A method is presented for constructing the basis functions of the irreducible representations \( \Gamma \) of the molecular point-group symmetry in terms of coordinate wave functions corresponding to a given total spin \( S \) of the molecule. The resulting functions are the eigenfunctions of the \( 2S+1 \Gamma \) molecular multiplets and lead to quasi-diagonalization of the secular equation. Examples are given of calculations for the energy levels of a system of four electrons in a tetrahedral field and for those of the six \( \pi \) electrons of benzene in the state with \( S = 0 \).

1. Construction of Basis Functions for the Molecular Symmetry Group

It had previously been shown [1, 2] that coordinate wave functions (made symmetrical with Young’s operators) serve to simplify the computation of matrix elements for the hamiltonian for a many-electron system. In addition, the energy matrix may be reduced to quasidiagonal form if the system has a point-group symmetry.

The hamiltonian for a symmetrical molecule is invariant under the transformations of the point symmetry, so the wave functions belonging to a given energy level should transform in accordance with the irreducible representations of the point-group symmetry of the molecule [3]. Hence to each energy level we may assign such a representation. The initial wave functions usually form the basis of a reducible representation in relation to the operations of this group, but construction from them of linear combinations belonging to the bases of the irreducible representations produces a considerable reduction in the order of the secular equations and sometimes leads to complete diagonalization.

The reason for this is the invariance of the complete spatial integral with respect to any transformation of the coordinate system, including the point-group symmetry operations. Hence the orthogonality of the matrix elements of irreducible representations (see [3]) allows us to show* that, by applying any operation of the group to a matrix element of the hamiltonian and summing over all the elements in the group, we get

\[
\langle a_\Gamma | H | \bar{a}_\Gamma \rangle = \delta_\Gamma \delta_\Gamma \langle a_\Gamma | H | \bar{a}_\Gamma \rangle.
\]  

(1)

Here \( \Gamma \) is the irreducible representation of the point group and \( \gamma \) enumerates the basis functions of this; \( a \) distinguishes repeated equivalent irreducible representations encountered in the expansion of the initial representation. Formula (1) implies that an expansion free from such repeated representations has a diagonal matrix, whereas if some irreducible representation occurs \( k \) times, it becomes necessary to solve a secular equation of order \( k \) to produce diagonalization.

The energy matrix may be found by taking one wave function from each \( \Gamma \), because the matrix elements of (1) are the same for all basis functions of a given irreducible representation. This feature reflects the degeneracy due to the spatial symmetry; deviation from symmetry violates (1) and so removes the degeneracy.

It is convenient to expand the initial reducible representation as irreducible parts by means of normalized projection operators [4, 5]**:

\[
\langle \gamma | R | \delta \rangle = \delta_\gamma \delta_\delta \langle \gamma | R | \delta \rangle.
\]

(2)

in which \( R \) represents all the operations of the point group, whose rank is \( N_R \); \( \langle \gamma | R | \delta \rangle \) is the element of matrix \( R \) for \( \Gamma \) at the intersection of row \( \gamma \) and column \( \delta \), \( f_\Gamma \)'s being the dimensions of \( \Gamma \). The effect of (2) on an arbitrary unsymmetrical function \( \psi_0 \) is to produce an orthonormal set \( f_\Gamma \) of basis functions \( \Phi_{\gamma\delta}^\Gamma \). It can be shown that the point-group symmetry operations transform functions with a given second subscript one into another (compare the analogous behavior of the \( \Phi_{\gamma\delta}^\Gamma \) of [1]):

* A necessary condition for (1) to be correct is that \( H \) is invariant with respect to the operations of the given point group, i.e., that \( H \) belongs to a single irreducible representation.

** The \( \Phi_{\gamma\delta}^\Gamma \) are the analogs of Young’s operator’s \( \theta_{\gamma\delta}^\Gamma \) for the point group and differ from the projection operators of [5] by normalizing factors.
The action of \( e^{\Gamma}_y \) on a function with a given spatial symmetry is to give either zero or a (nonnormalized) basis function.

Two conditions must thus be satisfied by the coordinate wave function of a symmetrical molecule for a state with a given total spin: 1) it must have the permutation symmetry \( [k] \), i.e., transform in accordance with the representation of the permutation group having \( [k] \) Young's scheme; 2) it must transform with respect to the irreducible representation \( \Gamma \) of the molecular point group. Permutation of the electron coordinates commutates with the transform operations of the point symmetry, so we have the operator equation

\[
\omega^{[\lambda]}_y e^{\Gamma}_y = e^{\Gamma}_y \omega^{[\lambda]}_y.
\]

Hence the order of operation of \( e^{\Gamma}_y \) and \( e^{\Gamma}_y \) on the initial function is unimportant and is governed solely by convenience.

The one-electron orbitals of MO theory often have a definite spatial symmetry as a consequence of the mode of construction; for instance, the following orthogonal orbitals are used [8] for the \( \pi \)-electron levels of benzene:

\[
\varphi_a = \frac{1}{V \delta_{a0}} \sum_{k=1}^{a} e^{\gamma k} \varphi_{a0}, \quad a = 0, \pm 1, \pm 2, 3,
\]

in which the \( \varphi_{ak} \) are one-electron orbitals localized on atom \( k \) and \( \delta_{a0} \) is a normalization factor. It is readily verified that the \( \varphi_a \) transform in accordance with the irreducible representations of group \( D_{6h} \), namely

\[
\varphi_0 \subset A_{2u}, \quad \varphi_1, \varphi_{-1} \subset E_{1g},
\]

\[
\varphi_{2}, \varphi_{-2} \subset E_{2u}, \quad \varphi_3 \subset B_{2g}.
\]

The wave functions are constructed from products of the one-electron orbitals of (5). It is convenient to employ the \( e^{\Gamma}_y \) to obtain linear combinations of these products that transform in accordance with the irreducible representations of the point group. The formulas of [2] are used to find the matrix elements when each orbital has one electron; a forthcoming paper will present the formulas for the matrix elements when the configuration contains coincident orbitals.

2. Computation Methods in the Heitler-London Approximation

Here AO are used as the \( \varphi_{ak} \); the action of \( \omega^{[\lambda]}_y \) on a product of these generates \( \Phi^{[\lambda]}_y \), which are symmetrical not only with respect to permutation of the electron coordinates but also with respect to that of the orbital numbers [1] and hence also with respect to permutation of the atoms (the latter provided that one orbital is specified for each atom and that ionic states are neglected). All the point-group transforms may also be represented as permutations of the corresponding atoms, but these operations do not run through all \( N! \) permutations, but only those that correspond to rotation or reflection of the molecule as a whole. This implies that the point group of the molecule is a subgroup of the permutation group for the atoms. The irreducible representations of a group may become reducible when we pass to a subgroup, and on appropriate transformation they split up into irreducible representations of the subgroup. The \( \Phi^{[\lambda]}_y \) form the basis of the \( [\lambda] \) irreducible representation of the permutation group for the atoms. Tables of characters for the irreducible representations of the permutation group and the point group readily allow one to determine the form of the expansion

\[
[\lambda] \rightarrow \sum_k a_k \Gamma_k,
\]

in which \( a_k \) denotes the number of occurrences of representation \( \Gamma_k \) in the expansion of \([\lambda]\). For this purpose we must draw up each operation of the point group for the corresponding permutation and expand in accordance with the standard procedure. The \([\lambda] \) Young's scheme is uniquely related to the \( S \) of the system, so (7) gives allowed multiplets for covalent structures whose derivation is best illustrated by the scheme

\[
\begin{array}{c}
[\lambda]_{\text{coord}} \\
\downarrow
\end{array} \quad \begin{array}{c}
[\lambda]_{\text{spin}} \\
\downarrow
\end{array} \quad \begin{array}{c}
\Gamma \\
\downarrow
\end{array} \quad \begin{array}{c}
S
\end{array}
\]

\* Wigner's [6] operator \( \sum \frac{\gamma}{\gamma} R | \gamma \rangle \langle \gamma | R \) (see also §94 in [1] and [7]) gives wave functions belonging to a single basis only when \( \Gamma \) occurs once in the expansion of the reducible representation; otherwise we obtain functions belonging to different bases, i.e., ones that do not transform one into another in response to the operations of the group.