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Energy Bands in Periodic Lattices—Green's Function Method

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The mathematical basis of calculations of energy bands in periodic lattices using the Green's function method is presented and the method's usefulness discussed. The original formulation of the method by Kohn and Rostoker is modified to achieve more efficient and accurate evaluation of "structure constants" using symmetry considerations and the full Ewald summation procedure. Formulas are derived giving the wave function both inside and outside the sphere inscribed in the unit cell. The method is demonstrated with the 3-dimensional Mathieu potential. Convergence is found to be very rapid both in this test case and in practical calculations on metals, and accurate energies and wave functions can be obtained without elaborate calculation even at points of low symmetry within the Brillouin zone.

I. INTRODUCTION

In separate papers we give the results of calculations on the energy bands of the alkali metals,[1] aluminum,[2] and the noble metals,[3] obtained by a procedure proposed by Kohn and Rostoker[4] which we shall call the Green's function method. (The same method was proposed previously by Korringa[5] from the different point of view of the multiple scattering of waves. This alternative approach has also been discussed by Morse.[6]) It is the purpose of this paper to present the mathematical basis of these calculations. Although the fundamental equations of the Green's function method were given by Kohn and Rostoker in their original paper,[4] we have found it essential to modify their procedures in several important respects to make the method suitable for extensive accurate calculations. In particular, accurate evaluation of the "structure constants" necessitates use of the full Ewald procedure of summation in both coordinate and reciprocal spaces, and advantage may be taken of symmetry to reduce to a minimum the number of independent structure constants that must be computed. We have extended the derivation to provide a formula for the wave function outside the sphere inscribed in the unit cell, and we have found a more accurate procedure for calculating the coefficients of terms in the wave function inside this sphere. Together with these new results, this paper summarizes the formulas of the Green's function method in the form we have found most convenient for practical use. We also give a brief demonstration of the method's accuracy by using it on the 3-dimensional Mathieu potential, exact eigenvalues of which are known.[7]

The Green's function method for calculating energy bands in solids shares with other methods such as those of augmented[8,9] or orthogonalized plane waves[10,11] and the various cellular methods[12–15] the advantage of taking accurate account of the polyhedral shape of the atomic cell. With these other methods, it thus represents a major advance over the spherical approximation of Wigner and Seitz,[16] which has been used extensively in band calculations on metals. This is especially so when one seeks departures from spherical energy surfaces such as occur even in a "nearly-free-electron" metal like sodium for states near the Brillouin zone surface. Recent interest, both theoretical and experimental, has attached particularly to the shape of the Fermi surface in metals,[17] and knowledge of band shapes in semiconductors and semimetals has been of vital importance in understanding the properties of these substances.

An especial advantage of the Green's function method is its rapid convergence. This is much better than that found in calculations with other methods as reported in the literature, though it is probably rivaled by recent work with forms of the augmented plane-wave method. In particular, the method permits accurate calculation at points of low symmetry within the Brillouin zone without requiring use of unmanageably large determinants. The method has the further advantage that the calculations are relatively simple and in many interesting cases can be done by hand, once tables are prepared of "structure constants" which are characteristic of lattice type but independent of the particular crystal potential or lattice constant. The method is a variational one leading to a stationary value for the

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[1] F. S. Ham (to be published).

[2] B. Segall, following paper [Phys. Rev. **124**, 1797 (1961)].

[3] B. Segall (to be published).

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

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

[6] P. M. Morse, Proc. Nat. Acad. Sci. **42**, 276 (1956).

[7] The Green's function method has been applied previously to the diamond structure and has been tested on a potential for which the tight-binding approximation is valid [B. Segall, J. Phys. Chem. Solids **8**, 371 (1959)].

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[12] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[13] F. von der Lage and H. Bethe, Phys. Rev. **71**, 612 (1947).

[14] D. J. Howarth and H. Jones, Proc. Phys. Soc. (London) **A65**, 355 (1952).

[15] W. Kohn, Phys. Rev. **87**, 472 (1952).

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

[17] *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

energy, but the convergence is sufficiently rapid to permit satisfactory calculation of wave functions as well.

We are concerned in the Green's function method with solving an integral equation within a single unit cell. As with "cellular" methods and the augmented plane-wave method, this is conveniently done only if the crystal potential can be represented approximately as being spherically symmetric about each ion and constant in the cell corners—the "muffin-tin" form of potential.[18] This restriction does not seem a severe handicap in dealing with most solids of current interest, particularly metals. This approximation to the potential can generally be corrected for by perturbation theory.

In the course of our work on the alkali metals and aluminum we have made extensive calculations of the structure constants for body-centered and face-centered cubic lattices. These have been collected in tables for some of the more interesting points in **k** space and are available from the authors.[19] If calculations are undertaken at more general points in **k**-space than those covered in the tables, the structure constants may be computed efficiently from the formulas of Sec. VII below using an automatic computer of capacity and speed comparable to that of the IBM 704.

We do not repeat in this paper the derivation of the Green's function method or of many of the formulas we use but instead refer the reader to the relevant portions of Kohn and Rostoker's paper for such proofs.[20] We conform so far as possible to Kohn and Rostoker's notation, although we have found it desirable to make some changes in their choice of the basic quantities, in order to facilitate calculation.

II. BASIC EQUATIONS

We seek propagating solutions $\psi(\mathbf{r})$ of Schrödinger's equation

$$[-\nabla^2+V(\mathbf{r})-E]\psi(\mathbf{r})=0, \tag{2.1}$$

in a periodic potential $V(\mathbf{r})$, so that

$$\psi(\mathbf{r}+\mathbf{r}_s)=\exp(i\mathbf{k}\cdot\mathbf{r}_s)\psi(\mathbf{r}). \tag{2.2}$$

Here **k** is the crystal momentum vector, and $\mathbf{r}_s$ is any translation vector of the lattice. Kohn and Rostoker have shown that $\psi(\mathbf{r})$ satisfies the integral equation (KR 2.14)

$$\psi(\mathbf{r})=\int_\tau G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')d\tau', \tag{2.3}$$

where the integral is over the interior of the unit cell of volume τ, and (KR 2.9)

$$G(\mathbf{r},\mathbf{r}')=-\frac{1}{\tau}\sum_n\frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot(\mathbf{r}-\mathbf{r}')]}{(\mathbf{K}_n+\mathbf{k})^2-E}. \tag{2.4}$$

Here the summation is over all vectors $\mathbf{K}_n$ of the reciprocal lattice, and E is the energy eigenvalue appropriate to $\psi(\mathbf{r})$. The Green's function $G(\mathbf{r},\mathbf{r}')$ satisfies

$$(\nabla^2+E)G(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}'), \tag{2.5}$$

$$G(\mathbf{r}',\mathbf{r})=G^*(\mathbf{r},\mathbf{r}'), \tag{2.6}$$

and

$$G(\mathbf{r}+\mathbf{r}_s,\ \mathbf{r}')=\exp(i\mathbf{k}\cdot\mathbf{r}_s)G(\mathbf{r},\mathbf{r}'), \tag{2.7}$$

for all $\mathbf{r}$, $\mathbf{r}'$ within the cell.

Kohn and Rostoker introduced a variational procedure (KR 2.15, 2.16) for solving (2.3) and showed that if the resulting wave function is in error by an amount $\xi x(\mathbf{r})$, the error in the energy is of order ξ^2. Restricting our discussion to a potential of the "muffin-tin" form—spherically symmetric about each ion within the sphere inscribed in the unit cell,[21,22] and constant elsewhere—we use a trial function of the form

$$\psi(\mathbf{r})=\sum_{l=0}^{l_N}\sum_j i^l C_{lj}R_l(r)\mathcal{Y}_{lj}(\mathbf{r}), \tag{2.8}$$

within the inscribed sphere. Here $R_l(r)$ is a radial function which is finite at $r=0$ and satisfies the radial differential equation

$$\left[-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{l(l+1)}{r^2}+V(r)-E\right]R_l(r)=0, \tag{2.9}$$

for the same value of E used in constructing $G(\mathbf{r},\mathbf{r}')$. The functions $\mathcal{Y}_{lj}(\mathbf{r})$ are linear combinations of spherical harmonics of angular momentum l, with argument the angular coordinates of **r**. These combinations are chosen such that they transform under the irreducible representations of the symmetry group of the wave vector **k**, and they are normalized, real, and mutually orthogonal:

$$\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta d\theta\mathcal{Y}_{lj}(\mathbf{r})\mathcal{Y}_{l'j'}(\mathbf{r})=\delta_{ll'}\delta_{jj'}. \tag{2.10}$$

Only those combinations having the same transforma-

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[18] The restriction of standard cellular methods to a muffin-tin form of potential has not generally been recognized, the usual tacit assumption being that it suffices if the potential within the entire unit cell is spherically symmetric about the central ion. But if the potential is not constant in the outer parts of the cell, one has no assurance that the usual spherical harmonic expansion of the wave function converges outside the inscribed sphere. This question is discussed in an article by Ham (reference 17, p. 9).

[19] B. Segall and F. S. Ham, "Tables of Structure Constants for Energy Band Calculations with the Green's Function Method." These unpublished tables for the bcc and fcc lattices may be obtained from the authors. They include the principal symmetry points and a few points on the symmetry axes, for a limited range of energy.

[20] Equations in reference 4 will be indicated by, for example, (KR 2.14) if reference to Kohn and Rostoker's Eq. (2.14) is intended.

[21] We restrict out attention to lattices with a single ion in each unit cell, located at the center of the cell. "Complex" lattices are considered by Segall in reference 22, and the methods of the present paper may be generalized directly to such cases.

[22] B. Segall, Phys. Rev. **105**, 108 (1957).

tion properties under the group of **k** enter (2.8) for a single $\psi(\mathbf{r})$.

If the zero of energy is adjusted to coincide with the constant value of $V(\mathbf{r})$ in the region outside the inscribed spheres, the integrand in (2.3) differs from zero only within the inscribed sphere. Kohn and Rostoker's variational principle then prescribes that the coefficients C_{lj} in (2.8) be chosen to make a functional (KR 2.16) stationary under variations in the C_{lj}. This requirement leads to equations determining the C_{lj} (KR 2.27)

$$\textstyle\sum_{l'j'}\Lambda_{lj;l'j'}C_{l'j'}=0. \tag{2.11}$$

Here (KR 3.15)

$$\begin{aligned}\Lambda_{lj;l'j'}=[R_l(r),j_l(\kappa r)]\{\mathfrak{B}_{lj;l'j'}[R_{l'}(r),j_{l'}(\kappa r)]&\\ +\kappa\delta_{ll'}\delta_{jj'}[R_l(r),n_l(\kappa r)]\}.&\end{aligned} \tag{2.12}$$

The coefficients $\mathfrak{B}_{lj;l'j'}$ derived from $G(\mathbf{r},\mathbf{r}')$ are functions of **k** and E and will be defined below. We define

$$[F,G]=[F(r)dG(r)/dr-G(r)dF(r)/dr]_{r=r_i}, \tag{2.13}$$

the functions being evaluated at the radius r_i of the inscribed sphere. In (2.12)

$$\begin{aligned}\kappa&=E^{\frac{1}{2}},\quad E>0\\ &=i(-E)^{\frac{1}{2}},\quad E<0\end{aligned} \tag{2.14}$$

and $j_l(\kappa r)$ and $n_l(\kappa r)$ are the spherical Bessel and Neumann functions,[23] which are related to the standard Bessel functions $J_\alpha(x)$ by

$$\begin{aligned}j_l(x)&=(\pi/2x)^{\frac{1}{2}}J_{l+\frac{1}{2}}(x),\\ n_l(x)&=(-)^{l+1}(\pi/2x)^{\frac{1}{2}}J_{-l-\frac{1}{2}}(x).\end{aligned} \tag{2.15}$$

A necessary condition for a nontrivial solution of (2.11) is (KR 2.28)

$$\operatorname{Det}\Lambda_{lj;l'j'}=0. \tag{2.16}$$

Since $\Lambda_{lj;l'j'}$ is a function of E through the structure constants, the spherical Bessel functions, and $R_l(r)$, (2.16) provides an equation for the approximate energy eigenvalue obtained for a given **k** from the trial function (2.8) with its summation terminated at l_N.

The Green's function $G(\mathbf{r},\mathbf{r}')$ can be expanded for $r<r'<r_i$ as (KR 3.13)

$$\begin{aligned}G(\mathbf{r},\mathbf{r}')=\sum_{l,j}\sum_{l'j'}[i^{(l-l')}\mathfrak{B}_{lj;l'j'}j_l(\kappa r)j_{l'}(\kappa r')&\\ +\kappa\delta_{ll'}\delta_{jj'}j_l(\kappa r)n_l(\kappa r')]\mathcal{Y}_{lj}(\mathbf{r})\mathcal{Y}_{l'j'}(\mathbf{r}').&\end{aligned} \tag{2.17}$$

Alternatively, since $G(\mathbf{r},\mathbf{r}')$ is a function of $\mathbf{R}=(\mathbf{r}-\mathbf{r}')$, we have (KR A2.8)

$$\begin{aligned}G(\mathbf{r},\mathbf{r}')=-(1/4\pi R)\cos\kappa R&\\ +\sum_{LJ}i^L\mathfrak{D}_{LJ}j_L(\kappa R)\mathcal{Y}_{LJ}(\mathbf{R}),&\end{aligned} \tag{2.18}$$

for $R<r_s$. The $\mathfrak{D}_{LJ}$ are the "structure constants" which we have evaluated. We have the relation (KR A2.14)

$$\mathfrak{B}_{lj;l'j'}=4\pi\sum_{LJ}\mathfrak{D}_{LJ}C^{LJ}{}_{lj;l'j'}, \tag{2.19}$$

where

$$C^{LJ}{}_{lj;l'j'}=\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta d\theta\,\mathcal{Y}_{LJ}(\mathbf{r})\mathcal{Y}_{lj}(\mathbf{r})\mathcal{Y}_{l'j'}(\mathbf{r}). \tag{2.20}$$

$C^{LJ}{}_{lj'l'j'}$ is zero unless $|l-l'|\leq L\leq(l+l')$ and $(l+l'+L)$ is an even integer. Hence

$$\mathfrak{B}_{lj;l'j'}=\mathfrak{B}_{l'j';lj},$$

and, from (2.12),

$$\Lambda_{lj;l'j'}=\Lambda_{l'j';lj}. \tag{2.21}$$

The equations above have been modified from the form given by Kohn and Rostoker, in order to eliminate powers of $i=(-1)^{\frac{1}{2}}$ that otherwise enter the final equations when $E>0$. Thus we use real angular functions $\mathcal{Y}_{lj}(\mathbf{r})$, and we introduce a factor i^l in (2.8) to permit choosing all the C_{lj}'s real in a lattice possessing inversion symmetry at the ion. Accordingly, $i^{(l-l')}\mathfrak{B}_{lj;l'j'}$ in (2.17) replaces $A_{lj;l'j'}$ in (KR 3.13), and from (2.18) and (KR A2.8) we find that our $\mathfrak{D}_{LJ}$ equals i^{-L} times Kohn and Rostoker's D_{LJ}. Our $\mathfrak{D}_{LJ}$ are real numbers for simple bcc and fcc lattices for $E>0$.

For $E<0$, κ becomes imaginary according to (2.14). In place of (2.12) we now express $\Lambda_{lj;l'j'}$ as

$$\begin{aligned}\Lambda_{lj;l'j'}=[R_l(r),U_l(|\kappa|r)]g_{ll'}\{h_{ll'}\mathfrak{B}_{lj;l'j'}&\\ \times[R_{l'}(r),U_{l'}(|\kappa|r)]+|\kappa|\delta_{ll'}\delta_{jj'}&\\ \times[R_l(r),-V_l(|\kappa|r)]\},&\end{aligned} \tag{2.22}$$

where

$$\begin{aligned}g_{ll'}&=i^{(l+l'-1)},\quad(l+l')\text{ odd}\\ &=i^{(l+l')},\quad(l+l')\text{ even,}\\ h_{ll'}&=i,\quad(l+l')\text{ odd}\\ &=1,\quad(l+l')\text{ even}\end{aligned}$$

and

$$\begin{aligned}U_l(|\kappa|r)&=i^{-l}j_l(\kappa r),\\ V_l(|\kappa|r)&=i^{-l-1}n_l(\kappa r),\end{aligned} \tag{2.23}$$

are real for $E<0$. $\mathfrak{B}_{lj;l'j'}$ is obtained from (2.19). When $E<0$, $\mathfrak{D}_{LJ}$ is real when L and $(l+l')$ are even, and $i\mathfrak{D}_{LJ}$ is real when L and $(l+l')$ are odd. Thus (2.22) permits calculation of $\Lambda_{lj;l'j'}$ in terms of real quantities when $E<0$, as does (2.12) for $E>0$.

III. PROCEDURE FOR EVALUATING EIGENVALUES

Energy eigenvalues are found by locating the values of E for which the determinant of the $\Lambda_{lj;l'j'}$ vanishes, according to (2.16). We have found it convenient to tabulate the structure constants $\mathfrak{D}_{LJ}$, the radial functions, and the spherical Bessel functions at a sequence of energies, evaluate the determinant at a few of these energies near an eigenvalue, and interpolate to locate the zero. Starting from a trial function com-

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[23] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, p. 622.

prising a single $\mathcal{Y}_{lj}(\mathbf{r})$, we have added independent terms until further increase in the size of the determinant makes no further change in the eigenvalue.

The quantity $[R_l,j_l]$ is a factor in all $\Lambda_{lj;l'j'}$ appearing in the (lj) row of the determinant. Hence if $[R_n,j_n]$ is zero at $E=E'$, all determinants arising from trial functions containing $\mathcal{Y}_{nj}(\mathbf{r})$ are zero at E'. However E' is not an eigenvalue of the original integral equation (2.3),[24] so that such roots of (2.16) must be distinguished and excluded.

An inconvenience in interpolation may occur if an eigenvalue falls near a value of $(\mathbf{K}_n+\mathbf{k})^2$, for $G(\mathbf{r},\mathbf{r}')$ as a function of E has simple poles at these points. Such singularities occur whenever there exist solutions to the homogeneous free electron Schrödinger equation

$$(-\nabla^2-E)\varphi(\mathbf{r})=0, \tag{3.1}$$

and to the boundary conditions (2.7) for the same $\mathbf{k}$ for which $G(\mathbf{r},\mathbf{r}')$ was constructed, since at this E a solution of the inhomogeneous equation (2.5) does not exist. A determinant of the $\Lambda_{lj;l'j'}$ is thus singular at this E if from these free electron solutions one can form a linear combination belonging to the same irreducible representation of the group of $\mathbf{k}$ as the $\mathcal{Y}_{lj}(\mathbf{r})$.

Eigenvalues frequently occur near such singularities, since an eigenvalue in a crystal is often close to the corresponding free electron energy. It is possible to reformulate the integral equation (2.3) to eliminate a singularity, and to construct a variational principle equivalent to the resulting inhomogeneous integral equation which leads to a stationary value for the energy. However, we have not found this to be as convenient a procedure for calculation as that based on the homogeneous integral equation (2.3). Accordingly, we have chosen to use the latter in all of our work and to tabulate the structure constants using a sufficiently small interval in E. Satisfactory interpolation has usually been possible if there is at least one tabulated point between an eigenvalue and the nearest singularity. The singularity in $\Lambda_{lj;l'j'}$ may of course be removed by multiplication by $[E-(\mathbf{K}_n+\mathbf{k})^2]$.

IV. CALCULATION OF WAVE FUNCTIONS

Within Inscribed Sphere

The wave function within the inscribed sphere is given by (2.8); the coefficients C_{lj} are determined by the linear homogeneous equations (2.11).

Instead of solving these equations directly at the eigenvalue, which necessitates evaluating the structure constants at that energy, we may set one of the coefficients equal to unity and solve for the $(n-1)$ others at the tabulated energies, using $(n-1)$ of the equations used in constructing the determinant that gave the eigenvalue. We then interpolate the resulting values for each C_{lj} to the eigenvalue. However, although many C_{lj} are small at the eigenvalue, they are often found in this fashion to vary rapidly with energy. Interpolation is consequently unreliable, and this procedure provides little means of estimating the accuracy of the final result.

We have chosen to calculate the coefficients by modifying this procedure to permit more accurate interpolation and to make evident the extent to which the value of the coefficient converges to a final result as n is increased. Let us denote the linear equations (2.11) by

$$\sum_{q=1}^{n} \Lambda_{iq}C_q=0, \quad i=1\cdots n, \tag{4.1}$$

where we have ordered the C_{lj} in order of decreasing importance in the construction of the wave function and have relabeled them for simplicity as C_q, $q=1\cdots n$. Setting

$$C_1=1, \tag{4.2}$$

we prove in Appendix I that for $q=2,\ 3,\ \cdots n$

$$C_q=-\frac{L_{q-1}}{K_q}+\sum_{m=q+1}^{n}\frac{H_{mq}L_{m-1}}{K_mK_{m-1}}. \tag{4.3}$$

Here L_m, K_m, and H_{mq} are determinants as follows:

$$L_m=(-)^{m+1}\begin{vmatrix} \Lambda_{11} & \Lambda_{12} & \Lambda_{13} & \cdots & \Lambda_{1m} \\ \Lambda_{21} & \Lambda_{22} & \Lambda_{23} & \cdots & \Lambda_{2m} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \Lambda_{m1} & \Lambda_{m2} & \Lambda_{m3} & \cdots & \Lambda_{mm} \end{vmatrix}, \tag{4.4}$$

$$K_m=\begin{vmatrix} \Lambda_{12} & \Lambda_{13} & \cdots & \Lambda_{1m} \\ \Lambda_{22} & \Lambda_{23} & \cdots & \Lambda_{2m} \\ \vdots & \vdots & \vdots & \vdots \\ \Lambda_{m-1,2} & \Lambda_{m-1,3} & \cdots & \Lambda_{m-1,m} \end{vmatrix}. \tag{4.5}$$

K_m is the $(m-1)$th order determinant obtained from $(-)^{m+1}L_m$ by suppressing the first column and last row. H_{mq} is (-1) times the determinant obtained from K_m by replacing the last row by zeros except for a one in the column that contained $\Lambda_{m-1,q}$ in K_m.

From (4.3) we see that C_q has been expressed as a series such that an increase in n, the number of equations and coefficients in (4.1), adds terms to the series without modifying the terms already present. L_m is the mth order determinant of the Λ_{ik}'s, the zeros of which give the eigenvalues in the approximation of retaining m terms in the trial function. Thus terms in the series (4.3), evaluated at the approximate eigenvalue obtained from L_n, should diminish in magnitude with increasing m as the eigenvalue obtained from L_m approaches that obtained from L_n. The individual determinants L_m, K_m, and H_{mq} vary smoothly with energy, except of course near a singularity, and they can be interpolated to the eigenvalue more satisfac-

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[24] This follows from Appendix 1 of reference 4, where the integral equation is converted to a set of linear equations for the C_{lj}. These equations differ from (2.11) in that the coefficient of $C_{l'j'}$ is $\Lambda_{lj;l'j'}/[R_l,j_l]$. The determinant of these equations does not vanish at the zeros of $[R_l,j_l]$.

torily and their error estimated more reliably than has been possible with the C_q themselves. Thus the advantage of (4.3) is that it exhibits the convergence of the value of C_q as n is increased and permits a satisfactory estimate of its error due to uncertainty both in the location of the eigenvalue and in the interpolation of the various necessary quantities.

The principal source of uncertainty in the C_q as obtained from (4.3) is in the interpolation of L_m, since a small absolute error in the value of L_m at the eigenvalue causes a large relative error in the corresponding term of (4.3) if L_m is small. To reduce this uncertainty we may take advantage of the fact that the different L_m usually vary with energy in a very similar fashion over a small energy range. We then determine constants α_m and β_m such that

$$z(E)=L_m(E)-\alpha_m-\beta_m L_n(E) \qquad (4.6)$$

is as small as possible over an energy range including three or four tabulated points E_i near the eigenvalue. In particular, we find the values of α_m and β_m which minimize $\sum_i [z(E_i)]^2$. If the zero of L_n defines the eigenvalue E', then by (4.6)

$$L_m(E')=\alpha_m+z(E'). \qquad (4.7)$$

If $z(E)$ is plotted at the few tabulated points, one usually finds that $z(E)$ is a smoothly varying function of energy and that one can estimate its value at E' with less uncertainty than one would have to attach to a direct interpolation of $L_m(E')$.

Outside Inscribed Sphere

Since the part of the unit cell outside the inscribed sphere does not have spherical symmetry, expansion of the wave function in spherical harmonics as in (2.8) does not provide a convenient representation in this region. Instead, we expand $\psi(\mathbf{r})$ in this region in plane waves.

We recall that $V(\mathbf{r})$ is zero for the muffin-tin potential outside the inscribed sphere, so that the domain of integration in the integral equation (2.3) is the interior of the sphere. We can then transform the integral equation to provide a representation of $\psi(\mathbf{r})$ for $r>r_i$ in terms of known quantities evaluated at the surface of the sphere.

Substituting for $[V(\mathbf{r}')\psi(\mathbf{r}')]$ in (2.3) from Schrödinger's equation (2.1), integrating by parts, and using (2.5), we obtain

$$\psi(\mathbf{r})=\int_{r'=r_i} \hat{n}\cdot[G(\mathbf{r},\mathbf{r}')\nabla'\psi(\mathbf{r}') -\psi(\mathbf{r}')\nabla'G(\mathbf{r},\mathbf{r}')]dS', \qquad (4.8)$$

where $\mathbf{r}$ lies within the unit cell but outside the inscribed sphere. We now use the expansion

$$G(\mathbf{r},\mathbf{r}')=\sum_{LJ}(-i)^L\mathfrak{D}_{LJ}(\mathbf{r})j_L(\kappa r')\mathcal{Y}_{LJ}(\mathbf{r}'), \qquad (4.9)$$

which is valid for $r'<r$, for $\mathbf{r}$ within the unit cell.[25] The function $\mathfrak{D}_{LJ}(\mathbf{r})$ may be expressed as

$$\mathfrak{D}_{LJ}(\mathbf{r})=-\frac{4\pi}{\tau}\frac{1}{j_L(\kappa s)}\sum_n \frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{r}]}{(\mathbf{K}_n+\mathbf{k})^2-E} \times j_L(|\mathbf{K}_n+\mathbf{k}|s)\mathcal{Y}_{LJ}(\mathbf{K}_n+\mathbf{k}), \qquad (4.10)$$

where s is arbitrary, $0\leq s<r$. Substituting from (4.9) and (2.8) into (4.8), we obtain for $r>r_i$

$$\psi(\mathbf{r})=r_i^2\sum_{lj}C_{lj}\mathfrak{D}_{lj}(\mathbf{r})[j_l(\kappa r_i),R_l(r_i)]. \qquad (4.11)$$

The functions $\mathfrak{D}_{LJ}(\mathbf{r})$ are closely related to the structure constants $\mathfrak{D}_{LJ}$, in particular to those of "complex" lattices.[22]

To obtain a plane-wave expansion for $\psi(\mathbf{r})$ outside the inscribed sphere, we use (4.10) directly in (4.11). However, whereas $\mathfrak{D}_{LJ}(\mathbf{r})$ is independent of the choice of s used in evaluating the series (4.10), the coefficients of the plane waves in the resulting expression for $\psi(\mathbf{r})$ *do* depend on the choice of s. This lack of uniqueness in the series is not surprising, for we require of the series only that it converge to the correct $\psi(\mathbf{r})$ for $r>r_i$; different plane wave expansions may represent the same function in this region but entirely different functions within the inscribed sphere.[26] To obtain the "best" possible approximation to $\psi(\mathbf{r})$ outside the sphere in terms of N given plane waves,

$$\psi(\mathbf{r})\approx\varphi_N(\mathbf{r})=\sum_{n=1}^{N} F_n \exp[i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{r}], \qquad (4.12)$$

we vary the F_n to minimize

$$\int_{r>r_i} |\psi(\mathbf{r})-\varphi_N(\mathbf{r})|^2 d\tau. \qquad (4.13)$$

On substituting from (4.11) for $\psi(\mathbf{r})$ using (4.10), we

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[25] $G(\mathbf{r},\mathbf{r}')$ satisfies the homogeneous equation $(\nabla'^2+E)G(\mathbf{r},\mathbf{r}')=0$ throughout the region $\mathbf{r}'<\mathbf{r}$ if $\mathbf{r}$ lies within the unit cell. $G(\mathbf{r},\mathbf{r}')$ therefore has an expansion of the form (4.9). Equation (4.10) follows in a manner analogous to the proof of Eq. (A.9) of reference 22.

[26] Morse (reference 6) has proposed an alternative plane-wave expansion for ψ outside the inscribed sphere. This is obtained by substituting into (4.8) from (2.4) and (2.8):

$$\psi(\mathbf{r})=\frac{4\pi r_i^2}{\tau}\sum_{lj} C_{lj}\sum_n \frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{r}]}{(\mathbf{K}_n+\mathbf{k})^2-E}\mathcal{Y}_{lj}(\mathbf{K}_n+\mathbf{k}) \times[R_l(r),j_l(|\mathbf{K}_n+\mathbf{k}|r_i)].$$

However, it appears to us that this series may not converge, because of the appearance of $[(d/dr)j_l(|\mathbf{K}_n+\mathbf{k}|r_i)]$. Even if the series should converge, its convergence is conditional and very slow, so that the series is at best inconvenient for practical use. On the other hand, the series (4.10) can be proved to converge for $s>0$, although conditionally, and it can be summed readily using the Ewald procedure (Sec. VII). The series in (4.14) converges absolutely for $s>0$.

obtain as equations for the F_n

$$\sum_{n'=1}^{N} F_{n'}\mu_{mn'} = -\frac{4\pi r_i^2}{\tau}\sum_{lj}\frac{C_{lj}}{j_l(\kappa s)}[j_l(\kappa r_i),R_l(r_i)]$$

$$\times\sum_{n=1}^{\infty}\frac{\mu_{mn}}{(\mathbf{K}_n+\mathbf{k})^2-E}j_l(|\mathbf{K}_n+\mathbf{k}|s)\mathcal{Y}_{lj}(\mathbf{K}_n+\mathbf{k}), \quad (4.14)$$

for $1\leq m\leq N$, where

$$\mu_{mn}=\int_{r>r_i}\exp[-i(\mathbf{K}_m-\mathbf{K}_n)\cdot\mathbf{r}]d\tau$$

$$=\tau\delta_{mn}-(4\pi r_i^2/|\mathbf{K}_m-\mathbf{K}_n|)j_1(|\mathbf{K}_m-\mathbf{K}_n|r_i). \quad (4.15)$$

A simple way to obtain the ratio

$$\omega=\left[\int_{r\geq r_i}|\psi(\mathbf{r})|^2d\tau\right]\Big/\left[\int_{\text{cell}}|\psi(\mathbf{r})|^2d\tau\right],$$

[and thereby to make possible normalization of $\psi(\mathbf{r})$ once the integral of $|\psi(\mathbf{r})|^2$ over the inscribed sphere is evaluated] is to shift the potential for $r<r_i$ by a small constant amount ΔV with respect to the constant level $V=0$ in the cell corners. We then find the new eigenvalue by the usual method of Sec. III. The difference ΔE between this and the original eigenvalue is also given by first-order perturbation theory as

$$\Delta E=\Delta V(1-\omega), \quad (4.16)$$

which then determines ω.

V. RELATION OF "MUFFIN-TIN" POTENTIAL TO CRYSTAL POTENTIAL

Direct application of the Green's function method has been restricted to potentials having the "muffin-tin" form. We shall show here how a suitable muffin-tin potential, $V_{mt}(\mathbf{r})$, may be derived from the actual crystal potential $V_x(\mathbf{r})$. We shall give expressions for their difference in a form convenient for the use of perturbation theory.

Inside the sphere of radius r_i inscribed in the cell, $V_x(\mathbf{r})$ may be expanded in terms of those linear combinations of spherical harmonics which are unchanged by the symmetry operations of the crystal. For a cubic crystal with one atom per unit cell, we have thus for $r<r_i$

$$V_x(\mathbf{r})=V_0(r)+V_4(r)L_4(\mathbf{r})+V_6(r)L_6(\mathbf{r})+\cdots. \quad (5.1)$$

Here L_4 and L_6 are $(4\pi)^{\frac{1}{2}}$ times the normalized symmetric "Kubic harmonic" (type α) of $l=4$ and 6, respectively, as defined by von der Lage and Bethe.[13] We choose the muffin-tin potential to be

$$V_{mt}(\mathbf{r})=V_0(r), \quad (5.2)$$

for $r<r_i$.

In the cell outside the sphere we choose

$$V_{mt}(\mathbf{r})=V_c, \quad (5.3)$$

where V_c is a constant chosen equal to the average of $V_x(\mathbf{r})$ in this region:

$$[\tau-(4\pi/3)r_i^3]V_c=\int_{\tau}V_x(\mathbf{r})d\tau-\int_{r<r_i}V_x(\mathbf{r})d\tau. \quad (5.4)$$

Here τ is the cell volume. In calculations we select the zero point in the energy scale such that $V_c=0$.

The difference $\delta V(\mathbf{r})=V_x(\mathbf{r})-V_{mt}(\mathbf{r})$ may be expressed throughout the cell as a Fourier series

$$\delta V(\mathbf{r})=\textstyle\sum_n \delta V_n\exp(i\mathbf{K}_n\cdot\mathbf{r}). \quad (5.5)$$

If, however, such a representation is to be used only in the region outside the sphere, the series is not unique. This was also the case for the wave function as discussed in Sec. IV. We may then choose a "best" representation for a given N plane waves, for use *only* in the region $r>r_i$,

$$\delta V(\mathbf{r})\approx W_N(\mathbf{r})=\sum_{n=1}^{N}W_n\exp(i\mathbf{K}_n\cdot\mathbf{r}), \quad (5.6)$$

by minimizing

$$\int_{r>r_i}|\delta V(\mathbf{r})-W_N(\mathbf{r})|^2d\tau, \quad (5.7)$$

with respect to W_n. We find that the W_n satisfy the equations

$$\sum_{n=1}^{N}W_n\mu_{mn}=\int_{r>r_i}\delta V(\mathbf{r})\exp(-i\mathbf{K}_m\cdot\mathbf{r})d\tau, \quad (5.8)$$

for $m=1\cdots N$, with μ_{mn} given by (4.15). Using (5.1) and (5.5), we have therefore

$$\sum_{n=1}^{N}W_n\mu_{mn}=\tau\delta V_m-4\pi\sum_{l=4,6\cdots}(-)^{l/2}L_l(\mathbf{K}_m)$$

$$\times\int_0^{r_i}r^2V_l(r)j_l(K_mr)dr. \quad (5.9)$$

This choice of the muffin-tin potential insures that perturbation corrections due to $\delta V(\mathbf{r})$ are small if the wave functions are simple. Thus if terms with $l\geq 2$ are negligible in the wave function, the terms involving L_4, L_6, etc., in $\delta V(\mathbf{r})$ for $r<r_i$ give no first-order correction. The choice of V_c in (5.4) leads to a zero first-order correction if $|\psi(\mathbf{r})|^2$ is constant for $r>r_i$. Thus this correction is small if $\psi(\mathbf{r})$ can be approximated accurately in this region by one plane wave.

First-order perturbation corrections may be calculated in a straightforward manner using (5.1) and (5.6) when $\psi(\mathbf{r})$ has been found for the muffin-tin potential. We have expressed $\psi(\mathbf{r})$ and $\delta V(\mathbf{r})$ in terms of spherical harmonics for $r<r_i$, and in terms of plane waves for $r>r_i$. Second-order corrections may also be calculated if other states of the same $\mathbf{k}$ and the same symmetry have been treated.

Explicit expressions for $V_l(r)$, V_c, and δV_n are given in Appendix II for a crystal potential which can be expressed as a sum of spherically symmetric terms centered on each lattice site,

$$V_x(\mathbf{r})=\sum_s U(|\mathbf{r}-\mathbf{r}_s|). \tag{5.10}$$

VI. THE MATHIEU POTENTIAL—AN EXAMPLE

As an example of the application of the Green's function method, we consider here the Mathieu problem for a simple cubic lattice. We shall compare our results with exact solutions obtained by separating Schrödinger's equation in Cartesian coordinates and using known properties of one-dimensional Mathieu functions.[27]

We take as the crystal potential,

$$V_x(\mathbf{r})=U_1+U_2[\cos(2\pi x/a)+\cos(2\pi y/a)+\cos(2\pi z/a)]. \tag{6.1}$$

Expanding $V_x(\mathbf{r})$ as in (5.1), we obtain

$$V_0(r)=U_1+(3U_2\xi^{-1})\sin\xi, \tag{6.2}$$

where $\xi=2\pi r/a$. The "muffin-tin" potential is then

$$\begin{aligned} V_{mt}(\mathbf{r})&=V_0(r), && \text{for } r<a/2,\\ &=V_c, && \text{for } r>a/2, \end{aligned} \tag{6.3}$$

where from (5.4)

$$V_c=U_1-U_2[9/\pi(6-\pi)]. \tag{6.4}$$

Choosing the zero of energy such that $V_c=0$, we have

$$U_1=U_2[9/\pi(6-\pi)]. \tag{6.5}$$

The "best" representation, (5.6) and (5.7), for $\delta V(\mathbf{r})=V_x(\mathbf{r})-V_{mt}(\mathbf{r})$ outside the sphere is trivial:

$$\begin{aligned} &W_n=U_2[9/\pi(6-\pi)], && \text{for } \mathbf{K}_n=0,\\ &W_n=\tfrac{1}{2}U_2, && \text{for } \mathbf{K}_n=(2\pi/a)(1,0,0), \text{ etc.},\\ &W_n=0, && \text{for } |\mathbf{K}_n|>2\pi/a. \end{aligned} \tag{6.6}$$

For a test case we choose $U_2=-\frac{1}{2}(2\pi/a)^2$. Calculated eigenvalues for several states at Γ (center of zone) and X (end of [100] axis) are listed in Table I along with the exact values for the Mathieu potential. The calculated values were obtained by including in the trial function all terms of correct symmetry with $l\leq 4$. The rapid convergence found as terms are added is illustrated by the results for X_1, in Table II.

TABLE I. Eigenvalues for the Mathieu potential and its "muffin-tin" approximation.

State[a]	ϵ for[b] the Mathieu potential	ϵ for[b] the muffin-tin approximation
$\Gamma_1(1)$	-0.843	-0.810
$\Gamma_1(2)$	$+0.364$	$+0.335$
Γ_{15}	$+0.250$	$+0.254$
$X_{4'}$	-0.263	-0.215
X_1	-0.756	-0.730

[a] The notation used for the irreducible representations of the simple cubic lattice is that of L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

[b] The parameter ϵ is related to the energy eigenvalue through

$$E=(2\pi/a)^2\epsilon.$$

We may also illustrate the usefulness of perturbation theory in correcting the calculated eigenvalues for the difference between the crystal potential, in this case the Mathieu potential, and its muffin-tin approximation. For the lowest state at Γ_1 in Table I, we find by the methods of Sec. IV that the normalized wave function outside the inscribed sphere is given by (4.12) with $a^{\frac{3}{2}}F_n=0.302$, 0.048, and 0.007 for the reciprocal vectors $\mathbf{K}_n=0$, $(2\pi/a,0,0)$, and $(2\pi/a,2\pi/a,0)$, respectively. The first-order perturbation correction due to $\delta V(\mathbf{r})$ given by (6.6) is then found to be $\Delta\epsilon^{(1)}=(a^2/4\pi^2)\times\Delta E^{(1)}=-0.025$. This is small, as expected from the fact that V_c is chosen so that $\int\delta V d\tau=0$. To estimate the second-order correction we replace the energy denominator in the second-order perturbation formula by an average energy of excitation, $\langle E_n-E_0\rangle$, and sum over excited states, obtaining

TABLE II. Convergence of the X_1 eigenvalue for the "muffin-tin" approximation to the Mathieu potential.[a]

l	Order of matrix	ϵ
0	1×1	-0.723
2	2×2	-0.730
4	4×4	-0.730

[a] The parameter ϵ is related to the energy eigenvalue through

$$E=(2\pi/a)^2\epsilon.$$

$$\Delta E^{(2)}=\frac{4\pi^2}{a^2}\Delta\epsilon^{(2)}=-\frac{\{\langle 0|(\delta V)^2|0\rangle-(\langle 0|\delta V|0\rangle)^2\}}{\langle E_n-E_0\rangle}. \tag{6.7}$$

Taking for $\langle E_n-E_0\rangle$ the difference between the two lowest states of symmetry Γ_1, we find $\Delta\epsilon^{(2)}\approx-0.01$. Thus $\Delta\epsilon^{(1)}+\Delta\epsilon^{(2)}\approx-0.03$, while the difference between the exact and approximate lowest Γ_1 eigenvalues in Table II is $\Delta\epsilon=-0.033$.

The Mathieu potential is a severe test of the Green's function method because the exact potential is represented poorly by the muffin-tin approximation, particularly in the region outside the inscribed sphere where the Mathieu potential varies considerably with $\mathbf{r}$. Nevertheless, the eigenvalues for the muffin-tin potential listed in Table I are not greatly different from the exact values for the Mathieu potential and it appears from the results for $\Gamma_1(1)$ that this difference can be calculated correctly and conveniently by perturbation theory from the difference in the potentials. The crystal potential for a real solid should usually vary less outside the inscribed sphere than is the case for the Mathieu potential. Thus these results indicate that the

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[27] P. M. Morse, Phys. Rev. **35**, 1310 (1930); *Tables Relating to Mathieu Functions* (Columbia University Press, New York, 1951).

muffin-tin approximation should usually suffice to yield fairly accurate eigenvalues for crystal potentials encountered in practical calculations, and that improved accuracy can be achieved if the difference between the crystal potential and muffin-tin potential is corrected for by perturbation theory.

VII. CALCULATION OF THE STRUCTURE CONSTANTS

Ewald's Method

Practical use of the Green's function method requires accurate tabulation of the structure constants $\mathfrak{D}_{LJ}$ appearing in the expansion (2.18) for $G(\mathbf{r},\mathbf{r}')$. In order to achieve a desired accuracy of six significant figures, we have found it necessary to use the complete Ewald method including summations in both coordinate and reciprocal spaces. The use of reciprocal space alone as proposed by Kohn and Rostoker in Eq. (KR A2.10) requires an inconveniently large number of terms in the sum. We present in this section the complete Ewald procedure.

An alternative representation of $G(\mathbf{r},\mathbf{r}')=G(\mathbf{R})$, where $\mathbf{R}=(\mathbf{r}-\mathbf{r}')$, is (KR A2.20)

$$G(\mathbf{R})=-\frac{1}{4\pi}\sum_s \frac{\exp[i\kappa|\mathbf{R}-\mathbf{r}_s|]}{|\mathbf{R}-\mathbf{r}_s|}\exp(i\mathbf{k}\cdot\mathbf{r}_s), \quad (7.1)$$

where the sum is over all lattice sites $\mathbf{r}_s$, and κ is related to E by (2.14).

Following Ewald[28] we use the relation

$$\frac{\exp[i\kappa|\mathbf{R}-\mathbf{r}_s|]}{|\mathbf{R}-\mathbf{r}_s|} =\frac{2}{\sqrt{\pi}}\int_{0(C)}^{\infty}\exp[-(\mathbf{R}-\mathbf{r}_s)^2\xi^2+\kappa^2/4\xi^2]d\xi, \quad (7.2)$$

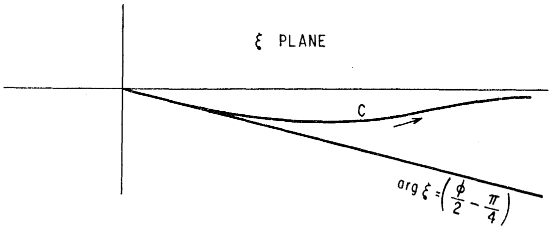

FIG. 1. Contour of integration C in complex ξ plane for integral in Eq. (7.2) of text; [$\phi=\arg\kappa$, $0<\phi<\pi$].

which follows by a simple transformation of an integral representation of the Hankel function $H_{-\frac{1}{2}}^{(1)}(z)$.[29] The contour of integration C in (7.2) is shown in Fig. 1, where $\phi=\arg\kappa$, and for the following manipulations we require that $0<\phi<\pi$. Thus we require that κ have a nonzero positive imaginary part in our derivation, but the final formulas are valid for arbitrary κ as may be proved by analytical continuation.

Distorting the contour of integration in (7.2) to run along the real axis beyond the point $\xi=\frac{1}{2}\eta^{\frac{1}{2}}$, where $\eta>0$ is arbitrary, we substitute from (7.2) into (7.1) and break each integral into two parts, $(0,\frac{1}{2}\eta^{\frac{1}{2}})$ and $(\frac{1}{2}\eta^{\frac{1}{2}},+\infty)$. $G(\mathbf{R})$ is thus expressed as the sum of two terms

$$G(\mathbf{R})=G_1(\mathbf{R})+G_2(\mathbf{R}). \quad (7.3)$$

An identity given by Ewald, which may be proved by Fourier analysis and is valid at each point along the contour $(0,\frac{1}{2}\eta^{\frac{1}{2}})$, then may be used to transform $G_1(\mathbf{R})$:

$$\textstyle\sum_s \exp[-(\mathbf{R}-\mathbf{r}_s)^2\xi^2+i\mathbf{k}\cdot(\mathbf{r}_s-\mathbf{R})] =(\pi^{\frac{3}{2}}/\tau\xi^3)\sum_n \exp[-(\mathbf{K}_n+\mathbf{k})^2/4\xi^2+i\mathbf{K}_n\cdot\mathbf{R}]. \quad (7.4)$$

We obtain, setting $E=\kappa^2$,

$$G_1(\mathbf{R})=-\frac{1}{\tau}\sum_n \frac{\exp[i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{R}]\exp\{[-(\mathbf{K}_n+\mathbf{k})^2+E]/\eta\}}{(\mathbf{K}_n+\mathbf{k})^2-E}, \quad (7.5)$$

$$G_2(\mathbf{R})=-\tfrac{1}{2}\pi^{-\frac{3}{2}}\int_{\frac{1}{2}\eta^{\frac{1}{2}}}^{\infty}\sum_s \exp[i\mathbf{k}\cdot\mathbf{r}_s-(\mathbf{r}_s-\mathbf{R})^2\xi^2+E/4\xi^2]d\xi. \quad (7.6)$$

These series converge absolutely for any finite $\eta>0$ and each term is an analytic function of E throughout the complex plane except at the simple poles of (7.5) at $E=(\mathbf{K}_n+\mathbf{k})^2$. Hence by analytical continuation, the sum of the series represents $G(\mathbf{R})$ for all E.

Expanding $G_1(\mathbf{R})$ and $G_2(\mathbf{R})$ termwise in spherical harmonics with respect to $\mathbf{R}$, and comparing with (2.18), we obtain

$$\mathfrak{D}_{LJ}=\mathfrak{D}_{LJ}^{(1)}+\mathfrak{D}_{LJ}^{(2)}+\mathfrak{D}_{00}^{(3)}\delta_{L0}. \quad (7.7)$$

Since $\mathbf{R}$ may be chosen arbitrarily in evaluating $\mathfrak{D}_{LJ}$, we take the limit $\mathbf{R}\rightarrow 0$, obtaining[30]

$$\mathfrak{D}_{LJ}^{(1)}=-(4\pi/\tau)\kappa^{-L}\exp(E/\eta) \times\sum_n \frac{|\mathbf{K}_n+\mathbf{k}|^L\exp[-(\mathbf{K}_n+\mathbf{k})^2/\eta]}{(\mathbf{K}_n+\mathbf{k})^2-E} \times\mathcal{Y}_{LJ}(\mathbf{K}_n+\mathbf{k}), \quad (7.8)$$

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[28] P. Ewald, Ann. Phys. 64, 253 (1921).

[29] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, New York, 1944), 2nd ed., p. 178, Eq. (4).

[30] Formulas equivalent to these have been derived also by Morse (reference 6).

$$\mathfrak{D}_{LJ}^{(2)}=\pi^{-\frac{1}{2}}(-2)^{L+1}i^{L}\kappa^{-L}\sum_{s}{}' r_s{}^{L}\exp(i\mathbf{k}\cdot\mathbf{r}_s)\mathcal{Y}_{LJ}(\mathbf{r}_s)\times\int_{\frac{1}{2}\eta^{\frac{1}{2}}}^{\infty}\xi^{2L}\exp\left[-\xi^2 r_s{}^2+\frac{E}{4\xi^2}\right]d\xi, \quad (7.9)$$

$$\mathfrak{D}_{00}^{(3)}=-\frac{\eta^{\frac{1}{2}}}{2\pi}\sum_{s=0}^{\infty}\frac{(E/\eta)^s}{s!(2s-1)}, \quad (7.10)$$

where in the summation in $\mathfrak{D}_{LJ}^{(2)}$ the term $\mathbf{r}_s=0$ is to be omitted. In deriving these results we have combined the term in $[(\cos\kappa R)/R]$ obtained from (2.18) for $L=0$ with the $\mathbf{r}_s=0$ term of $G_2(\mathbf{R})$ in (7.6). The singularities in each of these terms as $R\rightarrow 0$ cancel when they are combined, and $\mathfrak{D}_{00}^{(3)}$ in (7.10) results.

A similar derivation yields corresponding expressions for the structure constants of "complex" lattices,[22] or for the functions $\mathfrak{D}_{LJ}(\mathbf{r})$ introduced in (4.9) and (4.10) to express the wave function outside the inscribed sphere. For the latter we find $\mathfrak{D}_{00}^{(3)}(\mathbf{r})=0$ and

$$\mathfrak{D}_{LJ}^{(2)}(\mathbf{r})=\pi^{-\frac{1}{2}}(-2)^{L+1}i^{L}\kappa^{-L}\times\sum_s|\mathbf{r}_s-\mathbf{r}|^{L}\exp(i\mathbf{k}\cdot\mathbf{r}_s)\mathcal{Y}_{LJ}(\mathbf{r}_s-\mathbf{r})\times\int_{\frac{1}{2}\eta^{\frac{1}{2}}}^{\infty}\xi^{2L}\exp\left[-\xi^2(\mathbf{r}_s-\mathbf{r})^2+\frac{E}{4\xi^2}\right]d\xi, \quad (7.11)$$

where the sum is over all $\mathbf{r}_s$, including $\mathbf{r}_s=0$. $\mathfrak{D}_{LJ}^{(1)}(\mathbf{r})$ is given by (4.10) if the convergence factor

$$\exp\{[-(\mathbf{K}_n+\mathbf{k})^2+E]/\eta\}$$

is inserted in each term of the sum, and the limit $s\rightarrow 0$ taken.

Symmetry of Structure Constants

Setting $\mathbf{R}=(\mathbf{r}-\mathbf{r}')$, we see from (2.4) and (2.6) that $G(-\mathbf{R})=G^*(\mathbf{R})$. Since the $\mathcal{Y}_{LJ}(\mathbf{R})$ were chosen to be real, it follows from (2.18) that $\mathfrak{D}_{LJ}$ is real for $E>0$ and that $i^L\mathfrak{D}_{LJ}$ is real for $E<0$. Accordingly in (7.9) we may replace $i^L\exp(i\mathbf{k}\cdot\mathbf{r}_s)$ by $[\pm\cos(\mathbf{k}\cdot\mathbf{r}_s)]$ or $[\pm\sin(\mathbf{k}\cdot\mathbf{r}_s)]$ according as L is even or odd. [For "complex" lattices, $\mathfrak{D}_{LJ}$ is in general complex.]

It is evident from (2.4) that $G(\mathbf{S}\mathbf{R})=G(\mathbf{R})$ if the operator $\mathbf{S}$ is any symmetry operator belonging to the group of the wave vector $\mathbf{k}$. From (2.18) it then follows that only those $\mathfrak{D}_{LJ}$ are different from zero which correspond to a $\mathcal{Y}_{LJ}(\mathbf{R})$ belonging to the symmetric representation of the group of $\mathbf{k}$. This fact can be used to greatly reduce the number of independent $\mathfrak{D}_{LJ}$ that need be computed if the group of $\mathbf{k}$ contains more than the identity operator.

VIII. DISCUSSION

Our experience with the Green's function method from our work on the alkali metals[1] and aluminum[2] has borne out Kohn and Rostoker's expectation that the method converges rapidly as terms with increasing l are added to the trial function. We have found that a trial function including all independent terms with $l=0$, 1, 2 that are allowed by symmetry generally suffices to give an eigenvalue for the muffin-tin potential accurate to at least ±0.002 rydberg for states in the conduction bands of these metals. This is similar to the accuracy found in this paper for the Mathieu potential. At symmetry points (for example Γ, H, P, and N in a bcc lattice) where for $l\leq 2$ there are at most two independent terms, this accuracy can thus be achieved very simply since it requires at most a second-order determinant. Along symmetry axes such as [100], [111], and [110], and along certain lines in the Brillouin zone surface, three or four independent terms suffice for this accuracy. Such calculations can be done quite easily without the help of anything more than a desk calculator, once tables of the structure constants have been prepared and suitable radial functions obtained. Points of lower symmetry in the zone of course require more terms and are best done with the assistance of an automatic digital computer, but even for these the number of terms required for good accuracy is comparable to that required at symmetry points in a calculation by the orthogonalized plane wave method. Usually the simpler calculations on symmetry points and lines suffice to give valuable insight into the electronic structure. If a suitable interpolation formula is available, it is possible to get from these alone a good quantitative understanding of the entire band.

For states in unoccupied bands above the conduction bands, corrections due to terms with $l\geq 3$ increase with increasing energy. Many such states at symmetry points, however, require no more than 3 or 4 terms in the trial function for the accuracy discussed above. The ultimate accuracy that can in any case be obtained by adding terms to the trial function is limited by the accuracy with which interpolation of the determinants can be carried out between the energies at which the structure constants have been tabulated. Using a tabulation interval of $\Delta\epsilon=(a/2\pi)^2\Delta E=0.0333$ in most of our work, we estimate that interpolation can usually be made accurate to $\Delta\epsilon=\pm 0.001$.

Wave functions may also be calculated from the Green's function method, and the results using the procedure we have outlined have been gratifying in their convergence. Inside the inscribed sphere, the coefficients of the s, p, and d terms in the spherical harmonic expansion of the wave function of a conduction band state can be obtained with an accuracy which we estimate for the alkali metals and aluminum to be usually within 5%. If one of the coefficients is small compared to the others however, as in the case of $l\geq 3$ for conduction band states, or $l=1$ or 2 for $\mathbf{k}$ near $\mathbf{k}=0$, then the relative accuracy with which it is given is poorer. Outside the inscribed sphere the wave function is given as a Fourier series. We have found that the coefficients are reasonably small except for those plane waves having $(\mathbf{K}_n+\mathbf{k})^2$ close to the calculated energy eigenvalue. Thus a few plane waves usually suffice to represent $\psi(\mathbf{r})$ in this outer region, provided we use the "best" of the many equivalent Fourier series in this region, with the "best" series chosen as discussed in Sec. IV.

Explicit examples of the convergence of eigenvalues and wave functions are given in our papers reporting the results for the alkali metals and aluminum.

The Green's function method offers substantial advantage in a number of respects over other methods that have been described in the literature. Since it imposes via the Green's function the correct periodicity boundary conditions for the polyhedral unit cell, the method makes available results on distortions in energy band shapes, particularly near the zone surface, that cannot be provided by the widely used Wigner-Seitz method.[16] This latter replaces the boundary conditions on the polyhedral cell by similar conditions on the equivalent sphere and thus insures that the resulting bands will be spherical. Although usually an accurate method for obtaining the energy and effective mass of the conduction band of a metal at $\mathbf{k}=0$ (as we have verified with the Green's function method[1]), the Wigner-Seitz method thus cannot be used without substantial modification to obtain desirable information on the shape of the Fermi surface and the various band gaps at the zone faces.

Other cellular methods such as those proposed by Slater,[12] Kohn,[15] and Howarth and Jones,[14] either require the tedious evaluation of surface integrals over the cell surface or use the correct boundary conditions at only a few selected points on the cell surface. In the latter case the results have proved to be rather sensitive to the selection used, and in all the cellular methods there is good reason to doubt that the usual spherical harmonic expansion of the wave function converges in the part of the cell outside the inscribed sphere.[18] The Green's function method uses such an expansion only within the inscribed sphere, where it is unquestionably valid with a muffin-tin potential.

The convergence of the Green's function method is much better than that reported in published calculations with other methods that take account of the polyhedral shape of the unit cell, notably the orthogonalized plane wave (OPW) method. This is true even if core functions needed in the OPW method have been carefully determined to be appropriate to the crystal potential; if inaccurate core functions are used the OPW convergence is very much further worsened. Recent work[9] with forms of the augmented plane wave (APW) method, however, reportedly exhibits convergence comparable to that of the Green's function method, although hand calculations at symmetry points would appear easier with the latter if structure constant tables are available. Calculations have usually heretofore been limited to points of fairly high symmetry, in order to reduce to a manageable number the terms in the wave-function expansion needed for adequate convergence. Because of the rapid convergence of the Green's function method, calculations are practicable at general points in the Brillouin zone, although a stored-program computer is usually necessary for such work.

A great advantage of the Green's function method over all other methods, as pointed out by Kohn and Rostoker, is that much of the work in using the method is done once and for all for a particular lattice structure when tables of the structure constants, $\mathfrak{D}_{LJ}$, have been prepared for suitable values of $\mathbf{k}$ and E. These have proved rather more difficult to calculate than was believed at the time of Kohn and Rostoker's proposal of the method, as rather extensive tabulations have been required, and the infinite series for $\mathfrak{D}_{LJ}$ converges too slowly to give adequate accuracy unless the Ewald procedure is used and the sums in both spaces evaluated. But with the availability of high-speed digital computers with a large rapid-access memory, such as the IBM 704, the structure constants now can be computed readily.

The Green's function method, as well as the APW method (and in a rigorous formulation all cellular methods too), is convenient to use only with solids in which the potential can be approximated by one in the muffin-tin form. While the OPW method has the apparent advantage that the potential is not restricted to any particular form, this is offset by its relatively slow convergence and the need for accurate knowledge of the core states. For most solids of interest it should be possible to choose a muffin-tin potential that approximates the crystal potential sufficiently closely to permit correcting for the difference by perturbation theory. The muffin-tin potential need not be continuous at the inscribed sphere, so that it may be chosen in each region as in Sec. V to equal a suitable average in that region of the actual potential. As we have seen in Sec. VI, even for the Mathieu potential the difference between the exact eigenvalues and those obtained for the muffin-tin approximation is not large and is adequately corrected for by perturbation theory. A self-consistent potential for most solids departs relatively less from its muffin-tin approximation than is the case for the Mathieu potential. This is particularly so for a metal since for the latter the conduction electrons act to screen the electric field due to an ion within a distance typically $\frac{1}{3}$ to $\frac{1}{2}$ the lattice constant. Estimates of the perturbation corrections for occupied states in aluminum[2] using Heine's self-consistent potential, are only of the order 0.01 ry. In practice, of course, a self-consistent potential is not yet known with any reliability for most solids, and the region of principal uncertainty is the cell corners. Use of a suitable "muffin-tin" potential is therefore likely to be as accurate, particularly in metals, as other approximate potentials that have been used in calculations, and as our knowledge of potentials improves, perturbation theory should provide a means of making the necessary corrections.

We conclude, then, that the Green's function method is one of the most accurate and rapidly converging methods available for calculating eigenvalues and wave functions in solids. Structure constants may be calculated readily using the formulas developed in this paper, or in special cases are now tabulated and available from the authors. The further calculation of eigenvalues and wave functions for particular solids then may be carried out using the procedures we have outlined, and at many points and lines of symmetry in the Brillouin zone this work can be done with the use of only a desk calculator.

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APPENDIX I. PROOF OF SERIES SOLUTION FOR COEFFICIENTS C_q

We prove here that (4.3) is the solution of the first $(n-1)$ linear equations (4.1) if we set $C_1=1$ as in (4.2). We drop the equation with $i=n$ in (4.1), this being the one added in extending the trial function from $(n-1)$ to n independent terms. From Cramer's rule[31] and some simple manipulation of the determinants, we have

$$C_q=E_{nq}/K_n,\quad q=2,\cdots n \tag{A1.1}$$

where

$$E_{nq}=\begin{vmatrix} \Lambda_{12} & \cdots & \Lambda_{1q} & \cdots & \Lambda_{1n} & \Lambda_{11} \\ \Lambda_{22} & \cdots & \Lambda_{2q} & \cdots & \Lambda_{2n} & \Lambda_{21} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \Lambda_{n-1,2} & \cdots & \Lambda_{n-1,q} & \cdots & \Lambda_{n-1,n} & \Lambda_{n-1,1} \\ 0 & \cdots & 1 & \cdots & 0 & 0 \end{vmatrix}. \tag{A1.2}$$

The last row of E_{nq} has all zeros except for 1 in the column containing Λ_{iq}. We now apply a theorem of determinant theory[32] to the 2-rowed minor in the lower right corner of E_{nq}: "If D' is the adjoint of any determinant D, and M and M' are corresponding m-rowed minors of D and D', respectively, then M' is equal to the product of D^{m-1} by the algebraic complement of M." Using definitions of L_m, K_m, and H_{mq} given in Sec. VI, we have

$$E_{nq}K_{n-1}=\begin{vmatrix} E_{n-1,q} & -H_{nq} \\ L_{n-1} & K_n \end{vmatrix}, \tag{A1.3}$$

whence

$$\frac{E_{nq}}{K_n}=\frac{E_{n-1,q}}{K_{n-1}}+\frac{H_{nq}L_{n-1}}{K_nK_{n-1}}. \tag{A1.4}$$

Applying this recurrence relation for E_{mq}/K_m repeatedly, we obtain from (A1.4)

$$\frac{E_{nq}}{K_n}=\frac{E_{qq}}{K_q}+\sum_{m=q+1}^{n}\frac{H_{mq}L_{m-1}}{K_mK_{m-1}}, \tag{A1.5}$$

From (A1.2) and (4.4) we find that

$$E_{qq}=-L_{q-1}. \tag{A1.6}$$

The desired equation (4.3) follows from (A1.1), (A1.5), and (A1.6).

APPENDIX II. DEVIATIONS OF LATTICE SUM POTENTIAL FROM MUFFIN-TIN FORM

If the actual crystal potential is given by (5.10), we have in (5.1)

$$V_l(r)=(1/4\pi)\sum_s\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta d\theta L_l(\mathbf{r})U(|\mathbf{r}-\mathbf{r}_s|). \tag{A2.1}$$

We find

$$V_0(r)=U(r)+\frac{1}{2rr_s}\sum_s{}'\int_{r_s-r}^{r_s+r}\xi U(\xi)d\xi, \tag{A2.2}$$

and

$$V_l(r)=\frac{1}{2rr_s}\left(\frac{2l+1}{4\pi}\right)^{\frac{1}{2}}\sum_s{}'\alpha_{l0}{}^{(s)}\int_{r_s-r}^{r_s+r}\xi U(\xi)\times P_l\left(\frac{r^2+r_s{}^2-\xi^2}{2rr_s}\right)d\xi, \tag{A2.3}$$

where $P_l(x)$ is the Legendre polynomial of degree l, and the prime on the sum means that $\mathbf{r}_s=0$ is omitted. The coefficient $\alpha_{l0}{}^{(s)}$ is that of $[(2l+1)/4\pi]^{\frac{1}{2}}P_l(\cos\theta)$ in the expansion of $L_l(\theta,\varphi)$ in terms of normalized spherical harmonics with polar axis taken along $\mathbf{r}_s$. For a face-centered cubic crystal and "Kubic harmonics" as defined by von der Lage and Bethe,[13] we have for the nearest-neighbor sites, in the [110] directions,

$$\alpha_{40}=-(1/4)(7\pi/3)^{\frac{1}{2}},\quad \alpha_{60}=-(13/16)(2\pi)^{\frac{1}{2}}. \tag{A2.4}$$

Only these sites will contribute appreciably to $V_l(r)$ if $U(r)$ falls off sufficiently rapidly with increasing r to be negligible beyond adjacent cells.

The constant potential V_C is found from (5.4) to be given by

$$[\tau-(4/3)\pi r_i{}^3]V_C=4\pi\int_0^\infty r^2U(r)dr-4\pi\int_0^{r_i}r^2V_0(r)dr. \tag{A2.5}$$

The coefficients δV_m in the Fourier series (5.5) for $\delta V(\mathbf{r})$, valid throughout the cell, is

$$\delta V_m=(4\pi/\tau)\int_0^\infty U(r)j_0(K_mr)r^2dr-(4\pi/\tau)\int_0^{r_i}V_0(r)j_0(K_mr)r^2dr+(4\pi/\tau)(V_c/K_m)r_i{}^2j_1(K_mr_i)-V_c\delta_{m0}. \tag{A2.6}$$

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[31] M. Bocher, *Introduction to Higher Algebra* (The Macmillan Company, New York, 1907), p. 43.

[32] Reference 31, p. 31.