Theory of Symmetry Projections in Applied Quantum Mechanics*

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The Wigner projection operator used in group theory for finding symmetry-adapted states in quantum mechanics is represented as a matrix in a given basis of trial state vectors. By diagonalizing this projection matrix, the redundancies occurring when the projection operator is applied directly are removed automatically. A straightforward method is given for this diagonalization procedure using only general properties of projection matrices. This method has proved very powerful in numerical applications using electronic computers. Particularly for the ligand-field treatment of a part of a crystal or in the case of a molecule of general point-group symmetry, the projection matrix to be used in the MO-LCAO method is constructed and simplified. This is done also for the nonsymmorphic space groups of crystals in the tight-binding approximation of band theory. The whole procedure of constructing symmetry-adapted states in this case has been programmed for an electronic computer.

1. INTRODUCTION

THE importance of using group theory in applications of quantum theory is nowadays realized more and more. The symmetry properties of a quantum-mechanical system being investigated are useful not only in order to systematize the obtained results, but they also yield a considerable simplification for the numerical treatment of the problem. This is extremely essential also when big electronic computers are used.

The fundaments of group theory can be found in many text books which consider application to quantum theory.[1-4] For the construction of symmetry-adapted states in quantum theory the Wigner projection operator[1] is fundamental.

In many-particle quantum theory, the group of permutations among identical particles is necessary for systematization of the states. Particularly for the quantum theory of electrons in atoms, molecules, and solids, the antisymmetrical representation of this group describes the many-electron states in accordance with the Pauli exclusion principle. When it is possible to separate space and spin coordinates, however, other representations of the permutation group may also become important.

Except for the permutation symmetry, the space symmetry of the electronic potential due to the distribution of atomic nuclei in their equilibrium positions is the one of great importance. The theory presented here will be applied, in particular, to space groups for crystals using MO-LCAO methods.

Crystal space symmetry has been known for a long time to be the foundation by means of which the electronic structure of crystals can be investigated from first

principles. Bloch[5] in 1928 constructed electronic states symmetry adapted with respect to periodic potentials. Bethe[6] in 1929 gave an original band theory based on the symmetry properties of crystals. The theory of little groups, which is of basic interest for the symmetry of crystals, was considered first by Bouckaert, Smoluchowski, and Wigner[7] and by Herring.[8] The theory of irreducible representations of space groups have been thoroughly investigated recently by McIntosh,[9,10] Koster,[11] Zak,[12] and Raghavacharyulu.[13] Zak is constructing irreducible characters and Raghavacharyulu is tabulating full irreducible representations for all the 230 crystallographic space groups. When spin is taken into account, the so-called "double space groups" must be considered, containing many additional representations. These have been considered originally by Elliott.[14] In a review article by Johnston[15] in 1960 the relation between the double group and the homogeneous Lorentz group of rotations in four-dimensional space has been considered in the non-relativistic limit.

Elementary introductions to crystal symmetry and energy bands are found in several textbooks.[2,3,4,16,17] Many good review articles on group theory and band structure calculations in solids also occur, among others by Herman,[18] who gives a good survey of the many

[1] E. P. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Friedrich Vieweg und Sohn, Braunschweig, Germany, 1931).
[2] V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, New York, 1960).
[3] S. L. Altmann, *Group Theory, Quantum Theory* (Academic Press Inc., New York, 1962).
[4] J. S. Lomont, *Applications of Finite Groups* (Academic Press Inc., New York, 1959).
[5] F. Bloch, Z. Physik 52, 555 (1928).
[6] H. A. Bethe, Ann. Physik 3, 133 (1929).
[7] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).
[8] C. Herring, Phys. Rev. 52, 361 (1937).
[9] H. V. McIntosh, J. Mol. Spectry. 5, 269 (1960).
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[13] I. V. V. Raghavacharyulu, J. Mol. Spectry. 7, 341 (1961).
[14] R. J. Elliott, Phys. Rev. 96, 280 (1954).
[15] D. F. Johnston, Rept. Progr. Phys. 23, 66 (1960).
[16] H. Jones, *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960).
[17] P. H. E. Meijer and E. Bauer, *Group Theory. The Application to Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1962).
[18] F. Herman, Rev. Mod. Phys. 30, 102 (1958).

methods occurring. Pincherle[19] gives a comprehensive list of references. Sokolov and Shirokovskiĭ[20] also recently gave a comprehensive review on the subject, which was a continuation of a similar paper considering point group symmetry.[21] Symmetry properties of the localized Wannier functions[22] in energy band theory have been studied by des Cloizeaux.[23]

Among the methods of applied band theory the simplest one is based on the free-electron model originally given by Bethe[24] and further considered by Brillouin.[25] On account of its great simplicity, this theory is also used in recent applications,[26] although the results obtained only have qualitative value. A considerable improvement is introduced with orthogonalization with respect to the core states. This is done in the orthogonalized plane wave (OPW) method introduced by Herring[27] in 1940 and thoroughly discussed by Woodruff.[28] This method has many recent applications,[29,30] although the states of high symmetry, automatically orthogonal to the core states, show up a low convergence. The cellular method, originally given by Wigner and Seitz[31] in 1933 and applied among others by Altmann,[32] shows up similar difficulties. The automatically orthogonalized plane wave (APW) method, introduced by Slater[33] in 1937, takes the advantages of both these methods and is used frequently with quantitatively very good accuracy in comparison with the computational efforts involved.[34]

The tight-binding method comes very close to the Hartree-Fock theory used for electronic states of atoms and molecules. Generally, therefore, the method is very laborious when applied to crystals, even though effective one-electron potentials have to be used. This is due to the fact that a large number of molecular integrals must be calculated. In its simplest version given by Bloch[5] in 1928, each energy band is related to a certain atomic orbital. This is, however, not a very good description of the valence states. Serious errors may also occur because of the nonorthogonality of the atomic orbitals,

as was pointed out by Löwdin[35] in 1950. He therefore proposed a method of orthogonalization of the atomic orbitals by means of the overlap matrix,[35] which is an alternative way of constructing Wannier functions. This method is, however, extremely laborious. Löwdin[36] has also recently given a survey of band theory, valence bond, and tight-binding calculations.

An extension of the tight-binding method is done by introducing hydridization, which was done for example by Longuet-Higgins and de V. Roberts[37] for metal borides of cubic symmetry. This version of the tight-binding method is, however, still far from being accurate due to approximations such as neglect of all but nearest neighbors, supposition of effective energy elements being proportional to the corresponding overlap elements, the use of Slater atomic orbitals of free atoms in the ground state only. Approximations of this kind occur frequently in tight-binding calculations. The consideration of distant neighbors, exact calculation of molecular integrals involved, and the inclusion of excited atomic states of high symmetry have shown to be very important and will change even the qualitative picture of the energy bands quite a lot. This was found by the author in calculations for the same compound.[38,39] So far, this is the most accurate calculation done for this crystal, although it has also been treated with other methods.[40] Effective charges depending on the radial distance and the considered atomic orbital are also introduced in the one-electron Hamiltonian. The limitation indicated by the name "tight binding" does not have significance any longer in this modification of the method, and a better name is therefore the MO-LCAO method. The extension to include excited free-atom states in the basis corresponds closely to the use of orthogonalized plane waves. The convergence is more rapid than it is for plane waves, provided that the orbital exponents are chosen in a suitable way in order not to cause too large overlap, which would lead to the difficulties pointed out by Löwdin.[35] It was found that the orbital exponents for excited orbitals should be taken several times larger than the case would be in a free atom, where they may be chosen according to Slater's rules, and, furthermore, they depend on the $\mathbf{k}$ vector.

Certainly the procedure of calculation using this method is extremely time wasting, and, preferably, one would use an electronic computer for the complete computing procedure. A program has now been written for energy-band calculations in zirconium oxides of close-packed hexagonal symmetry. This program was constructed by the author for the Swedish electronic computer BESK, and has taken more than three years

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[20] A. V. Sokolov and V. P. Shirokovskiĭ, Usp. Fiz. Nauk **71**, 485 (1960) [translation: Soviet Phys.—Uspokhi **3**, 551 (1961)].

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[26] J. C. Slater, G. F. Koster, and J. H. Wood, Phys. Rev. **126**, 1307 (1962).

[27] C. Herring, Phys. Rev. **57**, 1169 (1940).

[28] T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 367.

[29] W. A. Harrison, Phys. Rev. **129**, 2503, 2512 (1963).

[30] F. Bassani and M. Yoshimine, Phys. Rev. **130**, 20 (1963).

[31] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[32] S. L. Altmann, Proc. Roy. Soc. (London) **A244**, 141, 153 (1958).

[33] J. C. Slater, Phys. Rev. **51**, 846 (1937).

[34] G. A. Burdick, Phys. Rev. **129**, 138 (1963).

[35] P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[36] P. O. Löwdin, J. Appl. Phys. **33**, 251 (1962).

[37] H. C. Longuet-Higgins and M. de V. Roberts, Proc. Roy. Soc. (London) **A224**, 336 (1954).

[38] S. Flodmark, Arkiv Fysik **14**, 513 (1959).

[39] S. Flodmark, Arkiv Fysik **18**, 49 (1960).

[40] M. Yamazaki, J. Phys. Soc. Japan **12**, 1 (1957).

to write. It may, however, serve as a basis for future calculations by means of the MO-LCAO method.

This program will also take care of symmetry transformations of the secular determinants, provided that the appropriate linear combinations are prescribed in certain data lists. It is the purpose of the present paper to give a formal method of obtaining these results. A preliminary paper on the subject was published by the author in 1962.[41] The theory has also been presented in parts at the Uppsala Conference in Quantum Chemistry in August 1960, at the Winter School of Quantum Chemistry and Solid-State Physics in Florida in January 1962, and also at the Latin American School of Physics in Mexico in July 1962.[42]

2. GENERAL THEORY

Consider a symmetry group G of order g. An arbitrary group element is denoted by P and the mnth matrix element of the jth unitary irreducible representation of P is denoted by $^jP_{mn}$. The order of this matrix is denoted by l_j. It is well known that the $l_j{}^2$ operators

$$^jS_{mn}=\frac{l_j}{g}\sum_P^{(G)} {}^jP_{mn}{}^*P \qquad (1)$$

fulfill the relations

$$^jS_{mn}{}^\dagger {}^{j'}S_{m'n'}=\delta_{jj'}\delta_{mm'}{}^jS_{nn'}. \qquad (2)$$

This is a direct consequence of the orthogonality relations in group theory.

Using equal indexes, $m=n$, in (1), the Wigner[1] projection operators are obtained. The Hermitian and idempotent properties of these operators follow from (1) and (2):

$$^jS_{nn}{}^\dagger={}^jS_{nn}, \quad {}^jS_{nn}{}^2={}^jS_{nn}. \qquad (3)$$

Let us introduce an arbitrary set of basis vectors,

$$\phi=(\phi_1, \phi_2, \cdots), \qquad (4)$$

in a vector space invariant under G, i.e.,

$$P\phi_i=\sum_k \phi_k P_{ki}; \quad \text{all} \quad P\in G. \qquad (5)$$

The matrix representative $\mathbf{P}=(P_{ki})$ of P is, in general, reducible. The application of the $\sum_j l_j$ different Wigner projection operators will provide the projections of (4) onto its irreducible subspaces. We are looking for a linear transformation reducing this basis.

The projection matrix

$$^j\mathbf{S}_{nn}=\frac{l_j}{g}\sum_P {}^jP_{nn}{}^*\mathbf{P} \qquad (6)$$

represents the Wigner operator in the basis (4)

$$^jS_{nn}\phi=\phi^j\mathbf{S}_{nn}. \qquad (7)$$

Like the projection operator itself, it is Hermitian and indempotent;

$$\mathbf{S}^\dagger=\mathbf{S}, \quad \mathbf{S}^2=\mathbf{S}. \qquad (8)$$

The symmetry-type indexes j and n will be dropped from now on, when no misunderstanding can occur. The first relation in (8) provides that there is a unitary transformation $\mathbf{T}$ which diagonalizes $\mathbf{S}$. The second relation says that the eigenvalues can be only 1 or 0:

$$\mathbf{T}^\dagger\mathbf{ST}=\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}\equiv\mathbf{E}. \qquad (9)$$

From (9) we see that

$$\mathbf{ST}=\mathbf{TE}=(\mathbf{t},0), \qquad (10)$$

where $\mathbf{t}$ is the rectangular part of $\mathbf{T}$ consisting of the columns of unit eigenvalue:

$$\mathbf{St}=\mathbf{t}. \qquad (11)$$

Transforming the basis (4) by means of $\mathbf{S}$ as in (7) yields a symmetry adaption, but not always a complete reduction, since the singular matrix $\mathbf{S}$ in general contains nonvanishing nondiagonal elements and, therefore, may yield several redundancies in the form of linear dependencies of the transformed basis vectors. Transforming further by means of $\mathbf{T}$, however, these redundancies are removed. Thus, a complete reduction is obtained by means of (10). Finally on account of (11), it is sufficient to use the rectangular matrix $\mathbf{t}$ instead of $\mathbf{S}$ for a complete symmetry reduction onto the basis of symmetry type (j,n). A set of independent basis vectors of the subspace of symmetry type (j,n) is thus given by the reduced row matrix $\phi\mathbf{t}$.

The problem now arises how to find the rectangular matrix $\mathbf{t}$. Given the Hermitian matrix $\mathbf{S}$, this certainly is of no principal difficulty, using standard methods of diagonalization. It is, however, possible to find this matrix more directly using the idempotent property of the projection matrix.

For this purpose we introduce the notation $\mathbf{S}_\nu$ for the νth column of $\mathbf{S}$ and $\mathbf{S}^\mu$ for the μth row, being the Hermitian conjugate of $\mathbf{S}_\mu$. Since $\mathbf{S}^2=\mathbf{S}$, apparently the columns $\mathbf{S}_\nu$ are eigencolumns of $\mathbf{S}$ with the eigenvalue 1, thus, fulfilling the relation (11) with $\mathbf{t}=\mathbf{S}_\nu$. These columns are, however, generally not orthonormal, since $\mathbf{S}_\mu{}^\dagger\mathbf{S}_\nu=\mathbf{S}^\mu\mathbf{S}_\nu=S_{\mu\nu}$ are the elements of the $\mathbf{S}$ matrix, which is generally not diagonal. The normalization, however, is easily done by introducing

$$\mathbf{t}_\mu=(S_{\mu\mu})^{-1/2}\mathbf{S}_\mu. \qquad (12)$$

The condition of linear independency is fulfilled for those eigencolumns (12) satisfying the orthogonality relations

$$\mathbf{t}_\mu{}^\dagger\mathbf{t}_\nu=S_{\mu\nu}(S_{\mu\mu}S_{\nu\nu})^{-1/2}=\delta_{\mu\nu}. \qquad (13)$$

The first part of (13) follows from (12); the second part is true only if $S_{\mu\nu}=0$ for $\mu\neq\nu$. A nonvanishing $S_{\mu\nu}$ will

[41] S. Flodmark, Arkiv Fysik **21**, 89 (1962).
[42] S. Flodmark, Scientific Technical Reports, written under a contract with the U. S. Army, available at the Institute of Theoretical Physics, University of Stockholm, Stockholm, Sweden.

therefore tell us that the μth and νth eigencolumns (12) are nonorthogonal, and thus involved in a linear relationship

$$\mathbf{t}_\nu = \sum_\mu \mathbf{t}_\mu S_{\mu\nu}(S_{\mu\mu}/S_{\nu\nu})^{1/2}. \tag{14}$$

Since all the nonvanishing eigenvalues of $\mathbf{S}$ are equal to 1, the rank of $\mathbf{S}$ is given by its trace, which is thus the number of independent $\mathbf{t}$ columns wanted. To see how these columns can be found most rapidly, consider first some simple properties of $\mathbf{S}$. From the general relations (8) it is found that

$$S_{\nu\nu} - S_{\nu\nu}{}^2 = \sum_{\substack{\mu \\ \mu \neq \nu}} |S_{\mu\nu}|^2. \tag{15}$$

Any diagonal element $S_{\nu\nu} = 1$ or 0 thus provides vanishing nondiagonal elements in the corresponding row and column. Therefore, the corresponding basis vectors need no transformation, being either completely inside or outside the symmetry-adapted subspace. The remaining subspace may then be divided further into subspaces corresponding to the different subblocks of $\mathbf{S}$ involved in linear relationships (14). The elements in such a submatrix fulfill the inequalities

$$0 < S_{\nu\nu} < 1; \quad |S_{\mu\nu}| < \tfrac{1}{2} \quad (\mu \neq \nu), \tag{16}$$

as follows from (15). When the trace of a submatrix is equal to 1, only one $\mathbf{t}$ column (12) is needed. If the trace is larger than or equal to 2, the first $\mathbf{t}$ column can be chosen arbitrarily. The remaining columns, $\mathbf{t}'$, may be orthogonalized to $\mathbf{t}$ using the Schmidt procedure of successive transformations

$$\mathbf{t}'' = [\mathbf{t}' - (\mathbf{t}^\dagger \mathbf{t}')\mathbf{t}](1 - |\mathbf{t}^\dagger \mathbf{t}'|^2)^{-1/2} \to \mathbf{t}', \tag{17}$$

$\mathbf{t}''$, when different from zero, still being an eigencolumn of (11) with the eigenvalue 1. The orthogonalization procedure is repeated for the remaining columns until a sufficient number of nonvanishing eigencolumns $\mathbf{t}$ are obtained.

For each symmetry type (j,n) a rectangular matrix $\mathbf{t}$ can thus be constructed according to the general procedure just given, each containing $\mathrm{Tr}(\mathbf{S})$ columns. The order of $\mathbf{S}$ is equal to the sum of $\mathrm{Tr}(\mathbf{S})$ over all the different symmetry types. The square matrix formed by putting together all the rectangular $\mathbf{t}$ matrices for different symmetry types (j,n) yields the total symmetry reduction of the reducible basis (4).

3. POINT SYMMETRY IN THE MO-LCAO THEORY

The method outlined in Sec. 2 is applicable to any symmetry group and to any trial basis set, which may be used in applied quantum mechanics to describe a physical system obeying the Schrödinger equation. In the quantum theory of atoms and molecules, one may start with a basis set of one-electron trial functions out of which the many-electron wave functions may be constructed and symmetry adapted with respect to space and permutation symmetry. The first step in this pro-

cedure may be the construction of space orbitals symmetry adapted with respect to the actual space group. We consider this problem here.

In the case of atoms, the states belonging to the irreducible representations of the group of pure rotations in three-dimensional space are, as is well known, the spherical harmonics. The potential felt by an electron in a molecule or crystal does not have spherical symmetry. Therefore, a set of spherical harmonics with respect to any atomic center is generally reducible under the actual molecular space group.

In the ordinary MO-LCAO theory, the trial basis is a set of atomic orbitals centered at all the different atoms in the molecule. The same treatment can be done for electrons moving in part of a crystal, which may consist of several atoms, in a molecular arrangement of a certain point-group symmetry. In this case the states must be symmetry adapted with respect to the point group of the molecular arrangement and the ligand-field potential. For general references on group theory and crystal-field theory we refer to a recent review article by Hertzfeld.[43]

Suppose our molecular arrangement contains a number of different chemical elements, which we denote by $A, B, C, \cdots$. Each chemical element, A, may occur in different positions $A', A'', \cdots$. Let us use truncated basis sets for each atomic center. In accordance with the MO-LCAO method, then

$$\phi = (\phi_{A'}, \quad \phi_{A''}, \cdots, \quad \phi_{B'}, \quad \phi_{B''}, \cdots,) \tag{18}$$

forms a basis for our approximate treatment. Suppose further that P is an element of the spatial point group G_P leaving the Hamiltonian invariant. Then the atom at A' is transformed into another position $A'' = P(A')$ by means of P, where A' and A'' are atomic centers of the same chemical element A. Let us introduce a block-diagonal matrix $\mathbf{P}$, the blocks being supermatrices $\mathbf{P}(A)$ for each chemical element A:

$$\mathbf{P}(A) = \begin{pmatrix} \mathbf{P}_{A'A'} & \mathbf{P}_{A'A''} \cdots \\ \mathbf{P}_{A''A'} & \mathbf{P}_{A''A''} \cdots \end{pmatrix}. \tag{19}$$

The submatrices $\mathbf{P}_{A''A'}$ in (19), defined by

$$\mathbf{P}_{A''A'} = \mathbf{P}_A \delta_{A'', \, P(A')} \tag{20}$$

vanish unless $P(A') = A''$. Thus, only one submatrix is different from zero in each row and in each column. The matrix $\mathbf{P}_A$ in (20) is the one representing P in the atomic basis of the chemical element A, when P is referred to the same center as A. Using spherical harmonics, thus $\mathbf{P}_A$ is a block-diagonal matrix, the blocks, $\mathbf{P}_A(L)$, being labeled by the angular momentum, L. This is a consequence of the fact that any point-group element can be written as a pure rotation, or a pure ro-

[43] C. M. Hertzfeld and P. H. E. Meijer, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 1.

tation times the inversion operator commuting with any rotation. The matrix $\mathbf{P}$ just defined is easily seen to be the representative of P in the basis (18). Diagonally placed subblocks of $\mathbf{P}$ are obviously labeled by the two indexes A and L.

The projection matrix (6) using this $\mathbf{P}$ matrix will, thus, also be block diagonal with respect to A and L. The diagonalization procedure of $\mathbf{S}$, described in Sec. 2, can therefore be performed separately for each A and L value. This means that $\mathbf{S}$ can be considered as a function of the four indexes j, n, A, and L. Still it has the matrix structure (19) and the submatrices, being of order $2L+1$, are given by

$$\{{}^{j}\mathbf{S}_{nn}(A,L)\}_{A'A''} = \frac{l_j}{g} \sum_{P}^{(G^{A'A''})} {}^{j}P_{nn}{}^{*}\mathbf{P}_{A}(L), \quad (21)$$

where the sum runs over the subset $G^{A'A''}$ of G_P containing all elements $P \in G_P$, satisfying $P(A'') = A'$.

The necessary diagonal elements, ${}^{j}P_{nn}$, of the irreducible representations can be found in the literature for all point groups. Melvin[44] has given such tables in a paper concerning a factoring of the projection operator. Explicit formulas for $\mathbf{P}_{A}(L)$, the possible A dependence coming only from the possibility of permitting the maximum L value to depend on A, have been given earlier by the author for $L \leq 3$ in terms of elements of the corresponding three-dimensional transformation matrix.[38,42]

The matrices (21) can thus be easily obtained by straightforward calculation for all the different index values occurring. The reduced symmetry-adapted basis can then be found according to the preceding section.

4. BAND THEORY AND SPATIAL SYMMETRY

Another interesting field for application of the methods in Sec. 2 is the solid-state theory. The electronic states in the band theory of crystals must be symmetry-adapted with respect to the total crystal space group. The author has treated this problem in a previous paper.[41] A further development of the final formula for the projection matrix will be presented here. Among others it has been block-diagonalized with respect to different chemical elements. In addition, a general program has been constructed for its computation by means of the electronic computer IBM 7090.

The representation theory for the crystallographic space groups is well known, and, therefore, the present investigation presumes all irreducible representations to be known. As a matter of fact, a complete tabulation of irreducible representations for all the 230 crystallographic space groups is under performance by Raghavacharyulu, who has also given a general method for their calculation.[13] For applications of the present method these tables are going to be extremely valuable, since tables of irreducible characters, being prepared by

[44] M. A. Melvin, Rev. Mod. Phys. **28**, 20 (1956).

Zak[12] are not sufficient for doing complete symmetry reductions, but their usefulness is limited mainly to the investigation of reducibility of representations.

As is well known, the crystallographic space group, G, is a so-called semidirect product group.[9,10] The group G_T of unit cell translations, being an invariant subgroup, has one-dimensional representations only, which are labeled by the reduced wave vector, $\mathbf{k}$.

The irreducible representations of the full crystal group are divided into submatrices, labeled by different prongs of the so-called "star" of $\mathbf{k}$, caused by operating on $\mathbf{k}$ with all elements P of the empty-lattice point group G_P.[11] There is only one submatrix of this kind in diagonal position, which does not vanish for all group elements, and the only elements which give a contribution are those of the "little group," or the "group of the wave vector," $G_{\mathbf{k}}$.[4,7,11] This is defined as the elements of G which are homomorphous with point-group elements $P \in G_P$ satisfying

$$P(\mathbf{k}) = \mathbf{k} + \mathbf{K}, \quad (22)$$

where $\mathbf{K}$ is a unit-zone translation in the reciprocal lattice. It is therefore true, as is well known, that it is sufficient to perform the symmetry adaptions with respect to the little groups of each $\mathbf{k}$ vector. This is consistent with the fact that the projection operator of the $\mathbf{k}$th irreducible representation of G_T commutes with the projection operators of all the irreducible representations of the factor group $F_{\mathbf{k}} = G_{\mathbf{k}}/G_T$. Forming a Bloch basis[5] of wave vector $\mathbf{k}$, the remaining symmetry adaption, therefore, has to be done with respect to $F_{\mathbf{k}}$, which is a finite group isomorphous with the point group G_P of the empty lattice. In the special case of a symmorphic space group, the factor group actually is a point group, but in the nonsymmorphic case, screw axes and glide reflection planes occur. It is always possible, however, to label the factor-group elements, $F \in F_{\mathbf{k}}$, by means of isomorphous point-group elements, $P \in G_P$. We denote by $\mathbf{d}$ the fractional-cell displacement, the translation $T_{\mathbf{d}}$ of which commutes with P and yields a factor-group element

$$F = P \cdot T_{\mathbf{d}} = T_{\mathbf{d}} \cdot P \equiv (\mathbf{d}, P). \quad (23)$$

In the tight-binding or MO-LCAO approximation, we use a Bloch basis analogous to (18) for each atom in the unit cell,

$$\psi_{\mathbf{k}} = (\psi_{A'\mathbf{k}}, \quad \psi_{A''\mathbf{k}}, \cdots \quad \psi_{B'\mathbf{k}}, \quad \psi_{B''\mathbf{k}}, \cdots), \quad (24)$$

where

$$\psi_{A'\mathbf{k}}(\mathbf{r}) \propto \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} \phi(\mathbf{r} - \mathbf{n} - \mathbf{a}')$$

is a basis of Bloch functions of atom A', the contribution coming from all the atomic bases ϕ with the same atomic-center position vector $\mathbf{a}'$ with respect to different unit cell vectors $\mathbf{n}$. The "little coset," $G^{A'A''\mathbf{k}}$, previously introduced by the author,[41] is defined as the subset of G_P, the elements P of which satisfy

$$P(\mathbf{a}'' + \mathbf{d}) = \mathbf{a}' + \mathbf{n}_{A'A''}{}^{P}; \quad F = P \cdot T_{\mathbf{d}} \in F_{\mathbf{k}}. \quad (25)$$

The little coset is, thus, analogous to the set $G^{A'A''}$ introduced in (20), although in the present case a possible unit-cell displacement $n_{A'A''}{}^P$ can be connected with the transformation between two different positions of the chemical element A. It has to be observed that no group element can combine two different chemical elements in this way.

In analogy to (19), we can now introduce the matrix $\mathbf{F}^k$ representing F in the basis (24). It is a block-diagonal matrix, the blocks $\mathbf{F}^k(A)$ being labeled by the chemical elements A:

$$\mathbf{F}^k(A) = \begin{bmatrix} \mathbf{F}_{A'A'}{}^k & \mathbf{F}_{A'A''}{}^k & \cdots \\ \mathbf{F}_{A''A'}{}^k & \mathbf{F}_{A''A''}{}^k & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix}. \qquad (26)$$

The submatrices of (26) are given by

$$\mathbf{F}_{A'A''}{}^k = \mathbf{P}_A \exp(-i\mathbf{k}\mathbf{n}_{A'A''}{}^P)\delta(A',P(A'')), \qquad (27)$$

where the Kronecker δ symbol vanishes unless A' and A'' are related to P according to (25). The matrix $\mathbf{P}_A$ is the same as in (20), and it is block diagonal in the azimuthal quantum number L.

A straightforward calculation now yields the symmetry projection matrix $\mathbf{S}$, labeled by the symmetry-type indexes j, n, and $\mathbf{k}$ and by the block-diagonal indexes A and L. The submatrix analogous to (21) is given by

$$\{^{jk}\mathbf{S}_{nn}(A,L)\}_{A'A''} = \frac{l_{jk}}{g_k} \sum_P^{(G^{A'A''k})} \exp(-i\mathbf{k}\mathbf{n}_{A'A''}{}^P) \times {}^{jk}F_{nn}{}^*\mathbf{P}_A(L). \qquad (28)$$

Here $^{jk}F_{nn}$ are diagonal elements of the jth irreducible representation of the factor group F_k, and the sum is extended over the little-coset elements. The order of F_k is denoted by g_k and the dimension of its jth irreducible representation is denoted by l_{jk}.

As is seen, the main difference from the molecular case appears in the exponential factor occurring in (28). Choosing $\mathbf{k}=0$, the molecular case is obtained as a special case. Also the case with only one atomic center, occurring in the ordinary ligand-field theory, is a special case, the little coset being put equal to the total point group in this case. Equation (28), therefore, represents the most general case for the treatment of space symmetry in the MO-LCAO theory of atoms, molecules, and crystals.

Since applications to (28) generally are very hard to perform by hand, a certain program for its calculation by means of the electronic computer IBM 7090 has been constructed by the author in FORTRAN language.[42] This program also takes care of the reduction of the projection matrix according to Sec. 2. Since it operates in the core memory of the computer only, it is limited to the following maximum values of ingoing quantities: 48 elements of the empty-lattice point group, 50 wave vectors, 30 little groups, 25 irreducible representations per little group, 6 chemical elements per unit cell, 5 atoms per chemical element and unit cell, and 4 shells of spherical harmonics (s,p,d,f). An unlimited number of different substances can, however, be symmetry adapted at the same machine run.

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