INTEGRAL INVARIANTS FOR HIGH-SYMMETRY OPEN-SHELL MOLECULES.

1. INVARIANT REPRESENTATIONS OF ELECTRON REPULSION INTEGRALS

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A numerical procedure for expanding electron repulsion integrals \( \langle m m | n n \rangle \) on degenerate molecular orbitals of \( \gamma \) symmetry (\( \gamma = e, t, g, h \)) into integral invariants (reduced matrix elements) \( H^k(\gamma, \gamma) \) is suggested. The latter are analogous in their sense to Slater-Condon parameters \( F^k(l, l) \) for atoms with an electronic configuration \( l^N \). The method is applicable to nonlinear molecules of arbitrary symmetries, including “not readily reducible” groups.

INTRODUCTION

Serious difficulties arise when open shell theory — restricted Hartree-Fock (RHF) method [1-4] — is applied to high-symmetry systems. The major problem is missing technique for calculating “vector coupling coefficients” (VCC), \( a_{mn} \) and \( b_{mn} \), used to specify the symmetry of the calculated spectroscopic state in the RHF method. Another difficulty involves asymmetry of VCC for some highly symmetric structures. These problems are discussed in detail in [5, 6].

The vector coupling coefficients enter into relations for the energy functional, the Fock operators, and the unified coupling operator. For degenerate open-shell systems \( \gamma^N \) (\( \gamma = p, d, \ldots \) for atoms; \( \gamma = e, t, g, h \) for nonlinear molecules), the energy functional is

\[
E^{(2S + 1 \Gamma, \gamma^N)} = E_r + f^2 \sum_{m} \sum_{n} (2a_{mn}J_{mn} - b_{mn}K_{mn}),
\]

where \( 2S + 1 \Gamma \) is the state under analysis; \( f = N / (2 \dim \gamma) \) is the occupation of an open shell; \( \dim \gamma \) is the dimension of the \( \gamma \) representation; \( E_r \) (\( E_{\text{rest}} \)) is the term that is the same for all states of \( \gamma^N \) configuration [1]:

\[
E_r = \sum_{u} H_{uu} + \sum_{u} \sum_{v} (2J_{uv} - K_{uv}) + 2f \left( \sum_{m} H_{mm} + \sum_{m} \sum_{n} (2J_{un} - K_{um}) \right)
\]

(in Eqs. (1), (2), the indices \( m, n \) label the open-shell orbitals, and the indices \( u, v \) label the closed-shell ones).

A general approach to determination of the VCC \( a_{mn} \) and \( b_{mn} \) was suggested in [5, 6]. This approach uses representations of open shell energy (1) and electron repulsion integrals \( \langle m m | n n \rangle \) on degenerate orbitals of \( \gamma \) symmetry \( (m, m, n, n \in \gamma) \) in terms of integral invariants (reduced matrix elements of electron repulsion). For atoms with \( l^N \) configuration \( (l = p, d, \ldots) \), such invariants are Slater-Condon parameters \( F^k(l, l) \) [7]. Analogous values may be introduced for molecules with \( \gamma^N \) configuration. If molecular invariants are denoted by \( H^k(\gamma, \gamma) \), the corresponding relations for the integrals and energy are [8]

\[
\langle m m | n n \rangle = \sum_{k} \alpha^{(k)}(m, m, n, n) \times H^k(\gamma, \gamma),
\]

\[ E^{(2S+1)\Gamma_N} = E_r + \sum_k c^{(k)} \times H^k(\gamma, \gamma), \]  
(4)

where \( \alpha^{(k)} \) and \( c^{(k)} \) are the numerical coefficients characterizing the integral and the state; \( \langle ij | kl \rangle \) is defined as

\[ \langle ij | kl \rangle = \int \phi_i^*(1) \phi_j^*(1) \phi_l^*(2) \phi_k^*(2) dV_1 dV_2. \]  
(5)

In the particular case of Coulomb and exchange integrals, expansion (3) may be represented in simpler form:

\[ J_{mn} = \sum_k p^{(k)}_{mn} H^k(\gamma, \gamma), \quad K_{mn} = \sum_k q^{(k)}_{mn} H^k(\gamma, \gamma), \]  
(6)

where

\[ p^{(k)}_{mn} = \alpha^{(k)}(m, m, n, n), \quad q^{(k)}_{mn} = \alpha^{(k)}(m, n, n, m). \]  
(7)

Calculating \( a_{mn} \) and \( b_{mn} \) by Eqs. (6) requires numerical values of the coefficients \( \alpha^{(k)} \) for all integrals in Eq. (3) and the coefficients \( c^{(k)} \) for the state in question \( (2S+1)\Gamma_N \). Here we suggest a simple method of calculating \( \alpha^{(k)} \) and \( c^{(k)} \) as applied to molecular structures of arbitrary symmetry with a \( \gamma_N \) electronic configuration, including “not readily reducible” groups.

**BRIEF SURVEY**

I. The values \( H^k(\gamma, \gamma) \) entering into Eqs. (3), (4) are reduced matrix elements of electron–electron Coulomb interaction [9, 10]. By definition these values are invariants under an arbitrary orthogonal transformation \( U \) of degenerate orbitals of \( \gamma \) symmetry

\[ \{ \varphi_m \} = \{ \varphi_m \}^0 \times U \]  
(8)

\( (m = 1, 2, \ldots, \text{dim} \gamma) \), where \( \{ \varphi_m \}^0 \) are the orbitals of the standard representation \( \gamma \) [11]. The orbitals \( \{ \varphi_m \}^0 \) may be obtained by acting on \( \{ \varphi_m \} \) with projection operators \( \varepsilon^\gamma \) [11].

Since \( H^k(\gamma, \gamma) \) is invariant under transformation (8), the dependence of the integrals \( \langle mn | nn \rangle \) on the choice of the basis \( \{ \varphi_m \} \) is transferred to the coefficients \( \alpha^{(k)} \) in Eq. (3). The coefficients \( c^{(k)} \) are independent of transformation (8). With a given set of invariants \( H^k(\gamma, \gamma) \), the coefficients \( c^{(k)} \) are unique for any nonmultiple state of \( \gamma_N \) configuration.

The number of invariants \( H^k(\gamma, \gamma) \) in expansions (3), (4) is denoted by \( L_\gamma \) and defined by a general formula [12]

\[ L_\gamma = [G]^{-1} \sum_{R \in G} \xi_T(R), \]  
(9)

where \([G]\) is the order of the group \( G \) under consideration; \( R \) is a symmetry element; \( \xi_T \) is the character of the reducible representation \( T \) determined by the internal symmetry of the tensor \( \langle mn | nn \rangle \). In the basis of real orbitals,

\[ T = [\gamma \otimes \gamma] [\gamma \otimes \gamma], \]  
(10)

where \( [\gamma \otimes \gamma] \) is a symmetric square of \( \gamma \).

The general method for calculating the coefficients \( \alpha^{(k)} \) in Eq. (3) for “readily reducible” groups is given by Wigner theory [13]. The applications of this theory are treated in many manuals, in particular, a detailed treatment for cubic groups is given in [14].

Many works are devoted to generalization of the approach [13] to “not readily reducible” groups, among which are, e.g., structures of icosahedral symmetry \( (I, I_h) \) (for references, see [9, 15]). For the problem under consideration (calculating matrix elements of electron–electron Coulomb interaction), a complete solution is given in [10].

As a matter of fact, method [10] is very complex and cumbersome (for the discussion, see [9]) and was not used for icosahedral systems. Other difficulties arising in an analysis of icosahedral groups is unavailability of irreducible representation matrices for the 4-fold degenerate representation \( G \) needed for calculating the coefficients \( \alpha^{(k)} \) and an ambiguous method of their construction [16, 17].