JOURNAL OF COMPUTATIONAL PHYSICS 12, 471–490 (1973)

Symmetry Projection of Crystal Wave Functions by Means of a Computer

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Received December 5, 1972

The theory of the irreducible representations of space groups and the symmetry projection of crystal wave functions can be written in a more concise form, when the irreducible representations of arbitrary finite groups can be calculated. Two computer programs have been written. Starting with a minimum of input they produce crystal space orbitals and plane waves respectively, symmetry adapted to the irreducible representations of any one of the 230 space groups. The irreducible representations are generated by the program itself.

1. INTRODUCTION

It is a laborious task to symmetrize crystal wave functions with respect to the irreducible representations (irreps for short) of the space groups. A computer program for symmetry adaptation of crystal space orbitals was written by Flodmark [1]. The present work is a generalization of his ideas.

Only in recent years there have appeared tables of the irreps of the space groups (Kovalev [2], Miller and Love [3], Zak e.a. [4], Bradley and Cracknell [5]). Luehrman [6] has written a program for symmetrizing plane waves with respect to the symmorphic space groups. Donato and Ruggeri [7] and Conklin [8] wrote similar programs as a part of their programs for energy band calculations. The tables of Miller and Love [3] are the most extensive ones and naturally they used a computer program, to produce these tables. They used the method of Raghavacharyulu [9].

It is possible to write a symmetry projection program, which uses these tables as input. But this would still leave much work for the user of such a program, since he would have to supply to the computer the contents of these tables, the point groups of the **k**-vector etc. (Flodmark's original program [1] was written in this way). It is not very practical to have the complete tables stored, since they consist of more than 1000 pages printed in code notation, where one letter represents a complete matrix.

It seemed more practical to let the computer calculate the necessary irreps at the moment when they are needed during the run of the symmetry adaptation program. In this way the user of such program needs to supply only a minimum of information as input. The problem of finding the irreps of a space group can be reduced to that of finding the irreps of a finite group. Since we have a general method to calculate the irreps of a finite group [10–14] we could write such a program. Part of this work was already reported in [12] and [15].

This method enables us to put the theory of irreps of the space groups in a more concise form. The author hopes that Section 2 may be an equivalent for space groups of Coleman's article on the symmetric group [16].

In Section 3, 4 and 5 we give the formulas for the projection matrices which are calculated in the programs. A short description of the programs is given in Section 6.

2. The Space Groups Made Easy

First we establish the usual set of conventions, with which the reader is assumed to be familiar. He can check them in most books on solid state theory and group theory applied to quantum mechanics.

A crystal lattice vector is denoted by

$$\mathbf{n} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \tag{2.1}$$

where n_i are integers and the $\mathbf{a}_i$ primitive lattice vectors. The reciprocal primitive lattice vectors are denoted by $\mathbf{b}_i$, $i = 1, 2, 3$. and

$$\mathbf{b}_i = \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)} \tag{2.2}$$

where i, j, k is a cyclic permutation of the indices 1, 2, 3. A reciprocal lattice vector is denoted by

$$\mathbf{K} = 2\pi(K_1\mathbf{b}_1 + K_2\mathbf{b}_2 + K_3\mathbf{b}_3) \tag{2.3}$$

with integers K_i and

$$\exp(i\mathbf{K} \cdot \mathbf{n}) = 1 \tag{2.4}$$

because of (2.2).

A space group operator $F = (P \mid \mathbf{t})$ transforms a vector $\mathbf{r}$ into

$$(P \mid \mathbf{t})\,\mathbf{r} = P\mathbf{r} + \mathbf{t} \tag{2.5}$$

Here P is a rotation or rotation-inversion, with respect to a fixed point, usually the origin of the coordinate system. In cartesian coordinates $\mathbf{r}$ is represented by a three-dimensional column r and P by a three-dimensional orthogonal matrix P. A pure translation is denoted by $(E \mid \mathbf{t})$ and a pure rotation by $(P \mid \mathbf{0})$ or just P for short. The identity operator is $(E \mid \mathbf{0})$. The product of two space group operators is given by

$$(P_1 \mid \mathbf{t}_1)(P_2 \mid \mathbf{t}_2) = (P_1P_2 \mid P_1\mathbf{t}_2 + \mathbf{t}_1) \tag{2.6}$$

and the inverse of F is

$$F^{-1} = (P^{-1} \mid -P^{-1}\mathbf{t}) \tag{2.7}$$

DEFINITION. The lattice translation group $T_{\mathbf{n}}$ consists of all the elements $(E \mid \mathbf{n})$ with $\mathbf{n}$ being a crystal lattice vector (2.1). We use the cyclic boundary conditions, stating that

$$(E \mid \mathbf{a}_1)^{N_1} = (E \mid \mathbf{a}_2)^{N_2} = (E \mid \mathbf{a}_3)^{N_3} = (E \mid \mathbf{0}) \tag{2.8}$$

where N_1, N_2, N_3 are large integers and

$$N = N_1N_2N_3 \tag{2.9}$$

is the number of unit cells in the region of periodicity and the number of elements in $T_{\mathbf{n}}$. When we use (2.6) for the elements of $T_{\mathbf{n}}$ we find that it is an abelian group, so it has N one dimensional irreps

$$\gamma_{\mathbf{k}}((E \mid \mathbf{n})) = \exp(-i\mathbf{k} \cdot \mathbf{n}) \tag{2.10}$$

with

$$\mathbf{k} = 2\pi \left(\frac{k_1}{N_1}\mathbf{b}_1 + \frac{k_2}{N_2}\mathbf{b}_2 + \frac{k_3}{N_3}\mathbf{b}_3\right) \tag{2.11}$$

$$k_i = 0, 1, 2, \ldots, N_i - 1, \qquad i = 1, 2, 3 \tag{2.12}$$

$\gamma_{\mathbf{k}}$ and $\gamma_{\mathbf{k}+\mathbf{K}}$ denote the same irreps because

$$\exp(-i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{n}) = \exp(-i\mathbf{k} \cdot \mathbf{n}) \tag{2.13}$$

and therefore we can label the irreps of $T_{\mathbf{n}}$ with another set of $\mathbf{k}$-vectors than (2.12). We choose

$$k_i = \frac{-N_i}{2} + 1, \frac{-N_i}{2} + 2, \ldots, 0, 1, 2, \ldots, \frac{N_i}{2} \tag{2.14}$$

We have supposed N_i to be even.

DEFINITION. The first Brillouin zone consists of all points $\mathbf{k}$, that lie closer to $\mathbf{K} = \mathbf{0}$ than to any other reciprocal lattice point. Its boundaries are the perpendicular bisecting planes of the lines connecting $\mathbf{K} = \mathbf{0}$ with the nearest (and sometimes with the next nearest) reciprocal lattice points $\mathbf{K}$.

So all the irreps of $T_{\mathbf{n}}$ are given by (2.10) where $\mathbf{k}$ has the form (2.11) and lies within or at the boundary of the Brillouin zone.

DEFINITION. The space group G of the crystal is the maximum set of operators $F_i = (P_i \mid \mathbf{u}_i + \mathbf{n})$ which map the crystal onto itself when acting on the atomic positions λ, μ, ν etc. according to

$$(P_i \mid \mathbf{u}_i + \mathbf{n})\,\boldsymbol{\lambda} = P_i\boldsymbol{\lambda} + \mathbf{u}_i + \mathbf{n} \tag{2.15}$$

Here the $\mathbf{n}$ are lattice vectors, $\mathbf{u}_i$ are vectors with lattice coordinates smaller than 1 and they are uniquely determined by the index i when the reference point of the point group operators P_i has been chosen. We have $P_1 = E$, $\mathbf{u}_1 = \mathbf{0}$ and for symmorphic space groups all $\mathbf{u}_i = \mathbf{0}$. Note that $T_{\mathbf{n}}$ is an invariant subgroup of G.

DEFINITION. The point group G_P of the space group G is the group of operators $\{P_i\}$ occurring in the elements $F_i = (P_i \mid \mathbf{u}_i + \mathbf{n})$ of the space group. Note that only for symmorphic space groups G_P is a subgroup of G. G_P is a finite group and each element P_i has finite order e_i

$$(P_i)^{e_i} = E,\ e_i \text{ finite integer} \tag{2.16}$$

Then

$$(P_i \mid \mathbf{u}_i + \mathbf{n})^{e_i} = (E \mid \mathbf{m}) \tag{2.17}$$

is a pure lattice translation. Because of (2.17) and (2.8) G is a finite group. We denote its order by g.

Each irrep of the space group is also a representation of the subgroup $T_{\mathbf{n}}$. But restricted to the elements of $T_{\mathbf{n}}$ that representation is in general reducible containing one or more $\gamma_{\mathbf{k}}$ several times. We can now classify the irreps of G by the irreps of $T_{\mathbf{n}}$ that they subduce: ${}^{j\mathbf{k}}\Gamma$ is such an irrep of G, that when ${}^{j\mathbf{k}}\Gamma((E \mid \mathbf{n}))$ is decomposed into irreps of $T_{\mathbf{n}}$, it contains $\gamma_{\mathbf{k}}$. The superscript j then enumerates the different irreps of this type.

DEFINITION. The little group of the second type of a space group G, with invariant subgroup $T_{\mathbf{n}}$, of the wave vector $\mathbf{k}$ (corresponding to irrep $\gamma_{\mathbf{k}}$ of $T_{\mathbf{n}}$) is

the subgroup of G (itself also a space group), denoted by $G_{\mathbf{k}}$, for wich the space group operators $F_i = (P_i \mid \mathbf{u}_i + \mathbf{n})$ are such that

$$P_i\mathbf{k} = \mathbf{k} + \mathbf{K} \tag{2.18}$$

where $\mathbf{K}$ is a reciprocal lattice vector (2.3).

Since $G_{\mathbf{k}}$ is also a space group, it contains $T_{\mathbf{n}}$ as an invariant subgroup. One can then form the cosets $T_{\mathbf{n}}(P_i \mid \mathbf{u}_i)$, with $(P_i \mid \mathbf{u}_i) \in G_{\mathbf{k}}$ and these cosets form a factor group $G_{\mathbf{k}}/T_{\mathbf{n}}$.

DEFINITION. An allowable irrep ${}^{j\mathbf{k}}\Gamma_A$ of $G_{\mathbf{k}}$ is one for which

$${}^{j\mathbf{k}}\Gamma_A((E \mid \mathbf{n})) = \exp(-i\mathbf{k} \cdot \mathbf{n})\,\mathsf{E} \tag{2.19}$$

where E is a unit matrix of the dimension $l_{j\mathbf{k}}$ of ${}^{j\mathbf{k}}\Gamma_A$.

THEOREM 1. *All the irreps ${}^{j\mathbf{k}}\Gamma$ of G can be constructed by taking all the allowable irreps ${}^{j\mathbf{k}}\Gamma_A$ of $G_{\mathbf{k}}$ and inducing from them the irreps of G; to each ${}^{j\mathbf{k}}\Gamma_A$ of $G_{\mathbf{k}}$ corresponds one ${}^{j\mathbf{k}}\Gamma$ of G.*

General accounts of the theory and proofs of the theorems can be found in the references [17–22].

The induction of ${}^{j\mathbf{k}}\Gamma$ from ${}^{j\mathbf{k}}\Gamma_A$ is formed as follows: Decompose G into cosets of subgroups $G_{\mathbf{k}}$:

$$G = \{G_{\mathbf{k}}, (P_l \mid \mathbf{u}_l)\, G_{\mathbf{k}}, (P_{l'} \mid \mathbf{u}_{l'})\, G_{\mathbf{k}}, \ldots\} \tag{2.20}$$

There are $g/g_{\mathbf{k}} = n_{\mathbf{k}}$ cosets, where $g_{\mathbf{k}}$ is the order of $G_{\mathbf{k}}$. We now renumber the elements of G in such way that the indices l of the coset representatives $(P_l \mid \mathbf{u}_l)$ are simply given by $l = 2, 3, 4, \ldots, n_{\mathbf{k}}$. If ${}^{j\mathbf{k}}\Gamma_A$ is an allowable irrep of $G_{\mathbf{k}}$ of dimension $l_{j\mathbf{k}}$, then the dimension of ${}^{j\mathbf{k}}\Gamma$ is

$$L_{j\mathbf{k}} = l_{j\mathbf{k}} n_{\mathbf{k}} \tag{2.21}$$

The matrices of ${}^{j\mathbf{k}}\Gamma$ have a subdivision into $n_{\mathbf{k}}$ matrix blocks of dimension $l_{j\mathbf{k}}$. The subblocks are labeled with row- and column indices l, which run from 1 to $n_{\mathbf{k}}$ and correspond to the enumeration of the coset representatives $(P_l \mid \mathbf{u}_l)$.

So the irrep of G is of the form

$${}^{j\mathbf{k}}\Gamma = \begin{pmatrix} {}^{j\mathbf{k}}\Gamma_{11} & {}^{j\mathbf{k}}\Gamma_{12} & \cdots & {}^{j\mathbf{k}}\Gamma_{1n_{\mathbf{k}}} \\ {}^{j\mathbf{k}}\Gamma_{21} & \cdots & & \\ \cdots & & & \\ \cdots & & & \\ {}^{j\mathbf{k}}\Gamma_{n_{\mathbf{k}}1} & \cdots & & {}^{j\mathbf{k}}\Gamma_{n_{\mathbf{k}}n_{\mathbf{k}}} \end{pmatrix}. \tag{2.22}$$

Each subblock ${}^{jk}\Gamma_{ll'}((P \mid \mathbf{u} + \mathbf{n}))$ is defined by

$$ {}^{jk}\Gamma_{ll'}((P \mid \mathbf{u} + \mathbf{n})) = {}^{jk}\Gamma_A((P_l \mid \mathbf{u}_l)^{-1}(P \mid \mathbf{u} + \mathbf{n})(P \mid \mathbf{u}_{l'})) \, \Delta_{ll'} \tag{2.23} $$

with $\Delta_{ll'} = 1$ if $(P_l \mid \mathbf{u}_l)^{-1}(P \mid \mathbf{u} + \mathbf{n})(P_{l'} \mid \mathbf{u}_{l'}) \in G_{\mathbf{k}}$; otherwise $\Delta_{ll'} = 0$. So the problem is reduced to that of finding the allowable irreps of $G_{\mathbf{k}}$.

DEFINITION. The little point group $P_{\mathbf{k}}$ is the point group of the space group $G_{\mathbf{k}}$.

$$ P_{\mathbf{k}} = \{P_i \text{ , with } (P_i \mid \mathbf{u}_i) \in G_{\mathbf{k}}\} \tag{2.24} $$

THEOREM 2. *If one or more of the following conditions is fulfilled,*

1. $\mathbf{k}$ *lies inside the first Brillouin zone*
2. G *is a symmorphic space group*
3. $G_{\mathbf{k}}$ *is a symmorphic space group*

then all the allowable irreps of $G_{\mathbf{k}}$ *are of the form*

$$ {}^{jk}\Gamma_A((P_i \mid \mathbf{u}_i + \mathbf{n})) = \exp(-i\mathbf{k} \cdot (\mathbf{u}_i + \mathbf{n})) \, {}^{j}\Gamma(P_i) \tag{2.25} $$

where ${}^{j}\Gamma(P_i)$ *is the j-th irrep of the little point group* $P_{\mathbf{k}}$ *of dimension* l_j .

So then also $l_{j\mathbf{k}} = l_j$. In this case there are as many allowable irreps of $G_{\mathbf{k}}$ as there are irreps of $P_{\mathbf{k}}$. Note that condition 2 always includes condition 3 but G may be nonsymmorphic with still $G_{\mathbf{k}}$ symmorphic.

If Theorem 2 cannot be used, that is when $\mathbf{k}$ lies on the Brillouin zone boundary and $G_{\mathbf{k}}$ is nonsymmorphic, then we must follow a slightly more complicated way to find the allowable irreps of $G_{\mathbf{k}}$.

DEFINITION. $T_{\mathbf{k}}$ is a subgroup of $T_{\mathbf{n}}$ with elements $(E \mid \mathbf{n})$ such that

$$ \exp(-i\mathbf{k} \cdot \mathbf{n}) = 1 \tag{2.26} $$

Decompose $G_{\mathbf{k}}$ into cosets of $T_{\mathbf{k}}$

$$ G_{\mathbf{k}} = \{T_{\mathbf{k}} \text{ , } (E \mid \mathbf{m}) \, T_{\mathbf{k}} \text{ ,..., } (P_i \mid \mathbf{u}_i) \, T_{\mathbf{k}} \text{ , } (P, \mid \mathbf{u}_i + \mathbf{m}) \, T_{\mathbf{k}} \text{ ,...}\} \tag{2.27} $$

where the elements $(E \mid \mathbf{m})$ do not belong to $T_{\mathbf{k}}$, that is

$$ \exp(-i\mathbf{k} \cdot \mathbf{m}) \neq 1 \tag{2.28} $$

These cosets form a factor group $G_{\mathbf{k}}/T_{\mathbf{k}}$.

DEFINITION. The little group of $\mathbf{k}$ of the first kind is the group $G_{\mathbf{k}}/T_{\mathbf{k}}$. Its elements are the cosets of (2.27). It is a finite group of not too high order.

DEFINITION. ${}^{j}\Gamma_A'$ is an allowable irrep of $G_{\mathbf{k}}/T_{\mathbf{k}}$ if

$$ {}^{j}\Gamma_A'((E \mid \mathbf{m})\, T_{\mathbf{k}}) = \exp(-i\mathbf{k} \cdot \mathbf{m})\, \mathsf{E} \tag{2.29} $$

THEOREM 3. *All the allowable irreps of $G_{\mathbf{k}}$ can be formed from the allowable irreps of $G_{\mathbf{k}}/T_{\mathbf{k}}$ as follows.*
Write each $(P_i \mid \mathbf{u}_i + \mathbf{n}) \in G_{\mathbf{k}}$ as

$$ (P_i \mid \mathbf{u}_i + \mathbf{n}) = (E \mid \mathbf{n}')(P_i \mid \mathbf{u}_i + \mathbf{m}) \tag{2.30} $$

with $(P_i \mid \mathbf{u}_i + \mathbf{m})$ being a coset representative in (2.27) and $(E \mid \mathbf{n}') \in T_{\mathbf{k}}$. Then

$$ \begin{aligned} {}^{j\mathbf{k}}\Gamma_A((P_i \mid \mathbf{u}_i + \mathbf{n})) &= {}^{j\mathbf{k}}\Gamma_A'((P_i \mid \mathbf{u}_i + \mathbf{m})\, T_{\mathbf{k}}) \\ &= \exp(-i\mathbf{k} \cdot \mathbf{m})\, {}^{j\mathbf{k}}\Gamma_A'((P_i \mid \mathbf{u}_i)\, T_{\mathbf{k}}) \\ &= \exp(-i\mathbf{k} \cdot \mathbf{n})\, {}^{j\mathbf{k}}\Gamma_A'((P_i \mid \mathbf{u}_i)\, T_{\mathbf{k}}) \end{aligned} \tag{2.31} $$

The group $G_{\mathbf{k}}/T_{\mathbf{k}}$ is in general not isomorphic to a point group. But its multiplication table can easily be constructed as follows: label each element $(P_i \mid \mathbf{u}_i + \mathbf{m})$ of the abstract group with the two indices i and s, where i is the index for the corresponding point group operator P_i and

$$ s = \exp(-i\mathbf{k} \cdot (\mathbf{u}_i + \mathbf{m})) \tag{2.32} $$

is determined by the translational part of the coset representative. Then for any product of two elements of $G_{\mathbf{k}}/T_{\mathbf{k}}$, the first index of the product is determined from the multiplication table of the point group $P_{\mathbf{k}}$ and the second index is calculated from the multiplication rule (2.6) and its definition (2.32). As soon as the multiplication table has been determined we can use the general method of finding the irreps of a finite group [10–14]. Finally we select the allowable irreps from the complete set of irreps of $G_{\mathbf{k}}/T_{\mathbf{k}}$ by a simple inspection of the representatives of the group elements selecting those irreps for which (2.29) holds.

This concludes the reduction of our problem. We started with the space group G for which the order g is a multiple of N, a very large number, in principle $N \to \infty$. We have shown that all the irreps ${}^{j\mathbf{k}}\Gamma$ of G, which subduce a specific $\gamma_{\mathbf{k}}$ of $T_{\mathbf{n}}$ can be found from the allowable irreps of $G_{\mathbf{k}}$. And the allowable irreps of $G_{\mathbf{k}}$ can be formed from the irreps of $P_{\mathbf{k}}$ or $G_{\mathbf{k}}/T_{\mathbf{k}}$. Their orders are independent of N. In order to specify a $\mathbf{k}$-vector one only gives the fractions

$$ \frac{q_i}{p_i} = \frac{k_i}{N_i} \tag{2.33} $$

in (2.11). The numbers N_i and N do not play any further role in the theory of irreps, than that they simplify the proofs of the theorems, but these can also be

worked out for discrete infinite space groups for which there is no restriction (2.8) for T_n.

The material above is just the usual theory of induced representations, conjugate representations, little groups etc. But we have been able to put it in a concise form because we cut off the discussion when we had reduced the problem to that of forming the irreps of a finite group of reasonable size, since that is a solved problem. A general method of calculating the irreps of arbitrary finite groups of such a size has been developed earlier [10–14].

3. Symmetry Projection

We introduce space group operators $\hat{F}$ that act on functions. The accent on $\hat{F}$ and other operators is to distinguish them from the previously introduced operators that act on position vectors. Definition of $\hat{F}$:

$$\hat{F}\psi(\mathbf{r}) = \psi(F^{-1}\mathbf{r}) \tag{3.1}$$

We shall interpret formula (3.1) as follows. At point $\mathbf{r}$ the function $\hat{F}\psi$ has the value of the function ψ at point $F^{-1}\mathbf{r}$. Other interpretations are possible [23], but we shall stick to this one. If $F_1F_2 = F_3$ then

$$\begin{aligned}\hat{F}_1\hat{F}_2\psi(\mathbf{r}) &= \hat{F}_2\psi(F_1^{-1}\mathbf{r}) = \psi(F_2^{-1}F_1^{-1}\mathbf{r}) \\ &= \psi(F_3^{-1}\mathbf{r}) = \hat{F}_3\psi(\mathbf{r})\end{aligned} \tag{3.2}$$

according to (3.1). So the group of operators $\hat{F}$ and F are isomorphic, and thus we shall drop the accent when it is not important and when misunderstanding is not possible.

So according to (3.1) and (2.7)

$$(P \mid \mathbf{t})\,\psi(\mathbf{r}) = \psi((P^{-1} \mid -P^{-1}\mathbf{t})\,\mathbf{r}) = \psi(P^{-1}(\mathbf{r} - \mathbf{t})) \tag{3.3}$$

The general formula for a symmetry projection operator [24] of a finite group of unitary operators $\hat{F}_i$ of order g is

$${}^{j}\hat{S}_{dd} = \frac{l_j}{g}\sum_{i=1}^{g} {}^{j}\Gamma^*(F_i)_{dd}\,\hat{F}_i \tag{3.4}$$

${}^{j}\Gamma$ is the j-th unitary irrep of the group, l_j its dimension, ${}^{j}\Gamma^*(F_i)_{dd}$ is the complex conjugate of the d-th diagonal element of the representative of F_i.

When the group is T_n and the irrep is γ_k (2.10) then (3.4) becomes

$$^kS = \frac{1}{N} \sum_{\mathbf{n}} \exp(i\mathbf{k} \cdot \mathbf{n})(E \mid \mathbf{n}) \tag{3.5}$$

where $\mathbf{n} = \sum_{i=1}^{3} n_i \mathbf{a}_i$, $n_i = 0, 1, 2, \ldots, N_i - 1$.

DEFINITION. The Bloch function $\psi_\mathbf{k}$ of a function $\psi(\mathbf{r})$ is the result of ^kS acting on $\psi(\mathbf{r})$:

$$\psi_\mathbf{k}(\mathbf{r}) = {}^kS\psi(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{n}} \exp(i\mathbf{k} \cdot \mathbf{n})\, \psi(\mathbf{r} - \mathbf{n}) \tag{3.6}$$

Note that the function $\psi_\mathbf{k}$ is not yet normalized. Starting with a set of basis functions $\Psi = (\psi_1 , \psi_2 , \ldots, \psi_r)$ one can form a Bloch basis $\Psi_\mathbf{k}$

$$\Psi_\mathbf{k} = {}^kS(\psi_1 , \ldots, \psi_r) = (\psi_{\mathbf{k}1} , \ldots, \psi_{\mathbf{k}r}) \tag{3.7}$$

It follows immediately from the way of construction of $^{j\mathbf{k}}\Gamma$ of G from $^{j\mathbf{k}}\Gamma_A$ of $G_\mathbf{k}$ in (2.22), (2.23) that, if φ_i , $i = 1, 2, \ldots, l_{j\mathbf{k}}$ is a basis for the irrep $^{j\mathbf{k}}\Gamma_A$ of $G_\mathbf{k}$, then

$$(P_l \mid \mathbf{u}_l)\, \varphi_i , \qquad i = 1, 2, \ldots, l_{j\mathbf{k}} , \qquad l = 1, 2, \ldots, n_\mathbf{k} \tag{3.8}$$

is the i-th function in the l-th block of a basis function of irrep $^{j\mathbf{k}}\Gamma$ of G. Formula (3.4) then has the form

$$^{j\mathbf{k}}S_{dd} = \frac{l_{j\mathbf{k}}}{g_\mathbf{k}} \sum_{(P\mid\mathbf{u}+\mathbf{m})\in G_\mathbf{k}} {}^{j\mathbf{k}}\Gamma^*((P \mid \mathbf{u} + \mathbf{m}))_{dd}\, (P \mid \mathbf{u} + \mathbf{m}) \tag{3.9}$$

Here $\mathbf{m}$ takes all the N values as in (3.5) and if the point group $P_\mathbf{k}$ of $G_\mathbf{k}$ is of order $g_\mathbf{k}'$ then

$$g_\mathbf{k} = N g_\mathbf{k}' \tag{3.10}$$

When (3.9) acts on a Bloch function (3.6), we get by means of (2.31) and (2.6)

$$\begin{aligned} {}^{j\mathbf{k}}S_{dd}\psi_\mathbf{k} &= \frac{l_{j\mathbf{k}}}{g_\mathbf{k}} \sum_{(P\mid\mathbf{u}+\mathbf{m})\in G_\mathbf{k}} {}^{j\mathbf{k}}\Gamma_A^*((P \mid \mathbf{u} + \mathbf{m}))_{dd}\, (P \mid \mathbf{u} + \mathbf{m})\, \psi_\mathbf{k} \\ &= \frac{l_{j\mathbf{k}}}{g_\mathbf{k}} \sum_{(P\mid\mathbf{u}+\mathbf{m})} e^{i\mathbf{k}\cdot\mathbf{m}}\, {}^{j\mathbf{k}}\Gamma_A^*((P \mid \mathbf{u}))_{dd}\, (P \mid \mathbf{u})(E \mid P^{-1}\mathbf{m})\, \psi_\mathbf{k} \end{aligned} \tag{3.11}$$

Now we have

$$(E \mid P^{-1}\mathbf{m})\,\psi_{\mathbf{k}}(\mathbf{r}) = (E \mid P^{-1}\mathbf{m})\,\frac{1}{N}\sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{n}}\,\psi(\mathbf{r}-\mathbf{n})$$

$$= \frac{1}{N}\,e^{-i\mathbf{k}\cdot\mathbf{m}}\sum_{\mathbf{n}} e^{i\mathbf{k}\cdot(\mathbf{n}+P^{-1}\mathbf{m})}\,\psi(\mathbf{r}-(\mathbf{n}+P^{-1}\mathbf{m})) = e^{-i\mathbf{k}\cdot\mathbf{m}}\,\psi_{\mathbf{k}}(\mathbf{r}) \qquad (3.12)$$

which is just the characteristic property of a Bloch function. We used in (3.12) the fact that for $P \in P_{\mathbf{k}}$, $\exp(-i\mathbf{k}\cdot P^{-1}\mathbf{m}) = \exp(-iP\mathbf{k}\cdot\mathbf{m}) = \exp(-i\mathbf{k}\cdot\mathbf{m})$. Then (3.11) becomes

$${}^{j\mathbf{k}}S_{dd}\psi_{\mathbf{k}} = \frac{l_{j\mathbf{k}}}{g_{\mathbf{k}}}\sum_{(P\mid\mathbf{u}+\mathbf{m})\in G_{\mathbf{k}}} {}^{j\mathbf{k}}\Gamma_A{}^{*}((P \mid \mathbf{u}))_{dd}\,(P \mid \mathbf{u})\,\psi_{\mathbf{k}} \qquad (3.13)$$

The terms under the summation sign are independent of $\mathbf{m}$, so each different term occurs N times and we can simplify (3.13) to

$${}^{j\mathbf{k}}S_{dd}\psi_{\mathbf{k}} = \frac{l_{j\mathbf{k}}}{g_{\mathbf{k}}'}\sum_{P\in P_{\mathbf{k}}} {}^{j\mathbf{k}}\Gamma_A{}^{*}((P \mid \mathbf{u}))_{dd}\,(P \mid \mathbf{u})\,\psi_{\mathbf{k}} \qquad (3.14)$$

where the summation now runs over only $g_{\mathbf{k}}'$ terms. For the cases where Theorem 2 can be applied, that is when

$${}^{j\mathbf{k}}\Gamma_A((P \mid \mathbf{u})) = e^{-i\mathbf{k}\cdot\mathbf{u}}\,{}^{j}\Gamma(P) \qquad (3.15)$$

the formula can be simplified further to

$${}^{j\mathbf{k}}S_{dd}\psi_{\mathbf{k}} = \frac{l_j}{g_{\mathbf{k}}'}\sum_{P\in P_{\mathbf{k}}} {}^{j}\Gamma^{*}(P)_{dd}\,(P \mid \mathbf{0})\,\psi_{\mathbf{k}} \qquad (3.16)$$

With (3.14) we have obtained a formula which is independent of the number N.

4. Symmetry Projection of Plane Waves

An augmented plan wave (*APW*) is a continuous function that is equal to a plane wave outside the sphere, inscribed in the Wigner Seitz cell. A space group operation transforms it to a similar function, continuous and equal to a plane wave outside a sphere. Therefore *APW*'s transform like plane waves and if

$$\psi = \sum_{n} \alpha_n e^{i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{r}} \qquad (4.1)$$

is symmetry adapted to some row of some irrep of a space group, then

$$\varphi = \sum_n \alpha_n \varphi_{\mathbf{k}n} \tag{4.2}$$

is also symmetry adapted. Here $\varphi_{\mathbf{k}n}$ is an *APW* that outside the sphere behaves like $\exp(i(\mathbf{k} + \mathbf{K}_n) \cdot \mathbf{r})$. So we can restrict our discussions to plane waves; all formulas will also be valid for *APW*'s.

Given a basis of plane waves

$$(\psi_{\mathbf{k}1}, \psi_{\mathbf{k}2}, \ldots, \psi_{\mathbf{k}r}) \tag{4.3}$$

where

$$\psi_{\mathbf{k}n} = \exp(i(\mathbf{k} + \mathbf{K}_n) \cdot \mathbf{r}) \tag{4.4}$$

and $\mathbf{K}_n$ is a reciprocal lattice vector (2.3). We want to obtain a basis symmetry adapted to $({}^{\mathbf{k}}\Gamma_A)_{dd}$ of $G_{\mathbf{k}}$. If we have constructed such a basis, we obtain the basis that is symmetry adapted to $({}^{\mathbf{k}}\Gamma)_{dd}$ of G according to (3.8)

Then we determine $P_{\mathbf{k}}$, the point group of $\mathbf{k}$, of order $g_{\mathbf{k}}'$ with elements $P_i \in P_{\mathbf{k}}$ and the reciprocal lattice vectors $\mathbf{K}^i$ according to

$$P_i\mathbf{k} = \mathbf{k} + \mathbf{K}^i \tag{4.5}$$

which gives

$$P_i(\mathbf{k} + \mathbf{K}_n) = \mathbf{k} + \mathbf{K}^i + P_i\mathbf{K}_n = \mathbf{k} + \mathbf{K}_n{}^i \tag{4.6}$$

Now extend the basis (4.4) so that all the functions

$$\psi_{\mathbf{k}+\mathbf{K}_n^i} = \exp(\mathrm{i}(\mathbf{k} + \mathbf{K}_n{}^i) \cdot \mathbf{r}) \tag{4.7}$$

are included for all $P_i \in P_{\mathbf{k}}$. Let this expanded basis be

$$\Psi_{\mathbf{k}} = (\psi_{\mathbf{k}1}, \psi_{\mathbf{k}2}, \ldots, \psi_{\mathbf{k}s}) \tag{4.8}$$

where we have supposed that the basis now consists of s plane waves. For such basis functions we then have

$$\begin{aligned}(P_i \mid \mathbf{u}_i)\,\psi_{\mathbf{k}n} &= (P_i \mid \mathbf{u}_i)\exp(\mathrm{i}(\mathbf{k} + \mathbf{K}_n) \cdot \mathbf{r}) = \exp(\mathrm{i}(\mathbf{k} + \mathbf{K}_n) \cdot (P_i^{-1} \mid -P_i^{-1}\mathbf{u}_i)\,\mathbf{r}) \\ &= \exp(-\mathrm{i}(\mathbf{k} + \mathbf{K}_n{}^i) \cdot \mathbf{u}_i)\exp(\mathrm{i}(\mathbf{k} + \mathbf{K}_n{}^i) \cdot \mathbf{r}) \\ &= \exp(-\mathrm{i}(\mathbf{k} + \mathbf{K}_n{}^i) \cdot \mathbf{u}_i)\,\psi_{\mathbf{k}m}\end{aligned} \tag{4.9}$$

for some index m. Thus

$$(P_i \mid \mathbf{u}_i)\,\Psi_{\mathbf{k}} = \Psi_{\mathbf{k}}\Gamma((P_i \mid \mathbf{u}_i)) \tag{4.10}$$

where $\Gamma((P_i \mid \mathbf{u}_i))$ is an $s \times s$ matrix with

$$\Gamma((P_i \mid \mathbf{u}_i))_{mn} = \exp(-i(\mathbf{k} + \mathbf{K}_m) \cdot \mathbf{u}_i) \tag{4.11}$$

if $P_i(\mathbf{k} + \mathbf{K}_n) = \mathbf{k} + \mathbf{K}_m$ and vanishing otherwise. Then we obtain from (3.14) and (4.10) that

$$^{j\mathbf{k}}S_{dd}\Psi_{\mathbf{k}} = \Psi_{\mathbf{k}}{}^{j\mathbf{k}}\mathsf{S}_{dd} \tag{4.12}$$

with

$$(^{j\mathbf{k}}\mathsf{S}_{dd})_{mn} = \frac{l_{j\mathbf{k}}}{g_{\mathbf{k}}'} \sum_{P_i \in P_{\mathbf{k}}} {}^{j\mathbf{k}}\Gamma_A{}^*((P_i \mid \mathbf{u}_i))_{dd}\, \Gamma((P_i \mid \mathbf{u}_i))_{mn} \tag{4.13}$$

Now orthonormalize the columns of $^{j\mathbf{k}}\mathsf{S}_{dd}$, skipping vanishing columns. The remaining columns form a matrix $^{j\mathbf{k}}\mathsf{t}_{dd}$ [1].

The elements of each column give the coefficients α_n in the linear combinations of plane waves (4.1) that are symmetry adapted to row d of irrep $^{j\mathbf{k}}\Gamma_A$ of $G_{\mathbf{k}}$. For each such linear combination of functions $\psi_{\mathbf{k}m}$ one obtains $n_{\mathbf{k}}$ linear combinations functions $\psi_{P_i\mathbf{k}m}$ $(l = 1, 2, \ldots, n_{\mathbf{k}})$ according to (3.8), belonging to the d-th row in the l-th block of $^{j\mathbf{k}}\Gamma$ of G.

5. Symmetry Projection of Space Orbitals

In this section we shall first develop the theory for atoms of only one chemical element in the unit cell. Their positions and orbitals are transformed into each other by the space group operators. At the end of the section we give then the simple generalization to several chemical elements, which shows that each chemical element can be treated separately.

We shall first extend our conventions, because we have to consider transformations by space group operators of functions in different coordinate systems. A function ψ, defined on the three-dimensional Euclidean space E^3 is a mapping of points in that space to numbers in the complex plane. The points of E^3 can be described by names like Q, S, etc. or by vectors like $\mathbf{q}$, $\mathbf{s}$. These vectors are then position vectors from an origin O to the points Q, S etc. By choosing a cartesian coordinate system with origin O, the vectors can be given by their coordinates q, s etc. in this system. We have

$$\mathbf{q} = (\boldsymbol{l}_x, \boldsymbol{l}_y, \boldsymbol{l}_z)\begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = \hat{\mathsf{x}}\mathsf{q} \tag{5.1}$$

Then ψ is given by the functional prescription ψ_O to obtain the function value for a point Q from the three real numbers q_x , q_y , q_z .

$$\psi(Q) = \psi_O(\mathbf{q}) \tag{5.2}$$

If we choose another origin $O(\mathbf{c})$ and cartesian coordinate axes parallel to the first system, we can denote the point Q by the coordinates $\mathbf{q}'$ in this system and

$$\psi(Q) = \psi_{O(\mathbf{c})}(\mathbf{q}') \tag{5.3}$$

$O(\mathbf{c})$ has coordinates $\mathbf{c}$ in the original coordinate system O so that

$$\mathbf{q} = \mathbf{c} + \mathbf{q}' \tag{5.4}$$

and

$$\psi_{O(\mathbf{c})}(\mathbf{q}') = \psi_O(\mathbf{c} + \mathbf{q}') \tag{5.5}$$

Remember that ψ, ψ_O , $\psi_{O(\mathbf{c})}$ are all different descriptions of the same function. Occasionally we may write $O(\mathbf{0})$ for O.

We introduce a shorter notation for the function $(E \mid \mathbf{a})\ \psi$

$$\psi_{\mathbf{a}} = (E \mid \mathbf{a})\ \psi \tag{5.6}$$

Also

$$(E \mid \mathbf{0})\ \psi = \psi_{\mathbf{0}} \tag{5.7}$$

and

$$(E \mid \mathbf{b})\ \psi_{\mathbf{a}} = (E \mid \mathbf{b})(E \mid \mathbf{a})\ \psi = (E \mid \mathbf{a} + \mathbf{b})\ \psi = \psi_{\mathbf{a}+\mathbf{b}} \tag{5.8}$$

If ψ is an atomic orbital for an atom at O, then $\psi_{\mathbf{a}}$ will be the equivalent atomic orbital for an atom at $O(\mathbf{a})$. Usually the description of the function $\psi_{\mathbf{a}}$ will be given in the coordinate system $O(\mathbf{a})$, $\psi_{\mathbf{a}O(\mathbf{a})}(\mathbf{q})$. According to (5.5), and (5.6) we have

$$\begin{aligned}\psi_{\mathbf{a}O(\mathbf{a})}(\mathbf{q}) &= \psi_{\mathbf{a}O(\mathbf{0})}(\mathbf{q} + \mathbf{a}) = (E \mid \mathbf{a})\ \psi_{\mathbf{0}O(\mathbf{0})}(\mathbf{q} + \mathbf{a}) \\ &= \psi_{\mathbf{0}O(\mathbf{0})}((E \mid \mathbf{a})^{-1}(\mathbf{q} + \mathbf{a})) = \psi_{\mathbf{0}O(\mathbf{0})}(\mathbf{q})\end{aligned} \tag{5.9}$$

We introduce a notation for the point group operators with different reference points.

$$(P \mid \mathbf{0}) = P = {}^{\mathbf{0}}P \tag{5.10}$$

${}^{\mathbf{0}}P$ is the point group operator that leaves $O(\mathbf{0})$ unchanged. Similarly we write ${}^{\boldsymbol{\mu}}P$ for a point group operator that leaves $O(\boldsymbol{\mu})$ fixed. We define, using $P\mathbf{q} = \hat{\mathbf{x}}\mathsf{P}\mathbf{q}$,

$$\hat{P}\psi_O(\mathbf{q}) = \psi_O(\mathsf{P}^{-1}\mathbf{q}) \tag{5.11}$$

$${}^{\boldsymbol{\mu}}\hat{P}\psi_{O(\boldsymbol{\mu})}(\mathbf{q}) = \psi_{O(\boldsymbol{\mu})}(\mathsf{P}^{-1}\mathbf{q}) \tag{5.12}$$

in agreement with (3.1). When ${}^{\mu}\hat{P}$ is applied to an orbital ψ_μ for an atom at $O(\mu)$ the resulting function is again an orbital for the atom at $O(\mu)$. The function ψ_μ has been rotated about its center $O(\mu)$.

Further we have to investigate the action of ${}^{0}\hat{P}$ on an orbital for an atom at $O(\mu)$. But we generalize the discussion directly to that of the action of the space group operator $({}^{0}P \mid \mathbf{u})$, where $\mathbf{u}$ is a nonprimitive lattice translation for nonsymmorphic space groups.

If we want to operate with $(P \mid \mathbf{u})$ on a function φ, given as $\varphi_{O(\mu)}(\mathbf{q})$ in coordinates of $O(\mu)$, we must first rewrite the function as a function of coordinates in $O(\mathbf{0})$, since only for such functions the action of $(P \mid \mathbf{u})$ was defined in (3.1). According to (5.5) we then have

$$\varphi_{O(\mu)}(\mathbf{q}) = \varphi_{O(0)}(\mathbf{q} + \mu) \tag{5.13}$$

and according to (3.1) we obtain

$$\begin{aligned}(P \mid \mathbf{u})\, \psi_{O(0)}(\mathbf{q} + \mu) &= \psi_{O(0)}((P \mid \mathbf{u})^{-1}(\mathbf{q} + \mu)) \\ &= \psi_{O(0)}(\mathsf{P}^{-1}\mathbf{q} + \mathsf{P}^{-1}\mu - \mathsf{P}^{-1}\mathbf{u})\end{aligned} \tag{5.14}$$

Let the atomic position μ be transformed by $(P \mid \mathbf{u})^{-1}$ into

$$(P \mid \mathbf{u})^{-1}\, \mu = P^{-1}\mu - P^{-1}\mathbf{u} = \nu + \mathbf{n}(F, \mu, \nu) \tag{5.15}$$

where ν is another atomic position vector in the unit cell with origin at $\mathbf{n}(F, \mu, \nu)$. Here $\mathbf{n}(F, \mu, \nu)$ is a lattice vector uniquely determined by $F = (P \mid \mathbf{u})$ and μ. So an atomic orbital at μ is transformed into an atomic orbital at $(P \mid \mathbf{u})^{-1}\mu$. Then (5.14) becomes equal to

$$\begin{aligned}\psi_{O(0)}(\mathsf{P}^{-1}\mathbf{q} + \nu + \mathsf{n}(F, \mu, \nu)) &= \psi_{O(\nu+\mathsf{n}(F,\mu,\nu))}(\mathsf{P}^{-1}\mathbf{q}) \\ &= {}^{\nu+\mathsf{n}(F,\mu,\nu)}\hat{P}\psi_{O(\nu+\mathsf{n}(F,\mu,\nu))}(\mathbf{q})\end{aligned} \tag{5.16}$$

where we used (5.12). We can recapitulate these results, taking for ψ the atomic orbital ψ_μ so that we obtain

$$(P \mid \mathbf{u})\, \psi_\mu = {}^{\nu+\mathbf{n}(F,\mu,\nu)}\hat{P}\psi_{\nu+\mathbf{n}(F,\mu,\nu)} \tag{5.17}$$

where the convention between μ and ν is given by (5.15).

Therefore $(P \mid \mathbf{u})\, \psi_\mu$ will usually be given as function of coordinates in $O(\nu + \mathbf{n}(F, \mu, \nu))$.

We make a slight generalization, to describe the action of $(P \mid \mathbf{u} + \mathbf{n}')$ on $\psi_{\mu+\mathbf{n}}$ where $\mathbf{n}'$ and $\mathbf{n}$ are lattice vectors.

$$\begin{aligned}(P \mid \mathbf{u} + \mathbf{n}')\, \psi_{\mu+\mathbf{n}} &= (E \mid \mathbf{n}')(P \mid \mathbf{u})(E \mid \mathbf{n})\, \psi_\mu = (E \mid \mathbf{n}')(E \mid P\mathbf{n})(P \mid \mathbf{u})\, \psi_\mu \\ &= (E \mid \mathbf{n}' + P\mathbf{n})\, {}^{\nu+\mathbf{n}(F,\mu,\nu)}\hat{P}\psi_{\nu+\mathbf{n}(F,\mu,\nu,)} = {}^{\nu+\mathbf{m}}\hat{P}\psi_{\nu+\mathbf{m}}\end{aligned} \tag{5.18}$$

with $\nu + \mathbf{n}(F, \mu, \nu) + \mathbf{n}' + P\mathbf{n} = \nu + \mathbf{m}$. For later use we note that we can write $\mathbf{n}$ as

$$\mathbf{n} = P^{-1}(\mathbf{m} - \mathbf{n}(F, \mu, \nu) - \mathbf{n}') \tag{5.19}$$

So we obtain that

$$(P \mid \mathbf{u} + \mathbf{n}')\, \psi_{\mu+\mathbf{n}} = {}^{\nu+\mathbf{m}}\hat{P}\psi_{\nu+\mathbf{m}} \tag{5.20}$$

Now we assume that we have a basis of L atomic orbitals

$$\Psi_0 = (\psi_0{}^1, \psi_0{}^2, \ldots, \psi_0{}^L) \tag{5.21}$$

for an atom at $O(\mathbf{0})$. Then an equivalent basis for an atom at $O(\mu)$ is given by

$$\Psi_\mu = (\psi_\mu{}^1, \psi_\mu{}^2, \ldots, \psi_\mu{}^L) \tag{5.22}$$

Further we assume that the basis has been chosen to be stable under the operations of the point group G_P of the space group, so that

$$\hat{P}\Psi_0 = \Psi_0{}^L\Gamma(P) \tag{5.23}$$

where the matrices ${}^L\Gamma(P)$ form a representation of G_P. Similarly

$${}^\mu\hat{P}\Psi_\mu = \Psi_\mu{}^L\Gamma(P) \tag{5.24}$$

We now construct a Bloch basis for atoms at position μ in the unit cells, by acting with (3.5) on (5.22) obtaining

$$\Psi_{\mathbf{k}\mu} = \frac{1}{N}\sum_{\mathbf{n}} \exp(i\mathbf{k}\cdot\mathbf{n})(E \mid \mathbf{n})\, \Psi_\mu = \frac{1}{N}\sum_{\mathbf{n}} \exp(i\mathbf{k}\cdot\mathbf{n})\, \Psi_{\mu+\mathbf{n}} \tag{5.25}$$

A similar Bloch basis is formed for each atomic position ν, λ etc. in the unit cell. Our complete Bloch basis is then

$$\Psi_{\mathbf{k}} = (\Psi_{\mathbf{k}\mu}, \Psi_{\mathbf{k}\nu}, \Psi_{\mathbf{k}\lambda}, \ldots) \tag{5.26}$$

When we operate with $(P \mid \mathbf{u} + \mathbf{n}')$ on $\Psi_{\mathbf{k}\mu}$ we obtain

$$\begin{aligned}(P \mid \mathbf{u} + \mathbf{n}')\, \Psi_{\mathbf{k}\mu} &= \frac{1}{N}\sum_{\mathbf{n}} \exp(i\mathbf{k}\cdot\mathbf{n})(P \mid \mathbf{u} + \mathbf{n}')\, \Psi_{\mu+\mathbf{n}} \\ &= \frac{1}{N}\sum_{\mathbf{n}} \exp(i\mathbf{k}\cdot\mathbf{n})\, {}^{\nu+\mathbf{m}}P\Psi_{\nu+\mathbf{m}} = \frac{1}{N}\sum_{\mathbf{n}} \exp(i\mathbf{k}\cdot\mathbf{n})\, \Psi_{\nu+\mathbf{m}}\, {}^L\Gamma(P)\end{aligned} \tag{5.27}$$

where we have used (5.25), (5.20) and an equivalent of (5.24).

We shall now rewrite the term $\exp(i\mathbf{k}\cdot\mathbf{n})$ using (5.19). Further we shall assume that $(P \mid \mathbf{u}+\mathbf{n}') \in G_{\mathbf{k}}$, so that $P\mathbf{k} = \mathbf{k} + \mathbf{K}$. Then

$$\begin{aligned}\exp(i\mathbf{k}\cdot\mathbf{n}) &= \exp(i\mathbf{k}\cdot(P^{-1}(\mathbf{m} - \mathbf{n}(F,\mu,\nu) - \mathbf{n}'))) \\ &= \exp(i\mathbf{k}\cdot(\mathbf{m} - \mathbf{n}(F,\mu,\nu) - \mathbf{n}'))\end{aligned} \tag{5.28}$$

Then (5.27) becomes equal to

$$\begin{aligned}&\exp(-i\mathbf{k}\cdot(\mathbf{n}(F,\mu,\nu)+\mathbf{n}'))\frac{1}{N}\sum_{\mathbf{m}}\exp(i\mathbf{k}\cdot\mathbf{m})\,\Psi_{\nu+\mathbf{m}}\,{}^{L}\Gamma(P) \\ &\quad= \exp(-i\mathbf{k}\cdot(\mathbf{n}(F,\mu,\nu)+\mathbf{n}'))\,\Psi_{\mathbf{k}\nu}\,{}^{L}\Gamma(P)\end{aligned} \tag{5.29}$$

So we have obtained that

$$(P \mid \mathbf{u}+\mathbf{n}')\,\Psi_{\mathbf{k}\mu} = \Psi_{\mathbf{k}\nu}\exp(-i\mathbf{k}\cdot(\mathbf{n}(F,\mu,\nu)+\mathbf{n}'))\,{}^{L}\Gamma(P) \tag{5.30}$$

When $\hat{F} = (P \mid \mathbf{u}+\mathbf{n}')$ acts on the complete Bloch basis (5.26) we get

$$\hat{F}\Psi_{\mathbf{k}} = \hat{F}(\Psi_{\mathbf{k}\mu}, \Psi_{\mathbf{k}\nu}, \ldots) = \Psi_{\mathbf{k}}\mathsf{F} \tag{5.31}$$

with

$$\mathsf{F} = \begin{pmatrix} \mathsf{F}_{\mu\mu} & \mathsf{F}_{\mu\nu} & \mathsf{F}_{\mu\lambda} & \cdots \\ \mathsf{F}_{\nu\mu} & \mathsf{F}_{\nu\nu} & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{5.32}$$

and

$$\mathsf{F}_{\mu\nu} = \delta((P \mid \mathbf{u})^{-1}\mu, \nu + \mathbf{n}(F,\mu,\nu))\exp(-i\mathbf{k}\cdot(\mathbf{n}(F,\mu,\nu)+\mathbf{n}'))\,{}^{L}\Gamma(P) \tag{5.33}$$

with $\delta((P \mid \mathbf{u})^{-1}\mu, \nu + \mathbf{n}(F,\mu,\nu)) = 1$ if $(P \mid \mathbf{u})^{-1}\mu = \nu + \mathbf{n}(F,\mu,\nu)$ and zero otherwise. When the projection operator (3.9)

$${}^{j\mathbf{k}}S_{\dot{a}\dot{d}} = \frac{l_{j\mathbf{k}}}{g_{\mathbf{k}}}\sum_{(P\mid\mathbf{u}+\mathbf{n}')\in G_{\mathbf{k}}} {}^{j\mathbf{k}}\Gamma^{*}((P \mid \mathbf{u}+\mathbf{n}'))_{\dot{a}\dot{d}}\,(P \mid \mathbf{u}+\mathbf{n}') \tag{5.34}$$

acts on the Bloch basis $\Psi_{\mathbf{k}}$ the terms $\exp(-i\mathbf{k}\cdot\mathbf{n}')$ in (5.33) will compensate the term $\exp(i\mathbf{k}\cdot\mathbf{n}')$ in ${}^{j\mathbf{k}}\Gamma^{*}((P \mid \mathbf{u}+\mathbf{n}'))_{\dot{a}\dot{d}}$ so that all terms in the summation with the same $(P \mid \mathbf{u})$ but different $\mathbf{n}'$ are equal. So each term occurs N times and we can restrict the summations to the different $(P \mid \mathbf{u})$ with $P \in P_{\mathbf{k}}$, obtaining like in (3.14) that

$${}^{j\mathbf{k}}S_{\dot{a}\dot{d}} = \frac{l_{j\mathbf{k}}}{g_{\mathbf{k}}'}\sum_{P\in P_{\mathbf{k}}} {}^{j\mathbf{k}}\Gamma_{A}^{*}((P \mid \mathbf{u})) \tag{5.35}$$

When ${}^{j\mathbf{k}}S_{\dot{a}\dot{d}}$ operates on $\Psi_{\mathbf{k}}$ we get

$$ {}^{j\mathbf{k}}S_{\dot{a}\dot{d}}\Psi_{\mathbf{k}} = \Psi_{\mathbf{k}}{}^{j\mathbf{k}}\mathsf{S}_{\dot{a}\dot{d}} \tag{5.36} $$

where the matrix ${}^{j\mathbf{k}}\mathsf{S}_{\dot{a}\dot{d}}$ has the same structure of subblocks as F in (5.32). To the block $({}^{j\mathbf{k}}\mathsf{S}_{\dot{a}\dot{d}})_{\mu\nu}$ do only those elements $(P \mid \mathbf{u})$ contribute for which

$$ (P \mid \mathbf{u})^{-1}\,\mu = \nu + \mathbf{n}(F, \mu, \nu) \tag{5.37} $$

because of (5.33). Denote this set by $G(\mu, \nu)$. Then using (5.31)–(5.33) and (5.36) we obtain

$$ ({}^{j\mathbf{k}}\mathsf{S}_{\dot{a}\dot{d}})_{\mu\nu} = \frac{l_{j\mathbf{k}}}{g_{\mathbf{k}}'} \sum_{(P\mid\mathbf{u})\in G(\mu,\nu)} {}^{j\mathbf{k}}\Gamma_A{}^*((P \mid \mathbf{u}))_{\dot{a}\dot{d}} \exp(-i\mathbf{k}\cdot\mathbf{n}(F, \mu, \nu))\, {}^{L}\Gamma(P) \tag{5.38} $$

with the same conventions for $l_{j\mathbf{k}}$, $g_{\mathbf{k}}'$ and ${}^{j\mathbf{k}}\Gamma_A{}^*((P \mid \mathbf{u}))$ as in sections two and three. ${}^{j\mathbf{k}}\Gamma_A$ is given by (2.25) or (2.31).

With the columns of ${}^{j\mathbf{k}}\mathsf{S}_{\dot{a}\dot{d}}$ we go through the same procedure as described at the end of section four, to obtain the symmetry adapted linear combinations of Bloch functions $\psi^i_{\mathbf{k}\mu}$ ($i = 1, 2, \ldots, L$; μ runs over the different atomic sites in the unit cell).

The generalization of the formulas for the case of several chemical elements in the unit cell is simple. Assume that the theory above was developed for atoms of chemical element α. We should then denote the basis (5.21) as $\Psi_{\alpha 0}$. Since the space group operators F_i map the crystal into itself, they will map the position of one atom into that of another atom of the same chemical element. Similarly, $\hat{F}_i$ will map orbitals of only one chemical element into each other. Let $\Psi_{\alpha 0}$ consist of L_α basis functions. Similarly $\Psi_{\beta 0}$ will be a stable basis of L_β basis functions for an atom of chemical element β at position $O(\mathbf{0})$. Then (5.23) can be generalized to

$$ P\Psi_{\kappa 0} = \Psi_{\kappa 0}{}^{L_\kappa}\Gamma(P) \tag{5.39} $$

for $\kappa = \alpha, \beta, \ldots$ Then form the basis

$$ \Psi_0 = (\Psi_{\alpha 0}, \Psi_{\beta 0}, \Psi_{\gamma 0}, \ldots) \tag{5.40} $$

When $\hat{P}$ acts on this basis we obtain

$$ \hat{P}\Psi_0 = \Psi_0\Gamma(P) \tag{5.41} $$

where $\Gamma(P)$ is blockdiagonal with blocks ${}^{L_\kappa}\Gamma(P)$ along the main diagonal. The Bloch basis will be

$$ \Psi_{\mathbf{k}} = (\Psi_{\alpha\mathbf{k}}, \Psi_{\beta\mathbf{k}}, \Psi_{\gamma\mathbf{k}}, \ldots) \tag{5.42} $$

with subbases $\Psi_{\alpha\mathbf{k}}$ of form (5.26). All derivations are then valid for each subbasis separately. When the projection operator (5.34) acts on (5.42) we obtain

$$ {}^{j\mathbf{k}}S_{\delta\delta}\Psi_{\mathbf{k}} = \Psi_{\mathbf{k}}\,{}^{j\mathbf{k}}S_{\delta\delta} \tag{5.43} $$

with ${}^{j\mathbf{k}}S_{\delta\delta}$ blockdiagonal in the same way as $\Gamma(P)$ in (5.41). The subblock ${}^{j\mathbf{k}}S_{\delta\delta\alpha}$ is a projection matrix for atoms of chemical element α and $({}^{j\mathbf{k}}S_{\delta\delta\alpha})_{\mu\nu}$ is of the form (5.38).

So each chemical element can be treated separately.

6. Short Description of the Programs

Two programs were written for the calculation of projection matrices (4.13) and (5.38). The programs SYMPRJ and SYMPW symmetrize atomic orbitals (spherical harmonics) and plane waves, respectively.

They have large parts in common, so we shall describe them simultaneously. Both contain the program IRREP for calculation of irreps as a subroutine. Both use some datasets stored on disks, which have been created by a program PRODAT. The program PRODAT is supplied with standard input and it has to be run only once per computer. It stores the multiplication tables of the point groups D_{6h} and O_h, from which the multiplication tables of all other point groups can be formed, with the help of an indexing system, also created by PRODAT. Further the elements of ${}^{L}\Gamma(P)$ in (5.38) for spherical harmonics Y_{lm} for $l = 0, 1, 2, 3$ are calculated and stored. It is possible to extend the program for larger values of l.

Common input to SYMRPJ and SYMPW is information about the primitive crystal unit cell and the space group. The primitive lattice vectors (2.1) are given by

$$ (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3) = (l_x, l_y, l_z)\,\mathsf{A} \tag{6.1} $$

where the elements of the matrix A are given as input to the programs. The space group is given by an index for the point group G_P and, for nonsymmorphic space groups only, the nonprimitive lattice translations $\mathbf{u}_i$.

For SYMPRJ one must also give the number of chemical elements, the number of atoms of each element and the positions μ of the atoms.

After this information the input may contain as many vectors $\mathbf{k}$ as wanted. For SYMPW the input must contain for each $\mathbf{k}$-vector the vectors $\mathbf{K}_n$ of (4.4) defining the plane waves $\psi_{\mathbf{k}n}$ to be included in the basis. The program itself extends this basis according to (4.6)–(4.8).

The program then produces the orthonormal columns of the projection matrix

${}^{j\mathbf{k}}S_{\alpha\delta}$ according to the theory described in the previous sections. First the program determines if $\mathbf{k}$ lies in the Brillouin zone or on its boundary. Then it forms $P_{\mathbf{k}}$ and, if necessary $G_{\mathbf{k}}/T_{\mathbf{k}}$. Then it calculates all irreps of $P_{\mathbf{k}}$ or $G_{\mathbf{k}}/T_{\mathbf{k}}$ and selects the allowable irreps. In SYMPRJ the sets $G(\mu, \nu)$ and the lattice vectors $\mathbf{n}(F, \mu, \nu)$ are also determined. Then all information to form the projection matrix (5.38) or (4.13) is available, and its elements are calculated for each irrep. After the orthonormalization of the columns of the projection matrix these columns are printed.

The programs have been written in Fortran for IBM360/75 in Stockholm. Detailed program description are available from Quantum Chemistry Program Exchange, Chemistry Dept., Indiana University, Bloomington, Indiana or directly from the authors.

8. Conclusion

In this paper the theory of symmetry projection is given only for single space groups, since our programs were written for this case. Extensions to double space groups and magnetic space groups are not difficult. One can again reduce the problem of finding their irreps to construction of irreps of finite groups.

At present the programs have been written for up to four-dimensional irreps. But when more computer space becomes available it will just be a question of changing dimensions of arrays, to extend the programs to six-dimensional irreps, which occur for some $\mathbf{k}$-vectors in a few space groups.

We are able to produce tables of symmetry adapted functions for all the space groups with our programs, but at present we do not plan to do so. The resulting output material would be so voluminous, that it would have to be edited in some coded form. It would then take a reader as much time to learn this code as it takes to learn to handle our programs, with which he can produce all the information for the relevant space group and $\mathbf{k}$-vectors within a few minutes of computer time.

Acknowledgments

I want to thank my teacher Dr. S. Flodmark for continuous help and support under the development of this project, which was initiated by him. Private communications with Dr. F. Harris, Dr. J. Cannon, Prof. J. Neubüser and Dr. J. D. Dixon helped to improve the method of calculating irreps. The Swedish Research Council supplied computer time. The quantum chemistry group of Prof. I. Fischer-Hjalmars was so kind as to let me use its computer time, when we ourselves temporarily ran out of money. I want to thank the Directors, the International Atomic Energy Agency and UNESCO for their hospitality at the 1972 Winter College on Electrons in Crystalline Solids at the International Centre for Theoretical Physics in Trieste, where I got the opportunity to prepare program SYMPW and some improvements of program IRREP.

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