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K. Balasubramanian

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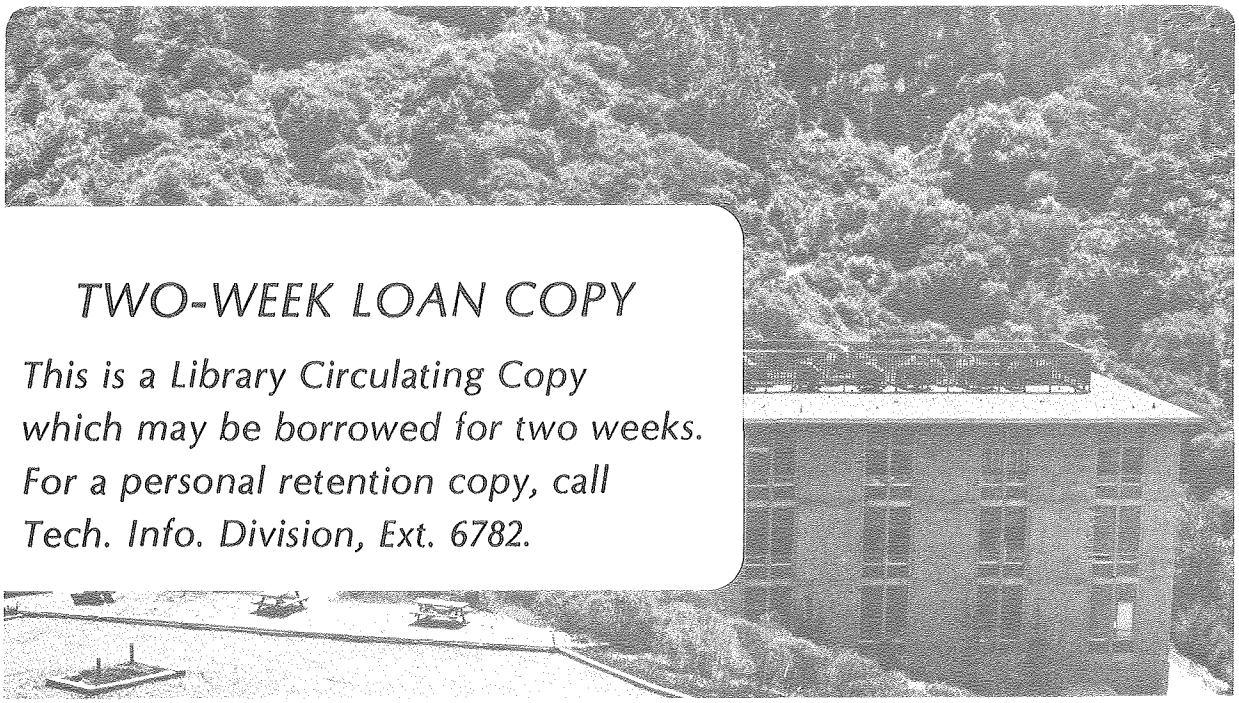

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Symmetry Simplifications of Space Types in Configuration Interaction Induced by Orbital Degeneracy

K. Balasubramanian

Department of Chemistry
and
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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 wherein all the space types in the same equivalence class with identical spin coupling make identical contributions to correlation. 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 the number of electrons. Method is illustrated with CI using the localized Löwdin orbitals of polyenes and CI in benzene 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 permutting the degenerate orbitals and consequently they have identical CI matrix elements and therefore, their CI expansion coefficients differ at most by a sign. Thus, if the CI matrix element of a representative of these equivalence classes of configurations is 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 Section 2 configuration symmetry groups are defined and shown to be expressible as generalized wreath products. In Section 3 we outline the generation of equivalence classes of space types and in Section 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 have identical CI matrix elements. This is also reflected in the corresponding coefficients of the CI wavefunction. For example, the two configurations of the localized Löwdin orbitals of butadiene shown below are equivalent.

This is because configurations I and II are transformable into each other by interchanging the degenerate occupied and virtual Löwdin orbitals. In fact, Ohmine *et al*[3] carried out a (S + D)-CI (CI which includes single and double excitations from the reference state) with $^1 1A_g$ reference state and obtained the same coefficient (-0.148) for these two configurations in the CI wavefunction

and showed that correlation to the $^1 1A_g$ ground state is predominantly introduced by these 2 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 2 configurations which are not equivalent in the above sense and yet may have coefficients of the same magnitude in the CI wavefunctions. 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) CI with $^1 1A_g$ reference state.[3]

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 Löwdin orbitals of butadiene by ω_1 and ω_2 and the virtual orbitals by ω_3 and ω_4, then any two space types that can be transformed into each other by the permutation (12)(34) of the Löwdin orbitals (where we denote ω_i by i) with the same spin coupling are equivalent. In the case of localized Löwdin 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 2 dimensional coupling to obtain a singlet state when there are 4 open shells). Each orbital can accommodate at most 2 electrons. Define a site

where an electron can be accommodated as a hole. Thus each orbital contains 2 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, eventhough, it motivates the formulation of a rigorous definition and helps to understand the problem. A precise definition and formulation of the configuration symmetry group are given in the next section.

B. Configuration Symmetry Groups as Generalized Wreath Products

Let Ω 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, Ω for the Löwdin orbitals of butadiene is the set $\{\omega_1, \omega_2, \omega_3, \omega_4\}$ and G is the set $\{(1)(2)(3)(4), (12)(34)\}$. Note that in this case the localized orbitals ω_1 and ω_2 cannot be permuted without permuting the corresponding virtual orbitals since they are localized to ethylenic units. However, delocalized degenerate 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 Ω and a group S_2 acting on the holes in each orbital of Ω. Let π be a map from Ω to H. Equivalently, for each orbital in Ω 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 $\{(g; \pi)/g\varepsilon G, \pi:\Omega \rightarrow H\}$. This is

precisely the wreath product G[H] used by the author in the context of symmetry groups of non-rigid molecules.[4] The product of 2 elements $(g;\ \pi)$ and $g';\ \pi')$ in G[H] is defined as

$$(g;\ \pi)(g';\ \pi') = (gg';\ \pi\pi_{g'})$$

where

$$\pi\pi_{g'}(i) = \pi(i)\ \pi'(g^{-1}i) \qquad \text{for } i\varepsilon\Omega.$$

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

$$e'(i) = {}^{1}H$$

where ${}^{1}H$ is the identity of the group H. Inverse of an element $(g;\ \pi)$ is $(g^{-1};\ \pi^{-1}_{g^{-1}})$.

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 π defined below.

$$\pi(1) = (12)$$

$$\pi(2) = (1)(2)$$

$$\pi(3) = (12)$$

$$\pi(4) = (12)$$

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

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

$$H_i = \{(e;\ \pi)/e \text{ is the identity of } G\},$$
$$G' = \{(g;\ e')/g \varepsilon G\},$$

and n is the number of elements in Ω. $H_1 \times H_2 \times \ldots \times H_n$ is an n-fold direct product of n copies of the group H. $H_1 \times H_2 \times \ldots \times H_n$ also denoted as H* is an invariant subgroup of G[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 Löwdin 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 ω_1, 3 and 4 to the orbitals ω_2, etc., then, for example, a permutation representation of the permutation ((12)(34); π), with π defined as in the above example, is

$$(12)(3)(4)(56)(78)(13)(24)(57)(68) = (1423)(58)(67).$$

Instead of the Löwdin orbitals of butadiene if Löwdin 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 $Y_1, Y_2, \ldots\ldots, Y_n$, and the group G permutes elements only within a set Y_i. Equivalently, G does not mix elements of different Y-sets. Let H_i be a group acting on the holes which correspond to orbitals in the set Y_i. Let π_i be a map from the set Y_i to H_i. The generalized wreath product $G[H_1, H_2, \ldots, H_m]$ consists of permutations $\{(g;\ \pi_1, \pi_2, \ldots, \pi_m)/g \varepsilon G,\ \pi_i : Y_i \rightarrow H_i\}$. If we denote the occupied Löwdin orbitals of decapentadiene by ω_1, ω_2, ω_3, ω_4 and ω_5 and the virtual orbitals by

ω_6, ω_7, ω_8, ω_9 and ω_{10} then the Y-sets are $Y_1 = \{\omega_1, \omega_5, \omega_6, \omega_{10}\}$, $Y_2 = \{\omega_2, \omega_4, \omega_7, \omega_9\}$ and $Y_3 = \{\omega_3, \omega_8\}$. The group G is

$$S_2(10) = \{(1)(2)(3)(4)(5)(6)(7)(8)(9)(10),\ (1,5)(2,4)(3)(6,10)(7,9)(8)\}$$

and the groups H_1, H_2 and H_3 are $S_2(2)$. Then the configuration symmetry group of the Löwdin orbitals of decapentadiene is $S_2(10)[S_2(2), S_2(2), S_2(2)]$. The order of this group is $2.2^4 \cdot 2^4 \cdot 2 = 1024$. In general, the order of generalized wreath product $G[H_1, H_2, \ldots, H_m]$, is $|G||H_1|^{|Y_1|}|H_2|^{|Y_2|}\ldots|H_m|^{|Y_m|}$.

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 f_1 from D to R which corresponds to the holes of the orbitals of butadiene is shown below.

$$f_1(1) = p$$
$$f_1(2) = a$$
$$f_1(3) = a$$
$$f_1(4) = a$$
$$f_1(5) = p$$
$$f_1(6) = p$$
$$f_1(7) = p$$
$$f_1(8) = a$$

The resulting space type is

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

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

For example, if $\tau = ((12)(34);\ \pi)$ with π defined as in the illustrative example of Section 2B 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

$$\tau f_1(1) = f_1((1324)(58)(67)\ 1) = f_1(3) = a$$
$$\tau f_1(2) = f_1((1324)(58)(67)\ 2) = f_1(4) = a$$
$$\tau f_1(3) = f_1((1324)(58)(67)\ 3) = f_1(2) = a$$
$$\tau f_1(4) = f_1((1324)(58)(67)\ 4) = f_1(1) = p$$
$$\tau f_1(5) = f_1((1324)(58)(67)\ 5) = f_1(8) = a$$
$$\tau f_1(6) = f_1((1324)(58)(67)\ 6) = f_1(7) = p$$
$$\tau f_1(7) = f_1((1324)(58)(67)\ 7) = f_1(6) = p$$
$$\tau f_1(8) = f_1((1324)(58)(67)\ 8) = f_1(5) = p$$

Thus the configuration is permuted to the configuration by the action of τ on the corresponding map f_1. The space type resulting from the action of τ 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 $\tau \varepsilon G[H_1, H_2,\ldots,H_m]$ such that the corresponding maps f_i and f_j satisfy the following condition.

$$f_i(d) = f_j(\tau d) \qquad \text{for every } d \varepsilon D.$$

All the maps that are equivalent can be grouped together and they form an

equivalence class. In the next Section 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 4 objects can be represented by (12)(34). This permutation has 2 cycles of length 2. (123)(4567) is another permutation of 7 objects containing a cycle of length 3 and a cycle of length 4. In general let a permutation τ have b_1 cycles of length 1, b_2 cycles of length 2,...,b_n cycles of length n. With this permutation we can associate the cycle representation $x_1^{b_1} x_2^{b_2} \ldots x_n^{b_n}$. 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,

$$P_T = \frac{1}{|T|} \sum_{\tau \varepsilon T} x_1^{b_1} x_2^{b_2} \ldots x_n^{b_n}$$

where a typical permutation $\tau \varepsilon T$ has b_1 cycles of length 1, b_2 cycles of length 2, etc. Consider T as the permutation group containing 6 elements shown below

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

Then the cycle index of this group is as follows.

$$P_T = \frac{1}{6} (x_1^3 + 3x_1x_2 + 2x_3)$$

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, $H_1, H_2, \ldots, H_t$. Recall that G is an intransitive group acting on a set Ω which is partitioned into the sets $Y_1, Y_2, \ldots, Y_m$. Let a $g \varepsilon G$

have $C_{ij}(g)$ cycles of length j in the set Y_i. Then the cycle representation of this $g\varepsilon G$ 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

$$Y_1 = \{1,5,6,10\},\ Y_2 = \{2,4,7,9\} \text{ and } Y_3 = \{3,8\}.$$

(We omitted the ω's for convenience.) Then this permutation $g\varepsilon G$ has 2 cycles of length 2 in the set Y_1 (they are (1,5) and (6,10)), 2 cycles of length 2 in the set Y_2 and 2 cycles of length 1 in the set Y_3. Consequently, the corresponding cycle representation is $x_{12}^2\ x_{22}^2\ x_{31}^2$. The cycle index of G is thus defined as follows:

$$P_G = \frac{1}{|G|} \sum_{g\varepsilon G} \prod_i \prod_j x_{ij}^{C_{ij}(g)}.$$

For the decapentadiene problem the cycle index of $S_2(10)$, is

$$P_{S_2(10)} = \frac{1}{2}\ (x_{11}^4 x_{21}^4 x_{31}^2 + x_{12}^2 x_{22}^2 x_{31}^2).$$

Let the cycle index of the group H_i, denoted by Z_i, be defined as follows.

$$Z_i(x_1,x_2,\ldots.) = \frac{1}{|H_i|} \sum_{h\varepsilon H_i} x_1^{b_1} x_2^{b_2} \ldots.$$

where $x_1^{b_1} x_2^{b_2} \ldots.$ is a cycle representation of an $h\varepsilon H_i$. 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 $G[H_1,H_2,\ldots,H_m]$, $Z(G[H_1,H_2,\ldots,H_m])$ is obtained as follows.

$$Z(G[H_1,H_2,\ldots,H_m]) = P_G(x_{ij} \to z_{ij}).$$

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 Löwdin 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 as follows.

$$Z_i = P_{H_i} = \frac{1}{2}\,(x_1^{\,2} + x_2).$$

Recall that $\qquad H_i = \{(1)(2),\ (12)\}.$

Thus

$$Z_{11} = Z_1 \ ;\ Z_{12} = Z_1(x_k \to x_{2k}) = \frac{1}{2}\,(x_2^{\,2} + x_4)$$

$$Z_{21} = Z_2 \ ;\ Z_{22} = Z_2(x_k \to x_{2k}) = \frac{1}{2}\,(x_2^{\,2} + x_4)$$

$$Z_{31} = Z_3.$$

Therefore, the cycle index of $S_2(10)[S_2(2),\ S_2(2),\ S_2(2)]$ is as follows.

$$Z(S_2(10)[S_2(2),\ S_2(2),\ S_2(2)]) = P_{S_2(10)}(x_{ij} \to z_{ij})$$

$$= \frac{1}{2}\,[\{\tfrac{1}{2}(x_1^{\,2}+x_2)\}^4\ \{\tfrac{1}{2}(x_1^{\,2}+x_2)\}^4\ \{\tfrac{1}{2}(x_1^{\,2}+x_2)\}^2$$

$$+\ \{\tfrac{1}{2}(x_2^{\,2}+x_4)\}^2\ \{\tfrac{1}{2}(x_2^{\,2}+x_4)\}^2\ \{\tfrac{1}{2}(x_1^{\,2}+x_2)\}^2]$$

$$= \frac{1}{2048}\,[(x_1^{\,2}+x_2)^{10} + 16(x_2^{\,2}+x_4)^4\ (x_1^{\,2}+x_2)^2].$$

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 $r \varepsilon R$, denoted as $w(r)$, which is just a formal symbol which book-keeps 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,

$$W(f) = \prod_{d \varepsilon D} w(f(d)).$$

To illustrate consider the map f_1 used as an illustrative example in Section 3A. The weight of this map $W(f_1) = w.1.1.1.w.w.w.1 = w^4$, since 4 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[6-7] which gives a generating function for equivalence classes of space types.

$$F = P_C(x_k \rightarrow (1+w)^k).$$

With C = 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 Löwdin orbitals of butadiene. The cycle index of butadiene problem is shown below.

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

$$= \frac{1}{32}\ [x_1{}^8+4x_1{}^6x_2 + 6x_1{}^4x_2{}^2 + 4x_1{}^2x_2{}^3 + 5x_2{}^4 + 8x_2{}^2x_4 + 4x_4{}^2].$$

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 4 electrons) in F which is shown below.

$$\frac{1}{32}\ [\binom{8}{4} + 4\binom{6}{4} + 4\binom{6}{2} + 6\binom{4}{2}\binom{2}{1} + 6\binom{4}{4}\binom{2}{2} + 6\binom{4}{4}\binom{2}{2} + 4\binom{2}{2}\binom{3}{1}$$

$$+ 4\binom{2}{2}\binom{3}{2} + 5\binom{4}{2} + 8\binom{2}{1} + 4\binom{2}{1}] = 352/32 = 11.$$

The eleven classes are shown in Table 1 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 shown below.

$$F = \frac{1}{16}\ ((1+w)^2 + (1+w^2))^4 = (1+w+w^2)^4.$$

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 a problem of 19 space types can be reduced to a problem involving 11 space types. Butadiene was used as a simple,however, a typical example. We now proceed to a few more examples such as Löwdin orbitals of hexatriene, benzene, etc. For the Löwdin orbitals of hexatriene the cycle index is shown below.

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

Thus the generating function F, is as follows

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

The coefficient of w^6 in the above expression is

$$\frac{1}{2}(1 + \binom{6}{411} + \binom{6}{222} + \binom{6}{3} + 1 + \binom{3}{111}) = 71.$$

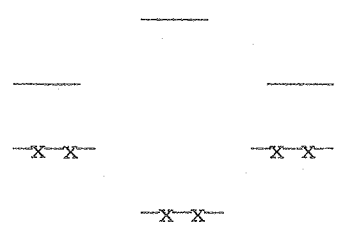
Thus there are 71 equivalence classes of space type. It will be interesting to compare this with the total number of space types which is the coefficient of w^6 in the expression $(1+w+w^2)^6$ and is shown below.

$$(1 + \binom{6}{141} + \binom{6}{222} + \binom{6}{3}) = 141.$$

Thus symmetry reduces CI involving 141 space types to CI involving just 71 unique space types. All are symmetry allowed in this example.

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 π electron approximation. The ground state is shown below in the delocalized representation



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 shown below.

$$P(S_2 \times S_2[S_2] \times S_2[S_2] \times S_2)$$

$$= \{\tfrac{1}{2}(x_1{}^2+x_2)\}^2 \quad \{\tfrac{1}{8}(x_1{}^4+2x_1{}^2x_2+3x_2{}^2+2x_4)\}^2.$$

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

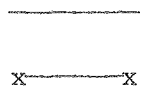
some reference states not necessarily the ground state. The total number of possible space types for benzene is 141. (This number is same as the number of space types for hexatriene as we would expect.)

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 a representative of each equivalence class 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 $S_m \times S_{n-m}$ 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 $s \varepsilon S_n$, 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 2 electrons and 2 orbitals shown below.



$$\binom{1234}{1234}$$

The space type shown above corresponds to the map f defined below.

$$f(1) = p$$

$$f(2) = p$$

$$f(3) = a$$

$$f(4) = a$$

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

$$\tau f(i) = f(\tau^{-1}\, i).$$

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

$$\tau f(1) = f((1432)\ 1) = f(4) = a$$

$$\tau f(2) = f((1432)\ 2) = f(1) = p$$

$$\tau f(3) = f((1432)\ 3) = f(2) = p$$

$$\tau f(4) = f((1432)\ 4) = f(3) = a.$$

Consequently, the resulting space type is . Hence this singly excited state can be generated by the permutation (1234) from the reference state.

Two elements s_1 and s_2 are said to be 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

$$(Ls_iC) \cap (Ls_jC) = \phi \text{ if } i \neq j,$$

where Φ 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 follows.

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

Brown <u>et al</u>. 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 2 degenerate orbitals with 2 electrons and their double coset representatives. The number of holes, n is 4. Since there are 2 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 shown below.

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

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

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)}

$$|LeC| = |L||C|/|L \cap C| = |C| = 8$$

(since $L \cap C = L$)

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 shown below.

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 shown below.

$$f_1(1) = p$$
$$f_1(2) = p$$
$$f_1(3) = a$$
$$f_1(4) = a.$$

Since $s_1 = e$, $s_1 f_1 = f_1$. Since $s_2 = (1342)$ the map $f_2 = s_2 f_1$ is shown below.

$$f_2(1) = (1342)\ f_1(1) = f_1((1243)\ 1) = f_1(2) = p$$
$$f_2(2) = (1342)\ f_1(2) = f_1((1243)\ 2) = f_1(4) = a$$
$$f_2(3) = (1342)\ f_1(3) = f_1((1243)\ 3) = f_1(1) = p$$
$$f_2(4) = (1342)\ f_1(4) = f_1((1243)\ 4) = f_1(3) = a$$

The resulting space types which correspond to f_1 and f_2 are shown below.

Of course, it can be easily seen that these are the 2 distinct representatives for 2 electrons in 2 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 Brown *et al*'s algorithm adapted to generalized wreath products using a computer.

In the present formalism we need to evaluate the CI symbolic formulas and the matrix elements between the representatives of the double cosets and a formula and a matrix element for a 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. If n is the total number of configurations the number of CI formulas and matrix elements that need to be evaluated is $n(n+1)/2$. Let m be the number of equivalence classes of configurations. Since we have to construct the formulas for CI matrix elements between the representatives of all the double cosets and a formula for a pair of elements in each equivalence class, the total number of formulas that need to be constructed is $m(m+1)/2 + m = m(m+3)/2$. For the localized orbitals of butadiene these numbers are 210 and 90, respectively, thus bringing down the number of unique formulas and matrix elements to 90 from 210.

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

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Table 1

The eleven equivalence classes of space types of Löwdin orbitals of Butadiene. Note that the ninth class can be coupled in 2 ways and thus gives rise to 2 configurations

Serial No				
1	—— ——	—— ——		
	x——x	x——x		
2	—— ——	—x—	—x—	—— ——
	—x—x—	—x—	—x—	—x—x—
3	—— ——	—x—	—x—	—— ——
	—x—	—x—x—	—x—x—	—x—
4	—x—x—	—— ——	—— ——	—x—x—
	—x—x—	—— ——	—— ——	—x—x—
5	—— ——	—x—x—	—x—x—	—— ——
	—x—x—	—— ——	—— ——	—x—x—
6	—x—	—x—	—x—	—x—
	—x—x—	—— ——	—— ——	—x—x—
7	—x—x—	—— ——	—— ——	—x—x—
	—x—	—x—	—x—	—x—
8	—x—x—	—x—	—x—	—x—x—
	—— ——	—x—	—x—	—— ——
9	—x—	—x—		
	—x—	—x—		
10	—x—x—	—x—x—		
	—— ——	—— ——		
11	—x—x—	—x—	—x—	—x—x—
	—x—	—— ——	—— ——	—x—