Space Groups and Wave-Function Symmetry in Crystals

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The procedure for setting up projection operators to derive symmetrized wave functions in crystals is discussed. This includes a description of the projection operator method, discussion of irreducible representations, basis functions, and the multiplication table for space groups, and the application of these methods to setting up symmetrized plane waves, and symmetrized linear combinations of atomic orbitals, for use with the OPW and APW methods of approximating to electronic wave functions in crystals.

1. PROJECTION OPERATORS AND SYMMMETRIZED PLANE WAVES

The group theory is practically essential for the discussion of the symmetry of wave functions in crystals, and yet it is not familiar enough to some of the workers in the field for them to use it with facility. The standard treatments of the problem[1] are rather abstract, and demand a good deal of knowledge of group theory. In this paper we outline a treatment of the problem which is direct, and requires a minimum of mathematical technique. This treatment is presented in detail in the text on "Quantum Theory of Molecules and Solids" which the author is in the process of writing.[2] The present paper is intended to introduce the method in a more analytical and consecutive manner than is used in that text, which proceeds mostly by the discussion of special cases, for pedagogic reasons.

Most treatments of the approximate solution of Schrödinger's equation for an electron moving in the type of periodic potential met in a crystal expand the wave function as a sum of functions each of which has the same type of symmetry as a plane wave. In the free-electron method these are plane waves themselves; but other methods use Bloch sums, orthogonalized plane waves, augmented plane waves, or other types of functions having the same symmetry behavior. It is well known that the Hamiltonian has no nondiagonal matrix elements between functions of different symmetry type. Hence if we can make linear combinations of plane waves, or of functions with equivalent symmetry properties, having the suitable symmetry type, we can build up a solution of Schrödinger's equation by combining such symmetrized functions, called symmetrized plane waves if we are dealing with the plane-wave case, with which we shall start our discussion. The main use of group theory in connection with the periodic potential problem is to show how to set up these symmetrized functions, and to define the types of symmetry which they can have. This involves one in the theory of irreducible representations of groups of operations.

The groups of operations with which we are concerned in crystal problems are the space groups, consisting of translations through whole numbers of lattice spacings, plus rotations and reflections, sometimes combined with additional so-called nonprimitive translations, all of which have the net result that if we apply such an operation to the crystal, it is indistinguishable from its original form. Technically, such operations commute with the Hamiltonian. When we have such groups of operations commuting with the Hamiltonian, it can be shown that any solution of Schrödinger's equation must have the symmetry of one of the basis functions for one of the irreducible representations of the space group. Our problem, then, is to investigate these irreducible representations and their symmetry properties.

The analytical statement of these facts is the following. Let R_k be one of the operators of the group. Let $u_b{}^P$ be the bth basis function for the Pth irreducible representation of the space group. Then a new function is generated by letting R_k operate on $u_b{}^P$; it is denoted as $R_k u_b{}^P$. The statement that $u_b{}^P$ forms a basis function for a representation means that the function $R_k u_b{}^P$ can be written as a linear combination

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[1] F. Seitz, Z. Krist. **88**, 433 (1934); **90**, 289 (1935); **91**, 336 (1935); **94**, 100 (1936). G. F. Koster, "Space Groups and their Representations," Solid State Phys. **5**, 173 (1957). G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (Technology Press, Cambridge, Massachusetts, 1963).

[2] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York), Vol. 1; Vol. 2 (to be published in 1965). Considerable material which will appear in Vol. 2 bearing on the present subject has appeared in various Quarterly Progress Reports of the Solid-State and Molecular Theory Group, MIT (unpublished). The following are by J. C. Slater: "Symmetry Properties in the Space Groups $D_{6h}{}^4$ and $C_{6v}{}^4$," 46, 67 (15 October 1962); "Symmetry Properties in the Space Groups $O_h{}^5(Fm3m)$, $O_h{}^7(Fd3m)$, and $T^2{}_d(F\bar{4}3m)$," 47, 4 (15 January 1963); "Symmetry Properties in the Space Groups $O_h{}^9(Im3m)$, $O_h{}^{10}(Ia3d)$, and $T_h{}^7(Ia3)$," 47, 27 (15 January 1963); "Symmetry Properties in the Space Groups $O_h{}^1(Pm3m)$ and $T_h{}^6(Pa3)$," 47, 54 (15 January 1963); "Symmetry Properties in the Space Group $D_{4h}{}^{14}(P4_2/mnm)$, 48, 15 (15 April 1963); "Symmetry Properties in the Space Groups $C_{3i}{}^2(R\bar{3})$, $D_3{}^7(R32)$, $D_{3d}{}^5(R\bar{3}m)$, and $D_{3d}{}^6(R3c)$," 48, 29 (15 April 1963); "Basis Functions for the Double Point Groups," 49, 4 (15 July 1963). Similar methods were also used and explained in the paper J. C. Slater, G. F. Koster, and J. H. Wood, Phys. Rev. **126**, 1307 (1962). Further contributions dealing with related topics in the Quarterly Progress Reports are the following: E. R. Keown, "The Slater Representation Theory," 51, 43 (15 January 1964); L. F. Mattheiss, "Symmetry Properties in the Space Group $O_h{}^3(Pm3n)$," 51, 54 (15 January 1964).

of the functions u_a^P, where a goes over the total set of basis functions. The number of basis functions is known as the order or dimensionality of the representation. The statement we have just made is expressed in the equation

$$R_k u_b^P = \sum(a) \Gamma_P(R_k)_{ab} u_a^P, \tag{1}$$

where the quantities $\Gamma_P(R_k)_{ab}$ are the coefficients of the linear combination. They form matrices with a number of rows and columns equal to the dimensionality of the representation (the rows and columns being denoted by a and b), and are said to form a representation of the group. This means that if we have three operators R_i, R_j, R_k of the group, such that $R_iR_j=R_k$, then the matrix elements satisfy the relation

$$\sum(c) \Gamma_P(R_i)_{ac} \Gamma_P(R_j)_{cb} = \Gamma_P(R_k)_{ab} \tag{2}$$

or the matrices multiply, by ordinary matrix multiplication, the same way that the operators multiply. It can be shown that if the u's are solutions of Schrödinger's equation, the various functions corresponding to different values of their subscript a, but the same P, are degenerate with each other. Hence we are led in this way to the analog of atomic multiplets, the dimensionality of the representation giving the number of degenerate states in the multiplet.

If one knows the representation matrices $\Gamma_P(R_k)_{ab}$, there is then a very powerful theorem which allows us to start with any arbitrary function and produce from it a function of the symmetry of one of the basis functions for one of the irreducible representations of the group. This is the method of projection operators. The theorem is the following. We start with an arbitrary function ψ, operate on it with each of the operators R_i of the group, and then form the linear combinations of the resulting functions defined as follows:

$$f_{bd}^P = \sum(R_i) \Gamma_P(R_i)_{bd}^* R_i\psi, \tag{3}$$

where the asterisk denotes the complex conjugate. The theorem states that f_{bd}^P so defined forms a basis function u_b^P for the pth irreducible representation, so that it satisfies Eq. (1). That is, we have

$$R_k \sum(R_i) \Gamma_P(R_i)_{bd}^* R_i\psi = \sum(a) \Gamma_P(R_k)_{ab} \sum(R_s) \Gamma_P(R_s)_{ad}^* R_s\psi. \tag{4}$$

The proof of this equation is given, for instance, in Ref. 2, Vol. 1, Eqs. (A12-26)–(A12-34). It holds no matter which value d has.

In order then to form symmetrized plane waves, we need two things. We first need the matrix elements $\Gamma_P(R_i)_{bd}$ for the group in question. Secondly, we need to know $R_i\psi$, where ψ is a plane wave. We shall show in the next section that $R_i\psi$ is another plane wave, with a wave vector having a different direction from that of ψ, though the same magnitude, so that the sum set up in Eq. (3) is a linear combination of plane waves, forming the symmetrized plane wave in question. In order to verify the correctness of an irreducible representation, we may want to substitute into Eq. (4). On the left of this equation we have a linear combination of quantities $R_kR_i\psi$, while on the right we have a linear combination of quantities $R_s\psi$. To verify the correctness of this equation, we must then be able to find the effect of two successive operations operating on a plane wave. It is a fundamental property of groups that such a succession of operations, R_kR_i, must be one of the operations of the group, and the statement of which operation it equals is called the multiplication table of the group. Consequently we wish to find the multiplication table. In the next sections we shall go on to discuss the meaning of space groups, their multiplication tables, and their effects on a plane wave, so as to provide the mathematical foundation for using the method of projection operators to set up symmetrized plane waves.

2. SPACE GROUPS AND THEIR MULTIPLICATION TABLES

An operation of a space group consists of the combination of a translation $\mathbf{T}_n=n_1\mathbf{t}_1+n_2\mathbf{t}_2+n_3\mathbf{t}_3$, where n_1, n_2, n_3 are integers, and $\mathbf{t}_1$, $\mathbf{t}_2$, $\mathbf{t}_3$ are the primitive translation vectors of the Bravais lattice in question; of a rotation, or rotation plus reflection, of the point group characteristic of the crystal class; and, for a nonsymmorphic space group, of a nonprimitive translation characteristic of the particular space group we are dealing with, different for different operations of the point group, but independent of which translation $\mathbf{T}_n$ we are dealing with. It is not generally realized that these rather vague and general statements can be interpreted to lead to various related, but quite different, detailed formulations of the problem. The situation can be greatly clarified if we understand precisely what we mean and choose the interpretation in a particular way.

We shall understand the operations to operate on a function, like a Schrödinger wave function, just as the Hamiltonian operator and other operators of wave mechanics do. We shall denote an operator of a space group by a symbol $\{R_i \mid \mathbf{T}_n\}$, where R_i is one of the operations of the point group, $\mathbf{T}_n$ one of the translations. Then we shall postulate that

$$\{R_i \mid \mathbf{T}_n\}\psi(x_1, x_2, x_3) = \psi(x_1', x_2', x_3'), \tag{5}$$

where x_1, x_2, x_3 are the rectangular coordinates x, y, z of a point, so that $\psi(x_1, x_2, x_3)$ is a function of the nature of a wave function for a one-particle problem. Here we are to understand that the quantities x_p' are defined by the linear equations

$$x_p' = \sum(q) \alpha_{pq}{}^i x_q + \tau_p{}^i + (\mathbf{T}_n)_p, \tag{6}$$

where p, q run from 1 to 3. In this expression, $\alpha_{pq}{}^{i}$ are the matrix components describing the rotation, or rotation plus reflection, associated with the operation R_i of the point group. These components satisfy the relation

$$(\alpha^i)_{qp}{}^{-1}=\alpha_{pq}{}^{i}, \tag{7}$$

where $(\alpha^i)^{-1}$ is the inverse or reciprocal matrix to α^i, so that we have the orthogonality relations

$$\sum(s)\,(\alpha^i)_{rs}{}^{-1}\alpha_{st}{}^{i}=\sum(s)\,\alpha_{sr}{}^{i}\alpha_{st}{}^{i}=\delta_{rt}$$

and

$$\sum(s)\,\alpha_{rs}{}^{i}(\alpha^i)_{st}{}^{-1}=\sum(s)\,\alpha_{rs}{}^{i}\alpha_{ts}{}^{i}=\delta_{rt}. \tag{8}$$

If the operation of the point group is a rotation, the determinant of the α's equals 1; if it is a rotation plus a reflection the determinant is -1. The quantity $\tau_p{}^{i}$ in Eq. (6) is the p component of the nonprimitive translation $\boldsymbol{\tau}^i$ associated with the operation R_i of the point group, in the space group in question, and $(\mathbf{T}_n)_p$ is the p component of the lattice translation.

If we consider the point group only [that is, if we set the translations $\boldsymbol{\tau}^i$ and $\mathbf{T}_n$ in Eq. (6) equal to zero], then Eq. (6) is very close to an equation describing a representation of the group. We can get an exact representation by rewriting $\alpha_{pq}{}^{i}$ in terms of its universe by Eq. (7). Then we have

$$R_i x_p=x_p{}'=\sum(q)\,(\alpha^i)_{qp}{}^{-1}x_q. \tag{9}$$

This equation is exactly analogous to Eq. (1), with the x_p's forming the basis functions, and the matrix elements $(\alpha^i)_{qp}{}^{-1}$ taking the place of $\Gamma_P(R_i)_{ab}$ in Eq. (1). Thus the three functions x_1, x_2, x_3, or x, y, z form basis functions for a three-dimensional representation of the point group. This representation is often reducible. Thus if all rotations are around the z axis, the function z is unchanged by the rotation, while x and y undergo linear transformations, so that z forms a basis function for a one-dimensional irreducible representation, and x and y for a two-dimensional irreducible representation. Since the quantities $(\alpha^i)_{qp}{}^{-1}$ form a representation of the point group, we may apply Eq. (2), and find

$$\sum(r)\,(\alpha^i)_{qr}{}^{-1}(\alpha^j)_{rs}{}^{-1}=(\alpha^k)_{qs}{}^{-1}, \tag{10}$$

where $R_iR_j=R_k$. This equation may be rewritten in the form

$$\sum(r)\,\alpha_{sr}{}^{j}\alpha_{rq}{}^{i}=\alpha_{sq}{}^{k} \tag{11}$$

which is an equation which we shall shortly wish wish to use.

The definition of Eq. (6) is not that used by all writers. Thus, Koster (Ref. 1) uses a definition which essentially describes the operations by the inverse of what we have used. At first sight this seems more reasonable, since then it is the matrix elements $\alpha_{pq}{}^{i}$ of the rotation which themselves form a representation of the point group, rather than their inverses. Nevertheless the writer feels that the procedure which we are adopting is more convenient than the alternative one. The reason comes from the very simple procedure which must be used to apply one of the operations to a given function. Since the point is rather subtle, we must emphasize just what Eq. (5) means. No matter what function ψ we may be dealing with, this equation means that we are to search through this function, and every time x_1 appears in it, we are to replace it by the linear combination of x_1, x_2, x_3 defined by Eq. (6); and similarly with x_2, x_3. This results in a new function, $\{R_i\,|\,\mathbf{T}_n\}\psi$, which still is a function of x_1, x_2, x_3. If we wish to use two successive operations of the space group, we apply the first one, resulting in a transformed function of x_1, x_2, x_3 defined in Eqs. (5) and (6); then we apply the second operation, which means that we are to search for every time x_1 appears in the function $\{R_i\,|\,\mathbf{T}_n\}\psi(x_1, x_2, x_3)$, and again replace it by an expression determined by Eq. (6).

We shall now carry through these steps analytically, so as to set up the multiplication table for the group. We shall find $\{R_i\,|\,\mathbf{T}_n\}\{R_j\,|\,\mathbf{T}_m\}\psi(x_1, x_2, x_3)$. Following the usual convention of quantum mechanics, we first find $\{R_j\,|\,\mathbf{T}_m\}\psi(x_1, x_2, x_3)$. If we proceed as in Eqs. (5) and (6), we find

$$\{R_j\,|\,\mathbf{T}_m\}\psi(x_1, x_2, x_3)=\psi[\sum(q)\alpha_{1q}{}^{j}x_q+\tau_1{}^{j}+T_{m1},$$
$$\sum(r)\alpha_{2r}{}^{j}x_r+\tau_2{}^{j}+T_{m2},\ \sum(s)\alpha_{3s}{}^{j}x_s+\tau_3{}^{j}+T_{m3}]. \tag{12}$$

If we wish to use matrix notation, we may set up $\boldsymbol{\alpha}^j$ as the square matrix

$$\begin{pmatrix}\alpha_{11}{}^{j} & \alpha_{12}{}^{j} & \alpha_{13}{}^{j}\\ \alpha_{21}{}^{j} & \alpha_{22}{}^{j} & \alpha_{23}{}^{j}\\ \alpha_{31}{}^{j} & \alpha_{32}{}^{j} & \alpha_{33}{}^{j}\end{pmatrix}$$

and $\mathbf{r}$ as the column vector

$$\begin{pmatrix}x_1\\ x_2\\ x_3\end{pmatrix},$$

and similarly $\boldsymbol{\tau}^j$ and $\mathbf{T}_m$ as column vectors. Then we may rewrite Eq. (12) in the form

$$\{R_j\,|\,\mathbf{T}_m\}\psi(\mathbf{r})=\psi[\boldsymbol{\alpha}^j\mathbf{r}+\boldsymbol{\tau}^j+\mathbf{T}_m]. \tag{12'}$$

We now apply the operator $\{R_i\,|\,\mathbf{T}_n\}$ to this function, which means that wherever x_p appears we are to replace it by $\sum(u)\alpha_{pu}{}^{i}x_u+\tau_p{}^{i}+T_{np}$, or in matrix language we are to replace the vector $\mathbf{r}$ by $\boldsymbol{\alpha}^i\mathbf{r}+\boldsymbol{\tau}^i+\mathbf{T}_n$.

Hence we find

$$\{R_i \mid \mathbf{T}_n\}\{R_j \mid \mathbf{T}_m\}\psi(x_1, x_2, x_3)$$
$$=\psi[\sum(qu)\alpha_{1q}{}^j\alpha_{qu}{}^i x_u+\sum(q)\alpha_{1q}{}^j(\tau_q{}^i+T_{nq})+\tau_1{}^j+T_{m1},$$
$$\sum(rv)\alpha_{2r}{}^j\alpha_{rv}x_v+\sum(r)\alpha_{2r}{}^j(\tau_r{}^i+T_{nr})+\tau_2{}^j+T_{m2},$$
$$\sum(sw)\alpha_{3s}{}^j\alpha_{sw}{}^i x_w+\sum(s)\alpha_{3s}{}^j(\tau_s{}^i+T_{ns})+\tau_3{}^j+T_{m3}]$$
$$=\psi\{\sum(u)\alpha_{1u}{}^k x_u+[\sum(q)\alpha_{1q}{}^j\tau_q{}^i+\tau_i{}^j]$$
$$+[\sum(q)\alpha_{1q}{}^jT_{nq}+T_{m1}],$$
$$\sum(v)\alpha_{2v}{}^k x_v+[\sum(r)\alpha_{2r}{}^j\tau_r{}^i+\tau_2{}^j]$$
$$+[\sum(r)\alpha_{2r}{}^jT_{nr}+T_{m2}],$$
$$\sum(w)\alpha_{3w}{}^k x_w+[\sum(s)\alpha_{3s}{}^j\tau_s{}^i+\tau_3{}^j]$$
$$+[\sum(s)\alpha_{3s}{}^jT_{ns}+T_{m3}]\}, \quad (13)$$

where

$$\alpha_{pu}{}^k=\sum(q)\alpha_{pq}{}^j\alpha_{qu}{}^i \quad (14)$$

or in matrix language

$$\{R_i \mid \mathbf{T}_n\}\{R_j \mid \mathbf{T}_m\}\psi[\boldsymbol{\alpha}^k\mathbf{r}+\boldsymbol{\alpha}^j(\boldsymbol{\tau}^i+\mathbf{T}_n)+\boldsymbol{\tau}^j+\mathbf{T}_m], \quad (13')$$

where

$$\boldsymbol{\alpha}^k=\boldsymbol{\alpha}^j\boldsymbol{\alpha}^i. \quad (14')$$

Now let us consider Eq. (13) or (13′). If our operators are to have a multiplication table, the argument of the function ψ in this equation must have the form given by Eq. (12), or (12′), for some operator $\{R_k \mid \mathbf{T}_l\}$ of the group. This requires first that the quantities $\sum(u)\alpha_{1u}{}^k x_u$, etc., or $\boldsymbol{\alpha}^k\mathbf{r}$, occurring in Eq. (13) or (13′), have the same form as the quantities $\sum(q)\alpha_{1q}{}^j x_q$, etc., or $\boldsymbol{\alpha}^j\mathbf{r}$, found in Eq. (12) or (12′), for some operation of the point group. To see that this is the case, consider the α's, which determine the point group. The expression $\sum(q)\alpha_{pq}{}^j\alpha_{qu}{}^i$, or $\boldsymbol{\alpha}^j\boldsymbol{\alpha}^i$, has the same form as the expression of Eq. (11), and by that equation it equals $\alpha_{pu}{}^k$, or $\boldsymbol{\alpha}^k$, the matrix for the kth operation of the point group, where $R_iR_j=R_k$. Hence as far as the point group is concerned, we have the necessary conditions for the existence of a multiplication table.

The second part of the proof must involve the statement that the translations found in Eq. (13) or (13′), which in matrix form are

$$\boldsymbol{\alpha}^j(\boldsymbol{\tau}^i+\mathbf{T}_n)+\boldsymbol{\tau}^j+\mathbf{T}_m, \quad (15)$$

must be of the form

$$\boldsymbol{\tau}^k+\mathbf{T}_l, \quad (16)$$

where $\boldsymbol{\tau}^k$ is the nonprimitive translation associated with the kth operation of the point group, in our definition of the space group, as given in Eq. (5) or (12), and where $\mathbf{T}_l$ is one of the lattice translations. These conditions are not automatically fulfilled for any arbitrary point group, and any arbitrary sets of primitive and nonprimitive translations. Rather, they furnish the restrictions on the point groups, on the nature of the primitive translation victors $\mathbf{t}_1$, $\mathbf{t}_2$, $\mathbf{t}_3$, and the nonprimitive translations $\boldsymbol{\tau}^i$, which limit the possible point groups to 32, the possible Bravais translation lattices to 14, and the possible space groups to 230. We shall not go into these individual cases, which have been adequately treated elsewhere (see Seitz, Ref 1). We point out only one fact, which we shall meet later in our discussion. If we apply in succession two operations of the space group each associated with zero translation, so that $\mathbf{T}_n=\mathbf{T}_m=0$, the translation found in Eq. (15), which will in this case have the form $\boldsymbol{\alpha}^j\boldsymbol{\tau}^i+\boldsymbol{\tau}^j$, can be written in the form of Eq. (16), namely, $\boldsymbol{\tau}^k+\mathbf{T}_{ij}$, but it does not follow that in all cases $\mathbf{T}_{ij}$ must be zero. We shall find that the values of $\mathbf{T}_{ij}$ appearing in this case are very characteristic quantities for the description of the space groups.

3. THE ACTION OF SPACE-GROUP OPERATORS ON PLANE WAVES

Let us now start with a plane wave, $\exp i\mathbf{k}\cdot\mathbf{r}$, where $\mathbf{k}$ is the wave vector, of rectangular components k_1, k_2, k_3, and $\mathbf{r}$ is the radius vector, of components x_1, x_2, x_3. If we wish to use matrix notation, we must regard $\mathbf{k}$ as a row vector (k_1, k_2, k_3). We then have for the plane wave the form

$$\psi(x_1, x_2, x_3)=\exp i\sum(p)k_px_p=\exp i\mathbf{k}\cdot\mathbf{r}. \quad (17)$$

We now let $\{R_i \mid \mathbf{T}_n\}$ operate on this, use Eq. (12′), and find

$$\{R_i \mid \mathbf{T}_n\}\exp i\mathbf{k}\cdot\mathbf{r}=\exp i\mathbf{k}\cdot(\boldsymbol{\alpha}^i\mathbf{r}+\boldsymbol{\tau}^i+\mathbf{T}_n)$$
$$=\exp i\mathbf{k}^i\cdot\mathbf{r}\exp i\mathbf{k}\cdot(\boldsymbol{\tau}^i+\mathbf{T}_n), \quad (18)$$

where

$$\mathbf{k}^i=\mathbf{k}\boldsymbol{\alpha}^i, \qquad k_q{}^i=\sum(p)k_p\alpha_{pq}{}^i. \quad (19)$$

Thus we see that the effect of performing the operation $\{R_i \mid \mathbf{T}_n\}$ on the plane wave can be described in two parts. First, it produces a new plane wave, with a transformed wave vector whose rectangular components are given in Eq. (19). Secondly, it multiplies by the factor $\exp i\mathbf{k}\cdot(\boldsymbol{\tau}^i+T_n)$, which depends on the translation.

In the transformation of Eq. (19) for finding the transformed wave vectors, the coefficients $\alpha_{pq}{}^i$ do not appear as they do in the expression of Eq. (6) for the transformed coordinates. Instead of summing over the second subscript q of $\alpha_{pq}{}^i$, as in Eq. (6), we sum over the first, p, which is shown in the matrix form by writing $\mathbf{k}$ as a row vector, and letting it precede the square matrix $\boldsymbol{\alpha}^i$. If we wished to regard $\mathbf{k}$ as a column

rather than a row vector, we could use Eq. (10), and write the transformation of Eq. (19) in the alternative form

$$\mathbf{k}_q{}^i=\sum(p)\,(\alpha^i)_{qp}{}^{-1}k_p, \qquad \mathbf{k}^i=(\boldsymbol{\alpha}^i)^{-1}\mathbf{k}, \qquad (19')$$

which shows that if $\mathbf{k}$ is regarded as a column vector, it transforms according to the inverse transformation to that transforming the coordinates. In other words, it is the matrices transforming the wave vector, in our scheme, which forms a representation of the group, rather than the matrices transforming the coordinates, as in the alternative scheme of Koster. We can have one or the other, but not both. In treating wave functions, we are more often interested in the wave vector than in the coordinates, suggesting that our procedure is more convenient than the usual one.

We can appreciate the advantage of our definition when we come to consider the translations associated with the operations, and in particular the translations involved in the successive application of two operations, as given in Eq. (15). If we wish to find $\{R_i\,|\,\mathbf{T}_n\}\{R_j\,|\,\mathbf{T}_m\}\exp i\mathbf{k}\cdot\mathbf{r}$, as in Eq. (13′), we first find $\{R_j\,|\,\mathbf{T}_m\}\exp i\mathbf{k}\cdot\mathbf{r}$. As we see from Eq. (18), the result is a plane wave $\exp i\mathbf{k}^j\cdot\mathbf{r}$, where $\mathbf{k}^j$ is determined by Eq. (19), as $\mathbf{k}\boldsymbol{\alpha}^j$, multiplied by the constant factor $\exp i\mathbf{k}\cdot(\boldsymbol{\tau}^j+\mathbf{T}_m)$. If we now allow $\{R_i\,|\,\mathbf{T}_n\}$ to act on this function, it has no effect on the constant factor. It results in a further transformed wave vector $\exp i\mathbf{k}^k\cdot\mathbf{r}$, where $\mathbf{k}^k$ is to be determined from $\mathbf{k}$ by use of the matrix of Eq. (14′), or $\mathbf{k}^k=\mathbf{k}\boldsymbol{\alpha}^j\boldsymbol{\alpha}^i$, times a further constant factor $\exp i\mathbf{k}^j\cdot(\boldsymbol{\tau}^i+\mathbf{T}_n)$. In other words, we have

$$\{R_i\,|\,\mathbf{T}_n\}\{R_j\,|\,\mathbf{T}_m\}\exp i\mathbf{k}\cdot\mathbf{r}$$
$$=\exp i\mathbf{k}^k\cdot\mathbf{r}\exp i\mathbf{k}_j\cdot(\boldsymbol{\tau}^i+\mathbf{T}_n)\exp i\mathbf{k}(\boldsymbol{\tau}^j+\mathbf{T}_m). \qquad (20)$$

The two constant factors taken together are just what result from the translation of Eq. (13′). In other words, this very straightforward way of operating on plane waves leads to the same result which we found in Eq. (13′). This direct possibility of operating on plane waves does not follow in the same way if we adopt the alternative definition of the operators of the space group.

4. SYMMETRIZED PLANE WAVES BY THE PROJECTION OPERATOR

We have now investigated the action of the space-group operators on plane waves, and have verified the method of operating with two operations in succession. We are next ready to attack our fundamental problem of setting up symmetrized plane waves by the projection operator. The main difficulty connected with this is the determination of the irreducible representations of the space group. Fortunately there are important general theorems which we can prove about these representations, though we cannot go the whole way toward finding them by straightforward methods. First we shall present these general theorems.

To understand them, we must first recall a few simple facts about wave functions in periodic potentials. It is well known (see for instance Ref. 2, Vol. 2, Chap. 5) that one can set up a so-called reciprocal lattice, and that any wave vector $\mathbf{k}$ can be written as the sum of a reduced wave vector $\mathbf{k}_0$, lying within the central Brillouin zone, and a vector $\mathbf{K}$ of the reciprocal lattice, which has the property that $\mathbf{K}\cdot\mathbf{T}_n=2\pi$ times an integer, where $\mathbf{T}_n$ is any one of the lattice translations. Furthermore, the reduced wave vector $\mathbf{k}_0$ can be located either at a so-called symmetry position, or at a general position. If it is at a general position, each of the vectors $\mathbf{k}^i$, formed from it according to Eq. (19) by one of the operations of the point group of the crystal, will have a distinct reduced wave vector. On the other hand, if it is at a symmetry position, a subgroup of the point group of the crystal operating on the wave vector will give vectors $\mathbf{k}^i$ corresponding to the same reduced wave vector. This subgroup of operations of the space group involving this subgroup of the point group is called the group of the wave vector. These facts are familiar, for example, from the well-known paper of Bouckaert, Smoluchowski, and Wigner.[3] It is only the cases where $\mathbf{k}_0$ is at a symmetry position that concern us here, for the symmetrized plane waves with which we work are formed from a number of plane waves with the same reduced wave vector.

The first general theorem which we shall prove is that the matrix element $\Gamma_P\{R_i\,|\,\mathbf{T}_n\}_{ab}$ for any operation of the group of the wave vector involves the translation $\mathbf{T}_n$ only through the simple factor $\exp i\mathbf{k}_0\cdot\mathbf{T}_n$. That is, we have

$$\Gamma_P\{R_i\,|\,\mathbf{T}_n\}_{ab}=\Gamma_P\{R_i\,|\,0\}_{ab}\exp i\mathbf{k}_0\cdot\mathbf{T}_n. \qquad (21)$$

We shall prove this theorem by assuming it to be true, and investigating what it would lead to when we set up basis functions for the irreducible representations by the method of projection operators.

We may use Eq. (3) and find that a basis function $f_{bd}{}^P$ for an irreducible representation P is to be given by

$$f_{bd}{}^P$$
$$=\sum(R_i,\mathbf{T}_n)\,\Gamma_P\{R_i\,|\,\mathbf{T}_n\}_{bd}{}^*\{R_i\,|\,\mathbf{T}_n\}\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}$$
$$=\sum(R_i,\mathbf{T}_n)\,\Gamma_P\{R_i\,|\,0\}_{bd}{}^*\exp-i\mathbf{k}_0\cdot\mathbf{T}_n$$
$$\{R_i\,|\,\mathbf{T}_n\}\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}$$
$$=\sum(R_i,\mathbf{T}_n)\,\Gamma_P\{R_i\,|\,0\}_{bd}{}^*\exp-i\mathbf{k}_0\cdot\mathbf{T}_n$$
$$\exp i\mathbf{k}^i\cdot r\exp i\mathbf{k}\cdot(\boldsymbol{\tau}^i+\mathbf{T}_n), \qquad (22)$$

[3] L. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).

in which we have used Eq. (18) for the last step. Here $\mathbf{k}$ is the wave vector $\mathbf{k}_0+\mathbf{K}$, and $\mathbf{k}^i$ is this vector transformed according to Eq. (19) or (19′). Now we note that the only way in which $\mathbf{T}_n$ appears in the quantity to be summed in Eq. (22) is in the factors

$$\exp -i\mathbf{k}_0\cdot\mathbf{T}_n \exp i\mathbf{k}\cdot\mathbf{T}_n=\exp i\mathbf{K}\cdot\mathbf{T}_n=1 \qquad (23)$$

on account of the fact that $\mathbf{K}\cdot\mathbf{T}_n=2\pi$ times an integer. Hence the quantity to be summed in Eq. (22) is independent of $\mathbf{T}_n$, and the sum equals the term for the case $\mathbf{T}_n=0$, multiplied by the number of translation operations. The latter is a constant, equal to the number of unit cells in the repeating range of the crystal (if we use periodic boundary conditions). Since multiplication of all basis functions by the same constant does not affect their property of forming basis functions, we may omit the summation over $\mathbf{T}_n$, and write

$$f_{bd}{}^P=\sum(R_i)\,\Gamma_P\{R_i\mid 0\}_{bd}{}^*\{R_i\mid 0\}\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}. \qquad (24)$$

The expression of Eq. (24) would give a basis function for the irreducible representation, provided Eq. (21) was correct. We must now verify this equation. To do so, we shall operate on $f_{bd}{}^P$ with the operator $\{R_j\mid\mathbf{T}_m\}$, to see if $\mathbf{T}_m$ occurs in the proper way in accordance with Eq. (21). If we use Eq. (20), we find that the effect of $\{R_j\mid\mathbf{T}_m\}$ on $f_{bd}{}^P$ includes a factor $\exp i(\mathbf{k}_0+\mathbf{K})^i\cdot\mathbf{T}_m$, which is the only way in which $\mathbf{T}_m$ enters the result. Since the operator R_i belongs to the group of the wave vector, this means that the transformed wave vector $(\mathbf{k}_0+\mathbf{K})^i$ equals $\mathbf{k}_0+\mathbf{K}^i$, the reduced wave vector $\mathbf{k}_0$ not being affected by the operation. Hence the factor is $\exp i\mathbf{k}_0\cdot\mathbf{T}_m \exp i\mathbf{K}^i\cdot\mathbf{T}_m$. Since $\mathbf{K}^i$ is one of the translation vectors of the lattice, we have $\exp i\mathbf{K}^i\cdot\mathbf{T}_m=1$, and the factor equals $\exp i\mathbf{k}_0\cdot\mathbf{T}_m$, verifying the dependence on $\mathbf{T}_m$ given in Eq. (21). Hence we have completed the proof that this theorem is true.

In case $\mathbf{k}_0$ lies within the Brillouin zone, rather than on its boundary, we can go further and give the form of the matrix elements of the irreducible representations of the space group completely from the matrix elements for the point group. Let the matrix elements for the point group of the wave vector be $\Gamma_P(R_i)_{ab}$. Then in this case we can prove that

$$\Gamma_P\{R_i\mid 0\}_{ab}=\Gamma_P(R_i)_{ab}\exp i\mathbf{k}_0\cdot\boldsymbol{\tau}^i \qquad (25)$$

or, from Eq. (21),

$$\Gamma_P\{R_i\mid\mathbf{T}_n\}_{ab}=\Gamma_P(R_i)_{ab}\exp i\mathbf{k}_0\cdot(\boldsymbol{\tau}^i+\mathbf{T}_n). \qquad (26)$$

To prove this result, we proceed as in the previous proof, by assuming its truth, setting up basis functions by the projection operator method, letting the operators operate on these functions, and showing that they are in fact basis functions, with the matrix elements given by Eq. (25) or (26). This proof is given in the Appendix. For a symmorphic space group (one in which the nonprimitive translations $\boldsymbol{\tau}^i$ are all zero), this proof holds also when $\mathbf{k}_0$ is on the boundary of the Brillouin zone, but for a nonsymmorphic space group it does not.

The proof of Eq. (25) in the Appendix depends on the assumption that the reduced wave vector $\mathbf{k}_0$ is not changed by the operation of the point group. However, if $\mathbf{k}_0$ lies on the surface of the Brillouin zone, the group of the wave vector can include operations which change $\mathbf{k}_0$, provided the transformed $\mathbf{k}_0$ equals the original $\mathbf{k}_0$ plus one of the wave vectors $\mathbf{K}$ of the reciprocal lattice. For instance, the operation could be one which transformed $\mathbf{k}_0$ into $-\mathbf{k}_0$, in case the vector $\mathbf{k}_0-(-\mathbf{k}_0)=2\mathbf{k}_0$ was one of the vectors of the reciprocal lattice. In such a case, for a nonsymmorphic space group, the proof in the Appendix breaks down, and we cannot assume that Eq. (25) holds. We do not have a general method of handling these reduced wave vectors on the surface of the Brillouin zone. In the next section we shall illustrate a method which can be used by a specific example. The problem is to find quantities $\Gamma_P\{R_i\mid 0\}_{bd}$ like those occurring in Eq. (24), such that the resulting functions will be basis functions for irreducible representations. By Eq. (1), these quantities must then satisfy the equations

$$\{R_i\mid 0\}\sum(R_j)\,\Gamma_P\{R_j\mid 0\}_{bd}{}^*\{R_j\mid 0\}\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}$$
$$=\sum(a)\,\Gamma_P\{R_i\mid 0\}_{ab}\sum(R_k)\,\Gamma_P\{R_k\mid 0\}_{ad}{}^*\{R_k\mid 0\}$$
$$\times\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}. \qquad (27)$$

On the left side of this equation, we have the product of two operators, $\{R_i\mid 0\}$ and $\{R_j\mid 0\}$, acting on the plane wave $\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}$. Now we have investigated the effect of the product of two such operators in Eqs. (13) to (16). We have found that

$$\{R_i\mid 0\}\{R_j\mid 0\}\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}$$
$$=\exp i(\mathbf{k}_0+\mathbf{K})^k\cdot\mathbf{r}\exp i(\mathbf{k}_0+\mathbf{K})\cdot(\boldsymbol{\tau}^k+\mathbf{T}_{ij}), \qquad (28)$$

where the modified wave vector is to be found from the matrix of Eq. (14). The primitive translation $\mathbf{T}_{ij}$ is the same one introduced following Eq. (16). If we compare with Eqs. (18) and (19), we see that Eq. (28) is very closely related to that defining the effect of the product operator $\{R_iR_j\mid 0\}$ on the plane wave, where $R_iR_j=R_k$. In fact,

$$\{R_i\mid 0\}\{R_j\mid 0\}\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}$$
$$=\exp i\mathbf{k}_0\cdot\mathbf{T}_{ij}\{R_iR_j\mid 0\}\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}, \qquad (29)$$

where in the factor $\exp i\mathbf{k}_0\cdot\mathbf{T}_{ij}$ we have made use of the fact that $\exp i\mathbf{K}\cdot\mathbf{T}_{ij}=1$. In other words, the effect of the successive application of two operators of the space group, corresponding to zero translation, on a

plane wave of reduced wave vector $\mathbf{k}_0$ is the same as that of the single operator of the space group whose point-group operator is the product of the point-group operators of the two factors with an additional constant factor $\exp i\mathbf{k}_0\cdot\mathbf{T}_{ij}$. By listing these factors for all products of operators of the point group, it is possible to get the multiplication table for the operators $\{R_i\,|\,0\}$ directly from that for the operators of the point group.

We may now insert the result of Eq. (29) in Eq. (27). This gives on each side of the equation a sum of operators like $\{R_iR_j\,|\,0\}$, or $\{R_k\,|\,0\}$, operating on the plane wave $\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}$, each multiplied by a coefficient. Since the plane waves arising from these various operations are independent of each other, and in fact are orthogonal if integrated over the repeating volume of the crystal, the two sides of the equation must agree term by term. That is, we may take the term bearing the index R_j from the left side of the equation, and equate it to that bearing the index R_k on the right, where $R_iR_j=R_k$. Thus we obtain the equation

$$\exp i\mathbf{k}_0\cdot\mathbf{T}_{ij}\Gamma_P\{R_j\,|\,0\}_{bd}^*=\sum(a)\,\Gamma_P\{R_i\,|\,0\}_{ab}\Gamma_P\{R_iR_j\,|\,0\}_{ad}^*. \quad (30)$$

Such an equation involving elements of the representation matrix $\Gamma_P\{R_i\,|\,0\}_{ab}$ must hold for each value of i, j, a, b, d, and P. If we can solve this set of equations, we shall have found our desired representation matrix elements for the irreducible representations for a wave vector on the surface of the Brillouin zone. In the next section we illustrate the sort of method which can be used in practice to get the desired solutions. We illustrate these methods by a simple case: the point A in the hexagonal close-packed structure, the space group D_{6h}^4.

5. THE SPACE GROUP D_{6h}^4 AS AN EXAMPLE

The point group D_{6h}, which is found in the space group D_{6h}^4, has 24 operations, which are described in Ref. 2 in terms of cylindrical coordinates. Though for many purposes it is more convenient to go to rectangular coordinates, we can illustrate our present point by retaining the cylindrical coordinates, which we shall take to be r, ϕ, z. We then have introduced in Ref. 2 the following notation for the operations of the point group:

$$\begin{aligned}
X_q\psi(r,\phi,z)&=\psi(r,\phi+\tfrac{1}{3}\pi q,z),\\
Y_q\psi(r,\phi,z)&=\psi(r,-\phi+\tfrac{1}{3}\pi,z),\\
X_q'\psi(r,\phi,z)&=\psi(r,\phi+\tfrac{1}{3}\pi q,-z),\\
Y_q'\psi(r,\phi,z)&=\psi(r,-\phi+\tfrac{1}{3}\pi,-z),
\end{aligned}\quad (31)$$

where $q=0,\ \pm1,\ \pm2,\ 3$. These notations are different from the standard ones for this group,[4] but they have the advantage that in terms of them the multiplication table for the point group can be expressed very simply. We have in fact

$$\begin{aligned}
X_pX_q&=X_{p+q} \qquad Y_pX_q=Y_{p+q},\\
X_pY_q&=Y_{-p+q} \qquad Y_pY_q=X_{-p+q},
\end{aligned}\quad (32)$$

as the reader can easily verify. The product of an unprimed by a primed operator has the same form as that of two unprimed operators, but the product operator is primed; the product of two primed operators is the same as of the corresponding two unprimed operators. In any case, if the subscript $p+q$ or $-p+q$ of the product operator lies outside the allowed range $0,\ \pm1,\ \pm2,\ 3$, we are to add or subtract integral multiples of 6 to bring it within this range.

From the multiplication table, it is simple to find the classes of operations. There are twelve classes, comprising the following operations respectively: X_0; X_1 and X_{-1}; X_2 and X_{-2}; X_3; Y_0, $Y_{\pm2}$; $Y_{\pm1}$, Y_3; and six equivalent classes formed from the primed operations. By general principles there are as many irreducible representations as classes, and the sum of the squares of the dimensionalities of the irreducible representations equals the number of operators. In this case there are eight one-dimensional irreducible representations, and four two-dimensional, satisfying these conditions. Basis functions for the one-dimensional representations may be taken to be 1, $\sin 6\phi$, $\cos 3\phi$, $\sin 3\phi$, and these same quantities multiplied by z; for the two-dimensional representations, $e^{i\phi}$ and $e^{-i\phi}$, $e^{2i\phi}$ and $e^{-2i\phi}$, and the same quantities multiplied by z. Matrix elements for the irreducible representations, using these basis functions, are given in Table I.

In the space group, we have a nonprimitive translation of $\mathbf{t}_3/2$, where $\mathbf{t}_3$ is the lattice spacing along the hexagonal or z axis, for the operations $X_{\pm1}$, X_3, $Y_{\pm1}$, Y_3, X_0', $X_{\pm2}'$, Y_0', $Y_{\pm2}'$, and no nonprimitive translations for the remaining operations of the point group. When we take account of these nonprimitive translations, we find values of the translation $\mathbf{T}_{ij}$, given in Eq. (29) in finding the effect of two successive applications of operations $\{R_i\,|\,0\}$ of the space group, as found in Table II.

Since the nonprimitive translation is along the z or hexagonal axis, it is only reduced wave vectors with a nonvanishing z component which will illustrate the effect of such a translation, since only for these will the factor $\exp i\mathbf{k}_0\cdot\mathbf{t}_3$ be nonvanishing. Let us therefore consider the following illustrative cases: first, $\mathbf{k}_0=0$, the point Γ in the notation of Herring (Ref. 4); secondly, $\mathbf{k}_0\neq0$, pointing along the z direction (the case Δ); thirdly, the boundary of the Brillouin zone in this direction (the point A), where $|\mathbf{k}_0|=\pi/|\mathbf{t}_3|$. For Γ, the factor $\exp i\mathbf{k}_0\cdot\mathbf{t}_3=1$, so that at Γ the matrix elements of the irreducible representations of the space

[4] C. Herring, J. Franklin Inst. **233**, 525 (1942).

TABLE I. Matrix elements and characters of the irreducible representations of the point group D_{6h}. The notations Γ_1^+, Γ_2^-, etc., are the notations of Herring (Ref. 4) for the corresponding irreducible representations of the space group D_{6h}^4 at the point $\mathbf{k}_0=0$. The matrix elements of the primed operators are equal to those of the unprimed operators for the first irreducible representations of each pair tabulated, and are the negative of those of the unprimed for the second representation tabulated. For propagation along the direction Δ, the group of the wave vector is C_{6v}, including the unprimed operators only. The irreducible representations for the space group, for $\mathbf{k}_0$ along the direction Δ, are obtained from the entries of the table, by multiplying the elements corresponding to operators with odd subscripts by the factor $\exp i\mathbf{k}_0\cdot\mathbf{t}_3/2$. The irreducible representations along Δ, as given by Herring, are indicated in the table. The abbreviation ω stands for $e^{2\pi i/3}$. Basis functions for the irreducible representations of D_{6h}, using the notation of Herring, are as follows:

Γ_1^+	1	Γ_2^-	z
Γ_2^+	$\sin 6\phi$	Γ_1^-	$z\sin 6\phi$
Γ_3^-	$\cos 3\phi$	Γ_4^+	$z\cos 3\phi$
Γ_4^-	$\sin 3\phi$	Γ_3^+	$z\sin 3\phi$
Γ_5^+	$e^{\pm i\phi}$	Γ_5^-	$z\,e^{\pm i\phi}$
Γ_6^-	$e^{\pm 2i\phi}$	Γ_6^+	$z\,e^{\pm 2i\phi}$

The operation X_3' is the inversion; Herring's notations have superscript + for functions even on inversion, − for those odd on inversion.

Representation	X_0	X_1	X_{-1}	X_2	X_{-2}	X_3	Y_0	Y_1	Y_{-1}	Y_2	Y_{-2}	Y_3
Γ_1^+, Γ_2^-, Δ_1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2^+, Γ_1^-, Δ_3	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
Γ_3^-, Γ_4^+, Δ_4	1	−1	−1	1	1	−1	−1	1	1	−1	−1	1
Γ_4^-, Γ_3^+, Δ_2	1	−1	−1	1	1	−1	1	−1	−1	1	1	−1
$(\Gamma_5^+, \Gamma_5^-, \Delta_5)_{11}$	1	ω	ω^2	ω^2	ω	1	0	0	0	0	0	0
$(\Gamma_5^+, \Gamma_5^-, \Delta_5)_{21}$	0	0	0	0	0	0	1	ω	ω^2	ω^2	ω	1
$(\Gamma_5^+, \Gamma_5^-, \Delta_5)_{12}$	0	0	0	0	0	0	1	ω^2	ω	ω	ω^2	1
$(\Gamma_5^+, \Gamma_5^-, \Delta_5)_{22}$	1	ω^2	ω	ω	ω^2	1	0	0	0	0	0	0
$\chi(\Gamma_5^+, \Gamma_5^-, \Delta_5)$	2	−1	−1	−1	−1	2	0	0	0	0	0	0
$(\Gamma_6^-, \Gamma_6^+, \Delta_6)_{11}$	1	$-\omega^2$	$-\omega$	ω	ω^2	−1	0	0	0	0	0	0
$(\Gamma_6^-, \Gamma_6^+, \Delta_6)_{21}$	0	0	0	0	0	0	1	$-\omega^2$	$-\omega$	ω	ω^2	−1
$(\Gamma_6^-, \Gamma_6^+, \Delta_6)_{12}$	0	0	0	0	0	0	1	$-\omega$	$-\omega^2$	ω^2	ω	−1
$(\Gamma_6^-, \Gamma_6^+, \Delta_6)_{22}$	1	$-\omega$	$-\omega^2$	ω^2	ω	−1	0	0	0	0	0	0
$\chi(\Gamma_6^-, \Gamma_6^+, \Delta_6)$	2	1	1	−1	−1	−2	0	0	0	0	0	0

group, $\Gamma_P\{R_i\,|\,0\}_{ab}$, are as given in Table I. The irreducible representations are labelled by Herring as shown in Table I. Along the direction Δ, the group of the wave vector includes the unprimed, but not the primed, operators. We may still use Table I for the matrix elements, but as in Eq. (25) we must multiply all those elements arising from operators having a nonprimitive translation by the factor $\exp i\mathbf{k}_0\cdot\mathbf{t}_3/2$. This factor goes from unity at the point Γ, to $e^{\pi i/2}=i$ at the point A. The irreducible representations along Δ, as given by Herring, are indicated in Table I, and the compatibility relations between the various irreducible representations at Γ and at Δ are obvious from the table; those representations having the same sets

TABLE II. Translation $\mathbf{T}_{ij}$ associated with product of two operations $\{R_i\,|\,0\}$ of the group D_{6h}, as in Eq. (29).

First operation	Second operation	$\mathbf{T}_{ij}$
$X_{\pm1}$, X_3, $Y_{\pm1}$, Y_3, X_0', $X_{\pm2}'$, Y_0', $Y_{\pm2}'$	$X_{\pm1}$, X_3, $Y_{\pm1}$, Y_3	$\mathbf{t}_3$
$X_{\pm1}$, X_3, $Y_{\pm1}$, Y_3, X_0', $X_{\pm2}'$, Y_0', $Y_{\pm2}'$	$X_{\pm1}'$, X_3', $Y_{\pm1}'$, Y_3'	$-\mathbf{t}_3$
All other cases		0

TABLE III. Basis functions for different irreducible representations and partners for propagation along direction Δ, immediately adjacent to point A. The functions $u_1, \cdots, u_{12}$ are obtained by applying projection operators formed from the various rows of the matrix of Table 1, modified for the point A. Note that we have arranged the order of these functions according to the subscript of Δ, giving a different order from that of Table I. The functions u_i' are obtained from the corresponding functions u_i by operating on them with X_0'.

Δ_1: $u_1=(X_0-iX_1-iX_{-1}+X_2+X_{-2}-iX_3+Y_0-iY_1-iY_{-1}+Y_2+Y_{-2}-iY_3)\psi$

Δ_2: $u_2=(X_0+iX_1+iX_{-1}+X_2+X_{-2}+iX_3+Y_0+iY_1+iY_{-1}+Y_2+Y_{-2}+iY_3)\psi$

Δ_3: $u_3=(X_0-iX_1-iX_{-1}+X_2+X_{-2}-iX_3-Y_0+iY_1+iY_{-1}-Y_2-Y_{-2}+iY_3)\psi$

Δ_4: $u_4=(X_0+iX_1+iX_{-1}+X_2+X_{-2}+iX_3-Y_0-iY_1-iY_{-1}-Y_2-Y_{-2}-iY_3)\psi$

$(\Delta_5)_{11}$: $u_5=(X_0-i\omega^2X_1-i\omega X_{-1}+\omega X_2+\omega^2X_{-2}-iX_3)\psi$

$(\Delta_5)_{21}$: $u_6=(Y_0-i\omega^2Y_1-i\omega Y_{-1}+\omega Y_2+\omega^2Y_{-2}-iY_3)\psi$

$(\Delta_5)_{12}$: $u_7=(Y_0-i\omega Y_1-i\omega^2Y_{-1}+\omega^2Y_2+\omega Y_{-2}-iY_3)\psi$

$(\Delta_5)_{22}$: $u_8=(X_0-i\omega X_1-i\omega^2X_{-1}+\omega^2X_2+\omega X_{-2}-iX_3)\psi$

$(\Delta_6)_{11}$: $u_9=(X_0+i\omega X_1+i\omega^2X_{-1}+\omega^2X_2+\omega X_{-2}+iX_3)\psi$

$(\Delta_6)_{21}$: $u_{10}=(Y_0+i\omega Y_1+i\omega^2Y_{-1}+\omega^2Y_2+\omega Y_{-2}+iY_3)\psi$

$(\Delta_6)_{12}$: $u_{11}=(Y_0+i\omega^2Y_1+i\omega Y_{-1}+\omega Y_2+\omega^2Y_{-2}+iY_3)\psi$

$(\Delta_6)_{22}$: $u_{12}=(X_0+i\omega^2X_1+i\omega X_{-1}+\omega X_2+\omega^2X_{-2}+iX_3)\omega$

$u_1'=(X_0'+iX_1'+iX_{-1}'+X_2'+X_{-2}'+iX_3'+Y_0'+iY_1'+iY_{-1}'+Y_2'+Y_{-2}'+iY_3')\psi$

$u_2'=(X_0'-iX_1'-iX_{-1}'+X_2'+X_{-2}'-iX_3'+Y_0'-iY_1'-iY_{-1}'+Y_2'+Y_{-2}'-iY_3')\psi$

$u_3'=(X_0'+iX_1'+iX_{-1}'+X_2'+X_{-2}'+iX_3'-Y_0'-iY_1'-iY_{-1}'-Y_2'-Y_{-2}'-iY_3')\psi$

$u_4'=(X_0'-iX_1'-iX_{-1}'+X_2'+X_{-2}'-iX_3'-Y_0'+iY_1'+iY_{-1}'-Y_2'-Y_{-2}'+iY_3')\psi$

$u_5'=(X_0'+i\omega^2X_1'+i\omega X_{-1}'+\omega X_2'+\omega^2X_{-2}'+iX_3')\psi$

$u_6'=(Y_0'+i\omega^2Y_1'+i\omega Y'_{-1}+\omega Y_2'+\omega^2Y_{-2}'+iY_3')\psi$

$u_7'=(Y_0'+i\omega Y_1'+i\omega^2Y_{-1}'+\omega^2Y_2'+\omega Y_{-2}'+iY_3')\psi$

$u_8'=(X_0'+i\omega X_1'+i\omega^2X_{-1}'+\omega^2X_2'+\omega X_{-2}'+iX_3')\psi$

$u_9'=(X_0'-i\omega X_1'-i\omega^2X_{-1}'+\omega^2X_2'+\omega X_{-2}'-iX_3')\psi$

$u_{10}'=(Y_0'-i\omega Y_1'-i\omega^2Y_{-1}'+\omega^2Y_2'+\omega Y_{-2}'-iY_3')\psi$

$u_{11}'=(Y_0'-i\omega^2Y_1'-i\omega Y_{-1}'+\omega Y_2'+\omega^2Y_{-2}'-iY_3')\psi$

$u_{12}'=(X_0'-i\omega^2X_1'-i\omega X_{-1}'+\omega X_2'+\omega^2X_{-2}'-iX_3')\psi$

of matrix elements are compatible, such as Δ_1 with Γ_1^+, Γ_2^-.

The point A is the one which introduces new features, which we are illustrating in the present section. Here the point group of the wave vector is the complete group D_{6h}, including the primed as well as the unprimed operations. The reason why the primed operations are included is that they correspond to changing z into $-z$, which means that the reduced wave vector, which has a magnitude of $\pi/|\mathbf{t}_3|$ and is along z, is transformed into its negative, differing from it by $2\pi/|\mathbf{t}_3|$, which is the fundamental interval in the reciprocal lattice along the z axis. Hence the transformed value of $\mathbf{k}_0$ equals one of the vectors of the reciprocal lattice plus $\mathbf{k}_0$, so that it corresponds to the same reduced wave vector.

Though the group of the wave vector at A is thus the same as at Γ, the multiplication table is quite different, on account of the factors $\exp i\mathbf{k}_0\cdot\mathbf{T}_{ij}$, which here have the value -1 for the products of operators given in Table II. Hence the irreducible representations are quite different from those at the point Γ, and must be found by independent methods. The first step in doing this is to look at the basis functions for the various irreducible representations along the direction Δ, for values of $\mathbf{k}_0$ immediately adjacent to the point A; we should naturally expect a continuity of properties as we approach A. We can set up such a function from each row of Table I, by using Eq. (3), and remembering that we have the extra factor i in all the rows having operators corresponding to nonprimitive translations. In this way we set up functions given in Table III, where we express the functions as linear combinations of various operators operating on ψ, which is assumed to be the plane wave $\exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r}$, where $\mathbf{k}_0$ is the value at the point A.

The functions found in this way are described as $u_1, \cdots, u_{12}$ in Table III. Each one forms a basis function for an irreducible representation of the group involving only the unprimed operators, but at the point A we have the primed operators as well. Therefore we may operate on these functions with the primed operators, and see what we get. In the first place, if we use only the primed operator X_0', and operate on each function in succession, we get the functions denoted by $u_1', \cdots, u_{12}'$ in Table III. We then find that these functions are all we need to describe the irreducible representations at point A. In fact, we find that u_1 and u_1' form basis functions for a two-dimensional irreducible representation, which we call A_1. The pair of functions u_2', u_2, form a second pair of basis functions for this same two-dimensional representation. Similarly u_3 and u_3' form basis functions for another two-dimensional irreducible representation, which we call A_2; and u_4', u_4 form another set of basis functions for this two-dimensional representation. Next, u_5, u_6, u_5', u_6' form basis functions for a four-dimensional irreducible representation. Additional sets of basis functions for this same

TABLE IV. Matrix elements and characters for the irreducible representations for the point A, D_{6h}^4.

	X_0	X_1	X_{-1}	X_2	X_{-2}	X_3	Y_0	Y_1	Y_{-1}	Y_2	Y_{-2}	Y_3	X_0'	X_1'	X_{-1}'	X_2'	X_{-2}'	X_3'	Y_0'	Y_1'	Y_{-1}'	Y_2'	Y_{-2}'	Y_3'
$(A_1)_{11}$	1	i	i	1	1	i	1	i	i	1	1	i	0	0	0	0	0	0	0	0	0	0	0	0
$(A_1)_{21}$	0	0	0	0	0	0	0	0	0	0	0	0	1	$-i$	$-i$	1	1	$-i$	1	$-i$	$-i$	1	1	$-i$
$(A_1)_{12}$	0	0	0	0	0	0	0	0	0	0	0	0	1	i	i	1	1	i	1	i	i	1	1	i
$(A_1)_{22}$	1	$-i$	$-i$	1	1	$-i$	1	$-i$	$-i$	1	1	$-i$	0	0	0	0	0	0	0	0	0	0	0	0
$\chi(A_1)$	2	0	0	2	2	0	2	0	0	2	2	0	0	0	0	0	0	0	0	0	0	0	0	0
$(A_2)_{11}$	1	i	i	1	1	i	-1	$-i$	$-i$	-1	-1	$-i$	0	0	0	0	0	0	0	0	0	0	0	0
$(A_2)_{21}$	0	0	0	0	0	0	0	0	0	0	0	0	1	$-i$	$-i$	1	1	$-i$	-1	i	i	-1	-1	i
$(A_2)_{12}$	0	0	0	0	0	0	0	0	0	0	0	0	1	i	i	1	1	i	-1	$-i$	$-i$	-1	-1	$-i$
$(A_2)_{22}$	1	$-i$	$-i$	1	1	$-i$	-1	i	i	-1	-1	i	0	0	0	0	0	0	0	0	0	0	0	0
$\chi(A_2)$	2	0	0	2	2	0	-2	0	0	-2	-2	0	0	0	0	0	0	0	0	0	0	0	0	0
$(A_3)_{11}$	1	$i\omega$	$i\omega^2$	ω^2	ω	i	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$(A_3)_{21}$	0	0	0	0	0	0	1	$i\omega$	$i\omega^2$	ω^2	ω	i	0	0	0	0	0	0	0	0	0	0	0	0
$(A_3)_{31}$	0	0	0	0	0	0	0	0	0	0	0	0	1	$-i\omega$	$-i\omega^2$	ω^2	ω	$-i$	0	0	0	0	0	0
$(A_3)_{41}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	$-i\omega$	$-i\omega^2$	ω^2	ω	$-i$
$(A_3)_{12}$	0	0	0	0	0	0	1	$i\omega^2$	$i\omega$	ω	ω^2	i	0	0	0	0	0	0	0	0	0	0	0	0
$(A_3)_{22}$	1	$i\omega^2$	$i\omega$	ω	ω^2	i	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$(A_3)_{32}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	$-i\omega^2$	$-i\omega$	ω	ω^2	$-i$
$(A_3)_{42}$	0	0	0	0	0	0	0	0	0	0	0	0	1	$-i\omega^2$	$-i\omega$	ω	ω^2	$-i$	0	0	0	0	0	0
$(A_3)_{13}$	0	0	0	0	0	0	0	0	0	0	0	0	1	$i\omega$	$i\omega^2$	ω^2	ω	i	0	0	0	0	0	0
$(A_3)_{23}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	$i\omega$	$i\omega^2$	ω^2	ω	i
$(A_3)_{33}$	1	$-i\omega$	$-i\omega^2$	ω^2	ω	$-i$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$(A_3)_{43}$	0	0	0	0	0	0	1	$-i\omega$	$-i\omega^2$	ω^2	ω	$-i$	0	0	0	0	0	0	0	0	0	0	0	0
$(A_3)_{14}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	$i\omega^2$	$i\omega$	ω	ω^2	i
$(A_3)_{24}$	0	0	0	0	0	0	0	0	0	0	0	0	1	$i\omega^2$	$i\omega$	ω	ω^2	i	0	0	0	0	0	0
$(A_3)_{34}$	0	0	0	0	0	0	1	$-i\omega^2$	$-i\omega$	ω	ω^2	$-i$	0	0	0	0	0	0	0	0	0	0	0	0
$(A_3)_{44}$	1	$-i\omega^2$	$-i\omega$	ω	ω^2	$-i$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\chi(A_3)$	4	0	0	-2	-2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

TABLE IV (*Continued*)

For the group C_{6v}^4, the point A is merely a special case of Δ, obtained by setting $\alpha=i$. Hence we have the following matrix elements and characters:

	X_0	X_1	X_{-1}	X_2	X_{-2}	X_3	Y_0	Y_1	Y_{-1}	Y_2	Y_{-2}	Y_3
A_1	1	i	i	1	1	i	1	i	i	1	1	i
A_2	1	$-i$	$-i$	1	1	$-i$	1	$-i$	$-i$	1	1	$-i$
A_3	1	i	i	1	1	i	-1	$-i$	$-i$	-1	-1	$-i$
A_4	1	$-i$	$-i$	1	1	$-i$	-1	i	i	-1	-1	i
$(A_5)_{11}$	1	$i\omega$	$i\omega^2$	ω^2	ω	i	0	0	0	0	0	0
$(A_5)_{21}$	0	0	0	0	0	0	1	$i\omega$	$i\omega^2$	ω^2	ω	i
$(A_5)_{12}$	0	0	0	0	0	0	1	$i\omega^2$	$i\omega$	ω	ω^2	i
$(A_5)_{22}$	1	$i\omega^2$	$i\omega$	ω	ω^2	i	0	0	0	0	0	0
$\chi(A_5)$	2	$-i$	$-i$	-1	-1	$2i$	0	0	0	0	0	0
$(A_6)_{11}$	1	$-i\omega^2$	$-i\omega$	ω	ω^2	$-i$	0	0	0	0	0	0
$(A_6)_{21}$	0	0	0	0	0	0	1	$-i\omega^2$	$-i\omega$	ω	ω^2	$-i$
$(A_6)_{12}$	0	0	0	0	0	0	1	$-i\omega$	$-i\omega^2$	ω^2	ω	$-i$
$(A_6)_{22}$	1	$-i\omega$	$-i\omega^2$	ω^2	ω	$-i$	0	0	0	0	0	0
$\chi(A_6)$	2	i	i	-1	-1	$-2i$	0	0	0	0	0	0

representation, which we call A_3, are the sets of functions u_7, u_8, u_7', u_8'; u_{12}', u_{11}', u_{12}, u_{11}; and u_{10}', u_9', u_{10},$^k u_9$.

We thus have found three irreducible representations at A, two two-dimensional and one four-dimensional. The sum of the squares of the dimensionalities, $2^2+2^2+4^2$, adds to 24, as it must to equal the number of operations, but we see that the whole situation is entirely different from what it is at Γ, even though we have the same number of operations. In Table IV we show the matrix elements of these irreducible representations. It is perfectly straightforward to find these matrix elements. Suppose for instance we operate on u_1 with the operator X_1. We use the rules of multiplication, and find that the result is

$$X_1u_1=(X_1+iX_2+iX_0+X_3+X_{-1}+iX_{-2}+Y_{-1}+iY_0+iY_{-2}+Y_1+Y_3+iY_2)\psi=iu_1. \quad (33)$$

Thus for the operator X_1 the entry $(A_1)_{11}$ in the table is i, indicating that we have iu_1 in Eq. (33), and the entry $(A_1)_{21}$ is zero. When we have found the table of matrix elements in this way, we then find that by applying projection operators formed from the various rows of the table, we get back just the functions of Table III, in the order in which we have enumerated them in the preceding paragraph. We can verify by substitution that these matrix elements satisfy Eq. (30).

We see, then, that a very simple procedure has sufficed to investigate the irreducible representations at the point A in the group D_{6h}^4. In many cases the problem is equally simple. Other cases lead to more complication. but it does not prove to be difficult in any case to work out the required matrices. In Ref. 2 some 20 space groups are worked out, and further explanation is given of methods which can be used in more complicated cases than the example which we have treated here.

6. MATRIX ELEMENTS OF THE HAMILTONIAN

We have now investigated all the steps required in applying the method of projection operators to set up symmetrized plane waves. In actual applications of the method, we are interested in finding the matrix elements of the Hamiltonian between different symmetrized plane waves. There are relations here which are more general than this special case, and we shall work them out in the present section. Let us start with two basis functions of the form given in Eq. (3), found by the method of projection operators, and find the matrix element of the Hamiltonian between them.

In order to check the general theorem that we have nonvanishing matrix elements of the Hamiltonian only between two functions of the same symmetry type, let us start out by taking functions of general symmetry, and show that it is only in the case where the symmetries are the same that we get a nonvanishing element. Let us then start with two functions, $f_{ab}^{P'}$ and $F_{cd}^{P'}$, determined by Eq. (3) from different functions ψ and ψ', and find the matrix element of the Hamiltonian between them. We have

$$\int f_{ab}^{P*}(H)_{op}F_{cd}^{P'}\,dv=\int\sum(R_i)\,\Gamma_P(R_i)_{ab}(R_i\psi)^*(H)_{op}\times\sum(R_j)\,\Gamma_{P'}(R_j)_{cd}^*(R_j\psi')\,dv. \quad (34)$$

Let us operate on the whole integrand with the operator $(R_i)^{-1}$. Since this is an operator which merely makes a rotation, reflection, or translation, it will have no effect on the value of the integral, though it will affect the integrand; it merely results in a change of variables in the integrand, of a type leaving the integral invariant. We shall have $(R_i)^{-1}R_i\psi=\psi$, in the first term. The operator $(R_i)^{-1}$ commutes with the Hamiltonian, so that the remainder of the integrand will involve $(R_i)^{-1}R_j\psi'$. Let

$$(R_i)^{-1}R_j=R_s, \qquad R_j=R_iR_s. \quad (35)$$

We may replace the summation over R_i and R_j by one over R_i and R_s. Then the expression of Eq. (34) is transformed into

$$\int f_{ab}^{P*}(H)_{op}F_{cd}^{P'}\,dv=\sum(R_i,\,R_s)\,\Gamma_P(R_i)_{ab}\Gamma_{P'}(R_iR_s)_{cd}^*\int\psi^*(H)_{op}(R_s\psi')\,dv. \quad (36)$$

We may use Eq. (2) to write $\Gamma_{P'}(R_iR_s)_{cd}^*$ in the form

$$\Gamma_{P'}(R_iR_s)_{cd}^*=\sum(e)\,\Gamma_{P'}(R_i)_{ce}^*\Gamma_{P'}(R_s)_{ed}^*. \quad (37)$$

Then the quantity multiplying the integral in Eq. (36) is

$$\sum(R_i,\,R_s,\,e)\,\Gamma_P(R_i)_{ab}\Gamma_{P'}(R_i)_{ce}^*\Gamma_{P'}(R_s)_{ed}^*. \quad (38)$$

We now use the general orthogonality theorem of matrix elements of the irreducible representations of a group, which is

$$\sum(R_i)\,\Gamma_P(R_i)_{ab}\Gamma_{P'}(R_i)_{ce}^*=(g/n_P)\;\delta_{PP'}\;\delta_{ac}\;\delta_{be}. \quad (39)$$

This theorem is proved in texts on group theory, and is discussed in Ref. 2, Vol. 2, Appendix 12. Here g is the number of operations in the group, n_P is the dimensionality of the P'th irreducible representation. When we use Eq. (39), we then have

$$\int f_{ab}^{P*}(H)_{op}F_{cd}^{P'}\,dv=(g/n_P)\delta_{PP'}\;\delta ac\sum(R_s)\,\Gamma_P(R_s)_{bd}^*\int\psi^*(H)_{op}(R_s\psi')\,dv. \quad (40)$$

The first thing which we note from Eq. (40) is that

the nondiagonal matrix element vanishes unless P and P' are the same, or we are dealing with matrix elements between basis functions for the same irreducible representation, and furthermore $a=c$, or we are dealing with basis functions for the same partner of the irreducible representation. In such a case we can find the matrix elements by carrying out a single summation over R_s, of integrals $\int\psi^*(H)_{op}(R_s\psi')\,dv$. In other words, we need to perform the symmetrizing operations only on the function ψ', and are not required to carry out these operations on ψ as well. The reason for this can be understood in the following way. An arbitrary function ψ can be decomposed into parts by the use of projection operators, each of which is a basis function for one of the partners for one of the irreducible representations of the group. The only part of this decomposed function which will have a nonvanishing matrix element with a symmetrized function $\sum(R_s)\Gamma_P(R_s)_{bd}{}^*R_s\psi'$, is the part which has the same symmetry as this symmetrized function. It is then unnecessary to symmetrize ψ before carrying out the integration. The most familiar example of this situation is found when we wish to find the matrix element of the Hamiltonian between two antisymmetrized or determinantal functions. The antisymmetrizing operator is a projection operator, of the type which we are considering. It is a well-known theorem that in computing such a matrix element, we need to antisymmetrize only the second function ψ', and can leave the first function ψ^* unsymmetrized.

Our functions $f_{ab}{}^P$ and $F_{cd}{}^{P'}$ are not normalized. Ordinarily we wish to find matrix elements between normalized functions. In this case we should divide Eq. (40) by the square root of the product of the normalizing integrals $\int f_{ab}{}^{P*}f_{ab}{}^P\,dv$ and $\int F_{cd}{}^{P'*}F_{cd}{}^{P'}\,dv$. To find the first of these integrals we may use Eq. (40), let $P'=P$, $c=a$, $d=b$, $\psi'=\psi$, and omit the operator $(H)_{op}$, replacing it by unity. Then we have

$$\int f_{ab}{}^{P*}f_{ab}{}^P\,dv=(g/n_P)\int\psi^*\sum(R_s)\Gamma_P(R_s)_{bb}{}^*R_s\psi\,dv \tag{41}$$

with a similar quantity for the other symmetrized function. Then we find for the matrix element of the Hamiltonian between normalized functions the quantity

$$\int f_{ab}{}^{P*}(H)_{op}F_{ad}{}^P\,dv\Big/\left(\int f_{ab}{}^{P*}f_{ab}{}^P\,dv\int F_{ad}{}^{P*}F_{ad}{}^P\,dv\right)^{\frac{1}{2}}$$

$$=\int\psi^*(H)_{op}\sum(R_s)\Gamma_P(R_s)_{bd}{}^*(R_s\psi')\,dv\Big/\left[\int\psi^*\sum(R_t)\Gamma_P(R_t)_{bb}{}^*R_t\psi\,dv\int\psi'{}^*\sum(R_u)\Gamma_P(R_u)_{dd}{}^*\psi'\,dv\right]^{\frac{1}{2}}. \tag{42}$$

We note that this result is independent of a, showing that we have the same matrix element no matter which partner of the set of basis functions we use. This is the origin of the degeneracy mentioned in Sec. 1, between the various basis functions of an irreducible representation.

7. APPLICATION TO TIGHT-BINDING, OPW, AND APW METHODS

A large part of the analysis in the preceding sections applies irrespective of the form of the function ψ; only a small part of the treatment is restricted to plane waves. Let us now consider how to build up functions of a suitable symmetry to serve as symmetry orbitals for the solution of Schrödinger's equation in a periodic potential, using different types of functions as a starting point. So far we have considered only plane waves, and an expansion of the wave function in plane waves is too slowly convergent to be of much practical value.

In many ways the simplest approximation to the wave function of an electron in a crystal is found by the method of linear combinations of atomic orbitals, the LCAO method, which for a crystal involves the Bloch sums. Suppose we let the function ψ be an atomic orbital on one of the atoms of the crystal. Then we can use our projection operator method, with the same matrix elements of the irreducible representations as before (these depend only on the symmetry of the problem, and are quite independent of the functions ψ). The only difference comes in the effect of the operators $\{R_i\,|\,\mathbf{T}_n\}$ on one of the atomic orbitals. If an atomic orbital is written as $a(\mathbf{r})$, where a can depend on the angle as well as the radial distance from the origin, which is taken to be the nucleus, then by Eq. (12′) we have

$$\{R_i\,|\,\mathbf{T}_n\}a(\mathbf{r})=a(\boldsymbol{\alpha}^i\mathbf{r}+\boldsymbol{\tau}^i+\mathbf{T}_n). \tag{43}$$

That is, the effect of operating on the atomic wave function with one of the operators of the space group is to produce a new atomic function, centered on an atom displaced by the amount $-\boldsymbol{\tau}^i-\mathbf{T}_n$ from the origin, and rotated in space by the operator related to the matrix $\boldsymbol{\alpha}^i$.

When we produce a symmetrized function by the projection operator method, we first take account of Eq. (21), which says that the matrix element $\Gamma_P\{R_i\,|\,\mathbf{T}_n\}_{ab}$ contains the factor $\exp i\mathbf{k}_0\cdot\mathbf{T}_n$. In setting up the projection operator, we use the complex conjugate of this

matrix element and sum over $\mathbf{T}_n$ (as well as over R_i). This summation of atomic orbitals displaced by the amount $-\mathbf{T}_n$, multiplied by the factor $\exp -i\mathbf{k}_0\cdot\mathbf{T}_n$, is simply an ordinary Bloch sum, showing that this procedure of using Bloch sums is a direct result of the translational symmetry of the space group.

We must give more attention, however, to the rotational operations, and to the nonprimitive translations $\boldsymbol{\tau}^i$. Suppose we have an atom at the origin, and suppose we consider the operations of the space group for which $\mathbf{T}_n=0$. There will be some of the operations of the point group for which $\boldsymbol{\tau}^i=0$, others for which it is not zero. For instance, in the space group of the diamond structure, if we take the origin at an atom, we find that the operations for which $\boldsymbol{\tau}^i=0$ are those of the tetrahedral group T_d; the additional operations for which $\boldsymbol{\tau}^i\neq 0$ are those belonging to the cubic group O_h which are not included in the tetrahedral group. If we start with an orbital of no special symmetry at the origin, the first set of operations will produce a symmetrized atomic orbital at the origin, having one of the appropriate symmetries for the point group T_d. The remaining operations corresponding to $\mathbf{T}_n=0$, in this particular case, will produce an atomic orbital at the location of the second atom in the unit cell, like that at the first atom, but suitably rotated or reflected to accord with the symmetry of the space group. When we have carried out these operations for $\mathbf{T}_n=0$, we can next sum over $\mathbf{T}_n$, producing Bloch sums of these symmetrized atomic orbitals extending over the whole crystal. Such a Bloch sum of suitably symmetrized atomic orbitals is the type of symmetrized function formed by the projection operator method when we start with an atomic orbital.

If we start with an atom which is not located at the origin, we can find the effect of the operators of the space group on this atomic orbital by transforming the expression of Eq. (43) to the new origin. We can understand the situation better if we consider what are called special positions in the crystal lattice. If we start with a given atom at position $\mathbf{r}$, and operate on this position vector with all the operations of the space group, each operation in general will produce from it another position $\mathbf{r}'=\boldsymbol{\alpha}^i\mathbf{r}+\boldsymbol{\tau}^i+\mathbf{T}_n$. Since the potential is assumed to be unchanged by any operation of the space group, there must be an identical atom at each position $\mathbf{r}'$. The number of operations equals the product of the number of operations of the point group, and the number of translations required to go from a given unit cell to each unit cell of the crystal. Hence the number of positions $\mathbf{r}'$ located inside a given unit cell will in general equal the number of operations in the point group. This is characteristic of so-called general positions in the crystal.

There are, however, certain special positions within the unit cell, such that if we construct all the positions $\mathbf{r}'$ as before, these positions will not all be distinct. The origin, in a symmorphic space group, is an extreme case of such a special position: every operation of the point group transforms the origin into itself. The existence of these special positions is of great importance in studying possible crystal structures. An atom located at a special position will be one of a number of equivalent atoms in the unit cell, this number equalling the number of operations in the point group, divided by the number of operations of the point group which transform the vector $\mathbf{r}$ out to the atom into itself. It is clear that in a space group connected with a point group with many operations, such as the cubic point group with 48 operations, any crystal with only a few atoms in the unit cell must have these atoms located at special positions.

We now see that if an atom is located at a special position, there will be several operations of the space group which will transform its position into itself. Other operations will transform it into another position, either in the same or another unit cell. The operations which transform it into itself will form a point group; they leave the atomic position invariant. They are like the operations T_d which transform the atom at the origin in the diamond case into itself. We may call this point group the group of the special position. It is analogous to the group of the wave vector, which in a similar way transforms a position in reciprocal space into itself. If we now choose the origin of coordinates at the special position where the atom is located, the point group of the special position will then appear in standard form, so that we can recognize it and consider its irreducible representations.

Any wave function forming a basis for an irreducible representation of the space group can be expanded in power series about such a special position, and the resulting polynomials of various powers in the coordinates will form basis functions for an irreducible representation of the point group of the special position. By such expansion, then, we can find what type of behavior at each atomic position is required to produce the desired type of symmetry. We now see the relation of this discussion to the study of linear combinations of atomic orbitals. For a function of a definite type of symmetry, the symmetry of an atomic orbital located at any special position is prescribed. If we start with an atomic orbital function of arbitrary type at this site, and use the projection operator, we shall remove everything except that part of the orbital which has the correct symmetry. The problem can be simplified, however, if we start from the beginning with atomic orbitals of the correct symmetry type. We thus have in our study of symmetry orbitals of space groups the machinery for setting up linear combinations of atomic orbitals of any desired symmetry, as well as of symmetrized plane waves of the same symmetry.

The OPW, or orthogonalized plane wave, method for approximating to the solution of a periodic potential problem can be described in the following way,

though this is not exactly the method ordinarily followed. We first set up a linear combination of symmetrized LCAO's, by the method just outlined, corresponding to each of the inner atomic orbitals in each of the atoms of the crystal. Since a linear combination of these by themselves will lead to a rather poor approximation for the true wave functions, we supplement them with symmetrized plane waves of the same symmetry. The linear combination of symmetrized LCAO's gives the wave function the proper behavior near the nuclei, and addition of a linear combination of symmetrized plane waves corrects the wave function in the regions between atoms. From our study we have learned how to set up these symmetrized functions. From Sec. 6 we understand how to find the matrix elements of the Hamiltonian between such symmetrized basis functions. In the discussion of that section, such as Eq. (42), there is nothing demanding that the functions ψ, ψ' which we are symmetrizing should be plane waves; one or both could be atomic orbitals. We then have the foundation of the method of computing the energy matrix for the OPW method, a matrix which must be diagonalized in the usual way to give the best OPW approximation to the solution of the periodic potential problem.

The APW, or augmented plane wave, method involves symmetry in a very similar way. Here we surround each atom by a sphere, within which we expand the wave function as a linear combination of spherical harmonics, each multiplied by a radial function which gives a solution of Schrödinger's equation for a spherically symmetrical potential approximating the true potential within the sphere. Outside the sphere we expand the wave function in plane waves. At a symmetry position in the Brillouin zone, we use a symmetrized plane wave outside the spheres. Inside, we have exactly the same symmetry problem as for the LCAO method. We use only those spherical harmonics or combinations of them which form basis functions for the suitable irreducible representations of the point group of the special position where the atomic sphere is located.

We shall not go further here into the details of the method used in these various schemes for setting up the symmetrized functions. In actual applications the process of symmetrizing is usually carried out by programming the computer. The underlying principles, however, are those which have been outlined in this paper, which are discussed for a number of individual cases in Ref. 2, and which are the same, no matter what method of approximation to the solution is used.

One remark should be made regarding the text mentioned in Ref. 2: it contains extensive bibliographies of topics related to the symmetry of wave functions, and methods of calculating them in molecules and solids. For this reason we have not included an extensive set of references in the present paper.

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APPENDIX

We start by finding $f_{bd}{}^P$ by Eq. (24), where

$$\Gamma_P\{R_i \mid 0\}_{ab}$$

is assumed to be given by Eq. (25). Thus we have

$$\begin{aligned} f_{bd}{}^P &= \sum (R_j)\, \Gamma_P(R_j)_{bd}{}^* \exp -i\mathbf{k}_0\cdot\boldsymbol{\tau}^j \\ &\qquad \{R_j \mid 0\} \exp i(\mathbf{k}_0+\mathbf{K})\cdot\mathbf{r} \\ &= \sum (R_j)\, \Gamma_P(R_j)_{bd}{}^* \exp -i\mathbf{k}_0\cdot\boldsymbol{\tau}^j \\ &\qquad \exp i(\mathbf{k}_0+\mathbf{K})^j\cdot\mathbf{r} \exp i(\mathbf{k}_0+\mathbf{K})\cdot\boldsymbol{\tau}^j \\ &= \sum (R_j)\, \Gamma_P(R_j)_{bd}{}^* \exp i(\mathbf{k}_0+\mathbf{K})^j\cdot\mathbf{r} \exp i\mathbf{K}\cdot\boldsymbol{\tau}^j, \end{aligned} \tag{A1}$$

where

$$(\mathbf{k}_0+\mathbf{K})_q{}^j = \sum (p)\, \alpha_{pq}{}^j (\mathbf{k}_0+\mathbf{K})_p. \tag{A2}$$

The group we are considering is the group of the wave vector. That is, it leaves $\mathbf{k}_0$ unchanged, or

$$(k_0)_q{}^j = \sum (p)\, \alpha_{pq}{}^j (k_0)_p = (k_0)_q \tag{A3}$$

so that $(\mathbf{k}_0+\mathbf{K})^j = \mathbf{k}_0+\mathbf{K}^j$.

Now we let the operator $\{R_i \mid 0\}$ operate on the function $f_{bd}{}^P$, to see if it forms a basis function for the Pth irreducible representation, with matrix elements given by Eq. (25). We have

$$\begin{aligned} \{R_i \mid 0\} f_{bd}{}^P &= \sum (R_j)\, \Gamma_P(R_j)_{bd}{}^* \exp i(\mathbf{k}_0+\mathbf{K}^k)\cdot\mathbf{r} \\ &\qquad \exp i\mathbf{k}_0\cdot\boldsymbol{\tau}^i \exp i\mathbf{K}^j\cdot\boldsymbol{\tau}^i \exp i\mathbf{K}\cdot\boldsymbol{\tau}^j, \end{aligned} \tag{A4}$$

where

$$K_q{}^k = \sum (p)\, \alpha_{pq}{}^k K_p \tag{A5}$$

with $\alpha_{pu}{}^k$ given in Eq. (14), and where again we have used the fact the $\mathbf{k}_0$ is not transformed by the operations of the group of the wave vector.

We now use Eqs. (15) and (16), which hold when we perform two operations in succession on a plane wave. We take the scalar product of the vector $\mathbf{K}$ with the expression of Eq. (15) set $\mathbf{T}_n$ and $\mathbf{T}_m$ equal

to zero, and find

$$\mathbf{K}^j\cdot\boldsymbol{\tau}^i+\mathbf{K}\cdot\boldsymbol{\tau}^j=\mathbf{K}\cdot\boldsymbol{\tau}^k+\mathbf{K}\cdot\mathbf{T}_{ij}. \tag{A6}$$

Hence we have

$$\exp i\mathbf{K}^j\cdot\boldsymbol{\tau}^i \exp i\mathbf{K}\cdot\boldsymbol{\tau}^j=\exp i\mathbf{K}\cdot\boldsymbol{\tau}^k, \tag{A7}$$

where the factor $\exp i\mathbf{K}\cdot\mathbf{T}_{ij}$ equals unity. Thus the expression of Eq. (A4) can be rewritten as

$$\{R_i\mid 0\}f_{bd}{}^P=\sum(R_j)\,\Gamma_P(R_j)_{bd}{}^* \times\exp i(\mathbf{k}_0+\mathbf{K}^k)\cdot\mathbf{r}\exp i\mathbf{k}_0\cdot\boldsymbol{\tau}^i\exp i\mathbf{K}\cdot\boldsymbol{\tau}^k. \tag{A8}$$

Following Eq. (1), we should like to prove that this expression is given by

$$\sum(a)\,\Gamma_P\{R_i\mid 0\}_{ab}f_{ad}{}^P. \tag{A9}$$

where $f_{ad}{}^P$ is given by Eq. (A1), with a substituted for b. That is, we should like to prove that the right side of Eq. (A8) equals

$$\sum(a)\,\Gamma_P(R_i)_{ab}\exp i\mathbf{k}_0\cdot\boldsymbol{\tau}^i\sum(R_k)\,\Gamma_P(R_k)_{ad}{}^* \times\exp i(\mathbf{k}_0+\mathbf{K}^k)\cdot\mathbf{r}\exp i\mathbf{K}\cdot\boldsymbol{\tau}^k, \tag{A10}$$

where we have used R_k as an index of summation rather than R_j as we have in Eq. (A1).

When we compare the expressions of Eqs. (A8) and A(10), we see that they would agree if we had

$$\sum(R_j)\,\Gamma_P(R_j)_{bd}{}^*=\sum(a,\,R_k)\,\Gamma_P(R_i)_{ab}\Gamma_P(R_k)_{ad}{}^*. \tag{A11}$$

The proof of this equation is similar to that for Eq. (4). We note that $R_iR_j=R_k$, where these are operators of the point group. Hence we can use the multiplication rule, Eq. (2). Furthermore, for matrix elements of irreducible representations, we can prove that

$$\Gamma_P(R_i)_{ab}=\Gamma_P(R_i^{-1})_{ba}{}^*, \tag{A12}$$

where R_i^{-1} is the inverse operation to R_i. Then the right side of Eq. (A11) can be rewritten in the form

$$\sum(R_k)\sum(a)\,\Gamma_P(R_i^{-1})_{ba}{}^*\Gamma_P(R_k)_{ad}{}^* =\sum(R_k)\,\Gamma_P(R_i^{-1}R_k)_{bd}{}^*=\sum(R_j)\,\Gamma_P(R_j)_{bd}{}^*, \tag{A13}$$

as was to be proved. We have carried out the final summation in Eq. (A13) over R_j rather than R_k, but we cover the same set of operations, namely all operations of the point group, in either case. With this equation we complete the proof that the matrix elements of the operators $\{R_i\mid 0\}$ for the basis functions of Eq. (A1) are those assumed in Eq. (25), so that these latter values form in fact the matrix elements for irreducible representations of the space group.