Relationship between the Augmented-Plane-Wave and Korringa-Kohn-Rostoker Methods of Band Theory*

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The augmented-plane-wave (APW) method and the recently proposed pseudopotential method of Ziman are derived from the "scattered-wave" or Green's-function approach, thus establishing their connection with the original Korringa-Kohn-Rostoker (KKR) method. It is shown that the differences between these various band-theoretical techniques can be understood in terms of the particular choices for the representations and basis sets used in the expansions of the composite wave function and the Green's function. It is proven that the APW method leads to the most rapidly convergent representation in plane waves of the exact solution to the ordinary wave equation outside the "muffin-tin" spheres, while the KKR scheme yields the most rapidly convergent partial-wave or angular momentum representation of the exact solution to the Schrödinger problem within the spheres. The relative advantages of these methods in computing energy bands and one-electron wave functions are discussed.

I. INTRODUCTION

It is well known to specialists working in the band theory of solids that two particular methods of calculating electronic energy bands, namely the "scattered-wave" technique of Korringa[1] and Morse[2] or equivalent Green's-function technique of Kohn and Rostoker[3] (KKR method) and the augmented-plane-wave (APW) method of Slater,[4] yield practically identical results when applied to the same crystal for identical crystal potentials. The attempt to develop a common theoretical framework for these two methods in terms of pseudopotential models has been the object of several recent papers by Ziman,[5] Lloyd,[6] and Slater.[7]

An important outcome of the pseudopotential approach has been to show that the KKR technique, originally cast in the angular momentum or partial-wave representation, can be recast in a plane-wave representation somewhat similar to that of the APW scheme. Since this representation was originally proposed by Ziman,[5] we shall call it the KKR-Z pseudopotential. Thus both the APW and KKR-Z secular determinants, which lead to the one-electron eigenvalues for the energy band problem, can be written symbolically as

$$\det|(k_n^2-E)\delta_{nn'}+\Gamma_{nn'}(\mathbf{k},E)|=0. \quad (1)$$

The quantity $\Gamma_{nn'}(\mathbf{k},E)$ is the pseudopotential matrix element which for energy E connects two plane waves of total wave vectors $\mathbf{k}_n=\mathbf{k}+\mathbf{K}_n$ and $\mathbf{k}_{n'}=\mathbf{k}+\mathbf{K}_{n'}$, respectively, ($\mathbf{k}$=point in reduced Brillouin zone; $\mathbf{K}_n$=principal translation vector of reciprocal lattice). In the case of the APW method, the pseudopotential takes the form (restricting our discussions to only one atom per unit cell)[4,6–8]

$$\Gamma_{nn'}{}^{(\mathrm{APW})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}\Bigg\{-(k_{n'}{}^2-E)\frac{j_1(|\mathbf{k}_{n'}-\mathbf{k}_n|R)}{|\mathbf{k}_{n'}-\mathbf{k}_n|}+\sum_l(2l+1)P_l(\cos\theta_{nn'})j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right]\Bigg\}, \quad (2)$$

while that for the KKR-Z method is[5–7]

$$\Gamma_{nn'}{}^{(\mathrm{KKR\text{-}Z})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}\Bigg\{\sum_l(2l+1)P_l(\cos\theta_{nn'})\times j_l(k_nR)j_l(k_{n'}R)\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right]\Bigg\}. \quad (3)$$

There is considerable similarity between these two expressions; for example, the appearance of the logarithmic derivatives of the radial wave functions (solutions of the radial Schrödinger equation for energy E) and the logarithmic derivatives of the spherical Bessel functions at the "muffin-tin" sphere radius R. However, there are also two notable differences. First of all, an extra Bessel function term $j_1(|\mathbf{k}_{n'}-\mathbf{k}_n|R)/|\mathbf{k}_{n'}-\mathbf{k}_n|$ appears in the APW pseudopotential. Secondly, the logarithmic derivatives of the Bessel functions for the KKR-Z pseudopotential have in their arguments the quantity $\kappa=(E)^{1/2}$, rather than the wave vector k_n as in expression (2).

It would be valuable to obtain additional insight into the origins of both the similarities and differences of the APW and KKR-Z methods, and to understand their relative convergence properties. The KKR-Z pseudopotential has not yet been applied in an actual

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[8] The APW matrix element written in Eq. (2) is actually an alternate form of the original expression derived by Slater. It was first suggested by Slater in *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1965), Vol. 2, p. 242.

energy-band calculation, so that such an investigation could help us to decide whether there will be any advantage to using one plane-wave method over the other in computations. The APW[9] and original KKR[10–13] schemes have been applied successfully many times. Since the KKR and KKR-Z representations are related (essentially by Fourier transform), an analysis of the relative properties of the two pseudopotentials could also lead to a more complete understanding of why the KKR and APW results agree so well, and whether an angular momentum or partial-wave representation is to be preferred over a plane-wave representation in setting up the eigenvalue problem.

Unfortunately, the pseudopotential derivations are primarily restatements of the original formulations and depend upon somewhat arbitrary replacements of the original potential by elaborate t-matrix and algebraic expansions[5] or delta-function singularities on the surface of the sphere.[6] They do not provide the type of common theoretical framework we are looking for. Moreover, Slater[7] has emphasized that while a common theoretical basis for the APW and KKR-Z methods may indeed be developed, there is sound reason to believe that it is impossible to transform one technique directly into the other. Slater's observation is based on the fact that the "muffin-tin" approximation to the crystal potential, which is used in both methods, introduces a lack of uniqueness in the composite wave functions. In other words, it is possible for two entirely different wave functions to converge to the proper solution of the energy-band problem outside or inside the nonoverlapping spheres. Outside the spheres, where the potential is assumed to be constant (adjusted to zero in the actual calculations), the Schrödinger equation is just the ordinary wave or scalar Helmholtz equation

$$r>R: \qquad (\nabla^2+\kappa^2)\Psi(\mathbf{r})=0. \tag{4}$$

Inside the spheres, where the potential is spherically averaged, the wave function is a solution of the Schrödinger equation or inhomogeneous wave equation

$$0\leq r<R: \qquad (\nabla^2+\kappa^2)\Psi(\mathbf{r})=V(r)\Psi(\mathbf{r}). \tag{5}$$

It has occurred to us that since the wave function in the region outside the spheres must be a proper solution to the "scattering" of a Bloch "wave" by the potential $V(r)$, the "scattered-wave" or Green's-function approach used to develop the original KKR method could also lead directly to both the KKR-Z and APW representations. This approach might be a more direct and revealing way to arrive at a common theoretical basis for comparing these band-theoretical models and their relative convergence properties.

It is well known that Eq. (4) can be transformed to the integral equation for the scattering of a wave by a sphere of radius R in the unit cell, namely[14]

$$\int_{r_0^s=R}[G(\mathbf{r},\mathbf{r}_0^s)\nabla_0\Psi(\mathbf{r}_0^s)-\Psi(\mathbf{r}_0^s)\nabla_0 G(\mathbf{r},\mathbf{r}_0^s)]\cdot\hat{n}_0 dS_0 = \begin{cases}\Psi(\mathbf{r}); & R<r<r^b\\ 0; & 0\leq r<R,\end{cases} \tag{6}$$

where $G(\mathbf{r},\mathbf{r}_0)$ is the single-particle Green's function in the "field" and "source" points $\mathbf{r}$ and $\mathbf{r}_0$, respectively, satisfying the inhomogeneous wave equation

$$(\nabla^2+\kappa^2)G(\mathbf{r},\mathbf{r}_0)=\delta(\mathbf{r}-\mathbf{r}_0). \tag{7}$$

The vector $\mathbf{r}_0^s$ refers to a point on the surface of the sphere and the unit vector n_0 points away from its center. It should be noted that an additional surface integral of the form (6) over the unit cell boundary $\mathbf{r}^b$ has identically vanished because both the wave function and Green's function satisfy the homogeneous periodic Bloch boundary conditions there. If we then allow the "field" point to approach the surface $\mathbf{r}^s$ of the sphere in the sense of taking the limit (to avoid the singularity in the Green's function when "source" point coincides with "field" point)

$$\lim_{R'\to R}\int_{r_0^s=R}[G(\mathbf{r}^s,\mathbf{r}_0^s)|_{r^s=R'}\nabla_0\Psi(\mathbf{r}_0^s) - \Psi(\mathbf{r}_0^s)\nabla_0 G(\mathbf{r}^s,\mathbf{r}_0^s)|_{r^s=R'}]\cdot\hat{n}_0 dS_0 = \lim_{R'\to R}\Psi(\mathbf{r}^s)|_{r^s=R'}, \tag{8}$$

and choose suitable expansions for both the Green's function and the "trial" wave function, we will be led to the original set of secular equations for the KKR technique (see Morse[2]). Since the wave function as represented by Eq. (6) is formally zero within the spheres, it is evident that one can set up the energy-band eigenvalue or secular problem entirely in terms of the solution outside or on the surface of the sphere. One can ensure that this wave function will join smoothly to the solution of the Schrödinger problem (5) within the sphere, i.e.,

$$0\leq r<R: \quad \Psi(\mathbf{r})=\int_{\Omega_s=4\pi R^3/3} G(\mathbf{r},\mathbf{r}_0)V(r_0)\Psi(\mathbf{r}_0)d\mathbf{r}_0, \tag{9}$$

by expressing the joining conditions in terms of inhomogeneous boundary conditions for the wave function on

[9] For a review of APW band calculations, see J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1963, No. 51, p. 14 (unpublished). This review is also published in *Advances in Quantum Chemistry*, edited by P. O. Löwdin (Academic Press Inc., New York, 1964), Vol. I, p. 35.

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[14] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, p. 805.

the surface of the sphere. Of course, one can also set up the secular problem entirely in terms of the solution (9) within and on the sphere, and then join it smoothly to the wave function outside the sphere. This was the original approach of Kohn and Rostoker[2] in their variational formulation of Eq. (9).

In attempting to derive the APW and KKR-Z representations, as compared with the KKR representation, directly from Eqs. (6) and (8), we should expect that the chief differences would arise, first of all, from the use of a plane-wave rather than partial-wave expansion of the "trial" wave function, and secondly from the choices of the Green's-function expansions and the boundary conditions on the surface of the sphere. In the case of the APW method, for example, the boundary condition will be just the one set up originally by Slater,[4] namely, the continuity of a single plane wave restricted to the region outside the spheres with a linear combination of spherical harmonic-radial function products which generate a solution to the Schrödinger equations (5) and (9) inside the spheres. The preservation of the original boundary conditions is an additional advantage of the "scattered-wave" or Green's-function approach over that of pseudopotentials in comparing the APW and KKR-Z representations.

We shall demonstrate, by both a simple use of projection operators and by the method of fitting a Fourier series, that the restriction of the plane-wave representation of the composite wave function to the region outside the "muffin-tin" spheres in the APW method leads to the most rapidly convergent plane-wave expansion of the wave functions there. The application of this argument to the KKR-Z and KKR representations leads to alternate secular equations which are related to the APW secular equations by a simple unitary transformation.

The option of using angular-momentum or partial-wave type expansions, rather than plane-wave expansions, for both the "trial" wave function and Green's function allows us to compare the plane-wave representation of the wave function outside the spheres directly with Korringa[1]-type wave functions expanded in "outgoing" spherical waves in this region. This, as we shall show below, also leads to useful information concerning the relative advantages and flexibility of these band-theoretical techniques.

These then are the objects of this paper. In Sec. II, we shall present the derivations of the APW and KKR-Z representations of the energy-band problem, with emphasis placed on the "best" choice of expanding the wave function outside the spheres. Section III will constitute a discussion of the outgoing-spherical-wave representation. In Sec. IV, we will summarize the properties of the various band-theoretical formulations and discuss the implications of these properties on practical calculations of energy bands.

II. THE PLANE-WAVE REPRESENTATIONS

A. The APW Method

Projection Operator Technique

The problem of determining solutions to the wave equation in the integral form (6) over the domain of the unit cell is reminiscent of similar problems in classical potential theory. We use the familiar plane-wave expansion of the Green's function, with the plane waves in this case normalized to the unit cell of volume Ω, i.e.,[3,15]

$$G(\mathbf{r},\mathbf{r}_0)=-\sum_n \frac{\Phi_n(\mathbf{r})\Phi_n^*(\mathbf{r}_0)}{k_n^2-E}, \tag{10}$$

$$\Phi_n(\mathbf{r})=(\Omega)^{-1/2}\exp(i\mathbf{k}_n\cdot\mathbf{r}). \tag{11}$$

The distinguishing feature of the APW method is the restriction of the plane-wave description of the wave function to the region outside the spheres, where the potential is flat. Therefore, in our approach, it would be improper to expand the "trial" APW solutions directly in the set (11). It is more appropriate here to generate basis functions which are plane waves Φ_n outside the sphere, but identically zero within the sphere. Let us call these functions χ_n. The resolution of the identity operator can be defined by the completeness of the set Φ_n over the unit cell. Thus we shall write

$$I=\sum_n \Phi_n\rangle\langle\Phi_n=\sum_n \Phi_n(\mathbf{r})\int_\Omega d\mathbf{r}'\Phi_n^*(\mathbf{r}'). \tag{12}$$

Since the cell is partitioned into the regions spanned respectively by the sphere of volume $\Omega_s=4\pi R^3/3$ and the region outside the sphere, of volume $\Omega-\Omega_s$, we can similarly partition our space of functions into two orthogonal complements defined by the projection operators

$$I=\mathcal{O}(\mathbf{r})+\mathcal{P}(\mathbf{r});\quad 0\leq r<r^b, \tag{13}$$

where

$$\mathcal{O}(\mathbf{r})=\sum_n \Phi_n(\mathbf{r})\int_{\Omega-\Omega_s} d\mathbf{r}'\Phi_n^*(\mathbf{r}'), \tag{14}$$

and

$$\mathcal{P}(\mathbf{r})=\sum_n \Phi_n(\mathbf{r})\int_{\Omega_s} d\mathbf{r}'\Phi_n^*(\mathbf{r}'). \tag{15}$$

The functions χ_n are obtained as the result of applying the projection operator $\mathcal{O}$ to the set Φ_n, i.e.,

$$\begin{aligned}\chi_{n'}(\mathbf{r})&=\mathcal{O}(\mathbf{r})\Phi_{n'}(\mathbf{r})\\ &=\sum_n \Phi_n(\mathbf{r})N_{nn'}=\Phi_{n'}(\mathbf{r});\quad R<r<r^b\\ &=0;\qquad\qquad\qquad\quad 0\leq r<R\end{aligned} \tag{16}$$

[15] B. Friedman, *Principles and Techniques of Applied Mathematics* (John Wiley & Sons, Inc., New York, 1956), p. 213.

where

$$N_{nn'}=\int_{\Omega-\Omega_s}\Phi_n^*(\mathbf{r})\Phi_{n'}(\mathbf{r})d\mathbf{r}. \quad (17)$$

Therefore, the functions χ_n have the properties we are looking for in a basis set, i.e., they are plane waves outside the sphere and identically zero inside. Moreover, the set is complete for the solution outside the spheres because the projection operator $\mathcal{O}$ defines the resolution of the identity in this region. It is important to note the linear dependence introduced between the original plane waves Φ_n in this region. That is, Eq. (16) is also a statement of the overcompleteness of the set of functions Φ_n (defined through the entire unit cell) if used to expand the wave function only outside the spheres.

Let us now write for the "trial" wave function to be used in Eqs. (6) and (8) the expansion

$$R\leq r<r^b: \quad \Psi(\mathbf{r})=\sum_{n'}A_{n'}\chi_{n'}=\sum_{n,n'}\Phi_n N_{nn'}A_{n'}, \quad (18)$$

where the equality $r=R$ should again be understood only in the sense of approaching the surface of the sphere as a limit. In practical applications, of course, the set (18) is truncated. Slater's[4] original boundary condition on the wave function at the sphere radius is that a single plane wave be continuous with a partial-wave solution of the Schrödinger equation (5) or (9). In our derivation, we shall translate this continuity condition into an inhomogeneous boundary condition satisfied by the "trial" wave function on the surface of the sphere. That is, we can write for the condition of the plane wave Φ_n appearing in (18) the equation

$$r_0^s=R: \quad \Phi_n(\mathbf{r}_0^s)=(\Omega)^{-1/2}\sum_{l,m}C_{lm}\mathcal{R}_l(E,R)\mathcal{Y}_{lm}(\mathbf{r}_0^s). \quad (19)$$

Employing the familiar expansion for the plane wave

$$\exp(i\mathbf{k}\cdot\mathbf{r})=4\pi\sum_{l,m}i^l j_l(kr)\mathcal{Y}_{lm}^*(\mathbf{k})\mathcal{Y}_{lm}(\mathbf{r}), \quad (20)$$

we can solve for the coefficients C_{lm}, obtaining

$$C_{lm}=i^l\frac{j_l(k_nR)}{\mathcal{R}_l(E,R)}\mathcal{Y}_{lm}^*(\mathbf{k}_n). \quad (21)$$

Substitution of (21) into (19) and then (19) into (18) yields for the "trial" wave function and its normal derivative on the sphere the respective expressions

$r_0^s=R$:

$$\Psi(\mathbf{r}_0^s)=(\Omega)^{-1/2}\sum_{n,n'}N_{nn'}A_{n'}\sum_{l,m}i^l j_l(k_nR)\times\mathcal{Y}_{lm}^*(\mathbf{k}_n)\mathcal{Y}_{lm}(\mathbf{r}_0^s) \quad (22)$$

and

$r_0^s=R$:

$$\hat{n}_0\cdot\nabla_0\Psi(\mathbf{r}_0^s)=(\Omega)^{-1/2}\sum_{n,n'}N_{nn'}A_{n'}\times\sum_{l,m}i^l\frac{j_l(k_nR)}{\mathcal{R}_l(E,R)}\mathcal{Y}_{lm}^*(\mathbf{k}_n)\mathcal{R}_l'(E,R)\mathcal{Y}_{lm}(\mathbf{r}_0^s), \quad (23)$$

where the prime denotes radial differentiation. We can also expand the plane waves $\Phi_n^*(\mathbf{r}_0)$ of the Green's function (10) in the series (20), obtaining for that function and its normal derivative on the surface of the sphere

$r>r_0^s=R$:

$$G(\mathbf{r},\mathbf{r}_0^s)=-(\Omega)^{-1/2}4\pi\sum_n\frac{\Phi_n(\mathbf{r})}{k_n^2-E}\sum_{l,m}i^{-l}j_l(k_nR)\times\mathcal{Y}_{lm}(\mathbf{k}_n)\mathcal{Y}_{lm}^*(\mathbf{r}_0^s), \quad (24)$$

$r>r_0^s=R$:

$$\hat{n}_0\cdot\nabla_0G(\mathbf{r},\mathbf{r}_0^s)=-(\Omega)^{-1/2}4\pi\sum_n\frac{\Phi_n(\mathbf{r})}{k_n^2-E}\sum_{l,m}i^{-l}j_l'(k_nR)\times\mathcal{Y}_{lm}(\mathbf{k}_n)\mathcal{Y}_{lm}^*(\mathbf{r}_0^s). \quad (25)$$

The direct substitution of expressions (22) through (25) into the surface integral of Eq. (6) yields for the wave function outside the spheres (after performing the integration over the "source" coordinates and using the completeness of the basis set χ_n)

$$R<r<r^b: \quad \Psi(\mathbf{r})=\sum_n\mathfrak{F}_n^{(\mathrm{APW})}(\mathbf{k},E)\exp(i\mathbf{k}_n\cdot\mathbf{r}) \quad (26)$$

in which

$$\mathfrak{F}_n^{(\mathrm{APW})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega^{3/2}}(E-k_n^2)^{-1}\times\sum_{n'}A_{n'}\sum_{l,m}j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathcal{R}_l'(E,R)}{\mathcal{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right]\mathcal{Y}_{lm}^*(\mathbf{k}_n)\mathcal{Y}_{lm}(\mathbf{k}_{n'}). \quad (27)$$

The quantities $\mathfrak{F}_n^{(\mathrm{APW})}(\mathbf{k},E)$ are the Fourier components of the exact wave function outside the spheres and are determined once the coefficients A_n have been established at the energy eigenvalues $E=E(\mathbf{k})$. The latter are calculated from the secular equations, which can be generated by performing the same substitutions at those carried out above in Eq. (8). The secular equations can be written in the form

$$\sum_{n'}[(k_{n'}^2-E)N_{nn'}+T_{nn'}(\mathbf{k},E)]A_{n'}=0, \quad (28)$$

where

$$N_{nn'}=\Omega^{-1}\int_{\Omega-\Omega_s}\exp[i(\mathbf{k}_{n'}-\mathbf{k}_n)\cdot\mathbf{r}]d\mathbf{r} \quad (29)$$

and

$$T_{nn'}(\mathbf{k},E)=\frac{(4\pi)^2R^2}{\Omega}\sum_{l,m}j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathcal{R}_l'(E,R)}{\mathcal{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right]\mathcal{Y}_{lm}^*(\mathbf{k}_n)\mathcal{Y}_{lm}(\mathbf{k}_{n'}). \quad (30)$$

Expression (29) is easily integrated and yields

$$N_{nn'}=\delta_{nn'}-\frac{4\pi R^2}{\Omega}\frac{j_1(|\mathbf{k}_{n'}-\mathbf{k}_n|R)}{|\mathbf{k}_{n'}-\mathbf{k}_n|}. \quad (31)$$

Both the Fourier coefficients (27) and the matrix elements (30) can be simplified by using the addition theorem for spherical harmonics. The new expressions are

$$\mathfrak{F}_n^{(\mathrm{APW})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega^{3/2}}(E-k_n^2)^{-1}\times\sum_{n'}A_{n'}\sum_l(2l+1)P_l(\cos\theta_{nn'})j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right] \quad (32)$$

and

$$T_{nn'}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}\sum_l(2l+1)P_l(\cos\theta_{nn'})\times j_l(k_nR)j_l(k_{n'}R)\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right]. \quad (33)$$

The secular equations can now be written as

$$\sum_{n'}[(k_{n'}^2-E)\delta_{nn'}+\Gamma_{nn'}^{(\mathrm{APW})}(\mathbf{k},E)]A_{n'}=0 \quad (34)$$

in which

$$\Gamma_{nn'}^{(\mathrm{APW})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}\left\{-(k_{n'}^2-E)\frac{j_1(|\mathbf{k}_{n'}-\mathbf{k}_n|R)}{|\mathbf{k}_{n'}-\mathbf{k}_n|}+\sum_l(2l+1)P_l(\cos\theta_{nn'})j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right]\right\}. \quad (35)$$

The determinant of the above matrix therefore agrees exactly with that written in Eqs. (1) and (2) for the APW method. Its zeros lead directly to the energy-band eigenvalues $E(\mathbf{k})$ and to the coefficients A_n of the augmented plane waves.

Fourier Series Technique

Let us return to the original question as to the choice of basis functions for expanding the APW wave function. Our adoption of the set χ_n, which are plane waves outside and zero inside the spheres, is not only compatible with Slater's[4] original definition of the augmented plane wave, but also with the fact that the wave function as represented by the integral equation (6) is formally zero within the spheres. Suppose we choose to expand the wave function directly in the set Φ_n, i.e.,

$$R\leq r<r^b:\quad \Psi(\mathbf{r})=\sum_n B_n\Phi_n, \quad (36)$$

apply the same boundary condition (19) and the same Green's-function expansions (24) and (25), and substitute all this in the integral equations (6) and (8), as before. We then find that the wave function and its Fourier components are identical to those of Eqs. (26) and (32), except for the substitution of the coefficients B_n for A_n, i.e.,

$$R\leq r<r^b:\quad \Psi(\mathbf{r})=\sum_n \mathfrak{F}_n(\mathbf{k},E)\exp(i\mathbf{k}_n\cdot\mathbf{r}), \quad (37)$$

$$\mathfrak{F}_n(\mathbf{k},E)=\frac{4\pi R^2}{\Omega^{3/2}}(E-k_n^2)^{-1}\times\sum_{n'}B_{n'}\sum_l(2l+1)P_l(\cos\theta_{nn'})j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right]. \quad (38)$$

However, the secular equations leading to the eigenvalues and to the coefficients B_n take the form

$$\sum_n[(k_{n'}^2-E)\delta_{nn'}+\Gamma_{nn'}(\mathbf{k},E)]B_n=0, \quad (39)$$

with

$$\Gamma_{nn'}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}\sum_l(2l+1)P_l(\cos\theta_{nn'})j_l(k_nR)\times j_l(k_{n'}R)\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right], \quad (40)$$

which differ from Eqs. (34) and (35), respectively, of the APW method in that the $j_1(|\mathbf{k}_{n'}-\mathbf{k}_n|R)/|\mathbf{k}_{n'}-\mathbf{k}_n|$ term is missing. This term, of course, appears only when the basis set for expanding the wavefunction is restricted to the region outside the spheres.

We should expect the secular problem described by Eqs. (39) and (40) to suffer from convergence difficulties for the very reasons stated earlier. The set Φ_n defined over the whole cell is improper and overcomplete for expanding a wave function which is plane-wave like only outside the spheres. The only way we can ensure that such a set is proper is to require that the wave function be a solution of the ordinary wave equation (4) inside as well as outside the sphere, and that it be reasonably continuous at the sphere radius. The full significance of this statement will be brought out more clearly in our discussion below of the KKR-Z representation. Thus the presence of the $j_1(|\mathbf{k}_{n'}-\mathbf{k}_n|R)/|\mathbf{k}_{n'}-\mathbf{k}_n|$ term in the APW matrix element must be directly connected with the fact that the APW method is the most rapidly convergent description of the plane-wave nature of the wave function outside the spheres.

We can arrive at this convergence property also from the point of view of fitting a Fourier series. It is well known that the expansion of an arbitrary function in a

Fourier series, e.g.,

$$f(x)=\sum_n B_n \exp(ik_n x) \tag{41}$$

should be understood as an equality in the sense of the space norm

$$\lim_{m\to\infty}\int |f(x)-\sum_{n=1}^{m} B_n \exp(ik_n x)|^2 dx=0, \tag{42}$$

the integral being over the domain of f. Let us therefore try to fit the exact wave function outside the spheres, as described by Eqs. (37) and (38), by a Fourier series. This can be accomplished by choosing for a "trial" function a finite series of the plane waves Φ_n, i.e.,

$$\Psi(\mathbf{r})\approx\sum_{n=1}^{m} B_n\Phi_n(\mathbf{r}), \tag{43}$$

minimizing the norm

$$\int_{\Omega-\Omega_s} |\Psi(\mathbf{r})-\sum_{n=1}^{m} B_n\Phi_n(\mathbf{r})|^2 dr \tag{44}$$

over the volume $\Omega-\Omega_s$ outside the sphere, and taking the limit as m goes to infinity. The substitution of expressions (37) and (38) for $\Psi(\mathbf{r})$ into (44) and the variation with respect to the coefficients of the trial function (43) then lead directly to the set of secular equations (34) and (35) for the APW method. This proves that the APW representation yields the "best" or most rapidly convergent plane-wave expansion of the wave function outside the "muffin-tin" spheres.

We have thus far restricted our discussion of convergence to the plane-wave aspect of the problem. However, each APW matrix element (35) involves a summation over the angular momentum quantum number l, a summation which has heretofore been assumed infinite. The convergence of this series is also very important, since it must be truncated at some $l_{\max}$ in actual band calculations. We may inquire, therefore, whether the APW form of the secular problem has optimum convergence in l. For example, it is well known that in the case of nearly-free-electron behavior, only a few plane waves should suffice to describe the energies and the wave functions outside the spheres. Since $E\cong k_n^2$ in this case, it would imply the near vanishing of the matrix elements $\Gamma_{nn'}{}^{(\mathrm{APW})}(\mathbf{k},E)$, which would, in turn, suggest some sort of cancellation of terms in the summation

$$\sum_l (2l+1)P_l(\cos\theta_{nn'})j_l(k_nR)\times j_l(k_{n'}R)\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(k_{n'}R)}{j_l(k_{n'}R)}\right]. \tag{45}$$

Slater[8] has already discussed in detail this aspect of the APW representation and has shown how the near vanishing of the off-diagonal matrix elements in the nearly-free-electron limit is related to the near vanishing of each l-dependent term in the summation of (45). However, the convergence of this sum for more general behavior of the energy bands is not as evident because of the explicit appearance of the wave vectors in the logarithmic derivatives of the Bessel functions. This brings us quite naturally to the KKR-Z representation of the energy-band problem.

B. The KKR-Z Representation

Let us first see how we can derive this representation directly from the integral equations (6) and (8). As Slater[7] has pointed out, an important difference between the APW and KKR-Z methods is that the wave functions of the latter technique are solutions to the ordinary wave equation (4) inside as well as outside the spheres. Thus one must assume continuity of the wave function outside the spheres not only with the partial-wave solutions of the Schrödinger equation (5) or (9) on the surface of the spheres, but also with the regular solutions of the wave equation within the spheres. The latter solutions can be written in the form

$$0\le r<R:\quad \Psi(\mathbf{r})=\sum_{l,m} B_{lm}j_l(\kappa r)\mathcal{Y}_{lm}(\mathbf{r}). \tag{46}$$

This can be accomplished by calling on the expansion of the "trial" wave function in plane waves inside as well as outside the spheres, as in Eq. (36), and then invoking the proper expansions of the Green's function plus the proper inhomogeneous boundary conditions. Let us put aside for the time being the convergence properties of such a plane-wave expansion and attempt to arrive at the KKR-Z secular problem.

The expansion of the Green's function and its normal derivative given in Eqs. (24) and (25) are not the only possible choices and, as we shall prove shortly, not the optimum choices. Ham and Segall[16] originally suggested that we use the fact that $G(\mathbf{r},\mathbf{r}_0)$ satisfies the ordinary homogeneous wave equation (4) in the unit cell for $0\le r_0<r$ to expand it in a complete set of regular spherical Bessel functions in the argument $\kappa=(E)^{1/2}$, i.e.,

$0\le r_0<r<r^b$:

$$G(\mathbf{r},\mathbf{r}_0)=\sum_{l,m} G_{lm}(\mathbf{k};E;\mathbf{r})j_l(\kappa r_0)\mathcal{Y}_{lm}(\mathbf{r}_0). \tag{47}$$

The coefficients G_{lm} are determined by simply identifying (47) with the expansion (10) of $G(\mathbf{r},\mathbf{r}_0)$ in plane waves, and then expanding $\Phi_n^*(\mathbf{r}_0)$ according to the identity (20). The result is given by

$$G_{lm}(\mathbf{k};E;\mathbf{r})=-(\Omega)^{-1/2}4\pi i^{-l}\times\sum_n \frac{\Phi_n(\mathbf{r})}{k_n^2-E}\frac{j_l(k_nr_0)}{j_l(\kappa r_0)}\mathcal{Y}_{lm}(\mathbf{k}_n). \tag{48}$$

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

Off-hand, it might seem that these coefficients should be an explicit function of the "source" point $\mathbf{r}_0$ as well as the "field" point $\mathbf{r}$. However, this cannot be true if $G(\mathbf{r},\mathbf{r}_0)$ is to be a solution of the wave equation. There is a "hidden identity" (to quote Ziman[5]) in expression (48) which ensures that these quantities will have the same value regardless of the value of $\mathbf{r}_0$ in the range $0\leq r_0<r<r^b$. Let us choose the magnitude of $\mathbf{r}_0$ as the sphere radius R. Thus we can write for the Green's function and its normal derivative for the "source" point on the sphere the respective expansions

$r>r_0{}^s=R$:

$$G(\mathbf{r},\mathbf{r}_0{}^s)=-(\Omega)^{-1/2}4\pi\sum_n\frac{\Phi_n(\mathbf{r})}{k_n{}^2-E}\sum_{l,m}i^{-l}j_l(k_nR)\times Y_{lm}(\mathbf{k}_n)Y_{lm}{}^*(\mathbf{r}_0{}^s), \quad (49)$$

$r>r_0{}^s=R$:

$$\hat{n}_0\cdot\nabla_0G(\mathbf{r},\mathbf{r}_0{}^s)=-(\Omega)^{-1/2}4\pi\sum_n\frac{\Phi_n(\mathbf{r})}{k_n{}^2-E}\sum_{l,m}i^{-l}\frac{j_l(k_nR)}{j_l(\kappa R)}\times Y_{lm}(\mathbf{k}_n)j_l'(\kappa R)Y_{lm}{}^*(\mathbf{r}_0{}^s). \quad (50)$$

Relation (49) is identical to (24) because of the cancellation of $j_l(\kappa R)$. However, relation (50), as compared with (25), involves the first derivatives of $j_l(\kappa R)$ rather than those of $j_l(k_nR)$.

Let us expand the "trial" wave function in a series of plane waves identical to (36) and introduce the inhomogeneous boundary condition that the wave function equal

$$r_0{}^s=R:\quad \Psi(\mathbf{r}_0{}^s)=\sum_{l,m}C_{lm}\mathfrak{R}_l(E,R)Y_{lm}(\mathbf{r}_0{}^s) \quad (51)$$

on the surface of the sphere. Solving for the coefficients C_{lm}, we obtain

$$C_{lm}=(\Omega)^{-1/2}\sum_n B_ni^l\frac{j_l(k_nR)}{\mathfrak{R}_l(E,R)}Y_{lm}{}^*(\mathbf{k}_n). \quad (52)$$

Thus we obtain for the "trial" wave function and its normal derivative on the sphere the expressions

$r_0{}^s=R$:

$$\Psi(\mathbf{r}_0{}^s)=(\Omega)^{-1/2}\sum_n B_n\sum_{l,m}i^lj_l(k_nR)\times Y_{lm}{}^*(\mathbf{k}_n)Y_{lm}(\mathbf{r}_0{}^s) \quad (53)$$

$r_0{}^s=R$:

$$\hat{n}_0\cdot\nabla_0\Psi(\mathbf{r}_0{}^s)=(\Omega)^{-1/2}\sum_n B_n\sum_{l,m}i^l\frac{j_l(k_nR)}{\mathfrak{R}_l(E,R)}Y_{lm}{}^*(\mathbf{k}_n)\times\mathfrak{R}_l'(E,R)Y_{lm}(\mathbf{r}_0{}^s). \quad (54)$$

The substitution of Eqs. (49), (50), (53), and (54) directly into the surface integral of Eq. (6) and the subsequent integration over the surface of the sphere yields for the exact wave function outside the spheres

$$R<r<r^b:\quad \Psi(\mathbf{r})=\sum_n\mathfrak{F}_n{}^{(\mathrm{KKR\text{-}Z})}(\mathbf{k},E)\exp(i\mathbf{k}_n\cdot\mathbf{r}), \quad (55)$$

where

$$\mathfrak{F}_n{}^{(\mathrm{KKR\text{-}Z})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega^{3/2}}(E-k_n{}^2)^{-1}\sum_{n'}B_{n'}\sum_l(2l+1)\times P_l(\cos\theta_{nn'})j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right]. \quad (56)$$

The secular equations for the coefficients B_n are obtained by making the same substitutions in Eq. (8). They may be written in the form

$$\sum_n\left[(k_{n'}{}^2-E)\delta_{nn'}+\Gamma_{nn'}{}^{(\mathrm{KKR\text{-}Z})}(\mathbf{k},E)\right]B_n=0 \quad (57)$$

in which

$$\Gamma_{nn'}{}^{(\mathrm{KKR\text{-}Z})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}\sum_l(2l+1)\times P_l(\cos\theta_{nn'})j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right]. \quad (58)$$

These matrix elements agree exactly with those (3) for the pseudopotential representation of the KKR method discussed by Ziman,[5] Lloyd,[6] and Slater.[7]

We can now reply to the question raised above concerning the convergence properties of the summation over l which appears in each element. The explicit occurrence of $\kappa=(E)^{1/2}$ in the arguments of the logarithmic derivatives of the Bessel functions allows us to quickly analyze the l dependence of the individual pseudopotential components

$$\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right]. \quad (59)$$

Zeros in this quantity imply continuity of the logarithmic derivatives of the radial wave functions with those of the regular spherical Bessel functions at the sphere radius. This is analogous to the Ramsauer effect[8,17] observed in the scattering of slow electrons from inert gas atoms, in that it corresponds to zero scattering amplitude or perfectly free-electron behavior of the lth partial-wave component of the wave function. In other words, the most important contributions to the summation over l in the pseudopotential matrix elements arise only from those partial-wave components which are appreciably different from free-electron behavior.

[17] C. Ramsauer, Ann. Phys. (N. Y.) **64**, 513 (1921); **66**, 545 (1921); **72**, 345 (1923).

For example, the distortion of the energy bands from free-electron parabolas in a transition or noble metal when a d band "hybridizes" or intersects the conduction band is predominantly due to the $l=2$ component of the pseudopotential. For energies in the vicinity of the atomic eigenvalue for a d level, the radial part R_2 of the $l=2$ partial wave is very much like that for an atomic bound d state. Its amplitude can be vanishingly small compared with its derivative R_2' at the sphere radius due to the "tailing off" of the wave function characteristic of a bound state. Thus the logarithmic derivative of the radial wave function can blow up relative to that of the Bessel function, and then one speaks of a "d-band resonance" of the pseudopotential component (59).

Such "resonances" can also occur, of course, with the pseudopotential elements (45) which describe the APW method. However, the cancellation of the logarithmic derivatives for the higher l components cannot take place as readily or over as wide an energy range in the APW form because of the occurrence of the wave vectors k_n, rather than κ, in the logarithmic derivatives of the Bessel functions. Therefore, we would expect the convergence in the summation over l to be somewhat poorer in general for the APW technique than for the KKR-Z method. There is a fair amount of direct computational evidence that this is indeed true, as a result of comparing the convergence in l of the presently used APW and KKR techniques. We shall discuss this evidence in the last section of the paper. No practical applications of the KKR-Z representation have yet been reported. In the case of very nearly-free-electron behavior, the convergence in the number of plane waves and the convergence in l should be very much the same for both the APW and KKR-Z schemes, because then it takes only a few plane waves to describe the wave function outside the spheres, and $k_n^2 \cong E=\kappa^2$.

C. Other APW Representations

While the KKR-Z representation should be very rapidly convergent in l, it does not lead to the most rapidly convergent plane-wave expansion of the wave function outside the spheres in general cases. As we have stressed in part A of this section, the APW form of the secular equations, where the plane-wave expansion of the wave function is confined to the region outside the spheres, requires the fewest number of plane waves to describe the exact solution in this region. This theorem also implies that any APW calculational scheme, regardless of the exact form of its secular equations, must have the same one-to-one plane wave convergence, although the convergence in l may vary from one version to another.

To illustrate this point let us first consider Slater's[4,8] original formulation of the APW secular problem. Its matrix elements are

$$\Gamma_{nn'}{}^{(\text{O-APW})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}\Bigg\{-(\mathbf{k}_n\cdot\mathbf{k}_{n'}-E)\times\frac{j_1(|\mathbf{k}_{n'}-\mathbf{k}_n|R)}{|\mathbf{k}_{n'}-\mathbf{k}_n|}+\sum_l(2l+1)P_l(\cos\theta_{nn'})j_l(k_nR)\times j_l(k_{n'}R)\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}\Bigg\}. \quad (60)$$

This version is the one presently programmed and the one which has been used almost exclusively in actual band calculations. It is related to the APW matrix elements (2) or (35), which we have emphasized in this paper, by the Bessel function identity

$$(\mathbf{k}_1\cdot\mathbf{k}_2)\frac{j_1(|\mathbf{k}_1-\mathbf{k}_2|R)}{|\mathbf{k}_1-\mathbf{k}_2|}=k_1{}^2\frac{j_1(|\mathbf{k}_1-\mathbf{k}_2|R)}{|\mathbf{k}_1-\mathbf{k}_2|}+\sum_l(2l+1)P_l(\cos\theta_{12})j_l'(k_1R)j_l(k_2R). \quad (61)$$

The secular problem based on the elements (60) is easier to program than that based on the elements (2), because the former are symmetric in the wave-vector indices and do not require the computation of the first derivatives of the Bessel function. However, the identity (61), which relates the two versions, is exact only if the summation over l in this expression is carried to infinity. Hence, there is no reason to expect that the convergence in l for (60) will be exactly the same as that we have discussed above for (2).

We should also mention several other modifications of the APW method. A revised approach was suggested by Slater[18] and extended by Saffren and Slater.[19] However, Saffren[20] studied the practicality of programming the revised method and came to the conclusion that Slater's[4] original version is simpler to use. A technique called the "wave-variational method" proposed by Schlosser and Marcus[21] has also proven to be basically the same as the original APW method, when the perturbation due to nonspherical components of the potential outside the spheres is treated in the latter approach.

Let us now derive an even further modification of the APW representation using the Green's-function method. We shall adopt the restricted basis set χ_n to describe the "trial" wave function, as in Sec. IIA [see Eq. (18)], but employ the Green's-function expansion (47) instead of (24). Carrying out the substitutions into the integral equations (6) and (8), essentially as in Sec. IIA, we find that the wave function outside the spheres and the

[18] J. C. Slater, Phys. Rev. **92**, 603 (1953).
[19] M. M. Saffren and J. C. Slater, Phys. Rev. **92**, 1126 (1953).
[20] M. M. Saffren, Ph.D. thesis, Massachusetts Institute of Technology, 1959 (unpublished).
[21] H. Schlosser and P. M. Marcus, Phys. Rev. **131**, 2529 (1963).

secular equations assume the respective forms:

$R<r<r^b$:

$$\Psi(r)=\sum_n \mathfrak{F}_n{}^{(\text{M-APW})}(\mathbf{k},E)\exp(i\mathbf{k}_n\cdot\mathbf{r}); \quad (62)$$

$$\mathfrak{F}_n{}^{(\text{M-APW})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega^{3/2}}(E-k_n{}^2)^{-1}\sum_{n'}A_{n'}\sum_l(2l+1)\times P_l(\cos\theta_{nn'})j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right]; \quad (63)$$

$$\sum_{n'}[(k_{n'}{}^2-E)\delta_{nn'}+\Gamma_{nn'}{}^{(\text{M-APW})}(\mathbf{k},E)]A_{n'}=0; \quad (64)$$

$$\Gamma_{nn'}{}^{(\text{M-APW})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}\left\{-(k_{n'}{}^2-E)\frac{j_1(|\mathbf{k}_{n'}-\mathbf{k}_n|R)}{|\mathbf{k}_{n'}-\mathbf{k}_n|}+\sum_l(2l+1)P_l(\cos\theta_{nn'})j_l(k_nR)j_l(k_{n'}R)\times\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right]\right\}. \quad (65)$$

These expressions are identical to Eqs. (26), (32), (34), and (35) for the APW method, except for the occurrence of $\kappa=(E)^{1/2}$ rather than the wave vector in the logarithmic derivatives of the Bessel functions. This representation can also be generated from the KKR-Z method by fitting the minimum number of plane waves to the KKR-Z form of the exact wave function outside the spheres using the Fourier series technique described in Sec. IIA.

The modified APW matrix elements above are related formally to the original APW matrix elements (2) or (35) by the same unitary transformation which takes the representation (47) for the Green's function into the original representation (24). However, in the present form the matrix elements combine the best features of the original APW and the KKR-Z elements, namely the rapid convergence of both the plane-wave expansion of the wave function outside the spheres and the summation over l.

III. THE OUTGOING-SPHERICAL-WAVE REPRESENTATION

Let us now take up the problem of describing the wave function outside the spheres in terms of partial waves or outgoing spherical waves. As we have pointed out in the beginning of the paper, the integral equation (6) is a statement of the fact that the wave function outside the spheres is a solution of the ordinary wave equation (4) and that these solutions can be considered to be "waves" emanating from suitably chosen "sources" on the surface of the spheres. Thus one can write these progressive solutions in the Bloch form

$R<r$:

$$\Psi(\mathbf{r})=\sum_n \exp(i\mathbf{k}\cdot\mathbf{R}_n)\times\sum_{l,m}A_{lm}h_l{}^{(1)}(\kappa|\mathbf{r}-\mathbf{R}_n|)\mathcal{Y}_{lm}(\mathbf{r}-\mathbf{R}_n), \quad (66)$$

where $\mathbf{R}_n$ is a principal translation vector of the direct lattice and $h_l{}^{(1)}$ is a spherical Hankel function of the first kind. To generate such a solution directly from the integral equation (6), we shall make use of an alternative form of the Green's function, namely[3]

$$G(\mathbf{r},\mathbf{r}_0)=-\frac{1}{4\pi}\sum_n\exp(i\mathbf{k}\cdot\mathbf{R}_n)\frac{\exp(i\kappa|\mathbf{r}-\mathbf{r}_0-\mathbf{R}_n|)}{|\mathbf{r}-\mathbf{r}_0-\mathbf{R}_n|}. \quad (67)$$

This is just a generalization of the familiar free-space Green's function[22]

$$G_{\text{f.s.}}(\mathbf{r},\mathbf{r}_0)=-\frac{1}{4\pi}\frac{\exp(i\kappa|\mathbf{r}-\mathbf{r}_0|)}{|\mathbf{r}-\mathbf{r}_0|} \quad (68)$$

to include the translational symmetry of the lattice. Furthermore, we can make use of the expansion[22]

$0<r_0<r$:

$$\frac{1}{4\pi}\frac{\exp(i\kappa|\mathbf{r}-\mathbf{r}_0|)}{|\mathbf{r}-\mathbf{r}_0|}=-i\kappa\sum_{l,m}h_l{}^{(1)}(\kappa r)j_l(\kappa r_0)\mathcal{Y}_{lm}(\mathbf{r})\mathcal{Y}_{lm}{}^*(\mathbf{r}_0) \quad (69)$$

for the free-space Green's function directly in (67). Thus we can write for the Green's function and its normal derivative on the surface of the sphere the respective expressions

$r>r_0{}^s=R$:

$$G(\mathbf{r},\mathbf{r}_0{}^s)=-i\kappa\sum_n\exp(i\mathbf{k}\cdot\mathbf{R}_n)\sum_{l,m}h_l{}^{(1)}(\kappa|\mathbf{r}-\mathbf{R}_n|)\times j_l(\kappa R)\mathcal{Y}_{lm}(\mathbf{r}-\mathbf{R}_n)\mathcal{Y}_{lm}{}^*(\mathbf{r}_0{}^s), \quad (70)$$

$r>r_0{}^s=R$:

$$\hat{n}_0\cdot\nabla_0 G(\mathbf{r},\mathbf{r}_0{}^s)=-i\kappa\sum_n\exp(i\mathbf{k}\cdot\mathbf{R}_n)\sum_{l,m}h_l{}^{(1)}(\kappa|\mathbf{r}-\mathbf{R}_n|)\times j_l'(\kappa R)\mathcal{Y}_{lm}(\mathbf{r}-\mathbf{R}_n)\mathcal{Y}_{lm}{}^*(\mathbf{r}_0{}^s). \quad (71)$$

As usual, the solutions outside the sphere are required to be continuous with the solution to the Schrödinger problem (5) or (9) at the sphere radius. We write this condition in the form of the inhomogeneous boundary values obeyed, respectively, by the "trial" wave function

[22] G. Goertzel and N. Tralli, *Some Mathematical Methods of Physics* (McGraw-Hill Book Company, Inc., New York, 1960), p. 179.

and its normal derivative on the sphere, namely

$$r_0^s=R: \qquad \Psi(\mathbf{r}_0^s)=\sum_{l,m} C_{lm}\mathfrak{R}_l(E,R)\mathcal{Y}_{lm}(\mathbf{r}_0^s), \quad (72)$$

$$r_0^s=R: \quad \hat{n}_0\cdot\nabla_0\Psi(\mathbf{r}_0^s)=\sum_{l,m} C_{lm}\mathfrak{R}_l'(E,R)\mathcal{Y}_{lm}(\mathbf{r}_0^s). \quad (73)$$

Substituting expressions (70) through (73) into the surface integral of Eq. (6) and performing the integration leads to the following expression for the wave function outside the spheres:

$$R<r: \quad \Psi(\mathbf{r})=-i\kappa R^2\sum_n \exp(i\mathbf{k}\cdot\mathbf{R}_n)\sum_{l,m} C_{lm}j_l(\kappa R) \times\mathfrak{R}_l(E,R)\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right] \times h_l^{(1)}(\kappa|\mathbf{r}-\mathbf{R}_n|)\mathcal{Y}_{lm}(\mathbf{r}-\mathbf{R}_n). \quad (74)$$

Direct comparison of (74) with (66) shows that the coefficients A_{lm} are related to those C_{lm} by the identity

$$A_{lm}=-i\kappa R^2 C_{lm}j_l(\kappa R) \times\mathfrak{R}_l(E,R)\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right]. \quad (75)$$

As has been pointed out in the literature several times, the coefficients A_{lm} are determined from the secular equations originally set up by Korringa,[1] while the coefficients C_{lm} are determined from the secular equations originally set up by Kohn and Rostoker.[2] Although Kohn and Rostoker[2] and Segall[23] have discussed the relationship between these two secular problems, in particular the connection between Korringa's "structure constants" and those of Kohn and Rostoker, the very useful identity (75) has not heretofore been presented.

Let us further remark that the KKR wave function (66) or (74) is related to the KKR-Z wave function (55) essentially by Fourier transform. This can be shown by first noting that the Green's function expansion in plane waves, Eq. (10), is the Fourier transform of the expansion (67) in spherical waves. The fundamental connecting relation is the well-known integral representation[3]

$$\frac{1}{4\pi}\frac{\exp(i\kappa|\mathbf{r}-\mathbf{r}_0|)}{|\mathbf{r}-\mathbf{r}_0|} =\lim_{\epsilon\to 0}\frac{1}{(2\pi)^3}\int\frac{\exp[i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_0)]}{K^2-(\kappa^2+i\epsilon)}d\mathbf{K} \quad (76)$$

for an "outgoing" spherical wave in terms of a plane wave of wave vector $\mathbf{K}$. Therefore by substituting the Green's-function expansions (49) and (50) (which are based on the plane-wave expansion) into the surface integral of Eq. (6), but using the "trial" wave function and its derivative in the forms (72) and (73), we can derive the following expression for the exact wave function in plane waves outside the spheres:

$$R<r<r^b: \quad \Psi(\mathbf{r})=\sum_n \mathfrak{F}_n^{(\mathrm{KKR})}(\mathbf{k},E)\exp(i\mathbf{k}_n\cdot\mathbf{r}), \quad (77)$$

$$\mathfrak{F}_n^{(\mathrm{KKR})}(\mathbf{k},E)=\frac{4\pi R^2}{\Omega}(E-k_n^2)^{-1}\sum_{l,m} C_{lm}j_l(k_nR) \times\mathfrak{R}_l(E,R)\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right] \times\mathcal{Y}_{lm}(\mathbf{k}_n). \quad (78)$$

The Fourier coefficients here involve the partial-wave coefficients C_{lm}, and are identical to expressions originally derived by Ham and Segall[16] [see their Eq. (4.11)]. However, by requiring that the partial-wave expansion (72) be continuous with a series of plane waves of the form (36) at the sphere radius, we are led to expression (52), which relates the coefficients C_{lm} to the coefficients B_n of the plane waves. Substitution of (52) directly into (78) then leads to the previously obtained expression (56) for the Fourier coefficients of the KKR-Z representation. Thus the KKR-Z form of the exact wave function outside the spheres is the Fourier transform of the KKR form of the wave function expressed in "outgoing" spherical waves. We could have shown this also by Fourier transforming the wave function (66) or (74) directly. The products of the spherical Hankel function and spherical harmonic can be put in the form[1,23,24]

$$h_l^{(1)}(\kappa r)\mathcal{Y}_{lm}(\mathbf{r})=i^{-l}\mathcal{Y}_{lm}(\nabla_r)h_0^{(1)}(\kappa r). \quad (79)$$

Using the identity

$$h_0^{(1)}(\kappa r)=\frac{\exp(i\kappa r)}{\kappa r}=\lim_{\epsilon\to 0}\frac{1}{2\pi^2\kappa}\int\frac{\exp(i\mathbf{K}\cdot\mathbf{r})}{K^2-(\kappa^2+i\epsilon)}d\mathbf{K}, \quad (80)$$

which is essentially the same as (76), we can immediately relate each multipole component of the "outgoing" spherical wave to the plane-wave representation.

We now have two basic expressions for the exact wave function outside the spheres, Eqs. (55) and (66) in plane waves and spherical waves, respectively, plus the expression (72) for the wave function which is a solution to the true Schrödinger equation (5) or (9) inside and on the surfaces of the spheres, all based upon the KKR calculational scheme. Korringa's[1] secular equations allow a determination of the coefficients A_{lm} appearing in (66). The secular equations of Kohn and Rostoker[2] lead to the coefficients C_{lm} of expression (72). The KKR-Z pseudopotential yields the coefficients B_n appearing in (55). All three versions should eventually converge to the same energy eigenvalues and wave func-

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

[24] R. Nozawa, Quantum Chemistry Group for Research in Atomic, Molecular and Solid-State Theory, Uppsala University, Uppsala, Sweden, 1965, Report No. 159, p. 9 (unpublished).

tions outside the spheres, so that once we have decided to adopt one of the methods, we can solve for its energies and coefficients, and then establish the other two sets of coefficients from the identities (52) and (75).

While the original KKR technique is very rapidly convergent in its angular-momentum representation of the wave function, we have already shown that the KKR-Z approach does not lead to as rapidly convergent a representation of the wave function in plane waves outside the spheres as does the APW technique. The APW wave function in this region must also be a proper solution for the "scattering" of a Bloch wave by the "muffin-tin" potential, since it is an exact solution to the ordinary wave equation (4) or (6). In Slater's[4] original derivation of the APW method, only the continuity of the wave function of the sphere radius was assumed at the outset, and this assumption was based on the use of infinite sums over the angular momentum l. It is evident now from first principles that in an actual band calculation by the APW scheme, continuity of the wave function is approximately achieved only if enough l values are included in the summations. Furthermore, continuity in the first derivative of the wave function is also practically achieved by combining a sufficient number of plane waves "fitted" to the exact wave function outside the spheres. Continuity in both the wave function and its first derivative therefore leads to the proper "scattered-wave" nature of the wave function. There is direct evidence in support of these statements obtained recently by Rudge[25] in the form of computer studies of APW wave functions.

Suppose in a given application we have already determined the energy bands by the KKR approach and have computed the coefficients C_{lm} or A_{lm} for the partial-wave description of the composite wave function. By-passing the KKR-Z form of the plane-wave representation, it is possible for one to arrive at the APW representation of the wave function outside the spheres directly in terms of the coefficients C_{lm} or A_{lm}. This can be accomplished by fitting the minimum number of plane waves to the KKR expression (74) of the exact wave function in this region using the method of Fourier series described in Sec. IIA. The coefficients of these plane waves A_n are determined from the set of equations

$$\sum_{n'} N_{nn'}A_{n'} = -\frac{4\pi R^2}{\Omega}\sum_{n''}\frac{N_{nn''}}{k_{n''}^2-E}\sum_{l,m} C_{lm}j_l(k_{n''}R) \times \mathfrak{R}_l(E,R)\left[\frac{\mathfrak{R}_l'(E,R)}{\mathfrak{R}_l(E,R)}-\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right]\mathcal{Y}_{lm}(\mathbf{k}_{n''}), \quad (81)$$

where $N_{nn'}$ is the integral defined in expressions (29) and (31). These equations were originally derived by Ham and Segall[16] [see their expression (4.14)], but the connection with the APW method was not pointed out.

[25] W. E. Rudge, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1966, No. 59, p. 8 (unpublished).

IV. SUMMARY AND CONCLUSIONS

It has been shown that both the KKR-Z and APW pseudopotentials can be generated from the same "scattered-wave" or Green's-function approach used to develop the original KKR scheme. The relationship between these three band-theoretical formulations is now quite clear. The KKR-Z secular problem is just the plane-wave counterpart or Fourier transform of the KKR angular momentum representation, agreeing with Ziman's[5] t-matrix and algebraic arguments. While the KKR method provides the "best" partial- or spherical-wave description of the exact composite wave function in the "muffin-tin" model, the APW technique leads to the "best least-squares" plane-wave description of the exact wave function outside the spheres. Both techniques converge rapidly to the correct energy bands $E(k)$ when carried out carefully. In comparing KKR and APW calculations on the same crystal for identical potentials, we should therefore not find it unusual that the resulting energy-band profiles and theoretical Fermi surfaces agree so well.

If we confine our interest in a particular application primarily to the bands and not the wave functions, the decision of which method to employ is largely arbitrary. The results of specific calculations and the computer experiments of Rudge[25] indicate that in the presently programmed APW method [described by the matrix elements (60)], the summations over l must be carried to at least $l_{\max}=6$ in order to reduce the error in the energy eigenvalues to ± 0.001 Ry. The convergence in l might be improved to agree with that $l_{\max}=2$ characteristic of the KKR method by programming the APW matrix elements in the form (65). The explicit separation of the KKR secular problem into the "structure constants," which depend only on the lattice structure, and the "phase shifts," which depend only on the nature of the potential, is of particular advantage when one has the structure constants available and wishes to carry out a band calculation fairly quickly and accurately at a desk calculator. However, the structure constants themselves, even in the improved Ewald form of Morse[2] or Ham and Segall,[16] require a large-scale computer of about the same speed and capacity as that used in present APW calculations. Therefore, as far as automating the band calculation is concerned, there is no significant advantage to using one method rather than the other. The only exception to this statement arises in the case of nearly-free-electron behavior. Here many of the off-diagonal matrix elements of the KKR-Z or APW pseudopotential naturally become very small or vanish, so that either of these representations is to be preferred over the KKR method, for which the structure constants actually are singular at the free-electron energies $E=k_n^2$.

It is only recently that band theorists have started to carry out their calculations to self-consistency and have attempted to compute accurate one-electron wave func-

tions. In most applications, this requires going beyond the "muffin-tin" model in order to correct for the effects of the non-spherical components of the crystal potential on the energy bands and wave functions. In many cases, particularly the heavier elements, it also necessitates the computation of spin-orbit and other relativistic effects. Thus it may be worthwhile to examine in greater detail whether initially determining the wave functions by one technique rather than another leads to a significant saving of computer time. For example, if one is interested in obtaining that part of the composite wave function which is the solution to the Schrödinger equation within the spheres, there is no doubt that the partial-wave representation of the KKR method is the most rapidly convergent one. Moreover, while the APW representation is the "best" way of describing the plane-wave nature of the wave function outside the spheres, it may be more convenient in some applications, e.g., the calculation of certain types of matrix elements, to use the KKR spherical-wave representation of the wave function there. In any case, as we have pointed out above, it is always possible to calculate the augmented-plane-wave components directly from the KKR partial-wave components by means of expression (81).

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Lattice Modulations in the CuAu Alloy*

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The lattice modulation in the long-period superlattice CuAu II is investigated on the basis of a theory recently developed by Teramoto and the author to explain the origin of the long-period superlattice and the phase transitions in the CuAu alloy. From a symmetry consideration, we find that there are two types of lattice modulations: one is uniform along the c axis and the other changes its sign alternately layer by layer along the c axis. The calculated atomic displacements are in semiquantitative agreement with the experimental results, if the repulsive interaction between atomic cores is considered as causing the lattice modulations. In addition, these lattice modulations explain some peculiar properties of the x-ray diffraction patterns: the asymmetry in the intensities of the split spots of the same order, and the intensities of the satellites around the ordinary Bragg diffraction spots.

I. INTRODUCTION

IN binary alloys, such as CuAu, Cu_3Au, Cu_3Pd, and Cu_3Pt, having ordered structures with long periods, experimental investigations have been made most extensively on CuAu.[1] This alloy has three phases, depending on the temperature. Below 380°C, the Cu atom layers and the Au atom layers are alternately stacked along the c axis of the face-centered lattice. This phase is called CuAu I. In this phase the crystal lattice is deformed tetragonally, and c/a is about 0.92.

In the temperature range between about 380°C and 410°C, the long-period superlattice is stable, and this phase is called CuAu II. This structure is constructed by shifting the crystal lattice of CuAu I by $(a/2, 0, c/2)$ at intervals of 5 lattice constants along the b axis as shown in Fig. 1. The domain size, 5 lattice constants, changes very little with temperature. In this phase the crystal lattice is deformed orthorhombically and b/a is 1.003. CuAu II makes a transition to the disordered state at 410°C.

Sato and Toth[2] added Al, Ga, Ni, Pd, etc. to CuAu, changing the number of conduction electrons, and they observed changes of domain size. They found that there is a close connection between the long periods and the number of conduction electrons, and pointed out that the conduction-electron contribution to the energy is important for the long-period structure.

After that, Tachiki and Teramoto[3] made a theoretical

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[1] See, for example, H. Sato, and R. S. Toth, in *Long Period Superlattices in Alloys, in Alloying Behavior and Effects in Concentrated Solid Soultions*, edited by T. B. Massalski (Gordon and Breach, Science Publishers, Inc., New York, 1965).

[2] H. Sato and R. S. Toth, Phys. Rev. **124**, 1833 (1961); Phys. Rev. Letters **8**, 239 (1962). See, also, H. Sato and R. S. Toth, Phys. Rev. **127**, 469 (1962); J. Appl. Phys. **33**, 3250 (1962); Solid State Commun. **2**, 249 (1964); Phys. Rev. **139**, A1581 (1965).

[3] M. Tachiki and K. Teramoto, J. Phys. Chem. Solids **27**, 335 (1966).