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,

$$[-\nabla^2 + V(\mathbf{r}) - E]\psi(\mathbf{r}) = 0, \qquad (1.1)$$

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.[1] 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.[2-5]

A straightforward application of this method was used by one of us [W. Kohn (unpublished); see reference 3] to find the ground-state energy $(k=0)$ of metallic Na.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[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_l, 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[6] 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

[1] See, e.g., W. Kohn, Phys. Rev. **87**, 472 (1952) where many references are given; also C. Herring, Phys. Rev. **57**, 1169 (1940).
[2] D. S. Saxon and R. A. Hutner, Philips Research Repts. 4, 81 (1949).
[3] R. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950).
[4] M. Dank and H. B. Callen, Phys. Rev. **86**, 622 (1952).
[5] M. Dank, Office of Naval Research Report, University of Pennsylvania, December, 1952 (unpublished).
[6] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. **79**, 382 (1950).

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. RÉSUMÉ OF GENERAL THEORY

Consider a monatomic lattice of nuclei at the equivalent positions,

$$\mathbf{r}_s = s_1\boldsymbol{\tau}_1 + s_2\boldsymbol{\tau}_2 + s_3\boldsymbol{\tau}_3, \quad s_i = 0, \pm 1, \pm 2, \cdots, \quad (2.1)$$

where the $\boldsymbol{\tau}_i$ are three fundamental translation vectors of the lattice. Let $V(\mathbf{r})$ be an effective potential with the periodicity property:

$$V(\mathbf{r}+\mathbf{r}_s) = V(\mathbf{r}). \quad (2.2)$$

We shall look for the "propagating" solutions,

$$\psi(\mathbf{r}+\mathbf{r}_s) = e^{i\mathbf{k}\cdot\mathbf{r}_s}\psi(\mathbf{r}), \quad (2.3)$$

of the Schrödinger equation,

$$[-\nabla^2 + V(\mathbf{r}) - E]\psi(\mathbf{r}) = 0. \quad (2.4)$$

These solutions satisfy the following boundary conditions in the central polyhedron, which surrounds the origin:

$$\psi(\mathbf{r}^c) = \exp(i\mathbf{k}\cdot\boldsymbol{\tau}_r)\psi(\mathbf{r}),$$
$$\partial\psi(\mathbf{r}^c)/\partial n^c = -\exp(i\mathbf{k}\cdot\boldsymbol{\tau}_r)\partial\psi(\mathbf{r})/\partial n, \quad (2.5)$$

where $\mathbf{k}$ is the wave vector of the solution, $\mathbf{r}^c$ and $\mathbf{r}$ are conjugate points on the surface of the polyhedron, and $\boldsymbol{\tau}_r$ is the fundamental translation vector joining them. (See Fig. 1.) From here on, it will be sufficient to
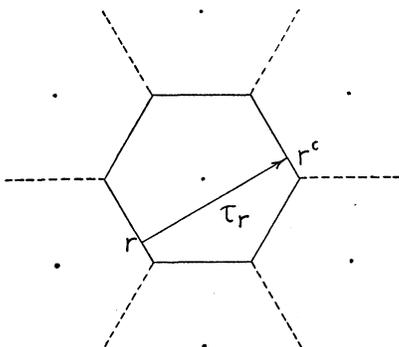

FIG. 1. Conjugate boundary points.

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

[8] We are greatly indebted in this connection to Drs. E. M. Baroady and R. J. Harrison of the Batelle Memorial Institute. We understand that Drs. Harrison and Trefftz are engaged in applications of Korringa's method which are similar to the work reported here.

consider the solution of (2.4) and (2.5) in the central polyhedron only.

We now introduce the Green's function $G(\mathbf{r},\mathbf{r}')$ defined by

$$(-\nabla^2 - E)G(\mathbf{r},\mathbf{r}') = -\delta(\mathbf{r}-\mathbf{r}'), \quad (2.6)$$

and, for conjugate boundary points $\mathbf{r}$ and $\mathbf{r}^c$

$$G(\mathbf{r}^c,\mathbf{r}') = \exp(i\mathbf{k}\cdot\boldsymbol{\tau}_r)G(\mathbf{r},\mathbf{r}'),$$
$$\partial G(\mathbf{r}^c,\mathbf{r}')/\partial n^c = -\exp(i\mathbf{k}\cdot\boldsymbol{\tau}_r)\partial G(\mathbf{r},\mathbf{r}')/\partial n. \quad (2.7)$$

Let $\mathbf{K}_n$ be the vectors of the reciprocal lattice defined by

$$\mathbf{K}_n\cdot\boldsymbol{\tau}_i = 2\pi\times(\text{integer}), \quad i=1, 2, 3. \quad (2.8)$$

Then G can be written as

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{\tau}\sum_n \frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{r}-\mathbf{r}')]}{(\mathbf{K}_n+\mathbf{k})^2 - E}, \quad (2.9)$$

where τ is the volume of the atomic polyhedron. Alternatively, G can be expressed in the form,

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{4\pi}\sum_s \frac{\exp[i\kappa|\mathbf{r}-\mathbf{r}'-\mathbf{r}_s|]}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_s|}\exp(i\mathbf{k}\cdot\mathbf{r}_s), \quad (2.10)$$

where

$$\kappa = +\sqrt{E}, \quad E>0,$$
$$= +i\sqrt{(-E)}, \quad E<0. \quad (2.11)$$

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,

$$G(\mathbf{r}',\mathbf{r}) = G^*(\mathbf{r},\mathbf{r}'), \quad (2.12)$$

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 $G^*(\mathbf{r},\mathbf{r}')$, and the complex conjugate of (2.6) by $\psi(\mathbf{r})$, subtract and integrate over $\mathbf{r}$ in the interior of the polyhedron. This leads to

$$\psi(\mathbf{r}') = \int_\tau G^*(\mathbf{r},\mathbf{r}')V(\mathbf{r})\psi(\mathbf{r})d\tau, \quad (2.13)$$

which, by (2.12) is equivalent to

$$\psi(\mathbf{r}) = \int_\tau G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')d\tau. \quad (2.14)$$

Our further considerations are based on this equation.[9]

[9] The final secular equation (3.17) is derived in the following from a variational formulation, which shows that the energy calculated from it will have an error of the second order compared to that of the trial function. A briefer, nonvariational derivation is given in Appendix 1. The reader who wishes to omit the variational discussion should proceed from here to the beginning of Sec. 3 up to (3.7) and then to Appendix 1.

The integral Eq. (2.14) is equivalent to the variational principle:

$$\delta\Lambda = 0, \qquad (2.15)$$

where

$$\Lambda \equiv \int_\tau \psi^*(\mathbf{r}) V(\mathbf{r}) \psi(\mathbf{r}) d\tau$$

$$- \int_\tau \int_{\tau'} \psi^*(\mathbf{r}) V(\mathbf{r}) G(\mathbf{r},\mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') d\tau d\tau', \quad (2.16)$$

as may be directly verified. It should be noted that $\delta\Lambda$ vanishes for arbitrary variations of ψ, 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 ψ be a solution of (2.14) corresponding to $\mathbf{k}$ and E (the latter enter through G); then, clearly,

$$\Lambda(\psi,\mathbf{k},E) = 0. \qquad (2.17)$$

If now ψ_t is a trial function,

$$\psi_t = \psi + \epsilon \chi,$$

where ϵ is a parameter of smallness, then by (2.15),

$$\Lambda(\psi_t,\mathbf{k},E) = O(\epsilon^2). \qquad (2.18)$$

Hence if for given $\mathbf{k}$ we calculate E_t from the equation,

$$\Lambda(\psi_t,\mathbf{k},E_t) = 0, \qquad (2.19)$$

then clearly,

$$E_t - E = O(\epsilon^2), \qquad (2.20)$$

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 $\mathbf{k}_t$ from

$$\Lambda(\psi_t,\mathbf{k}_t,E) = 0, \qquad (2.21)$$

we would have

$$\mathbf{k}_t - \mathbf{k} = O(\epsilon^2). \qquad (2.22)$$

The variational principle (2.15) lends itself to an application of the Rayleigh-Ritz technique. We use a trial function of the form:

$$\psi = \sum_0^n c_i \varphi_i, \quad c_i = a_i + ib_i, \qquad (2.23)$$

and substitute into (2.16). Calling

$$\Lambda_{i;j} \equiv \int_\tau \varphi_i^*(\mathbf{r}) V(\mathbf{r}) \varphi_j(\mathbf{r}) d\tau$$

$$- \int_\tau \int_{\tau'} \varphi_i^*(\mathbf{r}) V(\mathbf{r}) G(\mathbf{r},\mathbf{r}') V(\mathbf{r}') \varphi_j(\mathbf{r}') d\tau d\tau', \quad (2.24)$$

where $\Lambda_{i;j}$ is Hermitian, we have

$$\Lambda = \sum_{i,j=0}^n c_i^* \Lambda_{i;j} c_j. \qquad (2.25)$$

The conditions,

$$\partial\Lambda/\partial a_i = \partial\Lambda/\partial b_i = 0, \quad i = 0, 1, \cdots n, \qquad (2.26)$$

which follow from (2.15), give the linear equations

$$\sum_{j=0}^n \Lambda_{i;j} c_j = 0, \quad i = 0, 1, \cdots n, \qquad (2.27)$$

which are compatible only if

$$\text{Det}\Lambda_{i;j} = 0. \qquad (2.28)$$

Since, for given functions φ_i, the $\Lambda_{i;j}$ are functions only of $\mathbf{k}$ and E, Eq. (2.28) gives the required stationary connection between $\mathbf{k}$ 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 $\Lambda_{i;j}$ (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 $\mathbf{k}$ 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 $V(\mathbf{r})$ with the following properties:

$V(\mathbf{r}) = $ spherically symmetrical,

$$r < r_i = \text{radius of inscribed sphere}; \quad (3.1)$$

$$V(\mathbf{r}) = V_0 = \text{constant}, \quad r \geq r_i.$$

In that case we can first of all shift our zero of energy to make

$$V_0 = 0, \qquad (3.2)$$

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 Λ 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,

$$\sum_{l=0}^\infty \sum_{m=-l}^l C_{lm} R_l(r) Y_{lm}(\theta,\varphi), \qquad (3.3)$$

where $R_l(r)$ is defined by

$$\left[-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{l(l+1)}{r^2} + V(r) - E \right] R_l(r) = 0, \qquad (3.4)$$

$$R_l(0) = \text{finite}, \quad R_l(r_i) = 1;$$

and

$$Y_{lm}(\theta,\varphi) = \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}P_l^{|m|}(\cos\theta)e^{im\varphi}, \quad (3.5)$$

which is normalized to unity:

$$\int_0^\pi d\theta \int_0^{2\pi} d\varphi \, |Y_{lm}(\theta,\varphi)|^2 \sin\theta = 1. \quad (3.6)$$

It is therefore natural to use as trial function a finite series of the form (3.3),

$$\psi = \sum_{l=0}^{\bar{l}} \sum_{m=-l}^{l} C_{lm} R_l(r) Y_{lm}(\theta,\varphi), \quad (3.7)$$

which satisfies the wave equation exactly.

To deal properly with the singularities of G we must use a limiting procedure in evaluating Λ. We set

$$\Lambda = \lim_{\epsilon\to 0}\Lambda_\epsilon, \quad (3.8)$$

where

$$\Lambda_\epsilon = \int_{r<r_i-2\epsilon} d\tau \psi^*(\mathbf{r}) V(\mathbf{r})$$

$$\times\left[\psi(\mathbf{r}) - \int_{r'<r_i-\epsilon} d\tau' G(\mathbf{r},\mathbf{r}') V(\mathbf{r}')\psi(\mathbf{r}')\right]. \quad (3.9)$$

With the trial function (3.7), the volume integrals in (3.9) can be transformed into surface integrals by using the wave equation (2.4) satisfied by the trial $-\psi$ and (2.6) satisfied by G. Thus,

$$\psi(\mathbf{r}) - \int_{r'<r_i-\epsilon} d\tau' G(\mathbf{r},\mathbf{r}') V(\mathbf{r}')\psi(\mathbf{r}')$$

$$= \psi(\mathbf{r}) - \int_{r'<r_i-\epsilon} d\tau' G(\mathbf{r},\mathbf{r}')(\nabla'^2+E)\psi(\mathbf{r}')$$

$$= -\int_{r'=r_i-\epsilon} ds' \left[G(\mathbf{r},\mathbf{r}')\frac{\partial}{\partial r'}\psi(\mathbf{r}')\right.$$

$$\left. -\psi(\mathbf{r}')\frac{\partial}{\partial r'}G(\mathbf{r},\mathbf{r}')\right]. \quad (3.10)$$

Substituting into (3.9) and noting that, for $r>r'$,

$$\int_{r<r_i-2\epsilon} d\tau \psi^*(\mathbf{r}) V(\mathbf{r}) G(\mathbf{r},\mathbf{r}')$$

$$= \int_{r<r_i-2\epsilon} d\tau (\nabla^2+E)\psi^*(\mathbf{r})\cdot G(\mathbf{r},\mathbf{r}')$$

$$= \int_{r=r_i-2\epsilon} ds\left(\frac{\partial\psi^*(\mathbf{r})}{\partial r}G(\mathbf{r},\mathbf{r}')-\psi^*(\mathbf{r})\frac{\partial G(\mathbf{r},\mathbf{r}')}{\partial r}\right), \quad (3.11)$$

we find

$$\Lambda_\epsilon = \int_{r<r_i-2\epsilon} ds \int_{r'<r_i-\epsilon} ds'\left[\frac{\partial\psi^*(\mathbf{r})}{\partial r}-\psi^*(\mathbf{r})\frac{\partial}{\partial r}\right]$$

$$\times\left[\psi(\mathbf{r}')\frac{\partial}{\partial r'}G(\mathbf{r},\mathbf{r}')-G(\mathbf{r},\mathbf{r}')\frac{\partial}{\partial r'}\psi(\mathbf{r}')\right]. \quad (3.12)$$

Now it is shown in Appendix 2 that, for $r<r'<r_i$, G can be expanded in the form

$$G(\mathbf{r},\mathbf{r}') = \sum_{l,m}\sum_{l',m'}[A_{lm;l'm'}j_l(\kappa r)j_{l'}(\kappa r')$$

$$+\kappa\delta_{ll'}\delta_{mm'}j_l(\kappa r)n_l(\kappa r')]$$

$$\times Y_{lm}(\theta,\varphi)Y^*_{l'm'}(\theta',\varphi'), \quad (3.13)$$

where

$$j_l(x) = (\pi/2x)^{\frac{1}{2}}J_{l+\frac{1}{2}}(x),$$
$$n_l(x) = (\pi/2x)^{\frac{1}{2}}J_{-l-\frac{1}{2}}(x);^{10} \quad (3.14)$$

θ, φ and θ', φ' are polar angles of $\mathbf{r}$ and $\mathbf{r}'$, relative to some fixed system of coordinates; and the "structure constants" $A_{l,m;l',m'}$ which are functions of E and $\mathbf{k}$ are 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 $\epsilon\to 0$ is taken, one obtains for the matrix elements of Λ:

$$\Lambda_{lm;l'm'} = (L_l j_l - j_l')[(A_{lm;l'm'}j_{l'}'+\kappa\delta_{ll'}\delta_{mm'}n_{l'}')$$

$$-(A_{lm;l'm'}j_{l'}+\kappa\delta_{ll'}\delta_{mm'}n_{l'})L_{l'}], \quad (3.15)$$

where

$$L_l \equiv \frac{dR_l(r)}{dr}\Big/ R_l(r)\Big|_{r=r_i},$$

$$j_l' \equiv \frac{dj_l(\kappa r)}{dr}\Big|_{r=r_i}, \quad \text{etc.} \quad (3.16)$$

In deriving (3.15) we have used the normalization $R_l(r_i)=1$. 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,

$$\text{Det}\left|A_{lm;l'm'}+\kappa\delta_{ll'}\delta_{mm'}\frac{n_l'-n_l L_l}{j_l'-j_l L_l}\right| = 0. \quad (3.17)$$

This equation contains the required connection between E and $\mathbf{k}$. It is shown to be equivalent to Korringa's Eq. (19)[7] in Appendix 3.

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

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

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[10] For explicit expressions in terms of $\sin x$ and $\cos x$ see, e.g., L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1949), first edition, 77.

(2) For the first few l, the logarithmic derivatives L_l are obtained as functions of the energy. [It is understood here that the energy zero has already been shifted to make $V(r)=0$, $r \geq r_i$.] This may be done by numerical integration of (3.4) or directly from the observed term values of the atomic spectrum.[6]

(3a) If the energy is required for general $\mathbf{k}$'s (i.e., $\mathbf{k}$'s 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 κ) and to find those $\mathbf{k}$'s which make (3.17) vanish. Note that $\mathbf{k}$ enters only through the A's.

(3b) Certain points in $\mathbf{k}$ 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 considerations[11] that the wave function must have the form,

$$\psi = \sum_{l,i} C_l^{(i)} R_l(r) \sum_m \alpha_{lm}^{(i)} Y_{lm}(\theta,\varphi), \quad l=l_1, l_2, \cdots, \quad (3.18)$$

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

$$\sum_m \alpha_{lm}^{*(i)} \alpha_{lm}^{(j)} = \delta_{ij}. \quad (3.19)$$

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

$$\mathrm{Det} \left| B_{li;l'j} + \kappa \delta_{ll'} \delta_{ij} \frac{n_l' - n_l L_l}{j_l' - j_l L_l} \right| = 0,$$

$$l=l_1, l_2, \cdots, \quad (3.20)$$

$$l'=l_1, l_2, \cdots,$$

$$B_{li;l'j} = \sum_{m,m'} \alpha_{lm}^{*(i)} A_{lm;l'm'} \alpha_{l'm'}^{(j)}.$$

The order of this secular equation equals the number of independent functions (i.e., the number of $C_l^{(i)}$) introduced in (3.18).

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

For definitions of the $A_{lm;l'm'}$ see Appendix 2.

Wave Functions

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

[11] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

after the secular equation (3.17) or (3.20) has been solved.

For a "general" $\mathbf{k}$, the coefficients C_{lm} in (3.7) are given by

$$\sum_{l',m'} \left(A_{lm;l'm'} + \kappa \delta_{ll'} \delta_{mm'} \frac{n_l' - n_l L_l}{j_l' - j_l L_l} \right) \bar{C}_{l'm'} = 0, \quad (3.21)$$

$$C_{lm} = \bar{C}_{lm}/(j_l' - j_l L_l).$$

Similarly, for a symmetrically located $\mathbf{k}$, the coefficients $C_l^{(i)}$ in (3.18) are given by

$$\sum_{l',j} \left(B_{li;l'j} + \kappa \delta_{ll'} \delta_{ij'} \frac{n_l' - n_l L_l}{j_l' - j_l L_l} \right) \bar{C}_{l'}^{(i)} = 0, \quad (3.22)$$

$$C_l^{(i)} = \bar{C}_l^{(i)}/(j_l' - j_l L_l).$$

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 approximation 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 $A_{lm;l',m'}$ 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 $\mathbf{k}$) 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

TABLE I. The lithium potential.

r (atomic units)	$-rV$ (atomic units)	r (atomic units)	$-rV$ (atomic units)
0.02	5.727	0.92	2.4242
0.04	5.544	1.00	2.3766
0.06	5.450	1.08	2.3058
0.08	5.351	1.16	2.2458
0.10	5.253	1.24	2.2035
0.12	5.157	1.32	2.1661
0.14	5.058	1.40	2.1350
0.16	4.960	1.48	2.1090
0.18	4.862	1.64	2.0697
0.20	4.762	1.80	2.0466
0.24	4.563	1.96	2.0325
0.28	4.360	2.12	2.0288
0.32	4.1584	2.28	2.0292
0.36	3.9463	2.44	2.0228
0.40	3.7360	2.60	2.0124
0.44	3.5429	2.76	2.0065
0.48	3.3797	2.92	2.0031
0.52	3.2417	3.08	2.0015
0.56	3.1209	3.24	2.0008
0.60	3.0138	3.40	2.0004
0.68	2.8342	3.56	2.0002
0.76	2.6881	3.72	2.0001
0.84	2.5662		

procedure is not suitable. In many cases, however, the deviations from these conditions are small. One can then write

$$V(\mathbf{r}) = V^{(0)}(r) + V^{(1)}(\mathbf{r}), \qquad (4.1)$$

where $V^{(0)}$ satisfies (3.1), and $V^{(1)}$ is small. Thus for $r < r_i$ one might take for $V^{(0)}(r)$ the angular average of $V(\mathbf{r})$, and for $r > r_i$ the average value of $V(\mathbf{r})$ in the space between the inscribed sphere and the polyhedron. One then solves the problem with $V^{(0)}$, and adds to this a first-order perturbation correction using the wave functions determined by (3.21), (3.22).

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[12] 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:

$$V'(r) = V(r), \qquad r \leq r_i,$$
$$= V_0, \qquad r > r_i, \qquad (5.1)$$

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:

$$V_0 = -0.6629 \text{ ry.} \qquad (5.2)$$

[12] F. Seitz, Phys. Rev. 47, 400 (1953). In Table II of the paper by Seitz, the quantity rV_{II} was obtained from rV_I incorrectly by adding a small corrective potential with the wrong sign. Thus the correct rV_{II} can be obtained from the rV_I given by adding the difference $(rV_I - rV_{II})$ derived from Table II to the value of rV_I given in the table.

Figure 2 shows that this replacement is not likely to introduce an appreciable error, an expectation borne out by the calculation.

In the subsequent work the energy zero was shifted to V_0, so that the effective potential in our calculation was

$$\bar{V}(r) = V(r) - V_0, \qquad r \leq r_i,$$
$$= 0, \qquad r > r_i, \qquad (5.3)$$

and the effective energy was

$$\bar{E} = E - V_0. \qquad (5.4)$$

The lattice parameter (cube edge) was taken as

$$a = 6.5183 a_0, \qquad (5.5)$$

where a_0 is the Bohr radius.

At $\mathbf{k} = 0$, we used the trial function,

$$\psi = C_{00}(4\pi)^{-\frac{1}{2}} R_0(r), \qquad (5.6)$$

which, when substituted into (3.17), gave

$$E = -0.6832 \text{ ry.} \qquad (5.7)$$

This agrees to four figures with the energy calculated in the spherical approximation.[3] Since it is known that for $\mathbf{k} = 0$ 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 $\bar{E}$, the value of E relative to V_0, is very small (-0.0203 ry) for the ground-state.

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

$$\psi = \sum_{l=0}^{l} C_l R_l(r) Y_{l0}(\theta, \varphi), \qquad (5.8)$$

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 $\bar{E}$ was taken as $10(a_0/a)^2$ ry (near the Fermi level) and the corresponding $\mathbf{k}$'s were found 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

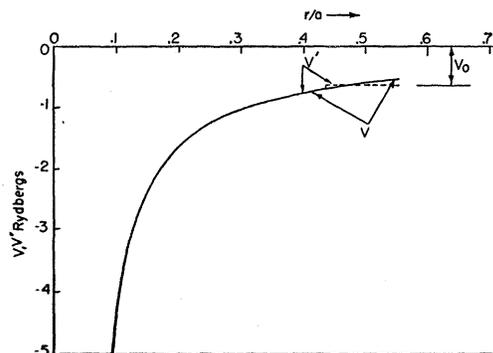
FIG. 2. The potentials V and V'.

(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 $\bar{E}$ for $k=0$ [Eq. (5.7)], we can fit an expression

$$E=E_0+E_2k^2+E_4^{(1)}k^4$$
$$+(5E_4^{(2)})(k_x^2k_y^2+k_y^2k_z^2+k_z^2k_x^2-\tfrac{1}{5}k^4) \quad (5.9)$$

to these points. (The smallness of $E_4^{(1)}$ and $E_4^{(2)}$ 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.[3]

As was to be expected, the band is not strictly spherically symmetrical in k space, i.e., $E_4^{(2)}\neq0$. (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 $E_4^{(1)}$ and $E_4^{(2)}$ terms are too small to be taken very seriously.[13] We believe, however, that the present method is useful when the band shape differs considerably from spherical symmetry as a result of the nonsphericity of the polyhedron. Such deviations from spherical symmetry, when substantial, play an important role in the theories of the Hall coefficient and of magnetoresistance.

We should like to express our thanks to Miss Alice Carroll for her expert assistance with the numerical calculations.

APPENDIX 1. NONVARIATIONAL DERIVATION OF THE SECULAR EQUATION 3.17

Let us consider a potential $V(r)$ with the properties:

$$V(r)=\text{spherically symmetrical,} \quad \text{for} \quad r\leq r_i-\epsilon$$
$$=0, \qquad\qquad\qquad \text{for} \quad r>r_i-\epsilon \quad (A1.1)$$

TABLE II. Three points of the energy band.

$\bar{E}(a/a_0)^2$ (ry)	(1,0,0)	$\lvert k\rvert a_0$	(1,1,1)
+ 2.0	$l=1:0.3026$ $l=2:0.3037$		
+10.0	$l=1:0.5757$ $l=2:0.5844$		$l=1:0.5845$ $l=2:0.5920$

<hr>

[13] A very rough estimate shows, for example, that the neighboring ions contribute a small term of the form $c(x^2y^2+y^2z^2+z^2x^2-\tfrac{1}{5}r^4)$ to the potential which gives rise to an $E_4^{(2)}$ 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 III. Expansion coefficients of the energy, Eq. (5.9).

	Spherical approximation	Present method
E_0	-0.6832	-0.6832
E_2	0.7270	0.723
$E_4^{(1)}$	-0.029	0.039
$E_4^{(2)}$	0.000	-0.033

(in the end $\epsilon\to0$). Then (2.14) becomes

$$\psi(\mathbf{r})=\int_{r'<r_i-\epsilon} G(\mathbf{r},\mathbf{r}')V(r')\psi(\mathbf{r}')d\tau'. \quad (A1.2)$$

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

$$0=\psi(\mathbf{r})-\int_{r'<r_i-\epsilon} G(\mathbf{r},\mathbf{r}')(\nabla'^2+E)\psi(\mathbf{r}')d\tau'$$

$$=\int_{r'=r_i-\epsilon}\left\{G(\mathbf{r},\mathbf{r}')\frac{\partial}{\partial r'}\psi(r')-\psi(r')\frac{\partial}{\partial r'}G(\mathbf{r},\mathbf{r}')\right\}ds'. \quad (A1.3)$$

In this equation, we substitute (3.13) for G and (3.3) for ψ, multiply by $Y_{lm}^*(\theta,\varphi)$ and integrate over the sphere $r=r_i-2\epsilon$. Finally, we let $\epsilon\to0$ and obtain:

$$\sum_{l',m'} j_l[A_{lm;l'm'}(j_{l'}L_{l'}-j_{l'}')$$

$$+\kappa\delta_{ll'}\delta_{mm'}(n_{l'}L_{l'}-n_{l'}')]C_{l'm'}=0, \quad (A1.4)$$

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:

$$P_l(\cos\Theta)=\frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{lm}(\theta,\varphi)Y_{lm}^*(\theta',\varphi'), \quad (A2.a)$$

where Θ is the angle between the directions (θ,φ) and (θ',φ') and the Y_{lm} are defined in (3.5).

Expansion of Plane Wave:

$$e^{i\mathbf{K}\cdot\mathbf{R}}=4\pi\sum_{l,m} i^l j_l(KR)Y_{lm}(\theta_R,\varphi_R)Y_{lm}^*(\theta_K,\varphi_K), \quad (A2.b)$$

where j_l is defined in (3.14), and θ_R, φ_R and θ_K, φ_K are the polar angles of $\mathbf{K}$ and $\mathbf{R}$ relative to some fixed coordinate system.

Expansion of Free Space Green's Function:

$$-\frac{1}{4\pi}\frac{e^{i\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}=\kappa\sum_{l,m}j_l(\kappa r)[n_l(\kappa r')-ij_l(\kappa r')]$$
$$\times Y_{lm}(\theta,\varphi)Y_{lm}^*(\theta',\varphi'),\quad\text{(A2.c)}$$

for $r<r'$, and a symmetrical expression when $r'<r$.

We now turn to the expansion of the Green's function in spherical harmonics. For this, either (2.9) or (2.10) can be used as a starting point, leading to alternative expressions for the expansion coefficients. ·

We begin with (2.9),

$$G(\mathbf{r},\mathbf{r}')=-\frac{1}{\tau}\sum_n\frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{r}-\mathbf{r}')]}{(\mathbf{K}_n+\mathbf{k})^2-E},\quad(2.9)$$

and introduce

$$D(\mathbf{r},\mathbf{r}')=G(\mathbf{r},\mathbf{r}')-G_0(\mathbf{r},\mathbf{r}'),\quad\text{(A2.1)}$$

where

$$G_0(\mathbf{r},\mathbf{r}')=-\frac{1}{4\pi}\frac{\cos(\kappa|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$
$$=\begin{cases}\kappa\sum_{l,m}j_l(\kappa r)n_l(\kappa r')Y_{lm}(\theta,\varphi)Y_{lm}^*(\theta',\varphi');\\ \qquad\qquad\qquad\qquad\qquad r<r',\\ \kappa\sum_{l,m}n_l(\kappa r)j_l(\kappa r')Y_{lm}^*(\theta,\varphi)Y_{lm}(\theta',\varphi');\\ \qquad\qquad\qquad\qquad\qquad r'<r,\end{cases}\quad\text{(A2.2)}$$

[see (A2.c)] and satisfies the same inhomogeneous wave equation as $G(\mathbf{r},\mathbf{r}')$ for $\mathbf{r}$, $\mathbf{r}'$ inside the atomic polyhedron. Consequently D satisfies the homogeneous wave equation in $\mathbf{r}$ and $\mathbf{r}'$, and hence for r, $r'<r_i$ must have an expansion of the form

$$D(\mathbf{r},\mathbf{r}')=\sum_{l,m}\sum_{l',m'}A_{lm;l'm'}j_l(\kappa r)j_{l'}(\kappa r')$$
$$\times Y_{lm}(\theta,\varphi)Y_{l'm'}^*(\theta',\varphi').\quad\text{(A2.3)}$$

Together with (A2.1) and (A2.2), this gives the form (3.13) for G. The Hermitian property of G, (2.12), implies the relationship

$$A_{l'm';lm}=A_{lm;l'm'}^*.\quad\text{(A2.4)}$$

Explicit expressions for the A's can be obtained by expanding each of the factors $\exp[i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{r}]$ and $\exp[-i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{r}']$ occurring in (2.9) in spherical harmonics and comparing the result with the expansion (3.13). Thus one finds

$$A_{lm;l'm'}=-\frac{(4\pi)^2}{\tau}i^{(l-l')}[j_l(\kappa r)j_{l'}(\kappa r')]^{-1}$$
$$\times\sum_n\frac{j_l(|\mathbf{K}_n+\mathbf{k}|r)j_{l'}(|\mathbf{K}_n+\mathbf{k}|r')Y_{lm}(\theta_n,\varphi_n)Y_{l'm'}(\theta_n,\varphi_n)}{(\mathbf{K}_n+\mathbf{k})^2-E}$$
$$-\kappa\delta_{ll'}\delta_{mm'}\frac{n_l(\kappa r')}{j_l(\kappa r)},\quad r<r'<r_i,\quad\text{(A2.5)}$$

where θ_n, φ_n are the polar angles of $\mathbf{K}_n+\mathbf{k}$ 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,

$$x\rightarrow\infty:\quad j_l(x)\rightarrow\frac{1}{x}\sin\left(x-l\frac{\pi}{2}\right),\quad\text{(A2.6)}$$

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,

$$\mathbf{R}=\mathbf{r}-\mathbf{r}'.\quad\text{(A2.7)}$$

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

$$G(\mathbf{R})\equiv-\frac{1}{\tau}\sum_n\frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{R}]}{(\mathbf{K}_n+\mathbf{k})^2-E}$$
$$=-\frac{1}{4\pi}\frac{\cos\kappa R}{R}+\sum_{L,M}D_{L,M}j_L(\kappa R)Y_{LM}(\Theta,\Phi),$$
$$\text{for}\quad R<r_s\quad(s=1,2,\cdots),\quad\text{(A2.8)}$$

where Θ, Φ are the polar angles of $\mathbf{R}$. The $D_{L,M}$ are given by

$$D_{L,M}=-\frac{4\pi}{\tau}i^L[j_l(\kappa R)]^{-1}$$
$$\times\sum_n\frac{j_L(|\mathbf{K}_n+\mathbf{k}|R)Y_{LM}^*(\theta_n,\varphi_n)}{(\mathbf{K}_n+\mathbf{k})^2-E}$$
$$+\frac{\kappa}{4\pi}\delta_{L0}\delta_{M0}\cot\kappa R,$$
$$D_{L,-M}=(-1)^LD_{L,M}^*\quad\text{(A2.9)}$$

where θ_n, φ_n are the polar angles of $(\mathbf{K}_n+\mathbf{k})$.

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

$$S(\eta)=\sum_n\frac{j_L(|\mathbf{K}_n+\mathbf{k}|R)Y_{LM}^*(\theta_n,\varphi_n)}{(\mathbf{K}_n+\mathbf{k})^2-E}$$
$$\times\exp\{[E-(\mathbf{K}_n+\mathbf{k})^2]/\eta\}.\quad\text{(A2.10)}$$

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

[14] P. Ewald, Ann. Physik **64**, 253 (1921).

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

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

$$\sum_{L,M} D_{L,M} j_L(\kappa R) Y_{LM}(\Theta,\Phi)$$

$$=\sum_{l,m} \sum_{l',m'} A_{lm;\,l',m'} j_l(\kappa r) j_{l'}(\kappa r')$$

$$\times Y_{l,m}(\theta,\varphi) Y_{l'm'}(\theta',\varphi'). \quad (A2.11)$$

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

$$j_L(\kappa R) Y_{LM}(\Theta,\Phi)$$

$$=\frac{1}{4\pi i^L}\int \exp(i\boldsymbol{\kappa}\cdot\mathbf{R}) Y_{LM}(\theta_\kappa,\varphi_\kappa) d\Omega_\kappa$$

$$=\frac{1}{4\pi i^L}\int \exp(i\boldsymbol{\kappa}\cdot\mathbf{r}) \exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}') Y_{LM}(\theta_\kappa,\varphi_\kappa) d\Omega_\kappa$$

$$=\frac{4\pi}{i^L}\sum_{l,m}\sum_{l',m'} i^{(l-l')} j_l(\kappa r) j_{l'}(\kappa r') Y_{lm}(\theta,\varphi)$$

$$\times Y_{l'm'}{}^*(\theta',\varphi') C_{LM;\,lm;\,l'm'}, \quad (A2.12)$$

where

$$C_{LM;\,lm;\,l'm'}$$

$$=\int Y_{LM}(\theta,\varphi) Y_{lm}{}^*(\theta,\varphi) Y_{l'm'}(\theta,\varphi) d\Omega. \quad (A2.13)$$

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

$$A_{lm;\,l',m'}=4\pi i^{(l-l')}\sum_L \frac{1}{i^L} D_{L,\,m-m'} C_{L,\,m-m';\,lm;\,l'm'}. \quad (A2.14)$$

Here we have used the fact that

$$C_{LM;\,l,m;\,l',m'}=0, \quad M\neq m-m'. \quad (A2.15)$$

The sum over L runs only over the values,

$$L=|l-l'|, \ |l-l'|+2, \cdots |l+l'|, \quad (A2.16)$$

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

In summary, the structure constants $A_{lm;\,l'm'}$ in the secular equation (3.17) are given either directly by (A2.5) or in terms of the smaller number of constants $D_{L,M}$ 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).[13] For this purpose we use the standard results:

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

$$=\delta(\mathbf{K}_n+\mathbf{k}-\mathbf{K}), \quad (A2.17)$$

$$\frac{1}{\tau}\sum_n \exp(i\mathbf{K}_n\cdot\boldsymbol{\varrho})=\sum_s \delta(\boldsymbol{\varrho}-\mathbf{r}_s), \quad (A2.18)$$

$$\lim_{\epsilon\to+0}\frac{1}{(2\pi)^3}\int \frac{\exp[i\mathbf{K}\cdot(\mathbf{R}-\mathbf{r}_s)]}{K^2-(E+i\epsilon)} d\mathbf{K}$$

$$=+\frac{1}{4\pi}\frac{\exp(i\kappa|\mathbf{R}-\mathbf{r}_s|)}{|\mathbf{R}-\mathbf{r}_s|}, \quad (A2.19)$$

$$\kappa=\begin{cases}\sqrt{E}, & E>0 \\ i\sqrt{-E}, & E<0.\end{cases}$$

Then,

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

$$=\lim_{\epsilon\to+0}\frac{1}{\tau}\sum_n \int \delta(\mathbf{K}_n+\mathbf{k}-\mathbf{K})\frac{\exp(i\mathbf{K}\cdot\mathbf{R})}{K^2-(E+i\epsilon)} d\mathbf{K}$$

$$=\lim_{\epsilon\to+0}\frac{1}{\tau}\frac{1}{(2\pi)^3}\sum_n \int\int \exp[i(\mathbf{K}_n+\mathbf{k}-\mathbf{K})\cdot\boldsymbol{\varrho}]$$

$$\times\frac{\exp(i\mathbf{K}\cdot\mathbf{R})}{K^2-(E+i\epsilon)} d\boldsymbol{\varrho} d\mathbf{K}$$

$$=\lim_{\epsilon\to+0}\frac{1}{(2\pi)^3}\sum_s \exp(i\mathbf{k}\cdot\mathbf{r}_s)$$

$$\times\int \frac{\exp[i\mathbf{K}\cdot(\mathbf{R}-\mathbf{r}_s)]}{K^2-(E+i\epsilon)} d\mathbf{K}$$

$$=-\frac{1}{4\pi}\sum_s \exp(i\mathbf{k}\cdot\mathbf{r}_s)\frac{\exp(i\kappa|\mathbf{R}-\mathbf{r}_s|)}{|\mathbf{R}-\mathbf{r}_s|}. \quad (A2.20)$$

If ϵ had been chosen negative, then for $E>0$, κ 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

$$G(\mathbf{r},\mathbf{r}')=-\frac{1}{4\pi}\sum_s \exp(i\mathbf{k}\cdot\mathbf{r}_s)\frac{\cos(\kappa|\mathbf{r}-\mathbf{r}'-\mathbf{r}_s|)}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_s|},$$

$$E>0, \quad (A2.21)$$

which, in contrast to (2.10), is manifestly Hermitian.

If (A2.20) is expanded in spherical harmonics relative to $\mathbf{R}$, using (A2.c), the following alternative expression

is found for the coefficients $D_{L,M}$ of (A2.8):

$$D_{L,M} = \kappa \sum_{s \neq 0} \exp(i\mathbf{k} \cdot \mathbf{r}_s)[n_L(\kappa r_s) - ij_L(\kappa r_s)]Y_{LM}^*(\theta_s, \varphi_s)$$

$$- \frac{i\kappa}{(4\pi)^{\frac{1}{2}}}\delta_{L0}\delta_{M0}, \quad (A2.22)$$

where θ_s, φ_s are the polar angles of $\mathbf{r}_s$. It may be noted that this series converges exponentially for $E < 0$ since $n_L(ix) - ij_L(ix) \sim e^{-x}/x$ for large x. Hence it provides a good check on evaluations of $D_{L,M}$ by (A2.9).

Convergence of the Green's Function Expansion

It has already been remarked that $D(\mathbf{r},\mathbf{r}')$, (A2.1) has an expansion of the form (A2.3) 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[7]

Consider the scattering in free space by the potential

$$\begin{aligned} V &= V(r), \quad r \leq r_i, \\ &= 0, \quad\quad r > r_i, \end{aligned} \quad (A3.1)$$

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

$$R(r) = A[j_l(\kappa r) - \tan\eta_l n_l(\kappa r)], \quad (A3.2)$$

where η_l is the phase shift. An elementary calculation shows that if L_l is the logarithmic derivative of R at r_i, then

$$\cot\eta_l = \frac{n_l'(\kappa r_i) - n_l(\kappa r_i)L_l}{j_l'(\kappa r_i) - j_l(\kappa r_i)L_l}. \quad (A3.3)$$

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

$$G_{lm; l'm'} = \kappa^{-1}A_{lm; l'm'} - i\delta_{ll'}\delta_{mm'}, \quad (A3.4)$$

(3.17) becomes

$$\text{Det}\left|G_{lm; l'm'} + \delta_{ll'}\delta_{mm'}\frac{e^{i\eta_l}}{\sin\eta_l}\right| = 0, \quad (A3.5)$$

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.[6]

Note added in proof.—Recently a calculation of the lithium conduction band was published by B. Schiff.[15] This author used a potential which differs from that constructed by Seitz, on which previous calculations by Seitz,[12] Bardeen,[16] Silverman and Kohn,[3] 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.

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[15] B. Schiff, Proc. Phys. Soc. (London) A67, 2 (1954).
[16] Bardeen, J. Chem. Phys. 6, 367 (1938).