Composite Wave Variational Method for Solution of the Energy-Band Problem in Solids*

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A method of solving the band problem is developed and applied which makes use of a composite representation of the wave function and of a variational expression for the energy applicable to trial functions with discontinuities in their values and derivatives on a surface within the cell. The composite representation consists of spherical waves belonging to the given potential within the inscribed sphere, and symmetrized combinations of plane waves for the given k outside the inscribed sphere. The potential is assumed spherical within the inscribed sphere but not outside. The calculated energy is variational even when the spherical waves are computed with trial energies differing from the true energy; hence, the process of iterating on the trial energies is strongly convergent. Results are obtained with the flattened Seitz potential for Li and the flattened Prokofiev potential for Na at many points, including points of general k. The Li energies check with high-precision values obtained independently, give a Fermi level at −0.429 eV and a Fermi surface that bulges toward, but does not touch, the zone face in the [110] direction. Comparisons are made with a number of other recent methods of solving the band problem.

I. INTRODUCTION

THE work reported here is a contribution to the solution of the band problem, namely to the determination of the one-electron energies and wave functions in a prescribed one-electron periodic potential. The importance of the band problem and its complexities are sufficiently great to have made it the subject of a long and continuing series of investigations by many workers,[1] quite apart from the complications of many-body effects and electron-phonon interactions. However, only recently have methods been developed and applied which, with the aid of high-speed digital computers, give accurate solutions to a reasonably general, although not completely general,[2] form of the band problem. Noteworthy examples of these recent methods are given in the calculations by Ham and Segall,[3] by Ham,[4] and by Segall[5] using the Green's-function method as developed by Kohn and Rostoker,[6] and the calculations with the augmented plane-wave method (APW) suggested by Slater[7] and applied in

recent years by Saffren,[8] Burdick,[9] Wood,[10] and other members of the MIT group. The common feature of these methods and the method of this paper is the power to solve the band problem with high precision, even for general values of k, the vector wave number characterizing the solutions (see Sec. II.1), hence, not aided by special symmetry. Unlike many of the older methods, they are, in principle, capable of an indefinite amount of refinement merely by adding more terms to the representation.

The method of this paper may conveniently be classified as one of a group of methods arising from the original APW.[7] The group is characterized by the use of a composite or dual representation of the wave function consisting, on the one hand, of a plane-wave expansion in the outer part of the atomic cell, which includes the boundary, and on the other hand, of an expansion in spherical waves in the inner part of the cell near the nucleus, more suited to represent the rapid oscillations of the wave function there. The various members of the group differ in the choice of the spherical wave functions, in the procedure for fixing the coefficients of the expansions, and in the exact form of the matrix elements of the secular equation. This group of methods then includes the original APW,[7–10] the APW method in the 1953 papers of Slater and Saffren,[11] and its application by Howarth,[12] the new APW procedure suggested by Saffren in his thesis,[8,13] the method of Leigh,[14] and the method of

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[1] For recent reviews, see L. Pincherle in *Reports on Progress in Physics* (The Physical Society, London, 1960), Vol. 23, p. 355; J. Callaway in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 100; J. C. Slater in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 1.

[2] The high-precision calculations assume the potential is spherically symmetric inside the inscribed sphere, and constant in the cell outside the inscribed sphere.

[3] F. S. Ham and B. Segall, Phys. Rev. **124**, 1786 (1961).

[4] F. S. Ham, Phys. Rev. **128**, 82 (1962); *ibid.* **128**, 2524 (1962).

[5] B. Segall, Phys. Rev. **124**, 1797 (1961).

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

[7] J. C. Slater, Phys. Rev. **51**, 846 (1937).

[8] M. M. Saffren, Ph.D. thesis, MIT, 1959 (unpublished).

[9] G. A. Burdick, Phys. Rev. Letters **7**, 156 (1961).

[10] J. H. Wood, Phys. Rev. **126**, 517 (1962).

[11] J. C. Slater, Phys. Rev. **92**, 603 (1953); M. M. Saffren and J. C. Slater, *ibid.* **92**, 1126 (1953).

[12] D. J. Howarth, Phys. Rev. **99**, 469 (1955).

[13] M. M. Saffren, in his thesis (Ref. 8), has moved toward the viewpoint of the composite representation. In Sec. 6 of the thesis,

Brown and Krumhansl,[15] as well as the method of this paper. It does not include the various cellular methods,[1] the Green's-function method,[3,6] and the orthogonalized plane wave (OPW) method,[1] which does not use a composite representation, but expands in a single set of functions obtained by orthogonalizing to prescribed core-state functions.

To introduce the new features of the method of this paper, we briefly compare it first with the original APW method and then with Leigh's method which anticipates a number of the new features; a more extended comparison appears in Sec. II.5. We first observe that the formulation of our method eliminates the intermediate stage in which augmented plane waves in a composite form are first constructed, and then the total wave function is expanded in these functions; rather we proceed directly to represent the total wave function in composite form. We then pay close attention to preserving the strict variational character of the expression for the energy with the actual trial wave function. Hence, we allow for discontinuities in the function, as well as its gradient, on the surface of separation between regions, and we take account of the use of approximate trial energies in the evaluation of radial functions in the inner expansion. These considerations lead to a secular equation with matrix elements which differ in three ways from those of the original APW; namely, (1) terms arising from the use of a general potential rather than one flattened in the outer region, (2) terms arising from the discontinuity in the trial wave function (a consequence of the finiteness of the spherical wave expansion), and (3) terms arising from the use of trial energies in the radial functions, which terms are linear in the difference of the trial energy from the variational energy (the root of the secular equation). Leigh also proceeds from a variational expression which allows for discontinuous trial wave functions, but is somewhat different from ours, and uses a general, nonflattened potential; his final matrix elements contain the terms of type (1) above, but only part of the terms of type (2), and none of the terms of type (3).

In Sec. II.1, the band problem is defined and stated as a cellular problem. In II.2 the idea of the composite expansion as a way of dealing with the difficulties of the band problem is developed, the strict variational point of view is introduced, and the idea of using discontinuous trial functions is discussed and defended. For the derivation of variational expressions, reference

is made to Appendix 1, where suitable variational expressions are obtained which have the desirable property of always giving real values of the energy. It is shown there that the energy expression of the APW is in fact variational when the trial function is continuous across the separation surface (but not necessarily its gradient). In Sec. II.3 the derivation of the secular equation is discussed, and the form of the matrix elements is described. Their simplicity is remarked on, and the fact that the eigenvalues depend only on logarithmic derivatives of the radial functions. Reference is made to Appendix 2 for the mathematical details and explicit formulas. The solution of the secular equation is described in II.4, with particular emphasis on the rapidly convergent procedure for finding the root, based on a variational expression for the energy even when calculated with estimated values of the energies of the spherical waves. The convergence is illustrated for a point in Li. Detailed comparison with other methods is given in II.5, particularly with the APW.

Section III describes the application of the method to Li and Na using the well-known potentials for these materials. Energies are found at many points in the Brillouin zone, including general points of $\mathbf{k}$. The potentials used are described in III.1, and a tabulation of their Fourier coefficients is in Table I. The energy bands obtained for Li are given in III.2, where quantitative comparison with the results of other workers is made; agreement to four figures is obtained with the values of Kohn and Rostoker.[6] From the calculated Li energies near the Fermi energy, the shape of the energy surfaces and the position of the Fermi surface are estimated by a systematic procedure using up to six kubic harmonic angular functions to represent a constant energy surface; for the potential used, the Fermi surface does not contact the zone face. The results for Na given in III.3 are similar and compare closely with results of other workers, although high-precision comparison is not available.

II. A COMPOSITE WAVE VARIATIONAL METHOD

1. The Energy-Band Problem

For a given one-electron potential energy function, $V(\mathbf{r})$, periodic in a given space lattice, i.e., $V(\mathbf{r}+\mathbf{R}_l) = V(\mathbf{r})$, where $\mathbf{R}_l$ is a lattice translation vector (an integral linear combination of the primitive translations, $\mathbf{a}_i$, $i = 1, 2, 3$), we seek those solutions of the Schrödinger equation,[16]

$$H\psi(\mathbf{r}) = [-\nabla^2 + V(\mathbf{r})]\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r}), \qquad (1)$$

which are satisfactory for describing bulk properties of the solid. With the use of periodic boundary conditions on the crystal,[17] the problem may be reduced to finding the solutions of (1) in a single primitive cell of the

he considers a composite basis of plane waves and spherical waves. However, his spherical waves are solutions of the Schrödinger equation which vanish on the surface of separation (the inscribed sphere), hence, each has a different, fixed energy, and the radial functions form a doubly indexed discrete infinity of functions $\mathfrak{R}_{nl}(r, \epsilon_{nl})$, whereas our radial functions all have the same energy, as determined by the solution of the secular equation, and thus are singly indexed functions $\mathfrak{R}_l(r, \epsilon)$ [see Sec. II.5].

[14] R. S. Leigh, Proc. Phys. Soc. (London) **69**, 388 (1956).

[15] E. Brown and J. A. Krumhansl, Phys. Rev. **109**, 30 (1958), E. Brown, *ibid.* **126**, 421 (1962).

[16] The usual units of energy band calculations are used, energies in rydbergs, and lengths in atomic units (a.u.), i.e., Bohr radii.

[17] See, for example, J. C. Slater, Ref. 1, p. 13.

lattice which satisfy the cellular boundary conditions given in (2). The cellular boundary conditions linearly relate values of ψ and its normal derivative at conjugate points of the boundary of the primitive cell; i.e., boundary points r_c and r_c+a_i separated by a primitive translation vector of the lattice a_i (see Fig. 1).

$$\psi(r_c+a_i, \ k) = e^{ik\cdot a_i}\psi(r_c,k) , \tag{2a}$$

$$\partial_{n_c}\psi(r_c+a_i, \ k) = -e^{ik\cdot a_i}\partial_{n_c}\psi(r_c,k) . \tag{2b}$$

In Eq. (2), n_c refers to the outward normal on the cell boundary, and the solutions are classified by the wave vector, k, which gives the change in phase of the wave function and its gradient on crossing the cell; namely, $k\cdot a_i$. This is the same change of phase shown by any of the plane waves $e^{ik_n\cdot r}$, where $k_n=k+K_n$, and K_n is a reciprocal lattice vector.[18] Since addition of any K_n to k leaves the boundary conditions unchanged, all the values of k giving distinct solutions are in a single primitive cell of the reciprocal lattice, usually chosen as the first Brillouin zone.[19]

Thus, the basic problem is the solution of the second-order, linear, homogeneous differential equation (1) in a polyhedral region, subject to the homogeneous boundary conditions (2); hence, for each k, the solutions form a discrete set of eigenfunctions $\psi_\nu(r,k)$, and the corresponding eigenvalues give the energies $\epsilon_\nu(k)$. For each value of the band index, ν, the energy as a function of k is referred to as the νth energy band. The difficulties in finding the energies and wave functions arise partly from the complicated shape of the boundary and partly from the singular nature of the potential near each nucleus; there is also the added labor of dealing with complex functions.

## 2. The Composite Wave Representation and Variational Procedures

Most methods of solving the band problem are designed to deal easily with one of the two difficulties noted above, and then must struggle with the other. On the one hand, the difficult boundary conditions are immediately satisfied by an expansion in the plane waves $e^{ik_n\cdot r}$, each of which satisfies (2), and which form a complete set of basis functions for functions satisfying (2). Unfortunately, such an expansion does not converge well enough near the nucleus, where the wave function is changing rapidly, to give an accurate representation in a practicable number of terms.[20] On

FIG. 1. Cross section of unit lattice cell with outer surface S_c, showing separation into inner and outer regions Ω_i and Ω_o by the inner surface S; n and n_c are the unit outward normals to the inner and outer surfaces, respectively; r_c and r_c+a_i are a pair of opposite points on the cell boundary separated by a lattice translation vector a_i.
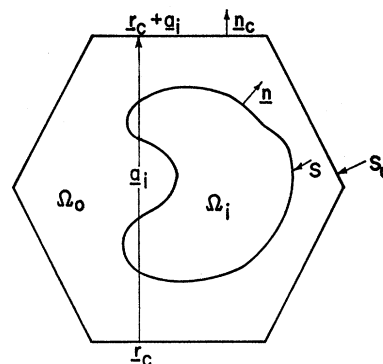
the other hand, expansions in spherical wave solutions of (1), (for a spherically symmetric potential and a definite energy), have trouble systematically satisfying (2), since the boundaries are not adapted to spherical coordinates. In addition, a more fundamental difficulty arises from the nonspherical nature of the potential in the outer part of the cell. Although $V(r)$ is nearly spherical near the nucleus it may differ substantially from spherical in the outer part of the cell near the cell boundary; indeed, the potential cannot be defined as spherical beyond the inscribed sphere.[21] Thus, a sphere larger than the inscribed sphere is partly in other cells and on the parts in other cells the potential will not be constant. Where the potential fails to be spherical, the original expansion fails to represent the wave function.[22]

A natural way of meeting both difficulties at once is to use both representations, each in the region in which it is most suitable, a representation conveniently termed a composite representation. However, it is then necessary to consider the new problem of determining the true energy from trial wave functions which have discontinuities in both the function and its gradient on the surface of separation between the regions. Now, the most efficient way to find a sequence of approximations to the energy using trial functions given in the composite representation, or, in fact, given in any representation, is to use a variational expression for the energy. This yields energies whose deviations from the true value are second order when the deviations of the wave function from the true function are first order; hence, when a sequence of variational energies is used in a systematic iterative procedure, one is quickly led to the correct solution.

In Appendix I, we consider at length the form of a variational expression for the energy suitable for trial functions discontinuous on a surface. Such variational

[18] Reference 17, p. 9; actually K_n is 2π times the reciprocal lattice of crystallography.

[19] Reference 17, p. 10; usually the first Brillouin zone is simply referred to as the Brillouin zone. Sections of the first Brillouin zone for the bcc lattice are shown in Figs. 5 and 6.

[20] This difficulty has been recognized since such expansions were first tried. The authors made some recent studies of the limitations on plane wave expansions which were reported briefly in Bull. Am. Phys. Soc. 4, 276 (1959), and are described at greater length in Ref. 26. A typical result is that by taking advantage of high-speed computers and modern methods of computing eigenvalues, the equivalent of 1055 plane waves can be used at the Γ_1 point.

This gave an energy within 5% of the correct value for Li, but was much worse for Na. The results at points of non-S character were better.

[21] Considering now the simple case of a monatomic Bravais lattice in which each nucleus is at the center of the primitive cell.

[22] Pointed out by F. Ham in The Fermi Surface, edited by Harrison and Webb (John Wiley & Sons, Inc., New York, 1960), p. 14.

expressions are found with the useful property of always yielding real values for the variational energy, ϵ_v. All these expressions require surface integrals over the discontinuity surface. However, if the class of trial functions is restricted to functions which have discontinuities on a surface only in the gradient, but the function is continuous there, then the form (A1.9) contains only a volume integral (of $|\nabla\psi|^2$) and is similar to that used in the development of the APW method.[23]

Objections are sometimes raised against the use of discontinuous functions as approximations to the wave function. For example, it is remarked that such functions are not admissible solutions of the Schrödinger equation, or that the Laplacian operator is singular at the discontinuity, so that variational expressions containing the Laplacian seem to be not well-defined. In reply, we note first that the discontinuous functions are being used merely as a computational device to approximate and approach the correct wave function which is, of course, continuous. Second, we note that the Laplacian is never applied at the discontinuity, but that in (A1.10), for example, the Laplacian is applied separately in Ω_i and Ω_o, in each of which the trial function is continuous. Finally, we note that the idea of using discontinuous trial functions has been successfully applied before, particularly by Kohn. Kohn[24] gives and tests a variational expression for band energies, adapted to the use of trial wave functions which do not satisfy the cellular boundary conditions (2); hence, these functions are discontinuous at the cell boundary. The variational expressions applied here generalize Kohn's expressions to hold for discontinuities on an arbitrary surface within the cell, and in fact (A1.10) goes over to the Kohn variational expression when $\Omega_o \to 0$, and S approaches the cell boundary.[25] Subsequently, Kohn and Rostoker[6] gave a quite different variational expression for the energy, also adapted for functions which do not satisfy (2), involving the lattice Green's function, and applied it in the Green's-function method of calculation of energy bands. Leigh[14] also generalizes Kohn's expressions to apply to functions discontinuous on a surface in the cell and discusses application to the calculation of eigenvalues.

3. Derivation and Structure of the Secular Equation

The determinantal secular equation for the energies is determined by a Rayleigh-Ritz procedure in which a trial wave function made up of a finite linear sum of suitable functions with undetermined coefficients is substituted in a variational expression for the energy, and equations for the coefficients are obtained from the

condition that the energy be stationary as a function of the finite set of coefficients. The wave function is taken in the composite form, i.e., a linear combination of N plane waves belonging to the given lattice and to the given $\mathbf{k}$ forms the outer trial function, while a linear combination of spherical waves out to order L, each belonging to a spherically symmetric potential within the sphere forming the inner region and each belonging to a trial energy ϵ_0, constitutes the inner trial function; the variational expression used is either (A1.10) or (A1.11), each of which contains volume integrals over the two regions, surface integrals over the spherical separation surface, S, and an operation of taking a real part. The somewhat lengthy details are given in Appendix 2, and we shall only comment here on the assumptions, on some special features of the derivation, and on the form of the results, giving references to the equations in Appendix 2.

A simplification is produced by an additional assumption which expresses the spherical-wave expansion coefficients linearly in terms of the N-plane-wave expansion coefficients A_n. It is assumed that the spherical waves out to order L of the inner trial function are equal on S, term by term, to the first L spherical wave components of the plane-wave expansion of the outer wave function (which, as given in (A2.3), depend only on ordinary Legendre functions, not associated functions, and on the spherical Bessel functions), i.e., that the inner and outer wave functions are matched to Lth order in spherical-harmonic expansion on S. This is not the only way the coefficients could be related. Normal derivatives, for example, could be similarly matched, or a homogeneous combination of function and derivative could be matched. However, matching in value on the sphere seemed simplest and the other possibilities mentioned above have not been examined in detail. As a result of this assumption, there are only N-independent expansion coefficients, and the secular equation will be of Nth order.

Since all terms of the variational expression are quadratic in the wave function, substitution of the composite expansion yields a linear equation, (A2.25), for ϵ_v, the variational approximation to the energy, all terms of which are quadratic in the A_n (actually bilinear in A_n^* and A_n). The explicit forms of the coefficients of the quadratic terms, referred to as matrix elements, are given in (A2.26) to (A2.29); the forms depend on the assumption that $V(\mathbf{r})$ is spherically symmetric in S, but not outside S; this assumption could be removed, in which case additional volume integrals appear in the matrix elements.[26] Before the final step using the variational character of ϵ_v, the operation of taking the real part must be carried out; in general, this requires making the matrix elements symmetric in the indexes $\mathbf{n}, \mathbf{n}'$ (although not if $L \to \infty$); the final index-symmetric

[23] J. C. Slater, Ref. 7, who does not discuss the variational character of the expression.

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

[25] Another way of stating this is that we allow trial wave functions which do not satisfy the *internal* boundary conditions of continuity of the function and its normal derivative on an internal boundary surface.

[26] A discussion of the nonspherical case is given in the unpublished Ph.D. thesis by H. Schlosser, Carnegie Institute of Technology, 1960 p. 28.

matrix elements are given in two forms in (A2.31), (A2.32).

Finally, holding ϵ_v stationary as the A_n and $A_{n'}{}^*$ are varied, yields homogeneous linear equations for the A_n, (A2.33); the condition for existence of a nonzero solution, the vanishing of the determinant of coefficients, then gives the secular equation

$$|H_{nn'}{}^{(s)}(\epsilon_0) - \epsilon_v D_{nn'}(\epsilon_0)| = 0. \tag{3}$$

The matrix elements in (3) depend on three types of quantities: (1) the logarithmic derivatives of the radial functions at $r = r_i$, $\mathcal{L}_{l\epsilon_0 i} = \mathcal{R}_l{}'(r_i,\epsilon_0)/\mathcal{R}_l(r_i,\epsilon_0)$, and their energy derivatives, $\partial \mathcal{L}_{l\epsilon_0 i}/\partial\epsilon_0$; [related to the integrals $I_{l\epsilon_0 i}$ by (A2.34)], which depend on the potential and the trial energy ϵ_0, (2) the outer Fourier coefficients of the potential (A2.17) which depend on the potential and the lattice structure, but not on ϵ_0; they are particularly simple for the flattened potential used in the applications, (3) the spherical Bessel functions and their derivatives $j_l(k_n r_i)$, $j_l{}'(k_n r_i)$, and Legendre polynomials, $P_l(\mathbf{k}_n \cdot \mathbf{k}_{n'}/k_n k_{n'})$, (but not the associated functions), which depend on the lattice structure, and on $\mathbf{k}$, but not on the potential or ϵ_0, i.e., they are structure constants.

The dependence on the radial functions only through their logarithmic derivatives at $r = r_i$ is a property possessed also by the Green's function and APW methods. Thus, the quantum defect procedure which Ham[4] combines with the Green's-function method, could be employed here.

We note that if $V(\mathbf{r})$ has inversion symmetry about the origin, then $V_{nn'}{}^o = V_{(n-n')}{}^o$ is clearly real from (A2.19), the matrix elements are all real, and the A_n's are real. This is the case for the applications to monatomic Bravais lattices described here.

4. Solution of the Secular Equation

Of the two forms of matrix elements in (A2.31) and (A2.32), (A2.31) is, in principle, more convenient to use because (A2.32) has an infinite sum over $l = L+1$ to ∞; however, if all the l series are carried effectively to convergence, this sum drops out, and then (A2.32) has the advantage of not requiring the $j_l{}'(k_n r_i)$.[27]

The two energies ϵ_0 and ϵ_v are kept distinct in (3), even though they become equal when the secular equation is fully solved at any finite N, because we want the equation for ϵ_v to be variational for any estimated trial ϵ_0 at which the radial functions are evaluated (which occurs before solving for ϵ_v). This variational property of the equation then makes possible a convenient rapidly convergent iterative procedure to fully solve the secular equation of finite N, from which the true energy is found in the limit $N \to \infty$. Thus, the ϵ_v found with an initial trial ϵ_0 is a variational approximation to the true energy, i.e., has second-order errors compared to the

errors in the wave function. But the final ϵ_v found when the secular equation is fully solved (i.e., when $\epsilon_0 = \epsilon_v$) is also variational, hence, we expect the initial ϵ_v to be close to the final value. This expectation is borne out when we iterate on ϵ_0, using the previous ϵ_v for the new ϵ_0; the ϵ_v from the second stage usually agrees closely with the ϵ_v from the initial stage (see the end of this subsection and Table I).

If the terms $(\epsilon_0 - \epsilon_v) \sum_l b_{lnn'} I_{l\epsilon_0 i}$ in $(H_{nn'} - \epsilon_v D_{nn'})$ were cancelled out by immediately taking $\epsilon_0 = \epsilon_v$ in these terms, the resulting equation yields an ϵ_v with a first-order error, namely, the linear term in $(\epsilon_0 - \epsilon_v)$ just discarded. This point is noted again in the next section in comparing the present method with the original APW procedure where this linear term is not included. Of course, the final value of ϵ_v does not depend on this term, but the convergence of the process for obtaining the final ϵ_v is faster when this term is included than when it is not included.[28]

It seems also worth noting another point about the trial ϵ_0's: namely, that from the point of view of the composite representation, the final energy in the spherical waves, i.e., the final value of ϵ_0 when ϵ_0 and ϵ_v coincide and in the limit of $N \to \infty$, should be the single true energy of the one-electron state we are evaluating, since the expansion represents the true wave function.[29] Thus, all the trial energies of the spherical waves should be chosen as close to the single final energy as can be estimated in advance from knowledge of the energy levels. They need not be exactly equal at any stage in the iterative process, but since they must approach equality as the iteration goes on, it is most convenient to choose them all equal in all stages.

The actual process of solving (3) for a given $\mathbf{k}$ consists of estimating ϵ_0, evaluating the matrix elements, and solving the equation for ϵ_v. Since the secular equation is not in standard form (ϵ_v appears in every term of the matrix), the most convenient procedure we have found is to evaluate the determinant for sets of trial values of ϵ_v, expanding the range until they bracket the root, i.e., until the determinants change sign; the root is then obtained by interpolation. The root is found this way for matrices of increasing order, until it converges as a function of order; call this root $\epsilon_v{}^{(1)}$. The process is then repeated, using as the ϵ_0 of the second stage, $\epsilon_v{}^{(1)}$, and leading to a new $\epsilon_v{}^{(2)}$. Usually $\epsilon_v{}^{(2)}$ agrees with $\epsilon_v{}^{(1)}$ to four or five decimal places, and $\epsilon_v{}^{(3)}$ with $\epsilon_v{}^{(2)}$ to five or six decimal places. The convergence for a typical case, at the point $\mathbf{k}a/2\pi = (0.1, 0.1, 0)$ in Li, is shown in Tables I and II. Table I exhibits the

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[27] Equation (A2.32) was used in the simple applications in this paper, since it was determined that by choosing $L = 11$, the remainder of the l series had a negligible effect on the energies calculated.

[28] The final ϵ_v thus depends only on the logarithmic derivatives $\mathcal{L}_{l\epsilon_v i}$ and not on their energy derivatives, $\partial \mathcal{L}_{l\epsilon_v i}/\partial\epsilon$, which, as noted in Appendix 2 [just after (A2.34)] are equivalent to the integrals $I_{l\epsilon_v i}$.

[29] If the final ϵ_0 had any other value than the true energy, the individual terms of the expansion of ψ_i would not satisfy the Schrödinger equation (with the correct energy); hence, the expansion would not represent the true wave function.

TABLE I. Convergence of the procedure for solving the secular equation (matrix order 16×16) at the point in the Li Brillouin zone, $\mathbf{k}a/2\pi = (0.1, 0.1, 0)$.

First stage	$\epsilon_0 = 0.665$	
	ϵ_v	Determinant values
	−0.685[a]	9.0172×10⁻²
	−0.665[a]	−2.4632×10⁻²
	−0.645[a]	−1.2450×10⁻¹
	−0.66956079[b]	1.8257×10⁻⁴
	−0.66952781[c]	3.5165×10⁻⁷
Second stage	$\epsilon_0 = -0.66952781$[d]	
	ϵ_v	Determinant values
	−0.68952781[a]	1.1811×10⁻¹
	−0.66952781[a]	1.0656×10⁻⁵
	−0.64952781[a]	−1.0288×10⁻¹
	−0.66952584[b]	−6.4914×10⁻⁸

[a] The three trial values of ϵ_v.
[b] Interpolation based on the three trial values and their determinants.
[c] A second interpolation based on the three nearest values to the root, including the result of (b).
[d] Using the result of the first stage to recalculate radial functions.

interpolation process on the determinants and the results of stage 1 and stage 2, which show five-place agreement. Table I refers to $N = 16$, hence uses a 16×16 secular determinant at which convergence in the order is effectively achieved; this is demonstrated in Table II where we see that the root of the 4×4 determinant agrees to three places, the 8×8 to four places, and the 12×12 to five places, with the root of the 16×16 determinant.

If successive eigenvalues at a given $\mathbf{k}$ happen to be closely spaced, as sometimes occurs near band edges, difficulties in locating the root can occur, but can usually be met by using a finer mesh of trial energies.

5. Comparison with Other Methods

Having shown in II.4 that the method of this paper is capable of calculating eigenvalues with high precision even at general points of $\mathbf{k}$, it becomes of interest to compare it with other methods of comparable power, and to exhibit similarities and differences. We compare, first, with the most closely related methods, the original APW method of Slater and Leigh's method; then some remarks are made about the relation to the Green's-function method and to the OPW.

The APW Method

We compare first the nature of the representations in the original APW and the present method. The former,

TABLE II. Convergence of the root of the secular equation as a function of matrix order for the point in the Li Brillouin zone, $\mathbf{k}a/2\pi = (0.1, 0.1, 0)$.

Matrix order	ϵ_v
4	−0.66935954
8	−0.66951509
12	−0.66952626
16	−0.66952781

as described in the recent paper of Wood,[10] which refers back to the original paper of Slater[7] in 1937, introduces as a basis for representing the total wave function, a set of augmented plane waves. These functions match on the surface, S, a single plane wave in Ω_o to a spherical wave expansion in Ω_i. Since this matching is possible for any choice of the energies of the spherical waves, these energies may be fixed in various ways. In the original APW method, these energies are taken to be the single final energy of the electronic state, whereas in a number of other papers the energy was fixed by matching the values and the gradients of the plane wave and its spherical wave tail on S.[11]

In the present method, the composite form described in II.2 and II.3 is adopted directly for the total wave function, rather than for the construction of an intermediate set of basis functions, as in the original APW. The main advantage of eliminating this intermediate stage is conceptual simplicity. Thus, the natural choice of the energy of each spherical wave is clearly the final energy of the total wave function, as noted in II.4, since the total wave function must satisfy the Schrödinger equation with that energy.[29] The ambiguity as to the best choice of energy introduced by construction of the APW's, which led to the other choice mentioned above,[11] is thus avoided. We also note that the matching between plane waves and spherical waves on the surface of separation between regions is made for the total wave function, which is the quantity required to be continuous, together with its gradient, rather than for individual plane waves. Finally, we note that it is somewhat simpler algebraically to deal with a single spherical-wave expansion, rather than with a separate expansion for each plane wave employed in Ω_o. However, it should be stated that since the basic elements of both methods are the same, i.e., spherical waves in Ω_i, plane waves in Ω_o, one could, if properly motivated, carry out any procedure with an augmented plane-wave expansion that can be carried out with the composite-wave expansion.[13]

A second area of difference between the methods arises from the strict attention given to variational formulation of the present method. The original APW formulation[7] does not explicitly introduce variational considerations in obtaining the secular equation for the energy, but obtains the secular equation essentially by the method of perturbation theory when the APW expansion is substituted into the Schrödinger equation. However, by suitable choice of the procedure used for evaluation of the matrix elements of kinetic energy, guided by plausible physical arguments, the result is, in fact, a variational secular equation provided that the trial functions are continuous and that the energies of the spherical waves are the final energy of the state; this is shown in Appendix 1. Direct proof of the variational character of the APW secular equation is also con-

tained in the work of Leigh[30] and Saffren.[31] Now, in the present formulation, close attention to preserving the variational character is made even when the trial function is discontinuous on S and when the trial energies of the spherical waves differ from the final energy of the state. In addition, a general nonflattened potential in Ω_o is used from the start, without interfering with the variational properties of the secular equation. In the APW formulations the potential has been generally assumed flattened in Ω_o, which is suggested by the desire to make the plane waves an exact solution in Ω_o. In fact, this is not necessary, and a general potential in Ω_o can be handled without loss of accuracy in the calculation procedure.[32]

The matrix elements of the secular equation obtained in Appendix 2 from this strict variational formulation, and discussed in II.3 contain three types of terms which do not appear in the usual APW matrix elements. These are specifically: (1) the terms

$$\tfrac{1}{2}r_i^2 \sum_{l=L+1}^{\infty} (k_n j_{lni}'/j_{lni}+k_{n'} j_{ln'i}'/j_{ln'i})b_{lnn'} \quad \text{in (A2.32)}$$

which arise from the discontinuity on S, and disappear as $L \to \infty$, (2) the terms $(\epsilon_0-\epsilon_v)r_i^2 \sum_{l=0}^{L} I_{l\epsilon_0 i}b_{lnn'}$ [putting (A2.27) and (A2.31) or (A2.32) in (A2.33)] which arise from preservation of variational character when the trial energy ϵ_0 differs from ϵ_v and are discussed in II.4, (3) the term $\Omega V_{nn'}{}^o$ in (A2.31) and (A2.32) arising from carrying along a general nonflattened potential in Ω_o, and discussed above.

Leigh's Method

The work of Leigh[14,30] anticipates several features of the present work; we should like to mention these explicitly, as well as various points of difference. Leigh introduces the same composite basis for the trial wave function, and also combines this with a variational expression adapted to functions with discontinuities on the surface of separation. Leigh's variational expression

is given in Appendix 1, (A1.16), where it is noted that (A1.16) is more restricted than (A1.9) or (A1.10); thus, (A1.16) requires that the potential, hence, also the surfaces, have inversion symmetry, and that the trial wave functions satisfy $\psi(-\mathbf{r})=\psi^*(\mathbf{r})$, a condition which may always be satisfied by the true wave functions for this kind of potential. For the applications to bcc lattices made here, however, the greater generality of (A1.9) or (A1.10) is not needed. In addition, Leigh discusses a class of variational expressions dependent on a parameter [Eq. (3) in Ref. 14] and attempts to select a best value of the parameter. The corresponding generalized formula is given in (A1.15). However, these variational expressions differ only by second-order terms from each other, and there seems to be no advantage in them over the simpler forms (A1.9) or (A1.10).

Some significant differences emerge when we compare matrix elements of the secular equation, in his Sec. 4, p. 393, with (A2.31) and (A2.32). His matrix elements contain all but two of the terms of $[(1+\alpha)H_{nn'}{}^{(1s)} -\alpha H_{nn'}{}^{(2s)}]$. These two are (1) $\epsilon_0 r_i^2 \sum_{l=0}^{L} I_{l\epsilon_0 i}b_{nn'}$ which plays a first-order role in determining ϵ_v with trial radial wave functions based on ϵ_0, as explained above in Sec. II.4, and (2) $-\alpha(r_i^2/2)\sum_{l=L+1}^{\infty}(k_n j_{lni}'/j_{lni} +k_{n'} j_{ln'i}'/j_{ln'i})b_{lnn'}$ which is clearly required in (A2.32) when (A2.31) is transformed by means of the simple and easily verified identity (A2.30). We have not, in fact, been able to verify the particular variational expression used in his Sec. 4, leading to his matrix elements. Finally, we note that we replace the sum $\sum_{m=-l}^{l} Y_{lm}^*(C_{n},r)Y_{lm}(C_{n'},r)$ which appears in his matrix elements, by the computationally much more convenient expression $(2l+1)P_{lnn'}$ (notation defined in Appendix 2).

The Green's-Function Method

The Green's-function method and the present method are similar in the sense that they are both based upon the use of discontinuous trial wave functions and variational principles for discontinuous trial wave functions. The Green's-function method trial wave function is discontinuous on the cell boundary, and the variational principle [Eq. (2.16) in Ref. 6] involves integrals over the cell of lattice Green's functions; on the other hand, in the present method, trial wave functions are discontinuous on an arbitrary surface within the cell, but are continuous at the cell boundaries, and the variational principle involves surface integrals over the surface of discontinuity.

The Green's-function method is made tractable by flattening the potential in the outer part of the cell, beyond the inscribed sphere. Then the variational expression reduces to integrals over the sphere when the flat part of the potential is taken as the zero reference level. The integrals over the sphere can then be easily evaluated for expansions in spherical waves. This simplification is not necessary in the present procedure.

[30] See Ref. 14; the proof from R. S. Leigh's work is not completely general, however, since his variational principle is restricted to potentials with inversion symmetry and his trial wave functions have a special form.

[31] See Ref. 8, p. 24; M. M. Saffren's proof is complicated by use of special properties of the APW expansion, whereas the proof in Appendix 1 applies for general trial functions, provided they are continuous on S.

[32] J. C. Slater (see Ref. 11), p. 607, has suggested taking account of the nonconstant nature of the potential by including the deviations from a constant in the matrix elements between APW's. This is equivalent to the term obtained here, $V_{n'n}{}^o$ from the nonconstant potential, but is still based in the perturbation theory point of view used in deriving the APW secular equation. Our derivation shows that the secular equation is still variational with this term. This fact is not widely known; for example, Callaway (Ref. 42) states that the APW requires a constant potential in Ω_o, Wood (Ref. 10) describes the APW as if the flattened potential were essential, and Pincherle (Ref. 1), p. 378, lists the APW under methods using a constant potential outside atomic spheres. However, Leigh has pointed out that the assumption is not necessary [Proc. Phys. Soc. (London) 71, 33 (1958)] and, in fact, estimates the error due to this assumption.

TABLE III. The first 25 Fourier coefficients, V_n, [see (A2.19)], corresponding to reciprocal lattice vectors $K_n = 2\pi n/a$, for flattened potentials of Li and Na; $a(\text{Li}) = 6.5183$ a.u., $a(\text{Na}) = 8.0427$ a.u.

n^2	$K_n(\text{Li})$	$-V_n(\text{Li})$	$K_n(\text{Na})$	$-V_n(\text{Na})$	n^2	$K_n(\text{Li})$	$-V_n(\text{Li})$	$K_n(\text{Na})$	$-V_n(\text{Na})$
0	0.0000	1.00221	0.0000	0.94063	26	4.9151	0.02039	3.9835	0.04721
2	1.3632	0.16889	1.1048	0.24782	30	5.2797	0.01857	4.2790	0.04200
4	1.9279	0.09435	1.5625	0.16619	32	5.4528	0.01783	4.4193	0.03974
6	2.3611	0.06388	1.9136	0.12976	34	5.6206	0.01708	4.5553	0.03762
8	2.7264	0.05166	2.2096	0.11158	36	5.7836	0.01630	4.6874	0.03559
10	3.0482	0.04576	2.4705	0.09980	38	5.9421	0.01548	4.8158	0.03366
12	3.3392	0.04141	2.7063	0.08997	40	6.0964	0.01466	4.9409	0.03186
14	3.6067	0.03720	2.9231	0.08935	42	6.2470	0.01385	5.0629	0.03020
16	3.8557	0.03305	3.1249	0.07269	44	6.3940	0.01309	5.1821	0.02871
18	4.0896	0.02926	3.3145	0.06547	46	6.5377	0.01240	5.2986	0.02739
20	4.3108	0.02607	3.4938	0.05941	48	6.6783	0.01179	5.4125	0.02625
22	4.5212	0.02358	3.6643	0.05447	50	6.8160	0.01127	5.5241	0.02528
24	4.7223	0.02173	3.8272	0.05048					

One advantage of the present method over the Green's-function method is the greater simplicity of our matrix elements. The matrix elements for the Green's-function method involve structure constants which arise from the expansion of the lattice Green's function. These structure constants are difficult to evaluate since they are complicated sums over functions of many variables and are singular for certain values of the variables. The independent variables include the energy, the wave number, the orders l, l' of the two spherical waves, and their degrees of association m, m'. In contrast, the matrix elements of the present method are nonsingular and just involve simply-computed standard functions such as the spherical Bessel functions, their derivatives and the ordinary Legendre polynomials.

The OPW Method

The OPW method has been used extensively in energy-band calculations, and has given many useful results. However, it differs from the methods discussed above in that it cannot give solutions of arbitrarily great accuracy. The difficulty with this method arises from inaccuracies in the core wave functions; the core functions to which the trial wave function is orthogonalized are not precise eigenfunctions of the given Hamiltonian; hence, the calculated energy eigenvalues will not stabilize at the upper energy levels desired but will continually descend toward the core values if the number of OPW's keeps increasing. Thus, there is always an uncertainty about the accuracy of OPW results which cannot be refined out by more extended calculations.

III. APPLICATION TO ENERGY BANDS OF Li AND Na

The method described above has been applied to calculate energies in the conduction bands of Li and Na using a FORTRAN II program and the IBM-704 digital computer. The calculations have been made with well-known potentials for these materials in order to test the method against results of other workers. These comparisons are along lines of high symmetry in the

Brillouin zone. Energies at many additional points of general k have also been found, and for Li used to estimate the position of the Fermi surface.

1. Potentials

The well-known empirical potentials of Seitz[33] for Li and Prokofiev[34] for Na, which reproduce the observed spectral term values of the free atom, were used in the calculations. However, the approximation of flattening the potential outside the inscribed sphere, used by other workers, was made here too.[35] The empirical ionic potential was used out to the radius of the inscribed sphere, and the potential in the outer part of the cell was replaced by its average value V_e. From the potential, the Fourier coefficients and outer Fourier coefficients [see (A2.18) and (A2.19)] were determined by integrations over the polyhedral cell. A short table of the Fourier coefficients of the flattened potential is given in Table III, and covers all values used in the calculations on Li and Na.[36]

2. Energy Bands in Li

The energy values of the conduction band at some 30 points in the Brillouin zone of Li are given in Table IV, including the next higher energy at three points on the zone surface, $ka/2\pi = (1,0,0)$, $(1,1,0)$, and $(1,1,1)$. The points fall mainly along the six directions [100], [110], [111], [221], [310], [311] and the $\epsilon(k)$ curve is plotted along these directions in Figs. 2, 3, and 4.

It is an important test of our method to establish the

[33] F. Seitz, Phys. Rev. 47, 400 (1935), who tabulated the potential incorrectly. Kohn and Rostoker (Ref. 6) give a correct tabulation of $-rV(r)$ which was exactly the potential used here (with quadratic interpolation between arguments where needed).

[34] W. Prokofiev, Z. Physik 58, 255 (1929).

[35] The method is, of course, not restricted to flattened potentials, and, in fact, no additional work is required to use matrix elements of a nonflattened potential in (A2.31) or (A2.32). The explicit formulas in (A2.31) and (A2.32) do require a spherically symmetrical potential for $r \leq r_i$, but a simple modification can handle general potentials (see Ref. 55).

[36] A much longer tabulation, of the first 125 Fourier coefficients for both Li and Na, is given in Ref. 26, where they were used for studies of simple plane-wave representations of the wave function.

TABLE IV. Energy values for Li at various points in the Brillouin zone. $a=6.5183$ a.u., $r_i=2.8225$ a.u.

$k_1a/2\pi$	$k_2a/2\pi$	$k_3a/2\pi$	BSW notation	ϵ
x	0	0	Δ line	
0	0	0	Γ_1	−0.68345
0.2	0	0		−0.65593
0.31505	0	0		−0.61538
0.5	0	0		−0.51040
0.60629	0	0		−0.42706
0.8	0	0		−0.23294
0.9	0	0		−0.11898
0.96	0	0		−0.06147
1	0	0	H_{15}	−0.04615
1	0	0	H_{12}	0.16337
x	x	0	Σ line	
0.1	0.1	0		−0.66953
0.3	0.3	0		−0.56176
0.5	0.5	0	N_1'	−0.41051
0.5	0.5	0	N_1	−0.19454
x	x	x	Λ line	
0.1	0.1	0.1		−0.66277
0.3	0.3	0.3		−0.49993
0.4	0.4	0.4		−0.35789
0.5	0.5	0.5	P_4	−0.18395
0.5	0.5	0.5	P_1	0.16265
$2x$	$2x$	x	ΓD_0 line	
0.2	0.2	0.1		−0.620
0.35	0.35	0.175		−0.4962
0.5	0.5	0.25	D_0	−0.353
$3x$	x	0	ΓG_0 line	
0.3	0.1	0		−0.61502
0.525	0.175	0		−0.47357
0.75	0.25	0	G_0	−0.294
$3x$	x	x	ΓF_0 line	
0.3	0.1	0.1		−0.60829
0.525	0.175	0.175		−0.45325
0.75	0.25	0.25	F_0	−0.2420
0.3	0.15	0.1		−0.59990
0.45	0.5125	0		−0.41161
0.4	0.5275	0		−0.41439

FIG. 2. Li energy values along the Δ line, [100], versus reduced wave number. $ka/2\pi$; points of other workers are also shown.

be made with the results of Ham,[38] who computed many points along the [100], [110], and [111] directions. His results along [100] are shown in Fig. 2, and correspond closely to our values, but lie slightly lower. Similar results hold in other directions. Since Ham's lattice constant was 2% larger, this would be expected to lower the energies slightly, and thus explain the difference between the two sets of results.[39]

Still less precise comparison is possible with the calculations of Glasser and Callaway[40] and of Callaway[41] who use the orthogonalized plane-wave method. Glasser and Callaway use the Seitz potential without flattening in the outer part of the cell, but continued spherically to the cell surface. The potential then has a strong

FIG. 3. Li energy bands in the [100], [110], and [111] directions versus $ka/2\pi$; points of other workers are also shown.

quantitative accuracy of the calculations by comparison with results of other workers using other methods. The best check is against the values obtained by Kohn and Rostoker[6] who used the identical potential and lattice constant. In our notation, they obtained energies, $\epsilon(ka/2\pi)$, at four values of k, three of which were also used in our calculations (and appear in Table IV), namely $\epsilon(0,0,0)=-0.6832$, $\epsilon(0.3151,0,0)=-0.6158$, $\epsilon(0.6063,0,0)=-0.4275$, which may be compared, respectively, with the values (from Table IV) −0.6834, −0.6154, and −0.4271. It is noteworthy that agreement is obtained to within a few units of the fourth figure, which is about the accuracy of their calculation.[37]

Less precise but more extensive comparisons may

[37] In fact, they assume ϵ and calculate k in two successive approximations corresponding to the use of two or three spherical waves in the expansion of the trial function. The k increased in the third figure between approximations, hence, the fourth figure is not established and probably lies slightly higher still, corresponding to the slightly higher values of Table IV, in which up to 12 spherical waves were used in the trial wave function.
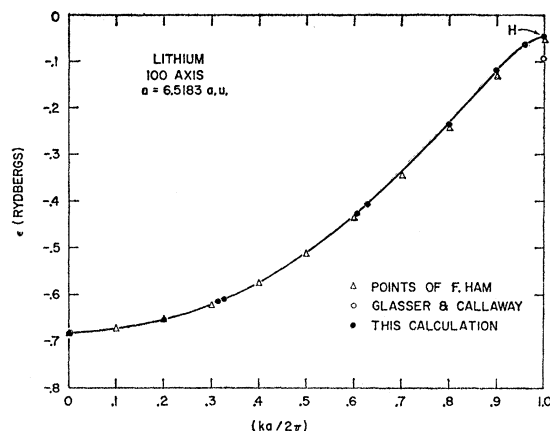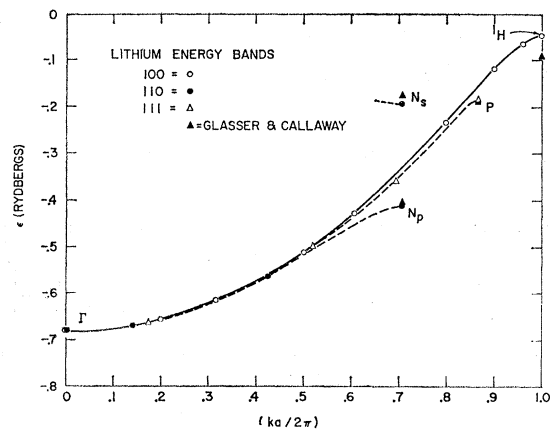
[38] Reference 22, p. 9; Fig. 1 on p. 16.
[39] When Ham uses the same lattice constant, he checks our results more closely (private communication). His calculations use the quantum defect method, rather than the Seitz potential, so we cannot easily say how close exact energies for the two calculations would be.
[40] M. L. Glasser and J. Callaway, Phys. Rev. 109, 1541 (1958).
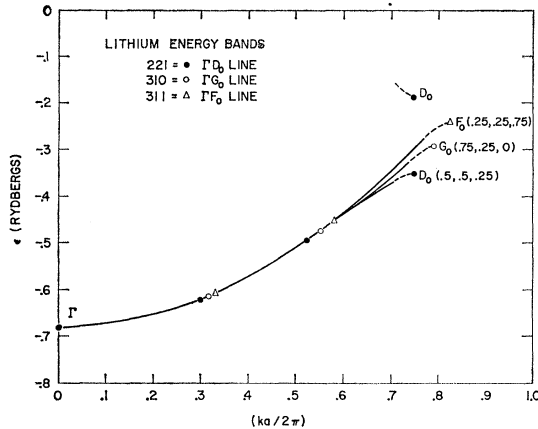[41] J. Callaway, Phys. Rev. 124, 1824 (1961).

FIG. 4. Li energy bands in the [221], [310], and [311] directions.

discontinuity of slope at the cell boundaries which pro-
duces a pronounced oscillation of the Fourier coeffi-
cients V_n as a function of $|n|^2$, and makes some energy
values quite different from the present calculations
(well outside the computation error), particularly the
point $ka/2\pi = (1,0,0)$ (Figs. 2 and 3), although the gap
at (0.5, 0.5, 0) is not very different. In Callaway's more
recent paper, the spurious discontinuity in slope of the
potential has been removed by a method other than
flattening.[42] The value of $\epsilon(1,0,0)$ rises from -0.092 to
-0.009 compared to our value of -0.046, while
$\epsilon(0.5,0.5,0)$ falls from -0.404 to -0.408 compared to
our -0.411, and $\epsilon(0.5,0.5,0.5)$ rises from -0.189 to
-0.177 compared to our -0.184. Thus, the new values
are somewhat closer to ours but still do not provide a
precise quantitative check. Presumably, the differences
are due to use of a different potential, but there is also
the residual uncertainty in OPW energies arising from
lack of precise orthogonality to the core functions in
the crystal.

3. The Fermi Energy and Fermi
Surface for Li

From the calculated energy values $\epsilon(k)$ listed in
Table I, an estimate of the Fermi energy ϵ_F and the
Fermi surface can be made. This cannot be made with
accuracy comparable to that of the individual $\epsilon(k)$,
since rather few points are available, but a systematic
procedure for evaluation of the energy will be used
which could be readily extended to a larger number of
points, and will give some idea of the accuracy attained.

If $g(\epsilon)$ is the density of electronic states in energy per
unit volume (including both spin states), then, measur-
ing energy from the bottom of the conduction band

at $k = 0$, we have

$$\int_0^{\epsilon_F} g(\epsilon)d\epsilon = \frac{2}{a^3}, \tag{4}$$

since $2/a^3$ is the conduction electron density (and, by
definition of ϵ_F, the number of states below ϵ_F is equal
to the number of electrons). Since the density of states
per unit volume is $1/4\pi^3$ in k space ($2/a^3$ in $\bar{k}$ space),
we also have for the number of states of energy less
than ϵ, per unit volume,

$$\int_0^\epsilon g(\epsilon)d\epsilon = (2/3a^3)\int_{4\pi} \bar{k}^3(\omega,\epsilon)d\omega, \tag{5}$$

where $\bar{k} = ka/2\pi$ is the reduced wave number, and $\bar{k}(\omega,\epsilon)$,
is its magnitude in the direction ω on the energy surface
ϵ. From (4) and (5) with $\epsilon = \epsilon_F$ we obtain a convenient
equation for ϵ_F,

$$\int_{4\pi} \bar{k}_F^3(\omega)d\omega = 3, \tag{6}$$

where $\bar{k}_F(\omega) \equiv \bar{k}(\omega,\epsilon_F)$.

An upper and a lower bound to ϵ_F are obtained by
using the fact that for given $\bar{k}$, the energies along [100]
lie highest and along [110] lie lowest of all directions,
as shown by Figs. 3 and 4. Now, from (6), the average
value of $\bar{k}_F$ (more precisely the cube root of the average
value of $\bar{k}_F^3$) is 0.6203; at this $\bar{k}$ along [100] Fig. 3 gives
a value of $\epsilon = -0.414$, whereas along [110], $\epsilon = -0.439$.
Thus, $\epsilon_F < -0.414$ (since the surface $\epsilon = -0.414$ would
everywhere lie outside the sphere with $\bar{k} = 0.6203$), and
cannot touch the Brillouin zone boundary whose lowest
energy is the N'_1 point, $\epsilon_{N'_1} = -0.4105$ (Table IV).

The appropriate average to take of the energies in
various directions to allow for the deviations from
spherical symmetry is conveniently found by using
the cubic symmetry of $\bar{k}(\omega,\epsilon)$ at given ϵ, and the fact
that the surface $\epsilon = \epsilon_F$ is a smooth surface (i.e., does
not intersect the zone boundary). Then $\bar{k}(\omega,\epsilon)$ may be
expanded in the complete orthogonal set of cubically
symmetric angular functions, the kubic harmonics.[43]
We seek a representation of the angular dependence of
$\bar{k}$ at given ϵ and not a polynomial expansion of $\epsilon(\bar{k})$
valid at all points within the Fermi surface, as is some-
times used.[44] At different energies, a different representa-
tion of $\bar{k}$ will be used, determined by its values along the

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[42] The potential of a unit point charge, $-2/r$, which gives
almost all the Seitz potential for $r \geq r_i$ ($97\frac{1}{2}\%$ of it), is replaced by
the easily calculable, smooth potential of a bcc lattice of unit
positive point charges screened by uniform negative charge;
the effect of this change has also been discussed by R. S. Leigh,
Proc. Phys. Soc. (London) 71, 33 (1958).

[43] These functions were defined and used by von der Lage and
Bethe, Phys. Rev. 71, 612 (1947), and later applied by D. D.
Betts, A. B. Bhatia, and Max Wyman, Phys. Rev. 104, 37 (1956).
We are concerned here with the functions of angle, rather than
with the kubic harmonic polynomials, which are homogeneous
polynomials in the components of $\bar{k}$ with cubic symmetry. A
general and simple procedure has been found for obtaining these
angular functions to all orders and will be reported separately.

[44] For example, J. Callaway (see Ref. 41) fits the energy values
in Li, as determined by his OPW calculation, to an expansion in
kubic harmonic polynomials through the sixth power, and uses
this expansion to fix the Fermi energy.

directions of the curves of $\epsilon(\bar{k})$ given in Figs. 3 and 4; it is clear that to fix ϵ_F we need consider at most only the portions of these curves between $\epsilon = -0.414$ and $\epsilon = -0.439$ (or between $\bar{k} = 0.592$ and $\bar{k} = 0.697$) and in fact the surface ϵ_F will be found to range between $\bar{k} = 0.603$ and 0.647.

The six directions in which $\epsilon(\bar{k})$ is given in Figs. 3 and 4 permit an expansion in six kubic harmonics, $K_i(\omega)$, $i = 1$ to 6, in the form

$$\bar{k}^3(\omega,\epsilon) = \sum_{i=1}^{6} A_i(\epsilon) K_i(\omega), \qquad (7)$$

where we take $K_1(\omega) = 1$. We choose to expand $\bar{k}^3$ rather than $\bar{k}$, since then A_1 gives immediately the integral in (5), (because of the orthogonality of the $K_i(\omega)$ over a sphere); then we have for the average value of $\bar{k}^3$,

$$(1/4\pi) \int_{4\pi} \bar{k}^3(\omega,\epsilon) d\omega = A_1(\epsilon). \qquad (8)$$

Betts, Bhatia, and Wyman[43] give the first six kubic harmonic polynomials (in fact, the first seven, which includes two polynomials of the 12th power), and also a set of integration formulas based on various sets of directions, up to six. However, they do not include all the directions used here, hence, we have extended their procedures; formulas (9) use the first 3, 4, and 6 kubic harmonics and invert (7) to find A_1 for the directions of interest here; then we can write the spherical average of a cubically symmetric function, $f(\omega)$, in the forms

$$(1/4\pi) \int_{4\pi} f(\omega) d\omega$$

$$\cong 0.285714 \, f(100) + 0.457143 \, f(110)$$
$$+ 0.257143 \, f(111), \qquad (9a)$$

$$\cong 0.0761905 \, f(100) + 0.270899 \, f(110)$$
$$+ 0.168750 \, f(111) + 0.484160 \, f(311), \qquad (9b)$$

$$\cong 0.022411 \, f(100) + 0.158678 \, f(110)$$
$$+ 0.037257 \, f(111) + 0.292624 \, f(311)$$
$$+ 0.280905 \, f(221) + 0.208125 \, f(310), \qquad (9c)$$

where $f(100)$ is the value of f in direction $[100]$, etc.

Application of (9) to $\bar{k}^3(\omega,\epsilon)$ at various ϵ between -0.414 and -0.439, and interpolation to satisfy (6), gives from (9.1), (9.2), and (9.3), respectively, $\epsilon_F = -0.431$, -0.429 and -0.429. This suggests $\epsilon_F = -0.429$ Ry, accurate to within 0.001 Ry, and that the three-point formula (9.1) over-emphasizes the $[110]$ direction.[45] This may be compared with Ham's[4] value of -0.433[46] and Callaway's[41] value of -0.433.[47]

FIG. 5. Central vertical section of Brillouin zone for Li through center of hexagonal face, $(1\bar{1}0)$ plane, showing section of energy surface at $\epsilon = -0.421$ eV and a section of the adjacent higher energy level at $\epsilon = -0.41$ eV which touches the zone face at the N point; the points at which the energy has been calculated are marked.

Finally, we note that the expansion (7) can also give a value for the density of states at energy ϵ. It is convenient to write this for the density of states per atomic volume, $g(\epsilon)a^3/2$, hence, from (5) and (8)

$$g(\epsilon)(a^3/2) = \frac{4\pi}{3} \frac{d}{d\epsilon} \left(\frac{1}{4\pi} \int_{4\pi} \bar{k}^3(\omega,\epsilon) d\epsilon \right) = \frac{4\pi}{3} \frac{dA_1(\epsilon)}{d\epsilon}, \qquad (10)$$

where $A_1(\epsilon)$ is given by formulas (9), when $f(\omega) = \bar{k}^3(\omega,\epsilon)$. Applying (9.3) to $A_1(\epsilon)$ around $\epsilon = -0.429$, gives $g(\epsilon_F)a^3/2 = 7.0$ states/Ry atom which may be compared with Ham's[4] value of 6.8 (or 0.312 state/Ry Å^3), given in his Fig. 1 (Part II).

Figures 5 and 6 give energy contours roughly sketched in vertical and horizontal sections of the Brillouin zone, at several energies. These show the outward bulge from spherical behavior in the $[110]$ directions, and the inward bulge from a sphere in the $[100]$ directions; at ϵ_F the former amounts to 4.4% and the latter to 2.7%.

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[45] This is the best we can do with $\epsilon(\bar{k})$ curves in six directions (and six kubic harmonics), but to check this apparent convergence of ϵ_F to -0.429 Ry, some additional directions would be desirable. In fact, the bulge in the constant energy surfaces in the $[110]$ direction is more localized than expansion (7) gives, and the value -0.429 may be low because the bulge is overemphasized. The true shape of the energy contours is indicated by the last two
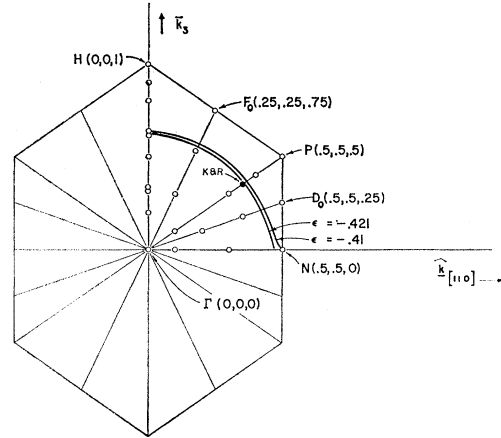
entries in Table IV which corresponds to energies of about -0.41 Ry at points of general $\bar{k}$; they have been used in Fig. 6 to fix the energy contours, which are rather spherical until close to $[110]$.

[46] Ham uses a lattice spacing of $a = 6.651$ a.u., 2% larger than ours, which could lower ϵ_F by 0.003 or 0.004 Ry, as shown by his Table III, Ref. 4, Part II; note in our Fig. 2 that his energy values lie below ours. Also Ham uses a special representation for the energies around each $[110]$ axis, which assumes independent cylindrically symmetric bulges from a sphere in each of these 12 directions; the accuracy of this assumption could be tested by use of our expansion (6). By interpolation in his computed values F. S. Ham (private communication) has found $\epsilon_F = -0.430$ Ry at our lattice spacing, which agrees with our value within the computational error.

[47] This value seems low for Callaway's energy values, since all his energies lie above ours (and Ham's) at the same $\bar{k}$, hence, one would expect his ϵ_F to be higher than our (and Ham's) value. In fact, a replotting of his tabulated energies near ϵ_F, and use of the three-point formula, (9.1), leads to $\epsilon_F = -0.429$ Ry, and this is probably low because (9.1) overemphasizes the low value in the $[110]$ direction; thus a reasonable estimate of ϵ_F from his energies would be -0.427 Ry.

TABLE V. Energy values for Na at various points in the Brillouin zone. $a=8.0427$ a.u., $r_i=3.4826$ a.u.

$k_1a/2\pi$	$k_2a/2\pi$	$k_3a/2\pi$	BSW symbol	ϵ
x	0	0	Δ line	
0	0	0	Γ_1	-0.60765
0	0	0	Γ_{12}	0.520
0	0	0	Γ_{15}	0.529
0.2	0	0		-0.58168
0.5	0	0		-0.44808
0.62895	0	0		-0.35732
0.8	0	0		-0.21039
0.9	0	0		-0.11228
0.96	0	0		-0.05207
1	0	0	H_{15}	-0.01977
1	0	0	H_1	0.08824
x	0	0	Σ line	
0.1	0.1	0		-0.59463
0.3	0.3	0		-0.49221
0.5	0.5	0	N_1	-0.29436
0.5	0.5	0	N'_1	-0.29385
x	x	x	Λ line	
0.1	0.1	0.1		-0.58816
0.3	0.3	0.3		-0.43562
0.4	0.4	0.4		-0.30629
0.5	0.5	0.5		-0.15464
0.5	0.5	0.5		-0.10476

4. Energy Bands in Na

Numerical results for calculations of the energy bands in Na are given in Table V using the same procedures as for Li. The conduction band is plotted in Fig. 7 and is seen to be almost spherical with very small deviations near the band edges in the various symmetry directions. These results are in good agreement with results of Ham[4] using the Green's-function method and of Saffren[48] using the APW method as shown in Table VI. The band gap at the N point is found to be approximately 0.0005 Ry, with N_S below N_P.
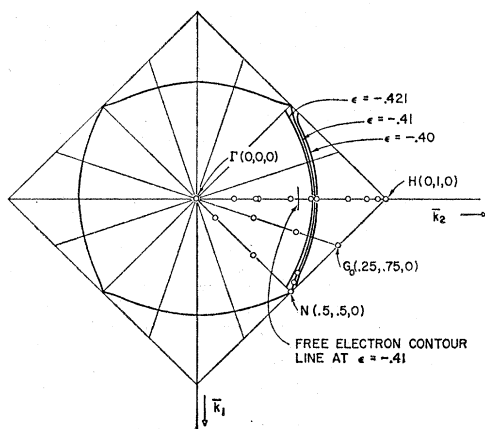
FIG. 6. Central horizontal section of Brillouin zone for Li, (001 plane), showing sections of three adjacent surfaces of constant energy.

[48] Unpublished; quoted by L. Allen in the Quarterly Progress Report of the Solid State and Molecular Theory Group (MIT), No. 29, 1958; and M. Saffren (private communication).
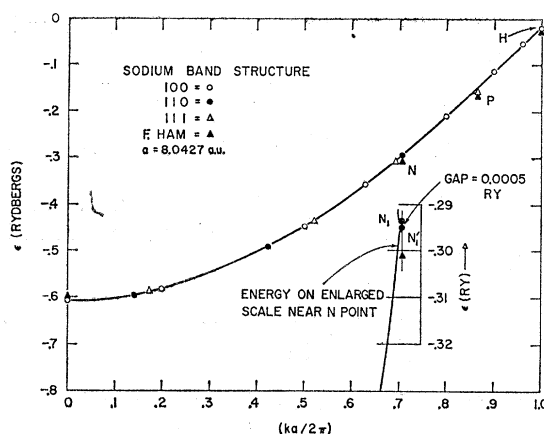
FIG. 7. Na energy bands in the [100], [110], and [111] directions versus reduced wave number; points of Ham are also shown. The structure near the N point is shown on an enlarged scale.

ACKNOWLEDGMENTS

TABLE VI. Comparative energy values for Na at a few points of high symmetry from Ham, Saffren, this paper, and Callaway.

$ka/2\pi$	ϵ (Ham)[a]	ϵ (Saffren)[b]	ϵ (This paper)	ϵ (Callaway)[c]
$(0, 0, 0)$ Γ_1	-0.6041	-0.6082	-0.6076	-0.5974
$(0.5, 0.5, 0)$ N_1	-0.2910	-0.2988	-0.2944	-0.263
$(0.5, 0.5, 0)$ N'_1	-0.3078	-0.2972	-0.2938	-0.316
$(0.5, 0.5, 0)$ P_4	-0.1669		-0.1546	-0.162

[a] Private communication (Ref. 4), $a=8.11$ a.u.; uses Green's-function method and quantum defect.
[b] Unpublished (Ref. 8); uses APW method.
[c] J. Callaway, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 131; based on a pseudopotential chosen to fit the S and P states of the free atom, and the OPW method.

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APPENDIX 1: VARIATIONAL EXPRESSIONS FOR THE ENERGY APPLYING TO TRIAL WAVE FUNCTIONS DISCONTINUOUS ON A SURFACE IN THE CELL

Variational expressions for the eigenvalues, ϵ, of the Schrödinger equation, (1), with boundary conditions (2) will be constructed which are valid for functions which have discontinuities on a prespecified but arbitrary surface S within the cell (see Fig. 1), but are continuous elsewhere in the lattice and satisfy the cellular boundary conditions (2). The effects of the discontinuities in the function (and its gradient) on S are allowed for by modifying the usual variational expression to include surface integrals over S. The first-order deviation of the energy from its correct value, computed from the variational expression, can then be made to vanish by cancellation of surface integrals arising from the discontinuities against the added surface integrals.

If ψ_i denotes the trial wave function in the inner region, Ω_i, and ψ_o the trial wave function in the outer region, Ω_o, then a suitable surface integral is added to the usual variational expression for the variational energy ϵ_v in the equation

$$\epsilon_v \int_\Omega d\Omega\, \psi^*\psi = \int_{\Omega_i+\Omega_o} d\Omega\, \psi^* H \psi$$
$$+ \int_S dS[a(\partial_n\psi_o^* + \partial_n\psi_i^*)(\psi_o - \psi_i)$$
$$- c(\psi_o^* + \psi_i^*)(\partial_n\psi_o - \partial_n\psi_i)]. \quad (A1.1)$$

The terms in the added surface integral are first order in the discontinuities on S (hence, first order in the deviations of the trial wave function from the true wave function) and, as will be seen below, the first-order variation of these terms has the same form as the surface terms arising from the first-order variation of the volume term.[49] It will be shown that (A1.1) is variational if

$$a = c = \tfrac{1}{2}, \quad (A1.2)$$

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[49] Note that the apparently more general form of the surface integral integrand, $(a\partial_n\psi_o^* + b\partial_n\psi_i^*)(\psi_o - \psi_i) - (c\psi_o^* + d\psi_i^*) \times (\partial_n\psi_o - \partial_n\psi_i)$, differs from the form in (A1.1) by second-order terms, $(\partial_n\psi_o^* - \partial_n\psi_i^*)(\psi_o - \psi_i)$ and $(\psi_o^* - \psi_i^*)(\partial_n\psi_o - \partial_n\psi_i)$, which are not of interest here. For a similar reason, we omit terms of the form $(\psi_o - \psi_i)(\psi_o^* - \psi_i^*)$ and $(\partial_n\psi_o^* - \partial_n\psi_i^*)(\partial_n\psi_o - \partial_n\psi_i)$. The complex conjugate terms to those in the surface integral in (A1.1) are omitted because their first-order variations [see (A1.4)] are of different form from the terms arising from the volume integral [see (A1.7)].

provided the trial wave function satisfies (2). Put

$$\psi = \psi_t + \delta\psi,\, \psi_i = \psi_t + \delta\psi_i,\, \psi_o = \psi_t + \delta\psi_t,\, \epsilon_v = \epsilon_t + \delta\epsilon_v, \quad (A1.3)$$

where ψ_t is the true wave function and ϵ_t the true eigenvalue, satisfying $H\psi_t = \epsilon_t\psi_t$. Then $\delta\epsilon_v$ is given to first order in the $\delta\psi$'s by

$$\delta\epsilon_v \int_\Omega d\Omega\, \psi_t^*\psi_t$$
$$= \int_{\Omega_i+\Omega_o} d\Omega\, \delta\psi^*(H - \epsilon_t)\psi_t + \int_{\Omega_i+\Omega_o} d\Omega\, \psi_t^*(H - \epsilon_t)\delta\psi$$
$$+ 2\int_S dS[a\partial_n\psi_t^*(\delta\psi_o - \delta\psi_i)$$
$$- c\psi_t^*(\partial_n\delta\psi_o - \partial_n\delta\psi_i)]. \quad (A1.4)$$

In (A1.4), the first volume integral on the right vanishes, and the second may be transformed by Green's theorems for a region Ω bounded by surface S,

$$\int_\Omega d\Omega\, \psi\nabla^2\phi = \int_\Omega d\Omega\, \phi\nabla^2\psi + \int_S dS(\psi\partial_n\phi - \phi\partial_n\psi) \quad (A1.5a)$$
$$= -\int_\Omega d\Omega\, \boldsymbol{\nabla}\psi\cdot\boldsymbol{\nabla}\phi + \int_S dS\,\psi\partial_n\phi. \quad (A1.5b)$$

Then (A1.5a) with $\psi = \psi_t^*$ and first with $\varphi = \delta\psi_i$, then with $\varphi = \delta\psi_o$ gives

$$\int_{\Omega_i} d\Omega\, \psi_t^*(H - \epsilon_t)\delta\psi_i$$
$$= -\int_S dS(\psi_t^*\partial_n\delta\psi_i - \partial_n\psi_t^*\delta\psi_i), \quad (A1.6a)$$

$$\int_{\Omega_o} d\Omega\, \psi_t^*(H - \epsilon_t)\delta\psi_o$$
$$= \int_S dS(\psi_t^*\partial_n\delta\psi_o - \partial_n\psi_t^*\delta\psi_o)$$
$$- \int_{S_c} dS(\psi_t^*\partial_{n_c}\delta\psi_o - \partial_{n_c}\psi_t^*\delta\psi_o). \quad (A1.6b)$$

In (A1.6b), $\mathbf{n}$ is the outward normal to Ω_i and $\mathbf{n}_c$ the outward normal to the cell. Since the trial functions (and $\delta\psi_o$) satisfy the cellular boundary conditions (2), the last integral in (A1.6b) vanishes by cancellation of contributions from opposite points on the cell boundary (points at which $\mathbf{n}_c$ has opposite directions). Hence, (A1.6a) and (A1.6b) give

$$\int_{\Omega_i+\Omega_o} d\Omega\, \psi_t^*(H - \epsilon_t)\delta\psi$$
$$= \int_S dS[\psi_t^*(\partial_n\delta\psi_o - \partial_n\delta\psi_i) - \partial_n\psi_t^*(\delta\psi_o - \delta\psi_i)]. \quad (A1.7)$$

Finally, using (A1.7) in (A1.4) shows that $\delta\epsilon_v$ vanishes (to first order) if (A1.2) holds, as is required to make (A1.1) a variational expression for ϵ_v.

A further useful property of (A1.1) is that ϵ_v is always real for any trial wave function. The terms are seen to group into conjugate pairs if we use the identity

$$\int_{\Omega_i+\Omega_o} d\Omega\, \psi^*H\psi = \int_{\Omega_i+\Omega_o} d\Omega(\nabla\psi^*\cdot\nabla\psi+\psi^*V\psi)$$
$$- \int_S dS(\psi_i^*\partial_n\psi_i-\psi_o^*\partial_n\psi_o),\quad \text{(A1.8)}$$

which follows from (A1.5b) and the cellular boundary conditions. Compact forms of (A1.1) are obtained with the use of the real part operator,

$$\epsilon_v\int_{\Omega_i+\Omega_o} d\Omega\, \psi^*\psi = \int_{\Omega_i+\Omega_o} d\Omega(\nabla\psi^*\cdot\nabla\psi+\psi^*V\psi)$$
$$+\mathrm{Re}\left\{\int_S dS(\psi_o^*-\psi_i^*)(\partial_n\psi_o+\partial_n\psi_i)\right\},\quad \text{(A1.9)}$$

$$\epsilon_v\int_{\Omega_i+\Omega_o} d\Omega\, \psi^*\psi = \mathrm{Re}\left\{\int_{\Omega_i+\Omega_o} d\Omega\, \psi^*H\psi\right.$$
$$\left.+\int_S dS(\psi_o^*\partial_n\psi_i-\psi_i^*\partial_n\psi_o)\right\}.\quad \text{(A1.10)}$$

The form (A1.10) has been previously published[50] in a preliminary note. Another form of (A1.10) follows from applying (A1.5b) just to Ω_o

$$\epsilon_v\int_{\Omega_i+\Omega_o} d\Omega\, \psi^*\psi$$
$$=\mathrm{Re}\left\{\int_{\Omega_i} d\Omega\, \psi^*H\psi+\int_{\Omega_o} d\Omega(\nabla\psi^*\cdot\nabla\psi+\psi^*V\psi)\right.$$
$$\left.+\int_S dS(\psi_o^*-\psi_i^*)\partial_n\psi_o+\int_S dS\,\psi_o^*\partial_n\psi_i\right\}\quad \text{(A1.11)}$$

and still other forms are obtained by forming linear combinations of (A1.9), (A1.10), and (A1.11).

If the class of trial functions is restricted to functions continuous on S, then (A1.9) and (A1.11) simplify to

$$\epsilon_v\int_{\Omega_i+\Omega_o} d\Omega\, \psi^*\psi$$
$$=\int_{\Omega_i+\Omega_o} d\Omega(\nabla\psi^*\cdot\nabla\psi+\psi^*V\psi)\quad \text{(A1.12)}$$
$$=\mathrm{Re}\left\{\int_{\Omega_i} d\Omega\, \psi^*H\psi+\int_{\Omega_o} d\Omega(\nabla\psi^*\cdot\nabla\psi+\psi^*V\psi)\right.$$
$$\left.+\int_S dS\,\psi_o^*\partial_n\psi_i\right\},\quad \text{(A1.13)}$$

[50] Quarterly Progress Report, Solid State and Molecular Theory Group (MIT), (see Ref. 48) No. 34, 1959 (unpublished), p. 86; No. 35, 1960 (unpublished), p. 61.

where in (A.12) the real part operator does not appear, since all terms are real.

A family of variational expressions for ϵ_v which differ from (A1.9) to (A1.11) by second-order terms is given by

$$\epsilon_v\int_\Omega d\Omega\, \psi^*\psi = \int_{\Omega_i+\Omega_o} d\Omega\, \psi^*H\psi$$
$$+\int_S dS\{[a\partial_n\psi_o^*+(1-a)\partial_n\psi_i^*](\psi_o-\psi_i)$$
$$-[(1-c)\psi_o^*+c\psi_i^*](\partial_n\psi_o-\partial_n\psi_i)\}\quad \text{(A1.14)}$$

for arbitrary a and c. If $a=c$, (A1.14) always gives real values of ϵ_v and may be compactly written

$$\epsilon_v\int_\Omega d\Omega\, \psi^*\psi = \int_{\Omega_i+\Omega_o} d\Omega\, \psi^*H\psi$$
$$+2\,\mathrm{Re}\left\{\int_S dS[a\partial_n\psi_o^*+(1-a)\partial_n\psi_i^*](\psi_o-\psi_i)\right\}.$$
$$\text{(A1.15)}$$

Other Work

Variational expressions with discontinuous trial functions have also been proposed by Leigh[14] and by Bevensee.[51] Leigh gives a formula equivalent to

$$\epsilon_v\int_{\Omega_i+\Omega_o} d\Omega\, \psi^*\psi = \int_{\Omega_i+\Omega_o} d\Omega\, \psi^*H\psi$$
$$+\int_S dS(\psi_o^*\partial_n\psi_i-\psi_i\partial_n\psi_o^*),\quad \text{(A1.16)}$$

which differs from (A1.10) only in omitting the operation of taking the real part of the right-hand side. Thus, his expression is not variational unless a special class of trial functions is used—namely, those which make ϵ_v in (A1.16) real. In fact, Leigh limits his trial functions in this way by assuming $V(\mathbf{r})$ has inversion symmetry and that S is a sphere; then the eigenfunctions and trial functions can be chosen to have their real parts even and their imaginary parts odd, in which case the integrals in (A1.16) are all real (since inversion and complex conjugation of the functions are equivalent), hence, so is ϵ_v.

Bevensee (his Eq. 83) has given a variational expression of the form

$$\epsilon_v\int_\Omega d\Omega\, \phi^*\psi = \int_\Omega d\Omega\, \phi^*H\psi+\frac{1}{2}\int_S [(\psi_o-\psi_i)(\partial_n\phi_o^*+\partial_n\phi_i^*)$$
$$-(\phi_o^*+\phi_i^*)(\partial_n\psi_o-\partial_n\psi_i)]dS,\quad \text{(A1.17)}$$

where ϕ and ψ may be discontinuous on S and satisfy cellular boundary conditions. Equation (A1.17) is

[51] Robert M. Bevensee, Ann. Phys. (N. Y.) 12, 222 (1961).

equivalent to (A1.1) with $a=c=\frac{1}{2}$, and with ψ^* and ψ treated as independent functions, in which case ϵ_v is not, in general, real.

APPENDIX 2: DERIVATION OF THE SECULAR EQUATION

Expansion of the Trial Wave Function

For detailed calculation, the inner surface S is chosen spherical, of radius r_i around the single atom in the cell,[52] and the trial wave function is expanded in the composite form using N plane waves and L spherical waves. Thus, the trial wave function in the outer region Ω_o, the outer trial wave function ψ_o, is written

$$\psi_o(\mathbf{r},\mathbf{k})=\sum_{n=1}^{N} A_n e^{i\mathbf{k_n \cdot r}}, \qquad (A2.1)$$

where $\mathbf{k_n}=\mathbf{k}+\mathbf{K_n}$, and $\mathbf{K_n}$ is a reciprocal lattice vector. Each of the plane waves $e^{i\mathbf{k_n \cdot r}}$ thus satisfies the cellular boundary conditions, (2). The summation runs over the first N vectors $\mathbf{k_n}$ arranged in order of increasing magnitude.

The expansion of ψ_o in spherical waves is obtained from the expansion of the individual plane waves in spherical waves, namely[53]

$$e^{i\mathbf{k_n \cdot r}}=\sum_{l=0}^{\infty} i^l(2l+1)j_{lnr}P_{lnr}. \qquad (A2.2)$$

In (A2.2),
$$j_{lnr}\equiv j_l(k_n r)\equiv (\pi/2k_n r)J_{l+\frac{1}{2}}(k_n r),$$
with
$$k_n\equiv|\mathbf{k_n}|, \quad r\equiv|\mathbf{r}|,$$

is the spherical Bessel function of order l,[54] and $P_{lnr}\equiv P_l(C_{n,r})$ is the Legendre polynomial of order l, with argument $C_{n,r}\equiv(\mathbf{k_n \cdot r})/(k_n r)$, the cosine of the angle between $\mathbf{k_n}$ and $\mathbf{r}$. Then ψ_o becomes

$$\psi_o=\sum_{n=1}^{N} A_n \sum_{l=0}^{\infty} s_{nlir}(j_{lnr}/j_{lni}), \qquad (A2.3)$$

where
$$s_{nlir}\equiv i^l(2l+1)j_{lni}P_{lnr}, \qquad (A2.4)$$

$$j_{lni}\equiv j_l(k_n r_i). \qquad (A2.5)$$

The trial wave function in the inner, spherical region Ω_i, the inner trial wave function ψ_i, is expanded in L spherical waves. It is convenient to assume $V(\mathbf{r})$ is spherically symmetrical within Ω_i, hence, a function of

scalar r, and this will be assumed in the applications. Then the spherical waves used in the expansion are exact solutions of the Schrödinger equation in Ω_i corresponding to a trial energy value, ϵ_0.[55] The simplest assumption about the coefficients of the expansion is that the L terms in ψ_i agree on S with the first L spherical wave terms of ψ_o, as given by (A2.3); i.e., the first L spherical harmonic components of ψ_i and ψ_o are matched on S. This fixes the coefficients of ψ_i in terms of the A_n, and we have

$$\psi_i(\mathbf{k},\mathbf{r})=\sum_{n=1}^{N} A_n \sum_{l=0}^{L} s_{nlir}(\mathcal{R}_{l\epsilon_0 r}/\mathcal{R}_{l\epsilon_0 i}), \qquad (A2.6)$$

where $\mathcal{R}_{l\epsilon_0 r}\equiv\mathcal{R}_l(r,\epsilon_0)$ is the solution of the radial Schrödinger equation for energy ϵ_0 and potential $V(r)$ which is regular at the origin,

$$\mathcal{R}_l''+2\mathcal{R}_l'/r+[\epsilon_0-V(r)-l(l+1)/r^2]\mathcal{R}_l=0, \qquad (A2.7)$$

and $\mathcal{R}_{l\epsilon_0 i}\equiv\mathcal{R}_l(r_i,\epsilon_0)$. Clearly, (A2.6) and the first L terms of (A2.3) are identical for $r=r_i$.

Evaluation of Volume and Surface Integrals

The evaluation of the variational expression for the energy in terms of the A_n requires evaluation of various volume and surface integrals of the trial wave function in terms of the A_n, hence, these are now tabulated for later use.

From (A2.6) and (A2.4), the inner normalization integral is given by

$$\int_{\Omega_i} \psi_i^*\psi_i d\Omega=r_i^2 \sum_{n,n'=1}^{N} A_n^* A_{n'} \sum_{l=0}^{L} b_{lnn'}I_{l\epsilon_0 i}. \qquad (A2.8)$$

In (A2.8), the angular integral over all directions of $\mathbf{r}$

$$\int_{4\pi} s_{nlir}^* s_{n'l'ir} d\omega_r$$
$$=4\pi(2l+1)j_{lni}j_{ln'i}P_{lnn'}\delta_{ll'}\equiv b_{lnn'}\delta_{ll'}, \qquad (A2.9)$$

depending on the orthogonality relation[56]

$$\int_{4\pi} P_{lnr}P_{l'n'r}d\omega_r=(4\pi/2l+1)P_{lnn'}\delta_{ll'}, \qquad (A2.10)$$

has served to eliminate one l summation, and the radial integral $I_{l\epsilon_0 i}$ is defined by

$$I_{l\epsilon_0 i}\equiv\left(\int_0^{r_i} r^2\mathcal{R}_{l\epsilon_0 r}^2 dr\right)/r_i^2\mathcal{R}_{l\epsilon_0 i}^2. \qquad (A2.11)$$

From (A2.1) the outer normalization integral is

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[52] This restricts the discussion to monatomic Bravais lattices, which are the crystal structures of the materials considered here. Straightforward generalizations to lattices with a basis are possible, in which separate spherical surfaces are introduced around each nonequivalent nucleus.

[53] See, for example, J. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Co., Inc., New York, 1941), p. 409. Note that the choice of $\mathbf{k_n}$ as the polar axis for $\mathbf{r}$ in the argument of P_l in (A2.2) avoids introduction of associated Legendre functions here and in (A2.6).

[54] Reference 53, p. 404.

[55] For nonspherical potentials the expansion can still be made in terms of a solution for a suitable spherical potential, for example, the spherical average of the actual potential. The development is the same as given here, but additional integrals appear in the matrix elements and the convergence to the eigenvalue might not be as good. This case is treated in Ref. 26.

[56] Reference 53, p. 407.

given by

$$\int_{\Omega_o} \psi_o{}^* \psi_o d\Omega = \Omega \sum_{n,n'=1}^{N} A_n{}^* A_{n'} O_{nn'}{}^o, \quad (A2.12)$$

on introducing the outer plane-wave overlap integrals

$$O_{nn'}{}^o \equiv \Omega^{-1} \int_{\Omega_o} e^{i(\mathbf{K}_{n'}-\mathbf{K}_n)\cdot \mathbf{r}} d\Omega \equiv O_{(n-n')}{}^o, \quad (A2.13)$$

where the single-index quantity

$$O_n{}^o \equiv \Omega^{-1} \int_{\Omega_o} e^{-i\mathbf{K}_n\cdot \mathbf{r}} d\Omega$$

$$= \begin{cases} \Omega_o/\Omega, & \text{for } \mathbf{K}_n = 0 \\ -3(j_1(K_n r_i)/K_n r_i)(\Omega_i/\Omega), & \text{for } \mathbf{K}_n \neq 0 \end{cases} \quad (A2.14)$$

is the outer nth Fourier component of a constant, and

$$j_1(x) \equiv (\pi/2x)^{1/2} J_{3/2}(x) = \sin x/x^2 - \cos x/x.$$

It follows from (A2.6) and (A2.7) that the inner average energy is

$$\int_{\Omega_i} \psi_i{}^* H \psi_i d\Omega = \epsilon_0 \int_{\Omega_i} \psi_i{}^* \psi_i d\Omega, \quad (A2.15)$$

while from (A2.1) the outer average energy is

$$\int_{\Omega_o} \psi_o{}^* H \psi_o d\Omega$$

$$= \Omega \sum_{n,n'=1}^{N} A_n{}^* A_{n'} (k_{n'}{}^2 O_{nn'}{}^o + V_{nn'}{}^o). \quad (A2.16)$$

In (A2.16) occur the outer matrix elements of the potential (which need *not* be spherically symmetrical in Ω_o),

$$V_{nn'}{}^o \equiv \Omega^{-1} \int_{\Omega_o} V(\mathbf{r}) e^{i(\mathbf{K}_{n'}-\mathbf{K}_n)\cdot \mathbf{r}} d\Omega \equiv V_{(n-n')}{}^o, \quad (A2.17)$$

where the outer Fourier coefficients of the potential

$$V_n{}^o \equiv \Omega^{-1} \int_{\Omega_o} V(\mathbf{r}) e^{-i\mathbf{K}_n\cdot \mathbf{r}} d\Omega$$

$$= V_n - (4\pi/K_n\Omega) \int_0^{r_i} r V(r) \sin(K_n r) dr, \quad (A2.18)$$

thus expressing $V_n{}^o$ in terms of the Fourier coefficients of the potential

$$V_n = \Omega^{-1} \int_{\Omega} V(\mathbf{r}) e^{-i\mathbf{K}_n\cdot \mathbf{r}} d\Omega. \quad (A2.19)$$

For flattened potentials, (Sec. II), $V(\mathbf{r})$ has the constant value V_e in Ω_o; hence, $V_n{}^o = V_e O_n{}^o$ and is given by (A2.14).

Finally, from (A2.1), the outer integral of $|\nabla \psi_o|^2$ is

$$\int_{\Omega_o} \nabla \psi_o{}^* \cdot \nabla \psi_o d\Omega = \Omega \sum_{n,n'=1}^{N} A_n{}^* A_{n'} \mathbf{k}_n \cdot \mathbf{k}_{n'} O_{nn'}{}^o. \quad (A2.20)$$

The surface integrals of interest are

$$\int_S \psi_o{}^* \partial_n \psi_i dS = r_i{}^2 \sum_{n,n'=1}^{N} A_n{}^* A_{n'} \sum_{l=0}^{L} \mathcal{L}_{l\epsilon_0 i} b_{lnn'}, \quad (A2.21)$$

$$\int_S \psi_i{}^* \partial_n \psi_o dS = r_i{}^2 \sum_{n',n=1}^{N} A_n{}^* A_{n'}$$

$$\times \sum_{l=0}^{L} k_{n'} (j_{ln'i}'/j_{ln'i}) b_{lnn'}, \quad (A2.22)$$

$$\int_S \psi_o{}^* \partial_n \psi_o dS = r_i{}^2 \sum_{n,n'=1}^{N} A_n{}^* A_{n'}$$

$$\times \sum_{l=0}^{\infty} k_{n'} (j_{ln'i}'/j_{ln'i}) b_{lnn'}, \quad (A2.23)$$

where the logarithmic derivative of the radial function on S

$$\mathcal{L}_{l\epsilon_0 i} \equiv \mathcal{R}_{l\epsilon_0 i}'/\mathcal{R}_{l\epsilon_0 i} \quad (A2.24)$$

and $j_{ln'i}' \equiv [\partial j_l(k_{n'} r)/\partial (k_{n'} r)]_{r=r_i}$. Note the difference in the l summation limits in (A2.22) and (A2.23).

Variational Expressions and the Secular Equation

Substitution of the composite expansion of the trial wave function, (A2.1) or (A2.3) and (A2.6), into various variational expressions for the energy leads to a linear equation for ϵ_v, all terms of which are quadratic in the A_n and $A_n{}^*$,

$$\text{Re}\left\{ \sum_{n,n'=1}^{N} A_n{}^* A_{n'} (H_{nn'} - \epsilon_v D_{nn'}) \right\} = 0. \quad (A2.25)$$

The variational character of this equation for ϵ_v means that the first-order variation of ϵ_v vanishes when a first-order variation of any A_n is made. Hence, linear equations for the $A_{n'}$ are obtained by differentiating (A2.25) with respect to the $A_n{}^*$, holding ϵ_v constant. The matrix elements obtained using (A1.10), denoted by superscript one, evaluated from (A2.15), (A2.8), (A2.16), (A2.21), (A2.22), and (A2.8), (A2.12) successively, are

$$H_{nn'}{}^{(1)} = \epsilon_0 r_i{}^2 \sum_{l=0}^{L} I_{l\epsilon_0 i} b_{lnn'} + \Omega(k_{n'}{}^2 O_{nn'}{}^o + V_{nn'}{}^o)$$

$$+ r_i{}^2 \sum_{l=0}^{L} (\mathcal{L}_{l\epsilon_0 i} - (k_{n'} j_{ln'i}'/j_{ln'i})) b_{lnn'}, \quad (A2.26)$$

and

$$D_{nn'}{}^{(1)} = r_i{}^2 \sum_{l=0}^{L} I_{l\epsilon_0 i} b_{lnn'} + \Omega O_{nn'}{}^o. \quad (A2.27)$$

Similarly, the matrix elements from (A1.11), superscript two, have the form

$$H_{nn'}{}^{(2)} = \epsilon_0 r_i^2 \sum_{l=0}^{L} I_{l\epsilon_0 i} b_{lnn'}$$

$$+ \Omega(\mathbf{k}_n \cdot \mathbf{k}_{n'} O_{nn'}{}^o + V_{nn'}{}^o) + r_i^2 \sum_{l=0}^{L} \mathcal{L}_{l\epsilon_0 i} b_{lnn'}$$

$$+ r_i^2 \sum_{l=L+1}^{\infty} k_{n'}(j_{ln'i}'/j_{ln'i}) b_{lnn'}, \quad (A2.28)$$

$$D_{nn'}{}^{(2)} = D_{nn'}{}^{(1)}. \quad (A2.29)$$

The equivalence of (A2.26) and (A2.28) also follows directly from the useful identity, obtained by applying Green's theorem (A1.5b) to two plane waves,

$$\Omega k_{n'}{}^2 O_{nn'}{}^o - r_i^2 k_{n'} \sum_{l=0}^{\infty} (j_{ln'i}'/j_{ln'i}) b_{lnn'}$$

$$= \Omega \mathbf{k}_n \cdot \mathbf{k}_{n'} O_{nn'}{}^o. \quad (A2.30)$$

Now to take the real part of the summation in (A2.25), observe that all parts of $H_{nn'}$ and $D_{nn'}$ are real, with the possible exception of $V_{nn'}$, which, however, always has the Hermitean property $V_{nn'} = V_{n'n}{}^*$. Thus, all parts which are real and symmetric in $\mathbf{n}$, $\mathbf{n'}$, or Hermitean, make a real contribution to the summation on combining the complex conjugate terms of (A2.25) with coefficients $A_n^* A_{n'}$ and $A_{n'}^* A_n$. This leaves the contributions of the real but unsymmetric parts of (A2.26) and (A2.28) which may be obtained by making these parts symmetric with respect to $\mathbf{n}$ and $\mathbf{n'}$. Hence, we introduce the index-symmetric matrix elements

$$H_{nn'}{}^{(1s)} = \epsilon_0 r_i^2 \sum_{l=0}^{L} I_{l\epsilon_0 i} b_{lnn'} + \Omega[(k_n^2 + k_{n'}^2) O_{nn'}{}^o/2 + V_{nn'}{}^o]$$

$$+ r_i^2 \sum_{l=0}^{L} [\mathcal{L}_{l\epsilon_0 i} - \tfrac{1}{2}(k_n j_{lni}'/j_{lni}$$

$$+ k_{n'} j_{ln'i}'/j_{ln'i})] b_{lnn'}, \quad (A2.31)$$

$$H_{nn'}{}^{(2s)} = \epsilon_0 r_i^2 \sum_{l=0}^{L} I_{l\epsilon_0 i} b_{lnn'} + \Omega(\mathbf{k}_n \cdot \mathbf{k}_{n'} O_{nn'}{}^o + V_{nn'}{}^o)$$

$$+ r_i^2 \sum_{l=0}^{L} \mathcal{L}_{l\epsilon_0 i} b_{lnn'} + \tfrac{1}{2} r_i^2 \sum_{l=L+1}^{\infty} (k_n j_{lni}'/j_{lni}$$

$$+ k_{n'} j_{ln'i}'/j_{ln'i}) b_{lnn'} \quad (A2.32)$$

for the matrix elements in (A2.25) and remove the real part operator.

Note that if the l summation goes to infinity, the original forms of the matrix elements (A2.26) and (A2.28) are already index-symmetric. This is apparent for $H_{nn'}{}^{(2)}$, and is true for the equivalent form $H_{nn'}{}^{(1)}$ as a consequence of (A2.30).

As noted above, linear equations for the A_n are obtained by differentiating (A2.25); instead of treating the real and imaginary parts of A_n as independent variables, it is convenient to use the linearly independent combinations A_n and A_n^*. This leads to a set of homogeneous linear equations for the A_n,

$$\sum_{n'=1}^{N} A_{n'}(H_{nn'}{}^{(s)} - \epsilon_v D_{nn'}) = 0, \quad n = 1 \text{ to } N, \quad (A2.33)$$

and since $H_{nn'}{}^{(s)}$ and $D_{nn'}$ are Hermitean, to the complex conjugate equations for the A_n^*. In either case, the condition for the solution gives the same secular equation from the vanishing of the determinant of the coefficients

$$|H_{nn'}{}^{(s)} - \epsilon_v D_{nn'}| = 0, \quad (A2.34)$$

whose roots ϵ_v are always real.[57]

Note that if $V(-\mathbf{r}) = V(\mathbf{r})$, corresponding to the nucleus being a center of inversion, $V_{nn'}$ and the matrix elements are all real, and the coefficients A_n are then real. This is the case for the lattices to which application is made here.[52]

Finally, note that the matrix elements do not require knowledge of the radial functions within S, but only of certain quantities at $r = r_i$, namely of the logarithmic derivative at r_i, $\mathcal{L}_{l\epsilon_0 i}$ and of the integral $I_{l\epsilon_0 i}$ which is, in fact, the energy derivative of the logarithmic derivative at ϵ_0 and on S, $-(\partial \mathcal{L}_{l\epsilon_0 i}/\partial \epsilon_0)$.[58]

Symmetrized Form of the Secular Equation

The theory has been developed to this point without explicit account of the symmetry of the lattice. However, at certain symmetry points and along certain symmetry axes in the Brillouin zone, one may greatly reduce the order of the secular equation which must be solved to obtain accurate energy eigenvalues by taking lattice symmetry into account in constructing the matrix elements entering into the secular equation. One notes that the accuracy of the representation is a function of the number of plane waves which are included in the expansion of the trial wave function; the greater the depth of the expansion in $\mathbf{k}$ space, the more accurate is the representation. The use of properly symmetrized matrix elements yields a smaller secular equation and the same energy for a given number of plane waves in the wave function expansion than the use of unsymmetrized functions. Hence, one can obtain greater accuracy at symmetry points than at general points with the same labor in solving the secular equation, or equal accuracy with less labor.

[57] Since the secular equation is not in standard form, this requires an extension of the theorem that the roots of a Hermitean matrix are real. Noting that the matrix $D_{nn'}$ is positive definite, the matrix $D_{nn'}{}^{-1/2} H_{n'n''} D_{n''n'''}{}^{-1/2}$ can be formed, whose secular equation has standard form and has the same roots as (A2.33).

[58] The relation was first published by R. A. Silverman, Phys. Rev. **85**, 227 (1952); for a simple proof, see H. Brooks, Nuovo Cimento **7**, Suppl. No. 2, 165 (1958); see p. 197, specifically.

Projection-operator techniques[59] are used to construct the symmetrized matrix elements. A projection operator has the property of projecting out of any arbitrary function the portion which transforms according to a particular irreducible representation of the group. A detailed discussion has been given by Schlosser,[60] who has tabulated symmetrized combinations of plane waves and matrix elements of the Hamiltonian for the simple cubic, face-centered cubic, and zincblende lattices, as well as the body-centered cubic lattice used in the applications here. We shall quote some results from that discussion. Let $\rho_{ij}{}^\alpha$ be the jth normalized projection operator transforming according to the ith row of the αth irreducible representation of the group of $\mathbf{k}$ defined by,

$$\rho_{ij}{}^\alpha = (\eta_\alpha/g) \sum_R \Gamma_{ij}{}^{\alpha*}(R)R, \qquad (A2.35)$$

where $\Gamma_{ij}{}^{\alpha*}(R)$ is the complex conjugate of the ijth element of the representation matrix for operation R of the αth irreducible representation of the group, η_α is the dimension of representation α, g is the order of the group and the sum is over all the operations R in the group.

The properties of projection operators can be used to show that matrix elements of the Hamiltonian between two symmetrized functions can be reduced to a matrix element between a symmetrized and an unsymmetrized function. Consider

$$H_{ij,kl}{}^{\alpha\beta,\mu\nu} \equiv \int (\rho_{ij}{}^\alpha\psi_\mu)^* H\rho_{kl}{}^\beta\psi_\nu d\Omega N_\mu N_\nu$$

$$= (\rho_{ij}{}^\alpha\psi_\mu, H\rho_{kl}{}^\beta\psi_\nu)N_\mu N_\nu, \qquad (A2.36)$$

[59] G. Koster, Tech. Rep. No. 8, Solid State and Molecular Theory Group, MIT, Cambridge, Massachusetts, 1956 (unpublished).
[60] H. Schlosser, J. Phys. Chem. Solids 23, 963 (1962).

where

$$\psi_\mu \equiv \psi(\mathbf{k}_\mu),$$

$$N_\mu \equiv (n_\mu)^{1/2},$$

and n_μ is the number of independent elements in the star of $\mathbf{k}_\mu$ (that is, the number of different independent $\mathbf{k}_\mu$'s which transform into each other under the operations of the group). We note that $H_{ij,kl}{}^{\alpha\beta,\mu\nu}$ has been normalized over the cell volume Ω. It follows easily[60] that

$$H_{ij,kl}{}^{\alpha\beta,\mu\nu} = (\psi_\mu, H\rho_{ji}{}^\beta\psi_\nu)N_\mu N_\nu \delta_{\alpha\beta}\delta_{ik}. \qquad (A2.37)$$

Thus, we have reduced $H_{ij,kl}{}^{\alpha\beta,\mu\nu}$ to a matrix element between a symmetrized wave function and an unsymmetrized wave function, and have demonstrated that the Hamiltonian does not have matrix elements between wave functions belonging to different irreducible representations of the group of $\mathbf{k}$, or between functions belonging to different rows of the same representation when the representation is degenerate.

Therefore, making use of (A2.37), we can write the symmetrized form of the secular equation for the αth irreducible representation of the group of $\mathbf{k}$,

$$\sum_{n'=1}^{N} A_{n'}N_n N_{n'}(\eta_\alpha/g)$$

$$\times \{\sum_R \Gamma_{ji}{}^{\alpha*}(R)[H_{n(Rn')} - \epsilon_v D_{n(Rn')}]\} = 0,$$

$$n = 1 \text{ to } N, \qquad (A2.38)$$

where $H_{n(Rn')}$ and $D_{n(Rn')}$ are obtained from the matrix elements $H_{nn'}$ and $D_{nn'}$, given in (A2.27), (A2.31), and (A2.32), by substituting in these expressions $R\mathbf{k}_{n'}$ for $\mathbf{k}_{n'}$.