Orthogonal Orbitals and Generalized Wannier Functions

JACQUES DES CLOIZEAUX*
University of California, San Diego, La Jolla, California
(Received 13 August 1962)

The invariance properties of a one-electron Hamiltonian $H=T+V$ with respect to the transformations of a space group G_H are used to show how the eigenfunctions of H can be expanded in terms of equivalent local orbitals. These orbitals are built from a suitable set of eigenfunctions and are shown to be orthogonal to each other. They are associated with the points M of a lattice $\mathfrak{L}$ which is invariant with respect to G_H and can be obtained from each other by space transformations. Group theory is used to write explicitly the unitary relations connecting the set of eigenfunctions of H and the corresponding orbitals. In crystals, it is shown that the eigenfunctions belonging to an energy band can often be described by means of one set of orbitals, provided that certain simple conditions are fulfilled. These conditions depend on the properties of the levels which correspond to the points Σ of maximum symmetry in the reciprocal space. These requirements determine also the nature of the lattice $\mathfrak{L}$ and the chemical bonding in the band.

I. INTRODUCTION

THE aim of this paper is to show how the symmetry properties of a one-electron Hamiltonian $H=T+V$ imply the possibility of expanding its eigenfunctions in terms of local orbitals. The Hamiltonian H is assumed to be invariant with respect to the transformations of a space group G_H. Equivalent orthonormal orbitals are defined as linear combinations of functions belonging to a suitable set of eigenfunctions of H. Two orbitals are said to be *equivalent* if they can be obtained from each other by some space transformation belonging to G_H. Conversely, it is shown that the eigenfunctions of H can be expanded in terms of the corresponding orbitals.

This problem is by no means a new one and it is possible to quote very well-known examples of localized orbitals such as the atomic orbitals used in the tight binding approximation (LCAO method) and the Wannier functions in a crystal. Hall,[1] among others, has studied the case of atomic orbitals but his treatment is incomplete. On the other hand, the properties of one-dimensional Wannier functions have been thoroughly investigated by Kohn,[2] for a one-dimensional infinite crystal with a center of symmetry. In particular, Kohn has proved that each band corresponds to a well-defined set of Wannier functions decreasing at infinity as fast as an exponential. Unfortunately, his method cannot be generalized because the analytic properties of the Bloch functions depend on the dimensionality of the space. In two and three dimensions, special cases have been considered by Blount[3]; however, a general treatment seems to be lacking.

Therefore, it is of interest to examine the question from a more general point of view. In this paper, we are mainly concerned with the group theoretical aspects of this problem, which can be investigated by using only elementary methods and a few basic theorems. The localizability properties of the orbitals are not discussed because they depend essentially on the phases of the eigenfunctions from which the orbitals are built. Of course, it is very important, especially in the case of crystals, to know how to determine suitable phase factors for these eigenfunctions; however, to solve this problem, it is necessary to examine carefully the analytic properties of the eigenfunctions of H and, in general, the problem is very complex. Therefore, this question is not studied here; we hope to carry out this task in another publication.

In Sec. II, we study the case where G_H is a general finite group, by applying the general methods of group theory. We show how orbitals can be built from a suitable set of eigenfunctions of H and conversely how these eigenfunctions can be expanded in terms of the orbitals. In Sec. III, we consider the special case of crystals. In a crystal, the energy levels form bands. Each band is usually made up of several branches which are connected; conversely and by definition, if two branches are connected, they belong to the same band. Thus, we study the possibility of representing a band by a set of orbitals which may be called generalized Wannier functions. In particular, it is shown that the nature of the orbitals which correspond to the bands of a crystal determines the nature of the chemical bonds in the crystal.

We hope that in spite of the apparent complexity of the formalism, the reader will appreciate the real simplicity of the theory. For the sake of clarity, all the symbols used in this paper are listed in Appendix I.

II. GENERAL DEFINITION OF LOCALIZED ORBITALS FOR A FINITE SPACE GROUP G_H

A. Definition of a General Lattice $\mathfrak{L}$ and of the Subgroups G_M Related to the Points M of $\mathfrak{L}$

A general lattice $\mathfrak{L}$ associated with a finite space group G_H is the set of all the distinct points M which can be obtained from a given point M_0 in space, by transformations belonging to G_H. All the points M of a lattice are equivalent and can be used to generate the

* On leave from the Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette, France.

[1] G. G. Hall, Proc. Roy. Soc. (London) **A202**, 336 (1950); G. G. Hall and J. E. Lennard-Jones, *ibid.* **A202**, 155 (1950).

[2] W. Kohn, Phys. Rev. **115**, 809 (1959).

[3] E. I. Blount (to be published).

whole lattice. If G_H is a translation group in a cyclical space (G_H must be finite), then $\mathfrak{L}$ is a Bravais lattice; but in general (even if G_H contains a subgroup of translations) $\mathfrak{L}$ is not a Bravais lattice. For instance, the corners of a square in ordinary space form a lattice which is not a Bravais lattice.

The group G_H itself is the space group which leaves the Hamiltonian H invariant. The orbitals to be deduced from eigenfunctions of H are attached to the points M of a lattice $\mathfrak{L}$; the choice of M_0 being arbitrary, the lattice $\mathfrak{L}$ is chosen at our convenience.

In the following we associate with each point M: (a) the subgroup G_M of G_H which contains all the transformations leaving M invariant, and (b) an element S_{MM_0} of G_H which transforms M_0 into M. Any element R which transforms M_0 into M can be written

$$R=S_{MM_0}R_{M_0}, \tag{1}$$

where R_{M_0} is an element of G_{M_0}. Thus, N being the number of points M, we can generate $(N-1)$ cosets of G_{M_0}. Therefore, g and g_{M_0} being, respectively, the numbers of elements of G_H and G_{M_0}, we have

$$N=g/g_{M_0}. \tag{2}$$

The groups G_M and G_{M_0} are isomorphic and a correspondence between the elements of G_{M_0} and the elements of G_M can be established in the following way:

$$R_M=S_{MM_0}R_{M_0}S_{MM_0}{}^{-1}. \tag{3}$$

Therefore, to any irreducible representation $\Gamma_{M_0}{}^m$ of the elements R_{M_0}, corresponds an identical representation $\Gamma_M{}^m$ of the elements R_M. The irreducible representations of G_H and G_{M_0} are connected by a relation which is very useful for our purpose. Any irreducible representation $\Gamma_H{}^l$ of G_H subduces[4] a usually reducible representation $[\Gamma_H{}^l]_M$ of G_M. In the following, it is assumed that all the representations $[\Gamma_H{}^l]_{M_0}$ are, in fact, completely reduced with respect to the irreducible representations $\Gamma_{M_0}{}^m$ of G_{M_0}:

$$[\Gamma_H{}^l]_{M_0}=\sum_m C(l|m)\Gamma_{M_0}{}^m. \tag{4}$$

All these representations are also assumed to be unitary.

B. Labeling and Transformation Properties of the Eigenstates of H

The invariance properties of H are now used to classify the eigenstates of H. It is possible to find a complete set of orthonormal eigenstates forming bases for the irreducible representations $\Gamma_H{}^l$ of G_H and for the irreducible representations $\Gamma_{M_0}{}^m$ of G_{M_0} contained in the reduced representation $[\Gamma_H{}^l]_{M_0}$. Such an eigenstate is denoted by the symbol $|l_p m_q \mu\rangle$. The index p is used to distinguish from each other the eigenstates which form independent bases of the same representation $\Gamma_H{}^l$. In general, eigenstates corresponding to different values of p are nondegenerate, but all the eigenstates labeled by the same index p are degenerate. In the same way, the index q is used to distinguish from each other the different equivalent representations $\Gamma_{M_0}{}^m$ contained in $[\Gamma_H{}^l]_{M_0}$ and to label the corresponding eigenstates of H. According to (4), q may take $C(l|m)$ different values; for instance, $q=1, \cdots, C(l|m)$. The index μ is used to label the basis vectors of a given representation $\Gamma_{M_0}{}^m$ of dimensionality $d_M{}^m$; it may be used also to specify the rows or the columns of a matrix of $\Gamma_{M_0}{}^m$. It takes the values $\mu=1, \cdots, d_M{}^m$. The eigenfunction $\varphi(l_p m_q \mu)$ corresponding to the state $|l_p m_q \mu\rangle$ can be defined by the identity

$$\varphi(l_p m_q \mu)\equiv\langle r|l_p m_q \mu\rangle. \tag{5}$$

An element R of G_H transforms this eigenfunction in the following way:

$$R\varphi(l_p m_q \mu)=\langle r|R|l_p m_q \mu\rangle=\sum_{l'p'm'q'\mu'}\langle r|l'_{p'}m'_{q'}\mu'\rangle \times\langle l'_{p'}m'_{q'}\mu|R|l_p m_q \mu\rangle. \tag{6}$$

This expression can now be simplified by introducing the elements $\langle m'_{q'}\mu'|{}^lR|m_q\mu\rangle$ of the unitary matrix ${}^lR$ which represents the operator R in $\Gamma_H{}^l$

$$R\varphi(l_p m_q \mu)=\sum_{m'q'\mu'}\varphi(l_p m'_{q'}\mu')\langle m'_{q'}\mu'|{}^lR|m_q\mu\rangle. \tag{7}$$

C. Construction of the Set $\mathcal{E}(\mathfrak{L},m)$ and Definition of the Orbitals

Now we would like to investigate the possibility of expressing a chosen set of eigenfunctions $\varphi(l_p m_q \mu)$ as linear combinations of localized orbitals associated with the sites M of some lattice $\mathfrak{L}$. However, this problem is difficult to solve directly. Therefore, we use a slightly different approach.

The nature of the orbitals is determined arbitrarily: (a) by choosing *a priori* a point M_0 which defines a lattice $\mathfrak{L}$ of points M, and (b) by assuming that the orbitals $M(m,\mu)$ which are associated with a site M form a basis for an irreducible representation $\Gamma_M{}^m$ of G_M isomorphic to a given representation $\Gamma_{M_0}{}^m$ of G_{M_0}. Thus, in the following, the index m remains fixed, while the index μ takes all possible different values. Now these orbitals have to be built by forming linear combinations of eigenfunctions $\varphi(l_p m_q \mu)$ which belong to a suitable set $\mathcal{E}(\mathfrak{L},m)$. This set, as is proved later, can be defined as follows.

A lattice $\mathfrak{L}$ and a representation $\Gamma_{M_0}{}^m$ being given, a set $\mathcal{E}(\mathfrak{L},m)$ contains, by definition, all the eigenfunctions $\varphi(l_p n_q \nu)$ belonging to any representation $\Gamma_H{}^l$ and labeled by an index p which, for each value of l, may take $C(l|m)$ different values. These requirements may seem a little strange but they stem from the Frobenius theorem (see Appendix I). In fact, the set of all the orbitals $M(m,\mu)$ form the basis of a representation of

[4] A definition of subduced and induced representations is given in the following book: J. S. Lomont, *Application of Finite Groups* (Academic Press Inc., New York, 1959), pp. 89 and 224.

the whole group G_H (induced representation) which is usually reducible. This means that it is, in general, possible to build several linear combinations of orbitals $\varphi(l_p m_q \mu)$ belonging to the same representation $\Gamma_H{}^l$ of G_H. Now the Frobenius theorem states that the number of these functions is really equal to the coefficient $C(l|m)$ of Eq. (4) and this fact explains the definition of a set $\mathcal{E}(\mathfrak{L},m)$. The $C(l|m)$ different values of p which correspond to the eigenfunctions of $\mathcal{E}(\mathfrak{L},m)$ are chosen somewhat arbitrarily but in the following it is assumed, for reasons of convenience, that p may take one of the values $p=1, \cdots, C(l|m)$. Therefore, d^l being the dimensionality of $\Gamma_H{}^l$, the number N_m of functions contained in $\mathcal{E}(\mathfrak{L},m)$ is

$$N_m=\sum_l C(l|m)d^l. \tag{8}$$

The orbitals associated with M_0 are defined in the following way:

$$M_0(m,\mu)=N_m{}^{-1/2}\sum_l \sum_{p=1}^{C(l|m)} (d^l)^{1/2}\varphi(l_p m_p \mu). \tag{9}$$

These functions are orthonormal and form a basis for $\Gamma_{M_0}{}^m$.

Now the orbitals $M(m,\mu)$ associated with a general site M of $\mathfrak{L}$, can be defined as the transforms of the orbitals $M_0(m,\mu)$ by S_{MM_0}

$$M(m,\mu)=S_{MM_0}M_0(m,\mu)$$
$$=N_m{}^{-1/2}\sum_l \sum_{p=1}^{C(l|m)} S_{MM_0}\varphi(l_p m_p \mu). \tag{10}$$

Since G_{M_0} and G_M are isomorphic and connected by (3), the orbitals $M(m,\mu)$ corresponding to a site M, form a basis for $\Gamma_M{}^m$. Using (7), we can now write explicitly

$$M(m,\mu)=N_m{}^{-1/2}\sum_{lpnq\nu} (d^l)^{1/2}\varphi(l_p n_q \nu)$$
$$\times\langle n_q\nu|\,{}^lS_{MM_0}|\,m_p\mu\rangle. \tag{11}$$

D. Expression Giving the Eigenfunctions $\varphi(l_p n_q \nu)$ in Terms of the Orbitals $M(m,\mu)$

N_m which is the number of eigenfunctions contained in $\mathcal{E}(\mathfrak{L},m)$, is also the total number of orbitals $M(m,\mu)$, as can be shown easily by applying a classical theorem[5] of group theory and by taking into account Eq. (2)

$$N_m=\sum_l C(l|m)d^l=(g/g_{M_0})d_M{}^m=Nd_M{}^m. \tag{12}$$

This equality suggests that by inversion of (10) the eigenfunctions $\varphi(l_p n_q \nu)$ might be expressed as a linear combination of orbitals. In fact, we have

$$\varphi(l_p n_q \nu)=N_m{}^{-1/2}(d^l)^{1/2}\sum_{M\mu} M(m,\mu)$$
$$\times\langle m_p\mu|\,{}^lS_{MM_0}{}^{-1}|\,n_q\nu\rangle. \tag{13}$$

[5] W. Burnside, *Theory of Groups of Finite Order* (Dover Publications, New York, 1955), Sec. 246, p. 330.

This formula is easily verified by replacing, in the second member of (13), $M(m,\mu)$ by its expansion (11) and by taking into account the relation (12) and the following closure relation which is proved in Appendix II.

$$\sum_{M\mu}\langle n'_{q'}\nu'|\,{}^{l'}S_{MM_0}|\,m_{p'}\mu\rangle\langle m_p\mu|\,{}^lS^{-1}{}_{MM0}|\,n_q\nu\rangle$$
$$=(g/g_M)(d_M{}^m/d^l)\delta_{ll'}\delta_{pp'}\delta_{nn'}\delta_{qq'}\delta_{\nu\nu'}. \tag{14}$$

E. Orthogonality of the Orbitals $M(m,\mu)$

The orthogonality of the orbitals which belong to the same site M is obvious because they form a basis for an irreducible unitary representation $\Gamma_M{}^m$. To prove the orthogonality of orbitals belonging to different sites, we need another closure relation which can be found in the following way. If, in formula (11) which defines $M(m,\mu)$, we replace $\varphi(l_p n_q \nu)$ by its expansion (13), we obtain

$$M(m,\mu)=N_m{}^{-1}\sum_{lpnq\nu M'\mu'} d^l\ M'(m,\mu')$$
$$\times\langle m_p\mu'|\,{}^lS_{M'M_0}{}^{-1}|\,n_q\nu\rangle\langle n_q\nu|\,{}^lS_{MM_0}|\,m_p\mu\rangle. \tag{15}$$

The orbitals $M(m,\mu)$ are linearly independent because an equal number N_m of orthogonal functions $\varphi(l_p n_q \nu)$ of $\mathcal{E}(\mathfrak{L},m)$ can be built from them, according to (13). Therefore, (14) must be satisfied identically and we get the following relation

$$\sum_{lpnq\nu} d^l\langle m_p\mu'|\,{}^lS_{M'M_0}{}^{-1}|\,n_q\nu\rangle\langle n_q\nu|\,{}^lS_{MM_0}|\,m_p\mu\rangle$$
$$=N_m\delta_{MM'}\delta_{\mu\mu'}. \tag{16}$$

On the other hand, an explicit expression for the scalar product of two orbitals can be derived directly from (11), because our representations are unitary.

$$\langle M'(m,\mu')|\,M(m,\mu)\rangle=N_m{}^{-1}\sum_{pMnq\nu} d^l\langle m_p\mu'|\,{}^lS_{MM_0}{}^{-1}|\,n_q\nu\rangle$$
$$\times\langle n_q\nu|\,{}^lS_{MM_0}|\,m_p\mu\rangle. \tag{17}$$

By using the closure relation (16), we get the orthogonality condition

$$\langle M'(m,\mu')|\,M(m,\mu)\rangle=\delta_{MM'}\delta_{\mu\mu'}. \tag{18}$$

F. Reality of the Orbitals

The Hamiltonian H is assumed to be spin independent and real. Therefore, it is often possible to build orbitals which are real. In fact, as we shall see, if the corresponding representations $\Gamma_M{}^m$ are real, or at least equivalent to their complex conjugate, and if we choose a proper set $\mathcal{E}(\mathfrak{L},m)$, then from this set we can get real orbitals.

If a space-group representation Γ is not real, the functions φ_j forming a basis for this representation cannot be real because a space symmetry always transforms a real function into another real one. When Γ is not real, the functions $\varphi_j{}^*$ form a basis for the complex

conjugate representation Γ^*. We now prove that if Γ and Γ^* are equivalent, they are also equivalent to a real representation. In fact, if Γ and Γ^* are equivalent, the matrices R and R^* corresponding to any element of the space group in the two representations, are related by a unitary transformation

$$R^* = URU^{-1}, \tag{19}$$

and we have also

$$\varphi_j^* = U\varphi_j. \tag{20}$$

Therefore, the functions φ_j and φ_j^* span the same space. In this space, we can now choose an orthonormal basis which is real, each basic vector being a real linear combination of the following vectors (which are not all independent):

$$\psi_j = \varphi_j + \varphi_j^*, \quad \chi_j = i(\varphi_j - \varphi_j^*). \tag{21}$$

The representation Γ' corresponding to this new basis is equivalent to Γ and Γ^* and is also real. Conversely, if Γ and Γ^* are not equivalent, the functions φ_j are independent of the functions φ_j^* and it is impossible to find for Γ any real basis because a representation of a space group of real transformations is real if its basis is real.

Now we can assume, without loss of generality, that any representation Γ_{M^m} which is equivalent to its complex conjugate is also real. The same property may be assumed to hold also for any representation Γ_{H^l} and is compatible with the complete reducibility of $[\Gamma_{H^l}]_{M_0}$. On the other hand, if Γ_{M^m} is real, a set $\mathcal{E}(\mathfrak{L},m)$ containing a basis for a representation Γ_H contains also a basis for the complex conjugate representation Γ_H^*.

Therefore, when Γ_{M^m} is real, it is possible to build sets $\mathcal{E}(\mathfrak{L},m)$ satisfying the following conditions: (a) If a function of $\mathcal{E}(\mathfrak{L},m)$ is real, it belongs to a real representation. (b) If a function φ of $\mathcal{E}(\mathfrak{L},m)$ is not real, it belongs to a complex representation Γ^l and the function φ^* is contained in $\mathcal{E}(\mathfrak{L},m)$ and belongs to a complex conjugate representation $\Gamma^{l'}$.

In the second case, by labeling our states in a proper way, we can write explicitly

$$\varphi^*(l_p n_q \nu) = \varphi(l'_p n_q \nu). \tag{22}$$

Now the reality of all the orbitals $M(m,\mu)$ results from the definition (9) of $M_0(m,\mu)$ and from the definition (10) of the other orbitals.

G. Localizability of the Orbitals. Choice of a Set $\mathcal{E}(\mathfrak{L},m)$

The orbitals which can be built from a given set $\mathcal{E}(\mathfrak{L},m)$ are not exactly well defined because the functions $\varphi(l_p n_q \nu)$ can always be transformed by a set of unitary matrices $U_{l_p n}$ into equivalent functions $\psi(l_p n_q \nu)$

$$\psi(l_p n_q \nu) = \sum_{q'} \varphi(l_p n_{q'} \nu)\langle q' | U_{l_p n} | q \rangle. \tag{23}$$

This ambiguity in the definition of the functions $\varphi(l_p n_q \nu)$ can be removed by requiring that the orbitals $M_0(m,\mu)$ be as well localized as possible around M_0. However, the concept of localizability is not well defined; therefore, the result depends on our precise requirements.

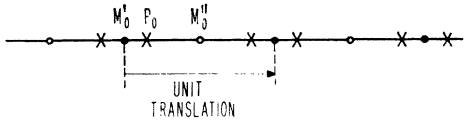

FIG. 1. Linear crystal.

The choice of a set $\mathcal{E}(\mathfrak{L},m)$ remains also really arbitrary, but we want to get orbitals as well localized as possible. A set $\mathcal{E}(\mathfrak{L},m)$ is suitable for this purpose, if the energies corresponding to the different eigenfunctions which are contained in this set are close to each other. Therefore, to achieve this result it may be reasonable and useful to use the following process to build a series of independent sets $\mathcal{E}(\mathfrak{L}_0,m_0)\cdots\mathcal{E}(\mathfrak{L}_n,m_n)\cdots$, containing all the eigenfunctions of H. Let $\mathcal{E}_0(E)$ be the set of all the eigenfunctions of H corresponding to eigenvalues smaller or equal to E. Let E_0 be the upper bound of the values of E such that $\mathcal{E}_0(E)$ does not contain any set $\mathcal{E}(\mathfrak{L},m)$ as a subset. Thus, $\mathcal{E}_0(E_0)$ contains at least one subset $\mathcal{E}(\mathfrak{L},m)$ and usually only one: This subset is the set $\mathcal{E}(\mathfrak{L}_0,m_0)$. Now by excluding from $\mathcal{E}_0(E)$ all the eigenfunctions belonging to $\mathcal{E}(\mathfrak{L}_0,m_0)$ we obtain a new set $\mathcal{E}_1(E)$. By using the same method as above, we can define a set $\mathcal{E}_1(E_1)$ which contains at least one subset $\mathcal{E}(L_1,m_1)$ and so on. In this way, we can build a complete series of sets $\mathcal{E}(L,m)$ corresponding, in general, to different lattices.

H. Example 1

Now, we apply the general formalism to the simple case of a cyclical linear crystal (Born-von Karman condition) with a center of symmetry. This crystal is assumed to contain $2n$ cells of length unity (n is an integer). When the number of cells is odd, the problem is simpler and can be treated exactly in the same way.

The elements of the group G_H can be classified as follows:

(a) The identity E forms a class by itself.

(b) The group G_H contains $(2n-1)$ translations. The symbol T_r represents a translation through r lattice spacings. For each $r=1\cdots(n-1)$ the translations T_r and T_{-r} together form a class. The element T_n forms a class by itself.

(c) The group G_H contains also two classes of reflections with respect to two sets of points M' and M'' which form two independent lattices $\mathfrak{L}'$ and $\mathfrak{L}''$ (see Fig. 1). A reflection with respect to a point of one sublattice is the product of a reflection with respect to a point of the other sublattice and of a translation through an odd number of lattice spacings. The elements belonging to these classes are denoted by the symbols $S_{M'}$ and $S_{M''}$.

The total number of classes of G_H is $(n+3)$ and this is also the number of the irreducible representations of G_H. The Bloch waves φ_k of wave number k belonging to a band $\mathfrak{B}$ form bases for these representations. We note that a translation leaves k invariant but that a reflection transforms k into $-k$. Therefore, the value of $|k|$ can be used to classify the representations of G_H, which are listed with their characters in Table I. The values of $|k|$ corresponding to the representations $\Gamma^{|k|}$ are given by the equality $|k|=\pi n'/n$ with $n'=1,\cdots(n-1)$.

TABLE I. Representation of the group of the linear crystal.

	E	$S_{M'}$	$S_{M''}$	T_τ
$\Gamma_H{}^{0s}$	1	1	1	1
$\Gamma_H{}^{0a}$	1	−1	−1	1
$\Gamma_H{}^{\pi s}$	1	1	−1	−1
$\Gamma_H{}^{\pi a}$	1	−1	1	−1
$\Gamma_H{}^{\lvert k\rvert}$	2	0	0	$2\cos k\tau$

For a given band $\mathfrak{B}$, φ_0 belongs either to $\Gamma_H{}^{0s}$ or $\Gamma_H{}^{0a}$ and φ_π belongs either to $\Gamma_H{}^{\pi s}$ or $\Gamma_H{}^{\pi a}$ depending on the symmetry properties of φ_0 and φ_π. On the other hand, if $k\neq 0, \pi$ the functions φ_k and φ_{-k} form always a basis for $\Gamma_H{}^{|k|}$.

Now, we try to describe the eigenfunctions of one or several bands by means of orbitals, but first we have to choose a lattice $\mathfrak{L}$ and find the nature of the orbitals.

Assumption 1

We assume that M_0 coincides with M_0'; thus $\mathfrak{L}$ and $\mathfrak{L}'$ are identical and it is convenient to define the elements S_{MM_0} as the translations which transform M_0 into M.

The group G_{M_0} contains only two elements E and S_{M_0}. The irreducible representations of this group are $\Gamma_{M_0}{}^s$ (unit representation) and $\Gamma_{M_0}{}^a$. The orbital associated with M_0 can be either symmetric or antisymmetric with respect to M_0. The sets $\mathcal{E}(\mathfrak{L},m)$ corresponding to these two possibilities are denoted by the symbols $\mathcal{E}(\mathfrak{L}',s)$ and $\mathcal{E}(\mathfrak{L}',a)$. For these sets $N_m=2n$ which is the number of eigenfunctions which are contained in a band.

From Table I, we deduce immediately the following equations which give the values of the coefficients $C(l|m)$ [see Eq. (4)]:

$$\begin{aligned}&[\Gamma_H{}^{0s}]_{M_0}=\Gamma_{M_0}{}^s, \quad [\Gamma_H{}^{\pi s}]_{M_0}=\Gamma_{M_0}{}^s,\\ &[\Gamma_H{}^{0a}]_{M_0}=\Gamma_{M_0}{}^a, \quad [\Gamma_H{}^{\pi a}]_{M_0}=\Gamma_{M_0}{}^a,\\ &[\Gamma_H{}^{|k|}]_{M_0}=\Gamma_{M_0}{}^a+\Gamma_{M_0}{}^s.\end{aligned} \tag{24}$$

According to the general definition of a set $\mathcal{E}(\mathfrak{L},m)$, we list for each representation of G_H the number of corresponding bases which are contained in a set $\mathcal{E}(\mathfrak{L}',s)$ or a set $\mathcal{E}(\mathfrak{L}',a)$. (See Table II.) Therefore, if φ_0 and φ_π are both either symmetric or antisymmetric with respect to M_0', the eigenfunctions belonging to $\mathfrak{B}$ constitute a set $\mathcal{E}(\mathfrak{L}',s)$ or a set $\mathcal{E}(\mathfrak{L}',a)$, respectively. If φ_0 and φ_π have not the same symmetry character, the band cannot be described by orbitals referred to the lattice $\mathfrak{L}'$; but the inspection of Table I shows that it can then be described by orbitals referred to the lattice $\mathfrak{L}''$. We return to this question in Sec. III.

As an illustration of our method, let us treat completely the case of a band $\mathfrak{B}$ which can be described by means of symmetric orbitals $M(s)$. We can now introduce functions $\varphi(l_p m_q \mu)$ which in our case can be denoted more simply by the symbol $\varphi(l,m)$. It is always possible to assume that

$$S_{M_0}\varphi_k=\varphi_{-k}, \tag{25}$$

and therefore we may put

$$\begin{aligned}&\varphi(0s,s)=\varphi_0,\\ &\varphi(\pi s,s)=\varphi_\pi,\\ &\varphi(|k|,s)=(\varphi_k+\varphi_{-k})/\sqrt{2},\\ &\varphi(|k|,a)=-i(\varphi_k-\varphi_{-k})/\sqrt{2}.\end{aligned}$$

The orbital $M_0(s)$ is given by the general formula (9) which in this case can be written

$$\begin{aligned}M_0(s)&=(2n)^{-1/2}\Big[\varphi(0s,s)+\varphi(\pi s,s)+\sqrt{2}\sum_{k=1}^{n-1}\varphi(|k|,s)\Big]\\ &\equiv(2n)^{-1/2}\sum_{k=-n+1}^{n}\varphi_k.\end{aligned} \tag{26}$$

The orbitals $M(s)$ are obtained from $M_0(s)$ by the translation S_{MM_0}. Note that the coefficient $\sqrt{2}$ in (26) comes from the dimensionality of the representation $\Gamma_H{}^{|k|}$. In this case, our orbitals are Wannier functions, and our definition coincides with the usual one.

Assumption 2

We may assume as well that we choose an arbitrary point P_0 of the crystal as the origin M_0. The group G_H generates from P_0 a lattice $\mathfrak{L}_P$ which is not a Bravais lattice and contains $4n$ points (twice as many as the lattice $\mathfrak{L}'$). In this case, G_{M_0} has only one element E and one representation $\Gamma_{M_0}{}^1$ (unity). There is only one kind of orbital $\mathcal{E}(\mathfrak{L}_P)$. For such a set, $N_m=4n$ which is the number of eigenfunctions contained in two bands. For any representation $\Gamma_H{}^l$ of G_H, we have

TABLE II. Nature of the sets $\mathcal{E}(\mathfrak{L}',s)$, $\mathcal{E}(\mathfrak{L}',a)$ and $\mathcal{E}(\mathfrak{L}_P)$.

	$\Gamma_H{}^{0s}$	$\Gamma_H{}^{0a}$	$\Gamma_H{}^{\pi s}$	$\Gamma_H{}^{\pi a}$	$\Gamma_M{}^{\lvert k\rvert}$
$\mathcal{E}(\mathfrak{L}',s)$	1	0	1	0	1
$\mathcal{E}(\mathfrak{L}',a)$	0	1	0	1	1
$\mathcal{E}(\mathfrak{L}_P)$	1	1	1	1	2

$$[\Gamma_H{}^l]_{M_0}=d^l\Gamma_{M_0}{}^1. \tag{27}$$

This equation indicates for each representation $\Gamma_H{}^l$ the number of bases which are contained in a set $\mathcal{E}(\mathfrak{L}_P)$ (see Table II).

Now it is clear that two bands $\mathfrak{B}_1$ and $\mathfrak{B}_2$ of Bloch waves $\varphi_k{}^1$ and $\varphi_k{}^2$ constitute together a set $\mathcal{E}(\mathfrak{L}_P)$ if the following conditions are fulfilled: (a) $\varphi_0{}^1$ and $\varphi_0{}^2$ must not have the same symmetry character; (b) $\varphi_\pi{}^1$ and $\varphi_\pi{}^2$ must not have the same symmetry character either.

Thus, we see that the connection between bands and orbitals is usually not a very simple one; this question is investigated with more details in Sec. III.

I. Example 2

The lattice $\mathfrak{L}$ is a regular tetrahedron and G_H is the full group of this tetrahedron (T_d). The point A is the origin. G_A is isomorphic to the group of an equilateral triangle (C_{3v}). The characters of the representations of G_H and G_A are listed[6] in Tables III and IV. Three types of orbitals are possible and Table V indicates the representations of the corresponding eigenfunctions of H.

The elements of G_A are the identity E, two rotations $C_{3A}{}^+$ and $C_{3A}{}^-$ and three reflections σ_{CD}, σ_{BD}, σ_{BC} with respect to planes passing through A and orthogonal, respectively, to CD, BD, and BC. In our case, the elements S_{MM_0} consist of E and of three reflections σ_{AB}, σ_{AC}, σ_{AD} with respect to planes passing through the center of the tetrahedron and orthogonal, respectively, to AB, AC, and AD. A representation of G_H is completely determined by specifying only the matrices representing the elements of G_A and the transformations σ_{AB}, σ_{AC}, σ_{AD} [see Eq. (1)]. Real irreducible representations of G_H characterized by the reducibility of the matrices belonging to G_A will now be given (see Sec. II B)

$$P_1(\epsilon=+1)\left[\begin{matrix}E=C_{3A}{}^+=C_{3A}{}^-=1,\\ \sigma_{AB}=\sigma_{AC}=\sigma_{AD}=\epsilon,\end{matrix}\right.\quad \left.\begin{matrix}\sigma_{CD}=\sigma_{BD}=\sigma_{BC}=\epsilon,\\ \end{matrix}\right]\begin{matrix}\Lambda_1(\epsilon=+1)\\ \Lambda_2(\epsilon=-1)\end{matrix}$$
$$P_2(\epsilon=-1)$$

$$P_3\left\{\begin{matrix}E=\begin{vmatrix}1&0\\0&1\end{vmatrix},\quad C_{3A}{}^+=\begin{vmatrix}-1/2&-\sqrt{3}/2\\ \sqrt{3}/2&-1/2\end{vmatrix},\quad C_{3B}{}^-=\begin{vmatrix}-1/2&\sqrt{3}/2\\ -\sqrt{3}/2&-1/2\end{vmatrix},\\ \sigma_{CD}=\begin{vmatrix}1&0\\0&-1\end{vmatrix},\quad \sigma_{BD}=\begin{vmatrix}-1/2&-\sqrt{3}/2\\ -\sqrt{3}/2&1/2\end{vmatrix},\quad \sigma_{BC}=\begin{vmatrix}-1/2&\sqrt{3}/2\\ \sqrt{3}/2&1/2\end{vmatrix},\\ \sigma_{AB}=\sigma_{CD},\qquad \sigma_{AC}=\sigma_{BD},\qquad \sigma_{AD}=\sigma_{BC},\end{matrix}\right\}\Lambda_3$$

$$P_4\left\{\begin{matrix}E=\begin{vmatrix}1&0&0\\0&1&0\\0&0&1\end{vmatrix},\quad C_{3A}{}^+=\begin{vmatrix}1&0&0\\0&-1/2&-\sqrt{3}/2\\0&\sqrt{3}/2&-1/2\end{vmatrix},\quad C_{3A}{}^-=\begin{vmatrix}1&0&0\\0&-1/2&\sqrt{3}/2\\0&-\sqrt{3}/2&-1/2\end{vmatrix},\\ \sigma_{CD}=\begin{vmatrix}1&0&0\\0&1&0\\0&0&-1\end{vmatrix},\quad \sigma_{BD}=\begin{vmatrix}1&0&0\\0&-1/2&-\sqrt{3}/2\\0&-\sqrt{3}/2&1/2\end{vmatrix},\quad \sigma_{BC}=\begin{vmatrix}1&0&0\\0&-1/2&\sqrt{3}/2\\0&\sqrt{3}/2&1/2\end{vmatrix},\\ \sigma_{AB}=\begin{vmatrix}-1/3&2\sqrt{2}/3&0\\2\sqrt{2}/3&1/3&0\\0&0&1\end{vmatrix},\quad \sigma_{AC}=\begin{vmatrix}-1/3&-\sqrt{2}/3&(2/3)^{1/2}\\ \sqrt{2}/3&5/6&\sqrt{3}/6\\(2/3)^{1/2}&\sqrt{3}/6&1/2\end{vmatrix},\quad \sigma_{AD}=\begin{vmatrix}-1/3&-\sqrt{2}/3&-(2/3)^{1/2}\\-\sqrt{2}/3&5/6&-\sqrt{3}/6\\-(2/3)^{1/2}&-\sqrt{3}/6&1/2\end{vmatrix},\end{matrix}\right\}\Lambda_1+\Lambda_3$$

$$P_5\left\{\begin{matrix}E=\begin{vmatrix}1&0&0\\0&1&0\\0&0&1\end{vmatrix},\quad C_{3A}{}^+=\begin{vmatrix}1&0&0\\0&-1/2&-\sqrt{3}/2\\0&\sqrt{3}/2&-1/2\end{vmatrix},\quad C_{3A}{}^-=\begin{vmatrix}1&0&0\\0&-1/2&\sqrt{3}/2\\0&-\sqrt{3}/2&-1/2\end{vmatrix},\\ \sigma_{CD}=\begin{vmatrix}-1&0&0\\0&1&0\\0&0&-1\end{vmatrix},\quad \sigma_{BD}=\begin{vmatrix}-1&0&0\\0&-1/2&-\sqrt{3}/2\\0&-\sqrt{3}/2&1/2\end{vmatrix},\quad \sigma_{BC}=\begin{vmatrix}-1&0&0\\0&-1/2&\sqrt{3}/2\\0&\sqrt{3}/2&1/2\end{vmatrix},\\ \sigma_{AB}=\begin{vmatrix}1/3&0&2\sqrt{2}/3\\0&-1&0\\2\sqrt{2}/3&0&-1/3\end{vmatrix},\quad \sigma_{AC}=\begin{vmatrix}1/2&-\sqrt{2}/3&-(2/3)^{1/2}\\-\sqrt{2}/3&-1/2&\sqrt{3}/6\\-(2/3)^{1/2}&\sqrt{3}/6&-5/6\end{vmatrix},\quad \sigma_{AD}=\begin{vmatrix}1/2&\sqrt{2}/3&-(2/3)^{1/2}\\ \sqrt{2}/3&-1/2&-\sqrt{3}/6\\-(2/3)^{1/2}&-\sqrt{3}/6&-5/6\end{vmatrix}.\end{matrix}\right\}\Lambda_2+\Lambda_3 \tag{28}$$

[6] G. F. Koster, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 5, p. 174.

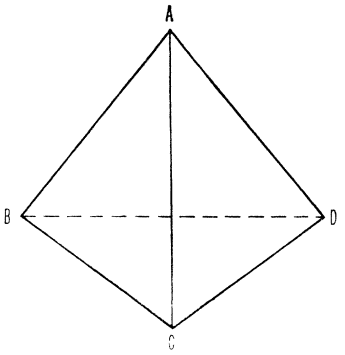

FIG. 2. The points A B C D form the lattice £ which is considered in example 2.

TABLE III. Representations of the group of the tetrahedron.

T_d	E	$8C_3$	$3C_2$	6σ	$6S_4$
P_1	1	1	1	1	1
P_2	1	1	1	−1	−1
P_3	2	−1	2	0	0
P_4	3	0	−1	1	−1
P_5	3	0	−1	−1	1

These representations are now used to illustrate our method in the special case where we want to build orbitals belonging to a representation Λ_3. Then, two orbitals $M(1)$ and $M(2)$ can be associated with each site M of £. They are built from eigenfunctions belonging to representations P_3, P_4, and P_5, namely, $\varphi(3,p)$ with $p=1, 2$, $\varphi(4,q)$ with $q=1, 2, 3$, and $\varphi(5,r)$ with $r=1, 2, 3$.

For instance, the orbitals $A(1)$ and $A(2)$ forming a basis for Λ_3 can be written explicitly in the following way [see Eq. (9)]:

$$A(1)=\tfrac{1}{2}\varphi(3,1)+\frac{\sqrt{6}}{4}\varphi(4,2)+\frac{\sqrt{6}}{4}\varphi(5,2),$$
$$A(2)=\tfrac{1}{2}\varphi(3,2)+\frac{\sqrt{6}}{4}\varphi(4,3)+\frac{\sqrt{6}}{4}\varphi(5,3). \tag{29}$$

The other orbitals are obtained by transforming $A(1)$ and $A(2)$ by the operations σ_{AB}, σ_{AC}, and σ_{AD}.

Conversely, by using the representations given above, the eigenfunctions $\varphi(3,p)$, $\varphi(4,q)$, and $\varphi(5,r)$ can be expanded in terms of the orbitals [Formula (13)]:

$$\varphi(3,1)=\tfrac{1}{2}A(1)+\tfrac{1}{2}B(1)+\tfrac{1}{4}C(1)-\frac{\sqrt{3}}{4}C(2)-\tfrac{1}{4}D(1)+\frac{\sqrt{3}}{4}D(2)$$
$$\varphi(3,2)=\tfrac{1}{2}A(2)-\tfrac{1}{2}B(2)-\frac{\sqrt{3}}{4}C(1)+\tfrac{1}{4}C(2)+\frac{\sqrt{3}}{4}D(1)+\tfrac{1}{4}D(2)$$
$$\varphi(4,1)=\frac{\sqrt{3}}{3}B(1)-\frac{\sqrt{3}}{6}C(1)+\tfrac{1}{2}C(2)-\frac{\sqrt{3}}{6}D(1)-\tfrac{1}{2}D(2)$$
$$\varphi(4,2)=\frac{\sqrt{6}}{4}A(1)+\frac{\sqrt{6}}{12}B(1)+\frac{5\sqrt{6}}{24}C(1)+\frac{\sqrt{2}}{8}C(2)+\frac{5\sqrt{6}}{24}D(1)-\frac{\sqrt{2}}{8}D(2)$$
$$\varphi(4,3)=\frac{\sqrt{6}}{4}B(1)+\frac{\sqrt{6}}{4}B(2)+\frac{\sqrt{2}}{8}C(1)+\frac{\sqrt{6}}{8}C(2)-\frac{\sqrt{2}}{8}D(1)+\frac{\sqrt{6}}{8}D(2) \tag{30}$$
$$\varphi(5,1)=\frac{\sqrt{3}}{3}B(2)-\tfrac{1}{2}C(1)-\frac{\sqrt{3}}{6}C(2)+\tfrac{1}{2}D(1)-\frac{\sqrt{3}}{6}D(2)$$
$$\varphi(5,2)=\frac{\sqrt{6}}{4}A(1)-\frac{\sqrt{6}}{4}B(1)-\frac{\sqrt{6}}{8}C(1)+\frac{\sqrt{2}}{8}C(2)-\frac{\sqrt{6}}{8}D(1)-\frac{\sqrt{2}}{8}D(2)$$
$$\varphi(5,3)=\frac{\sqrt{6}}{4}A(2)-\frac{\sqrt{6}}{12}B(2)+\frac{\sqrt{2}}{8}C(1)-\frac{5\sqrt{6}}{24}C(2)-\frac{\sqrt{2}}{8}D(1)-\frac{5\sqrt{6}}{24}D(2)$$

III. GENERALIZED WANNIER FUNCTIONS IN CRYSTALS

A. Energy Bands and Representations of a Crystal Group G_H

In the following sections, the general theory is applied to crystals. To take full advantage of all the symmetries of the problem, we consider only cyclical crystals (Born-von Karman conditions). By definition, a crystal group is a group containing an invariant subgroup of translations T. This case is very important in practice and also very interesting from a mathematical point of view. In fact, by repeating an initial crystal, it is possible to build very big or even infinite crystals

TABLE IV. Representations of the group of the equilateral triangle.

C_{3V}	E	$2C_3$	3σ
A_1	1	1	1
A_2	1	1	−1
A_3	2	−1	0

having the same kind of symmetries as the initial one and it turns out that all the properties of a finite crystal can be deduced from the properties of the equivalent infinite crystal. For instance, Bloch waves in a finite crystal are special Bloch waves of the infinite crystal, corresponding to proper discrete values of the wave number $\mathbf{k}$. Therefore, in the following, very large or infinite crystals are studied first and the results are extended afterwards to finite crystals.

In an infinite crystal, the energy levels (and the corresponding Bloch waves) form energy bands $\mathfrak{B}$. In each band the energy $E_\mathbf{k}$ is a multivalued continuous function of the real wave vector $\mathbf{k}$. Our definition of a band is the following: A band consists usually of several different branches; two connected branches belong always to the same band; two bands are never connected. In a given band, the number of levels corresponding to any value $\mathbf{k}$ is a constant n. On the other hand, the elements of G_H which leave invariant the wave vector $\mathbf{k}$ of a Bloch function form a subgroup $G_\mathbf{k}$ having irreducible representation $\Gamma_\mathbf{k}{}^{ka}$. These representations are used to generate all the irreducible representations $\Gamma_H{}^{*ka}$ of G_H which are characterized by a star[4] of equivalent values of $\mathbf{k}$ in the reciprocal space and by the index a of the generating representation $\Gamma_\mathbf{k}{}^{ka}$. To indicate that the representations $\Gamma_H{}^{*ka}$ are induced according to Frobenius' method, by a representation $\Gamma_\mathbf{k}{}^{ka}$ of the subgroup $G_\mathbf{k}$, we write

$$\Gamma_H{}^{*ka}=\{\Gamma_\mathbf{k}{}^{ka}\}_H. \tag{31}$$

Now it happens very often that there exists some lattice $\mathfrak{L}$ such that a complete band forms a set $\mathcal{E}(\mathfrak{L},m)$ and therefore can be described by a set of orbitals associated with each point of this lattice. In the following, it is shown that to determine, in fact, whether a band forms a set $\mathcal{E}(\mathfrak{L},m)$ or not, it is sufficient to know the nature of the representations $\Gamma_H{}^{*ka}$ corresponding to the points of maximum symmetry in reciprocal space. The orbitals corresponding to a band will be called generalized Wannier functions. The nature of these orbitals is well defined and therefore determines mathematically the exact nature of the chemical bonds in the crystal. Unfortunately, as it is seen later, a band cannot always be described by only one set of orbitals. The relations between Bloch waves and Wannier functions will also be investigated.

TABLE V. Correspondence between orbitals and eigenfunctions of H.

G_A	G	N_m
A_1	$P_1\,P_4$	4
A_2	$P_2\,P_5$	4
A_3	$P_3\,P_4\,P_5$	8

B. Properties of a Band $\mathfrak{B}$ Forming a Set $\mathcal{E}(\mathfrak{L},m)$

Let us give first the general conditions fulfilled by a band $\mathfrak{B}$, when its eigenfunctions form a set $\mathcal{E}(\mathfrak{L},m)$. Let $n(\mathbf{k}a|\mathfrak{B})$ be the number of distinct bases for representations $\Gamma_\mathbf{k}{}^{ka}$, which can be built from Bloch waves $\varphi_\mathbf{k}$ belonging to $\mathfrak{B}$. According to (31), $n(\mathbf{k}a|\mathfrak{B})$ is also the number of corresponding representations $\Gamma_H{}^{*ka}$ in the band $\mathfrak{B}$. Each irreducible representation $\Gamma_H{}^{*ka}$ associated to a star of $\mathbf{k}$, subduces a reducible representation of G_{M_0}, the group of the origin M_0 of $\mathfrak{L}$ and Eq. (4) can be written

$$[\Gamma_H{}^{*ka}]_{M_0}=\sum_m C(*\mathbf{k}a|m)\Gamma_{M_0}{}^m. \tag{32}$$

From the definition of a set $\mathcal{E}(\mathfrak{L},m)$ (see Sec. I-C), we deduce the following criterion insuring that the eigenfunctions belonging to $\mathfrak{B}$ form a set $\mathcal{E}(\mathfrak{L},m)$

$$n(\mathbf{k}a|\mathfrak{B})=C(*\mathbf{k}a|m) \tag{33}$$

for any $\mathbf{k}$.

This criterion is now simplified. First, a precise definition of what we call *points of maximum symmetry* in reciprocal space must be given. A set of points of maximum symmetry is a minimal set of points Σ such that any point P in the Brillouin zone can be connected to at least one point Σ by a path having the following property: If $P(\mathbf{k})$ is any point of wave number $\mathbf{k}$ lying between Σ and P in the path and if $P(\mathbf{k}')$ is any point of wave number $\mathbf{k}'$ lying between $P(\mathbf{k})$ and P in the path, then $G_{\mathbf{k}'}$ is either identical to $G_\mathbf{k}$ or is a subgroup of $G_\mathbf{k}$. The points Σ are isolated and in the cases of interest, the definition of the points of maximum symmetry is unique. The wave vectors associated with these points are denoted by $\mathbf{k}(\Sigma)$. The center of the Brillouin zone is a point Σ, the other points Σ being in general corners of the polyhedron limiting the Brillouin zone. Now using this definition of the points Σ, we can reformulate criterion (33) in a simpler way by means of the following theorem:

Theorem. If the eigenfunctions belonging to a band form a set $\mathcal{E}(\mathfrak{L},m)$, the relation

$$n(\mathbf{k}a|\mathfrak{B})=C(*\mathbf{k}a|m) \tag{34}$$

is true for any vector wave $\mathbf{k}$. Conversely, if for a given band for some lattice $\mathfrak{L}$ and some representation $\Gamma_M{}^m$ this relation is true for any vector $\mathbf{k}(\Sigma)$, then it is true for any vector $\mathbf{k}$ and the eigenfunctions belonging to $\mathfrak{B}$ form a set $\mathcal{E}(\mathfrak{L},m)$.

Lemma. Let $\Gamma_A{}^a$ and $\Gamma_B{}^b$ be two irreducible representations of two subgroups A and B of a group G.

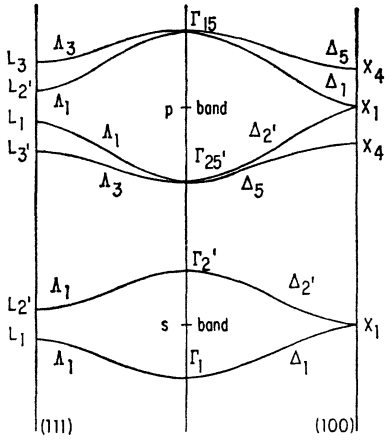

FIG. 3. Energy bands for a diamond-type crystal. Tight binding.

From these representations, by using Frobenius' method, it is possible to induce[4] representations $\{\Gamma_A{}^a\}_G$ and $\{\Gamma_B{}^b\}_G$ of the group G. In turn, these representations subduce representations usually reducible of B and A, respectively:

$$\begin{aligned}[\{\Gamma_A{}^a\}_G]_B&=\sum_b C(Aa\,|\,Bb)\Gamma_B{}^b,\\ [\{\Gamma_B{}^b\}_G]_A&=\sum_a C(Bb\,|\,Aa)\Gamma_A{}^a,\end{aligned}\tag{35}$$

where

$$C(Aa\,|\,Bb)=C(Bb\,|\,Aa).\tag{36}$$

Using this lemma which is proved in Appendix III, it is now possible to prove our theorem.

Proof of the Theorem. As was shown before, if a band $\mathfrak{B}$ forms a set $\mathcal{E}(\mathfrak{L},m)$, then for each point Σ we must have

$$n(\mathbf{k}(\Sigma)a\,|\,\mathfrak{B})=C(*\mathbf{k}(\Sigma)a\,|\,m).\tag{37}$$

Let us now prove that the converse is also true by showing that when the conditions (37) hold, the general condition (33) is valid for any vector $\mathbf{k}$ of the reciprocal space. We note that any point in the Brillouin zone can by attained by starting from some point Σ and by passing through points of decreasing symmetry. Therefore, to establish the theorem, it is sufficient to prove that if the relation (33) holds for a vector $\mathbf{k}$, it holds also for any vector $\mathbf{k}'$ in the neighborhood of $\mathbf{k}$, provided that $G_{k'}$ is a subgroup of G_k. This last result can be derived as follows.

If $G_{k'}$ is a subgroup of G_k, any irreducible representation $\Gamma_k{}^{ka}$ of G_k subduces a representation of $G_{k'}$ which is usually reducible with respect to the irreducible representations $\Gamma_{k'}{}^{k'a'}$

$$[\Gamma_k{}^{ka}]_{k'}=\sum_{a'} C(\mathbf{k}a\,|\,\mathbf{k}'a')\Gamma_{k'}{}^{k'a'}.\tag{38}$$

Thus, by passing from $\mathbf{k}$ to $\mathbf{k}'$, we remove usually some degeneracies, and from (38) we deduce easily by continuity the relations which connect the coefficients $n(\mathbf{k}a\,|\,\mathfrak{B})$ and $n(\mathbf{k}'a'\,|\,\mathfrak{B})$

$$n(\mathbf{k}'a'\,|\,\mathfrak{B})=\sum C(\mathbf{k}a\,|\,\mathbf{k}'a')n(\mathbf{k}a\,|\,\mathfrak{B}).\tag{39}$$

TABLE VI. Nature of the Wannier functions for a linear crystal.

φ_0		φ_π		
M_0'	M_0''	M_0'	M_0''	Orbitals
S	S	S	A	S on $\mathfrak{L}'$
S	S	A	S	S on $\mathfrak{L}''$
A	A	A	S	A on $\mathfrak{L}'$
A	A	S	A	A on $\mathfrak{L}''$

The lemma given above can now be used to derive very analogous relations connecting $C(*\mathbf{k}a\,|\,m)$ and $C(*\mathbf{k}'a'\,|\,m)$.

According to (31) and (32) we may write

$$[\{\Gamma_k{}^{ka}\}_H]_{M_0}=[\Gamma_H{}^{*ka}]_{M_0}=\sum_m C(*\mathbf{k}a\,|\,m)\Gamma_{M_0}{}^m.\tag{40}$$

Application of the preceding lemma gives

$$[\{\Gamma_{M_0}{}^m\}_H]_k=\sum_a C(*\mathbf{k}a\,|\,m)\Gamma_k{}^{ka}.\tag{41}$$

But $G_{k'}$ is a subgroup of G_k; therefore, by taking (38) into account, we can write

$$\begin{aligned}[\{\Gamma_{M_0}{}^m\}_H]_{k'}&=[[\{\Gamma_{M_0}{}^m\}_H]_k]_{k'}\\ &=\sum_{aa'} C(*\mathbf{k}a\,|\,m)C(\mathbf{k}a\,|\,\mathbf{k}'a')\Gamma_{k'}{}^{k'a'}.\end{aligned}\tag{42}$$

We can also write more directly [see Eq. (41)]:

$$[\{\Gamma_{M_0}{}^m\}_H]_{k'}=\sum_{a'} C(*\mathbf{k}'a'\,|\,m)\Gamma_{k'}{}^{k'a'}.\tag{43}$$

By comparing Eqs. (42) and (43), we obtain the following relations:

$$C(*\mathbf{k}'a'\,|\,m)=\sum_a C(\mathbf{k}a\,|\,\mathbf{k}'a')C(*\mathbf{k}\alpha\,|\,m).\tag{44}$$

Now Eqs. (39) and (44) show that the validity of the condition

$$n(\mathbf{k}a\,|\,\mathfrak{B})=C(*\mathbf{k}a\,|\,m),\tag{45}$$

implies also the equality

$$n(\mathbf{k}'a'\,|\,\mathfrak{B})=C(*\mathbf{k}'a'\,|\,m).\tag{46}$$

Therefore, if (45) is true for all the points Σ, it is true

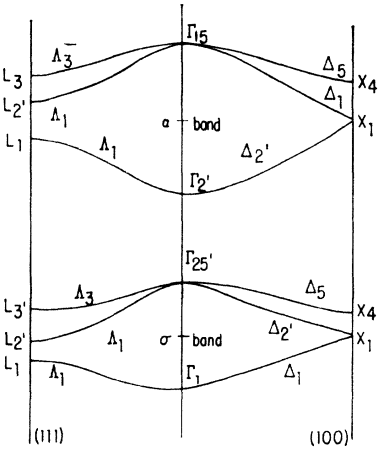

FIG. 4. Energy bands for a diamond-type crystal. Valence binding.

everywhere in the Brillouin zone, and as a consequence the eigenfunctions of $\mathfrak{B}$ form a set $\mathcal{E}(\mathfrak{L},m)$.

Example. As a very simple application of the theorem we consider the case of a linear crystal with a center of symmetry which has been studied in Sec. II-H. For such a crystal the points Σ are the center of the Brillouin zone ($k=0$) and the point at the boundary ($k=\pi$). For a given band, the corresponding eigenfunctions are φ_0 and φ_π. From the structure of the representations of G_H (see Table I), it is easy to see that φ_0 is either completely symmetric or completely antisymmetric with respect to any point of $\mathfrak{L}$ or $\mathfrak{L}''$; on the other hand, if φ_π is symmetric with respect to the points of $\mathfrak{L}'$, it is antisymmetric with respect to the points of $\mathfrak{L}''$ and conversely.

All the possible cases are listed in Table VI. The type of the lattice $\mathfrak{L}$ and the nature of the orbitals which are carried by points of this lattice are deduced from the theorem given above, in full agreement with the results of Kohn.[2]

C. Remarks on the Possibility of Representing a Band by a Set of Orbitals

The theorem derived in Sec. II-C is useful because it shows that, to know whether the eigenfunctions of a band $\mathfrak{B}$ form a set $\mathcal{E}(\mathfrak{L},m)$ or not, we have only to examine a finite number of conditions related to the points Σ. Now, we may ask, what determines exactly the nature of the orbitals associated with a given band and whether a band can always be represented by a set of orbitals.

Let us assume in the following that G_H is fixed and that the Hamiltonian H depends on a few parameters. When the values of the parameters change, levels belonging to different representations of G_H can easily cross each other, whereas those belonging to the same representations cannot. For instance, energy levels corresponding to points of high symmetry in the Brillouin zone and belonging to different representations of G_H may cross each other but general energy surfaces are never allowed to cross. Therefore, if for a point Σ there is a crossing of levels belonging to two different bands, there must be a complete rearrangement of both bands. Under this rearrangement an energy level corresponding to a given representation can be transferred from one band to the other. Thus, the structure of the bands depends very much on the values of the parameters of H. A fictitious example will now be given for a diamond-type crystal.[7] In Fig. 3, we plotted S and P bands in the tight binding limit; as the reader may verify, in this case $\mathfrak{L}$ is the lattice of the carbon atoms and the Wannier functions associated with each band are atomic orbitals of S and P type, respectively. Now, let us assume that for some change of the parameters in H, the levels Γ_{25}' and Γ_2' at the center of the Brillouin zone, happen to cross each other; in this case, we may obtain the band structure indicated in Fig. 4 which corresponds to covalent binding; the lattice $\mathfrak{L}$ which corresponds to this new band structure consists of the midpoints of the lines joining nearest neighbor carbon atoms; the Wannier functions associated with each band are now bond orbitals which are symmetrical (σ) or antisymmetrical (α).

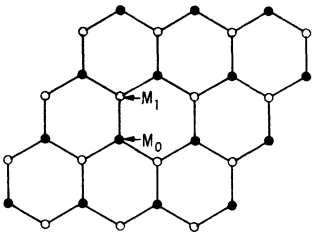

FIG. 6. The lattice $\mathfrak{L}$ is made of two Bravais sublattices: sublattice $\mathfrak{L}_0$ = black circles; sublattice $\mathfrak{L}_1$ = white circles.

On the other hand, when the parameters change in H, the same kind of process may lead to a complex band as a result of the overlapping of two simple bands. An example of such overlapping is given in Fig. 5. It is obvious that, in general, complex bands cannot be described by means of a single set of Wannier functions. However, let us remark that this overlapping of bands can never occur in one dimension. So, in this case, each band can always be described by means of Wannier functions. In summary, we can say that, in simple cases, the bands of a crystal can be described by means of a single set of Wannier functions, the nature of which is determined by the ordering of the energy levels at the points of highest symmetry Σ. On the other hand, if in a crystal the valence band and the conduction band can be represented by Wannier functions, these functions define the chemical nature of the crystal.

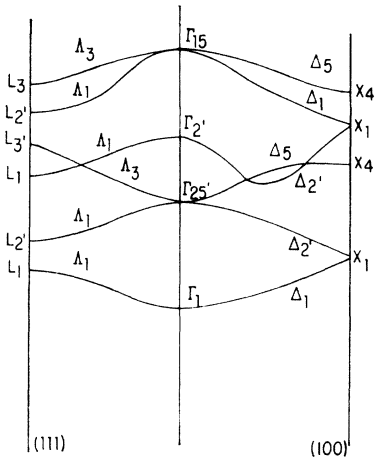

FIG. 5. Energy bands for a diamond-type crystal. Mixed bands.

D. Expansion of the Bloch Waves in Terms of Orbitals. Definition of the Quasi-Bloch Waves $\varphi(\mathbf{k},m,\mathfrak{u})$

When in a crystal, a band can be represented by a set of Wannier functions, any Bloch wave belonging to

[7] J. Callaway, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 99.

the band can be expressed as a linear combination of these orbitals. Unfortunately, the coefficients of this expansion are usually rather complicated: In fact, the general formulas given in Sec. II cannot be applied directly. Therefore, in this section, we write the expansion somewhat schematically: In a band, the Bloch waves of wave vector $\mathbf{k}$ forming a basis for an irreducible representation $\Gamma_{\mathbf{k}}^{k\alpha}$ of $G_{\mathbf{k}}$ can be denoted by the symbol $\varphi(\mathbf{k}a_p\alpha)$. The index p is used to distinguish different bases belonging to the same representation. The index α is used to label the row of different vectors belonging to a given basis. Thus, we may have $\alpha=1, \cdots, d^{k\alpha}$ where $d^{k\alpha}$ is the dimensionality of the representation. On the other hand, in a crystal, each lattice $\mathfrak{L}$ can be split into a certain number of sublattices which are Bravais lattices and which can be found in the following way. Let T be the subgroup of the translations contained in G_H. By applying the transformations T to the point M_0, we generate a Bravais lattice $\mathfrak{L}_0$. Now if $\mathfrak{L}_0$ is not identical to $\mathfrak{L}$, it is possible to find in the vicinity of M_0 a point M_1 of $\mathfrak{L}$ which does not belong to $\mathfrak{L}_0$. Then by applying the translations T to the point M_1, we generate another Bravais lattice $\mathfrak{L}_1$, and so on (see Fig. 6). In this way, we can split the lattice $\mathfrak{L}$ into J different Bravais sublattices $\mathfrak{L}_0$, $\cdots \mathfrak{L}_{J-1}$ generated from points $M_0, \cdots M_{J-1}$. Each sublattice, of course, contains the same number of points $N_T=N/J$. Now, we can associate with each sublattice $\mathfrak{L}_j$, a quasi-Bloch wave $\varphi_j(\mathbf{k},m,\mu)$. Calling $\mathbf{t}$ the displacement corresponding to an operation T of T, we put

$$\varphi_j(\mathbf{k},m,\mu)=(N_T)^{-1/2}\sum_T \exp[i\mathbf{k}(\mathbf{M}_0\mathbf{M}_j+\mathbf{t})] \times A_{TM_j}(m,\mu). \quad (47)$$

It is clear that the Bloch waves $\varphi(\mathbf{k}a_p\alpha)$ of given $\mathbf{k}$ are related to the functions $\varphi_j(\mathbf{k},m,\mu)$ having the same wave vector, by a unitary transformation which can be written in the following way

$$\varphi(\mathbf{k}a_p\alpha)=\sum_{j\mu} \varphi_j(\mathbf{k}m\mu)\langle j\mu|\, U_{\mathbf{k}m}\,|\, a_p\alpha\rangle. \quad (48)$$

We note that the coefficients of this expansion do not depend really on the exact value of $\mathbf{k}$ but merely on the nature of the star of $\mathbf{k}$. Therefore, for a crystal of a given type, in order to write explicitly the expansion (47) in any case, it is sufficient to calculate only a finite number of coefficients. Unfortunately, these coefficients cannot be completely determined by group theoretical arguments: They depend also on the analytic structure of the band. Anyway, the functions $\varphi_j(\mathbf{k},m,\mu)$ are very useful in practical cases and, in fact, can be found directly[8] without calculating in detail the Bloch waves.

IV. SUMMARY

The results of this study can now be reviewed briefly. Taking advantage of the invariance properties of a one-electron Hamiltonian with respect to the elements of a space group G_H we have shown in Sec. II that the eigenfunctions of H can be expanded in terms of equivalent local orbitals. These orbitals are attached to the points M of a lattice $\mathfrak{L}$, which is generated by applying the operations of G_H to an arbitrary given point M_0. To each point M there corresponds a subgroup G_M consisting of those transformations of G_H which leave M invariant. According to our assumptions (Sec. II A) the orbitals $M(m,\mu)$ associated with a point M must form a basis for a given irreducible representation Γ_M^m of G_M. In Sec. II B, we classify the eigenfunctions of H according to their symmetry properties and in Sec. II C the orbitals are obtained by a unitary transformation from a suitable set $\mathcal{E}(\mathfrak{L},m)$ of eigenfunctions of H. The properties of this set are determined by the initial choice of the lattice $\mathfrak{L}$ and of the representation $\Gamma_{M_0}^m$. Conversely, in Sec. II D, the eigenfunctions belonging to $\mathcal{E}(\mathfrak{L},m)$ have been expanded in terms of the orbitals. These orbitals are orthonormal (Sec. II E) and can be deduced from each other by symmetry transformations. Moreover, we have shown in Sec. II F that if H and $\Gamma_{M_0}^m$ are real the corresponding orbitals are real provided that the set $\mathcal{E}(\mathfrak{L},m)$ is defined in a reasonable way. Section II G is devoted to a few remarks concerning the localizability properties of the orbitals and the possibility of choosing suitable sets $\mathcal{E}(\mathfrak{L},m)$. As an illustration of our formalism, the case of a linear chain is treated in Sec. II H and another example (tetrahedron) is given in Sec. II I.

Section II is devoted to a special study of the case of crystals. We try to investigate whether it is possible or not to describe a band by means of one set of orbitals. Notations and definitions are introduced in Sec. II A and in Sec. II B, we prove that if a finite number of simple conditions are fulfilled, then the eigenfunctions belonging to a band form a set $\mathcal{E}(\mathfrak{L},m)$. These conditions are related to the points of maximum symmetry in reciprocal space. In Sec. II C, it is shown that if a band can be described by one set of orbitals only, the nature of the band determines the nature of the lattice $\mathfrak{L}$ and of the orbitals; therefore it determines also the nature of the chemical bonds. The orbitals which correspond to a band can be called generalized Wannier functions. Unfortunately, a band cannot always be described by only one set of Wannier functions because in crystals different bands may overlap. The application of the formalism to the special case of crystals is discussed in Sec. III D.

The possibility of building really localized orbitals depends on the analytic properties of the eigenfunctions of H; an examination of this question will be carried out in a later paper.

ACKNOWLEDGMENTS

The author is grateful to Professor Walter Kohn for making possible his stay at La Jolla as well as for nu-

[8] This point will be discussed in a subsequent paper.

merous interesting and helpful discussions. He also wishes to thank Dr. J. J. Pearson and Dr. R. Balian for their assistance in the preparation of the manuscript.

APPENDIX I. LIST OF SYMBOLS

G_H	general space group leaving the Hamiltonian H invariant,
g	number of elements of G_H,
R	element of G_H,
$\Gamma_H{}^l$	irreducible representation of G_H,
d^l	dimensionality of $\Gamma_H{}^l$,
${}^lR$	matrix representing R in $\Gamma_H{}^l$,
$\mathfrak{L}$	lattice invariant with respect to G_H,
M_0	origin of $\mathfrak{L}$,
M	any point of $\mathfrak{L}$,
S_{MM_0}	special element of G_H transforming M_0 into M,
N	number of points M in $\mathfrak{L}$,
G_{M_0}	subgroup of G_H containing the elements of G_H which leave M_0 invariant,
R_{M_0}	element of G_{M_0},
$\Gamma_{M_0}{}^m$	irreducible representation of G_{M_0},
G_M	subgroup of G_H containing the elements of G_H, which leave M invariant, isomorphic to G_{M_0},
g_m	number of elements of G_M and of G_{M_0},
R_M	element of G_M,
$\Gamma_M{}^m$	irreducible representation of G_M, corresponding to $\Gamma_{M_0}{}^m$,
$d_M{}^m$	dimensionality of $\Gamma_M{}^m$,
$[\Gamma_H{}^l]_M$	representation of G_M subduced by an irreducible representation $\Gamma_H{}^l$ of G_H,
$\{\Gamma_M{}^m\}_H$	representation of G_H induced by an irreducible representation $\Gamma_M{}^m$ of G_M,
$C(l\|m)$	number of representations $\Gamma_M{}^m$ contained in $[\Gamma_H{}^l]_M$,
$C(\mathrm{A}a\|\mathrm{B}b)$	coefficient referring to the irreducible representations $\Gamma_\mathrm{A}{}^a$ and $\Gamma_\mathrm{B}{}^b$ of two subgroups A and B of a group G,
$\|l_p m_q \mu\rangle$	eigenstate of H belonging to a representation $\Gamma_H{}^l$ and a representation $\Gamma_M{}^m$,
$\varphi(l_p m_q \mu)$	wave function corresponding to $\|l_p m_q \mu\rangle$,
$\langle m'_{q'}\mu'\|{}^lR\|m_q\mu\rangle$	matrix element of ${}^lR$,
$M(m,\mu)$	orbital centered on M and belonging to a representation $\Gamma_M{}^m$,
$\mathfrak{B}$	energy band of a crystal,
T	subgroup of translations of G_H in a crystal,
N_T	number of elements of T,
$G_\mathbf{k}$	in a crystal, subgroup of G_H the elements of which leave invariant the wave vector $\mathbf{k}$ of a Bloch wave,
$\Gamma_\mathbf{k}{}^{\mathbf{k}a}$	irreducible representation of $G_\mathbf{k}$,
$\Gamma_H{}^{*\mathbf{k}a}$	in a crystal, irreducible representation of G_H, induced by an irreducible representation $\Gamma_\mathbf{k}{}^{\mathbf{k}a}$,
$n(\mathbf{k}a\|\mathfrak{B})$	number of bases of eigenfunctions belonging to a representation $\Gamma_H{}^{*\mathbf{k}a}$ and contained in a band,
Σ	point of maximum symmetry in reciprocal space,
$\varphi(\mathbf{k}a_p\alpha)$	Bloch wave belonging to a band and a representation $\Gamma_\mathbf{k}{}^{\mathbf{k}a}$,
$\mathfrak{L}_j$	one of the Bravais sublattices of a crystal,
$\varphi_j(\mathbf{k}m\mu)$	quasi Bloch wave.

APPENDIX II. A CLOSURE RELATION

The closure relation (13)

$$\sum_{M\mu}\langle n'_{q'}\nu'|{}^{l'}S_{MM_0}|m_{p'}\mu\rangle\langle m_p\mu|{}^lS_{MM_0}{}^{-1}|n_q\nu\rangle = (g/g_M)(d_M{}^m/d^l)\delta_{ll'}\delta_{pp'}\delta_{nn'}\delta_{qq'}\delta_{\nu\nu'} \quad \text{(A2.1)}$$

is a consequence of the orthogonality relations[9] satisfied by the matrices ${}^lR$ forming an irreducible representation $\Gamma_G{}^l$ of the elements R of G_H.

$$\sum_R\langle b'|{}^{l'}R|a'\rangle\langle a|{}^lR^{-1}|b\rangle=(g/d^l)\delta_{ll'}\delta_{aa'}\delta_{bb'}. \quad \text{(A2.2)}$$

Using our previous notation, we may write as well

$$\sum_R\langle n'_{q'}\nu'|{}^{l'}R|m'_{p'}\mu'\rangle\langle m_p\mu|{}^lR^{-1}|n_q\nu\rangle = (g/d^l)\delta_{ll'}\delta_{mm'}\delta_{pp'}\delta_{\mu\mu'}\delta_{nn'}\delta_{qq'}\delta_{\nu\nu'}. \quad \text{(A2.3)}$$

Now each operator R can be considered as a product [see Eq. (1)]

$$R=S_{MM_0}R_{M_0}. \quad \text{(A2.4)}$$

The matrices ${}^mR_{M_0}$ forming a representation $\Gamma_{M_0}{}^m$ obey orthogonality relations analogous to (A2.2):

$$\sum_{R_{M_0}}\langle\xi'|{}^{m'}R_{M_0}|\mu'\rangle\langle\mu|{}^mR_{M_0}{}^{-1}|\xi\rangle = (g_M/d_M{}^m)\delta_{mm'}\delta_{\mu\mu'}\delta_{\xi\xi'}. \quad \text{(A2.5)}$$

On the other hand, relation (A2.4) can be used to transform (A2.3):

$$\sum_{M_0R_{M_0}}\sum_{\xi\xi'}\langle n'_{q'}\nu'|{}^{l'}S_{MM_0}|m'_{p'}\xi'\rangle \times\langle\xi'|{}^{m'}R_{MM_0}|\mu'\rangle\langle\mu|{}^mR_{MM_0}{}^{-1}|\xi\rangle\langle m_p\xi|{}^lS_{MM_0}{}^{-1}n_q\nu\rangle = (g/d^l)\delta_{ll'}\delta_{mm'}\delta_{pp'}\delta_{\mu\mu'}\delta_{nn'}\delta_{qq'}\delta_{\nu\nu'}. \quad \text{(A2.6)}$$

Let us simplify the first member of this equation by using (A2.5) to eliminate all the terms referring to R_{M_0}. Now putting $m=m'$ and $\mu=\mu'$, we obtain (A2.1).

APPENDIX III. ON FROBENIUS' THEOREM AND A RELATED LEMMA

Frobenius' Theorem

Let $\Gamma_\mathrm{A}{}^a$ be the irreducible representation of a subgroup A of a group G and $\{\Gamma_\mathrm{A}{}^a\}_\mathrm{G}$ the corresponding induced representations of G. These representations

[9] A. Speiser, *Die Theorie der Gruppen* (Dover Publications, New York, 1945), Satz 146, p. 164.

are usually reducible with respect to the irreducible representations $\Gamma_G{}^g$ of G

$$\{\Gamma_A{}^a\}_G=\sum_g C(Aa|Gg)\Gamma_G{}^g. \tag{A3.1}$$

Conversely, any irreducible representation $\Gamma_G{}^g$ subduces a representation $[\Gamma_G{}^g]_A$ which is usually reducible

$$[\Gamma_G{}^g]_A=\sum_a C(Gg|Aa)\Gamma_A{}^a. \tag{A3.2}$$

According to the Frobenius theorem

$$C(Aa|Gg)=C(Gg|Aa). \tag{A3.3}$$

By means of this theorem,[10] the following lemma, which is used in Sec. III B, is derived.

Lemma

Let $\Gamma_A{}^a$ and $\Gamma_B{}^b$ be irreducible representations of the two subgroups A and B of a group G. These representations induce two representations $\{\Gamma_A{}^a\}_G$ and $\{\Gamma_B{}^b\}_G$ of the full group. These new representations subduce usually reducible representations of B and A, respectively, namely, $[\{\Gamma_A{}^a\}_G]_B$ and $[\{\Gamma_B{}^b\}_G]_A$ and we have

$$\begin{aligned}[\{\Gamma_A{}^a\}_G]_B&=\sum_b C(Aa|Bb)\Gamma_B{}^b,\\ [\{\Gamma_B{}^b\}_G]_A&=\sum_a C(Bb|Aa)\Gamma_A{}^a.\end{aligned} \tag{A3.4}$$

The lemma states that

$$C(Aa|Bb)=C(Bb|Aa). \tag{A3.5}$$

[10] A. Speiser, *Die Theorie der Gruppen* (Dover Publications, New York, 1945), Satz 179, p. 200.

(Let us remark, however, that these coefficients still depend on G.)

Proof of the Lemma

The induced representations $\{\Gamma_A{}^a\}_G$ and $\{\Gamma_B{}^b\}_G$ are usually reducible with respect to the irreducible representations $\Gamma_G{}^g$ of G

$$\begin{aligned}\{\Gamma_A{}^a\}_G&=\sum_g C(Aa|Gg)\Gamma_G{}^g,\\ \{\Gamma_B{}^b\}_G&=\sum_g C(Bb|Gg)\Gamma_G{}^g,\end{aligned} \tag{A3.6}$$

and we obtain also the following reduction for the representations $[\Gamma_G{}^g]_A$ and $[\Gamma_G{}^g]_B$ subduced by a representation $\Gamma_G{}^g$

$$\begin{aligned}[\Gamma_G{}^g]_A&=\sum_a C(Gg|Aa)\Gamma_A{}^a,\\ [\Gamma_G{}^g]_B&=\sum_b C(Gg|Bb)\Gamma_B{}^b.\end{aligned} \tag{A3.7}$$

By combining these two sets of equalities, we obtain

$$\begin{aligned}[\{\Gamma_A{}^a\}_G]_B&=\sum_g C(Aa|Gg)[\Gamma_G{}^g]_B\\ &=\sum_{gb} C(Aa|Gg)C(Gg|Bb)\Gamma_B{}^b,\\ [\{\Gamma_B{}^b\}_G]_A&=\sum_g C(Bb|Gg)[\Gamma_G{}^g]_A\\ &=\sum_{ga} (CBb|Gg)C(Gg|Aa)\Gamma_B{}^a.\end{aligned} \tag{A3.8}$$

The equality (A3.5) is an obvious consequence of the Frobenius theorem [Eq. (A3.3)].