathbf{r}}=4\pi\sum\nolimits_{l,m}i^l j_l(kr)Y_{lm}(\mathbf{r})Y_{lm}{}^*(\mathbf{k}). \tag{A-4}$$

Upon comparison with (24), the equation defining the structure constants, we find that

$$A_{lm;l'm'}{}^{(j,j')}=\frac{-(4\pi)^2 i^{l-l'}}{\tau j_l(\kappa r_j)j_l(\kappa r_{j'}{}')}\sum_{\mathbf{K}_n}\frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{a}_j-\mathbf{a}_{j'})]}{(\mathbf{K}_n+\mathbf{k})^2-E}\times j_l(|\mathbf{K}_n+\mathbf{k}|r_j)j_{l'}(|\mathbf{K}_n+\mathbf{k}|r_{j'}{}')\times Y_{lm}{}^*(\mathbf{K}_n+\mathbf{k})Y_{l'm'}(\mathbf{K}_n+\mathbf{k}). \tag{A-5}$$

In analogy with the corresponding work of Kohn and Rostoker, we can obtain a more useful means of evaluating the A's by noting that the Green's function has as its argument the single vector $\mathbf{R}_{jj'}=\mathbf{r}_j-\mathbf{r}_{j'}{}'$. A new set of coefficients, $D_{LM}{}^{(j,j')}$, is then defined by the expansion of $\mathcal{G}^{(j,j')}(\mathbf{R}_{jj'})$ in the single series of spherical harmonics

$$\mathcal{G}^{(j,j')}(\mathbf{R}_{jj'})=\sum\nolimits_{L,M}D_{LM}{}^{(jj')}j_L(R_{jj'})Y_{LM}(\mathbf{R}_{jj'}). \tag{A-6}$$

The relationship between the $D^{(j,j')}$'s and $A^{(j,j')}$'s is the same as one relating the corresponding "diagonal" quantities which can be shown by the arguments used for the "simple" lattices.[3] The relationship is

$$A_{lm;l'm'}{}^{(j,j')}=4\pi i^{l-l'}\sum\nolimits_L i^{-L}C_{lm;l'm'}{}^{Lm-m'}D_{Lm-m'}{}^{(j,j')}, \tag{A-7}$$

where

$$C_{lm;l'm'}{}^{LM}=\int Y_{LM}(\mathbf{r})Y_{lm}{}^*(\mathbf{r})Y_{l'm'}(\mathbf{r})d\Omega_r. \tag{A-8}$$

Except when $l_{\max}$ is very small, the number of D's required in a calculation is considerably smaller than the number of A's. The C's are, of course, quite general coefficients and have been tabulated.[8]

The structure constants $D_{LM}{}^{(j,j')}$ can be determined readily by employing (A-4) in (A-3) and comparing with (A-6); and we find that

$$D_{LM}{}^{(jj')}=-\frac{4\pi}{\tau}\frac{i^L}{j_L(\kappa R_{jj'})}\sum_{\mathbf{K}_n}\frac{\exp\{i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{a}_j-\mathbf{a}_{j'})\}}{(\mathbf{K}_n+\mathbf{k})^2-E}\times j_L(|\mathbf{K}_n+\mathbf{k}|R_{ji})Y_{LM}{}^*(\mathbf{K}_n+\mathbf{k}). \tag{A-9}$$

Another representation for the structure constants can be obtained by starting with the Green's function expressed as the sum over the real lattice. We write

$$\begin{aligned}\mathcal{G}^{(j,j')}(\mathbf{R}_{jj'})&=-\frac{1}{4\pi}\sum_{\mathbf{r}_n}\exp(i\mathbf{k}\cdot\mathbf{r}_n)\frac{\exp\{i\kappa|\mathbf{R}_{jj'}-(\mathbf{r}_n-\mathbf{a}_j+\mathbf{a}_{j'})|\}}{|\mathbf{R}_{jj'}-(\mathbf{r}_n-\mathbf{a}_j+\mathbf{a}_{j'})|}\\&=-\frac{1}{4\pi}\exp[i\mathbf{k}\cdot(\mathbf{a}_j-\mathbf{a}_{j'})]\sum_{\mathbf{s}_{jj';n}}\exp(i\mathbf{k}\cdot\mathbf{s}_{jj';n})\times\frac{\exp\{i\kappa|\mathbf{R}_{jj'}-\mathbf{s}_{jj';n}|\}}{|\mathbf{R}_{jj'}-\mathbf{s}_{jj';n}|},\end{aligned} \tag{A-10}$$

where the lattice sum extends over the whole of the lattice defined by

$$\mathbf{s}_{jj';n}=\mathbf{r}_n-(\mathbf{a}_j-\mathbf{a}_{j'})\,(j\text{ and }j'\text{ fixed}). \tag{A-11}$$

To put (A-10) in the form (A-6), use is made of the Neumann expansion[9]

$$-\frac{1}{4\pi}\frac{\exp(i\kappa|\mathbf{R}-\mathbf{s}|)}{|\mathbf{R}-\mathbf{s}|}=\kappa\sum_{l,m}j_l(\kappa R)[n_l(\kappa s)-ij_l(\kappa s)]\times Y_{lm}(\mathbf{R})Y_{lm}{}^*(\mathbf{s})\quad\text{for}\quad R<s. \tag{A-12}$$

In this manner we obtain

$$D_{LM}{}^{(j,j')}=\kappa\exp[i\mathbf{k}\cdot(\mathbf{a}_j-\mathbf{a}_{j'})]\sum_{\mathbf{s}_{jj';n}}\exp(i\mathbf{k}\cdot\mathbf{s}_{jj';n})\times[n_L(\kappa s_{jj';n})-ij_L(\kappa s_{jj';n})]Y_{LM}{}^*(\mathbf{s}_{jj';n}). \tag{A-13}$$

It is of interest to compare (A-9) and (A-13) with the corresponding expressions for the "simple" lattices

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[8] Closely related coefficients are discussed in E. V. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 175 ff. Also, an extensive tabulation of the coefficients (A-8) has been carried out by F. S. Ham (unpublished).

[9] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Part II, p. 1574.

as given by Kohn and Rostoker.[3] In both the lattice sum and the reciprocal lattice sum representations, the "diagonal" structure constants contain a term which arises from the singular part of the Green's function. Because of the assumption of nonoverlapping spheres, this term does not appear in our expressions. The only other difference between the two in the reciprocal-space representation is the appearance of the phase factors $\exp[i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{a}_j-\mathbf{a}_{j'})]$, the origin of which has been discussed in Sec. III. In the lattice sum representation, the summands have exactly the same form for both cases, but in the case of the "off-diagonal" structure constants the sum extends over a sublattice displaced from the lattice $\mathbf{r}_n$ by the vector $(\mathbf{a}_j-\mathbf{a}_{j'})$. This also can be readily understood in terms of the discussion in Sec. III.

The property (A-2) of the $A_{lm;l'm'}{}^{(j,j')}$ suggests that there must be a corresponding relation for the $D_{LM}{}^{(j,j')}$. Using

$$Y_{lm}{}^*(x)=(-1)^m Y_{l-m}(x),$$

one can readily verify from an explicit representation of the D's such as (A-9), that they have the property that

$$D_{LM}{}^{(j,j')}=(-1)^{L+M}D_{L-M}{}^{(j',j)*}. \tag{A-14}$$

APPENDIX B

In this section we will consider the band structure problem from Korringa's point of view,[2] that is, in terms of the scattering of the electron wave by the crystalline array of atomic spheres. We note that the wave function can be expressed as

$$\psi_{-\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{r}_n}\exp(-i\mathbf{k}\cdot\mathbf{r}_n)\sum_{j'}\varphi^{(j')}(\mathbf{r}-\mathbf{r}_n-\mathbf{a}_{j'})$$
$$=\sum_{j'}\exp(i\mathbf{k}\cdot\mathbf{a}_{j'})\sum_{\mathbf{r}_{nj'}}\exp(-i\mathbf{k}\cdot\mathbf{r}_{nj'})\varphi^{(j')}(\mathbf{r}-\mathbf{r}_{nj'}), \tag{B-1}$$

where $\mathbf{r}_{nj'}=\mathbf{r}_n+\mathbf{a}_{j'}$ and the functions $\varphi^{(j')}$ are, in general, different.

In the regions of constant potential the solution of the Schrödinger equation can be expressed in terms of $j_l(x)$ and $h_l{}^{(1)}(x)$, the spherical Bessel function and the spherical Hankel function of the first kind, respectively. Thus, in the region outside the "atomic sphere" centered at $\mathbf{r}=\mathbf{a}_j$ the wave function can be taken to be

$$\psi_{-\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{a}_j}\sum_{l,m}\{b_{lm}{}^{(j)}j_l(\kappa|\mathbf{r}-\mathbf{a}_j|)$$
$$+a_{lm}{}^{(j)}h_l{}^{(1)}(\kappa|\mathbf{r}-\mathbf{a}_j|)\}Y_{lm}{}^*(\mathbf{r}-\mathbf{a}_j). \tag{B-2}$$

The second term of (B-2) behaves asymptotically as

$$a_{lm}{}^{(j)}|\mathbf{r}-\mathbf{a}_j|^{-1}\exp(i\kappa|\mathbf{r}-\mathbf{a}_j|)$$

and is singular at $\mathbf{a}_j$, and thus is identified as the wave scattered by the atom at $\mathbf{a}_j$. The first term, which is regular at $\mathbf{a}_j$, is, of course, the incident wave.

We are now in a position to interpret our problem in terms of a scattering picture. Our principle of approach is to consider the wave incident upon a particular atom to be built up of the waves scattered from all the other atoms of the lattice. This establishes a relationship between the scattering amplitudes, $a_{lm}{}^{(j)}$, and the coefficients of the incident wave, $b_{lm}{}^{(j)}$. The waves incident on and scattered from a particular atom are related by the phase shift of ordinary scattering theory. These conditions are sufficient to determine all the amplitudes and the dispersion relationship, which yields the energy as a function of $\mathbf{k}$.

The problem can be defined mathematically by rewriting (B-1) as

$$\psi_{-\mathbf{k}}(\mathbf{r})=\varphi^{(j)}(\mathbf{r}-\mathbf{a}_j)$$
$$+\sum_{r_{nj'},j'}{}' e^{i\mathbf{k}\cdot\mathbf{a}_{j'}}\{e^{-i\mathbf{k}\cdot\mathbf{r}_{nj'}}\varphi^{(j')}(\mathbf{r}-\mathbf{r}_{nj'})\}, \tag{B-1a}$$

where the prime over the summation indicates that the term specified by $\mathbf{r}_n=0$ and $j'=j$ is to be omitted. In the regions exterior to the spheres $\varphi^{(j')}(\mathbf{r}-\mathbf{r}_{nj'})$ is taken to be the purely outgoing scattered wave emanating from the atom at $\mathbf{r}_{nj'}$. The problem is then to show that the second term of (B-1a) corresponds to the first term of (B-2), and to derive the equations satisfied by the scattering amplitudes.

To proceed with the details, we first consider the sum of the waves scattered on the atom centered at $\mathbf{r}=\mathbf{a}_j$ by the remaining atoms of the sublattice $\mathbf{r}_{nj}$. This is

$$\exp(i\kappa\cdot\mathbf{a}_j)\sum_{\mathbf{r}_{nj}\neq 0}\exp(-i\mathbf{k}\cdot\mathbf{r}_{nj})\sum_{l,m}a_{lm}{}^{(j)}$$
$$\times h_l{}^{(1)}(\kappa|\mathbf{r}-\mathbf{r}_{nj}|)Y_{lm}{}^*(\mathbf{r}-\mathbf{r}_{nj}). \tag{B-3}$$

Now, it can be shown that[10]

$$h_l{}^{(1)}(\kappa r)Y_{lm}(\mathbf{r})=i^{-l}\mathcal{Y}_{lm}(\nabla_r)h_0{}^{(1)}(\kappa r), \tag{B-4}$$

where

$$\mathcal{Y}_{l,m}(\nabla_r)=\left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{\frac{1}{2}}$$
$$\times Q_m\left(\frac{\partial}{\partial(ikx)},\frac{\partial}{\partial(iky)}\right)\mathcal{P}_l{}^{|m|}\left(\frac{\partial}{\partial(ikz)}\right),$$
$$Q_{m=\pm|m|}(x,y)=(x\pm iy)^{|m|}, \tag{B-5}$$
$$\mathcal{P}_l{}^{|m|}(z)=(d^{|m|}/dz^{|m|})P_l(z),$$

and $P_l(z)$ is the conventional Legendre polynomial. (B-3) can then be written

$$\exp(i\mathbf{k}\cdot\mathbf{a}_j)\sum_{\mathbf{r}_{nj}\neq 0}\exp(-i\mathbf{k}\cdot\mathbf{r}_{nj})\sum_{l',m'}(-1)^{m'}i^{l'}a_{l'm'}{}^{(j)}$$
$$\times\mathcal{Y}_{l'-m'}(\nabla_{r_{nj}})h_0{}^{(1)}(\kappa|\mathbf{r}-\mathbf{r}_{nj}|) \tag{B-6}$$

where the derivatives act on the coordinates $\mathbf{r}_{nj}$.

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[10] N. Kasterin, Proc. Acad. Sci. Amsterdam **6**, 460 (1897/98); J. Korringa, reference 2.

We now wish to relate (B-6), which corresponds to the sum of the waves scattered from the atoms of the sublattice $\mathbf{r}_{nj}(\neq a_j)$, to the wave incident on the atom centered at $\mathbf{a}_j$. Mathematically, this means that we want to expand (B-6) in terms of Bessel functions $[j_l(x)]$ of the argument $|\mathbf{r}-\mathbf{a}_j|$. For this purpose we make use of the expansion

$$h_0^{(1)}(\kappa|\mathbf{r}-\mathbf{r}'|)$$
$$=4\pi\sum_{l,m}[h_l^{(1)}(\kappa r')Y_{lm}(\mathbf{r}')]j_l(\kappa r)Y_{lm}^*(\mathbf{r}), \quad \text{(B-7)}$$

when $r'>r$.[9] Then

$$h_0^{(1)}(\kappa|\mathbf{r}-\mathbf{r}_{nj}|)=h_0^{(1)}(\kappa|(\mathbf{r}-\mathbf{a}_j)-\mathbf{r}_n|)$$
$$=4\pi\sum_{l,m}[i^{-l}\mathcal{Y}_{lm}(\nabla_{r_n})h_0^{(1)}(\kappa r_n)]$$
$$\times j_l(\kappa|\mathbf{r}-\mathbf{a}_j|)Y_{lm}^*(\mathbf{r}-\mathbf{a}_j), \quad \text{(B-8)}$$

and by a simple transformation of the derivative operators in (B-6), we obtain for (B-6) the following:

$$e^{i\mathbf{k}\cdot\mathbf{a}_j}\sum_{l,m}\sum_{l'm'}\Gamma_{lm;l'm'}^{(j,j)}a_{l'm'}^{(j)}$$
$$\times j_l(\kappa|\mathbf{r}-\mathbf{a}_j|)Y_{lm}^*(\mathbf{r}-\mathbf{a}_j), \quad \text{(B-9)}$$

where

$$\Gamma_{lm;l'm'}^{(j,j')}=4\pi(-1)^{m'}i^{l-l'}\sum_{\mathbf{r}_n\neq 0}e^{i\mathbf{k}\cdot\mathbf{r}_n}$$
$$\times\mathcal{Y}_{lm}(\nabla_{r_n})\mathcal{Y}_{l'-m'}(\nabla_{r_n})h_0^{(1)}(\kappa r_n). \quad \text{(B-10)}$$

The above corresponds to the coefficients derived by Korringa. It can be rewritten in the form used by Korringa:

$$\Gamma_{lm;l'm'}^{(j,j)}=4\pi(-1)^{m'}i^{l'-l-1}$$
$$\times[\mathcal{Y}_{lm}(\nabla_r)\mathcal{Y}_{l'-m'}(\nabla_r)S(\mathbf{r})]|_{r=0}, \quad \text{(B-11)}$$

with

$$S(\mathbf{r})=\sum_{\mathbf{r}_n\neq 0}\exp(i\mathbf{k}\cdot\mathbf{r}_n)\frac{\exp\{i\kappa|\mathbf{r}-\mathbf{r}_n|\}}{|\mathbf{r}-\mathbf{r}_n|}. \quad \text{(B-12)}$$

(The slight differences between Korringa's expressions and the above expression result from different choices of the phases of the various functions employed.)

The contribution to the wave incident on $\mathbf{a}_j$ from centers of another sublattice, for example, the one defined by $\mathbf{r}_{nj'}$, can be calculated in a manner similar to the one used above. Here it is, of course, necessary to take into account the scatterings from all "atomic" spheres of the sublattice. Also, we note that the point $\mathbf{a}_j$ is separated from the sublattice $\mathbf{r}_{nj'}$ by the vectors $\mathbf{s}_{jj';n}$, defined by (A-11), so that in this case we require the expansion of

$$h_0^{(1)}(\kappa|\mathbf{r}-\mathbf{r}_{nj'}|)=h_0^{(1)}(\kappa|(\mathbf{r}-\mathbf{a}_j)-\mathbf{s}_{jj';n}|)$$

in terms of $j_l(\kappa|\mathbf{r}-\mathbf{a}_j|)$. We then find that the contribution of the waves scattered from the atoms of the sublattice $\mathbf{r}_{nj'}$ on to the atom located at $\mathbf{r}=\mathbf{a}_j$ is

$$e^{i\mathbf{k}\cdot\mathbf{a}_j}\sum_{l,m}\sum_{l',m'}\Gamma_{lm;l'm'}^{(j,j')}a_{l'm'}^{(j')}$$
$$\times j_l(\kappa|\mathbf{r}-\mathbf{a}_j|)Y_{lm}^*(\mathbf{r}-\mathbf{a}_j), \quad \text{(B-13)}$$

where

$$\Gamma_{lm;l'm'}^{(j,j')}=4\pi(-1)^{m'}i^{l-l'}e^{i\mathbf{k}\cdot(\mathbf{a}_{j'}-\mathbf{a}_j)}$$
$$\times\sum_{\mathbf{s}_{jj';n}}\exp(i\mathbf{k}\cdot\mathbf{s}_{jj';n})\mathcal{Y}_{lm}(\nabla_{s_{jj';n}})$$
$$\times\mathcal{Y}_{l'-m'}(\nabla_{s_{jj';n}})h_0^{(1)}(\kappa s_{jj';n}). \quad \text{(B-14)}$$

The incident wave is the sum of (B-9) and all the terms (B-13) with $j'\neq j$, and we find from (B-2) that

$$b_{lm}^{(j)}=\sum_{l',m'}\sum_{j'}\Gamma_{lm;l'm'}^{(j,j')}a_{l'm'}^{(j')}. \quad \text{(B-15)}$$

The wave incident on and the wave scattered from a particular "atomic" sphere are also related by the condition that the wave function and its derivative be continuous at the surface of the sphere. In terms of the phase shift, $\eta_l^{(j)}$, this requires that

$$b_{lm}^{(j)}=-ia_{lm}^{(j)}\csc\eta_l^{(j)}\exp[-i\eta_l^{(j)}]. \quad \text{(B-16)}$$

The system of equations determining the scattering amplitudes $a_{l,m}^{(j)}$ is then

$$\sum_{l',m'}\sum_{j'}\{\Gamma_{lm;l'm'}^{(j,j')}+i\delta_{ll'}\delta_{mm'}\delta_{jj'}$$
$$\times\csc\eta_l^{(j)}\exp[-i\eta_l^{(j)}]\}a_{l'm'}^{(j')}=0. \quad \text{(B-17)}$$

The secular equation associated with this linear homogeneous system of equations determines the dispersion relation for the electron waves; and it is

$$\det\{\Gamma_{lm;l'm'}^{(j,j')}$$
$$+i\delta_{ll'}\delta_{mm'}\delta_{jj'}\csc\eta_l^{(j)}\exp[-i\eta_l^{(j)}]\}=0. \quad \text{(B-18)}$$

Equations (B-17) and (B-18) are the desired generalizations of Korringa's equations.

Kohn and Rostoker noted that by using

$$i\csc\eta_l e^{-i\eta_l}=1+i\left.\frac{n_l'-n_lL_l}{j_l'-j_lL_l}\right|_{r=R}. \quad \text{(B-19)}$$

Korringa's results could be recast into the same form as their equations. This also holds true for the "complex" lattices. We can rewrite (B-18) as

$$\det\left\{F_{lm;l'm'}^{(j,j')}+\kappa\delta_{ll'}\delta_{mm'}\delta_{jj'}\left.\left[\frac{n_l'-n_lL_l^{(j)}}{j_l'-j_lL_l^{(j)}}\right]\right|_{r=R_j}\right\}=0, \quad \text{(B-20)}$$

where

$$F_{lm;l'm'}^{(j,j')}=-i\kappa[\Gamma_{lm;l'm'}^{(j,j')}+\delta_{ll'}\delta_{mm'}\delta_{jj'}]. \quad \text{(B-21)}$$

Furthermore, it is possible to prove that

$$A_{lm;l'm'}^{(j,j')*}=F_{lm;l'm'}^{(j,j')} \quad \text{(B-22)}$$

so that (B-20) and (28) are, in fact, exactly equivalent.