Symmetry Simplifications of Space Types in Configuration Interaction Induced by Orbital Degeneracy

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Abstract

Symmetry simplifications are introduced in configuration interaction (CI) by reducing the number of symmetry-allowed space types if there is degeneracy in some of the molecular orbitals by constructing the unique space types. A new symmetry group which we call the configuration symmetry group is defined and is shown to be expressible as a generalized wreath product group. Generating functions are derived for enumerating the equivalence classes of space types. A double coset method is expounded which constructs the representatives of all equivalence classes of space types using the cycle index of generalized wreath product and the double cosets of label subgroup with generalized wreath product in the symmetric group $S_n$, if $n$ is twice the number of occupied and virtual orbitals. Method is illustrated with CI using the localized orbitals of polyenes, CI in benzene, and atomic CI for several reference states.

1. Introduction

Configuration interaction [1] (CI) is a powerful technique which introduces correlation to the self-consistent field (SCF) reference state. Electrons are excited to virtual orbitals and the resulting electronic states are known as configurations. A configuration is essentially characterized by two components known as space types and spin types. The space type of a configuration specifies the orbitals and the occupancy of the electrons in various orbitals and ignores the spin couplings of electrons which are specified by the appropriate symmetry-adapted spin functions either in the unitary group $U(n)$ or the symmetry group $S_n$, where $n$ is the number of electrons. In recent years symmetry simplifications of the symbolic formulas used in constructing the CI matrix elements were accomplished using the unitary symmetry of the spin states or the associated Gel'fand states of the electrons [2]. The number of space types can be reduced by selecting the symmetry-allowed space types from a set of all possible space types. This is a consequence of the totally symmetric Hamiltonian which has nonvanishing matrix elements only if the direct product of the two states of the CI matrix element contains the totally symmetric representation. This, of course, cuts down the number of space types when a molecule possesses symmetry elements.

In this paper we accomplish an additional symmetry reduction of the symmetry-allowed space types if some of the SCF orbitals or the orbitals used in
constructing configurations are degenerate. In such a case several configurations are transformable into one another by permuting the degenerate orbitals. Often, their CI expansion coefficients differ at most by a sign. Thus, if the CI matrix elements of a representative of these equivalence classes of configurations with all representatives of other equivalence classes are determined then the matrix elements of the other configurations in this class are obtained. In this paper we consider this symmetry simplification. We define and formulate a new symmetry group which we call the configuration symmetry group and show that it is expressible as a generalized wreath product. The equivalence classes of space types are enumerated using the cycle indices of generalized wreath products as generators and constructed using the double cosets of label subgroup with configuration symmetry group in the symmetric group $S_n$. A computer algorithm can also be formulated for generating the representatives of equivalence classes of space types.

In Sec. 2 configuration symmetry groups are defined and shown to be expressible as generalized wreath products. In Sec. 3 we outline the generation of equivalence classes of space types and in Sec. 4 a double coset method is formulated for constructing these representatives of equivalence classes of space types.

2. Configuration Symmetry Groups

A. Formulation

Two configurations which can be transformed into each other by permuting degenerate orbitals can be considered equivalent. This is also reflected in the corresponding coefficients of the CI wave function. For example, the two configurations of the localized orbitals of butadiene shown below are equivalent:

\[
\begin{align*}
\text{(I)} & \quad -x-x- -x-x- \\
\text{(II)} & \quad -x-x- -x-x-
\end{align*}
\]

This is because configurations I and II are transformable into each other by interchanging the degenerate occupied and virtual localized orbitals. Ohmine et al. [3] carried out a $(S + D)$-CI (CI which includes single and double excitations from the reference state) with $^1\text{A}_g$ reference state and obtained the same coefficient ($-0.148$) for these two configurations in the CI wave function and showed that correlation to the $^1\text{A}_g$ ground state is predominantly introduced by these two configurations. In general, such configurations have CI coefficients which differ at most by a sign. However, the converse may not necessarily be true. We may have two configurations which are not equivalent in the above sense and yet may have coefficients of the same magnitude in the CI wave functions. For example, the two configurations of butadiene shown below, which are constructed using the delocalized SCF orbitals of butadiene have the same
coefficient (0.054) in \((S+D)-\text{CI}\) with \(^{1}A\) reference state [3]:

\[
\begin{array}{cccc}
\times & \times & \times & \times \\
\times & \times & \times & \times \\
\times & \times & \times & \times \\
\times & \times & \times & \times \\
\end{array}
\]

Of course, this need not bother us for we are interested in introducing symmetry
simplifications when there is configuration equivalence, but we must be aware
of this.

If we denote the degenerate occupied localized orbitals of butadiene by \(w_1\)
and \(w_2\) and the virtual orbitals by \(w_3\) and \(w_4\), then any two space types that can
be transformed into each other by the permutation (12)(34) of the localized
orbitals (where we denote \(w_i\) by \(i\)) with the same spin coupling are equivalent.
In the case of localized orbitals the occupied and virtual orbitals have to be
permuted simultaneously because of their localization to ethylenic units. Let us
look at the equivalence of space types without considering the spin couplings
which are determined depending on the reference state. However, we must be
aware that the same space type can have more than one spin coupling. (For
example, a two dimensional coupling to obtain a singlet state when there are
four open shells.) Each orbital can accommodate at most two electrons. Define
a site where an electron can be accommodated as a hole. Thus each orbital
contains two holes. Two holes in the same orbital are equivalent because putting
an electron in any one of these holes would generate the same space type or
configuration. Consequently, let us define the configuration symmetry group as
the group that includes the permutations of the degenerate orbitals and the
permutations of the holes in each orbital. Such a definition is a little vague, even
though, it motivates the formulation of a rigorous definition and helps to under-
stand the problem. A precise definition and formulation of the configuration
symmetry group are given in Sec. 2.B.

**B. Configuration Symmetry Groups as Generalized Wreath Products**

Let \(\Omega\) be a set of orbitals some of which are degenerate. Let \(G\) be a
permutation group which consists of permutations of degenerate orbitals. For
example, \(\Omega\) for the localized orbitals of butadiene is the set \(\{\omega_1, \omega_2, \omega_3, \omega_4\}\) and
\(G\) is the set \(\{(1)(2)(3)(4), (12)(34)\}\). Localized orbitals of polynes are construc-
ted from the delocalized \(\text{SCF}\) orbitals by an appropriate unitary transformation
as described in Ref. 3. Note that in this case the localized orbitals \(\omega_1\) and \(\omega_2\)
cannot be permuted without permuting the corresponding virtual orbitals since
they are localized to ethylenic units. However, delocalized degenerate \(\text{SCF}\) orbitals
(both occupied and virtual) can be permuted independently because there is no
such localization to a particular unit cell. Since the two holes in each orbital are
equivalent these holes can also be permuted. If we denote them by 1 and 2 then
the permutation group of these holes is \(S_2 = \{(1)(2), (12)\}\). We have a symmetry
group $G$ acting on $\Omega$ and a group $S_2$ acting on the holes in each orbital of $\Omega$. Let $H$ be the permutation group of the two holes in any orbital. Let $\pi$ be a map from $\Omega$ to $H$. Equivalently, for each orbital in $\Omega$ we assign a permutation in $H$, which determines the permutations of the holes in that orbital. The problem is reminiscent of the symmetry groups of nonrigid molecules [4] where the group $G$ acts on the rigid structure and a group $H$ corresponds to the set of torsional permutations in the structure. Define the configuration symmetry group as the set of permutations $\{(g; \pi)/g \in G, \pi: \Omega \rightarrow H\}$. This is precisely the wreath product $G[H]$ used by the author in the context of symmetry groups of nonrigid molecules [4]. The product of two elements $(g; \pi)$ and $(g'; \pi')$ in $G[H]$ is defined as $(g; \pi)(g'; \pi') = (gg'; \pi\pi'_e)$, where

\[
\pi\pi'_e(i) = \pi(i)\pi'(g^{-1}i) \quad \text{for} \quad i \in \Omega.
\]

It can be seen that $(e; e')$ is the identity of the group $G[H]$, with $e$ being the identity of $G$ and $e'$ defined by $e'(i) = ^1H$, where $^1H$ is the identity of the group $H$. Inverse of an element $(g; \pi)$ is $(g^{-1}; \pi_{e^{-1}})$.

Let us illustrate the above definition with the localized orbitals of butadiene. The configuration symmetry group of these orbitals is the wreath product of $G = S_2(4) = \{(1)(2)(3)(4), (12)(34)\}$, with $H = S_2(2) = \{(1)(2), (12)\}$. Let $S_m(n)$, in general, denote the permutation group of $n$ objects containing $m!$ elements. For example, a permutation in the configuration symmetry group $S_2(4)[S_2(2)]$ would be of the form $((12)(34); \pi)$, with $\pi$ defined below:

\[
\pi(1) = (12),
\pi(2) = (1)(2),
\pi(3) = (12),
\pi(4) = (12).
\]

That is, permute the degenerate occupied and virtual localized orbitals. In addition, permute the holes in the localized orbitals 1, 3, and 4.

A permutation representation of $G[H]$ is obtained as $(H_1 \times H_2 \times \cdots \times H_n) \cdot G'$, where

\[
H_i = \{(e; \pi)/e \text{ is the identity of } G\},
\]

and $G'$ is $(\{g; e'/g \in G\},$ and $n$ is the number of elements in $\Omega$. $H_1 \times H_2 \times \cdots \times H_n$ is an $n$-fold direct product of $n$ copies of the group $H$. Thus the group product $H^*G'$ is also a semidirect product. The order of the group $G[H]$ is $|G||H|^{|\Omega|}$, where the modulus sign is used to denote the number of elements in a set.

If the eight holes of the localized orbitals of butadiene are denoted as 1, 2, 3, 4, 5, 6, 7, and 8 with the holes 1 and 2 belonging to the orbital $\omega_1$, 3, and 4
to the orbitals ω₂, etc., then, for example, a permutation representation of the permutation ((12)(34); π), with π defined as in the above example, is


Here we adopt the convention of left-to-right multiplication of permutations.

Instead of the localized orbitals of butadiene if localized orbitals of hexatriene or decapentadiene need to be considered then the above formalism has to be generalized. Such a generalization of wreath product to generalized wreath product is possible when G is intransitive [4]. The group G acting on Ω is intransitive if Ω can be partitioned into mutually disjoint sets Y₁, Y₂, ..., Yₙ, and the group G permutes elements only within a set Yᵢ. Equivalently, G does not mix elements of different Y sets. Let Hᵢ be a group acting on the holes which correspond to orbitals in the set Yᵢ. Let πᵢ be a map from the set Yᵢ to Hᵢ. The generalized wreath product G[H₁, H₂, ..., Hₘ] consists of permutations \{(g; π₁, π₂, ..., πₘ)/g ∈ G, πᵢ: Yᵢ → Hᵢ\}. If we denote the occupied localized orbitals of decapentadiene by ω₁, ω₂, ω₃, ω₄, and ω₅ and the virtual orbitals by ω₆, ω₇, ω₈, ω₉ and ω₁₀ then the Y sets are Y₁ = {ω₁, ω₅, ω₆, ω₁₀}, Y₂ = {ω₂, ω₄, ω₇, ω₉} and Y₃ = {ω₃, ω₈}. The group G is

S₂(10) = {(1)(2)(3)(4)(5)(6)(7)(8)(9)(10), (1,5)(2,4)(3)(6,10)(7,9)(8)}

and the groups H₁, H₂, and H₃ are S₂(2). Then the configuration symmetry group of the localized orbitals of decapentadiene in S₂(10)[S₂(2), S₂(2), S₂(2)]. The order of this group is 2^2 · 2^4 · 2 = 2048. In general, the order of generalized wreath product G[H₁, H₂, ..., Hₘ] is |G||H₁|^Y₁||H₂|^Y₂|...|Hₘ|^Yₘ|.

3. Generation of Equivalence Classes of Space Types

A. Preliminaries and Formulation

Let D be the set of holes in all orbitals. Let R be a set consisting of two elements p and a, p representing the presence of an electron in a hole in D, while a represents the absence of an electron in a hole in D. Then any space type is just a map from the set D to the set R. An example of such a map fᵢ from D to R which corresponds to the holes of the orbitals of butadiene is

f₁(1) = p,

f₁(2) = a,

f₁(3) = a,

f₁(4) = a,

f₁(5) = p,

f₁(6) = p,

f₁(7) = p,

f₁(8) = a.
The resulting space type is

\[ \begin{array}{c}
\times \\
\times \\
\times \\
\times \\
\end{array} \quad \begin{array}{c}
\times \\
\times \\
\times \\
\times \\
\end{array} \]

The group \( G[H_1, H_2, \ldots, H_m] \) defined in Sec. 2.B acts on \( D \) in that it permutes the holes in \( D \). This in turn permutes the set of functions from \( D \) to \( R \) by

\[ \tau f(i) = f(\tau^{-1}i) \text{ for } \tau \in G[H_1, H_2, \ldots, H_m]. \]

For example, if \( \tau = (12)(34); \pi \) with \( \pi \) defined as in the illustrative example of Sec. 2.B and \( f_1 \) defined as above,

\[ \tau f_1(i) = f_1(((1423)^{-1}(58)^{-1}(67)^{-1}i) = f_1((1324)(58)(67)i). \]

Thus,

\[ \begin{align*}
\tau f_1(1) &= f_1((1324)(58)(67)1) = f_1(3) = a, \\
\tau f_1(2) &= f_1((1324)(58)(67)2) = f_1(4) = a, \\
\tau f_1(3) &= f_1((1324)(58)(67)3) = f_1(2) = a, \\
\tau f_1(4) &= f_1((1324)(58)(67)4) = f_1(1) = p, \\
\tau f_1(5) &= f_1((1324)(58)(67)5) = f_1(8) = a, \\
\tau f_1(6) &= f_1((1324)(58)(67)6) = f_1(7) = p, \\
\tau f_1(7) &= f_1((1324)(58)(67)7) = f_1(6) = p, \\
\tau f_1(8) &= f_1((1324)(58)(67)8) = f_1(5) = p.
\end{align*} \]

Thus the configuration

\[ \begin{array}{c}
\times \\
\times \\
\times \\
\times \\
\end{array} \quad \begin{array}{c}
\times \\
\times \\
\times \\
\times \\
\end{array} \]

is permuted to the configuration

\[ \begin{array}{c}
\times \\
\times \\
\times \\
\times \\
\end{array} \quad \begin{array}{c}
\times \\
\times \\
\times \\
\times \\
\end{array} \]

by the action of \( \tau \) on the corresponding map \( f_1 \). The space type resulting from the action of \( \tau \) is another map \( f_2 \) from \( D \) to \( R \) and these two maps or the corresponding space types are equivalent. In general, two space types are said to be equivalent if there exists a \( \tau \in G[H_1, H_2, \ldots, H_m] \) such that the corresponding maps \( f_i \) and \( f_j \) satisfy

\[ f_i(d) = f_j(\tau d) \quad \text{for every } d \in D. \]
All the maps that are equivalent can be grouped together and they form an equivalence class. In Sec. 3.B we obtain generators of equivalence classes of space types in terms of group structures known as cycle indices.

### B. Cycle Indices as Generators

Any permutation can be represented by its cycle decomposition. For example, a permutation of four objects can be represented by (12)(34). This permutation has two cycles of length 2. (123)(4567) is another permutation of seven objects containing a cycle of length 3 and a cycle of length 4. In general let a permutation \( \tau \) have \( b_1 \) cycles of length 1, \( b_2 \) cycles of length 2, \ldots, \( b_n \) cycles of length \( n \). With this permutation we can associate the cycle representation \( x_1^{b_1} x_2^{b_2} \cdots x_n^{b_n} \).

For example, the cycle representations associated with the permutations (12)(34) and (123)(4567) are \( x_2^2 \) and \( x_3^1 x_4^1 \), respectively. Define the cycle index of a permutation group \( T \), denoted as \( P_T \), as the sum of cycle representations of the elements in \( T \) divided by \( |T| \), the number of elements in \( T \). Symbolically,

\[
P_T = \frac{1}{|T|} \sum_{\tau \in T} x_1^{b_1} x_2^{b_2} \cdots x_n^{b_n},
\]

where a typical permutation \( \tau \in T \) has \( b_1 \) cycles of length 1, \( b_2 \) cycles of length 2, etc. Consider \( T \) as the permutation group containing six elements

\[
T = \{(1)(2)(3), (12)(3), (13)(2), (1)(23), (132), (123)\}.
\]

Then the cycle index of this group is

\[
P_T = \frac{1}{6} (x_1^3 + 3 x_1^2 x_2 + 2 x_3).
\]

The cycle index of the group \( G[H_1, H_2, \ldots, H_m] \) can be obtained in terms of the cycle indices of \( G, H_1, H_2, \ldots, H_m \). Recall that \( G \) is an intransitive group acting on a set \( \Omega \) which is partitioned into the sets \( Y_1, Y_2, \ldots, Y_m \). Let a \( g \in G \) have \( C_{ij}(g) \) cycles of length \( j \) in the set \( Y_i \). Then the cycle representation of this \( g \in G \) would be

\[
\prod_{i,j} x_{ij}^{C_{ij}(g)},
\]

where \( x_{ij} \) stands for a \( j \) cycle in the set \( Y_i \). For example, consider the permutation (1,5)(2,4)(3)(6,10)(8)(7,9) of the decapentadiene problem for which

\[
Y_1 = \{1, 5, 6, 10\}, \quad Y_2 = \{2, 4, 7, 9\}, \quad \text{and} \quad Y_3 = \{3\}.
\]

(We omitted the \( \omega \)'s for convenience.) Then this permutation \( g \in G \) has two cycles of length 2 in the set \( Y_1 \) (they are (1, 5) and (6, 10)), two cycles of length 2 in the set \( Y_2 \), and two cycles of length 1 in the set \( Y_3 \). Consequently, the corresponding cycle representation is \( x_2^2 x_2^2 x_{31}^2 \). The cycle index of \( G \) is thus defined as

\[
P_G = \frac{1}{|G|} \sum_{g \in G} \prod_{i,j} x_{ij}^{C_{ij}(g)}.
\]
For the decapentadiene problem the cycle index of \( S_2(10) \) is
\[
P_{S_2(10)} = \frac{1}{2}(x_{11}^2 x_{21} x_{31}^2 + x_{12}^2 x_{22} x_{31}^2).
\]
Let the cycle index of the group \( H_n \) denoted by \( Z_n \) be defined as
\[
Z_i(x_1, x_2, \ldots) = \frac{1}{|H_i|} \sum_{h \in H_i} x_1^{h_1} x_2^{h_2} \ldots
\]
where \( x_1^{h_1} x_2^{h_2} \ldots \) is a cycle representation of an \( h \in H_i \). Define \( Z_{ij} \) as \( Z_i \) with every \( x_k \) in \( Z_i \) replaced by a \( x_{jk} \), where \( jk \) is the product of \( j \) and \( k \). In symbols,
\[
Z_{ij} = Z_i(x_k \rightarrow x_{kj}).
\]
Then it can be shown [5] that the cycle index of \( G[H_1, H_2, \ldots, H_m] \)
\[
Z(G[H_1, H_2, \ldots, H_m]) = P_G(x_{ij} \rightarrow Z_{ij}).
\]
That is, the cycle index of \( G[H_1, H_2, \ldots, H_m] \) is obtained by replacing every \( x_{ij} \) in \( P_G \) by \( Z_{ij} \).

Let us illustrate this with the localized orbitals of decapentadiene. For this problem \( P_G \) was already obtained. The three groups \( H_1, H_2, \) and \( H_3 \) are \( S_2(2) \). Thus the cycle index of any \( H_i, Z_i \) is
\[
Z_i = P_{H_i} = \frac{1}{2}(x_1^2 + x_2).
\]
Recall that \( H_i = \{(1)(2), (12)\} \). Thus
\[
Z_{11} = Z_1; \quad Z_{12} = Z_1(x_k \rightarrow x_{2k}) = \frac{1}{2}(x_2^2 + x_4),
\]
\[
Z_{21} = Z_2; \quad Z_{22} = Z_2(x_k \rightarrow x_{2k}) = \frac{1}{2}(x_2^2 + x_4),
\]
\[
Z_{31} = Z_3.
\]
Therefore, the cycle index of \( S_2(10)[S_2(2), S_2(2), S_2(2)] \) is
\[
Z(S_2(10)[S_2(2), S_2(2), S_2(2)]) = P_{S_2(10)}(x_{ij} \rightarrow Z_{ij})
\]
\[
= \frac{1}{2}[(\frac{1}{2}(x_1^2 + x_2))^4(\frac{1}{2}(x_1^2 + x_2))^4(\frac{1}{2}(x_1^2 + x_2))^2
\]
\[
+ (\frac{1}{2}(x_2^2 + x_4))^2(\frac{1}{2}(x_2^2 + x_4))^2(\frac{1}{2}(x_2^2 + x_4))^2]
\]
\[
= \frac{1}{2048}(x_1^2 + x_2)^{10} + 16(x_2^2 + x_4)^{4}(x_1^2 + x_2)^2).
\]
In this case the order of configuration group was 2048 whose cycle index was very efficiently obtained without enumerating all the 2048 permutations of the configuration symmetry group and summing all their cycle representations.

Having obtained the cycle index, the next step is to obtain generators of equivalence classes of space types. To accomplish this we introduce the concept of a weight of an element \( r \in R \), denoted as \( w(r) \), which is just a formal symbol which "bookkeeps" the number of electrons in a configuration. For example, we may associate a weight 1 if the electron is absent and a weight \( w \) if it is present. Then define the weight of any map \( f \) from \( D \) to \( R \) as the product of
the weights of the corresponding images. In symbols,

\[ W(f) = \prod_{d \in D} w(f(d)). \]

To illustrate consider the map \( f_1 \) used as an illustrative example in Section 3.A. The weight of this map \( W(f_1) = w.1.1.1.w.w.1 = w^4 \), since four electrons are present in this configuration. In general, since we suppress the absence of an electron with the weight 1, for any configuration with \( k \) electrons, the weight would be \( w^k \).

Then we have the following theorem due to Pólya [6] and reviewed by DeBruijn [7], which gives a generating function for equivalence classes of space types

\[ F = P_C(x_k \to 1 + w^k), \]

with \( C \) the configuration symmetry group which is, in general, a generalized wreath product. That is, we obtain the generating function for equivalence classes of space types by replacing every \( x_k \) by \( 1 + w^k \). The coefficient of a typical term \( w^l \) in \( F \) gives the number of equivalence classes of space types containing \( l \) electrons.

Let us illustrate the method with several examples starting from the localized orbitals of butadiene. The cycle index of butadiene problem is shown:

\[ P_T = \frac{1}{2}[(\frac{1}{2}(x_1^2 + x_2))^4 + (\frac{1}{2}(x_2^2 + x_4))^2] \]

\[ = \frac{1}{2}[x_1^8 + 4x_1^6x_2 + 6x_1^4x_2^2 + 4x_1^2x_2^3 + 5x_2^4 + 8x_2^2x_4 + 4x_4^2]. \]

Thus \( F \) for butadiene is

\[ F = \frac{1}{32}[(1 + w)^8 + 4(1 + w)^6(1 + w^2) + 6(1 + w)^4(1 + w^2)^2 \]

\[ + 4(1 + w)^2(1 + w^2)^3 + 5(1 + w^2)^4 + 8(1 + w^2)^2(1 + w^4) + 4(1 + w^4)^2]. \]

Note that \( F \) generates space types with all probable occupancies, even though, for the present problem we are interested in the coefficient of \( w^4 \) (since there are four electrons) in \( F \) which is

\[ \frac{1}{32}[(\frac{1}{8}) + 4(\frac{1}{4}) + 4(\frac{1}{2}) + 6(\frac{1}{8})(\frac{1}{2}) + 6(\frac{1}{2})(\frac{3}{2}) + 4(\frac{3}{2})(\frac{5}{2}) \]

\[ + 4(\frac{3}{2})(\frac{3}{2}) + 5(\frac{5}{2}) + 8(\frac{5}{2}) + 4(\frac{5}{2})] = 352/32 = 11. \]

The 11 classes are shown in Table I where space types in the same row belong to the same equivalence class.

It is also possible to obtain just the generating function for space types by letting \( G \) be the group containing only the identity in the generalized wreath product. The modified cycle index is as follows for the butadiene problem:

\[ P_T = \frac{1}{16}(x_1^2 + x_2)^4. \]

The generating function for just the space types is

\[ F = \frac{1}{16}[(1 + w)^2 + (1 + w^2)]^4 = (1 + w + w^2)^4. \]
TABLE I. Eleven equivalence classes of space types of localized orbitals of butadiene. Note that the ninth class can be coupled in two ways and thus gives rise to two configurations.

<table>
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<tr>
<th>Serial No</th>
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</table>

For an $n$-orbital problem it can be easily shown that the generating function for space types is

$$F = (1 + w + w^2)^n.$$  

The coefficient of $w^4$ in the generating function for the space types of butadiene is

$$1 + \binom{4}{2} + \binom{4}{121} = 19.$$
Thus there are 19 space types for butadiene which are grouped into 11 equivalence classes. Butadiene was used as a simple, however, a typical example. We now proceed to a few more examples such as localized orbitals of hexatriene, benzene, etc. For the localized orbitals of hexatriene the cycle index is

\[
P(S_2[S_2, S_3]) = \frac{1}{2} \left( \frac{1}{2^6} (x_1^2 + x_2)^6 + \frac{1}{2^3} (x_2^2 + x_4)^3 \right).
\]

Thus the generating function \( F \), is

\[
F = \frac{1}{2^7} \left( 2^6(1 + w + w^2)^6 + 8 \cdot 2^3(1 + w^2 + w^4)^3 \right).
\]

The coefficient of \( w^6 \) in the above expression is

\[
\frac{1}{3} \left( 1 + (\frac{6}{41}) + (\frac{6}{222}) + (\frac{6}{4}) + 1 + (\frac{3}{1111}) \right) = 71.
\]

Thus there are 71 equivalence classes of space types. It will be interesting to compare this with the total number of space types which is the coefficient of \( w^6 \) in the expression \( (1 + w + w^2)^6 \) and is

\[
[1 + (\frac{6}{41}) + (\frac{6}{222}) + (\frac{6}{4})] = 141.
\]

As a last example consider benzene. In this case we generate all possible space types. However, for a particular reference state only some of these would contribute because others may be symmetry forbidden. Nevertheless, our procedure must be general since if we want to look at different reference states we need to generate all possible space types and then select the space types allowed by symmetry. Benzene is considered here within the framework of \( \sigma \) electron approximation. The ground state is shown below in the delocalized representation

\[
\begin{align*}
\text{-------} & \quad \text{-------} \\
\text{---x---} & \quad \text{---x---} \\
\text{-------} & \quad \text{-------}
\end{align*}
\]

The configuration symmetry group can be seen to be

\[
S_2 \times S_2[S_2] \times S_2[S_2] \times S_2.
\]

The cycle index of a direct product of groups is the product of the cycle indices. In this case the electrons in different sets of orbitals can be identified by different weights also. In such a case we get some more details of enumeration. The cycle index for benzene is

\[
P(S_2 \times S_2[S_2] \times S_2[S_2] \times S_2) = \{\frac{1}{2}(x_1^2 + x_2)\}^2 \{\frac{1}{8}(x_1^4 + 2x_1^2x_2 + 3x_2^2 + 2x_4)\}^2.
\]

If one collects the coefficient of \( w^6 \) in the appropriate generating function obtained by replacing every \( x_k \) by \( 1 + w^k \) we find this to be 58. Thus the number of equivalence classes of space types for a CI of benzene is 58. Actually for a given reference state this number will be smaller because one has to choose
symmetry-allowed space types from these equivalence classes. Nevertheless, any space type will contribute to some reference states not necessarily the ground state. The total number of possible space types for benzene is 141. (This number is same as the number of space types for hexatriene as we would expect.)

Table II lists the number of space types and equivalence classes of space types for CI of some atoms. These space types are constructed with all possible excitations up to $3p$ orbitals.

<table>
<thead>
<tr>
<th>Atom</th>
<th>No. of space types</th>
<th>No. of equivalence classes</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>45</td>
<td>17</td>
</tr>
<tr>
<td>Li</td>
<td>156</td>
<td>42</td>
</tr>
<tr>
<td>Ne</td>
<td>414</td>
<td>86</td>
</tr>
<tr>
<td>B</td>
<td>882</td>
<td>148</td>
</tr>
<tr>
<td>C</td>
<td>1554</td>
<td>223</td>
</tr>
<tr>
<td>N</td>
<td>2304</td>
<td>295</td>
</tr>
<tr>
<td>O</td>
<td>2907</td>
<td>349</td>
</tr>
<tr>
<td>F</td>
<td>3139</td>
<td>368</td>
</tr>
</tbody>
</table>

In retrospect, for a general problem one adopts the following rules to enumerate the space types and their equivalence classes. If there are $n$ orbitals (both occupied and virtual) and $m$ electrons the coefficient of $w^m$ in the generating function for the space types gives the number of space types. Then all the degenerate orbitals in the set of orbitals are identified and grouped in to the same $Y$ set. This generates all the sets $Y_1, Y_2, \ldots$. The next step is to construct the appropriate configuration symmetry group which is a generalized wreath product. Subsequently, the cycle index and generating function are obtained. The coefficient of $w^m$ in the resulting generating function enumerates the equivalence classes of space types.

4. Double Coset Method for the Construction of a Representative of the Equivalence Classes of Space Types

It is probably not just enough to enumerate the equivalence classes of space types even though this enumeration is important since it helps to construct a double coset decomposition which enables the construction of a representative
in the equivalence class. There should be a method or an algorithm for the construction of representatives of equivalence classes so that one may carry out \( CI \) with these representatives. There are such procedures in the literature. The formulation that we present here is essentially the idea of Ruch et al. [8] who used the double cosets for enumerating isomers of chemical structures. However, in this section we reformulate this method to adapt it to generalized wreath product groups. Brown et al. [9] formulated a computer algorithm and program for constructing these representatives of double cosets. The double coset method was also used by Davidson [10] to construct the symmetry-distinct basis set integrals. However, this double coset was constructed in the molecular point group which is a group of much lower order in comparison to the generalized wreath product groups.

Let \( n \) be the number of holes in all the orbitals. Let \( m \) be the number of electrons. The group \( S_n \times S_{n-m} \) for the present problem is called the label subgroup and let us denote it by \( L \). Let \( C \) be the configuration symmetry group. Note that both \( L \) and \( C \) are subgroups of \( S_n \). For an element \( s \in S_n \), the set \( LsC \) is called a double coset of \( L \) and \( C \) in \( S_n \). Any space type can be considered as an element of \( S_n \). This is because we may consider the identity of \( S_n \) as the space type in which the holes of first \( m \) orbitals contain electrons. Then any other space type can be described by a permutation in \( S_n \). Let us illustrate this concept with two electrons and two orbitals

\[
\begin{array}{c}
\begin{array}{c}
\text{---(1234)} \\
\times \times \times (1234) \\
\end{array}
\end{array}
\]

The space type shown above corresponds to the map \( f \) defined as

\[
\begin{align*}
f(1) &= p, \\
f(2) &= p, \\
f(3) &= a, \\
f(4) &= a,
\end{align*}
\]

where \( a \) and \( p \) have the same meaning as in Sec. 3.A. Then a permutation such as \( \tau = (1234) \) acts on \( f \) by the recipe given in Sec. 3.A which is

\[
\tau f(i) = f(\tau^{-1} i).
\]

Since \( \tau^{-1} = (1432) \),

\[
\begin{align*}
\tau f(1) &= f((1432)1) = f(4) = a, \\
\tau f(2) &= f((1432)2) = f(1) = p, \\
\tau f(3) &= f((1432)3) = f(2) = p, \\
\tau f(4) &= f((1432)4) = f(3) = a.
\end{align*}
\]
Consequently, the resulting space type is

\[ \begin{array}{c}
\times \\
\times 
\end{array} \]

Hence this singly excited state can be generated by the permutation (1234) from the reference state.

Two elements \( s_1 \) and \( s_2 \) are in the same double coset if

\[ s_1 = Ls_2C. \]

The corresponding space types are then equivalent. Thus the unique space types are just the representatives of the double coset decomposition of \( S_n \). The elements \( S = \{ s_1, s_2, \ldots, s_t \} \) of \( S_n \) are the distinct representatives if

\[ S_n = \bigcup_{i=1}^{t} Ls_iC \]

and

\[ (Ls,C) \cap (Ls,C) = \phi \quad \text{if } i \neq j, \]

where \( \phi \) is the null set. We enumerated the number of distinct representatives in Section 3 using cycle indices as generators.

The number of elements in any double coset \( LsC \), denoted as \( |LsC| \) is given as

\[ |LsC| = |L||C|/|s^{-1}Ls \cap C| = |L||C|/|L \cap sCs^{-1}|. \]

Brown et al. have formulated a computer algorithm and a program for constructing these distinct representatives. Details of this algorithm can be found in their paper.

We now give an example of two degenerate orbitals with two electrons and their double coset representatives. The number of holes, \( n \) is 4. Since there are two electrons in these holes, the label subgroup is \( L = S_2 \times S_2 \). The configuration symmetry group \( C = S_2[S_2] \). The cycle index \( P_C \) and the generating function \( F \) for this problem are

\[ P_C = \frac{1}{8}(x_1^4 + 2x_1^2x_2 + 3x_2^2 + 2x_4), \]

\[ F = \frac{1}{8}((1 + w)^4 + 2(1 + w)^2(1 + w^2) + 3(1 + w^2)^2 + 2(1 + w^4)). \]

The coefficient of \( w^2 \) in \( F \) is 2. Hence we look for \( s_1 \) and \( s_2 \) in \( S_4 \) such that

\[ (Ls_1C) \cup (Ls_2C) = S_4 \]

and

\[ (Ls_1C) \cap (Ls_2C) = \phi. \]

We will illustrate this by explicitly writing out all the elements of each double coset. One obvious choice is \( s_1 = e \), the identity of \( S_4 \). The resulting double coset
is shown below.

\[ LeC = \{(1)(2), (12), (34), (12)(34), (13)(24), (14)(23), (1423), (1324)\}, \]

\[ |LeC| = |L||C|/|L \cap C| = |C| = 8 \quad (since \ L \cap C = L \ in \ this \ case). \]

The second double coset which has no common element with \( LeC \) is the double coset \( L(1342)C \). \( (1342) \) was chosen since it is not present in the first double coset. This choice is, of course, not unique for we could have chosen \( (1243) \), or \( (123) \), etc. However, any such choice would lead to the same double coset. The second double coset thus obtained is

\[ L(1342)C = \{(1342), (134), (142), (14), (23), (1243), (243), (123), (234), (1234), (24), (124), (132), (143), (1432), (13)\} \]

Note that

\[ (LeC) \cup (L(1342)C) = S_4 \]

and

\[ (LeC) \cap (L(1342)C) = \phi. \]

Hence \( \{e, (1342)\} \) is a set of distinct representatives. The corresponding space types are obtained by operating \( s_1 \) and \( s_2 \) on the map \( f_1 \)

\[ f_1(1) = p, \]
\[ f_1(2) = p, \]
\[ f_1(3) = a, \]
\[ f_1(4) = a. \]

Since \( s_1 = e, s_1f_1 = f_1 \). Since \( s_2 = (1342) \), the map \( f_2 = s_2f_1 \) is

\[ f_2(1) = (1342)f_1(1) = f_1((1243)1) = f_1(2) = p, \]
\[ f_2(2) = (1342)f_1(2) = f_1((1243)2) = f_1(4) = a, \]
\[ f_2(3) = (1342)f_1(3) = f_1((1243)3) = f_1(1) = p, \]
\[ f_2(4) = (1342)f_1(4) = f_1((1243)4) = f_1(3) = a. \]

The resulting space types which correspond to \( f_1 \) and \( f_2 \) are

\[ \longleftrightarrow --x--x-- \longleftrightarrow, \quad --x-- \longleftrightarrow --x--. \]

Of course, it can be easily seen that these are the two distinct representatives for two electrons in two degenerate orbitals. This was only an illustrative example used to exemplify the concept of double coset method. In general, for more complex systems these double coset decompositions can be constructed with the help of cycle indices, and the Brown et al. algorithm adapted to generalized wreath products using a computer.
For a general CI one first enumerates the equivalence classes of space types using the formalism outlined in Sec. 3. Then one constructs the double cosets of the label subgroup $S_m \times S_{n-m}$ and the configuration symmetry group. The representatives of the resulting double cosets construct the actual equivalence classes of space types.

In the present formalism we need to evaluate the CI symbolic formulas and the matrix elements between one representative of a double coset and all space types in another equivalence class and formulas and matrix elements for each pair of elements in each equivalence class. Consequently, the number of space types, the number of symbolic formulas and the number of CI matrix elements that need to be constructed are brought down.

It should be interesting to look at the combinatorics of the CI formulas constructed using the double cosets of space types and all the space types. For the butadiene problem, since there are 20 configurations the total number of formulas is 210. When CI formulas are obtained in terms of the members of the double cosets first formulas are needed for a member in an equivalence class containing more than one space type with all the other members in all the subsequent classes. This is because, for example, the matrix element between the first member of the second class and the first member of the fifth class is not the same as the matrix element between the first member of the second class and the second member of the fifth class. (In fact the former differs by a single excitation, while the latter differs by a triple excitation.) Nevertheless, the matrix element between the first member of the second class and the first member of the fifth class is identical with the matrix element between the second member of the second class and the second member of the fifth class. Further, one needs to evaluate matrix elements for a representative with itself and with other members in the same class. When one enumerates all these combinations for the localized orbitals of butadiene (taking into account that the ninth class can be coupled in two ways) one obtains the number of unique matrix elements to be 113. Thus the number of matrix elements is brought down from 210 to 113.

The formalism outlined here can be easily adapted to $(S + D)$-CI or any other CI including the full CI.

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