Simplified LCAO Method for the Periodic Potential Problem*

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(Received February 17, 1954)

The LCAO, or Bloch, or tight binding, approximation for solids is discussed as an interpolation method, to be used in connection with more accurate calculations made by the cellular or orthogonalized plane-wave methods. It is proposed that the various integrals be obtained as disposable constants, so that the tight binding method will agree with accurate calculations at symmetry points in the Brillouin zone for which these calculations have been made, and that the LCAO method then be used for making calculations throughout the Brillouin zone. A general discussion of the method is given, including tables of matrix components of energy for simple cubic, face-centered and body-centered cubic, and diamond structures. Applications are given to the results of Fletcher and Wohlfarth on Ni, and Howarth on Cu, as illustrations of the fcc case. In discussing the bcc case, the splitting of the energy bands in chromium by an antiferromagnetic alternating potential is worked out, as well as a distribution of energy states for the case of no antiferromagnetism. For diamond, comparisons are made with the calculations of Herman, using the orthogonalized plane-wave method. The case of such crystals as InSb is discussed, and it is shown that their properties fit in with the energy band picture.

I. THE LCAO METHOD FOR SOLIDS

ONE of the standard methods for solving the periodic potential problems met in the theory of the electronic motions in solids is the LCAO (linear combination of atomic orbitals) or Bloch or tight binding method. This was originally proposed by Bloch,[1] and consists of making a linear combination of atomic orbitals located on the various atoms of the crystal, the coefficients being the values of the plane wave $\exp(i\mathbf{k}\cdot\mathbf{R})$ at the various positions $\mathbf{R}$ at which the atoms are located. In the present paper, we shall examine this method, noting that it becomes almost impossibly difficult to carry out with full rigor, on account of the enormous number of difficult integrals which must be computed. On the other hand, it has many attractive qualitative features, since it gives solutions showing all the correct symmetry properties of the energy bands, and it is rather easy to get solutions for energy bands at an arbitrary point in the Brillouin zone, whereas most other approximate methods become too difficult to carry out except at certain symmetry points of the Brillouin zone. With this in mind, we shall suggest using the LCAO method, not as a primary method of accurate calculation, but rather as an interpolation method. We shall arbitrarily discard many of the terms which make trouble with the accurate calculation, but shall retain those which are necessary to give qualitative correctness to the method. Instead of computing the various integrals analytically, we shall use them as disposable constants, to be chosen so that we shall fit the results of more accurate calculation made by other methods, such as the cellular method or the method of orthogonalized plane waves, which are capable of more accurate results, but only at restricted symmetry points of the Brillouin zone. We shall give formulas useful in such applications of the LCAO method, and shall describe its use in discussing certain problems, including the face-centered and body-centered cubic and diamond structures.

If we start with an atomic orbital $\phi_n(\mathbf{r}-\mathbf{R}_i)$, located on an atom at vector position $\mathbf{R}_i$, and with quantum numbers symbolized by the subscript n, then we can form the Bloch sum $\sum(\mathbf{R}_i)\exp(i\mathbf{k}\cdot\mathbf{R}_i)\phi_n(\mathbf{r}-\mathbf{R}_i)$, where the sum is to be extended over the atoms in equivalent positions in all the unit cells of the crystal. The sum as it stands is not normalized, but we shall later take up its normalization. We can set up such Bloch sums corresponding to each atomic orbital of an atom, and corresponding to each atom in the unit cell of the crystal. We find that there are no nondiagonal matrix components of the Hamiltonian operator, consisting of the kinetic energy and the periodic potential function, between two Bloch sums with different $\mathbf{k}$'s. On the other hand, in general there are nonvanishing matrix components of the Hamiltonian between Bloch sums of the same $\mathbf{k}$ value, corresponding either to different atomic orbitals on the same atom, or to atomic orbitals on different atoms in the unit cell. Some of these nondiagonal matrix components vanish at special symmetry points of the Brillouin zone, or special values of $\mathbf{k}$, and it is this vanishing which leads to the special properties of the energy bands at these symmetry points.

We can then set up an approximate solution of the periodic potential problem in the following way. We take a finite set of atomic orbitals on each of the atoms of the unit cell, going up from the lowest atomic states to those concerned in the highest levels occupied in the crystal, or somewhat higher. From each of these atomic orbitals, we construct a Bloch sum. For a given $\mathbf{k}$ value, we can then set up a wave function consisting of a linear combination of all these Bloch sums. In general, except at special $\mathbf{k}$ values, there will be matrix

* Supported in part by the U. S. Office of Naval Research, in part by the Army, Navy, and Air Force.
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[1] F. Bloch, Z. Physik 52, 555 (1928).

components of energy between all these Bloch sums, so that we shall have a secular problem whose order equals that of the total number of atomic orbitals concerned, though at special $\mathbf{k}$ values there will be factoring of the secular equation, and resulting simplification. With modern digital computers, such secular equations can be solved, and the resulting wave functions and energy levels form useful approximations to the solution of the periodic potential problem. At a general $\mathbf{k}$ value, all roots of the secular equation will be distinct, and we group together the functions of different $\mathbf{k}$ value having the lowest energy as the lowest-energy band, those having the second lowest energy as the second-energy band, and so on, though at special symmetry points several energy bands can be degenerate with each other. This is, in principle, a quite good method for approximating the periodic potential problem. Its practical difficulties arise only from the enormous amount of numerical work involved in computing rigorously the various matrix components of energy, and as mentioned earlier, we shall later suggest certain simplications which make it practical.

It is rather surprising that many writers who have considered this method in the literature have not understood certain rather fundamental points. Thus, many writers have felt that in crystals of certain symmetry there were sets of wave functions which did not combine with each other, resulting in splitting of energy bands, which in fact do not occur. Bloch, in his original paper, only computed the diagonal matrix component of energy for a single Bloch sum, and gave no thought to setting up a secular problem relating to the combination of several Bloch sums. The first writer who specifically thought of anything but s atomic orbitals seems to have been Wilson,[2] who computed the diagonal energy of Bloch sums of p orbitals, but erroneously concluded that there would be no nondiagonal matrix components of energy between Bloch sums formed from the p_x, p_y, and p_z atomic orbitals. He made this error on account of a misinterpretation of the results of Bethe[3] concerning the symmetry properties of wave functions in crystals in which the potential has various types of rotational and inversion symmetry, as well as translational symmetry. Bethe had shown that electronic wave functions in such crystals can be chosen to transform under the symmetry operations of the point group like the various irreducible representations of this group, and by using such arguments had been able to derive results on the splitting of energy levels in the crystal, and on the vanishing of certain nondiagonal matrix components of energy. Some of the early writers on energy band theory failed to note the fact, pointed out later by Bouckaert, Smoluchowski, and Wigner,[4] that one cannot, in general, choose wave functions in this way and simultaneously diagonalize the translational operations in the crystal.

A wave function which diagonalizes the translational operations is one which, like a Bloch sum, is multiplied by the factor $\exp i(\mathbf{k}\cdot\mathbf{R})$ when we make a translation $\mathbf{R}$ which carries the lattice into itself; the factor $\exp i(\mathbf{k}\cdot\mathbf{R})$ is the eigenvalue connected with the translational operation. Bouckaert, Smoluchowski, and Wigner pointed out that associated with one $\mathbf{k}$ vector are several others, into which the first one transforms by one of the symmetry operations of the point group of the crystal. Thus, for instance, a general $\mathbf{k}$ vector in a cubic crystal is one of 48 vectors derived from the first one by interchanging x, y, and z, or changing signs; such vectors are said to form a star. It now proves necessary to make linear combinations of Bloch-type wave functions corresponding to all $\mathbf{k}$ vectors in this star, in order to form a wave function transforming according to Bethe's prescription, according to an irreducible representation of the point group of the crystal. Conversely, in order to build up a function connected with one $\mathbf{k}$ value, and hence diagonalizing the translational operations, one must make a linear combination of functions transforming according to the various irreducible representations of the point group. Put more simply, a wave function of a given $\mathbf{k}$ value must be made up as a linear combination of functions having the symmetry properties of s, p_x, p_y, p_z, $\cdots$ orbitals, and will not have the characteristics of any one of these types of orbitals. The exceptions come only for certain special $\mathbf{k}$ values, such as $\mathbf{k}=0$.

We see, then, that Bethe's rules do not apply to wave functions of the Bloch type, corresponding to a definite $\mathbf{k}$, except at special values like $\mathbf{k}=0$. But as we have pointed out, this fact was not clear to various writers at first. In the LCAO method, we make up suitable wave functions at an arbitrary $\mathbf{k}$ value by making linear combinations of the Bloch sums made up of different atomic orbitals, in the way already described, and in general we have contributions coming from all the Bloch sums. The first paper in which it was realized that a secular equation must be solved between the various Bloch sums formed from different atomic orbitals seems to have been that of Jones, Mott, and Skinner[5] dealing with x-ray emission bands of metals, in which wave functions were made up by solving a secular problem between s, p_x, p_y, and p_z Bloch functions. Oddly enough, however, in a later paper by Jones and Mott[6] the error was made of thinking that a threefold d band, formed from the functions of symmetry xy, yz, zx, was separated from a twofold band formed from functions like x^2-y^2 and $3z^2-r^2$; no nondiagonal matrix components of energy between the Bloch sums formed from these two types of atomic

[2] A. H. Wilson, Proc. Roy. Soc. (London) **A133**, 458 (1931).
[3] H. Bethe, Ann. Physik **3**, 133 (1929).
[4] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).
[5] Jones, Mott, and Skinner, Phys. Rev. **45**, 379 (1934).
[6] H. Jones and H. F. Mott, Proc. Roy. Soc. (London) **A162**, 49 (1937).

orbitals were considered. Actually, here as in other cases, there are nondiagonal matrix components of energy between all these types of Bloch functions, at an arbitrary **k** value, and the d band does not split into two subbands. This unwarranted simplification is also found in the first work of Fletcher and Wohlfarth[7] on nickel, though it is removed in their second paper,[8] which seems to be the first proper treatment of the structure of the d band by the LCAO method.

In addition to the misunderstanding which we have just been describing, there is another widespread misconception about the method. This is the supposition that it is desirable for some reason to start by hybridizing the atomic orbitals, for instance, to introduce directed orbitals of some sort suggested by the symmetry of the crystal. This misconception occurs particularly in the writings of those who, like for instance Pauling[9] and Ganzhorn,[10] do not make it clear whether they are using an energy band calculation, or a modified Heitler-London method. In the case of Lennard-Jones and his associates,[11] using their equivalent orbitals, one gathers that they feel that there is some virtue in using hybridized orbitals of one type or another (that is, linear combinations of several atomic orbitals, on the same or adjacent atoms) for a straightforward calculation of energy bands, or of molecular orbitals in a molecular problem. This procedure is in fact of no value in most cases.

One can start with atomic orbitals of the ordinary sort, space quantized with respect to a particular direction in space, or can use orbitals set up with reference to cubic axes, such as the p_x, p_y, p_z combinations of the p orbitals and the d orbitals varying as xy, yz, zx, x^2-y^2, and $3z^2-r^2$, or finally one can use more complicated hybridized orbitals, such as the four tetrahedral directed orbitals formed from the s and the three p functions. With any one of these starting points, one can set up the Bloch sums of the atomic orbitals, and then can solve the secular problem between these Bloch sums. The final result will obviously be the same no matter which set of atomic orbitals we start with. In fact, if we were going to use n atomic orbitals per unit cell, we could make any n linear combinations of the original orbitals, form Bloch sums of these modified orbitals, and solve a secular problem using the modified Bloch sums, and in every case come out with the same answer in the end. The only advantage in one choice of atomic orbitals over another is convenience in calculating the matrix components or solving the secular equation. We shall be dealing in the present paper with cubic crystals, and shall use orbitals of the p_x, p_y, p_z, xy, yz, etc., type, since they give about as much simplification as we can get. But in addition, these are just as useful in discussing the diamond structure as tetrahedral orbitals would be. At an arbitrary point of **k** space, in any case the matrix components will not simplify, no matter what form of atomic orbitals we use. Along special symmetry lines and planes, we can sometimes choose atomic orbitals leading to a factoring of the secular equation, and this is obviously useful; but the choice is different for different symmetry lines and planes.

For solving the one-electron problem, in other words, there is no advantage in using hydridized or directed orbitals when dealing with crystals, or similarly in using directed or equivalent orbitals in solving the molecular orbital problem in a molecule. The advantages of such orbitals, if there are any, seem to lie in treating the many-electron problem, either by methods of configuration interaction or by other methods. It seems likely that by using directed or hybridized or equivalent orbitals, one can set up approximate treatments of electron correlation which express the preference of two electrons of opposite spin to be found in an orbital representing a covalent bond. But this use of such orbitals lies entirely outside the scope of the present paper, which deals with energy band theory, or one-electron solutions of Schrödinger's equation for a periodic potential.

II. SIMPLIFICATION OF THE LCAO METHOD

We have seen in the preceding section the general outlines of the LCAO method for solids. We shall now examine it in more detail, show how complicated it is when applied rigorously, but indicate the simplifications which can be made if we treat it as an interpolation method. There is one complication which we can remove at the outset. If we start with the atomic orbitals ϕ_n, located on the various atoms of a unit cell, and make Bloch sums from them, then we shall find that these Bloch sums are not orthogonal to each other. The reason is that the ϕ_n's connected with orbitals on different atoms are not orthogonal to each other. We can remove this difficulty by immediately setting up new atomic orbitals, linear combinations of the original ones, which are orthogonal to each other. This can be done most symmetrically by the method of Löwdin.[12] We shall assume that this is done, and shall call the resulting orbitals ψ_n. By this procedure we still have not solved the periodic potential problem. We shall still find nondiagonal matrix components of energy between the Bloch sums formed from different Löwdin

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[8] G. C. Fletcher, Proc. Phys. Soc. (London) **A65**, 192 (1952).
[9] L. Pauling, Phys. Rev. **54**, 899 (1938).
[10] K. Ganzhorn, "Gruppentheorie und Quantenmechanik der Übergangs metall-Strukturen," thesis, Technischen Hochschule, Stuttgart, 1952 (unpublished); Z. Naturforsch. **7a**, 291 (1952); Z. Naturforsch. **8a**, 330 (1953).
[11] J. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949); J. Lennard-Jones and G. G. Hall, Proc. Roy. Soc. (London) **A202**, 155 (1950); J. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) **A202**, 166 (1950); G. G. Hall, Proc. Roy. Soc. (London) **A202**, 336 (1950); Proc. Phys. Soc. (London) **A66**, 1162 (1953). (This last reference, which was not available when the present paper was written, has some resemblance to it in its general point of view.)
[12] P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

functions ψ_n. But the technique of solving the secular problem will be much simplified. These Löwdin functions ψ_n show symmetry properties like those of the atomic orbitals ϕ_n from which they were derived. (See the Appendix for a proof of this.) For instance, if we start with a p_x atomic orbital and construct orthogonalized atomic orbitals according to Löwdin's prescription, in a cubic crystal, we shall find that the orthogonalized orbital formed from p_x and from contributions of other orbitals on adjacent atoms, will still have the symmetry of a p_x function.

From these Löwdin functions, we can now construct Bloch sums, and if we write them in the form $N^{-\frac{1}{2}}\sum(\mathbf{R}_i)\exp i(\mathbf{k}\cdot\mathbf{R}_i)\psi_n(\mathbf{r}-\mathbf{R}_i)$, where $\mathbf{R}_i$ is the vector position of the atom on which the orbital is located, we shall find that these Bloch sums are normalized and orthogonal. We are assuming periodic boundary conditions, and the number of unit cells in the repeating region is N; the normalization is over this repeating region. The sum is over unit cells. That is, a Bloch function is to be formed from just one atomic orbital per unit cell. If we have several atoms per unit cell, even if some are identical with each other, as the two atoms per unit cell in the diamond structure, we are to use different Bloch sums for each atom in the unit cell. On the other hand, we are to choose our unit cells as small as possible. For instance, in the face-centered or body-centered cubic structures, we are to choose unit cells containing only one atom in the unit cell, instead of the conventional cube, which holds four atoms per cube in the face-centered structure, two per cube in the body-centered structure.

We must now find the matrix component of energy between two such Bloch sums. If H is the Hamiltonian operator, this matrix component is clearly

$$N^{-1}\sum(\mathbf{R}_i,\mathbf{R}_j)\exp i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_i)\times\int\psi_n^*(\mathbf{r}-\mathbf{R}_i)H\psi_m(\mathbf{r}-\mathbf{R}_j)dv. \quad (1)$$

The sum is over the N unit cells. We must remember that $\mathbf{R}_i$ ranges over the positions of the atoms on which orbitals ψ_n are located, while $\mathbf{R}_j$ ranges over the positions of orbitals ψ_m. These may well be different, for these orbitals may be located on different atoms in the unit cell. But now we notice that one of the summations in the double sum of (1) can be eliminated, for it merely amounts to multiplying the single summation by N, which cancels the factor N^{-1}. In particular, let us eliminate the summation over $\mathbf{R}_i$, letting it be for instance the position of the atom in the central unit cell on which the orbital ψ_n is located, and carrying out a single sum over $\mathbf{R}_j$, which amounts to summing over all neighbors of the original atom. Then in place of (1) we have

$$\sum(\mathbf{R}_j)\exp i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_i)\int\psi_n^*(\mathbf{r}-\mathbf{R}_i)H\psi_m(\mathbf{r}-\mathbf{R}_j)dv. \quad (2)$$

In this formula, $\mathbf{R}_j-\mathbf{R}_i$ is the vector displacement from the atom on which the orbital ψ_n is located, to one of its neighbors on which an orbital ψ_m is located.

The convenient feature which we observe from (2) is the very simple way in which each term depends on the propagation constant $\mathbf{k}$, and the fact that each term of the summation can be identified with a pair of orbitals on neighboring atoms. The actual calculation of the integrals, however, can be extremely difficult. First we must find the orthogonalized Löwdin functions, from the atomic orbitals, and this is a very considerable task. When this is done, each ψ_n in (2) is a combination of atomic orbitals on many nearby atoms. Thus the integral in (2) can be made up as a linear combination of many integrals of the form of $\int\phi_n^*(\mathbf{r}-\mathbf{R}_i)\times H\phi_m(\mathbf{r}-\mathbf{R}_j)dv$. Now the Hamiltonian H, involving a periodic potential, can be written as the sum of a kinetic energy operator, and a potential, which is approximately a sum of spherically symmetrical potential wells located at all the atoms of the crystal. Hence our integral is a linear combination of integrals of a product of an atomic function $\phi_n^*(\mathbf{r}-\mathbf{R}_i)$ located on the atom at position $\mathbf{R}_i$, another atomic function $\phi_m(\mathbf{r}-\mathbf{R}_j)$ on the atom at $\mathbf{R}_j$, and a spherical potential function located on still a third atom. In other words, we have three-center integrals, of the form which are being worked on so extensively in the present study of molecules, and whose calculation is very difficult. All these complications add up to make the rigorous calculation of the matrix components of energy an almost impossible task, not only because the individual terms are difficult to work out, but also because there are so many of them, combined in such complicated ways. The possibility is not excluded that eventually ways will be found to do this work by means of high-speed computers, but it will certainly be quite out of the question without such help. No calculations which have yet been made by the LCAO method for crystals approach real rigor, and Dr. R. H. Parmenter, in this laboratory, who has tried to estimate the labor involved in such a rigorous calculation, has concluded that by present methods it would be quite out of the question.

We now come to the point where it is desirable to introduce our simplifications, which convert the method from a rigorous one to a rather simple interpolation method. We merely use the form (2) for the matrix components of energy, but replace the integrals by disposable constants, which we choose to fit accurate determination of energies at particular $\mathbf{k}$ values. We must be more precise about the way this is done, however. We wish only a finite number of arbitrary constants, for we have to fit only a finite number of accurate calculations of energy. To choose a finite number, we proceed as follows. We note first that there is every reason to think that the integrals in (2) will get smaller numerically as the atoms in question get farther apart. If the functions ψ_n were atomic orbitals, instead of Löwdin's orthogonalized combinations, then

such an integral would be zero unless the two atoms were close enough so that their orbitals overlapped to an appreciable extent. The orthogonalized Löwdin functions contain contributions located on neighboring atoms, and hence extend outward farther than atomic orbitals, so that the actual integrals in (2) will be appreciable for greater interatomic distances than if they were formed from simple atomic orbitals. Still our general statement almost certainly remains true, that the integrals will decrease fairly rapidly as the interatomic distance decreases. A first natural simplification, then, is to assume arbitrarily that all integrals are to be disregarded except those for neighbors lying closer than a certain minimum distance. We can use only nearest neighbors, or only nearest and second nearest, or only nearest and second and third nearest, according to how many disposable constants we wish to use.

There is one thing to be noticed about the integrals in (2). Many of them must be related, through demands of crystal symmetry. Thus, if symmetry operations of rotation and inversion about the atom at position $\mathbf{R}_i$, where the orbital ψ_n is located, will carry the atom at $\mathbf{R}_j$ into another similar atom, in the same or another unit cell, then there will be relations between the integrals between the orbital ψ_n and orbitals of type ψ_m on these various atoms, which clearly must all be at the same distance from the first atom. As a very simple example, in a simple cubic crystal the interaction integrals between an s orbital on the atom at the origin and s orbitals on atoms displaced by equal distances along the $\pm x$, $\pm y$, and $\pm z$ axes must all be equal. Rules like this, which can be studied by inspection or by the group theory, decrease greatly the number of independent integrals. When we take account of such rules, we find in some important practical cases, which we shall mention later, that if we use the integrals between nearest neighbors, or nearest and second-nearest neighbors, we have about the right number of disposable constants to fit the results of accurate calculation at the various symmetry points in the Brillouin zone for which calculations have been made. This results in rather simple formulas for matrix components of energy, set up according to (2).

Another simplification which we can make is to consider only atomic orbitals whose energy is somewhere near that of the energy bands we are interested in. Thus, if we are dealing with diamond, we can reasonably disregard the $1s$ atomic orbitals, treating only the $2s$ and $2p$. Or, with an element in the $3d$ transition group, we can consider $3d$, $4s$, and possibly $4p$ atomic orbitals, but can disregard the rest, when we are concerned with the valence and conduction bands. We could not make such an approximation if we were making a rigorous calculation; we remember that one hazard of such calculations is that, if we use wave functions for outer electrons which are not orthogonal to those of the inner electrons and then apply the variation method, we can arrive at entirely erroneous results. We are saved from such difficulties in our present method. By choosing our parameters so as to fit certain accurately determined energies, we know that we cannot possibly make a serious error. The use of relatively few atomic orbitals then reduces the order of the secular problem to a point where we can handle it without serious difficulty. Thus, for instance, in diamond, we need eight orbitals: $2s$ and the threefold degenerate $2p$, on each of the two atoms of the unit cell. Hence we have an eighth-order secular equation, which is not difficult to solve with a digital computer. For an element of the iron group, the five d functions and the one $4s$ lead to a sixth-order secular equation and give quite good results; under some circumstances, we can simplify even further, disregarding the $4s$, and having a fifth-order equation.

There is a still further simplification which is sometimes desirable, sometimes not, involving the neglect of three-center integrals. This is complicated enough so that we devote the next section to its discussion. Then we shall go on to the application of our method to several specific cases.

III. THE TWO-CENTER APPROXIMATION

Many writers on molecular problems have assumed that three-center integrals were negligible compared to two-center integrals. This is not really the case. Nevertheless they are certainly smaller than the two-center integrals. And since we are neglecting many terms, and trying to reduce our problem to a form where it has just enough arbitrary constants to fit whatever information we may have, there may be cases where it is desirable to assume that we can disregard three-center integrals, thereby simplifying the situation even further. If we treat the potential energy in H as being the sum of spherical potentials located on the various atoms and disregard three-center integrals, then the only part of the potential energy we retain in (2) is the sum of spherical potentials located on the two atoms on which the atomic orbitals are located. Thus the integral becomes similar to the type which we should have in a diatomic molecule. If we consider the vector $\mathbf{R}_j-\mathbf{R}_i$, stretching from one atom to the other, to be an axis like that of a diatomic molecule, we can express each of the functions ψ as a sum of functions space quantized with respect to that axis. Thus if ψ were an atomic p orbital, we could express it as a linear combination of a $p\sigma$ and a $p\pi_\pm$ function with respect to the axis, and if it is a d function it is a combination of $d\sigma$, $d\pi_\pm$, and $d\delta_\pm$, where as usual σ, π, and δ refer to the component of angular momentum around the axis. Actually, the ψ's are not atomic orbitals, but rather the Löwdin orthogonalized functions, but we have seen that they still have the same symmetry properties with respect to the crystal as the atomic orbitals, and it is not a bad approximation to assume that they can

be expanded in the same way. In the integral (2), we shall get a nonvanishing contribution only if we are dealing with σ components of both ψ_n and ψ_m, or π_+ components of both, or π_- components of both, etc. Hence we can reduce all the various integrals appearing in (2) to a relatively small number.

It is a straightforward matter of rotating axes and transforming spherical harmonics in terms of one set of axes into spherical harmonics with respect to another set, to find the nature of these integrals. Thus, let the atomic orbitals be set up with respect to a set of rectangular axes. We shall symbolize the p_x, p_y, p_z functions by x, y, z; the various d functions by xy, yz, zx, x^2-y^2, and $3z^2-r^2$, which stand for the various functions whose dependence on angle is like that of the polynomials we have written, multiplied by appropriate functions of r. Then to set up the integrals in (2), we need contributions consisting of a product of an atomic orbital of this type on the atom located at $\mathbf{R}_i$, another atomic orbital on the atom at $\mathbf{R}_j$, and spherical potentials centered on these two atoms. Let the direction cosines of the direction of the vector $\mathbf{R}_j-\mathbf{R}_i$, pointing from one atom to the other, be l, m, n. Then we can symbolize one of the integrals by such a symbol as $E_{x,xy}(l,m,n)$, meaning an integral in which the function ψ_n is a p_x-like function; ψ_m, a d function with symmetry properties like xy. This particular function can be written approximately in terms of two integrals: that between a $p\sigma$ orbital on the first atom and a $d\sigma$ orbital on the second; and that between a $p\pi$ on the first and a $d\pi$ on the second. Let the first of these be symbolized by $(pd\sigma)$ and the second by $(pd\pi)$; we shall assume that the first index, such as p, refers to the first orbital, the second, as d, to the second, and note that interchanging the order of the indices has no effect if the sum of the parities of the two orbitals is even, but changes the sign if the sum of the parities is odd. We now find, by carrying out the analysis mentioned earlier, that $E_{x,xy}(l,m,n)=\sqrt{3}l^2m(pd\sigma)+m(1-2l^2)(pd\pi)$. Similar formulas can be worked out for each of the combinations of functions, and are listed in Table I for all combinations of s, p, and d functions. The entries not given in the table can be found by cyclically permuting the coordinates and direction cosines. It is to be realized, of course, that the integrals like $(pd\sigma)$ are functions of the distance between the atoms, so

TABLE I. Energy integrals for crystal in terms of two-center integrals.

$E_{s,s}$	$(ss\sigma)$
$E_{s,x}$	$l(sp\sigma)$
$E_{x,x}$	$l^2(pp\sigma)+(1-l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma)-lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma)-ln(pp\pi)$
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$
E_{s,x^2-y^2}	$\frac{1}{2}\sqrt{3}(l^2-m^2)(sd\sigma)$
$E_{s,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)](sd\sigma)$
$E_{x,xy}$	$\sqrt{3}l^2m(pd\sigma)+m(1-2l^2)(pd\pi)$
$E_{x,yz}$	$\sqrt{3}lmn(pd\sigma)-2lmn(pd\pi)$
$E_{x,zx}$	$\sqrt{3}l^2n(pd\sigma)+n(1-2l^2)(pd\pi)$
E_{x,x^2-y^2}	$\frac{1}{2}\sqrt{3}l(l^2-m^2)(pd\sigma)+l(1-l^2+m^2)(pd\pi)$
E_{y,x^2-y^2}	$\frac{1}{2}\sqrt{3}m(l^2-m^2)(pd\sigma)-m(1+l^2-m^2)(pd\pi)$
E_{z,x^2-y^2}	$\frac{1}{2}\sqrt{3}n(l^2-m^2)(pd\sigma)-n(l^2-m^2)(pd\pi)$
$E_{x,3z^2-r^2}$	$l[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}ln^2(pd\pi)$
$E_{y,3z^2-r^2}$	$m[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}mn^2(pd\pi)$
$E_{z,3z^2-r^2}$	$n[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)+\sqrt{3}n(l^2+m^2)(pd\pi)$
$E_{xy,xy}$	$3l^2m^2(dd\sigma)+(l^2+m^2-4l^2m^2)(dd\pi)+(n^2+l^2m^2)(dd\delta)$
$E_{xy,yz}$	$3lm^2n(dd\sigma)+ln(1-4m^2)(dd\pi)+ln(m^2-1)(dd\delta)$
$E_{xy,zx}$	$3l^2mn(dd\sigma)+mn(1-4l^2)(dd\pi)+mn(l^2-1)(dd\delta)$
E_{xy,x^2-y^2}	$\frac{3}{2}lm(l^2-m^2)(dd\sigma)+2lm(m^2-l^2)(dd\pi)+\frac{1}{2}lm(l^2-m^2)(dd\delta)$
E_{yz,x^2-y^2}	$\frac{3}{2}mn(l^2-m^2)(dd\sigma)-mn[1+2(l^2-m^2)](dd\pi)+mn[1+\frac{1}{2}(l^2-m^2)](dd\delta)$
E_{zx,x^2-y^2}	$\frac{3}{2}nl(l^2-m^2)(dd\sigma)+nl[1-2(l^2-m^2)](dd\pi)-nl[1-\frac{1}{2}(l^2-m^2)](dd\delta)$
$E_{xy,3z^2-r^2}$	$\sqrt{3}lm[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)-2\sqrt{3}lmn^2(dd\pi)+\frac{1}{2}\sqrt{3}lm(1+n^2)(dd\delta)$
$E_{yz,3z^2-r^2}$	$\sqrt{3}mn[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}mn(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}mn(l^2+m^2)(dd\delta)$
$E_{zx,3z^2-r^2}$	$\sqrt{3}ln[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}ln(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}ln(l^2+m^2)(dd\delta)$
$E_{x^2-y^2,x^2-y^2}$	$\frac{3}{4}(l^2-m^2)^2(dd\sigma)+[l^2+m^2-(l^2-m^2)^2](dd\pi)+[n^2+\frac{1}{4}(l^2-m^2)^2](dd\delta)$
$E_{x^2-y^2,3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2-m^2)[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}n^2(m^2-l^2)(dd\pi)+\frac{1}{4}\sqrt{3}(1+n^2)(l^2-m^2)(dd\delta)$
$E_{3z^2-r^2,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)]^2(dd\sigma)+3n^2(l^2+m^2)(dd\pi)+\frac{3}{4}(l^2+m^2)^2(dd\delta)$

that we shall have different values for nearest neighbors, second-nearest neighbors, and so on; these can be indicated by subscripts 1, 2, etc. Sometimes it is more convenient to indicate the argument of $E_{x,xy}$, and similar quantities, not by l, m, n, but by the actual coordinates of the second atom with respect to the first, perhaps expressed as a multiple of the lattice spacing. Such notations will be given later for the various special cases we consider.

By the use of Table I, we can approximately express the various E integrals concerned in the problem in terms of a smaller number of integrals like $(pd\sigma)$, etc. In some cases, we shall find that the number of integrals like $(pd\sigma)$ is exactly equal to the number of E integrals involved with neighbors of a particular interatomic distance, and in such a case one method has no advantage over the other; we can compute one set of integrals from the other. In other cases, however, there are considerably more E integrals than integrals of the two-center type. In such a case, we must be guided by convenience as to which method to use. If we have to fit a considerable number of points by means of our disposable constants, we shall normally want to use the E integrals, since we have more of them. When we do this, we find in practice that they cannot be accurately derived from the smaller number of two-center integrals, showing that the two-center approximation is not very good. However, if we have fewer points to fit, it may happen that we cannot determine all the E integrals from the information at hand. In such a case, we may choose to assume that they can be expressed according to Table I in terms of two-center integrals, thereby having a smaller number of disposable constants, which we may be able to determine from the available information. Certainly the results will not be as reliable as if we do not make the two-center approximation; but the two-center approximation may not be very bad and such a procedure may be better than nothing. Another use for Table I is that in some cases there are existing calculations using the LCAO approximation, which almost invariably assume two-center integrals; our table will make it convenient to compare our method with these existing calculations.

IV. THE SIMPLE CUBIC STRUCTURE

Though real crystals do not ordinarily show the simple cubic structure, nevertheless it is convenient to begin with it, both on account of its simplicity, and also because from the results of it we can immediately derive the behavior of the face-centered and body-centered cubic structures. Our task is to express the matrix components of the Hamiltonian, which we have written in (2), in a form convenient for use in the simple cubic case. As before, we use s, p, and d atomic orbitals, which we choose so as to form basis functions for irreducible representations of the cubic point group. These s, p, and d functions will have transformation properties like the sets s; x, y, z; xy, yz, zx; x^2-y^2, $3z^2-r^2$. We let the atoms be located at the vector positions $pa\mathbf{i}+qa\mathbf{j}+ra\mathbf{k}$, where p, q, r are integers, a is the lattice spacing of the simple cubic crystal, and $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors along the x, y, z axis. Let the subscripts n, m refer to two out of the set of symbols s, x, y, z, xy, etc. Then we shall denote our integrals by the expression

$$E_{n,m}(p,q,r)=\int \psi_n^*(\mathbf{r})H\psi_m(\mathbf{r}-pa\mathbf{i}-qa\mathbf{j}-ra\mathbf{k})dv. \quad (3)$$

That is, in this case, rather than using l, m, n as the arguments of the E symbols, it is more convenient to use actual atomic coordinates, so that $l=p(p^2+q^2+r^2)^{-\frac{1}{2}}$, etc. The integrals occurring in (3) are the ones to be inserted in formula (2) for the matrix components of energy.

We now wish to express our matrix components of energy between the Bloch sums in terms of the smallest set of integrals of this nature that is possible. We make use of all relations between integrals which symmetry permits to reduce the number of atomic integrals which appear in the matrix elements of Bloch functions. Making use of these relations, the matrix elements for the simple cubic crystal are given in Table II. A symbol like (n/m), such as (s/x), etc., denotes the matrix component of the Hamiltonian between a Bloch sum of atomic functions of symmetry type n and one of symmetry type m. We have also used the abbreviation $\xi=ak_x$, $\eta=ak_y$, $\zeta=ak_z$.

The various E symbols occurring in Table II are all independent, so that in fitting known energy values, we may treat them all as disposable constants. On the other hand, in some cases we may wish to express these symbols in terms of the smaller number of two-center integrals, as discussed in the preceding section. In this case, we may use Table I to write all of the E's in terms of these two-center integrals. In doing this, we must remember that the direction cosines in Table I are proportional to, but not equal to, the p, q, r of Table II. It is not hard to introduce the expressions of Table I into Table II, and we give in Table III the results of this substitution. Comparison of these tables allows us to see the considerable reduction in the number of disposable parameters introduced by using the two-center approximation. Thus, for instance, for interactions of d electrons on second-nearest neighbors, we have six independent integrals in Table II: $E_{xy,xy}(110)$, $E_{xy,xy}(011)$, $E_{xy,xz}(011)$, $E_{xy,3z^2-r^2}(110)$, $E_{3z^2-r^2,3z^2-r^2}(110)$, and $E_{x^2-y^2,x^2-y^2}(110)$. In Table III, these are all expressed in terms of three two-center integrals: $(dd\sigma)_2$, $(dd\pi)_2$, $(dd\delta)_2$. In some cases the reduction in number is less, or there is no reduction at all, as we have mentioned earlier. Each case is different, and must be separately examined by comparison of Tables II and III.

There are obviously many different independent

TABLE II. Matrix components of energy for simple cubic crystals.

(s/s)	$E_{s,s}(000)+2E_{s,s}(100)(\cos\xi+\cos\eta+\cos\zeta)+4E_{s,s}(110)(\cos\xi\cos\eta+\cos\xi\cos\zeta+\cos\eta\cos\zeta)+8E_{s,s}(111)\cos\xi\cos\eta\cos\zeta$
(s/x)	$2iE_{s,x}(100)\sin\xi+4iE_{s,x}(110)(\sin\xi\cos\eta+\sin\xi\cos\zeta)+8iE_{s,x}(111)\sin\xi\cos\eta\cos\zeta$
(s/xy)	$-4E_{s,xy}(110)\sin\xi\sin\eta-8E_{s,xy}(111)\sin\xi\sin\eta\cos\zeta$
(s/x^2-y^2)	$\sqrt{3}E_{s,3z^2-r^2}(001)(\cos\xi-\cos\eta)+2\sqrt{3}E_{s,3z^2-r^2}(110)(-\cos\xi\cos\zeta+\cos\eta\cos\zeta)$
$(s/3z^2-r)$	$E_{s,3z^2-r^2}(001)(-\cos\xi-\cos\eta+2\cos\zeta)-2E_{s,3z^2-r^2}(110)(-2\cos\xi\cos\eta+\cos\xi\cos\zeta+\cos\eta\cos\zeta)$
(x/x)	$E_{x,x}(000)+2E_{x,x}(100)\cos\xi+2E_{y,y}(100)(\cos\eta+\cos\zeta)+4E_{x,x}(110)(\cos\xi\cos\eta+\cos\xi\cos\zeta)+4E_{x,x}(011)\cos\eta\cos\zeta$ $+8E_{x,x}(111)\cos\xi\cos\eta\cos\zeta$
(x/y)	$-4E_{x,y}(110)\sin\xi\sin\eta-8E_{x,y}(111)\sin\xi\sin\eta\cos\zeta$
(x/xy)	$2iE_{x,xy}(010)\sin\eta+4iE_{x,xy}(110)\cos\xi\sin\eta+4iE_{x,xy}(011)\sin\eta\cos\zeta+8iE_{x,xy}(111)\cos\xi\sin\eta\cos\zeta$
(x/yz)	$-8iE_{x,yz}(111)\sin\xi\sin\eta\sin\zeta$
$(x/x-y^2)$	$\sqrt{3}iE_{x,3z^2-r^2}(001)\sin\xi+2\sqrt{3}iE_{z,3z^2-r^2}(011)(\sin\xi\cos\eta+\sin\xi\cos\zeta)+2iE_{z,x^2-y^2}(011)(\sin\xi\cos\eta-\sin\xi\cos\zeta)$ $+8iE_{x,x^2-y^2}(111)\sin\xi\cos\eta\cos\zeta$
$(x/3z^2-r^2)$	$-iE_{x,3z^2-r^2}(001)\sin\xi-2iE_{z,3z^2-r^2}(011)(\sin\xi\cos\eta+\sin\xi\cos\zeta)+2\sqrt{3}iE_{z,x^2-y^2}(011)(\sin\xi\cos\eta-\sin\xi\cos\zeta)$ $-(8/\sqrt{3})E_{x,x^2-y^2}(111)\sin\xi\cos\eta\cos\zeta$
$(z/3z^2-r^2)$	$2iE_{z,3z^2-r^2}(001)\sin\zeta+4iE_{z,3z^2-r^2}(011)(\cos\xi\sin\zeta+\cos\eta\sin\zeta)+(16/\sqrt{3})iE_{x,x^2-y^2}(111)\cos\xi\cos\eta\sin\zeta$
(xy/xy)	$E_{xy,xy}(000)+2E_{xy,xy}(100)(\cos\xi+\cos\eta)+2E_{xy,xy}(001)\cos\zeta+4E_{xy,xy}(110)\cos\xi\cos\eta$ $+4E_{xy,xy}(011)(\cos\xi\cos\zeta+\cos\eta\cos\zeta)+8E_{xy,xy}(111)\cos\xi\cos\eta\cos\zeta$
(xy/xz)	$-4E_{xy,xz}(011)\sin\eta\sin\zeta-8E_{xy,xz}(111)\cos\xi\sin\eta\sin\zeta$
(xy/x^2-y^2)	zero
$(xy/3z^2-r^2)$	$-4E_{yx,3z^2-r^2}(110)\sin\xi\sin\eta-8E_{xy,3z^2-r^2}(111)\sin\xi\sin\eta\cos\zeta$
(xz/x^2-y^2)	$2\sqrt{3}E_{xy,3z^2-r^2}(110)\sin\xi\sin\zeta+4\sqrt{3}E_{xy,3z^2-r^2}(111)\sin\xi\cos\eta\sin\zeta$
$(xz/3z^2-r^2)$	$2E_{xy,3z^2-r^2}(110)\sin\xi\sin\zeta+4E_{xy,3z^2-r^2}(111)\sin\xi\cos\eta\sin\zeta$
(x^2-y^2/x^2-y^2)	$E_{3z^2-r^2,3z^2-r^2}(000)+\frac{3}{2}E_{3z^2-r^2,3z^2-r^2}(1001)(\cos\xi+\cos\eta)+2E_{x^2-y^2,x^2-y^2}(001)(\frac{1}{4}\cos\xi+\frac{1}{4}\cos\eta+\cos\zeta)$ $+3E_{3z^2-r^2,3z^2-r^2}(110)(\cos\xi\cos\zeta+\cos\eta\cos\zeta)+4E_{x^2-y^2,x^2-y^2}(110)(\cos\xi\cos\eta+\frac{1}{4}\cos\xi\cos\zeta+\frac{1}{4}\cos\eta\cos\zeta)$ $+8E_{3z^2-r^2,3z^2-r^2}(111)\cos\xi\cos\eta\cos\zeta$
$(3z-r/3z-r^2)$	$E_{3z^2-r^2,3z^2-r^2}(000)+2E_{3z^2-r^2,3z^2-r^2}(001)(\frac{1}{4}\cos\xi+\frac{1}{4}\cos\eta+\cos\zeta)+\frac{3}{2}E_{x^2-y^2,x^2-y^2}(001)(\cos\xi+\cos\eta)$ $+4E_{3z^2-r^2,3z^2-r^2}(110)(\cos\xi\cos\eta+\frac{1}{4}\cos\xi\cos\zeta+\frac{1}{4}\cos\eta\cos\zeta)+3E_{x^2-y^2,x^2-y^2}(110)(\cos\xi\cos\zeta+\cos\eta\cos\zeta)$ $+8E_{3z^2-r^2,3z^2-r^2}(111)\cos\xi\cos\eta\cos\zeta$
$(x^2-y^2/3z^2-r^2)$	$\frac{1}{2}\sqrt{3}E_{3z^2-r^2,3z^2-r^2}(001)(-\cos\xi+\cos\eta)-\frac{1}{2}\sqrt{3}E_{x^2-y^2,x^2-y^2}(001)(-\cos\xi+\cos\eta)$ $+\sqrt{3}E_{3z^2-r^2,3z^2-r^2}(110)(\cos\xi\cos\zeta-\cos\eta\cos\zeta)-\sqrt{3}E_{x^2-y^2,x^2-y^2}(110)(\cos\xi\cos\zeta-\cos\eta\cos\zeta)$

integrals and types of atomic functions in Tables II and III, and we should not try in any case to set up a problem so complicated as to include all types. In special cases, the problem will simplify greatly by the omission of many types of orbitals. In such cases, it may well be that the secular equation set up from these matrix components will be simple enough along certain special directions or in certain special planes so that it can be solved by elementary means; this arises mostly because many of the nondiagonal matrix components have factors $\sin\xi$, etc., which vanish in special cases. However, since real crystals do not show the simple cubic structure, we shall not try to set up special cases and discuss them here, but shall rather go on to the structures which actually occur in nature, starting with the face-centered cubic structure.

V. THE FACE-CENTERED CUBIC STRUCTURE

The face-centered cubic structure is that in which the atoms are located at points $pa\mathbf{i}+qa\mathbf{j}+ra\mathbf{k}$, where $p+q+r$ is an even integer. The nearest neighbors of a given atom are located at the twelve points whose p, q, r are like (110). The second-nearest neighbors are at the six points like (200), and the third nearest at the 24 points like (211). We see that as far as the nearest and second-nearest neighbors are concerned, the problem is very similar to what we have already met with the simple cubic structure. That is, the nearest neighbors with the face-centered structure are precisely the same as the second-nearest neighbors with the simple cubic structure, and the second-nearest neighbors with the face-centered structure are like the nearest neighbors with the simple cubic structure, only twice as far away. Thus, if we are interested only in nearest and second-nearest neighbors, we can deduce the matrix components of energy immediately from the results of Tables II and III. For the diagonal matrix component of an s state, for instance, the quantity (s/s) of Tables II and III, the corresponding formulas are

$$\begin{aligned}(s/s)&=E_{s,s}(000)+4E_{s,s}(110)(\cos\xi\cos\eta+\cos\xi\cos\zeta\\&\quad+\cos\eta\cos\zeta)+2E_{s,s}(200)(\cos2\xi+\cos2\eta+\cos2\zeta)\\&=E_{s,s}(000)+4(ss\sigma)_1(\cos\xi\cos\eta+\cos\xi\cos\zeta\\&\quad+\cos\eta\cos\zeta)+2(ss\sigma)_2(\cos2\xi+\cos2\eta+\cos2\zeta).\quad(4)\end{aligned}$$

In a similar way, we can find all the other matrix components of energy.

From the matrix components of energy, we can easily demonstrate all the various cases of symmetry found at various points of the Brillouin zone with a crystal of this type. For instance, at the center of the Brillouin zone, where $\xi=\eta=\zeta=0$, we see by inspection that all nondiagonal matrix components of energy vanish, so that our original Bloch functions are the correct wave functions to form solutions of Schrödinger's equation. We find, of course, that the diagonal energies of the three p states are all equal, so that they are degenerate at the origin. The d states, however, split into a threefold degenerate and a twofold degenerate set, as we should expect from Bethe's rules. The reason why Bethe's rules apply is that at this symmetry point, the star of $\mathbf{k}$ vectors contains only one member, and as a result we can diagonalize the symmetry operations of the point group and the translation operation at the same time. The energies of the two d states at $\mathbf{k}=0$ are found to be

$$\begin{aligned}(xy/xy)&=(yz/yz)=(zx/zx)\\&=E_{xy,\,xy}(000)+4E_{xy,\,xy}(110)+8E_{xy,\,xy}(011)\\&\qquad+4E_{xy,\,xy}(200)+2E_{xy,\,xy}(002),\\(x^2-y^2,\,x^2-y^2)&=(3z^2-r^2,\,3z^2-r^2)\\&=E_{3z^2-r^2,\,3z^2-r^2}(000)+6E_{3z^2-r^2,\,3z^2-r^2}(110)\\&\quad+6E_{x^2-y^2,\,x^2-y^2}(110)+3E_{3z^2-r^2,\,3z^2-r^2}(002)\\&\qquad+3E_{x^2-y^2,\,x^2-y^2}(002).\end{aligned}\tag{5}$$

As we depart from $\mathbf{k}=0$, however, nondiagonal matrix components of energy between the various functions appear, proportional to k for small $\mathbf{k}$ values, and the degeneracy is removed. If we expand the matrix components in power series in ξ, η, ζ, and retain only the lowest terms, we can find the behavior of the energy bands in the neighborhood of $\mathbf{k}=0$, and are led to secular equations of the type discussed by Shockley.[13] Our method, however, is not limited to small k values, and we can solve for the behavior of the energy bands throughout the Brillouin zone.

The Brillouin zone for the face-centered cubic structure if of course identical with the Wigner-Seitz cell for the body-centered structure. We can easily demonstrate this fact from our matrix components of energy. By examining the reciprocal lattice, we find that the origin of the Brillouin zone, and the points $\xi=\pm\pi$, $\eta=\pm\pi$, $\zeta=\pm\pi$, lying at the corners of the cube, must be equivalent points. The first Brillouin zone includes the region closer to the origin than to these points. To demonstrate the body-centered nature of the reciprocal lattice, we must show that when we increase ξ, η, ζ, by $\pm\pi$ each, the energy is unchanged. When we examine the matrix components of energy, like those given in (4), we find that in fact each of them is unchanged when we make this change. Each of the components relating to a second-nearest neighbor in the simple cubic case, or a nearest neighbor in the face-centered structure, has a product of two sines or cosines in the expression in Table II or III, whereas each component relating to a nearest neighbor for the simple cubic case, or a second-nearest neighbor for the face-centered structure, has a single cosine, or the product of three, and these relations are just such as to assure the periodicity in the momentum space. The same thing would hold, of course, if more distant neighbors were included. Such simple considerations allow us to study all the symmetry properties of the wave functions and energy levels, and show that the LCAO method is particularly well suited for pedagogical purposes, in discussing the degeneracy properties of wave functions. Since such deductions are very elementary in nature, we shall not carry them further.

Many important crystals have the face-centered cubic structure, and the type of treatment we have sketched can be very useful for discussing their energy bands. A beginning in this direction is furnished by the discussion of Fletcher and Wohlfarth,[7,8] of the energy bands of nickel. They have considered the five d electrons of nickel, omitting discussion of the $4s$ band which really overlaps the d bands. They have considered only nearest neighbors, and have computed the integrals $(dd\sigma)$, $(dd\pi)$, $(dd\delta)$, using a two-center approximation, and suitable atomic orbitals and spherical potentials. They do not state their result in terms of these two-center integrals, but rather in terms of six quantities, which they call A_1, A_2, $\cdots A_6$, which are very closely related to our quantities $E_{xy,\,xy}(110)$, etc. We have already stated that for the interaction of d electrons on second-nearest neighbors in the simple cubic structure, there are six such integrals, and these are simply related to Fletcher and Wohlfarth's A's. However, since they were determined from a two-center approximation, we should be able to work back from these A's to find $(dd\sigma)$, etc. When we examine the numerical values of Fletcher and Wohlfarth's A's, we find that in fact they satisfy the relations necessary to be derived from two-center integrals, and working backward from them, we find that they must be given by $(dd\sigma)=-0.2504E_0$, $(dd\pi)=0.1348E_0$, $(dd\delta)=-0.0204E_0$, where $E_0=1.349$ ev. It is interesting to see the rapid decrease in the numerical values of these integrals, as we go from the σ orbital, which of course will overlap the most, through the π to the δ orbital, which overlaps the least. The alternation of sign of the integrals is demanded by the symmetry of the orbitals.

If we use these values of the integrals and the matrix components of energy from Table III for the nearest neighbors in a face-centered cubic structure (that is, the second-nearest neighbors in a simple cubic structure), and consider the five d states, we then find precisely the matrix components of energy considered by Fletcher and Wohlfarth. They have solved the five-by-five secular equation at many points throughout

[13] W. Shockley, Phys. Rev. **78**, 173 (1950).

TABLE III. Matrix components of energy for simple cubic crystals, two-center approximation.

(s/s)	$s_0+2(ss\sigma)_1(\cos\xi+\cos\eta+\cos\zeta)+4(ss\sigma)_2(\cos\xi\cos\eta+\cos\xi\cos\zeta+\cos\eta\cos\zeta)+8(ss\sigma)_3\cos\xi\cos\eta\cos\zeta$
(s/x)	$2i(sp\sigma)_1\sin\xi+2\sqrt{2}i(sp\sigma)_2(\sin\xi\cos\eta+\sin\xi\cos\zeta)+(8/\sqrt{3})i(sp\sigma)_3\sin\xi\cos\eta\cos\zeta$
(s/xy)	$-2\sqrt{3}(sp\sigma)_2\sin\xi\sin\eta-(8/\sqrt{3})(sd\sigma)_3\sin\xi\sin\eta\cos\zeta$
(s/x^2-y^2)	$\sqrt{3}(sd\sigma)_1(\cos\xi-\cos\eta)+\sqrt{3}(sd\sigma)_2(\cos\xi\cos\zeta-\cos\eta\cos\zeta)$
$(s/3z^2-r^2)$	$(sd\sigma)_1(-\cos\xi-\cos\eta+2\cos\zeta)+(sd\sigma)_2(-2\cos\xi\cos\eta+\cos\xi\cos\zeta+\cos\eta\cos\zeta)$
(x/x)	$p_0+2(pp\sigma)_1\cos\xi+2(pp\pi)_1(\cos\eta+\cos\zeta)+2(pp\sigma)_2(\cos\xi\cos\eta+\cos\xi\cos\zeta)$ $+2(pp\pi)_2(\cos\xi\cos\eta+\cos\xi\cos\zeta+2\cos\eta\cos\zeta)+[(8/3)(pp\sigma)_3+(16/3)(pp\pi)_3]\cos\xi\cos\eta\cos\zeta$
(x/y)	$-2[(pp\sigma)_2-(pp\pi)_2]\sin\xi\sin\eta-(8/3)[(pp\sigma)_3-(pp\pi)_3]\sin\xi\sin\eta\cos\zeta$
(x/xy)	$2i(pd\pi)_1\sin\eta+(\sqrt{6})i(pd\sigma)_2\cos\xi\sin\eta+2\sqrt{2}i(pd\pi)_2\sin\eta\cos\zeta+[(8/3)(pd\sigma)_3+(8/3\sqrt{3})(pd\pi)_3]i\cos\xi\sin\eta\cos\zeta$
(x/yz)	$[-(8/3)(pd\sigma)_3+(16/3\sqrt{3})(pd\pi)_3]i\sin\xi\sin\eta\sin\zeta$
(x/x^2-y^2)	$\sqrt{3}(pd\sigma)_1\sin\xi-(3/2)^{\frac{1}{2}}(pd\sigma)_2i\sin\xi\cos\zeta+2\sqrt{2}(pd\pi)_2i[\sin\xi\cos\eta+\frac{1}{2}\sin\xi\cos\zeta]+(8/\sqrt{3})(pd\pi)_3i\sin\xi\cos\eta\cos\zeta$
$(x/3z^2-r^2)$	$-(pd\sigma)_1i\sin\xi+\sqrt{2}(pd\sigma)_2i[\sin\xi\cos\eta-\frac{1}{2}\sin\xi\cos\zeta]-(\sqrt{6})(pd\pi)_2i\sin\xi\cos\zeta-(8/3)(pd\pi)_3i\sin\xi\cos\eta\cos\zeta$
$(z/3z^2-r^2)$	$2i(pd\sigma)_1\sin\zeta+[(1/\sqrt{2})(pd\sigma)_2+(\sqrt{6})(pd\pi)_2]i[\cos\xi\sin\zeta+\cos\eta\sin\zeta]+(16/3)(pd\pi)_3i\cos\xi\cos\eta\sin\zeta$
(xy/xy)	$d_0+2(dd\pi)_1(\cos\xi+\cos\eta)+2(dd\delta)_1\cos\zeta+3(dd\sigma)_2\cos\xi\cos\eta+2(dd\pi)_2(\cos\xi\cos\zeta+\cos\eta\cos\zeta)$ $+(dd\delta)_2(\cos\xi\cos\eta+2\cos\xi\cos\zeta+2\cos\eta\cos\zeta)+[(8/3)(dd\sigma)_3+(16/9)(dd\pi)_3+(32/9)(dd\delta)_3]\cos\xi\cos\eta\cos\zeta$
(xy/xz)	$2[-(dd\pi)_2+(dd\delta)_2]\sin\eta\sin\zeta+[-(8/3)(dd\sigma)_3+(8/9)(dd\pi)_3+(16/9)(dd\delta)_3]\cos\xi\sin\eta\sin\zeta$
(xy/x^2-y^2)	zero
$(xy/3z^2-r^2)$	$\sqrt{3}[(dd\sigma)_2-(dd\delta)_2]\sin\xi\sin\eta+(16/3\sqrt{3})[(dd\pi)_3-(dd\delta)_3]\sin\xi\sin\eta\cos\zeta$
(xz/x^2-y^2)	$-\frac{3}{2}[(dd\sigma)_2-(dd\delta)_2]\sin\xi\sin\zeta-(8/3)[(dd\pi)_3-(dd\delta)_3]\sin\xi\cos\eta\sin\zeta$
$(xz/3z^2-r^2)$	$\frac{1}{2}\sqrt{3}[-(dd\sigma)_2+(dd\delta)_2]\sin\xi\sin\zeta-(8/3\sqrt{3})[(dd\pi)_3-(dd\delta)_3]\sin\xi\cos\eta\sin\zeta$
(x^2-y^2/x^2-y^2)	$d_0+\frac{3}{2}(dd\sigma)_1(\cos\xi+\cos\eta)+(dd\delta)_1(\frac{1}{2}\cos\xi+\frac{1}{2}\cos\eta+2\cos\zeta)+4(dd\pi)_2\cos\xi\cos\eta$ $+[\frac{3}{4}(dd\sigma)_2+(dd\pi)_2+(9/4)(dd\delta)_2](\cos\xi\cos\zeta+\cos\eta\cos\zeta)+[(16/3)(dd\pi)_3+(8/3)(dd\delta)_3]\cos\xi\cos\eta\cos\zeta$
$(3z^2-r^2/3z^2-r^2)$	$d_0+(dd\sigma)_1(\frac{1}{2}\cos\xi+\frac{1}{2}\cos\eta+2\cos\zeta)+\frac{3}{2}(dd\delta)_1(\cos\xi+\cos\eta)+(dd\sigma)(\cos\xi\cos\eta+\frac{1}{4}\cos\xi\cos\zeta+\frac{1}{4}\cos\eta\cos\zeta)$ $+3(dd\pi)_2(\cos\xi\cos\zeta+\cos\eta\cos\zeta)+3(dd\delta)_2(\cos\xi\cos\eta+\frac{1}{4}\cos\xi\cos\zeta+\frac{1}{4}\cos\eta\cos\zeta)$ $+[(16/3)(dd\pi)_3+(8/3)(dd\delta)_3]\cos\xi\cos\eta\cos\zeta$
$(x^2-y^2/3z^2-r^2)$	$\frac{1}{2}\sqrt{3}[-(dd\sigma)_1+(dd\delta)_1](\cos\xi-\cos\eta)+[\frac{1}{4}\sqrt{3}(dd\sigma)_2-\sqrt{3}(dd\pi)_2+\frac{3}{4}\sqrt{3}(dd\delta)_2](\cos\xi\cos\zeta-\cos\eta\cos\zeta)$

the unit cell of reciprocal space, obtaining the distribution of energy levels in energy in this way. They also show that the secular equation can be factored, leading to no factor worse than a quadratic equation, in the 100, 110, and 111 directions. This of course is to be expected. We can consider the symmetry of the wave functions for $\mathbf{k}$ vectors in these directions and can see that if we combine the various d functions to give combinations belonging to the appropriate irreducible representations for these directions, we shall get the factoring of the secular equation which they have found.

The results of this calculation of Fletcher and Wohlfarth are very interesting, but the reader will see that they are not carried out exactly according to the spirit of the present discussion. Our present view would be that more accurate values of the energies at certain symmetry points could probably be found by other methods, such as the method of orthogonalized plane waves, and that it would be better to use the present method as an interpolation, determining the integrals as disposable constants. Fortunately, we have such a calculation of a crystal having the face-centered structure. Recent results of Howarth[14] on copper, by the cellular method, provide us with some of the necessary information. Howarth's calculations are very accurate but unfortunately are carried out only at $\mathbf{k}=0$ and at the edge of the Brillouin zone in the 001 direction or at the point $\zeta=\pi$, $\xi=\eta=0$. We shall examine these calculations and see what information they can give us, using this as an illustration of the application of the method.

If we let ζ be arbitrary but assume $\xi=\eta=0$, the matrix components of energy for the face-centered structure take on the following form:

$$\begin{aligned}
&(s/s)=E_{s,s}(000)+4E_{s,s}(110)+8E_{s,s}(110)\cos\zeta,\\
&(xy/xy)=E_{xy,xy}(000)+4E_{xy,xy}(110)\\
&\qquad\qquad+8E_{xy,xy}(011)\cos\zeta,\\
&(xz/xz)=(yz/yz)=E_{xy,xy}(000)+4E_{xy,xy}(011)\\
&\qquad\qquad+4E_{xy,xy}(110)+4E_{xy,xy}(011)\cos\zeta,\\
&(x^2-y^2/x^2-y^2)\\
&\quad=E_{3z^2-r^2,3z^2-r^2}(000)+4E_{x^2-y^2,x^2-y^2}(110)\\
&\qquad+6E_{3z^2-r^2,3z^2-r^2}(110)+2E_{x^2-y^2,x^2-y^2}(110)\cos\zeta,\\
&(3z^2-r^2/3z^2-r^2)\\
&\quad=E_{3z^2-r^2,3z^2-r^2}(000)+4E_{3z^2-r^2,3z^2-r^2}(110)\\
&\qquad+6E_{x^2-y^2,x^2-y^2}(110)+2E_{3z^2-r^2,3z^2-r^2}(110)\cos\zeta,\\
&(s/3z^2-r^2)=4E_{s,3z^2-r^2}(110)-4E_{s,3z^2-r^2}(110)\cos\zeta.
\end{aligned}\tag{6}$$

All other nondiagonal matrix components vanish. We see that at $\mathbf{k}=0$, where $\cos\zeta=1$, all nondiagonal matrix

[14] D. J. Howarth, Proc. Roy. Soc. (London) **A220**, 513 (1953).

components vanish, so that we are left with three energy levels: the nondegenerate s level; the threefold degenerate state formed from the functions xy, yz, zx; and the twofold degenerate state formed from x^2-y^2 and $3z^2-r^2$. A twofold degeneracy between the states xz, yz persists for all ζ values, but otherwise the degeneracy is all removed when ζ departs from zero, so that at $\zeta=\pi$ we have five distinct energies. Howarth has determined the three energy values we have just described at $\zeta=0$, and the five at $\zeta=\pi$. Let us see what information this gives us about the E integrals.

When we count up in Eq. (6), we find that there are nine independent E integrals concerned in the formulas. Hence it is clear that we can determine all but one of these from Howarth's calculations. When we examine the numbers, we see that we can proceed as follows. The nondiagonal matrix component $(s/3z^2-r^2)$ serves only to push apart the diagonal energies (s/s) and $(3z^2-r^2/3z^2-r^2)$ at $\zeta=\pi$. But the numerical values indicate that these two states are already far apart at this point in the Brillouin zone, so that a small nondiagonal matrix component would have almost no effect in pushing them further apart. We can then assume with very slight error that this nondiagonal matrix component is negligible at $\zeta=\pi$. We then use Eq. (6) to determine the eight integrals aside from $E_{s,\,3z^2-r^2}(110)$, which we neglect. This integral would become important only over the relatively small range of ζ where the s function was having an energy close to that of the $3z^2-r^2$ function; it would determine the details of the interaction of s and d functions where their energies cross. We cannot get information about this from calculations at the center and edges of the Brillouin zone.

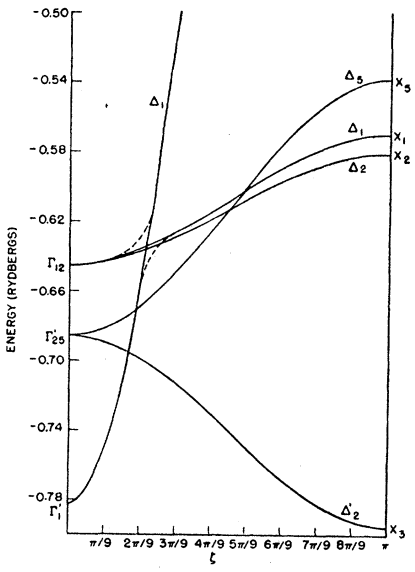


FIG. 1. Variation of energy with wave vector in the 001 direction for Cu calculated using Howarth's energy values at the center and boundary of the zone. (Symmetry symbols are taken from reference 4.)

Proceeding in this way, from Howarth's numerical values, we can compute the values of the remaining eight integrals. These are tabulated in Table IV in rydbergs. The reader can find Howarth's values, if he wishes, by substituting these integrals in Eq. (6). We plot the functions of ζ, given from Eq. (6), in Fig. 1. We see the way in which the s function cuts across the d band steeply; we recall that if the matrix component $(s/3z^2-r^2)$ were known, we should be able to show that the s function does not cut the d function $3z^2-r^2$, but that their energies are pushed apart in the immediate neighborhood of the crossover point as schematically indicated by the dotted line in Fig. 1. Since, however, the energy of the s state varies so rapidly with $\mathbf{k}$, we expect that this effect will not be felt far from this crossover point. It is this fact which makes it a rather good approximation to treat the problem of the five d electrons in a transition metal as independent of the s electron, merely superposing their final energy bands, as Fletcher and Wohlfarth have done.

Comparison of Fig. 1 with Fig. 1 of Fletcher and Wohlfarth's paper (reference 8) shows that the energies, as a function of $\mathbf{k}$, in the 100 direction, show a surprising similarity though one energy level, that arising from the $3z^2-r^2$ state, behaves quite differently, rising with increasing ζ in Howarth's case, falling in Fletcher and Wohlfarth's. But nevertheless the similarities are close. This is shown from Table IV, where we have given not only Howarth's values of the integrals, but also those computed from Fletcher and Wohlfarth's integrals $(dd\sigma)$, etc., which we have already mentioned, expressed in rydberg units so that they are comparable with Howarth's integrals. The agreement of the integrals $E_{xy,\,xy}(110)$ and $E_{xy,\,xy}(011)$ is surprisingly good. The disagreement of the other two integrals computed by both methods is, of course, a result of the discrepancy between the behavior of the $3z^2-r^2$ state, showing that the behavior of this state cannot be described in terms of two-center integrals. Fletcher and Wohlfarth's calculations, of course, assume identical values for the quantities $E_{xy,\,xy}(000)$ and $E_{3z^2-r^2,\,3z^2-r^2}(000)$, since these must be equal in the two-center approximation. Since this quantity merely appears as an additive constant in Fletcher and Wohlfarth's calculation, we cannot determine it in their case. It is interesting to see that the difference between the two integrals as determined by Howarth's calculations, though appreciable, is by no means large. Fletcher and Wohlfarth's calculations of course give no information about the s state, and neither theirs nor Howarth's give information about the interaction between s and d states, as we have pointed out.

This discussion of the resemblances and differences between the calculations of Fletcher and Wohlfarth on nickel, and of Howarth on copper, carried out by quite different methods, suggests that in the future, when more accurate calculations are made for more metals showing the face-centered structure, comparisons of

this type may prove quite valuable in discussing the variation of the energy bands from one element to the next. Further calculations now being carried out in this laboratory by Howarth on copper, if successful, should provide more complete information about this substance, perhaps filling in some of the gaps in Table IV.

VI. THE BODY-CENTERED CUBIC STRUCTURE

The body-centered cubic structure can be handled by methods similar to those we have just used for the face-centered structure. It has atoms at points $pa\mathbf{i}+qa\mathbf{j}+ra\mathbf{k}$, where p, q, r are all even, or all odd, integers. The nearest neighbors of a given atom are the eight of type (111), the second nearest are the six of type (200), and the third nearest are the twelve of type (220). We see that all three of these types are similar to those met in the simple cubic structure, the first being equivalent to the third-nearest neighbors in the simple cubic structure, the second to the nearest neighbors in the simple cubic structure, but twice as far away, and the third being equivalent to the second-nearest neighbors in the simple cubic structure, but twice as far away. Thus we can read the matrix components of the energy for all these types of neighbors directly from the results of Tables II and III. For the s state, for instance, we have

$$(s/s)=E_{s,s}(000)+8E_{s,s}(111)\cos\xi\cos\eta\cos\zeta+4E_{s,s}(200)(\cos2\xi\cos2\eta+\cos2\xi\cos2\zeta+\cos2\eta\cos2\zeta)+2E_{s,s}(220)(\cos2\zeta+\cos2\eta+\cos2\zeta). \quad (7)$$

As with the face-centered structure, it is interesting to check the relationship between these energy expressions and the periodicity in the reciprocal lattice and the structure of the Brillouin zone. The reciprocal space must show a face-centered cubic type of symmetry, the points such as $\xi=0, \eta=\zeta=\pi$ being equivalent to the origin. If we make this transformation, we see that the expression (7) is unchanged, and examination of Tables II and III shows that the same thing will be true of each matrix component. We can also easily check the special symmetry properties at the center and other symmetry points of the Brillouin zone.

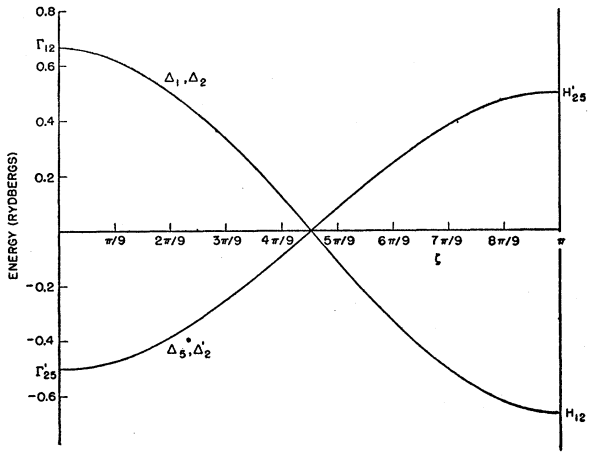
There are a number of important metals which show the body-centered structure: the alkalies, on the one hand, and some of the transition metals, on the other. The alkalies have of course been the subject of much study, and the indications from both the cellular method and the method of orthogonalized plane waves are that the conduction band is rather closely like that characteristic of free electrons, explaining the success of the free-electron model in treating these simple metals. The fact that the alkali metal energy band is so nearly free-electron-like throws some interesting light on our approximation method. The fact appearing from the free-electron nature is that the curvature of the energy surface at $\mathbf{k}=0$ is much less than that at the boundaries of the Brillouin zone. We see from Eq. (7) that in the 100 direction, for $\eta=\zeta=0$, the energy is given by $8E_{s,s}(111)\cos\xi+[8E_{s,s}(200)+2E_{s,s}(220)]\times\cos2\xi+$constant. Now if the quantities $E_{s,s}(200)$ and $E_{s,s}(220)$ were determined as real energy integrals from atomic orbitals, they would have to be negative, just as $E_{s,s}(111)$ is. We then see at once that these terms would increase the curvature already present from the first term at $\xi=0$ but would decrease it at $\xi=\pi$. In other words, if we had this sign for $E_{s,s}(200)$ and $E_{s,s}(220)$, we should have a curvature of the energy surface which (numerically) would be greater at $\mathbf{k}=0$ than at the boundary of the zone, which is contrary to our other information. It must be, then, that to fit the known properties of the energy surface, we must choose the quantities $E_{s,s}(200)$ and $E_{s,s}(220)$ of opposite sign to what we should find if we regarded them as energy integrals between atomic orbitals, and we may by no means neglect them. This emphasizes the importance of our principle that these quantities are really to be regarded as disposable parameters rather than atomic integrals; we may be led seriously astray if we disregard this fact. On the other hand, if we computed the integrals properly from Löwdin functions, we might well get this opposite sign for the integrals for more distant neighbors; for the characteristic of the orthogonalized functions is that they must have contributions on rather distant atoms, of opposite sign to those on the central atom where the orbital is located, which might change the sign of the integral.

The greatest interest of the body-centered structure comes not from the alkali metals, however, but from the tight bound transition metals showing this structure, vanadium, chromium, one of the forms of iron, molybdenum, tantalum, and tungsten. These metals, on account of their tight binding, and on account of the slight antiferromagnetic properties of chromium and the ferromagnetic behavior of body-centered iron, have a very great interest and practical importance. Unfortunately, we do not have any really reliable determination of the structure of their energy bands, by any method.

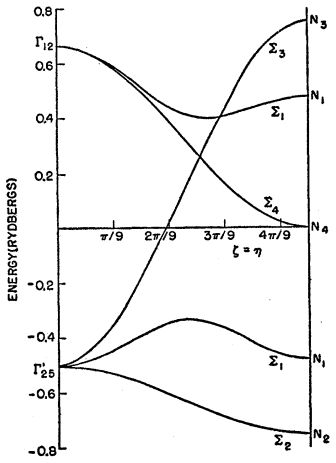
TABLE IV. Energy integrals (in rydbergs) for face-centered cubic structure of Ni (Fletcher and Wohlfarth) and Cu (Howarth).

Integral	Fletcher and Wohlfarth (Ni)	Howarth (Cu)
$E_{s,s}(000)$		+0.0366
$E_{s,s}(110)$		−0.0683
$E_{xy,xy}(000)$		−0.6388
$E_{3z^2-r^2,3z^2-r^2}(000)$		−0.5925
$E_{xy,xy}(110)$	−0.01928	−0.0253
$E_{xy,xy}(011)$	+0.00574	+0.00683
$E_{3z^2-r^2,3z^2-r^2}(110)$	−0.00786	−0.00375
$E_{x^2-y^2,x^2-y^2}(110)$	+0.01353	−0.00500
$E_{xy,xz}(011)$	−0.03116	
$E_{xy,3z^2-r^2}(110)$	−0.03917	

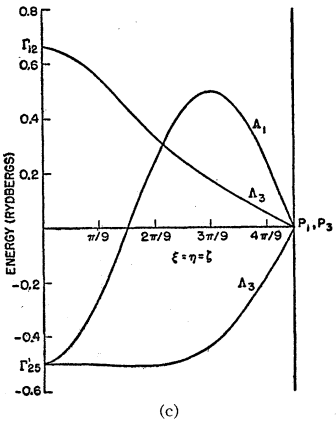
Lacking such information, it is tempting to ask how much our simplified LCAO method can tell us. Accordingly, we shall give here a treatment of the behavior of the *3d* band in such a metal, though, since we have no correct calculation to start with, we must arbitrarily assume values for the various integrals. Even in this way we can derive interesting results, and our present work can form a framework for more accurate treatments of this structure, when calculations by better methods become available in the future.



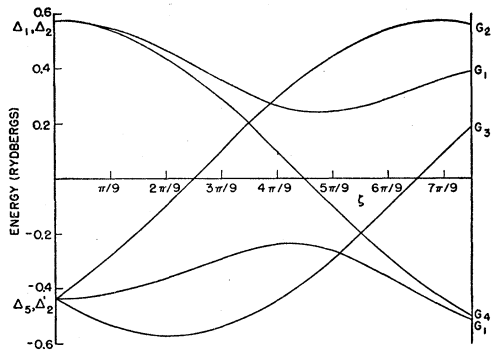
(a)



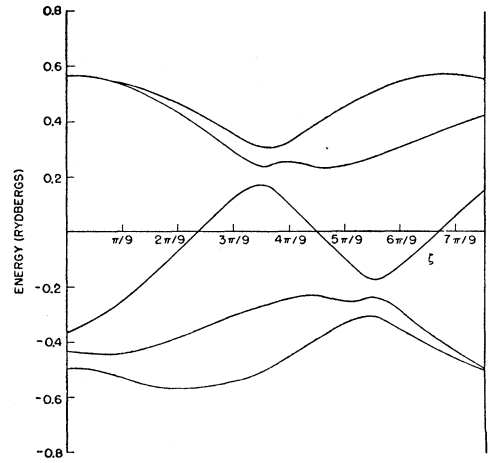
(b)



(c)



(d)



(e)

FIG. 2. Variation of energy with wave vector along various lines in reciprocal space calculated for body-centered structure using Fletcher and Wohlfarth's values for the nearest-neighbor *d* interactions. (a) 001 direction; (b) 011 direction; (c) 111 direction; (d) parallel to 001 direction with $\xi=0$, $\eta=\pi/6$; (e) parallel to 001 direction with $\xi=\pi/18$, $\eta=\pi/6$. (Symmetry symbols are taken from reference 4.)

Since we have no better information, we shall use the two-center approximation, and since we have no values for the integrals $(dd\sigma)$, $(dd\pi)$, $(dd\delta)$, we shall use the same ones determined by Fletcher and Wohlfarth for nickel. The absolute values of these integrals would certainly be different for the elements having the body-centered structure, but very likely the ratios of the three integrals would not be very different. Hence it seems likely that our treatment can give some idea of the general form of the energy bands, though not of the absolute width. We assume, of course, only nearest-neighbor interactions, as Fletcher and Wohlfarth did for nickel. Then the matrix components of energy are found from Table III, using the values appropriate for third-nearest neighbors in the simple cubic case.

We have taken the secular equation and values of the integrals which we have just described, and have solved the five-by-five secular equation at many points through

the Brillouin zone. This calculation was made on the Whirlwind digital computer, and we wish to thank the authorities in charge of that computer, and in particular to thank Dr. Alvin Meckler, who assisted in the programming, for their help in making the calculations. Energy levels were computed on a network of points 10 degrees apart along the axes (that is, for intervals of $\pi/18$) for ξ, η, and ζ. Calculations had to be made at 220 independent points in the Brillouin zone:[15] for $\xi<\eta\leq\zeta\leq\pi/2$. The limitation that ξ, η, ζ be less than $\pi/2$ will be discussed in a later paragraph; it proves to be the case that the roots for larger values of these quantities can be obtained at once from values when they are less than $\pi/2$.

Calculations at these points did not all have to be made by solving the secular equation, since it proves to to be possible to get an analytical solution at all points in the xy plane, or for $\zeta=0$. If we take the matrix components, and insert this value of ζ, we find that the only nondiagonal matrix components of energy which do not vanish are (xz/yz) and $(xy/3z^2-r^2)$. Thus the secular equation factors into a quadratic equation, involving the functions xz and yz; another quadratic, involving xy and $3z^2-r^2$; and the function x^2-y^2, which is a solution as it stands.

In Fig. 2,[15a] we show the energy levels as computed in this way, along a number of lines in the reciprocal lattice. In Fig. 2a, 2b, and 2c we show the energy along the 001, 011, and 111 directions. By comparison with Fig. 1, or with the figures in Fletcher and Wohlfarth's papers, we see that the arrangement of energy bands is quite different in the body-centered structure from what it is in the face-centered structure: at the origin, the energy levels are near the top and bottom of the band rather than near the center, as in the face-centered structure. This would lead us to expect a large density of levels near the top and bottom of the band, with a dip in the middle, which as we shall show in a moment really occurs. We also show two curves indicating the way in which the degeneracy is removed as we move away from symmetry positions in the Brillouin zone. In Fig. 2d, we show curves for the energy levels for $\xi=0$, $\eta=\pi/6$, ζ arbitrary. By comparison with Fig. 2a, we see that the double and triple degeneracies found in the 001 direction are split, but that an accidental degeneracy is still permitted, since we are still in a symmetry plane. In Fig. 2e, we have $\xi=\pi/18$, $\eta=\pi/6$, ζ arbitrary. The accidental degeneracy present in Fig. 2d is now removed, the energy levels being modified so that they cannot cross at all. This is a sample of what happens in other general directions in the Brillouin zone.

From these calculations, we have found values of $N(E)$, the number of states in a given energy range. We have done this in the following way. We have set up curves, like Figs. 2a, 2d, and 2e, for all the calculated values of ξ and η. In each of these curves, we have subdivided the energy range into small intervals (0.05 unit) and have measured the relative extent of the ζ axis for which the curve lay within each of these intervals. This results in a step curve for $N(E)$ determined from each of these energy curves. We have finally added these step curves for all the various energy curves, weighting each one properly. Since we have used a finite net, and a finite energy interval, this of course does not give a smooth curve, and one could get better results by more elaborate methods of calculation; but since our problem is only illustrative anyway, it did not seem worth while to take greater pains in calculating the energy distribution. The results of this calculation are shown in Fig. 3. We see, as we suspected, that there is a decided dip in the density of states curve in the center. There is a good deal of experimental evidence, based on electronic specific heat and other evidence, for such a dip, though we shall not go into the details here. The curve of Fig. 3 is symmetrical about its midpoint, for reasons which we shall now discuss.

The reason for this symmetry is the existence of a type of reflection symmetry of the whole problem

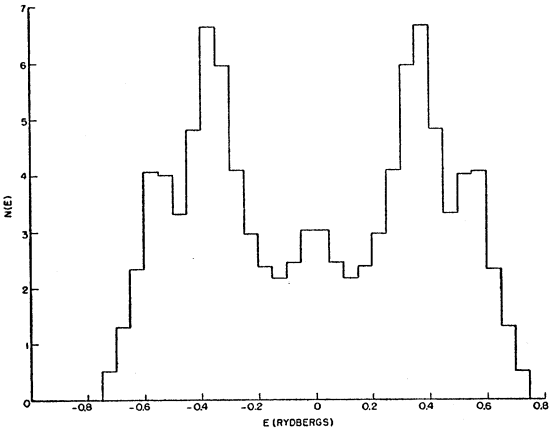


FIG. 3. Density of states curve for body-centered structure calculated using Fletcher and Wohlfarth's parameters for the nearest-neighbor d interactions. The total area under the $N(E)$ curve is five corresponding to five states.

[15] A complete table of the eigenvalues of the 220 secular equations, in hectographed form, may be obtained by writing the authors. This table has also been deposited as Document No. 4225 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[15a] In the ordinates of Figs. 2 and in the abscissa of Fig. 3, the unit of energy is incorrectly indicated. Instead of the rydberg the unit of energy should be $E_0=1.349$ ev. (The unit of energy in terms of which Fletcher and Wohlfarth express their nearest-neighbor interactions between d functions for the face-centered structure.) In any case, the scale of energy in these diagrams should not be taken seriously. There is little reason to believe anything but the ratios of the nearest-neighbor d interactions is correct as we have used them. We expect that the broad features of the curves are correct but do not believe that the actual numerical values of the energies are significant.

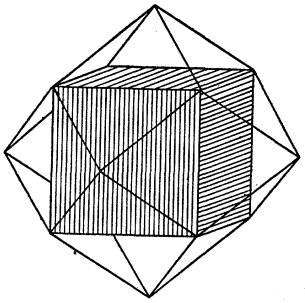


FIG. 4. First Brillouin zone for the body-centered cubic structure showing the inscribed cube bounded by the planes $\xi=\pm\pi/2$, $\eta=\pm\pi/2$, $\zeta=\pm\pi/2$.

about the planes $\xi=\pm\pi/2$, or $\eta=\pm\pi/2$, etc. These planes enclose a cubic volume half the volume of the Brillouin zone. This is made clear from Fig. 4 in which we show the whole Brillouin zone and the cube under discussion. The Brillouin zone consists of the cube and of pyramids extending outward from each face of the cube. If these pyramids were reflected in the faces of the cube, so that they extended inside rather than outside the cube, they would just fill the cube. The symmetry property to which we have referred can then be stated as follows: the energies of the five states at a point in one of the pyramids, outside the cube, and at the mirror image of this point reflected in the face of the cube, therefore located in the corresponding pyramid inside the cube, are the negatives of each other. (In this statement, we are assuming that the additive term in the energy, $E_{xy,xy}(000)$, is zero.) Thus all the energies inside the cube occur with the opposite sign at corresponding points outside the cube, proving the symmetry of the $N(E)$ curve to which we have just referred.

To prove this theorem, we wish to show that the roots of the secular equation are unchanged if, for instance, we change ζ to $\pi-\zeta$, and leave ξ and η unchanged. That is, we change the sign of $\cos\zeta$ but leave all other sines and cosines unchanged in our matrix components. We can now examine the matrix components in detail. Let us change the sign of $\cos\zeta$; change the sign of the energy E in the secular equation; and furthermore, change the functions xz and yz to $-xz$ and $-yz$, thereby changing the sign of all matrix components containing one of these functions, but leaving those components unchanged which contain neither or two of the functions. When we do this, we discover that the sign of every term in the secular equation has changed, so that its roots are the same as before. Since these roots now give the negative of the energy, on account of changing the sign of E, we have proved our theorem. One very useful result of this theorem is that it reduces by half the volume of the Brillouin zone in which we must compute the energies, in order to find $N(E)$.

One account of the reflection property just proved, we see that on the faces of the cube equal positive and negative energy levels must occur in pairs. That is, since there are five levels, one must be zero, and the others must be plus and minus two values. This suggests that the secular equation should factor into quadratics along these faces, and this is in fact the case. It does not follow from the vanishing of matrix components, but if we multiply out the whole secular equation, we find that it has a factor E, and the remaining fourth-order equation becomes a quadratic for E^2, leading to the properties described. We shall not write down this quadratic equation, but it is not hard to derive and it obviously leads to additional points in the Brillouin zone where we can solve the secular equation analytically, rather than having to use the digital computer.

The cube which we have introduced in Fig. 4 has a special significance. Suppose we considered the problem in which the atom at the center of our body-centered cubic structure was of one type, but its eight nearest neighbors were of another sort. We should then have a simple cubic structure with two atoms in the unit cell, the cube having a side of $2a$, in our present notation, and one atom being at the corner, the other at the center, of the unit cell. The cube in the Brillouin zone which we have been discussing is then just the Brillouin zone for this simple cubic structure. It is now easy to modify our discussion so as to take up this case of two unlike atoms. This case is of considerable importance. It is met in some alloys; for instance, in the ordered form of CuZn, though in that case we should be more interested in the $4s$ and $4p$ levels than in the $3d$. But in particular, it is probably met in chromium, on account of the antiferromagnetic nature of that element. It has been suggested by one of the writers[16] that electrons of one spin, in an antiferromagnetic substance, may see an alternating potential, having one value in atoms whose spin is preponderately in the same direction as the spin of the electron in question, but having a higher value in atoms of opposite spin. We know from the work of Shull and Wilkinson[17] that chromium appears to show a small antiferromagnetism, corresponding to about 0.4 Bohr magneton per atom. Thus we must conclude that the electrons feel such an alternating potential, and that as far as they are concerned the crystal is made of two unlike centers of force, forming the simple cubic structure with two unlike atoms per unit cell, of the type which we have just described. This situation is somewhat similar to that suggested by Ganzhorn (reference 10), though his discussion is so confused, as between energy band and Heitler-London approaches, that it is hard to understand the details of his argument.

Let us now ask how our problem is to be formulated in terms of the simple cubic structure containing two atoms per unit cell. We must set up ten Bloch functions, the first five corresponding to the five d orbitals on the atoms at the corners of the cubic unit cells, the second

[16] J. C. Slater, Phys. Rev. **82**, 538 (1951).
[17] C. G. Shull and M. F. Wilkinson, Revs. Modern. Phys. **25**, 100 (1953).

five corresponding to the five d orbitals on the atoms at the centers. The nearest neighbor of an atom of one type is now an atom of the other type. Hence since we are considering only interactions between nearest neighbors, the only nonvanishing matrix components of energy will be nondiagonal components between an atom of one type and an atom of the other type. Thus, for instance, the nondiagonal matrix component between an xy orbital on the atom of one type, and the xy on the atom of the other type, will be the expression (xy/xy) which we have already considered; and so on. For convenience in writing, let us label these matrix components H_{11}, H_{12}, $\cdots H_{15}$, H_{21}, $\cdots H_{55}$. There will be no nondiagonal matrix components between Bloch functions formed from two types of orbital on the same type of atom, for such nondiagonal matrix components would involve interactions between second-nearest neighbors, which we are disregarding. The diagonal matrix component of energy of one of the Bloch wave functions will be independent of $\mathbf{k}$ for the same reason. If the atoms of the two types are really identical, then the diagonal matrix components of atoms of either type will be the same; but, if they are not identical, these diagonal components will be different, and it is just the effect of this difference which we wish to investigate.

Let the diagonal energies of the two types of atoms be H_a and H_b. Then the secular equation can be written as given in Eq. (8). We can solve this equation, if we assume that we have already solved the corresponding five-by-five secular equation whose matrix components are $H_{11}\cdots H_{55}$. For that solution tells us how to find linear combinations of our five functions, which diagonalize this matrix,

$$\begin{vmatrix} H_a-E & 0 & 0 & 0 & 0 & H_{11} & H_{12} & H_{13} & H_{14} & H_{15} \\ 0 & H_a-E & 0 & 0 & 0 & H_{21} & H_{22} & H_{23} & H_{24} & H_{25} \\ 0 & 0 & H_a-E & 0 & 0 & H_{31} & H_{32} & H_{33} & H_{34} & H_{35} \\ 0 & 0 & 0 & H_a-E & 0 & H_{41} & H_{42} & H_{43} & H_{44} & H_{45} \\ 0 & 0 & 0 & 0 & H_a-E & H_{51} & H_{52} & H_{53} & H_{54} & H_{55} \\ H_{11} & H_{12} & H_{13} & H_{14} & H_{15} & H_b-E & 0 & 0 & 0 & 0 \\ H_{21} & H_{22} & H_{23} & H_{24} & H_{25} & 0 & H_b-E & 0 & 0 & 0 \\ H_{31} & H_{32} & H_{33} & H_{34} & H_{35} & 0 & 0 & H_b-E & 0 & 0 \\ H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & 0 & 0 & 0 & H_b-E & 0 \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & 0 & 0 & 0 & 0 & H_b-E \end{vmatrix} = 0. \tag{8}$$

Let the eigenvalues be E_1, E_2, $\cdots E_5$. Let us now apply this linear transformation to the five d functions on atom a, and the same transformation to the five on atom b. This will diagonalize the upper right corner and lower left corner of the matrix in (8). It will not interfere, however, with the other two corners of the matrix, on account of the degeneracy of the problem, the fact that all five functions have the same diagonal energy. When we have made this transformation, Eq. (8) will be transformed into

$$\begin{vmatrix} H_a-E & 0 & 0 & 0 & 0 & E_1 & 0 & 0 & 0 & 0 \\ 0 & H_a-E & 0 & 0 & 0 & 0 & E_2 & 0 & 0 & 0 \\ 0 & 0 & H_a-E & 0 & 0 & 0 & 0 & E_3 & 0 & 0 \\ 0 & 0 & 0 & H_a-E & 0 & 0 & 0 & 0 & E_4 & 0 \\ 0 & 0 & 0 & 0 & H_a-E & 0 & 0 & 0 & 0 & E_5 \\ E_1 & 0 & 0 & 0 & 0 & H_b-E & 0 & 0 & 0 & 0 \\ 0 & E_2 & 0 & 0 & 0 & 0 & H_b-E & 0 & 0 & 0 \\ 0 & 0 & E_3 & 0 & 0 & 0 & 0 & H_b-E & 0 & 0 \\ 0 & 0 & 0 & E_4 & 0 & 0 & 0 & 0 & H_b-E & 0 \\ 0 & 0 & 0 & 0 & E_5 & 0 & 0 & 0 & 0 & H_b-E \end{vmatrix} = 0. \tag{9}$$

We can now immediately solve Eq. (9). Let us rearrange the rows and columns so that first we have the first row and column, then the sixth, then the second, then the seventh, and so on. Then we see that it factors into a set of two-by-two secular equations, the first one being

$$\begin{vmatrix} H_a-E & E_1 \\ E_1 & H_b-E \end{vmatrix} = 0. \tag{10}$$

The solution of this is

$$E=\tfrac{1}{2}(H_a+H_b)\pm[E_1^2+\tfrac{1}{4}(H_a-H_b)^2]^{\frac{1}{2}}. \tag{11}$$

The rest of the two-by-two secular equations are handled in the same way. We shall now discuss first the case where $H_a=H_b=0$, so that the two atoms are really alike, but are handling the problem using a unit cell twice as large as necessary, so that there are two like atoms in the unit cell. In this case, the solutions are $E=\pm E_1$, $\pm E_2$, etc.

This is just what we should expect. We are using the cubic Brillouin zone, half as large as the correct Brillouin zone for the body-centered structure. We must describe, in this smaller zone, all the energy levels which should properly be found inside the larger zone. But we have

already found that the energy levels at any point of one of the pyramids extending outside the cube are the negatives of the values found at the point inside the cube which is the mirror image in a cube face. Alternatively, the energy levels at any point of one of the pyramids are the negatives of those at the point inside the cube to which this pyramid would be shifted by a translation of π along the x, y, or z axes. Thus the solution E_1, E_2, etc., of our secular equation give the energies which belong inside the cubic part of the Brillouin zone, and the solutions $-E_1$, $-E_2$, etc., are those corresponding to the pyramids outside the cube, in the body-centered cubic case. We see the way, then, in which our present description leads to just the same energy levels as before, for the case where the two atoms are really identical. This shows us that our requirement, which we stated earlier, that the unit cell be chosen as small as possible, in applying the LCAO method, is dictated by convenience, not by necessity. It leads to a smaller secular equation, but the final results are the same in either case.

Now let us consider the case where the atoms are really different, so that H_a is not equal to H_b. For convenience, we may take $H_b=-H_a$, so that the center of gravity of the band is not disturbed by making the atoms unlike. Then we see from Eq. (11) that the effect of a nonvanishing value of H_a-H_b is to push the two energies $\pm E_1$ apart, enough so that the higher one is always greater than $\frac{1}{2}(H_a-H_b)$, the lower one always less than the negative of this quantity. In other words, the effect of this perturbation is to make a real energy gap, holding throughout the Brillouin zone, such that no energy levels whatever will be found within a gap of width H_a-H_b. This of course has an effect over the bounding planes of the new cubic Brillouin zone. We have already seen that in the absence of our perturbation, there would always be one energy level equal to zero on these planes. With our doubled number of energy levels, this level now splits into two, one of positive and one of negative energy. But there is a similar situation wherever, inside the Brillouin zone, an energy level of the unperturbed problem is equal to zero. In Fig. 3, under the action of this perturbation, a gap where $N(E)$ is zero appears in the center of the figure, of width H_a-H_b. Of course, the area under the curve cannot be changed, and it is not hard to show that $N(E)$ will become infinite at the edges of the gap, and rapidly fall to approximately its original value at a distance from the gap of the order of the gap width, the added height of the curve near the gap being just enough to keep the original area. Such a gap has been considered by Ganzhorn (reference 10); but it is not clear from his argument whether he realizes that it exists only for unlike atoms, vanishing when the two atoms a and b become alike.

It is interesting next to ask what is the effect of this perturbation on the wave functions, with particular reference to the problem of the antiferromagnetism of chromium. There are two cases: first, for those energy levels far from the gap; secondly, for those close to the gap. For those far from the gap E_1, which plays the part of the nondiagonal matrix component of energy in Eq. (10), is large compared to H_a-H_b. That is, as far as the secular equation is concerned, we have almost a degenerate problem, and the solutions are almost exactly the sum or difference of the two unperturbed wave functions. The sum gives a solution involving equal amplitudes of disturbances on the atoms of both types, with phase relations just like those arising from the Bloch sums for the problem where the atoms are alike. That is, it reduces to our former solution, and the wave functions are unperturbed far from the gap. The difference is similar to this, except for the difference in phase, which is just what is needed to describe the former solution for ζ between $\pi/2$ and π, or in the pyramidal region of the Brillouin zone of Fig. 4. Close to the gap, however, E_1, the nondiagonal matrix component of energy in Eq. (10), is small compared to the diagonal component, and the solution consists largely of the one unperturbed solution or the other. The wave functions corresponding to energies below the gap, and near to it, consist of contributions coming almost entirely from the lower potential wells, while those corresponding to energies just above the gap consist of contributions from the atoms with higher potential wells.

We can now ask what is the application of this situation to the antiferromagnetic case, as found in chromium. We must assume that a gap of this type really exists in the d band of chromium, as a result of an alternating potential arising from the antiferromagnetism itself. This would give a lower band capable of accommodating five d electrons per atom. We must further assume that the s band, which will overlie the d band, is located at such a height that the Fermi level, coming when one electron per atom is located in the s band, lies within the gap in the d band. This would amount to a numerical coincidence, which would not be particularly improbable. If we had this situation, then in the ground state of chromium, we should have one electron in the s band, five in the lower d band. At the Fermi level, the electron density $N(E)$ would arise only from the s electron, and hence would be quite small, consistent with the known low electronic specific heat of chromium. The upper occupied d levels would correspond to a considerable concentration of electrons of one spin in sites of one type, electrons of the other spin in sites of the other type, thus leading to the type of antiferromagnetism observed. The lower occupied d levels would have no such alternation of spin, so that the net magnetic moment on each atomic site would be far less than five Bohr magnetons. The magnitude of the net magnetization would depend on the ratio of the gap width to the whole band width, and the observed small value would be consistent with a rather narrow gap width. All of these predictions

seem to be consistent with what is known about chromium.

This type of argument is not able to lead to a prediction as to the expected magnitude of the gap width or magnetic moment per atom. To do that, we should calculate the energy of the whole crystal, as a function of the magnitude of the antiferromagnetic moment, and find that value of antiferromagnetic moment which minimizes the energy. This would demand finding the cohesive energy very accurately as a function of magnetic moment, and the calculation of cohesive energy, involving a many-electron problem, is very much more difficult than a discussion of one-electron energies, which alone can be handled by the present simplified methods. It is surely not adequate merely to identify the cohesive energy of the crystal with the sum of the one-electron energies, which is all that can be found by the present methods. We can see qualitatively, however, by considering the one-electron energies, why we should expect a result such as is observed. If we start with a model in which there is no antiferromagnetism, there would be no gap. If we now introduce an antiferromagnetic moment and alternating potential, the gap will appear, and as a result the energies of the upper energy levels of the lower occupied d band will decrease. It certainly seems likely that this decrease of one-electron energy is the feature of the problem which stabilizes the antiferromagnetic state. On the other hand, if we used only our simple one-electron arguments, we should conclude that the one-electron energies, and hence the energy of the crystal, would continue to decrease as the gap width increased. This would suggest that the stable state was one with a complete antiferromagnetic effect, with a moment of five Bohr magnetons per atom, as was once suggested by Zener.[18] This is known not to occur by the results of Shull and Wilkinson (reference 17).

The reason for this is moderately clear, if we ask what happens to our prediction of energy bands as the antiferromagnetic moment gets large. In Eq. (11), this is the limit where $H_a - H_b$ is large compared to any of the E_1's, or where the effect of the alternating potential, arising from exchange, is large compared to the effect of band splitting on account of the interaction of neighboring atoms. Then Eq. (11) shows us that, though the two halves of the d band are split widely apart, each half-band is greatly narrowed (since in this limit the effect of E_1 is found only as a second-order correction to the energy). This narrowing is real and has a perfectly simple physical meaning. In this limit, all electrons of plus spin are found on atomic sites of one type, those of minus spin on sites of the other type. The energy bands are set up only from electrons of one spin, and as far as these are concerned, the electrons are found only on atoms forming a simple cubic lattice of side $2a$. These atoms are much further apart than the nearest neighbors in the nonmagnetic case, so that we expect practically no broadening of the bands. The energy difference between the two half-bands will be independent of interatomic distance, and the broadening of the bands, being very small, will hardly vary with interatomic distance.

We shall thus lose, in this limit, the principal feature undoubtedly contributing to the cohesive energy of chromium. The fact that the body-centered transition metals are so tightly bound unquestionably arises on account of the contribution of the d electrons to the binding energy.[19] On our interpretation, the lower half of the d band is occupied, consisting of those wave functions contributing most strongly to the bonding, while the upper half, containing the antibonding orbitals, is empty. This view implies that it is the change in average energy of the occupied d levels with internuclear distance which is the important feature in the binding. Clearly we lose this binding if the occupied d band shrinks to a very narrow width, as it does for very large antiferromagnetism. But a quantitative calculation of these effects demands a thorough study of the many-electron problem, as we have stated. In the limit of large antiferromagnetism, the energy difference between the two d bands, the occupied and the unoccupied ones, will come entirely from an intra-atomic exchange integral of a type which can only be properly treated by a study of the energy of the many-electron problem and of the configuration interaction involved in the correct behavior of the system as the interatomic distance increases to infinity. We do not feet that there is any simplified way to estimate these effects and must hope that at some future time a sufficiently exact treatment of the cohesive energy of chromium can be given so that a reliable estimate of the antiferromagnetic moment can be made. In the meantime, it seems quite legitimate to use the observed magnitude of this quantity to derive results, as we have done here, regarding the energy bands, and to use these results in a qualitative way to correlate information on such quantities as electronic specific heat.

If our views are correct, the case of chromium can be rather unique. It is known from the work of Shull and Wilkinson, quoted above, that molybdenum and tungsten, which have the same electronic structure as chromium, are not antiferromagnetic and that vanadium, lying before chromium in the periodic table, also is not antiferromagnetic. Molybdenum and tungsten would have to be explained by supposing that the coincidence by which the Fermi edge for the s electrons lay within the gap for d electrons did not occur in those elements. Thus the d band would be either more or less than half-filled (it does not seem to make much difference which), and we could not get a stabilizing effect

[18] C. Zener, Phys. Rev. **81**, 440 (1951).

[19] This is in agreement with the views of Pauling (reference 9). Pauling in that reference intimated that those who believe in the energy band theory of the d band did not accept this view but this is by no means the case.

by introducing the gap, since if the band were more than half-filled there would be approximately equal numbers of electrons increasing and decreasing their energy, and if it were less than half-filled the energies of the occupied levels would hardly be changed. According to the remarks made earlier, we feel that the tight binding of these elements arises from the fact that the d band is approximately half-filled and that it is strongly bonding; but the antiferromagnetic effect would have small effect on this, and we do not feel that the present methods are adapted to making a calculation of the cohesive energy. As for vanadium, with one less electron than chromium, the energy levels in the neighborhood of the middle of the d band are empty in any case, and there would be no stabilizing effect from introducing an antiferromagnetic moment, so that we expect a complete lack of antiferromagnetism, and a very close approximation to an ordinary energy band picture, for this element.

As we proceed in the other direction in the periodic table from chromium, we come to manganese, which has a different crystal structure and so cannot be treated by the present discussion. Its structure is unfortunately so complicated that it would be very difficult to handle it even by the present simplified method, since it has many atoms in the unit cell. One would guess, from the fact that it is known to be slightly antiferromagnetic, that proper treatment, if it could be given, would perhaps lead to a gap in this case too, somewhat similar to that in chromium, but separating the occupied from the unoccupied levels; but this is entirely speculative. The next element is iron, which of course is ferromagnetic in its body-centered form. Surely our arguments would not lead to antiferromagnetism for it; and one should be able to apply a rather straightforward energy-band argument to its ferromagnetism.

The only difference between this case and the standard one is that, if we ask what is probably the saturation magnetization to be expected, we can conclude that very likely it should be less than the value of approximately 2.6 Bohr magnetons which would be deduced by extrapolating the well-known curve of saturation magnetization of nickel and cobalt *versus* atomic number. The probable reason is that as enough electrons have their spin reversed so that electrons of plus spin will come somewhere near filling the d band, those of minus spin will be reduced to something like 2.5 per atom, so that their one-electron energies will lie near the minimum of the distribution curve of Fig. 3. In this case, it will require quite a large one-electron energy to reverse the spin of an electron, so that the magnetization will probably stop at this point, rather than continuing until there are quite five electrons per atom in the d band with plus spin. This could well lead to the observed moment of something like 2.2 Bohr magnetons. This argument, as we seen, is not very different from Pauling's.[9] However, it is based on an energy-band theory rather than an attempted Heitler-London explanation. Furthermore, unlike Pauling, we believe that the proper quantitative discussion of the problem would involve an accurate calculation of cohesive energy as a function of magnetization, just as in the case of chromium, and we are of the opinion that no simple and easy argument can lead to a reliable calculation of the saturation magnetization, such as Pauling attempted in his paper already quoted or in a more recent and entirely different discussion.[20]

In this section we have attempted to show that rather simple arguments can lead to a qualitative interpretation of some of the features of the body-centered metals, though those properties depending on cohesive energy are necessarily hard to treat. Our discussion of chromium has depended on the very simplified tight binding approximation involving only nearest neighbors. It is easy to see that if second nearest-neighbor interactions are included, the gap arising from the alterating potential can disappear. In such a case, in Eq. (8), the upper-left and lower-right corners of the secular determinant would no longer have the simple form assumed, and our arguments would entirely break down. Of course, we should still have energy gaps appearing at each point of the face of the cubic Brillouin zone of the simple cubic structure, but these gaps would no longer all be centered at the same energy, and they could well not result in a gap in the $N(E)$ curve as a whole. To maintain our explanation, then, we must assume that these terms are at least small. It does not seem absurd that this should be the case, so that our treatment really might represent a valid approximation to the facts. The d electrons have rather concentrated wave functions and second-nearest neighbor interactions would really be expected to be small. This would be in entire contrast to the $4s$ electrons, whose interactions surely are so great that no gap would appear in the $4s$ band. Only later calculations by more accurate methods can answer these questions properly.

VII. THE DIAMOND STRUCTURE

The diamond structure may most conveniently be described as a face-centered cubic structure, but with two atoms in the unit cell, rather than one. That is, we have atoms at the points $pa\mathbf{i}+qa\mathbf{j}+ra\mathbf{k}$, where p, q, r are integers, and $p+q+r$ is an even integer, just as in the face-centered structure; but also we have atoms at points identical with the first, but displaced by a vector $\frac{1}{2}a(\mathbf{i}+\mathbf{j}+\mathbf{k})$. The first lattice we shall denote by 1, the second by 2. We must now set up Bloch functions of s, p_x, p_y, p_z orbitals on each of the two types of atomic sites, so that we shall have eight Bloch sums. By the methods we have previously used, we can find the matrix components of energy between these Bloch sums. We shall denote these matrix components by such symbols as $(s/x)_{11}$, signifying a matrix component

[20] L. Pauling, Proc. Natl. Acad. Sci. **39**, 551 (1953).

TABLE V. Matrix components of energy for diamond structure.

$(s/s)_{11}=(s/s)_{22}$	$E_{s,s}(000)+4E_{s,s}(110)(\cos\xi\cos\eta+\cos\eta\cos\zeta+\cos\xi\cos\zeta)$
$(x/x)_{11}=(x/x)_{22}$	$E_{x,x}(000)+4E_{x,x}(110)(\cos\xi\cos\eta+\cos\xi\cos\zeta)+4E_{x,x}(011)\cos\eta\cos\zeta$
$(s/s)_{12}=(s/s)_{21}^*$	$4E_{s,s}(\frac{1}{2}\frac{1}{2}\frac{1}{2})(\cos\frac{1}{2}\xi\cos\frac{1}{2}\eta\cos\frac{1}{2}\zeta-i\sin\frac{1}{2}\xi\sin\frac{1}{2}\eta\sin\frac{1}{2}\zeta)$
$(s/x)_{12}=-(s/x)_{21}^*$	$4E_{s,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})(i\sin\frac{1}{2}\xi\cos\frac{1}{2}\eta\cos\frac{1}{2}\zeta-\cos\frac{1}{2}\xi\sin\frac{1}{2}\eta\sin\frac{1}{2}\zeta)$
$(s/x)_{11}=-(s/x)_{22}^*$	$-4E_{s,x}(011)\sin\xi\sin\eta+4iE_{s,x}(110)(\sin\xi\cos\eta+\sin\xi\cos\zeta)$
$(x/x)_{12}=(x/x)_{21}^*$	$4E_{x,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})(\cos\frac{1}{2}\xi\cos\frac{1}{2}\eta\cos\frac{1}{2}\zeta-i\sin\frac{1}{2}\xi\sin\frac{1}{2}\eta\sin\frac{1}{2}\zeta)$
$(x/y)_{12}=(x/y)_{21}^*=(y/x)_{12}$	$4E_{x,y}(\frac{1}{2}\frac{1}{2}\frac{1}{2})(i\cos\frac{1}{2}\xi\cos\frac{1}{2}\eta\sin\frac{1}{2}\zeta-\sin\frac{1}{2}\xi\sin\frac{1}{2}\eta\cos\frac{1}{2}\zeta)$
$(x/y)_{11}=(x/y)_{22}^*$	$-4E_{x,y}(110)\sin\xi\sin\eta-4iE_{x,y}(011)(\sin\xi\cos\zeta-\sin\eta\cos\zeta)$

between an s and a p_x Bloch sum on the sites 1, or $(s/x)_{12}$ for the component between an s function on site 1, a p_x on site 2. We shall include interactions between nearest and second-nearest neighbors. The nearest neighbors of a given atom are four forming a tetrahedral array around it, belonging to the other lattice. Thus the four nearest neighbors of the atom at the origin are located at the positions $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}-\frac{1}{2}-\frac{1}{2})$, $(-\frac{1}{2}\frac{1}{2}-\frac{1}{2})$, $(-\frac{1}{2}-\frac{1}{2}\frac{1}{2})$, all times a. The second-nearest neighbors of a given atom belong to the same lattice, and are the twelve neighbors of type $a(110)$. When we include these interactions, and use the same notation as previously, we find the matrix components given in Table V.

From the two-center approximation, we can derive values which the various integrals of Table V would have to have if this approximation were valid. We find the following results:

$$\begin{aligned}
&E_{s,s}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})=(ss\sigma)_1,\\
&E_{x,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})=\tfrac{1}{3}(pp\sigma)_1+\tfrac{2}{3}(pp\pi)_1,\\
&E_{x,y}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})=\tfrac{1}{3}(pp\sigma)_1-\tfrac{1}{3}(pp\pi)_1,\\
&E_{s,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})=3^{-\frac{1}{2}}(sp\sigma)_1,\\
&E_{s,s}(110)=(ss\sigma)_2,\\
&E_{x,x}(011)=(pp\pi)_2,\\
&E_{x,y}(110)=\tfrac{1}{2}(pp\sigma)_2-\tfrac{1}{2}(pp\pi)_2,\\
&E_{x,x}(110)=\tfrac{1}{2}(pp\sigma)_2+\tfrac{1}{2}(pp\pi)_2,\\
&E_{s,x}(110)=2^{-\frac{1}{2}}(sp\sigma)_2,\\
&E_{s,x}(011)=E_{x,y}(011)=0.
\end{aligned}\tag{12}$$

For the nearest-neighbor interactions, we see that we have four of the E integrals, and also four of the two-center integrals, so that either scheme gives the same degree of generality. For the second-nearest neighbors, we have seven E integrals, and only four two-center integrals, so that we lose disposable constants by using the two-center approximation.

We can now use the results of Table V to investigate propagation in special directions, in particular the 100 and 111 directions, in which the secular equations simplify enough so that we can get part of the solution analytically. First we shall consider the origin, the case $\mathbf{k}=0$. Here it is clear that the secular equation factors into four two-by-two secular equations, one each for the s, p_x, p_y, and p_z functions. Furthermore, the diagonal matrix components of energy of the two lattices are the same, so that the energies equal the diagonal component, plus or minus the nondiagonal component, and the wave functions are the sums and differences of the atomic orbital functions on the two lattices. The energies are the following: for the s states, $E_{s,s}(000)+12E_{s,s}(110)\pm4E_{s,s}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$; (+ sign, Γ_1 symmetry,[21] − sign, Γ_2') and for the p states, which of course are threefold degenerate, $E_{x,x}(000)+8E_{x,x}(110)+4E_{x,x}(011)\pm4E_{x,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. (+ sign, Γ_{15} symmetry, − sign, Γ_{25}').

Next let us consider the 100 direction, so that $\eta=\zeta=0$. We then find by inspection of Table V that there are no nondiagonal matrix components between any of the four Bloch functions formed from the s or p_x functions on either lattice, and those formed from the p_y or p_z functions on either lattice. We have thus, in the first place, a fourth-order secular equation for the s and p_x like functions. Let us denote the s function on the first lattice as function 1, the p_x on the first lattice as function 2, the s on the second lattice as function 3, the p_x on the second lattice as function 4. When we write out the secular equation, we find that certain terms are imaginary; but these can all be made real by multiplying the second and fourth columns by $-i$, the second and fourth rows by i, which has the effect of using imaginary coefficients for the x functions, real coefficients for the s functions. When we do this, the modified matrix components prove to be

$$\begin{aligned}
&H_{11}=H_{33}=E_{s,s}(000)+4E_{s,s}(110)+8E_{s,s}(110)\cos\xi,\\
&H_{22}=H_{44}=E_{x,x}(000)+4E_{x,x}(011)+8E_{x,x}(110)\cos\xi,\\
&H_{12}=H_{34}=8E_{s,x}(110)\sin\xi,\\
&H_{13}=4E_{s,s}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\cos\tfrac{1}{2}\xi,\\
&H_{14}=H_{23}=4E_{s,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\sin\tfrac{1}{2}\xi,\\
&H_{24}=4E_{x,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\cos\tfrac{1}{2}\xi.
\end{aligned}\tag{13}$$

The matrix in this form, since it is real, is symmetric about the diagonal.

The biquadratic equation determined from these matrix components can now be further factored into a

[21] For the meaning of symmetry symbols for diamond structure see C. Herring, J. Franklin Inst. **233**, 525 (1942).

form giving two quadratic equations. To do this, we need only assume that $S_3=S_1$, $S_4=S_2$ (Δ_1 symmetry), or $S_3=-S_1$, $S_4=-S_2$ (Δ_2' symmetry), where the S's are the coefficients of the functions. These quadratic equations are

$$\begin{vmatrix} H_{11}+H_{13}-E & H_{12}+H_{14} \\ H_{12}+H_{14} & H_{22}+H_{24}-E \end{vmatrix}=0, \tag{14}$$

and a similar equation in which the signs of H_{13}, H_{14}, and H_{24} are to be changed each time they appear. There is a very interesting feature regarding this quadratic. If we take Eq. (14), but use values of ζ between π and 2π, we find that it becomes identical with the other quadratic equation in the range from 0 to π. Specifically, if we find the solutions of (14) for a value of ξ between π and 2π, this solution equals the solution of the other quadratic for a value $2\pi-\xi$. The energy is a smooth function of ξ for this whole range, and this means that the two quadratics have common roots for $\xi=\pi$, which is the edge of the Brillouin zone in this direction. This is similar to a case of accidental degeneracy; the roots separate as we depart from this point in any direction in the momentum space. Another result is that at this special point, the energy, regarded as a function of ξ, approaches the edge of the Brillouin zone with a finite slope, instead of with a zero slope as we usually find.

At this special point $\xi=\pi$, since we have degeneracy, the wave functions are not uniquely determined. There is one way to set them up, however, which is interesting and informing. We can set up one wave function as a combination of the s functions on lattice 1 and the p_x on lattice 2, and the other as a combination of the s functions on lattice 2 and the p_x on lattice. 1. This situation seems very peculiar at first sight, but when we consider it we see that it is entirely reasonable. If $\xi=\pi$, the wavelength equals $2a$. Now the x component of the distance between an atom of the first lattice and one of the second is $a/2$, and hence a quarter wavelength. If we have, then, a wave function which goes to a maximum on the atoms of one lattice, represented by s atomic orbitals, this wave function must be passing through zero on the atoms of the other lattice, so that it must be made up on that lattice out of p_x orbitals, with a nodal plane through the atoms. There will be, of course, two degenerate states of this type (symmetry type X_1).

We have now considered the four nondegenerate levels formed from the s and p_x functions for propagation along the 100 direction, and the special degeneracy that occurs for $\xi=\pi$, at the edge of the Brillouin zone. Next let us consider the doubly degenerate levels formed from the p_y and p_z functions on the two lattices. Let us denote the p_y function on the first lattice as function 1, the p_z on the first lattice as function 2, the p_y on the second as function 3, the p_z on the second as function 4. Then the matrix components of energy between these four functions are

$$\begin{aligned} H_{11}=H_{22}=H_{33}=H_{44}&=E_{x,x}(000)+4E_{x,x}(110) \\ &\quad+[4E_{x,x}(110)+4E_{x,x}(011)]\cos\xi, \\ H_{13}=H_{24}&=4E_{x,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\cos\tfrac{1}{2}\xi, \\ H_{14}=H_{23}&=4iE_{x,y}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\sin\tfrac{1}{2}\xi, \\ H_{12}=H_{34}&=0. \end{aligned} \tag{15}$$

We find at once that the secular problem given by (15) can be solved by assuming either that the coefficients S_1 and S_2 of the first two functions are the same, and similarly that $S_3=S_4$, or by assuming that $S_2=-S_1$, $S_4=-S_3$. Either solution leads at once to a quadratic, and the energies are the same: $E=H_{11}\pm(H_{13}^2+H_{14}H_{14}^*)^{\frac{1}{2}}$. One of these solutions corresponds to a function of type p_y+p_z, and the other to a function of type p_y-p_z (Δ_5 symmetry). We verify at once that these solutions lead to the value already found at $k=0$. At the edge of the Brillouin zone, $\xi=\pi$, the solutions are $E_{x,x}(000)-4E_{x,x}(011)\pm4E_{x,y}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ (X_4 symmetry).

We have now finished our discussion of propagation along the 100 direction, and have found that in this direction, out of our eight energy levels, there are four single levels, which however join to form two doubly degenerate levels at the edge of the Brillouin zone, and two doubly degenerate levels. Next we may take up in a similar way the solutions in the 111 direction. We shall not give such a complete discussion of this case, though it is carried through in a similar way. We first set up matrix components of energy, using Table V, and setting $\xi=\eta=\zeta$. We may then take advantage of our knowledge of the symmetry properties of the solution along the trigonal 111 axis to factor the resulting secular equation. We know that all solutions must belong to one of the irreducible representations of the threefold rotation group. One of these representations is one-dimensional. This is a function which is unchanged when we make a rotation of 120° about the threefold axis; that is, when we cyclically permute the letters x, y, z. In other words, for this type of function, the p_x, p_y, p_z functions must have equal coefficients. We may set up such a solution by assuming that the s function on one lattice has one coefficient; the p_x, p_y, p_z functions on that lattice have a second coefficient, all equal; the s on the other lattice has a third coefficient; and the p_x, p_y, p_z on the second lattice have a fourth coefficient (Λ_1 symmetry). When we make these substitutions, we find that all the eight linear equations leading to the eight-by-eight secular equation reduce to four independent equations, leading thus to a fourth-order secular equation with four roots.

This fourth-order secular equation for the four nondegenerate functions cannot be further simplified, except at the boundary of the Brillouin zone, which in this direction comes for $\xi=\eta=\zeta=\pi/2$. For this propagation vector, as often at the midpoints of faces of Brillouin zones, we have a symmetry relation which

we lack otherwise: the wave function must be symmetric or antisymmetric with respect to inversion in the midpoint of the line joining the atom at the origin, and the atom at position $a/2$, $a/2$, $a/2$, which is displaced from it along the direction of propagation. If we assume that the coefficients of the atomic orbital on the two lattices are related in such a way that we have either this symmetry or antisymmetry, we find that we have an additional simplification of the secular equation. It breaks down into two quadratic equations, each of which can be solved by formula, though no additional degeneracies are introduced: the four roots are still distinct. The solutions of these quadratics is given in Eq. (16). The solutions with the upper sign (aside from the sign in front of the radical, which is $\pm$ in either case) refer to the symmetric (L_1 symmetry), those with the lower sign to the antisymmetric (L_2' symmetry), functions with respect to the inversion mentioned.

$$\begin{aligned}E=&\tfrac{1}{2}[E_{s,s}(000)+E_{x,x}(000)]\mp E_{s,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\\&\pm E_{x,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\mp 2E_{x,y}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})-4E_{x,y}(110)\\&\pm[\{\tfrac{1}{2}[E_{s,s}(000)-E_{x,x}(000)]\mp E_{s,s}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\\&\mp E_{x,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\pm 2E_{x,y}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})+4E_{x,y}(110)\}^2\\&+3\{\pm 2E_{s,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})+4E_{s,x}(011)\}^2]^{\frac{1}{2}}.\end{aligned}\quad(16)$$

In addition to these four nondegenerate solutions in the 111 direction, we also have twofold degenerate solutions. We can build up the wave functions by using only the p_x, p_y, and p_z functions, omitting the s, and using two arbitrary linear combinations of p_x, p_y, and p_z which are orthogonal to the sum $p_x+p_y+p_z$ which is used in the solution which we have already discussed. The method of making these linear combinations is arbitrary; we can, for instance, use the combination p_x-p_y, and $p_z-\frac{1}{2}(p_x+p_y)$. If we do this, we find a quadratic equation for the energy, identical in either case, leading to twofold degenerate energy values (Λ_3 symmetry). The roots of this quadratic, at the edge of the Brillouin zone, where $\xi=\eta=\zeta=\pi/2$, are

$$\begin{aligned}E=&E_{x,x}(000)+4E_{x,y}(110)\\&\pm[2E_{x,x}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})+2E_{x,y}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})]\end{aligned}\quad(17)$$

(+ sign L_3 symmetry, − sign L_3' symmetry).

We have now found formulas for the energies of all eight bands, at the center of the Brillouin zone, and at the edges of the zone along the 100 and 111 directions. Fortunately, for this problem we have good calculations of the energy bands of diamond at these points in the Brillouin zone, carried out by Herman[22] by the method of orthogonalized planes waves. We therefore can make a good quantitative application of our method. Herman's calculations provide enough information to determine uniquely the parameters listed in Table VI. These parameters are sufficient to fit all of Herman's calculations. The parameters $E_{s,x}(110)$ and $E_{x,y}(011)$ cannot be determined from Herman's calculations.

TABLE VI. Energy integrals (in Rydbergs) for diamond, from Herman's calculations.

$E_{s,s}(000)$	−1.37
$E_{x,x}(000)$	−0.378
$E_{s,s}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	−0.325
$E_{x,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.0563
$E_{x,y}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.277
$E_{s,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.122
$E_{s,s}(110)$	0.019
$E_{x,x}(011)$	−0.064
$E_{x,y}(110)$	−0.022
$E_{x,x}(110)$	−0.006
$E_{s,x}(011)$	0.119

It is interesting to take the parameters from Table VI, and see how accurately they fit in with the two-center approximation, and also to what extent they justify us in feeling that the integrals decrease as we go to more and more distant neighbors. From Eq. (12), we see that as far as the nearest neighbors are concerned, we can derive the integrals uniquely from the values of Table VI: we have $(ss\sigma)_1=-0.325$ rydbergs, $(pp\sigma)_1=0.610$, $(pp\pi)_1=-0.221$, $(sp\sigma)_1=0.211$. These values are reasonable. They all have the right signs for two-center integrals of the corresponding atomic orbitals, and the right order of magnitude: the largest interaction is $(pp\sigma)_1$, between two p orbitals pointing along the bond, while $(ss\sigma)_1$, the interaction of s orbitals, is considerably smaller, and the other interactions still smaller.

As far as second-nearest neighbors are concerned, we cannot derive two-center integrals uniquely from the values of Table VI, showing that the two-center approximation is not valid. We can, however, test its correctness and get orders of magnitude for the integrals. From Eq. (12), we know that $E_{s,s}(110)$, which equals 0.019, uniquely equals $(ss\sigma)_2$, and it is encouraging to find it so much smaller than $(ss\sigma)_1$. It is also interesting to find it of the opposite sign; this is in line with earlier remarks made in connection with the body-centered structure in the alkalies, where we pointed out that the s interaction between second-nearest neighbors might often be of the opposite sign to the nearest-neighbor interactions. The integral $E_{x,x}(011)$ should equal $(pp\pi)_2$, and its value -0.064 shows that this quantity is considerably smaller than $(pp\pi)_1$, so that again we verify that the second-nearest neighbor interaction is considerably smaller than the nearest-neighbor terms. But from Eq. (12), we see that we can also solve for $(pp\pi)_2$, as well as $(pp\sigma)_2$, from $E_{x,y}(110)$ and $E_{x,x}(110)$. When we do this, we find $(pp\sigma)_2=-0.028$, $(pp\pi)_2=0.016$. These are both small, in line with the fact that they represent second-nearest neighbor interactions, but the value of $(pp\pi)_2$ determined in this way does not agree at all with the value found from $E_{x,x}(011)$. This shows that the two-center approximation is not valid. This is shown even more by the

[22] F. Herman, Phys. Rev. **88**, 1210 (1952); F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953). We are indebted to Dr. Herman for supplying numerical data regarding his calculations.

considerable value of the integral $E_{s,x}(011)$, which is 0.119, the largest of the second-nearest neighbor terms. For this is an integral which would vanish entirely if we used the two-center approximation and can appear only because the tetrahedral surroundings of each atom in the diamond structure do not have the complete cubic symmetry. In spite of this failure of the two-center approximation, still it is possible to choose integrals of a two-center type which form a passable approximation to Herman's results; but since they cannot be chosen uniquely, but only as a compromise between various errors, it does not seem worth while pursuing this matter further.

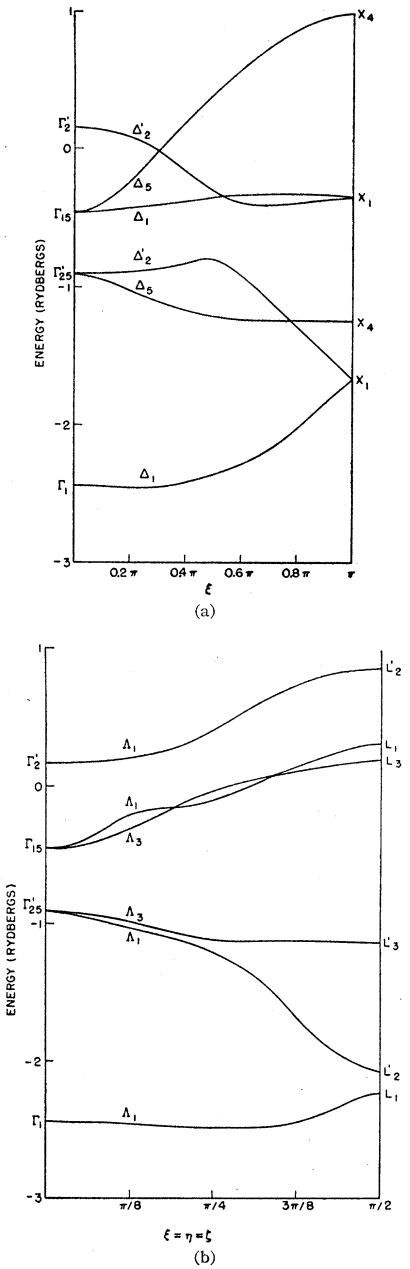


FIG. 5. Variation of energy with wave vector for diamond calculated using Herman's values at the center and boundaries of the zone. (a) 100 direction; (b) 111 direction; (see reference 21 for the meaning of the symmetry symbols).

It is interesting to use the integrals given in Table VI to calculate the energy at other points in the Brillouin zone than those symmetry points for which Herman has made calculations; this after all is the fundamental object of the present study. To do this, we need the two integrals $E_{s,x}(110)$ and $E_{x,y}(011)$ which cannot be determined from Herman's values. Lacking further information, we have arbitrarily chosen the values 0.021 and 0 for these two integrals; these are of the order of magnitude of what would be deduced from a two-center approximation. We have then used these values (which are of small importance in the final calculations) and the values of Table VI, and have calculated the curves of Fig. 5, giving the energy as a function of $\mathbf{k}$ along the 100 and 111 directions. This demanded solving the fourth-order secular equation in the 111 direction numerically. These curves of course reduce exactly to Herman's values at the edges of the zone. Herman has made interpolations in his paper, but our computed curves differ from his in some significant details, such as in the peculiar nature of the nondegenerate levels in the conduction band in the 100 direction, in which we have found accidental degeneracy to occur. Nevertheless, the general form of energy bands is similar to that deduced by Herman, giving of course the energy gap between the four lower occupied bands and the four higher empty bands. Similar calculations of course could be made for germanium, since Herman and Callaway[22] have made orthogonalized plane-wave calculations for this material too. However, we understand that they are improving the published numerical values for germanium, and feel it better to wait for the revised values before making numerical calculations. It is clear from Fig. 5 that we have the possibility, as has been frequently suggested, that the top of the valence band and bottom of the conduction band should not lie at $\mathbf{k}=0$. In our case, it appears that the top of the valence band would lie at six equivalent points along the 100 directions

It is interesting to compare these results for diamond with various other calculations which have been made for crystals of this type. The first calculation by the tight binding method is by Morita.[23] His calculations are like those of the present section, in most respects; his values for the various integrals are just like those of Table V. He does not express his integrals in terms of two-center integrals, though he calculates them by a two-center approximation. His results are known to come out very differently from the results of Herman and of the present study in that he finds the nondegenerate level in the conduction band lying below the threefold degenerate level at the center of the

[23] A. Morita, Sci. Rep. Tôhoku Univ. 33, 92 (1949).

Brillouin zone. This discrepancy is so serious that it has thrown considerable doubt on the use of the tight binding approximation for diamond. It appears to us likely, however, that this discrepancy is the result of some unfortunate numerical error in Morita's work. If we work back from the numerical values of his integrals, we find that some of the two-center integrals which we derive from them are surprisingly close to those which we have found from Herman's calculations; for instance, the values of $(ss\sigma)_1$ are almost exactly the same. However, Morita's value for $(pp\sigma)_1$ comes out to be 0.179 and for $(pp\pi)_1$, -0.349, as compared to our values of 0.61 and -0.22, respectively. We should certainly expect that $(pp\pi)$ would be smaller numerically than $(pp\sigma)$, since the $p\pi$ wave functions will overlap less than the $p\sigma$'s, so that it seems likely that Morita's calculations of these quantities are in error. This probably ties in with the fact that Morita finds that the s-like level is the lowest in the conduction band, which we have already mentioned. This is largely a result of the integrals which seem to be in error. We therefore suspect that a tight binding calculation made correctly by the method Morita used might well give a good account of the conduction as well as the valence band in diamond and germanium.

Another, and quite different, calculation of diamond by the tight binding approximation has been made by Hall.[24] Hall has used the equivalent orbitals which have been discussed by him, Lennard-Jones, and others. In the present case, he interprets these equivalent orbitals as being the symmetric, or bonding, combinations of directed orbitals on adjacent pairs of atoms. He sets up Bloch functions made from each such directed orbital, and solves the secular equation between these Bloch functions. Each bond in the unit cell then has a directed symmetric orbital along it. There are four such bonds in the unit cell (each of the two atoms in unit cell has four bonds attached to it, but each bond is shared between two atoms), so that we have a four-by-four secular equation, and we may expect in this way to get four states, and a description of the valence band, but not of the conduction band. If Hall had chosen to do so, he could also have set up a four-by-four secular equation involving combinations of antisymmetric or antibonding orbitals on each bond and have thus got a description of the conduction band.

The results which Hall obtains are not in very good agreement with experiment, or with the results which we have so far been discussing. In particular, he finds the levels at $\mathbf{k}=0$ to be split essentially as in Fig. 5, but the twofold degenerate level in the 100 or 110 direction proves to have an energy independent of $\mathbf{k}$, or to be a zero-width band, a peculiarity found also in the cellular treatment[25] of this problem, to which Hall's results have close resemblance. There is no physical reason to think that the band really has this property and this is a shortcoming of Hall's calculation.

It is useful to consider the relation of Hall's calculation to the one which we have been describing earlier in this section, since at first sight one might think them equivalent; Hall[26] clearly feels that his calculation has a fundamental significance which we do not believe that it possesses. In our discussion, we have already seen that the lower band is made up at $\mathbf{k}=0$ of symmetric combinations of s and p functions on the two lattices, and the upper band of antisymmetric combinations. From the s and p functions we can of course build up tetrahedral directed orbitals, so that for $\mathbf{k}=0$ we can build up the wave function properly for the valence band from the symmetric combinations of directed orbitals. In other words, Hall's method would give the same values for the energy at $\mathbf{k}=0$ that we have found by our more general treatment. However, as $\mathbf{k}$ departs from zero, we have seen that the correct combinations for the lower band are no longer the symmetric combinations of orbitals on the two lattices. By solving our eight-by-eight secular equation we have automatically found the correct combinations, and our results depart increasingly from Hall's as $\mathbf{k}$ increases. Of course, our energies will be lower than Hall's, since we are making a better approximation to a solution of the Schrödinger equation. In particular, the band which Hall finds to be of zero width is depressed in the more accurate calculation, as $\mathbf{k}$ increases.

If we had carried out the calculations by Hall's method of equivalent orbitals, using his calculation of the valence band by symmetric orbitals, and a similar calculation of the conduction band by antisymmetric orbitals, we should then find that there were nondiagonal matrix components of energy between the two bands, which vanished for $\mathbf{k}=0$, but increased with $\mathbf{k}$. By including these nondiagonal matrix components, we should find an eight-by-eight secular equation which would have the same roots as our secular equation, since the symmetric and antisymmetric equivalent orbitals are linear combinations of the s and p orbitals on the two lattices which we have used as our starting point. It might be convenient to use Hall's procedure, as amplified in this way, to make an actual calculation. For by using Hall's equivalent orbitals, but disregarding the nondiagonal matrix components of energy between valence and conduction band, we find an energy gap between these two bands. Introduction of the nondiagonal matrix components will then have the effect of pushing certain levels apart, push the levels of the valence band down and those of the conduction band up. Since these levels are not degenerate, even in the absence of nondiagonal matrix components, it is possible that a second-order perturbation calculation would be adequate for considering the effect of these nondiagonal matrix components of energy, thereby making possible

[24] G. G. Hall, Phil. Mag. **43**, 338 (1952).
[25] G. E. Kimball, J. Chem. Phys. **3**, 560 (1935).
[26] G. G. Hall, Phys. Rev. **90**, 317 (1953).

an approximation to the exact solution of the correct secular equation. Since this secular equation is not very difficult to handle anyway, however, it seems better to use it directly, and in this case there is no advantage in Hall's procedure. In any case, Hall's calculation for the valence band alone is clearly a poorer approximation than the one considered in the present section.

Before leaving the problem of the diamond structure, we should say a few words about the compounds, such as InSb, crystallizing in the zincblende structure. This is the case in which the two interpenetrating face-centered lattices are no longer equivalent. For instance, the atom at the origin might be In, that at the point $a/2$, $a/2$, $a/2$ might be Sb. We shall lose, then, any results depending on symmetry or antisymmetry between these two lattices, but otherwise the results of the calculations will be essentially unchanged. We can introduce the modification by using one set of diagonal energy values, $E_{s,s}(000)$ and $E_{x,x}(000)$, for the atoms of one type, another set for the atoms of the other type, much as we did in our earlier treatment of the body-centered cubic structure when modified to have unlike atoms at the centers and corners of the cube. Here, however, in contrast to that case, the treatment we have already given has the correct unit cell, holding two atoms, even if the atoms are unlike.

We shall still have eight bands arising from our s and p orbitals on the two lattices. At $\mathbf{k}=0$, we shall still have two nondegenerate bands of s-like type and two threefold degenerate bands of p-like type, and the other consequences of symmetry will mostly be the same as for diamond. One exception is the degeneracy between the two bands formed from s and p_x functions, at the point $\xi=\pi$, $\eta=\zeta=0$. We remember that the wave functions for one of these bands consisted of s orbitals on one lattice, p_x on the other, and for the other band the role of the two lattices was interchanged. If the two lattices are no longer equivalent, it is quite clear that these two wave functions will have different energies. This is one of the few qualitative differences between the energy band structures in the two cases, however. The general situation, according to which we have a lower set of bands capable of holding eight electrons per unit cell, and an upper set of bands holding the same number, will still hold, so that since we have just eight electrons per cell in any of these crystals, we shall in every case fill the valence band, leaving the conduction band empty, and shall have an insulator or semiconductor as with the diamond group of elements. The situation is quite different from what we had in the body-centered cubic case, where making the two types of atoms unlike introduced an energy gap which was not present previously. Here, we have an energy gap anyway, on account of the lack of equivalence of the two atoms in unit cell even in diamond, and this gap can be modified in width by making the two atoms unlike, but no new gaps are introduced.

There can be a good deal of qualitative difference between the wave functions for diamond and for a crystal forming the zincblende structure, however, and in some cases there can be reversals of the order of the bands, which we can understand from general qualitative arguments. To have a specific example, let us take InSb, formed from the elements on the two sides of Sn. The potential wells about the Sb atoms will be deeper than around the In atoms, and if the atoms were electrically neutral, there would be three outer electrons around each In atom, five around each Sb atom. We cannot of course guarantee this neutrality; the chemists often speculate in such cases whether the crystal is formed from neutral atoms or ions, and in a case like this we could even speculate as to which sign the charges on the ions were. We could take extreme points of view. We could say that the crystal was completely ionic, the In forming a positive ion with triple charge, losing its three electrons, which would go onto the Sb to form a closed shell of eight electrons. Or we could take a quite opposite point of view, supposing that the In took up an extra electron, forming a negative ion, so as to have four outer electrons like a tetravalent atom, and that similarly the Sb lost an electron, again so as to have four outer electrons. There is no good reason for thinking that either of these extreme points of view has any close relation to the actual facts of the situation. We can, however, from our general approach, get a much sounder view of the charge distribution in this crystal, which points the way to an interpretation of many other crystals in which there is an ambiguity between different points of view.

We remember that our determination of one-electron wave functions is one part of a self-consistent field calculation, and that the final decision as to how much charge lies on each type of atom is one that is to be made by carrying through a self-consistent problem. Let us assume that at a given stage of this calculation we are given a periodic potential and are trying to find the wave functions, that is, we are solving our eight-by-eight secular equations. When we have done this, for each $\mathbf{k}$ value, we find the total charge density of electrons distributed in the lower or valence band, leaving the conduction band empty, and we use this charge density in computing a potential to use in the next stage of the self-consistent calculation. If, for instance, as seems highly likely, the final result of the self-consistent method should be that each of the atoms is approximately electrically neutral in the crystal, then the charge distribution corresponding to the valence band would actually correspond to three electrons per atom in the In atoms, five per atom in the Sb atoms. We shall now show that such a result is altogether probable.

For any particular $\mathbf{k}$ value, we have to determine the eight wave functions corresponding to the various energy bands. As a very simple example, let us consider $\mathbf{k}=0$; the other $\mathbf{k}$ values, though more complicated, will not be different in principle. We know that at $\mathbf{k}=0$,

our problem factors on account of symmetry, so that we find two s-like states, two p_x like, two p_y like, two p_z like. Each of these is handled in a similar way. In the s-like states, for instance, we know that if we are dealing with the diamond structure we have a quadratic secular equation in which the two diagonal matrix components are equal, since the diagonal energies will be the same whether the atomic orbitals are on the one face-centered lattice or on the other. The two linear combinations, then, will be the sum and difference of the unperturbed functions, so that in either case the resulting charge density will have equal values on the atoms of both lattices.

With the InSb, however, this secular problem for the two s-like states no longer has this property of degeneracy. The diagonal energy of an s orbital on an In atom will be considerably higher than that of an s orbital on an Sb atom, since the Sb has a deeper potential well. The nondiagonal matrix component between the two states may well be much as in the diamond case, but the perturbation will have a very different effect, on account of the lack of degeneracy. It will separate the energies of the two states somewhat. But the wave function of the lower of the two resulting states will be a mixture of a large fraction of that unperturbed wave function whose diagonal energy is lower (that is, an s function on the Sb) and a much smaller fraction of that function whose diagonal energy is higher (that is, an s function on the In). Conversely, for the upper state, we shall have a combination in which most of the charge density is on the In, a lesser amount on the Sb. Only the lower state is filled, however, so that we are left with more charge on the Sb, less on the In. The same situation will hold for the p states with $\mathbf{k}=0$, and in fact for every $\mathbf{k}$ value; so that it is quite certain that the charge distribution corresponding to the electrons in the valence band will have a good deal more charge on the Sb than on the In. It is entirely possible, as has been suggested above, that the final result would come out with almost complete electrical neutrality, about five-eighths of the charge being on the Sb, three-eights on the In. Certainly we should have something much closer to this than to either of the extreme ionic states which we discussed earlier.

The final type of wave function, and charge distribution, which we have found in this case can throw a good deal of light on the question of ionic or nonionic crystals in general. We have different amounts of charge on the atoms of the two types; we do not even have to have integral charges, on the average, on each type of atom. And yet our total charge distribution consists of the entirely filled valence bands, entirely empty conduction bands, just as in diamond. The total charge density has the same sort of spherical symmetry about each atom (modified by overlap with the neighboring atoms) which we should have in diamond, and which we should find from filling s, p_x, p_y, p_z bands. The interesting feature is the way in which, by making up our energy band functions as linear combinations of atomic orbitals, we can simultaneously achieve these two results of variable total charge, and yet the characteristics of a closed shell of electrons. Our wave function for the crystal as a whole is set up as a single determinant, since we have only filled energy bands. We have all the advantages which we meet in the molecular orbital model of molecules, including the way in which that model leads naturally to the interpretation of the polarity of molecules, and the possibility of having fractional amounts of electronic charge on each atom. We must now forget that we have the drawbacks of the molecular orbital model as well; we could get better results if we took a certain amount of configuration interaction into account. Thus, in particular, if we wished to give a proper account of the energy bands in our crystals of the diamond or zincblende type as a function of internuclear separation, we should have to consider a configuration interaction, of a practically impossible degree of difficulty, between the single determinantal state we have been describing, and other configurations in which varying numbers of electrons are excited to the antibonding energy bands. Even in the absence of such configuration interaction, however, our energy band method gives a good general account of the situation.

From the discussion which we have given of the zincblende structure, we can see that in certain cases the order of energy levels may be different in it from what it is in the diamond structure, as shown in Fig. 5. In Fig. 5, we saw that the lowest state of the valence band and the highest of the conduction band were of the s-like type, while the top of the valence band and the bottom of the conduction band were of the p-like type. The reason for this arrangement is seen in the magnitudes of the various matrix components of energy. Thus we found that the energies of the s states, for $\mathbf{k}=0$, were $E_{s,s}(000)+12E_{s,s}(110)\pm 4E_{s,s}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=-1.14 \pm 1.30$ rydbergs, and for the p states we had $E_{x,x}(000) +8E_{x,x}(110)+4E_{x,x}(011)\pm 4E_{x,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=-0.68\pm 0.23$. The smaller nondiagonal matrix component for the p states is responsible for the fact that these two states are not widely separated. On the other hand, as we go to a compound like InSb, where we shall no longer have a degenerate problem, the diagonal s and p components on the Sb sites will lie considerably below those on the In sites. Furthermore, we may expect that the diagonal energy of the s state, on either site, will lie considerably below that of the p state on the same site, on account of the general rule that s states lie lower than p states; this is consistent with our value of -1.14 for the s energy, -0.68 for the p, above. Hence as far as diagonal energies are concerned, the lowest level of all will be the s Sb orbital, next the p Sb orbitals, next the s In orbital, with the p In orbitals highest. If the orbitals on the two sites are considerably separated in energy, the nondiagonal matrix components,

even if they are still of the same general magnitude as those given above, still will not produce nearly as much displacement of the energy as in the diamond case, since they will produce only a second-order change in energy rather than a first-order change in a nondegenerate problem. Consequently, it may well be that they will not invert the order of the s and p states in the conduction band, but will rather leave the lowest state in the conduction band an s-like rather than a p-like state. This would explain an observation of Pearson and Tanenbaum,[27] according to which the conduction band of InSb appears to be nondegenerate at its lowest energy value.

Many of the properties of the crystals like InSb, then, seem to be interpreted easily in terms of our approximate tight binding method. In fact, the diamond structure appears to be the one in which, at the moment, we are able to make the best use of it, partly on account of the results of Herman by means of the orthogonalized plane-wave method. This, in particular, is the only case in which we are at present able to evaluate the effect of second-nearest neighbors, by comparison of our LCAO method with values calculated by other methods; and it is particularly gratifying that the contributions of second-nearest neighbors appear to be a good deal less than those of nearest neighbors, lending support to our hypothesis that we really are dealing with a series of terms which decrease rapidly as we go to more distant neighbors. If this turns out to be a general situation, it really may be that the method possesses a rather fundamental significance and need not be regarded merely as a convenient interpolation method.

APPENDIX

We wish to show in this appendix that the transformation properties of the Löwdin functions ψ_n are the same as those of the nonorthogonal functions ϕ_n from which they arise. Let us suppose that under some operation O, of the group of the crystal, the transformation properties of the nonorthogonal functions are given by

$$O\phi_n=\sum(m)\phi_m\Gamma(O)_{mn}. \tag{A1}$$

Here $\Gamma(O)_{mn}$ is a unitary matrix ($[\Gamma(O)^{-1}]_{mn}=\Gamma(O)^*_{nm}$). We must show that the transformation properties of the ψ_n's are the same; that is,

$$O\psi_n=\sum(m)\psi_m\Gamma(O)_{mn}. \tag{A2}$$

[27] G. L. Pearson and M. Tanenbaum, Phys. Rev. **90**, 153 (1953).

The relation between the ψ_n's and the ϕ_n's is given by Löwdin,[12]

$$\psi_n=\sum(m)\phi_m(\Delta^{-\frac{1}{2}})_{mn}. \tag{A3}$$

Here $(\Delta^{-\frac{1}{2}})_{mn}$ is the mnth matrix element of the reciprocal of the square root of the overlap matrix Δ_{mn},

$$\Delta_{mn}=\int\phi_m^*\phi_n d\tau. \tag{A4}$$

[The same orbitals are included in this summation in Eq. (A3) as in the summations expressing the transformation properties of the ϕ_n's.] Applying the operator O to Eq. (A3) we see that

$$O\psi_n=\sum(l)\sum(m)\phi_l\Gamma(O)_{lm}(\Delta^{-\frac{1}{2}})_{mn}. \tag{A5}$$

In order to prove our theorem, we must show that the right-hand sides of Eq. (A5) and Eq. (A2) are equal. Explicitly, we must prove the equality

$$\sum(l)\sum(m)\phi_l(\Delta^{-\frac{1}{2}})_{lm}\Gamma(O)_{mn}=\sum(l)\sum(m)\phi_l\Gamma(O)_{lm}(\Delta^{-\frac{1}{2}})_{mn}. \tag{A6}$$

In Eq. (A6), the left-hand side was obtained from Eq. (A2) through the use of Eq. (A5). To establish the validity of Eq. (A6), it suffices to show that

$$\sum(m)(\Delta^{-\frac{1}{2}})_{lm}\Gamma(O)_{mn}=\sum(m)\Gamma(O)_{lm}(\Delta^{-\frac{1}{2}})_{mn}. \tag{A7}$$

Multiplying both sides by $[\Gamma(O)^{-1}]_{ql}$ and summing over l yields the result

$$\begin{aligned}\sum(l)\sum(m)[\Gamma(O)^{-1}]_{ql}(\Delta^{-\frac{1}{2}})_{lm}\Gamma(O)_{mn}&=\sum(l)\sum(m)[\Gamma(O)^{-1}]_{ql}\Gamma(O)_{lm}(\Delta^{-\frac{1}{2}})_{mn}\\&=\sum(l)\sum(m)\delta_{qm}(\Delta^{-\frac{1}{2}})_{mn}=(\Delta^{-\frac{1}{2}})_{qn}.\end{aligned} \tag{A8}$$

In other words, we have established our theorem if we can show that the reciprocal of the square root of the overlap matrix is invariant with respect to the unitary matrix $\Gamma(O)_{mn}$. Under certain very general conditions, this is true if the overlap matrix itself is invariant with respect to the unitary transformation. This, however, is easily seen to be true since

$$\begin{aligned}\Delta_{mn}&=\int\phi_m^*\phi_n d\tau=\int O\phi_m^* O\phi_n d\tau\\&=\sum(q)\sum(l)\Gamma(O)_{qm}^*\Gamma(O)_{ln}\int\phi_q^*\phi_l d\tau\\&=\sum(q)\sum(l)[\Gamma(O)^{-1}]_{mq}\Delta_{ql}\Gamma(O)_{ln}.\end{aligned} \tag{A9}$$

Thus we have established our theorem.