Note

Symmetry Transformation of Crystal Wave Functions

1. INTRODUCTION

A number of operating computer programs for the complete symmetry adaptation of electronic wavefunctions with respect to crystallographic groups have been carefully tested, and certain corrections in the earlier theoretical description of the symmetrization procedure are made.

Using group algebra to decompose the Hamiltonian of a quantum system, it is necessary to know the irreducible representations. In the case of finite-order groups a general technique of finding the irreducible representations has been presented [1] and programmed for a computer [2]. The symmetrization procedure has been performed in explicit terms for crystallographic states [3] and has also been programmed for a computer [4]. This program is used in combination with programs for computing energy bands according to the tight-binding and augmented-plane-wave (APW) methods. A review article is available describing the techniques to be used for magnetic space groups [5], although this procedure has not been programmed so far. Also, nonnumerical methods are possible in using computers to find the irreducible representatives [6].

One of the most useful contributions to the theory of symmetry adaptation of trial states in quantum mechanics was given by Wigner [7]. By using his projection operator [8],

$$^jS_{mm} = (l_j/g) \sum_{A \in G} {}^jD^*(A)_{mm}A, \tag{1}$$

states belonging to the symmetry type $| jm \rangle$ with respect to the group G of the Hamiltonian are obtained. The notations used in (1) are standard: A is an element of G, which is supposed to have finite order g, and $^jD(A)_{mn}$ are matrix elements of one of its irreducible representations, the order of which is denoted by l_j.

The matrix representative of (1) in a trial basis of finite order N is singular (when the basis is reducible). Denoting by n_j the number of times the jth irreducible representation is found in the basis, there are only $n_j l_j$ linearly independent columns in this matrix. By orthonormalizing the columns of the projection matrix, a rectangular matrix ^jt_m of order $n_j l_j \times N$ is thus obtained [3]. This is the so-called "reduction matrix" by means of which the Hamiltonian matrix can be reduced from order N to order $n_j l_j$ according to

$$^{jm}\mathbf{H} = {}^jt_m{}^\dagger \mathbf{H} \, {}^jt_m . \tag{2}$$

The main difficulty of performing this procedure is to find the irreducible matrix

representatives occurring in the expression (1) for the projection operator. This problem has been solved for arbitrary finite groups [1], and the method has been programmed for a computer. The corresponding program, IRREP, is available at the Quantum Chemistry Exchange Program (QCPE) of Indiana Univ., Bloomington, Indiana [2]. The symmetry adapatation procedure has also been programmed in the cases of the tight-binding and APW methods for computing electron states in crystals [4].

These programs are very general and are now in full use, combined with other available programs for energy band calculations.

The procedure of symmetry adaptation of crystallographic states is also described by Blokker [9]. This paper was written under guidance of the present author, but it contains a number of mistakes which are due, partly, to using an unnecessarily complicated transformation scheme. This makes it necessary to rewrite some of the derivations in detail.

2. TRANSFORMATION OF CRYSTAL ORBITALS

Consider a primitive crystallographic lattice vector $\mathbf{n}$ and a vector $\boldsymbol{\mu}$ defining the position of an atomic site in the unit cell. A space group operation $F = (P \mid \mathbf{t})$ is defined as the combination $T(\mathbf{t}) P$ between a point group operator P and a translation $T(\mathbf{t})$ through the distance $\mathbf{t}$. When F operates on the atomic position vector $\mathbf{n} + \boldsymbol{\mu}$ another atomic position vector $\mathbf{n}' + \boldsymbol{\nu}$ is obtained where $\mathbf{n}'$ is a primitive lattice vector. Thus,

$$F\boldsymbol{\mu} = \boldsymbol{\nu} + \mathbf{n}(F, \boldsymbol{\mu}, \boldsymbol{\nu}), \tag{3}$$

where $\mathbf{n}(F, \boldsymbol{\mu}, \boldsymbol{\nu}) = \mathbf{n}' - P\mathbf{n}$ defines a primitive lattice vector. This definition is the same as given by [3], but it differs from Blokker's formula [9, (5.15)].

Now consider a wavefunction $\psi(\mathbf{r})$ which may be localized to a lattice site, used as the origin of the coordinate system. Translating this function by $T_{op}(\mathbf{n} + \boldsymbol{\mu})$ one obtains the function $\psi(\mathbf{r} - \mathbf{n} - \boldsymbol{\mu}) = \psi_{\mathbf{n}+\boldsymbol{\mu}}(\mathbf{r})$. This is thus a function localized to the atomic position $\mathbf{n} + \boldsymbol{\mu}$. By means of (3) and the definition $F_{op}\psi_0(\mathbf{r}) = \psi_0(F^{-1}\mathbf{r})$ for F_{op}, then

$$F_{op}\psi(\mathbf{r} - \mathbf{n} - \boldsymbol{\mu}) = \psi(F^{-1}\mathbf{r} - \mathbf{n} - \boldsymbol{\mu}) = \psi(P^{-1}(\mathbf{r} - \boldsymbol{\tau})), \tag{4}$$

where

$$\boldsymbol{\tau} = \boldsymbol{\nu} + P\mathbf{n} + \mathbf{n}(F, \boldsymbol{\mu}, \boldsymbol{\nu}) \tag{5}$$

is the center of localization for the transformed function (4). This result coincides with Blokker's formula [9, (5.17)], although his definition of $\mathbf{n}(F, \boldsymbol{\mu}, \boldsymbol{\nu})$ is not the same as in (3). This is erroneous, since Blokker has used Wigner's definition for transformation of functions, forgetting that certain operations are forbidden in his transformation scheme [7, p. 106]. In our scheme a geometrical definition is used where it is important to keep the same variable $\mathbf{r}$ in a series of consecutive operations, as is done in (4).

In the linear-combination-of-atomic-orbitals (LCAO) method, one uses a basis of localized wave functions

$$\psi_{n+\mu} = (\psi^1_{n+\mu}, \psi^2_{n+\mu}, \ldots). \tag{6}$$

These wavefunctions form a closed set which is invariant under point group operation through the center of localization given by the position vector $n + \mu$. Using this set to form a set of Bloch wavefunctions

$$\psi_{k,\mu} = \sum_n e^{ik \cdot n} \psi_{n+\mu}, \tag{7}$$

we obtain [3]

$$F_{op}\psi_{k,\mu} = \psi_{Pk,\nu}F_{\nu\mu}. \tag{8}$$

In the case when F belongs to the little group of k, Pk can be replaced by k in (8), and

$$F_{\nu\mu} = \delta(F\mu, \nu + n(F, \mu, \nu))e^{-ik \cdot n(F,\mu,\nu)}P, \tag{9}$$

where $\delta(F\mu, \nu + n(F, \mu, \nu)) = 1$ if (3) is fulfilled and zero otherwise.

The matrix P represents the corresponding point group operator with respect to the center $n + \mu$ in the basis (6). Forming a basis of Bloch functions according to the tight-binding approximation,

$$\Psi_k = (\psi_{k,\mu}, \psi_{k,\nu}, \ldots), \tag{10}$$

where all atomic positions μ, $\nu, \ldots$ of the primitive unit cell occur, we thus obtain

$$F_{op}\Psi_k = \Psi_k F. \tag{11}$$

Here F is the block matrix

$$F = \begin{pmatrix} F_{\mu\mu} & F_{\mu\nu} & \cdots \\ F_{\nu\mu} & F_{\nu\nu} & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} \tag{12}$$

given by the submatrices (9).

In [9, Eq. (5.33)], μ and ν have been interchanged in $F_{\nu\mu}$ by mistake; the erroneous occurrence of the inverse of F in the definition of $n(F, \mu, \nu)$ as discussed above makes this formula again correct. The computer program [4] for symmetry adaptation of crystal orbitals which works according to [9, (5.33)] in the tight-binding case therefore gives correct results.

3. SYMMETRY ADAPTATION OF CRYSTAL ORBITALS

Starting with a trial basis of Bloch wavefunctions (7), it suffices to use Wigner's projection operator for the allowable irreducible representations of the factor group G_k/T_k in order to find a completely symmetry-adapted basis with respect to the

crystallographic group G. Here G_k is the little group of k defined by the subgroup of G whose elements $F = (P \mid t)$ fulfill the condition

$$P\mathbf{k} = \mathbf{k} + \mathbf{K}, \tag{13}$$

where $\mathbf{K}$ is 2π times a primitive reciprocal-lattice vector and T_k is a subgroup of the group G_T of primitive lattice translations $T(\mathbf{n})$, the elements, $T(\mathbf{n}')$, of T_k determined by the condition

$$e^{-i\mathbf{k}\cdot\mathbf{n}'} = 1. \tag{14}$$

Setting $F = (P_l \mid \mathbf{u}_l + \mathbf{n})$, where $\mathbf{n} = \mathbf{n}' + \mathbf{m}$ is a primitive lattice vector and $\mathbf{m}$ does not satisfy the condition (14) when $\mathbf{m} \neq 0$, the elements of G_k/T_k are related to the coset representatives $(P_l \mid \mathbf{u}_l + \mathbf{m})$. To find the multiplication table of G_k/T_k, we label the elements (l, s) of this group by two indices; l is a label for the point group elements in the little group and s is defined by

$$s = \exp(-i\mathbf{k} \cdot (\mathbf{u}_l + \mathbf{m})), \tag{15}$$

which can take only a small number of different values. Thus G_k/T_k is a group of finite order. Its multiplication table is obtained using (15) and the product rule for space group elements,

$$(P_l \mid \mathbf{u}_l + \mathbf{m})(P_{l'} \mid \mathbf{u}_{l'} + \mathbf{m}') = (P_l P_{l'} \mid P_l(\mathbf{u}_{l'} + \mathbf{m}') + \mathbf{u}_l + \mathbf{m}). \tag{16}$$

Once this multiplication table for the group G_k/T_k is obtained, there is a general method for finding its irreducible representatives [1]. This method is used in the program IRREP [2] occurring as a subprogram in the symmetry projection programs [4]. Having found the irreducible representations of G_k/T_k one must select irreducible representations $^{jk}\Gamma_A((P \mid \mathbf{u} + \mathbf{m}))$ which are "allowable." These representations satisfy the condition that a primitive translation $T(\mathbf{m})$ occurring as a factor in the space group element $F = T(\mathbf{m}) F'$ related to the elements of G_k/T_k is represented by the irreducible representative of F' multiplied by the factor $\exp(-i\mathbf{k} \cdot \mathbf{m})$.

The irreducible representations are particularly simple, when $\mathbf{k}$ is a vector inside the Brillouin zone or when G_k is symmorphic. In these cases the factor (15) is just multiplied by the irreducible representation of the point group. In other cases the general method discussed above must be used. Using the basis (10) the projection matrix will be built up from subblocks

$$(^{jk}\mathbf{S}_{dd})_{\nu\mu} = (l_{jk}/g_k) \sum_{(P|t)\in G_k(\mu,\nu)/T_k} {}^{jk}\Gamma_A{}^*((P \mid t))_{dd} \exp[-i\mathbf{k} \cdot \mathbf{n}(F, \mu, \nu)]\mathbf{P}. \tag{17}$$

Here the sum is limited to elements of G_k/T_k combining the atomic sites μ and ν according to (3), thus forming the subset $G_k(\mu, \nu)/T_k$.

The projection matrix thus obtained is automatically block-diagonal with respect to different chemical elements in the atomic basis. It is also block-diagonal with respect to the angular momentum quantum number, in the case when the basis functions are spherical harmonics. It is a straightforward procedure to compute the

reduction matrices from (17) and reduce the Hamiltonian matrix according to (2). In the more general case of magnetic crystallographic space groups, a generalization of (17) is obtained [5, Eq. (175)]. By means of the program IRREP [2] it is possible to produce tables for all the crystallographic space groups, magnetic as well as nonmagnetic. The literature is not at all complete at this point. The results would, however, be enormously comprehensive. It is therefore preferable to make use of the programs [2, 4] in each particular application.

The symmetrization procedure described here has now been combined with an energy band program. Several test runs are made and the agreement between symmetrized and unsymmetrized versions is excellent. The band program uses the method of linear combinations of muffin-tin orbitals (LMTO) described in [10, 11]. This particular band program is orders of magnitude faster than conventional band programs. Symmetrization was found to be very important for classifying the crystallographic states.

A complete energy band calculation has been made on EuO [12], using the LMTO program combined with SYMPRJ [4]. The advantage of using symmetrization is particularly stressed when more complicated compounds with several atoms per unit cell are investigated.

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