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Application of the Augmented Plane Wave Method to Copper*

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An application of the augmented plane wave method of solving the periodic potential problem has been made to metallic copper. The aim is to investigate the value of the method and to learn details of the energy band structure of copper. The method has been found to converge very rapidly; eigenvalues of three- or four-figure accuracy can be obtained for any point in *k*-space without involving the solution of very large secular determinants. Throughout, good results can be obtained by considering only a single augmented plane wave; these appear to be good one-electron wave functions by themselves, and the possible use of these as a starting point in a self-consistent calculation is discussed. The method proves suitable ground for the application of a high-speed computer, by which the present computation has been carried out.

The numerical results for copper are not in agreement with the results of a cellular calculation. Recalculation of certain states by the cellular method indicates that the dominant reason lies in the different potentials employed, the augmented plane wave method dealing with a potential constant in a region between the atoms. The sensitivity of the energy levels upon the exact crystal potential has become more apparent, though copper may be expected to show greater sensitivity than other materials. The present calculation of the width of the 3*d* band is 3.935 ev, compared with 3.46 ev by the cellular method and 2.7 ev by the tight-binding method. The appearance of a high density of states near the top of the 3*d* band is confirmed.

In recent years, various methods have been used in attempts to make accurate solutions of the periodic potential problem. By limiting consideration to points in momentum space possessing high symmetry, the cellular method has proved capable of accurate results; calculations have been made on sodium,[1,2] lithium,[3] copper,[4] and lead sulfide,[5] using this method. The orthogonalized plane wave method originally proposed by Herring[6] can also be used with accuracy at certain points in momentum space, and studies have been made by this means of beryllium,[7] lithium,[8,9] and, more recently, of diamond[10] and germanium.[11–13]

An alternative approach to the periodic potential problem was suggested by Slater[14] and extended by Saffren and Slater[15]; the purpose of the present paper is to describe an application of this method and to estimate its value as a practical approach to the investigation of energy band structures. The method is obviously simple mathematically; its practical value depends upon the rate of convergence of an expansion of the wave function in terms of "augmented plane waves," and it is hence of immediate interest to apply the method to a particular substance. Metallic copper has been selected for two reasons. Firstly, the form and relative positions of the 4*s* and 3*d* bands are of interest, in particular since it is an indication of the band structure of the transition elements preceding copper in the periodic table. Secondly, a calculation by the cellular method has already been carried out for copper,[4] and confidence in such calculations would be greatly improved by obtaining equivalent results by the two approaches. Comparison can also be made with the calculations in the 3*d* band in nickel using the "tight-binding" approximation,[16,17] although this makes no claims to be an exact solution of the problem.

The conclusion arising from the present work is that the method provides an excellent approach to the solution of the periodic potential problem. Without undue numerical labor, it is possible to obtain eigenvalues of greater accuracy than those resulting from the cellular method as it is used at present. In addition, it is possible to extend the calculation to deal with points in momentum space possessing no symmetry properties. The numerical results for copper are not in agreement with the results of the cellular calculation; the difference is apparently due to the different crystal potential assumed in the two calculations. The present work is to be regarded as an analysis of the practical use of the augmented plane wave method rather than an evaluation of physically significant results for copper.

THEORY OF THE AUGMENTED PLANE WAVE METHOD

The mathematical details of the method used here have been given by Saffren and Slater,[15] subsequently referred to as I. Only a brief recapitulation of the necessary formulas will be given here.

We assume the crystal potential in which the electron moves to be spherically symmetrical inside a sphere, radius r_s, surrounding each atom and constant between these spheres. We shall here consider a material con-

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taining only one atom per unit cell. Inside the sphere, the wave function is expanded in a series of spherical harmonics of angle, and radial wave functions of r, $u_l(r)$, satisfying the equation

$$\frac{d^2(ru_l)}{dr^2}=\left(\frac{l(l+1)}{r^2}+V(r)-E\right)ru_l, \tag{1}$$

$V(r)$ being the potential inside the sphere.

Outside the sphere, we assume the solution to be a single plane wave of propagation constant $\mathbf{k}$; if we choose the constant potential to be zero in this region, the energy of this wave is $|\mathbf{k}|^2$. By suitable choice of constants in the expansion inside the sphere, the two functions can be made equal at the boundary of the sphere. The wave function so obtained may be written in unnormalized form [see I, Eq. (2)] as

$$\psi=\epsilon_1\exp(i\mathbf{k}\cdot\mathbf{r})+\epsilon_2\cdot 4\pi\sum_l(2l+1)j_l(|\mathbf{k}|r_s)\times i^lP_l(\cos\theta)u_l(E,r)/u_l(E,r_s). \tag{2}$$

$j_l(|\mathbf{k}|r_s)$ are spherical Bessel functions, θ is measured relative to the direction of $\mathbf{k}$ as polar axis, and ϵ_1, ϵ_2 are defined as

$$\epsilon_1=1,\quad \epsilon_2=0,\quad \text{when}\quad r>r_s;$$
$$\epsilon_1=0,\quad \epsilon_2=1,\quad \text{when}\quad r<r_s.$$

The function (2) we call an augmented plane wave. It will, in general, possess a discontinuity in first derivative at the boundary of the sphere; to obtain the "best" single function of the type (2) possible, the parameter E is chosen to make the expectation value of the energy of (2) a minimum. The result of this process, which can be carried through analytically, is to set the expectation value of the energy equal to the parameter E. The spurious contribution arising from the plane wave outside the sphere is exactly cancelled by the contribution to the kinetic energy integral of the discontinuity in first derivative over the surface of the sphere. The resulting equation for E [see I, Eq. (5)] is

$$\Omega(E-|\mathbf{k}|^2)-4\pi r_s^2\sum_l(2l+1)j_l^2(|\mathbf{k}|r_s)\times[d\ln u_l(E,r)/dr]_{r=r_s}=0. \tag{3}$$

Ω is the volume of the unit cell lying outside the sphere.

The dependence of E upon $|\mathbf{k}|^2$ implicit in (3) has been discussed previously from theoretical considerations;[18] a typical example is shown in Fig. 1. By solving (3), we have determined an augmented plane wave for a given $\mathbf{k}$. Such functions are used as initial functions in a variational procedure. As pointed out by Slater,[14] we can use functions with the same propagation vector $\mathbf{k}$ but corresponding to different energies E; we can also use functions with $\mathbf{k}$ ranging through a number of Brillouin zones, arising from the same reduced wave vector, corresponding to energies E which join smoothly to each other as $\mathbf{k}$ is varied. The overlap integrals and matrix components of energy between the various augmented plane waves are easily determined. We find three contributions to the energy matrix elements, arising from the regions inside and outside the sphere, and from the discontinuity in first derivative over the surface of the sphere. The calculation of these matrix elements follows the treatment of reference 14. For completeness, we give here the resulting formulas for matrix elements between two augmented plane waves $\psi_1(E_1,\mathbf{k}_1)$ and $\psi_2(E_2,\mathbf{k}_2)$. If we denote the Hamiltonian operator H and the unit operator I by the symbol 0, we find that

$$[\psi_1,0,\psi_2]=J(\psi_1,0,\psi_2)+4\pi\sum_l(2l+1)j_l(|\mathbf{k}_1|r_s)\times j_l(|\mathbf{k}_2|r_s)P_l(\mathbf{k}_1\cdot\mathbf{k}_2/|\mathbf{k}_1|\,|\mathbf{k}_2|)K_l(\psi_1 0,\psi_2), \tag{4}$$

where

$$J(\psi_1,I,\psi_2)=-4\pi r_s^2 j_1(|\mathbf{k}_1-\mathbf{k}_2|r_s)/|\mathbf{k}_1-\mathbf{k}_2|,\qquad (\mathbf{k}_1\neq\mathbf{k}_2) \tag{5}$$

$$=\Omega,\qquad (\mathbf{k}_1=\mathbf{k}_2) \tag{6}$$

$$J(\psi_1,H,\psi_2)=\mathbf{k}_1\cdot\mathbf{k}_2 J(\psi_1,I,\psi_2), \tag{7}$$

$$K_l(\psi_1,I,\psi_2)=r_s^2[d\ln u_l(E_2,r)/dr-d\ln u_l(E_1,r)/dr]\times[E_1-E_2]^{-1},\qquad (E_1\neq E_2) \tag{8}$$

$$=\left[\int_0^{r_s}u_l^2(E_1,r)r^2dr\right]u_l^{-2}(E_1,r_s),\qquad (E_1=E_2) \tag{9}$$

$$K_l(\psi_1,H,\psi_2)=r_s^2[E_1d\ln u_l(E_2,r)/dr-E_2d\ln u_l(E_1,r)/dr][E_1-E_2]^{-1},\qquad (E_1\neq E_2) \tag{10}$$

$$=E_1K_l(\psi_1,I,\psi_2)+r_s^2[d\ln u_l(E_1,r)/dr]_{r=r_s},\qquad (E_1=E_2). \tag{11}$$

The functions ψ_1, ψ_2 are unnormalized. The normalization constant $n(E,\mathbf{k})$ is easily seen from (6) and (9) to be given by

$$n^2=\Omega+4\pi\sum_l(2l+1)j_l^2(|\mathbf{k}|r_s)\times\left[\int_0^{r_s}u_l^2(E,r)r^2dr\right][u_l^{-2}(E,r_s)]. \tag{12}$$

With the exception of (9) and (11), these matrix elements have a dependence on the radial wave functions only through their logarithmic derivatives at the surface of the sphere. Formulas (9) and (11) can be reduced to a similar form by use of the relationship

$$\int_0^{r_s}u_l^2(E,r)r^2dr=-r_s^2u_l^2(E,r_s)\frac{d}{dE}[d\ln u_l(E,r)/dr]_{r=r_s}. \tag{13}$$

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[18] M. M. Saffren, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1953 (unpublished), p. 16.

For computational purposes, however, accuracy is most easily maintained by using (9) and (11) as they stand.

As shown by Slater,[14] we find that when $\mathbf{k}_1$ and $\mathbf{k}_2$ are equal and when (3) is satisfied both energy and overlap matrix elements are zero (except when E_1 and E_2 are also equal). Hence, in particular, the augmented plane waves corresponding to electrons in the valence or conduction bands will be orthogonal to those corresponding to electrons in the ion core states, so that, if we restrict our discussion to the former, the lowest eigenvalue will converge to the required eigenvalue in the valence or conduction band.

If we include augmented plane waves of different wave vectors in the variational problem, however, both overlap and energy matrix elements are nonzero; the resulting secular equation will thus, in general, be one involving a nondiagonal overlap matrix, i.e., with the energy parameter occurring in nondiagonal terms as well as along the diagonal. The method used to solve such an equation will be outlined in the following section.

METHOD OF COMPUTATION

It is obvious that the computation involved in this work is simple, but laborious. It must also be borne in mind that when a method of solving the periodic potential problem has been found, a desirable feature of such a process would be the ease with which it could be used in a self-consistent type of calculation (that this may be necessary even in calculations on simple metals is apparent from the results of the present work). These features of the calculation suggest the use of a high-speed computer; throughout this work therefore, use has been made of the Whirlwind I high-speed digital computer to enable the entire process to be carried out automatically and at high speed.

The first step is to solve Eq. (3). For this we require the radial wave functions $u_l(E,r_s)$ for various l and E; these are obtained by the Noumerov process.[19] The spherical Bessel functions $j_l(|\mathbf{k}|r_s)$ are most accurately determined[20] by use of the auxiliary function Λ_l, defined by

$$\Lambda_{l+\frac{1}{2}}(x)=(2/x)^l(2/\sqrt{\pi})\Gamma(l+\tfrac{3}{2})j_l(x). \qquad (14)$$

For high l, simple series expansions of $\Lambda_{l+\frac{1}{2}}(x)$ are possible, from which functions of lower l may be generated from the recurrence relation

$$\Lambda_{l-\frac{1}{2}}(x)=\Lambda_{l+\frac{1}{2}}(x)-\frac{x^2}{(2l+1)(2l+3)}\Lambda_{l+\frac{3}{2}}(x). \qquad (15)$$

In practice, this was found to produce negligible loss in accuracy for all l and $x(=|\mathbf{k}|r_s)$ required here.

Having computed the function on the right-hand side of (3), we wish to specify a value of $|\mathbf{k}|$ corresponding to a particular point in the Brillouin zone, and to determine the solutions $E(\mathbf{k})$ of (3). Regarded as a function of E, however, (3) has the undesirable property of discontinuities at values of E such that $u_l(E,r_s)$ is zero. In addition, the computation of (3) at values of E forming a fine enough mesh for accurate interpolation of zeros is a lengthy calculation owing to the occurrence of the radial wave functions. A more tractable approach is to regard (3) as a function of $\mathbf{k}$ for a given value of E, and to determine the zeros of this function, which varies slowly with $\mathbf{k}^2$. Graphical interpolation then yields the desired values of E for the particular wave vectors required.

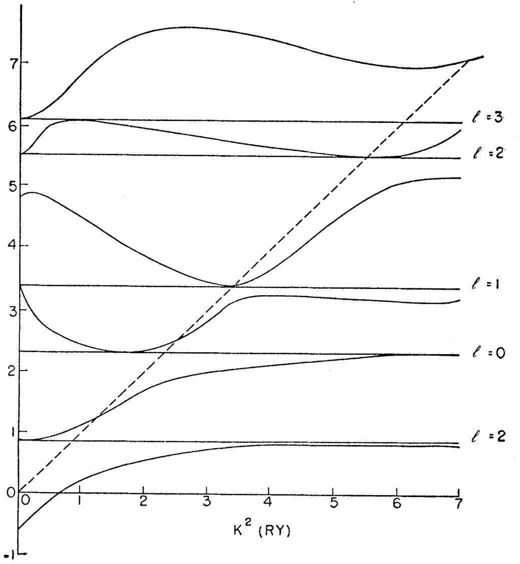

FIG. 1. Energy of augmented plane wave, E, as a function of wave vector, $|\mathbf{k}|$, of plane wave portion (Hartree atomic potential for Cu$^+$, $(3d)^{10}$ configuration, touching radius of sphere). Asymptotes corresponding to zeros of $u_l(E,r_s)$ are shown with relevant values of l. Broken line indicates $E=|\mathbf{k}|^2$.

One fact of some importance arises as a result of this method of solution. The values of E and $\mathbf{k}$ subsequently used to calculate the matrix elements do not necessarily satisfy (3) exactly, since they depend upon the accuracy with which one can select points from a graph. Hence, the orthogonality relations mentioned in the preceding section are not exactly satisfied. It has been found that the eigenvalues of the resulting secular equation are highly sensitive to small changes in the matrix elements, and considerable errors can arise by assuming that overlap and energy matrix elements between functions of the same k are zero. The original formulas (4) to (11) were therefore used to calculate these matrix elements also. By this means, the formulation of the variational problem remains consistent, although the augmented plane waves with which we start are not the "best" functions possible.

The method used to solve the secular equation is

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[19] For a detailed account of this method, see G. W. Pratt, Phys. Rev. **88**, 1217 (1952).

[20] *Tables of Spherical Bessel Functions* (National Bureau of Standards, Washington, 1948), Vols. I and II.

that of Löwdin.[21] The equations written in matrix notation as

$$(\mathbf{H}-\mathbf{\Delta}E_j)\mathbf{X}_j=0 \tag{16}$$

are reduced to the canonical form

$$(\mathbf{H}'-\mathbf{1}E_j)\mathbf{C}_j=0, \tag{17}$$

where E appears only in the diagonal elements of the matrix by the transformation

$$\mathbf{H}'=\mathbf{\Delta}^{-\frac{1}{2}}\mathbf{H}\mathbf{\Delta}^{-\frac{1}{2}}, \quad \mathbf{X}_j=\mathbf{\Delta}^{-\frac{1}{2}}\mathbf{C}_j. \tag{18}$$

The matrix $\mathbf{\Delta}^{-\frac{1}{2}}$ can be found by first diagonalizing $\mathbf{\Delta}$, and forming the inverse square root of the diagonal matrix; the problem hence reduces to one of ordinary matrix diagonalization. The process of matrix diagonalization, used twice here, can be carried out at high speed and with great accuracy on the Whirlwind I computer by a routine developed by Dr. A. Meckler. This fact makes the present method of determining $\mathbf{\Delta}^{-\frac{1}{2}}$ simpler and more accurate than that used by Löwdin.

APPLICATION TO METALLIC COPPER

In order to apply this method to any material, suitable choice must be made of the spherically symmetric potential $V(r)$ around each atom. In the cellular calculation on copper, an atomic potential was used as an approximation to the crystal potential. In order to conform as closely as possible to the data used in this previous investigation, the same potentials have been used, modified to be continuous with the zero constant potential at the boundary of the sphere. In the present work, the spheres were taken to be touching, giving the best facilities for approaching as closely as possible to the actual crystal potential with this form of potential. In all cellular calculations, the electron under consideration is supposed to move in the field of the nucleus and all other electrons. In the case of the $4s$ band, therefore, a suitable potential is that for Cu^+ in configuration $(3d)$.[10] Two atomic potentials are available for this configuration, the Hartree atomic potential,[22,23] and the Hartree-Fock potential[24] which includes exchange between the ion core electrons. Separate calculations have therefore been carried out using both of these potentials, in order to investigate the difference in energy band structure arising from the two different assumptions. In the case of the $3d$ band, a modified Hartree potential was formed to represent the $(3d)^9(4s)$ configuration by subtracting from the Hartree Cu^+ potential the contribution from one $3d$ electron and adding that of an atomic $4s$ electron, both normalized to unity inside the atomic sphere. It is recognized that these potentials are probably only crude approximations to the actual crystal potential, and the marked dependence of the relative positions of the electronic energy levels upon the potential found subsequently indicates that greater care is necessary in the choice of potential in order to obtain results of real physical significance.

The computation was carried out as already described. A typical plot of the energy of an augmented plane wave as a function of $\mathbf{k}^2$ is shown in Fig. 1. The example shown is obtained by using the Hartree Cu^+ potential inside the sphere; the lattice constant is taken to be the observed value, 6.8124 Bohr units. The asymptotes shown correspond to values of E for which $u_l(E,r_s)$ is zero; the relevant values of l are shown for each asymptote. In carrying out the summation over l, the series in (3) is in practice terminated at a given l, determined by the properties of the spherical Bessel functions. However, it may be observed that the aim in solving (3) is simply to obtain the best possible one-electron wave functions to use as unperturbed functions in the subsequent variational calculation. It has been found that this latter process converges so rapidly that functions which only satisfy (3) approximately are still sufficiently good unperturbed wave functions. Hence, a reduction in numerical labor can be achieved at this stage of the computation by including only terms of low l in the summation in (3). Results for copper have shown that inclusion of terms for which $l<7$ in (3) gives values of E determining wave functions which are equally good unperturbed functions for the variational process as are functions resulting from the inclusion of all terms for which $l<13$. In setting up the matrix elements between two augmented plane waves, however, we maintain sufficient values of l to ensure accuracy in the summations in (4). Although the augmented plane waves determined by this means possess, in general, a discontinuity in first derivative at the boundary of the sphere, the contribution of this discontinuity to the energy vanishes if $E=|\mathbf{k}|^2$.[25] It is seen from Fig. 1 that over much of the range the curves E *versus* $|\mathbf{k}|^2$ lie close to the line $E=|\mathbf{k}|^2$, indicating that the individual augmented plane waves are themselves quite good approximations to the true solutions of the wave equation.

To form a wave function corresponding to a point $\mathbf{k}$ in the Brillouin zone as a linear combination of augmented plane waves, we can use functions with wave vectors $\mathbf{k}_\mathrm{n}=\mathbf{k}+\mathbf{K}_\mathrm{n}$, $\mathbf{K}_\mathrm{n}$ being a vector of the reciprocal lattice. The expression for the wave function is hence

$$\Psi(\mathbf{k},E)=\sum_{\mathrm{n},m} a_\mathrm{n}{}^m\psi(k_\mathrm{n},E_{m,\,\mathrm{n}}), \tag{19}$$

ψ being an augmented plane wave, and $a_\mathrm{n}{}^m$ being constants to be determined by solution of a secular equation. The index m refers to functions with differing E but the same $\mathbf{k}$. It is immediately apparent that in general a large number of terms can appear in (19).

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[21] P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[22] D. R. Hartree, Proc. Roy. Soc. (London) **A141**, 282 (1933).

[23] D. R. Hartree, Proc. Roy. Soc. (London) **A143**, 516 (1934).

[24] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

[25] See analysis in references 14 and 15.

For a face-centered cubic crystal such as copper, the lowest nonzero $\mathbf{K}_n$ are of the form $\mathbf{K}_{004}=(0,0,4\pi/a)$, the next of the form $\mathbf{K}_{044}=(0,4\pi/a,4\pi/a)$ and so on, together with similar vectors formed by interchange of the three components and alteration of signs. Thus, inclusion of only terms in which $\mathbf{K}_n=(0,0,0)$ and $\mathbf{K}_n=(0,0,4\pi/a)$ results in $7m$ unknown constants in (19) and hence a secular equation of order $7m$, where m is the number of "branches" of Fig. 1 being used. Inclusion of the next set of $\mathbf{K}_n$ gives a secular equation of order $19m$. Thus, unless the series (19) converges very rapidly in both n and m, the resulting secular equation will be of very high order.

At points in the Brillouin zone possessing high symmetry, however, the permissible wave functions possess known symmetry properties.[26] In such case, some of the coefficients $a_n{}^m$ are interdependent, and, compared with the general case described above, an equivalent number of terms can be included in (19) with fewer undetermined coefficients. For example, at the center of the zone, $\mathbf{k}=(0,0,0)$, for the state possessing s-like symmetry (referred to in reference 26 as the state Γ_1), we find that

$$a_{004}{}^m=a_{040}{}^m=a_{400}{}^m=a_{00-4}{}^m=a_{0-40}{}^m=a_{-400}{}^m,$$

and similarly, all coefficients of the type $a_{044}{}^m$ are equal. Hence, to consider the Γ_1 state, a secular equation of order $2m$ replaces one of order $7m$ in the general case, and one of order $3m$ replaces one of order $19m$, and so on. Thus, as in all such calculations, this method will be most powerful at points possessing high symmetry in k-space, for this allows the inclusion of more terms in (19) without involving secular equations of an equivalently high order. Much of the present calculation has therefore been limited to points of high symmetry in k-space.

To discuss the convergence of the sum (19), it is convenient to consider an example; that selected is the state X_s,[27] having reduced wave vector $(0,0,2\pi/a)$, and having the symmetry of the free electron function $\cos(2\pi z/a)$. After applying the symmetry conditions, the following independent coefficients remain in (19):

$$a_{002}{}^m,\ a_{042}{}^m,\ a_{006}{}^m,\ a_{442}{}^m,\ a_{406}{}^m,\ \cdots.$$

Table I shows the lowest eigenvalue resulting from solutions of a secular equation involving varying numbers of these coefficients. The first entry in the first column shows the energy of the single symmetry combination of augmented plane waves, coefficient $a_{002}{}^1$. The second entry in this column shows the result of including $a_{002}{}^1$, $a_{042}{}^1$; the second entry of the second column results from the inclusion of $a_{002}{}^1$, $a_{042}{}^1$, $a_{002}{}^2$, $a_{042}{}^2$, and so on. More terms have been included in this example than in any other state considered in order to demonstrate the convergence. The excellent convergence shown in Table I is typical of results for all the states considered here; in no case was any improvement obtained by inclusion of more than two values of E for each $\mathbf{k}$ ($m=1$, 2 in the notation given above), and in no case was it necessary to consider values of $\mathbf{K}_n$ greater than $\mathbf{K}_{044}$. This latter observation is not surprising in the case of copper, and may not be true for other substances. Previous calculations[4] have shown that the energy of a conduction electron in copper approximates closely to that of a free electron, and hence the wave function, except in the immediate vicinity of the nucleus, can be well approximated by a single plane wave. In the case of the electrons in the $3d$ band, the wave functions are principally concentrated inside the atomic sphere, and are small in the region of constant potential between the spheres. The accurate representation of this part of the wave function is therefore of little importance in determining the energy.

TABLE I. Example of convergence of lowest eigenvalue of secular equation, using different numbers of augmented plane waves. State X_s using Hartree potential.

Number of wave vectors	Number of E per k 1	2	3	4	5	6
1	0.3760	0.3752	0.3747	0.3747	0.3746	0.3746
2	0.3754	0.3746	0.3746	0.3746	0.3746	0.3746
3	0.3748	0.3746	0.3746	0.3746	0.3746	0.3746

The rapid convergence obtained for states of high symmetry in the Brillouin zone, of which Table I is a typical example, suggest that the method could be applied at points of no symmetry in k-space. A calculation has been made at one such point, the point $A=(\pi/2a,\pi/a,3\pi/2a)$. Results of four figure accuracy can be obtained from the solution of a secular equation of order 14. This is the highest order equation it has been found necessary to solve in the present work.

The method is hence more powerful than the cellular method, which has so far only been applied with accuracy at points of high symmetry in k-space. The orthogonalized plane wave method has also been used to investigate general points in k-space[28]; approximately the same numerical labor is required in the two methods, and the present method would appear to show a more rapid convergence.

Higher eigenvalues of the secular equations possess slower convergence and, in most cases, it is necessary to include further $\mathbf{K}_n$ to obtain accurate results for such states. No attempt has been made to complete the calculation of these eigenvalues except in a few cases; for this reason, the results given here do not exhaust the data of interest. The aim of the present calculation has been to demonstrate the power of the

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[26] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936). See also reference 4 for a general description of these symmetries.

[27] The notation used to denote the states of various symmetries is an adaptation of that used by Bouckaert *et al.* (reference 26), and is fully described in references 2 and 4.

[28] F. Herman (private communication).

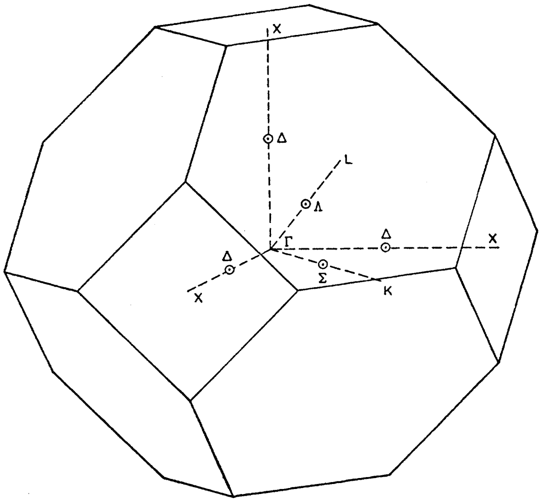

FIG. 2. Brillouin zone for a face-centered cubic crystal, showing points of high symmetry.

augmented plane wave method rather than to calculate every eigenvalue of interest for copper. The ultimate aim in such a calculation is the determination of the entire density of electronic energy states; this would be possible by the augmented plane wave method, but, even making full use of a high-speed computer, would be a very laborious operation. The calculation of an eigenvalue at a general point in k-space involved here the solution of a secular equation of order 14, and the evaluation of over 70 radial wave functions. However, there have recently been suggested methods of interpolating, from accurate results at a few points in momentum space, the energy at any point in k-space, and hence obtaining the density of electronic states.[29,30] Such methods become more powerful if there exist accurate results at more points in momentum space. Thus, the ability to investigate any point in momentum space with accuracy, even at the cost of extensive numerical labor, affords very valuable assistance in applying any such interpolation scheme.

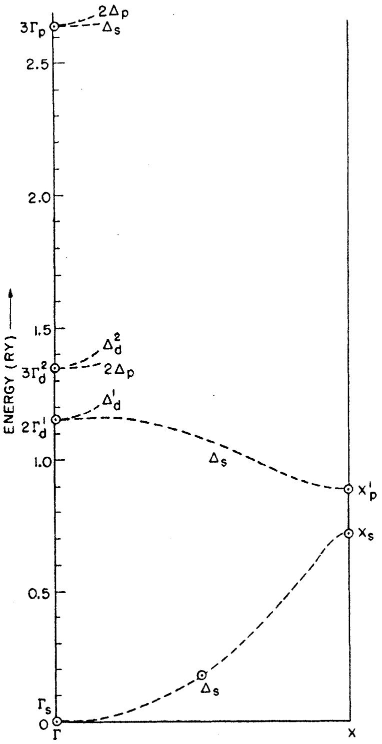

FIG. 3. Energy as a function of wave vector in [002] direction: Conduction band using Hartree potential. Energy in Rydberg units relative to the ground state Γ_s. Figure preceding description of state indicates degree of degeneracy.

DISCUSSION OF RESULTS

The numerical results obtained for copper are shown in Tables II and III. For convenience of reference, the states are given both in the notation of the previous cellular calculation[4] (HJ notation) and in that of Bouckaert *et al.*[26] (BSW notation). The points of high symmetry in the Brillouin zone are shown in Fig. 2. The results are quoted to the accuracy that has been obtained by investigating the successive convergence of the secular equations. The points along the axes of high symmetry referred to as Δ, Λ, Σ represent the center points along these axes [i.e., Δ is the point $(0,0,\pi/a)$]. The dependence of E upon k along the principal directions in k-space is shown in Figs. 3–11. The calculated points are shown, together with schematic diagrams of the $E-k$ curves through these points. The manner in which the various states are connected along the axes can be derived from the compatability conditions of Bouckaert *et al.*[26]

TABLE II. Eigenvalues of conduction band of copper using (a) Hartree and (b) Hartree-Fock atomic potentials. Energies in Rydberg units.

State HJ notation	BSW notation	(a)	(b)
Γ_s	Γ_1	−0.558	−0.354
Γ_d^1	Γ_{12}	0.671	0.803
Γ_d^2	Γ_{25}'	0.7982	0.907
Γ_p	Γ_{15}	1.697	2.308
Σ_s	Σ_1	−0.451	−0.240
K_s	K_1	−0.147	0.086
K_p^1	K_3	−0.136	0.0951
Λ_s	Λ_1	−0.391	−0.1702
L_s	L_1	−0.0519	0.2219
L_p^1	L_2'	0.0887	0.3263
Δ_s	Δ_1	−0.471	−0.174
X_s	X_1	0.080	0.375
X_p^1	X_4'	0.2409	0.502
A	···	0.124	0.361

The eigenvalues of the conduction band show that the states at the top of this band are predominantly

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[29] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[30] L. Allen (private communication); Phys. Rev. 98, 993 (1955).

s-like in character along each of the principal directions. The energy gap across the faces of the first Brillouin zone varies from 2.18 ev along the [002] direction to 0.15 ev along the [011] direction when the Hartree potential is used, and from 1.72 ev in the [002] direction to 0.12 ev in the [011] direction in the case of the Hartree-Fock potential. There is a considerably closer correspondence between the results for the two potentials than was observed in the cellular calculation. The use of the Hartree-Fock potential results in a larger width for the conduction band, and a smaller energy gap across the faces of the zone along each of the principal directions, but the relative positions of the states possessing s- and p-like symmetries at the edges of the zone is unaltered. The eigenvalues lie close to the "free-electron" values along the [002] and [111] directions, but are lower than these values along the [011] direction. Calculations at the center points along these axes confirm the approximate parabolic dependence of E upon $\mathbf{k}$, with the consequence of an effective mass slightly less than unity in the [002] and [111] directions, and considerably less than unity in the [011] direction. The presence of an s-like state at the top of the conduction band in the [111] direction does not agree with the prediction of Mott,[31] based on x-ray absorption measurements by Cauchois[32] that this state would be predominantly p-like in character.

TABLE III. Eigenvalues of d band of copper. Energies in Rydbergs.

State			State		
HJ notation	BSW notation	Eigen-value	HJ notation	BSW notation	Eigen-value
Γ_d^1	Γ_{12}	-0.155	Δ_s	Δ_1	-0.235
Γ_d^2	Γ_{25}'	-0.0541	Δ_d^1	Δ_2	-0.13
Σ_s	Σ_1	-0.2853	Δ_d^2	Δ_2'	-0.067
K_s	K_1	-0.3448	Δ_p	Δ_5	-0.0643
K_s	K_1	-0.14	X_s	X_1	-0.335
K_d	K_2	-0.1621	X_d^1	X_2	-0.1062
K_p^1	K_3	-0.1528	X_d^2	X_3	-0.0742
K_p^2	K_4	-0.0688	X_d^3	X_5	-0.066
Λ_s	Λ_1	-0.1355	X_p^2	X_5'	$+0.64$
Λ_p	Λ_3	-0.152	X_f^1	X_2'	$+1.527$
Λ_p	Λ_3	-0.061	X_f^2	X_3'	$+1.60$
L_s	L_1	-0.2756	A	A	-0.2693
L_d	L_3	-0.1456			-0.194
L_p^2	L_3'	-0.0652			-0.127

The eigenvalues of the $3d$ band show a spread of 3.935 ev from the Γ_d^2 state at the center of the zone to the state K_s at $\mathbf{k}=(0,3\pi/4,3\pi/4)$. This value is in general agreement with the predictions of x-ray absorption measurements by Cauchois,[32] who predicts a value of less than 5 ev, and by Gyorgy and Harvey,[33] who predict a width of 3.5 ev. It also agrees with the result of 3.8 ev quoted by Chodorow[34] obtained from an application of an earlier form of this method,[35] using

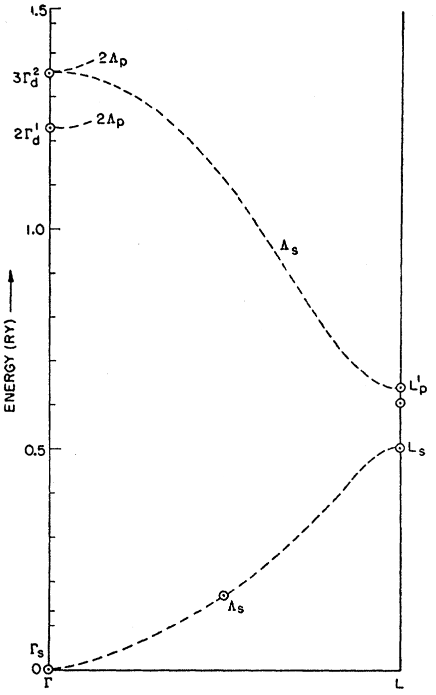

FIG. 4. Energy as function of wave vector in [111] direction: Conduction band using Hartree potential.

the same form of potential. The width of the band in the [002] direction in fact agrees exactly with that of Chodorow.

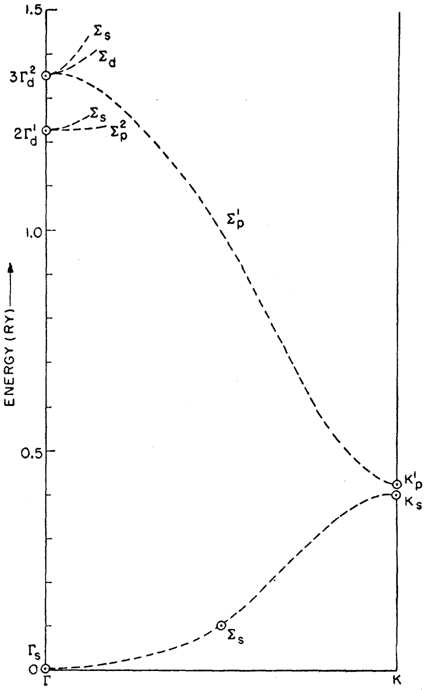

FIG. 5. Energy as function of wave vector in [110] direction: Conduction band using Hartree potential.

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[31] N. F. Mott, Phil. Mag. **44**, 187 (1953).

[32] Y. Cauchois, Phil. Mag. **44**, 173 (1953).

[33] E. M. Gyorgy and G. G. Harvey, Phys. Rev. **93**, 365 (1954).

[34] M. Chodorow, Phys. Rev. **55**, 675 (1939).

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

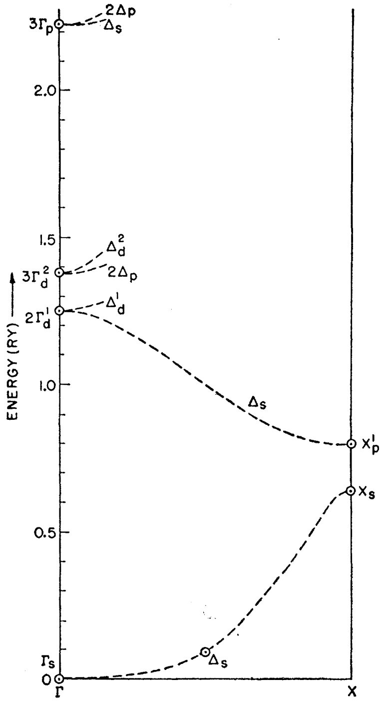

FIG. 6. Energy as function of wave vector in [002] direction: Conduction band using Hartree-Fock potential. Energy in Rydberg units relative to the ground state Γ_s.

It will be seen from the figures quoted that not all the states in the d band have been evaluated at each point in k-space considered; further states would involve the solution of higher order secular equations, which is not considered necessary in the present work. The distribution of states in the d band is consistent with the assumption of a high density of states at the top of the band, agreeing with a previous calculation for nickel by the "tight binding" method.[16,17,36]

These results are to be compared with those of the cellular calculation on copper[4] since both claim to be accurate solutions to the periodic potential problem. Serious differences are immediately apparent, especially in the eigenvalues in the d band. The total band width does not differ greatly, the cellular calculation giving a width of 3.46 ev, but the distribution of states in the band differs widely in the two calculations. Similar differences occur in the case of excited levels of the d band.[37] It has, however, been observed previously that the eigenvalues appear to depend markedly on the crystal potential used in the calculations, and, unlike the cellular calculation, the present work has assumed a constant potential outside the atomic spheres. A cellular calculation has therefore been repeated using the exact potential employed in the present work. In particular, the two states at the center of the zone in the d band were considered, both of which are easily amenable to an accurate cellular calculation. The results agreed with those of the augmented plane wave method to within the accuracy one can claim from the cellular method. It is therefore concluded that the difference in the results is predominantly due to different potentials used in the two calculations.

The same may be assumed to be true in the case of the conduction band. The augmented plane wave method may be the more reliable for these states. Doubt has recently been cast on the accuracy of cellular calculations involving the matching of boundary conditions at points on the cell boundaries,[38] and this may affect the reliability of the results for the conduction band of copper carried out by that method. The agreement with experiment is equally good for both sets of results.

It must be pointed out that the use of two different potentials in considering the 3d and 4s bands makes it impossible to predict the relative positions of the bands by direct use of the augmented plane wave method. This method is only used to solve the periodic potential problem for a single assumed potential. The two calculations are therefore to be regarded as distinct energy

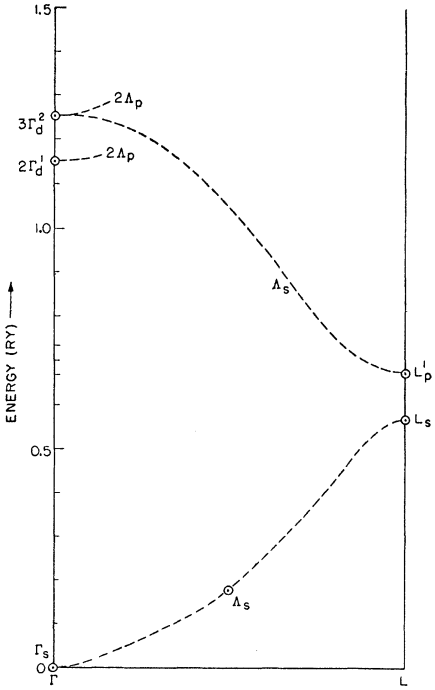

FIG. 7. Energy as function of wave vector in [111] direction: Conduction band using Hartree-Fock potential.

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[36] G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1954 (unpublished), p. 4.

[37] I am indebted to Mr. J. Hubbard for permission to see results on the excited states of the d band carried out by the cellular method.

[38] F. Ham, Ph.D. thesis, Harvard University, 1954 (unpublished). I am indebted to Dr. Ham for several discussions on this matter.

band calculations. In the cellular calculation, an attempt was made to determine the relative positions of the two bands by an approximate solution of the Hartree equations for the crystal. Such a calculation is necessarily very approximate in the absence of a full self-consistent treatment of the two bands, and no such attempt has been made in the present work.

The sensitivity of the eigenvalues upon the exact crystal potential has been noted previously in the case of copper and of germanium. Copper and the transition metals preceding it in the periodic table may be expected to show more sensitivity than other materials, for it is known that the radial wave functions for $l=2$ are exceptionally sensitive to the potential; in the crystal, this effect will be particularly noticeable in the *3d* band. It becomes more apparent that a self-consistent type of calculation is necessary even in the case of simple metals. In this connection, the augmented plane wave method has a marked advantage over other existing methods of solving the periodic potential problem. It has already been observed from Fig. 1 that a single augmented plane wave may well be a good approximation to the true wave function. This is borne out in Table I and in every other state considered. Energies in error by not more than 0.003 Rydberg unit can be obtained before entering upon the variational problem, that is, by considering an augmented plane wave to be a sufficiently good wave function. Although the wave functions themselves may be expected to show greater error, it still appears that an augmented plane wave forms a fair approximation to the true solution. This is a significant observation when the problem of self-consistency is approached. The contribution to the potential of these one-electron functions could be estimated; this new potential could then be used to repeat the calculation and to obtain self-consistency. Alternatively, the new potential could be regarded as a perturbation to the original potential, to be included in the variational calculation. Hence, a practical consequence of the extremely rapid convergence of the augmented plane wave method is the feasibility of a self-consistent energy band calculation.

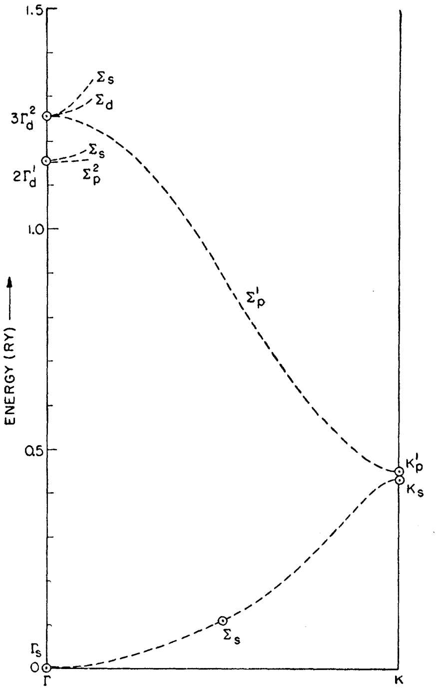

FIG. 8. Energy as function of wave vector in [110] direction: Conduction band using Hartree-Fock potential.

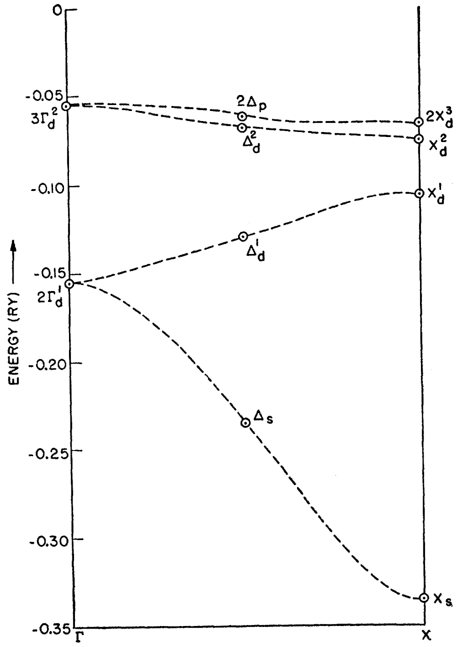

FIG. 9. Energy as function of wave vector in [002] direction: *3d* band. Energy in Rydberg units.

CONCLUSION

The work on copper has shown that the augmented plane wave method is among the most powerful of the existing methods for the solution of the one-electron periodic potential problem. Results of greater accuracy than those obtainable by the cellular method as currently used can be obtained with no greater numerical difficulty. In addition, the application is not so severely limited to points of high symmetry in momentum space. The method thus compares favorably with the method of orthogonalized plane waves, which has also been applied to points of no symmetry in momentum space. Although the method used here deals with a restricted form of potential, it has been pointed out by Slater that more general forms of potential could be considered with some ease; it remains to be seen whether the rapid

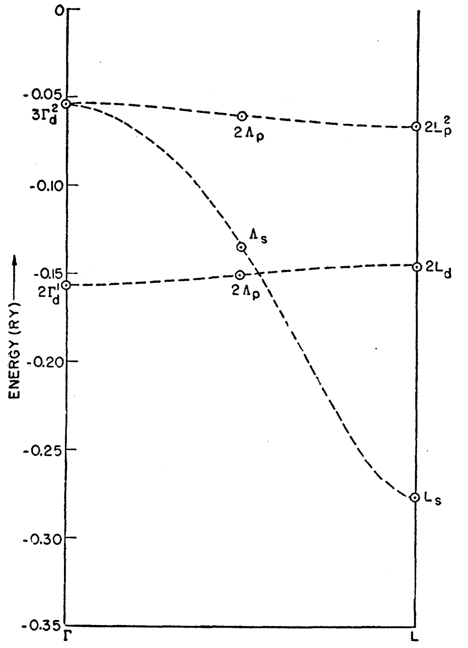

FIG. 10. Energy as function of wave vector in [111] direction: 3*d* band.

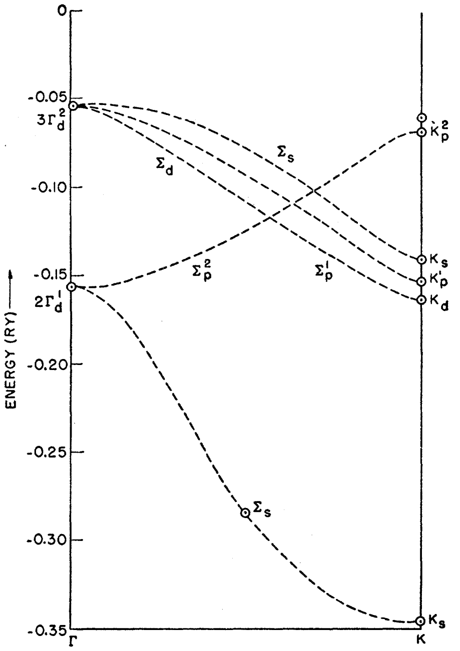

FIG. 11. Energy as function of wave vector in [110] direction: 3*d* band.

rate of convergence observed in the present work would also result from the inclusion of different forms of potential. Although the calculation of an entire density of states by the augmented plane wave method would be a calculation of prohibitive length, the ability to obtain accurate eigenvalues at any point in *k*-space affords a valuable means of checking any interpolation procedure used to obtain a density of states curve.

In view of the differences between the results of the present calculation on copper and those of the cellular calculation, which difference appears entirely due to the different potentials employed, it cannot be claimed that the results of such solutions to the periodic potential problem necessarily bear any great physical significance. As more accurate solutions are carried out, it becomes increasingly apparent that the exact form of the potential inside the atomic cell is an important factor in determining the energy levels. The need for a self-consistent calculation is obvious, and the present method would appear to make such a calculation feasible. Such a calculation has not been carried out for copper, and the present work is therefore to be regarded as an investigation into the value of the augmented plane wave method, rather than an investigation of the physical properties of metallic copper.

ACKNOWLEDGMENTS

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