Solution of the Schrödinger Equation in Periodic Lattices with an Application to Metallic Lithium

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The problem of solving the Schrödinger equation in a periodic lattice is studied from the point of view of the variation-iteration method. This approach leads to a very compact scheme if the potential \( V(r) \) is spherically symmetrical within the inscribed spheres of the atomic polyhedra and constant in the space between them. The band structure of the lattice is then determined by (1) geometrical structure constants, characteristic of the type of lattice and (2) the logarithmic derivatives, at the surface of the inscribed sphere, of the \( s, p, d, \ldots \) functions corresponding to \( V(r) \). By far the greater part of the labor is involved in the calculation of (1), which needs to be done only once for each type of lattice; (2) can be obtained by numerical integration or directly from the atomic spectra. Although derived from a different point of view, this scheme turns out to be essentially equivalent to one proposed by Korringa on the basis of the theory of lattice interferences. The present paper also contains an application to the conduction band of metallic lithium.

1. INTRODUCTION

One of the central problems in the band theory of solids is to find the propagating solutions of a Schrödinger equation,

\[
[-\nabla^2 + V(r) - E]\psi(r) = 0,
\]

in which the potential has the periodicity of the lattice under consideration. Exact solutions of this problem are in general not possible, and so a number of approximation methods have been used in the past. The present paper deals with the application of the variation-iteration method to this problem, a method which has in recent years been found to be a very useful tool for the approximate solution of the wave equation in nuclear and electromagnetic theory and whose practicability in solid state physics is just beginning to be explored.

A straightforward application of this method was used by one of us [W. Kohn (unpublished); see reference 3] to find the ground-state energy \( (k=0) \) of metallic Na. While the result was very satisfactory, the labor involved discouraged him from calculating the rest of the band in this way.

Dank and Callen\textsuperscript{4,5} have proposed a technique based on repeated iteration. Apart from orthogonality questions, not yet fully clarified, which arise from the fact that the wave functions of interest in band theory do not correspond to the lowest eigenvalues, their method has the advantage of being a general and systematic technique. It involves, however, a major computational effort for each physical problem, requiring the assistance of large scale computing machines.

After our original attempts we noticed that under two conditions the whole problem simplified enormously, namely when the effective potential was spherically symmetrical within the inscribed spheres of the atomic polyhedra and constant in the space between them. Both of these are rather well satisfied in many solids. If necessary, small deviations from these conditions can be taken into account by a perturbation calculation.

The most attractive feature of the scheme which then emerges is that by far the greater part of the work of calculating energy bands consists of the calculation of certain geometrical "structure constants" which must be calculated once and for all for each type of lattice. Beside these, the only other information required are the logarithmic derivatives \( L_k \) at the surface of the inscribed sphere, of the \( s, p, d, \ldots \) solutions of the Schrödinger equation with the given \( V(r) \). These can be easily obtained either by numerical integration or, in some cases, directly from the atomic spectra\textsuperscript{4} without explicit introduction of \( V(r) \).

It should be emphasized that in spite of the assumption of a spherical \( V(r) \) the method is not equivalent to the spherical approximation of Wigner and Seitz in which also the atomic polyhedron is approximated by a sphere. The present method takes the actual shape of the polyhedron exactly into account.

We have used this method to calculate the filled part of the conduction band of metallic lithium (Sec. 5). On the basis of our experience with this calculation, we believe that once the structure constants are tabulated, the method affords a very convenient way of calculating energy bands when the potential satisfies approximately the aforementioned conditions.

A program of preparing systematic tables of the structure constants for body- and face-centered cubic

lattices has been started, and the results will be published when available.

When this work was completed, a paper by Korringa\(^7\) was brought to our attention\(^8\) in which an essentially equivalent scheme was developed from a different point of view. We have felt, however, that a presentation of our work in substantially its original form was advisable, since it brings out a number of new points which did not appear in Korringa’s work.

2. RESUMÉ OF GENERAL THEORY

Consider a monatomic lattice of nuclei at the equivalent positions,
\[ r_i = s_1 \tau_1 + s_2 \tau_2 + s_3 \tau_3, \quad s_i = 0, \pm 1, \pm 2, \ldots, \] (2.1)
where the \( \tau_i \) are three fundamental translation vectors of the lattice. Let \( V(r) \) be an effective potential with the periodicity property:
\[ V(r + r_i) = V(r). \] (2.2)
We shall look for the “propagating” solutions,
\[ \psi(r + r_i) = \exp(ik \cdot r_i)\psi(r), \] (2.3)
of the Schrödinger equation,
\[ [-\nabla^2 + V(r) - E]\psi(r) = 0. \] (2.4)
These solutions satisfy the following boundary conditions in the central polyhedron, which surrounds the origin:
\[ \psi(r') = \exp(iK \cdot \tau_i)\psi(r), \]
\[ \partial\psi(r')/\partial n' = -\exp(iK \cdot \tau_i)\partial\psi(r)/\partial n, \] (2.5)
where \( K \) is the wave vector of the solution, \( r' \) and \( r \) are conjugate points on the surface of the polyhedron, and \( \tau_i \) is the fundamental translation vector joining them. (See Fig. 1.) From here on, it will be sufficient to consider the solution of (2.4) and (2.5) in the central polyhedron only.

We now introduce the Green’s function \( G(r, r') \) defined by
\[ (-\nabla^2 - E)G(r, r') = \delta(r - r'), \] (2.6)
and, for conjugate boundary points \( r \) and \( r' \)
\[ G(r', r') = \exp(iK \cdot \tau_i)G(r, r'), \]
\[ \partial G(r', r')/\partial n' = -\exp(iK \cdot \tau_i)\partial G(r, r')/\partial n. \] (2.7)
Let \( K_n \) be the vectors of the reciprocal lattice defined by
\[ K_n \cdot \tau_i = 2\pi \times (\text{integer}), \quad i = 1, 2, 3. \] (2.8)
Then \( G \) can be written as
\[ G(r, r') = \frac{1}{\sum_{\tau}} \exp[iK_n \cdot (r - r')]/(K_n + K)^2 - E, \] (2.9)
where \( \tau \) is the volume of the atomic polyhedron. Alternatively, \( G \) can be expressed in the form,
\[ G(r, r') = \frac{1}{4\pi} \sum_{\tau} \exp[iK_n \cdot (r - r')]/|r - r'| \exp(iK_n \cdot \tau), \] (2.10)
where
\[ \kappa = +\sqrt{E}, \quad E > 0, \]
\[ = -i\sqrt{(-E)}, \quad E < 0. \] (2.11)
The correctness of (2.9) and (2.10) may be verified by direct substitution. Equation (2.9) is the standard expansion of a Green’s function in terms of the eigenfunctions of the homogeneous boundary value problem and (2.10) can easily be derived from it. (See Appendix 2.) The Green’s function has the hermitian property,
\[ G(r', r) = G^*(r, r'), \] (2.12)
as is apparent from (2.9).

To replace the boundary value problem (2.4), (2.5) by an integral equation, we multiply (2.4) by \( G^*(r, r') \), and the complex conjugate of (2.6) by \( \psi(r) \), subtract and integrate over \( r \) in the interior of the polyhedron. This leads to
\[ \psi(r') = \int \psi(r)G(r, r')V(r)\psi(r')dr, \] (2.13)
which, by (2.12) is equivalent to
\[ \psi(r) = \int G(r, r')V(r')\psi(r')dr. \] (2.14)

Our further considerations are based on this equation.\(^9\)

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\(^7\) J. Korringa, Physica 13, 392 (1947).
\(^8\) We are greatly indebted in this connection to Drs. E. M. Barady and R. J. Harrison of the Batelle Memorial Institute.
\(^9\) We understand that Drs. Harrison and Trefftz are engaged in applications of Korringa’s method which are similar to the work reported here.
The integral Eq. (2.14) is equivalent to the variational principle:
\[ \delta \Lambda = 0, \quad (2.15) \]
where
\[ \Lambda = \int \psi^*(r)V(r)\psi(r)dr \]
\[ - \int \int \psi^*(r)V(r)G(r,r')V(r')\psi(r')d\tau dr', \quad (2.16) \]
as may be directly verified. It should be noted that $\delta \Lambda$ vanishes for arbitrary variations of $\psi$, in particular also such as do not satisfy the boundary conditions (2.5). This allows one much greater freedom of choice of the trial functions.

The variational formulation has considerable practical usefulness. For let $\psi$ be a solution of (2.14) corresponding to $k$ and $E$ (the latter enter through $G$); then, clearly,
\[ \Lambda(\psi, k, E) = 0. \quad (2.17) \]
If now $\psi_i$ is a trial function,
\[ \psi_i = \psi + \epsilon \chi, \]
where $\epsilon$ is a parameter of smallness, then by (2.15),
\[ \Lambda(\psi_i, k, E) = O(\epsilon^2). \quad (2.18) \]
Hence if for given $k$ we calculate $E_i$ from the equation,
\[ \Lambda(\psi_i, k, E_i) = 0, \quad (2.19) \]
then clearly,
\[ E_i - E = O(\epsilon^2), \quad (2.20) \]
i.e., the error of the energy is of the second order compared to that of the trial function. Similarly, if we considered $E$ given and calculated $k_i$ from
\[ \Lambda(\psi_i, k_i, E) = 0, \quad (2.21) \]
we would have
\[ k_i - k = O(\epsilon^2). \quad (2.22) \]

The variational principle (2.15) lends itself to an application of the Rayleigh-Ritz technique. We use a trial function of the form:
\[ \psi = \sum_{i=0}^{n} c_i \varphi_i, \quad c_i = a_i + ib_i, \quad (2.23) \]
and substitute into (2.16). Calling
\[ \Lambda_{ij} = \int \varphi_i^*(r)V(r)\varphi_j(r)dr \]
\[ - \int \int \varphi_i^*(r)V(r)G(r,r')V(r')\varphi_j(r')d\tau dr', \quad (2.24) \]
where $\Lambda_{ij}$ is Hermitian, we have
\[ \Lambda = \sum_{i=0}^{n} c_i^* \Lambda_{ij} c_j. \quad (2.25) \]
The conditions,
\[ \partial \Lambda/\partial a_i = \partial \Lambda/\partial b_i = 0, \quad i = 0, 1, \ldots, n, \quad (2.26) \]
which follow from (2.15), give the linear equations
\[ \sum_{j=0}^{n} \Lambda_{ij} c_j = 0, \quad i = 0, 1, \ldots, n, \quad (2.27) \]
which are compatible only if
\[ \text{Det} \Lambda_{ij} = 0. \quad (2.28) \]

Since, for given functions $\varphi_i$, the $\Lambda_{ij}$ are functions only of $k$ and $E$, Eq. (2.28) gives the required stationary connection between $k$ and $E$.

If desired, the coefficients $c_i$ can be determined from (2.27) after (2.28) has been solved.

3. SIMPLIFICATION FOR A CERTAIN CLASS OF POTENTIALS

While the method described in the preceding section does formally represent a solution of our problem its practicability depends on whether the $\Lambda_{ij}$ (2.24) can be evaluated with a reasonable effort. Unfortunately this is in general quite a formidable task, involving first of all the calculation of the Green's function for various $k$ and $E$ but then also the evaluation of the 6-dimensional integrals occurring in (2.24); the latter is made harder by the fact that the Green's function is singular for equal arguments, and that the region of integration is the rather complicated atomic polyhedron.

A great simplification can be achieved if one confines oneself to potentials $V(r)$ with the following properties:
\[ V(r) = \text{spherically symmetrical}, \quad r < r_i = \text{radius of inscribed sphere}; \quad (3.1) \]
\[ V(r) = V_0 = \text{constant}, \quad r \geq r_i. \quad (3.2) \]
In that case we can first of all shift our zero of energy to make
\[ V_0 = 0, \quad (3.3) \]
and can therefore restrict our discussion to potentials which vanish for $r \geq r_i$. We then notice from (2.16) that the contribution to $\Lambda$ come only from the spheres $r < r_i$, $r' < r_i$.

Now for $r < r_i$ the true solution of our problem, for energy $E$, can be expanded in spherical harmonics,
\[ \varphi_i(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_{lm} R_l(r) Y_{lm}(\theta, \phi), \quad (3.3) \]
where $R_l(r)$ is defined by
\[ \left[ \frac{1}{r^2} \frac{d}{dr} \frac{d}{dr} + \frac{l(l+1)}{r^2} + V(r) - E \right] R_l(r) = 0, \quad (3.4) \]
$R_l(0)$ is finite, $R_l(r_i) = 1$;
we find
\[ \Lambda_\varepsilon = \int_{r<r_1-\varepsilon} dr \int_{r'<r_1-\varepsilon} dr' \left[ \frac{\partial \psi^*(r)}{\partial r} \psi(r') - \psi^*(r) \frac{\partial \psi(r')}{\partial r} \right] \]
\[ \times \left[ \psi(r') \frac{\partial G(r,r')}{\partial r'} - G(r,r') \frac{\partial \psi(r')}{\partial r'} \right]. \] (3.12)

Now it is shown in Appendix 2 that, for \( r' < r, \)
\( G \) can be expanded in the form
\[ G(r,r') = \sum_{l,m} \sum_{l',m'} \left[ \lambda_{lm} j_{l'}(x) j_{l'}(y') + \kappa \delta_{l'} \delta_{m'} n_{l'}(x) n_{l'}(y') \right] \]
\[ \times Y_{lm}(\theta,\phi) Y_{lm'}^{*}(\theta',\phi'), \] (3.13)
where
\[ j_{l}(x) = (\pi/2x)^{1/2} J_{l}(x), \] (3.14)
\[ n_{l}(x) = (\pi/2x)^{1/2} J_{l}(x), \] (3.14)_{0}
\( \theta, \phi \) and \( \theta', \phi' \) are polar angles of \( r \) and \( r' \), relative to some fixed system of coordinates; and the “structure constants” \( A_{lm,m'} j_{l'}(x) j_{l'}(y') \) are functions of \( E \) and \( k \) characteristic for the lattice under consideration. They are explicitly given in the form of infinite sums (for details see Appendix 2).

When (3.13) and (3.7) are substituted into (3.12) and the limit \( \varepsilon \rightarrow 0 \) is taken, one obtains for the matrix elements of \( \Lambda \):
\[ \lambda_{lm,m'} = \left( L_{l} j_{l} - j'_{l} \right) \left[ (A_{lm,m'} j_{l'}(x) j_{l'}(y') + \kappa \delta_{l'} \delta_{m'} n_{l'}(x) n_{l'}(y')) \times Y_{lm}(\theta,\phi) Y_{lm'}^{*}(\theta',\phi') \right], \] (3.15)
where
\[ L_{l} \equiv \frac{dR_{l}(r)}{dr} \bigg|_{r=r_{l}}, \]
\[ j_{l} \equiv \frac{dJ_{l}(x)}{dx} \bigg|_{x=x_{l}}, \] etc.

In deriving (3.15) we have used the normalization \( R_{l}(r_{l}) = 1 \). Before equating the determinant of (3.15) to zero, we divide each row by \( (L_{l} j_{l} - j'_{l}) \), and each column by \( (L_{l'} j_{l'} - j'_{l'}) \) which gives the secular equation,
\[ \det A_{lm,m'} \delta_{m'm} n_{l'} - n_{l} L_{l} = 0. \] (3.17)

This equation contains the required connection between \( E \) and \( k \). It is shown to be equivalent to Köringsa’s Eq. (19) in Appendix 3.

In practice, (3.17) may be used as follows:

1) The structure constants \( A_{lm,m'} \) are tabulated once and for all, for each type of lattice, as functions of \( E \) and \( k \).

For explicit expressions in terms of \( \sin \theta \) and \( \cos \theta \) see, e.g., L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1949), first edition, 17.
(2) For the first few \( l \), the logarithmic derivatives \( L_l \)
are obtained as functions of the energy. [It is under-
stood here that the energy zero has already been
shifted to make \( V(r) = 0, \ r \geq r_c \). This may be done by
numerical integration of (3.4) or directly from the
observed term values of the atomic spectrum.]

(3a) If the energy is required for general \( k \)'s (i.e., \( k \) which
are not invariant under any of the symmetry
operations of the lattice), the most convenient way of
solving (3.17) is to fix \( E \) (and hence \( k \)) and to find
those \( k \)’s which make (3.17) vanish. Note that \( k \) enters
only through the \( A \)’s.

(3b) Certain points in \( k \) space are invariant under
some of the symmetry operations of the lattice. The
procedure (3a) does, of course, still apply to such
points, but in general (3.17) can now be factored and
it is advantageous to perform this factorization in
advance.

Suppose then we know from group-theoretical con-
siderations\(^{11} \) that the wave function must have the form,

\[
\psi = \sum_{l_1} C_l^{(0)} R_l(r) \sum_{m} a_{lm}^{(0)} Y_{lm}(\theta, \phi), \ l = l_1, l_2, \ldots , \quad (3.18)
\]

where the \( a_{lm}^{(0)} \) are given by group theory and may be
chosen so that

\[
\sum_{m} a_{lm}^{(0)} a_{lm}^{(0)\ast} = \delta_{ij}. \quad (3.19)
\]

Substituting (3.18) into (3.12) and demanding that
\( \delta A/\delta C_l^{(0)} = 0 \) gives, in the limit \( \epsilon \to 0 \),

\[
\text{Det} \left[ B_{ij}; v_{j} + \kappa \delta_{ij}\delta_{ij'} - \frac{n_i - n_i L_l}{j' - j L_l} \right] = 0 ,
\]

\[ l = l_1, l_2, \ldots , \quad (3.20) \]

\[ l' = l_1, l_2, \ldots \]

\[ B_{ij} = \sum_{m, m'} a_{lm}^{(0}\ast} A_{lm n_{m'} m'} a_{lm}^{(0)}. \]

The order of this secular equation equals the number of
independent functions (i.e., the number of \( C_l^{(0)} \) intro-
duced in (3.18).

If the energy is wanted at an isolated point of high
symmetry, e.g., \( k = 0 \), then (3.20) must be solved by
varying \( E \). However the energy is required on a
symmetry axis or plane, e.g., along the axis \( k_x = k_y = 0 \),
along which the \( a_{lm}^{(0)} \) remain constant, it is simpler to
fix \( E \) and solve (3.20) for \( k_x \).

For definitions of the \( A_{lm n_{m'} m'} \) see Appendix 2.

**Wave Functions**

For some purposes one requires, besides the energy
\( E(k) \), also the wave functions \( \psi \). As usual, these can be
obtained from the set of linear equations (2.26),

\[ \sum_{j'} \left( A_{lm n_{j} n_{j'}} + \kappa \delta_{ij}\delta_{ij'} - \frac{n_i - n_i L_l}{j' - j L_l} \right) \cdot \psi_{nm} = 0, \quad (3.21) \]

\[ C_{im} = \bar{C}_{im}/(j_i^2 - j L_l). \]

Similarly, for a symmetrically located \( \kappa \), the coefficients
\( C_l^{(0)} \) in (3.18) are given by

\[ \sum_{j'} \left( B_{ij} + \kappa \delta_{ij}\delta_{ij'} - \frac{n_i - n_i L_l}{j' - j L_l} \right) \cdot \psi_{nm} = 0, \quad (3.22) \]

\[ C_l^{(0)} = \bar{C}_{l}^{(0)}/(j_i^2 - j L_l). \]

One should remember, however, that in a variational
procedure such as the present one the accuracy of the
wave function is much poorer than that of the energy.

**4. USEFULNESS AND LIMITATIONS**

In this section we shall try to appraise the advantages
and limitations of the method just described.

In cases where an effective potential is given which
has the properties (3.1) to a sufficient degree of approxi-
mation we believe that the present method offers an
extremely convenient way of calculating the energy
bands. By far the greatest part of the work consists of
the calculation of the structure constants \( A_{lm n_{m'} m'} \)
which are characteristics of the geometry of the lattice
and whose computation is well suited for high-speed
calculating machines.

The only other ingredients necessary for obtaining
the band structure are the logarithmic derivatives of
the radial functions, which are easily obtained.

The convergence of the procedure is very good, as
illustrated in the application to metallic lithium which
is described in the following section. Very accurate
results for the energies are obtained there with as few
as 2 or 3 trial functions. There are three factors which
favor rapid convergence:

(1) The secular equation results from a variational
principle so that the error of \( E \) (or \( k \)) is of the second
order compared to the error of the trial function.

(2) As a rule, variational principles based on the
integral equation, as the present one is, give much more
accurate results than those based on the differential
equation.\(^{1} \)

(3) The trial function is required only inside the
inscribed sphere. In this limited region a smaller number
of partial waves will give a good approximation to
the correct function than is needed to describe the wave
function in the entire polyhedron.

The chief limitation of the method is, of course, its
restriction to potentials of the class (3.1). When the
actual potential violates these conditions radically the

\[^{11} \] F. C. Von der Lage and H. A. Bethe, Phys. Rev. 71, 612
(1947).
Table I. The lithium potential.

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<th>( r ) (atomic units)</th>
<th>( \frac{V}{r} ) (atomic units)</th>
<th>( \frac{V}{r} ) (atomic units)</th>
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5. APPLICATION TO METALLIC LITHIUM

As a first test of this method we have calculated the filled part of the 2s conduction band of metallic lithium. As potential we took that which was used by Seitz in his original calculation, but due to an error was not correctly printed in his published paper. It is correctly listed in Table I.

This potential, while spherically symmetrical, is not strictly constant outside the inscribed sphere. We have therefore replaced it by the potential:

\[
V'(r) = \begin{cases} 
V(r), & r \leq r_0, \\
V_0, & r > r_0,
\end{cases}
\]

where \( V_0 \) was chosen as the average value of \( V(r) \) in the space between the inscribed sphere and the boundary of the polyhedron:

\[
V_0 = -0.6629 \text{ ry.}
\]

This agrees to four figures with the energy calculated in the spherical approximation. Since it is known that for \( k = 0 \) the spherical approximation gives very accurate results for the alkalis, this agreement represents a good check on the validity of replacing \( V \) by \( V' \), Eq. (5.1). We may also note that \( E' \), the value of \( E \) relative to \( V_0 \), is very small (\( -0.0203 \text{ ry} \)) for the ground-state.

Next the energy was fixed at \( E = 2(a_0/a)^2 \text{ ry} \) and the corresponding \( k \) along the \((1,0,0)\) direction was determined. As trial functions we used

\[
\psi = \sum_{i=0}^{1} C_i R_i(r) Y_{l0}(\theta, \phi),
\]

with the \( Y_{l0} \) referred to the \((1,0,0)\) direction. To test the convergence, \( l \) was taken as 1 and 2 (2 and 3 trial functions). The results are listed in Table II.

Finally \( E' \) was taken as \( 10(a_0/a)^2 \text{ ry} \) (near the Fermi level) and the corresponding \( k \) was determined along the \((1,0,0)\) and \((1,1,1)\) directions. The trial functions were again of the form (5.8) with the \( Y_{l0} \) referred to the

![Fig. 2. The potentials V and V'.](image-url)
(1,0,0) and (1,1,1) directions, respectively. The results are listed in Table II.

It will be seen that the convergence is very rapid. With 2 trial functions the error is less than 2 percent, so that with 3 functions it is presumably quite negligible.

Adopting the three values of $|k|$ calculated with $l=2$ and the $E$ for $k = 0$ [Eq. (5.7)], we can fit an expression

$$E = E_0 + E_k \delta^2 + E_{4(k)} \delta^4$$

$$+ (5E_{4(k)}) (k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2 - \frac{1}{2} k^4)$$

(5.9)

to these points. (The smallness of $E_{4(k)}$ and $E_{4(k)}$ justifies the use of this form, which is strictly correct only for small $k$'s.) The result is listed in Table III, where it is also compared with the corresponding result obtained in the spherical approximation.

As was to be expected, the band is not strictly spherically symmetrical in $k$ space, i.e., $E_{4(k)} \neq 0$. (In the spherical approximation the band has, of course, spherical symmetry.) However, the smallness of both fourth order coefficients is quite remarkable. It means that the entire filled part of the band is very nearly parabolic, although the top of the filled region is quite close to the boundary of the Brillouin zone.

From a physical standpoint the $E_{4(k)}$ and $E_{4(k)}$ terms are too small to be taken very seriously. \footnote{A very rough estimate shows, for example, that the neighboring ions contribute a small term of the form $c(z^2r^2 + r^2z^2 + r^2z^2 + 1/\rho)$ to the potential which gives rise to an $E_{4(k)}$ whose order of magnitude (probably within a factor of 5) is $= - 0.006$. Furthermore, it is very doubtful if the band picture can be trusted for such fine effects.}

TABLE II. Three points of the energy band.

| $\delta$ (a/0.9 a) | (1,0,0) | $|k|$ (a) |
|-------------------|---------|----------|
| 0.9               | 2.0     | 2.03026  |
| 1.0               | 2.0     | 2.03087  |
| 1.1               | 2.0     | 2.05737  |
| 1.2               | 2.0     | 2.08444  |

Finally, it is observed that the $E_k$ is negligible.

<table>
<thead>
<tr>
<th>$E_k$</th>
<th>$E_k(1)$</th>
<th>$E_k(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>-0.029</td>
<td>0.039</td>
</tr>
</tbody>
</table>

TABLE III. Expansion coefficients of the energy, Eq. (5.9).

<table>
<thead>
<tr>
<th>$E_k$</th>
<th>Present method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>-0.033</td>
</tr>
</tbody>
</table>

(In the end $\epsilon \to 0$). Then (2.14) becomes

$$\psi(r) = \int _{r'=r-2\epsilon} ^{r} G(r,r') V(r') \psi(r') dr'$$

(A1.2)

Now consider an $r$ for which $r=r_1-2\epsilon$, and use (2.4) and (2.6). This gives

$$0 = \psi(r) - \int _{r'=r_1-\epsilon} ^{r} G(r,r') (V(r') + E) \psi(r') dr'$$

$$= \int _{r'=r_1-\epsilon} ^{r} \left[ G(r,r') \frac{\partial}{\partial r'} \psi(r') - \psi(r') \frac{\partial}{\partial r'} G(r,r') \right] ds'.$$

(A1.3)

In this equation, we substitute (3.13) for $G$ and (3.3) for $\psi$, multiply by $Y_{lm}(\theta,\phi)$ and integrate over the sphere $r=r_1-2\epsilon$. Finally, we let $\epsilon \to 0$ and obtain:

$$\sum _{l',m'} [A_{lm;lm'} (j_L^* L - j_{l'}) + \epsilon \delta_{l,l'} \delta_{m,m'} (n_L^* - n_{l'}) ] C_{lm'} = 0,$$

(A1.4)

where the symbols are explained in (3.13), (3.14), and (3.16). These linear equations lead at once to the compatibility condition (3.17).

APPENDIX 2. EXPANSION OF THE GREEN'S FUNCTION

We begin by setting down three standard results which will be used in what follows:

**Addition Theorem:**

$$P_t (\cos \theta) = \frac{4\pi}{2l+1} \sum _{m=-l} ^{l} Y_{lm}(\theta,\varphi) Y_{lm}^*(\theta',\varphi'),$$

(A2.a)

where $\Theta$ is the angle between the directions $(\theta,\varphi)$ and $(\theta',\varphi')$ and the $Y_{lm}$ are defined in (3.5).

**Expansion of Plane Wave:**

$$e^{i\mathbf{K} \cdot \mathbf{R}} = 4\pi \sum _{l,m} j_l (\mathbf{K} \mathbf{R}) Y_{lm}(\theta_R,\varphi_R) Y_{lm}^*(\theta_K,\varphi_K),$$

(A2.b)

where $j_l$ is defined in (3.14), and $\theta_R, \varphi_R$ and $\theta_K, \varphi_K$ are the polar angles of $\mathbf{K}$ and $\mathbf{R}$ relative to some fixed coordinate system.
Expansions of Free Space Green's Function:

\[ \frac{1}{4\pi} \frac{\exp[i(\mathbf{K}_n+k) \cdot (r-r')]}{|r-r'|} = \sum_{l,m} j_l(\alpha r') Y_l(\theta', \phi') \times Y_{l*}(\theta, \phi) \] (A2.1)

where \( \theta, \phi \) are the polar angles of \( \mathbf{K}_n+k \) relative to the fixed coordinate system. The right-hand side is of course independent of the particular choice of \( r \) and \( r' \). It should be noted that in view of the asymptotic behavior,

\[ x \to \infty : \quad j_l(x) \sim \frac{1}{x} \sin \left( x - \frac{x^2}{2} \right), \] (A2.6)

the sum in (A2.5) is absolutely convergent.

Apart from the Hermitian relationships (A2.4) the \( A \)'s are not all independent but are derivable from a smaller number of independent constants. It may be noted that \( G \) is a function only of the single vector,

\[ \mathbf{R} = r - r'. \] (A2.7)

We shall now show how the \( A \)'s can all be expressed in terms of the expansion coefficients of \( G \) relative to \( \mathbf{R} \).

Proceeding exactly as before, we find that \( G \) can be written in the form

\[ G(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \sum_{\tau \kappa} \frac{\exp[i(\mathbf{K}_n+k) \cdot \mathbf{R}]}{|\mathbf{K}_n+k|^2 - E} \] (A2.8)

where \( \Theta, \Phi \) are the polar angles of \( \mathbf{R} \). The \( D_{L,M} \) are given by

\[ D_{L,M} = -\frac{4\pi}{\tau} \frac{\exp[i(\mathbf{K}_n+k) \cdot \mathbf{R}]}{|\mathbf{K}_n+k|^2 - E} \] (A2.9)

\[ = \sum_{\tau \kappa} j_l(\mathbf{K}_n+k | \mathbf{R}) Y_{LM}(\Theta, \Phi) \] (A2.10)

where \( \Theta, \Phi \) are the polar angles of \( \mathbf{K}_n+k \).

The infinite sum in (A2.9) converges, but only slowly. A convenient practical scheme of evaluating this sum is based on Ewald's method.\(^{14}\) We consider

\[ S(\tau) = \sum_{\tau \kappa} j_l(\mathbf{K}_n+k | \mathbf{R}) Y_{LM}(\Theta, \Phi) \] (A2.11)

\[ \times \exp[iE - (\mathbf{K}_n+k)^2/\eta]. \] (A2.12)

We require \( S(\tau) \). Now Ewald has shown that \( S(\tau) \to S(\tau) = S(\infty) \) approaches zero exponentially as \( \eta \to \infty \). Hence, by choosing for \( \eta \) a sufficiently large value (which in practice turns out to be remarkably small), we can without appreciable error evaluate \( S(\eta) \) instead of

\[^{14}\text{P. Ewald, Ann. Physik 64, 253 (1921).}\]
SCHRODINGER EQUATION IN PERIODIC LATTICES

This is a great practical advantage since the sum for $S(r)$, because of its exponential factor, converges much more rapidly than for $S(\infty)$.

The $A_{lm;v';m'}$ are expressible in terms of the $D_{LM}$. Comparing (3.13) with (A2.8), we see that

$$
\sum_{LM} D_{LM} j_L(\kappa R) Y_{LM}(\Theta, \Phi)
= \sum_{LM} \sum_{l',m'} A_{lm;v';m'} j_l(\kappa R) j_{l'}(\kappa R') \times Y_{l,m}(\Theta, \Phi) Y_{l',m'}(\Theta', \Phi').
$$

(A2.11)

Now by a double application of (A2.12),

$$
j_L(\kappa R) Y_{LM}(\Theta, \Phi)
= \frac{1}{4\pi l!} \int \exp(i\kappa \cdot R) Y_{LM}(\Theta, \Phi) d\Omega,
$$

(A2.12)

where

$$
C_{LM; l, m; l', m'} = \int Y_{LM}(\Theta, \Phi) Y_{l,m}^*(\Theta, \Phi) Y_{l', m'}(\Theta, \Phi) d\Omega.
$$

(A2.13)

Substituting (A2.11) into (A2.10) and comparing coefficients of $Y_{lm}(\Theta, \Phi) Y_{l'm'}(\Theta', \Phi')$, gives

$$
A_{lm; v'; m'} = 4\pi \delta^{(l-l')} \sum_L \frac{1}{2^L} D_{LM} \sum_{m-m'} C_{LM; l, m; l', m'}.
$$

(A2.14)

Here we have used the fact that

$$
C_{LM; l, m; l', m'} = 0, \quad M \neq m - m'.
$$

(A2.15)

The sum over $L$ runs only over the values

$$
L = |l-l'|, |l-l'| + 2, \ldots |l+l'|,
$$

(A2.16)
as, by (A2.13), the C's vanish for other $L$'s.

In summary, the structure constants $A_{lm; v'; m'}$ in the secular equation (3.17) are given either directly by (A2.5) or in terms of the smaller number of constants $D_{LM}$ by (A2.14, 13 and 9). A practical method for evaluating the sum in (A2.9) is indicated in connection with (A2.10).

**Alternative Definitions of Structure Constants**

As already mentioned, the Green's function can also be expanded by starting from the expression (2.10).

We begin by deriving (2.10) from (2.9). For this purpose we use the standard results:

$$
\frac{1}{(2\pi)^3} \int \exp[i(\mathbf{K}_n + \mathbf{k} - \mathbf{K}) \cdot \mathbf{p}] d\mathbf{p} = \delta(\mathbf{K}_n + \mathbf{k} - \mathbf{K}),
$$

(A2.17)

$$
\frac{1}{(2\pi)^3} \int \exp[i\mathbf{K} \cdot (\mathbf{R} - \mathbf{r}_z)] d\mathbf{K} = \frac{1}{4\pi} \frac{\exp(i\kappa |\mathbf{R} - \mathbf{r}_z|)}{|\mathbf{R} - \mathbf{r}_z|},
$$

(A2.19)

Then,

$$
G(\mathbf{R}) = \lim_{\epsilon \to 0} \frac{1}{\tau} \sum_{\mathbf{K}_n + \mathbf{k} - \mathbf{K}} \exp[i\mathbf{K} \cdot (\mathbf{R} - \mathbf{r}_z)] d\mathbf{K} = \frac{1}{K^2 - (E + i\epsilon)} \exp[i\mathbf{K} \cdot \mathbf{R}]
$$

(A2.20)

$$
\times \sum_{\mathbf{K}_n + \mathbf{k} - \mathbf{K}} \exp[i\mathbf{K} \cdot (\mathbf{R} - \mathbf{r}_z)]
$$

(A2.20)

If $\epsilon$ had been chosen negative, then for $E > 0$, $\kappa$ in (A2.20) is replaced by $-\kappa$. Both of these expressions are correct since their difference is evidently a solution of the homogeneous problem and hence zero. Thus, instead of (2.10) we can also write

$$
G(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi} \sum_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}_z) \frac{\cos(\epsilon |\mathbf{r} - \mathbf{r}' - \mathbf{r}_z|)}{|\mathbf{r} - \mathbf{r}' - \mathbf{r}_z|},
$$

(A2.21)

which, in contrast to (2.10), is manifestly Hermitian.
is found for the coefficients $D_{L,M}$ of $(2.8)$:

$$D_{L,M}=\kappa \sum_{\nu=0}^{\infty} \exp(i\mathbf{k} \cdot \mathbf{r}) \left[ n_L(\kappa r) - i j_L(\kappa r) \right] Y_{LM}^* (\theta, \phi) \frac{\kappa}{(4\pi)^{1/2}} \delta_{L,M_0},$$

where $\theta$, $\phi$ are the polar angles of $\mathbf{r}$. It may be noted that this series converges exponentially for $E < 0$ since $n_L(ix) - i j_L(ix) \sim e^{-x^2}/x$ for large $x$. Hence it provides a good check on evaluations of $D_{L,M}$ by $(2.9)$.

**Convergence of the Green's Function Expansion**

It has already been remarked that $D(\mathbf{r}, \mathbf{r}')$, $(2.1)$ has an expansion of the form $(2.3)$ which converges, provided both $\mathbf{r}$ and $\mathbf{r}'$ are inside the inscribed sphere of the polyhedron. On the other hand, a consideration of $(2.10)$ shows that the expansion does not converge for all other $\mathbf{r}$ and $\mathbf{r}'$ inside the atomic polyhedron. This must be borne in mind when one considers applications of the integral equation method to potentials which are not constant outside the inscribed sphere.

**APPENDIX 3. CONNECTION WITH THE WORK OF KORRINGA**

Consider the scattering in free space by the potential

$$V = V(\mathbf{r}), \quad r \leq r_1,$$

$$= 0, \quad r > r_1,$$

(A3.1)

at an energy $E$. Let $R_l$ be the radial part of the solution corresponding to angular momentum $l$, which for $r \leq r_1$ satisfies $(3.4)$ and for $r > r_1$ has the form

$$R(\mathbf{r}) = A \left[ j_l(\kappa r) - \text{tan} \theta_0 \delta_l(\kappa r) \right],$$

(A3.2)

where $\eta_0$ is the phase shift. An elementary calculation shows that if $L_l$ is the logarithmic derivative of $R$ at $r_1$, then

$$\cot \eta_0 = \frac{n_l(\kappa r_1) - n_l(x) L_l}{j_l(\kappa r_1) - j_l(x) L_l}.$$

(A3.3)

When this is introduced into $(3.17)$, together with the constants,

$$G_{lm; am'} = \kappa^{-1} A_{lm; am'} - i \delta_{ll'} \delta_{mm'},$$

(A3.4)

(3.17) becomes

$$\text{Det} \left\{ G_{lm; am'} + \delta_{ll'} \delta_{mm'} \frac{e^{\kappa r_1}}{\sin \eta_0} \right\} = 0,$$

(A3.5)

which corresponds to Korringa's Eq. (19). Equation (3.17) appears to be slightly more convenient than (A3.5), as its elements are Hermitian for positive and negative $E$, and as it involves the logarithmic derivatives which are the quantities directly obtained from numerical integration or extrapolation of atomic data.

**Note added in proof.**—Recently a calculation of the lithium conduction band was published by B. Schiff,\textsuperscript{18} This author used a potential which differs from that constructed by Seitz, on which previous calculations by Seitz,\textsuperscript{15} Bardeen,\textsuperscript{16} Silverman and Kohn,\textsuperscript{9} as well as the present work were based.

The results of Schiff for the position of the lowest level in the conduction band, relative to the ionization energy of the atom, and for the width of the filled part of the band, differ from the results of the other authors by 13 and 23 percent, respectively. However, the cohesive energies are in good agreement.

This discrepancy is presumably due to the difference between the potentials used. According to the theory of Wigner and Seitz the potential should be the best effective potential for the valence electron in the free atom. The potential of Seitz does indeed reproduce all atomic energy levels with great accuracy. Schiff's potential is substantially weaker than that of Seitz in the vicinity of the nucleus, in places by as much as 15 percent. As a result his calculated ionization energy for the atomic $2s$ electron is 8 percent smaller than the observed value, while the Seitz potential gives agreement with experiment within a fraction of a percent.

\textsuperscript{19} Bardeen, J. Chem. Phys. 6, 367 (1938).