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Relativistic double group spinor representations of nonrigid molecules

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The character theory of relativistic double group spinor representations is developed in order to represent the total rovibronic states of nonrigid molecules. It is shown that the double groups can be represented in terms of wreath products and powerful matrix cycle type generators that are used to construct their character tables. It is shown that these tables are of use when spin–orbit coupling is included in the Hamiltonian even for molecules containing lighter atoms. Applications to nonrigid molecules such as $Tl_2H_4 / Tl_2H_4^+$ are considered. It is shown that the tunneling splittings and the nuclear spin statistical weights can be obtained for such species using the character tables thus constructed. The spinor double groups of several other molecules such as hexamethyl dilead and heavy weakly bound clusters such as $(PoH_2)_4$ are also considered. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1648636]

I. INTRODUCTION

Relativistic spinor representations of molecules require a double group approach due to the incorporation of spin–orbit interaction terms into the Hamiltonian.[1–7] Many years ago, Longuet-Higgins[8] formulated the symmetry groups of non-rigid molecules as permutation–inversion groups. Longuet-Higgins[8] noted that the treatment of rovibronic levels of nonrigid molecules, which typically exhibit potential energy surfaces with surmountable energy barriers, requires a group-theoretical approach that includes all feasible permutations of the nuclei under fluxional motions. In conclusion Longuet-Higgins[8] noted that the inclusion of spin–orbit coupling for nonrigid molecules needs to be considered as a separate topic. Up to now it appears that this has not been considered systematically for heavy nonrigid species for which spin–orbit effects become important.

The double group theory of rigid point groups has been considered by a number of workers. In particular Pyykkö and co-workers[2,4] have provided relativistic double group treatments for D_{3h} and T_h groups while the current author has considered the double group of the icosahedral group.[5] The present author[9] has also considered the development of non-rigid molecular groups as wreath product groups and as generalized wreath products. The permutation and wreath product groups have also been used in a number of chemical applications[10–16] such as enumeration of isomers, weakly bound van der Waals or hydrogen-bonded complexes,[11,14,17–19] polyhedral structures,[20,21] spectroscopy,[11,16,22] and clusters. King[20,21] has used the wreath product groups to represent the symmetries of four-dimensional analogues of polyhedra. Up to now many of these applications were restricted only for nonrigid species without consideration of spin–orbit coupling. Introduction of the spin–orbit term into the Hamiltonian results in an addi-

tional R operation, which leads to a sign change for a rotation by 360°. The new group that has twice the number of elements as the permutation–inversion group is not a direct product of the PI group and the group with R and identity operations. This is due to the fact that some conjugacy classes double by the introduction of R, while the others do not.[3,7] Moreover, the character values for some conjugacy classes of the double group are irrational numbers. Consequently, the generation of the double group character tables of nonrigid molecules is far more challenging than the normal point group tables.

Spin–orbit effects become very significant for molecules containing very heavy atoms,[1–7] and even for systems with second and third row elements spin–orbit effects can be appreciable if one seeks to obtain results of spectroscopic accuracies. Species that have overall half-integral spin states cannot be treated correctly within the normal permutation–inversion groups or point groups. Molecules containing very heavy atoms such as Tl often exhibit weaker Tl–Tl bonding, and thus internal rotation around such bonds would have small and surmountable energy barriers. The barrier to internal rotation around the Tl–Tl bond is only 5–8 kcal/mole in Tl_2H_4.[23] Pyykkö and co-workers[24] have shown that intermolecular dimerization energies for species such as $(H_2E–EH_2)_2$, $(HE–EH)_2$ for E = As to Po are only 8 to 13 kJ/mole suggesting the nonrigid nature of these species. In fact PoH_2 exists as a liquid in its most stable form. Likewise hexamethyl dilead[25] would have a low surmountable barrier to rotation around the Pb–Pb bond due to rather weak bonding between Pb atoms caused by spin–orbit destabilization. The rovibronic levels of such species have to be considered as direct products of rotational, vibrational, and electronic levels as classified in the double group of the nonrigid molecule. The rotational levels are well known to exhibit tunneling splittings due to nonrigid motions. This would in turn be reflected as split rovibronic levels in the double group. Con-

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sequently, the correct treatment of the spectroscopic properties of such molecules exhibiting both spin–orbit coupling and nonrigid motions must be considered in the double group of the nonrigid permutation–inversion groups.

In the current work, we provide a systematic approach to the character tables of the double groups of nonrigid molecules. We use the matrix-cycle-type generators for the construction of the character tables. The method provides both the conjugacy classes and the character values of the double groups of wreath product groups. It is shown that the rovibronic levels and nuclear spin statistical weights of such species can be obtained from the double group character tables. We illustrate our techniques with a number of examples to show that these groups can be expressed as double groups of wreath products of permutation groups S_n.[26] We have provided three complete illustrative examples of double groups, $\{S_2[S_2]\}^2$, $\{S_2[S_3]\}^2$, and $\{S_4[S_2]\}^2$. There could be higher order double wreath product groups for larger weakly bound clusters, and the current technique can be extended to apply to those systems as spectroscopic data become available.

II. WREATH PRODUCT DOUBLE GROUP APPROACH TO NONRIGID MOLECULES

The motivation for the development of double groups of nonrigid molecules containing very heavy atoms stems from the computations of species such as Tl_2H_4.[23] Molecules containing such very heavy metal–metal bonds exhibit surmountable barriers to rotation around the metal–metal bonds due to the weaker dimer bonds of sixth row elements as a consequence of the relativistic inert pair effect. In the case of Tl, Pb, Bi, Po, etc., the bonding between themselves is weakened by large spin–orbit coupling. In fact, the Pb–Pb bond energy is wakened by a factor of 2 by spin–orbit coupling due to the mixing of the antibonding orbitals with bonding orbitals in the spinor representations. Our computed barrier for the internal rotation around the Tl–Tl bond to convert the twisted structure into the planar structure is 7 kcal/mole at the MP2 level and 7.9 kcal/mole at the CCSD(T) level.[23] The spin–orbit coupling weakens the Tl–Tl bond substantially and thus we expect the barrier to reduce by less than 4 kcal/mole in the presence of spin–orbit effects.[23]

The Pb–Pb internal rotation should also have a small barrier. This appears to be the case for the reported structure of hexamtethyl di-lead.[25] Other cases that would involve molecules containing heavy atoms with surmountable barriers are clusters of PoH_2, which are weakly bound. For even molecules containing lighter elements such as Si, As, P, etc., the spin–orbit effects need to be considered if spectroscopic accuracy is desired. In those cases, we need to consider double groups of the nonrigid molecular groups should the molecule exhibit a potential energy surface with surmountable energy barriers. It is thus evident that the gap in the literature for the character theory of double groups of nonrigid molecular frameworks needs to be filled.

The ordinary symmetry group of a nonrigid molecule can be expressed as permutations and inversion operations of the nuclei in the molecular framework.[8] Let G, be a set of permutations (and in general permutation–inversion operations) of the rigid part of a molecule. In some cases G may become isomorphic to the complete set of $n!$ permutations of n objects, in which case, it is denoted by the permutation group S_n. In general the S_n group[26] consists of $n!$ permutations of n objects in a set Ω of chosen nuclei in the molecule to represent the rigid framework. As an example we may consider the Tl_2H_4 molecule. The rigid part of the molecule consists only of the Tl atoms and thus the permutations of the Tl nuclei span a permutation group of two permutations isomorphic to the S_2 permutation group. The internal rotation around the T–Tl bond switches the hydrogen atoms attached to each of the Tl atom. Let the permutations of each pair of hydrogen atoms be the group H which in this case, is also isomorphic to the S_2 group of permutations of the hydrogens on each Tl atom. The overall group of Tl_2H_2 then becomes the wreath product of G with H, denoted by $G[H]$. In this case, the permutation group of the nonrigid Tl_2H_2 molecule is the wreath product group, $S_2[S_2]$ since both G and H are S_2 groups. In general, the wreath product group $G[H]$ consists of permutations

$$\{(g;\pi)| \quad \pi \text{ mapping of } \Omega \text{ into } H, \ g\varepsilon G\}$$

such that the product of two permutations is defined as

$$(g;\pi)(g;\pi')=(gg';\pi\pi'_g),$$

where

$$\pi_g(i)=\pi(g^{-1}i), \ \forall \ i\varepsilon\Omega,$$

$$\pi\pi'(i)=\pi(i)\pi'(i), \ \forall \ i\varepsilon\Omega.$$

A given element of $G[H]$ is represented by $(g;h_1,h_2,\ldots,h_n)$, where $g\varepsilon G$ and $h_i\varepsilon H$. Thus the group $G[H]$ contains $|G||H|^n$ elements where n is the order of Ω. For Tl_2H_4 the order of the nonrigid permutation group is

$$|S_2[S_2]|=2! \ (2!)^2=8.$$

It can be seen that the group $G[H]$ is isomorphic with

$$G[H]=(H_1\times H_2\times\cdots H_n)\wedge G',$$

where $H_1,H_2,\ldots,H_n$ are all isomorphic copies of the same group H, x symbol stands for direct product while symbol represents a semidirect product. The group $H_1\times H_2\times\cdots H_n$ is an invariant subgroup of $G[H]$, which is why the product outside parentheses is a semidirect product.

The character theory of the wreath product groups and the generalized wreath product groups are quite well developed.[10,12,15] The current author[10] has developed generating function algorithms for the character values of the various irreducible representations of wreath product groups. Before we start the double group formalism, the character generating method of wreath products is briefly outlined. The conjugacy classes of wreath product $S_n[H]$ groups are characterized by matrix types obtained from the permutation cycle type or orbit structure of g and the conjugacy class information of H. Let a permutation $g\varepsilon G$ give rise to a_1 cycles of length 1, a_2 cycles of length 2,...,a_n cycles of length n upon its action on the set Ω. The cycle type of G is then denoted by $T_g=(a_1,a_2,\ldots,a_n)$. To illustrate a permutation (12) of the Tl nuclei would have the cycle type (0,1). If we denote the conjugacy classes of H by $C_1,C_2,\ldots,C_s$, and

TABLE I. Conjugacy classes of the $S_2[S_2]$ group.

No.	Matrix type	Permutation	Number of elements
1	$\begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix}$	(1)(2)(3)(4)	1[a]
2	$\begin{bmatrix} 0 & 0 \\ 2 & 0 \end{bmatrix}$	(12)(34)	1
3	$\begin{bmatrix} 1 & 0 \\ 1 & 0 \end{bmatrix}$	(1)(2)(34)	2
4	$\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$	(13)(24)	2
5	$\begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$	(1423)	2[a]

[a]Classes that generate new classes in the double group.

since G is a complete S_n group of $n!$ permutations, we can express the cycle type of an element in the wreath product $G[H]$ by a $s \times n$ matrix, $T(g;\pi)$ also known as the cycle type of $(g;\pi)$. Let a_{ik} of the cycle products of G belong to the conjugacy class C_i, we thus define the cycle type of $(g;\pi)$, which represents the conjugacy class of $S_n[H]$ as

$$T(g;\pi) = a_{ik} (1 \leqslant i \geqslant s, \ 1 \leqslant k \geqslant n).$$

Table I shows the cycle matrix types for the conjugacy classes of the nongroup of Tl_2H_4 or the $S_2[S_2]$ group. We construct these matrices first by getting the two cycle types of the elements in G, $(2,0)$, $(0,1)$ and then using the above algorithm. Let $P(m)$ denote the number of partitions of integer m with the convention that $P(0)=1$. Let n be partitioned into ordered s-tuples, where s is the number of conjugacy classes of H, $(n) = (n_1, n_2, \ldots, n_s)$ such that $\Sigma_i n_i = n$. Then the number of conjugacy classes of $S_n[H]$ is given by

$$\sum_n P(n_1) P(n_2) \cdots P(n_s).$$

As an illustration for Tl_2H_4, the $S_2[S_2]$ group has the ordered partitions $(2,0)$, $(0,2)$, $(1,1)$, since the S_2 group has two conjugacy classes. Substituting the values of $P(2)=2$, $P(1)=1$, and $P(0)=1$ in the above expression we obtain the number of conjugacy classes of $S_2[S_2]$ as $2+2+1=5$. Five conjugacy classes thus obtained are shown in Table I. The number of elements in each conjugacy class of $S_n[H]$ is given by

$$\frac{|S_n[H]|}{\Pi_{i,k} a_{ik}! (k.|H|/|C_i|)^{a_{ik}}}.$$

To illustrate consider the number of elements in the third conjugacy class with the matrix type $\begin{bmatrix} 1 & 0 \\ 1 & 0 \end{bmatrix}$ given by

$$\frac{2!.(2!)^2}{1!(1.2/1)^1 1!(1.2)^1} = 2.$$

All conjugacy classes thus obtained with the number of elements in each class are shown in Table I. It is interesting to note that the $S_2[S_2]$ group is isomorphic with the D_4 point

group of eight elements. The complete PI group is obtained as the direct product of $S_2[S_2]$ and the I group, which has the identity and inversion operations.

The character tables of the $S_n[H]$ groups can be obtained with combinatorial generating functions that employ matrix type polynomials. All possible irreducible representations of the $S_n[H]$ group are constructed using induced representations from a smaller group to a larger group.[9] It is well known that the irreducible representations of the S_n group[26] are represented by the partitions of n, denoted by $[n_1, n_2, \ldots, n_m]$, where $n_1, n_2, \ldots, n_m$ is a partition of the integer n. Thus the irreducible representations of the S_2 group are $[2]$ and $[1^2]$. The irreducible representations of $S_n[H]$ are constructed by first forming the outer tensor (outer direct) products of the irreducible representations of H n times, the finding the inertia factor of each such product, and subsequently inducing the representation from the inertia factor group to the whole group. For example, the unique outer products for the irreducible representations of $S_2 \times S_2$ are given by

$$[2]\#[2], \quad [2]\#[1^2], \quad \text{and} \quad [1^2]\#[1^2].$$

The inertia factor groups (subgroup of G) of the above products are S_2', S_1' (identity group), and S_2', respectively. The overall representations of the $S_n[H]$ groups are obtained by multiplying the unique outer products of irreducible representations of H with the irreducible representations of the factor group G' for each product, and then inducing the whole representation into $G[H]$. That is, the irreducible representations of $G[H]$ are given by

$$F^* = (F_1 \# F_2 \# \cdots F_n) \otimes F' \uparrow G[H],$$

where $F_1 \# F_2 \# \cdots F_n$ is the outer tensor product of the irreducible representations $(F_1, F_2, \ldots, F_n)$ from the group H, # is the outer product, F' is an irreducible representation of the factor group G', $\otimes$ represents an inner product, and the $\uparrow$ stands for an induced representation to the whole group $G[H]$.

The above technique of enumerating the irreducible representations of the $S_2[S_2]$ group can be illustrated for the Tl_2H_4 molecule. The five representations of the $S_2[S_2]$ group are given by

$$A_1 = ([2]\#[2]\#) \otimes [2]', \quad A_2 = ([2]\#[2]) \otimes [1^2]',$$

$$E = ([2]\#[1^2]) \otimes [1]' \uparrow S_2[S_2],$$

$$B_1 = ([1^2]\#[1^2]) \otimes [2]' \uparrow S_2[S_2],$$

$$B_2 = ([1^2]\#[1^2]) \otimes [1^2]'.$$

The whole permutation–inversion group can be obtained as the direct product of $S_2[S_2]$ with the I group since the inversion operation does not generate any new permutation, it is denoted by E^*.

The character tables of the $S_n[H]$ groups can be generated using the generating functions as polynomials of matrix cycle types. Balasubramanian[10] has developed a general algorithm for the characters of the wreath product groups. In

this method suppose P_G^χ is the generalized character cycle index polynomial of the irreducible representation χ of the factor subgroup G' of G, and it is given by

$$P_G^\chi = \frac{1}{|G|} \sum_{g \varepsilon G} \chi(g) s_1^{b_1} s_2^{b_2} \cdots s_n^{bn}.$$

Let $T(M)_i$ be the matrix type of the representation of the inertia factor. The generating function for the irreducible representation F^* of $S_n[H]$ is obtained by the following replacement:

$$T(G[H])^{F^*} = P_G^\chi(s_i \to T(M)_i).$$

That is, in the above expression every s_i is replaced by the corresponding matrix type $T(M)_i$, where all algebraic manipulations are done with the cycle type matrices. We introduce $\oplus$, $\otimes$, $-$ operations for additions, multiplications, and subtractions to contrast that these are not ordinary matrix multiplications, etc. To illustrate, consider the Tl_2H_4 case.

$$\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}^2 = \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix}, \quad \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 1 & 0 \end{bmatrix}.$$

Since this procedure involves several steps, let us consider a few examples. The B_2 irreducible representation given by $([2]\#[2])\otimes[1^2]'$. The generalized character cycle index of $[1^2]'$, the factor group irreducible representation, is given by

$$P_{S_2}^{[1^2]} = \tfrac{1}{6}[S_1^2 - S_2].$$

For the representation[2], the matrix type expressions $T(M)_i$ are given as follows:

$$T(M)_1^{[2]} = \frac{1}{2}\left[\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}\right],$$

$$T(M)_2^{[2]} = \frac{1}{2}\left[\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}\right].$$

Replacing every s_i by $T(M)_i$ in the expression for $P_{S_2}^{[1^3]}$ we obtain

$$GF_{B_2} = \frac{1}{2}\left[\frac{1}{2^2}\left\{\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}\right\}^2 - \frac{1}{2^1}\left\{\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}\right.\right.$$
$$\left.\left. \oplus \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}\right\}\right].$$

Using the matrix manipulations indicated above for the cycle types, we can simplify the above expression into

$$GF_{B_2} = \frac{1}{2}\frac{1}{2^2}\left[\begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} + 2\begin{bmatrix} 1 & 0 \\ 1 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ 2 & 0 \end{bmatrix} - 2\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}\right.$$
$$\left. - 2\begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}\right].$$

The above expression is a generating function for the character values with the order of the group (8) factored out. That is, the string of coefficients $\{1,2,1,-2,-2\}$ in the above expression gives the product of the character value and the number of elements in each conjugacy class. Thus the expression generates the character values $\{1,1,1,-1,-1\}$ when

the number of elements in each conjugacy class is factored out. This corresponds to the character values of the B_2 representation. Let us consider an induced representation, that is, the $E = ([1^2]\#[2])\otimes[1]'\uparrow S_2[S_2]$ irreducible representation of the $S_2[S_2]$ group. The expression for the character generating function is shown below,

$$GF_E = \frac{1}{2}\left[\frac{1}{2}\left\{\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}\right\}\right]$$
$$\times \left[\left\{\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}\right\}\right].$$

The above expression upon simplification yields

$$GF_E = \frac{1}{2}\frac{1}{2^2}\left[2\begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} - 2\begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix}\right].$$

From the above expression we obtain the string $\{2, -2,0,0,0\}$ from which the character for E is generated.

Next we go to the double group of the wreath products. The introduction of the spin–orbit coupling into the Hamiltonian results in a symmetry analogous to the symmetry of a "Mobius surface," and thus rotation by 360° results in a sign change. This is usually characterized by an operation R that is added to the PI group. This doubles the number of elements in the double group. However, the result of including the R operation into the PI group does not result in a direct product since some of the conjugacy classes double in their order, while other conjugacy classes result in new conjugacy classes upon multiplication by R. Consequently the first step to constructing the character table of the double groups of wreath products is to construct the conjugacy class structures after the introduction of the R operation.

If the double operation R (rotation by 360°) when multiplied by the permutation operation generates an equivalent operation to the permutation then both P and RP belong to the same conjugacy class. This can be determined by visualizing the permutation operation as a proper or improper rotation. For example, routinely pure C_2 types of operations are two-sided axes in that the C_2 and C_2R become equivalent since C_2 often changes its direction by application of another operation. Thus the C_2 operation and C_2R belong to the same conjugacy class. On the other hand, all other pure higher-order C_n rotational axes lead to new conjugacy classes as C_n and C_nR are not equivalent. This is because C_n and $C_n^{(n-1)}$ do not belong to the same conjugacy class in the double group as

$$C_n C_n^{(n-1)} = R.$$

Thus for $n > 2$, C_n and $C_n^{(n-1)}$ belong to different conjugacy classes in the double group. We simply identify this as $C_n R$ as a new conjugacy class. Once all proper rotations have thus been completed we would be left with only composite operations or improper rotations. Once these are expressed as products of the corresponding proper rotation and planes (inversions), we can identify if the operation will generate a new conjugacy class upon multiplication with R or not.

The above technique of generating conjugacy classes of the double groups is demonstrated for the wreath product

TABLE II. Character table of $\{S_2[S_2] \times I]^2$.

| | 1^4 | 2^2 | $1^2 2$ | 2^2 | 4 | 1^{4*} | 2^{2*} | $1^2 2^*$ | 2^{2*} | 4^* | $R1^4$ | $R4$ | $R1^{4*}$ | $R4^*$ |
	1	1[2]	2[4]	2[4]	2	1	1[2]	2[4]	2[4]	2	1	2	1	2
A_1^+	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2^+	1	1	-1	-1	1	1	1	-1	-1	1	1	1	1	1
B_1^+	1	1	-1	1	-1	1	1	-1	1	-1	1	-1	1	-1
B_2^+	1	1	1	-1	-1	1	1	1	-1	-1	1	-1	1	-1
A_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1
A_2^-	1	1	-1	-1	1	-1	-1	1	1	-1	-1	-1	-1	-1
B_1^-	1	1	-1	1	-1	-1	-1	1	-1	1	-1	1	-1	1
B_2^-	1	1	1	-1	-1	-1	-1	-1	1	1	-1	1	-1	1
E^+	2	-2	0	0	0	2	-2	0	0	0	2	0	2	0
E^-	2	-2	0	0	0	-2	2	0	0	0	2	0	-2	0
$E_{1/2}^+$	2	0	0	0	$\sqrt2$	2	0	0	0	$\sqrt2$	-2	$-\sqrt2$	-2	$-\sqrt2$
$E_{3/2}^+$	2	0	0	0	$-\sqrt2$	2	0	0	0	$-\sqrt2$	-2	$\sqrt2$	-2	$\sqrt2$
$E_{1/2}^-$	2	0	0	0	$\sqrt2$	-2	0	0	0	$-\sqrt2$	-2	$-\sqrt2$	2	$\sqrt2$
$E_{3/2}^-$	2	0	0	0	$-\sqrt2$	-2	0	0	0	$\sqrt2$	-2	$\sqrt2$	2	$-\sqrt2$

$S_2[S_2]$ in Table I. As can be seen there, the identity operation will always generate a new class denoted by R. The classes 2, 3, and 4 correspond to twofold rotations or composite twofold operations and thus do not generate a new class. Only the class 5 which has a permutational orbit structure of length 4 (pure) is not a two-sided operation and thus $(1324)R$ generates a new conjugacy class. The conjugacy classes for which the operation R produces equivalent operations double in number while those that do not produce equivalent operations produce new classes with equal number of elements as the original class. Thus for the $S_2[S_2]$ group the orders of conjugacy classes 2, 3, and 4 double while the conjugacy classes 1 and 5 generate two new classes with the same number of elements as the original class. Once this has been identified, we can find the character values of the new irreducible representations of the double groups.

The character values of all even representations (single valued) in the double group are identical to the values of the corresponding conjugacy classes before the multiplication of the R operation. New irreducible representations that equal the number of new conjugacy classes are generated and they correspond to double-valued or half-integral irreducible representations. These new representations have to be even dimensional. This combined with the fact that the sum of the squares of the dimensions of these irreducible representations must add up to the order of the single group will provide us information on the dimensions of the new double valued representations. For the wreath product $S_2[S_2]$, the case of Tl_2H_4, there should be two two-dimensional double-valued representations since $2^2 + 2^2 = 8$, the order of $S_2[S_2]$. The character values of these representations under the new conjugacy classes should be opposite in sign to the character values of the corresponding classes prior to multiplying by R. Also character values of all classes that double must be zero since we have

$$\chi(pR) = -\chi(P),$$

and since p and pR belong to the same class we have

$$\chi(pR) = \chi(P).$$

Thus combining the above two equations we get the result that the character value must be zero if p and pR belong to the same conjugacy class.

The character values of those classes that do not double can be obtained by identifying the rotational degree of the permutation operation and then by using the formula

$$\chi^{(j)}(C_n) = \frac{\sin(j+\frac{1}{2})(2\pi/n)}{\sin(\pi/n)}.$$

The first and the last irreducible representations, which are typically two dimensional, are obtained using the above formula. While the remaining ones are linear combination with the others to yield $D^{(j)}$. This combined with the great orthogonality theorem uniquely determine the character values. Again the character values of the operations pR should have opposite signs compared to the character values of p.

As a first illustration for the double group of wreath product, consider the $\{S_2[S_2]\}^2$ group of Tl_2H_4. Since only classes 1 and 5 do not double only two new classes are generated in the double group, which yield two irreducible representations for the double group $\{S_2[S_2]\}^2$. These two irreducible representations have to be two-dimensional to comply with the stipulation that sum of the squares of the dimensions must be 8. The two irreducible representations can be thus denoted as $E_{1/2}$ and $E_{3/2}$. Both of these representations should have nonzero character values only under the classes 1, 5 and the new double group classes. The character values under the identity operation have already been determined as 2 for both of those. The character values under class 5 are determined using the formula above for $\chi^{(j)}$.

Once the character values of the double-valued representations have been determined, we can find the character table of the whole permutation–inversion double group. For the example of Tl_2H_4, since the double group of the PI group is a direct product of $\{S_2[S_2]\}^2$ with the inversion group, the full character table is constructed as a direct product of the two tables. The entire character table of $\{S_2[S_2] \times I\}^2$ is shown in Table II. The $+$ and $-$ super labels correspond to the parities of the representations relative to the inversion operation. The table can also be found in Ref. 27.

TABLE III. Conjugacy classes of the $S_2[S_3]$ group.

No.	Matrix type	Permutation	Number of elements	No.	Matrix type	Permutation	Number of elements
1[a]	$\begin{bmatrix} 2 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}$	1^6	1	2	$\begin{bmatrix} 1 & 0 \\ 1 & 0 \\ 0 & 0 \end{bmatrix}$	$1^4 2$	6
3[a]	$\begin{bmatrix} 1 & 0 \\ 0 & 0 \\ 1 & 0 \end{bmatrix}$	$1^3 3$	4	4	$\begin{bmatrix} 0 & 0 \\ 2 & 0 \\ 0 & 0 \end{bmatrix}$	$1^2 2^2$	9
5[a]	$\begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 2 & 0 \end{bmatrix}$	3^2	4	6[a]	$\begin{bmatrix} 0 & 0 \\ 1 & 0 \\ 1 & 0 \end{bmatrix}$	123	12
7	$\begin{bmatrix} 0 & 1 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}$	2^3	6	8[a]	$\begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 1 \end{bmatrix}$	6	12
9[a]	$\begin{bmatrix} 0 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix}$	24	18				

[a]Classes that generate new classes in the double group.

The character tables of the double groups of nonrigid molecules grow quickly and exponentially. Consider analogues of the ethane molecule such as hexamethyl dilead, digermane (Ge_2H_6), Sn_2H_6, etc. For example, Pyykkö[25] has considered the nuclear spin–spin coupling constants of $Pb_2(CH_3)_6$, which exhibits ethanelike structure. The ground state of digermane is known to be D_{3d} for its rigid equilibrium structure. The internal rotation around the Pb–Pb bond would lead to a nonrigid group and nonrigid NMR group. Thus we consider the double group of the wreath product $S_2[S_3]$, which we denote by $\{S_2[S_3]\}^2$, where S_3 is the permutation group that contains 3! permutation of three objects. The conjugacy classes of the $S_2[S_3]$ group are shown in Table III with those classes that generate new classes in the double group upon multiplication by R. The classes are characterized by 3×2 matrices since there are three conjugacy classes in the S_3 group and two Pb nuclei. For each class we have also provided the overall permutation of the carbon nuclei for $Pb_2(CH_3)_6$. Thus the classes 1, 3, 5, 6, 8, and 9 generate new classes upon multiplication by R on the basis of their cycle structures and equivalent rotational operations. The remaining classes, which are two-sided double, and thus the character values for these classes in the double-values representations are zero. Table III also shows the order of each conjugacy class as obtained by the formulas that we discussed before. There are nine conjugacy classes in $S_2[S_3]$ and 15 conjugacy classes in the double group, $\{S_2[S_3]\}^2$.

Since there are six new conjugacy classes in the $\{S_2[S_3]\}^2$ double group, there should be six new double-valued representations in the double group. The dimensions of the even-dimensional representations should satisfy, $l_1^2 + l_2^2 + \cdots + l_6^2 = 72$, and thus only possible solution with the above constraints is two two-dimensional and four-dimensional irreducible representations should be present in the $\{S_2[S_3]\}^2$ double group. Since the character values of the

classes that double must be zero, we need to determine the character values of only classes 1,3,5,6,8, and 9. The first class has the character value equal to the dimension of the representation. The character values of the sixth, eighth, and ninth representations are irrational and given by the character formulas. The characters of the class 3 and 5 are also obtained by identifying them with the appropriate rotational operations. In addition we have developed a computer code to ensure compliance of the great orthogonality theorem in the double group. The character values of the new conjugacy classes are the same as those of the corresponding classes without the R operation multiplied by -1. The character table thus constructed for the $\{S_2[S_3]\}^2$ double group, which contains 144 operations, is shown in Table IV. If the inversion operation needs to be included the whole double group of the PI group is a direct product in this case, and would contain 288 operations. Note that in Table IV, the double-valued irreducible representations are denoted by primes above the labels. Generation of the character table of the $\{S_2[S_3]\}^2$ double group turned out to be tedious as we had to ensure of the places that have irrational characters and also compliance with the great orthogonality theorem.

As the next case we consider the $\{S_4[S_2]\}^2$ double group which has $2.4!.2^4 = 768$ operations. The $S_4[S_2]$ wreath product group occurs in a number of other chemistry and physics applications, as it is the octahedral group in the fourth dimension[20,21] and also the orthogonal group in the fourth dimension. In the context of molecules containing very heavy atoms, Klinkhammer and Pyykkö[24] and co-workers have shown that the dimerization energies for molecules such as $(BiH_2)_2$, $(H–Po–PoH)_2$, etc., are quite small in the range of 8 to 13 kJ/mole. This means a cluster such as $(TeH_2)_4$ or $(PoH_2)_4$ would be quite nonrigid due to the low intermolecular binding energy. This is consistent with the observed liquid state of PoH_2. The symmetry group of any

TABLE IV. Character table of $\{S_2[S_3]\}^2$ double group.

Conj.	1^6	1^42	1^33	1^22^2	3^2	123	2^3	6	24	$R1^6$	$R1^33$	$R3^2$	$R123$	$R6$	$R24$
Order	1	6[12]	4	9[18]	4	12	6[12]	12	18	1	4	4	12	12	18
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	1	-1	-1	-1	1	1	1	1	-1	-1
A_3	1	-1	1	1	1	-1	-1	-1	1	1	1	1	-1	-1	1
A_4	1	-1	1	1	1	-1	1	1	-1	1	1	1	-1	1	-1
E	2	0	2	-2	2	0	0	0	0	2	2	2	0	0	0
G_1	4	0	-2	0	1	0	2	-1	0	4	-2	2	0	-1	0
G_2	4	0	-2	0	1	0	-2	1	0	4	-2	1	0	1	0
G_3	4	2	1	0	-2	-1	0	0	0	4	1	1	-1	0	0
G_4	4	-2	1	0	-2	1	0	0	0	4	1	-2	1	0	0
E'_1	2	0	-2	0	2	0	0	$\sqrt{3}$	0	-2	0	2	0	$-\sqrt{3}$	0
E'_2	2	0	-2	0	2	0	0	$-\sqrt{3}$	0	-2	0	2	0	$\sqrt{3}$	0
G'_1	4	0	2	0	1	0	0	0	$\sqrt{2}$	-4	-2	-1	0	0	$-\sqrt{2}$
G'_2	4	0	2	0	1	0	0	0	$-\sqrt{2}$	-4	-2	-1	0	0	$\sqrt{2}$
G'_3	4	0	-1	0	-2	$\sqrt{3}$	0	0	0	-4	1	2	$-\sqrt{3}$	0	0
G'_4	4	0	-1	0	-2	$-\sqrt{3}$	0	0	0	-4	1	2	$\sqrt{3}$	0	0

such nonrigid molecule would be characterized by the $S_4[S_2]$ group in the absence of spin–orbit coupling. Once spin–orbit coupling is introduced into the Hamiltonian, the relativistic spinor representation requires the $\{S_4[S_2]\}^2$ double group for the treatment of rovibronic levels of such clusters which typically undergo tunneling in the higher group. With these species in mind, we have obtained the character table of the $\{S_4[S_2]\}^2$ double group.

Table V shows the conjugacy classes of the $S_4[S_2]$ group in terms of matrix cycle types. Since there are only two conjugacy classes in the S_2 group and S_4 acts on four objects, the cycle type matrices are 2×4, as seen from Table

V. The ordered partitions of 4 into 2 parts are (4,0), (0,4), (3,1), (1,3), and (2,2). From these the number of conjugacy classes of $S_4[S_2]$ is generated as $P(4)+P(4)+P(3)P(1)+P(1)P(3)+P(2)P(2)$, where $P(m)$ is the number of partitions of the integer m. Since $P(4)=5$, $P(3)=3$, and $P(2)=2$, we get, $5+5+3+3+2\times2=20$. For each of the 20 conjugacy classes the matrix for the cycle types are constructed and are shown in Table V. From each of the matrix types, the number of elements in the conjugacy class is directly obtained using the formulas discussed before. The results are shown in Table V.

The conjugacy classes of the $\{S_4[S_2]\}^2$ double group are

TABLE V. Conjugacy classes of the $S_4[S_2]$ group.

No.	Matrix type	Permutation	Number of elements	No.	Matrix type	Permutation	Number of elements
1ª	$\begin{bmatrix} 4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	1^8	1	2	$\begin{bmatrix} 3 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$	1^62	4
3	$\begin{bmatrix} 2 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 \end{bmatrix}$	1^42^2	6	4	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 \end{bmatrix}$	1^22^3	4
5	$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 \end{bmatrix}$	2^4	1	6	$\begin{bmatrix} 2 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	1^42^2	12
7	$\begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$	1^22^3	24	8	$\begin{bmatrix} 0 & 1 & 0 & 0 \\ 2 & 0 & 0 & 0 \end{bmatrix}$	2^4	12
9ª	$\begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$	1^44	12	10	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{bmatrix}$	1^224	24
11	$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 2 & 1 & 0 & 0 \end{bmatrix}$	2^24	12	12ª	$\begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	1^23^2	32
13	$\begin{bmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$	23^2	32	14	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	1^26	32
15	$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 \end{bmatrix}$	26	32	16	$\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	4^2	48
17ª	$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	8	48	18	$\begin{bmatrix} 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	2^4	12
19	$\begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$	2^24	24	20ª	$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \end{bmatrix}$	4^2	12

ªClasses that generate new classes in the double group.

obtained by identifying those classes that would generate new conjugacy classes when multiplied by the R operation. These are identified in Table V as classes 1, 9, 12, 17, and 20. This was accomplished by identifying the proper/ improper rotational operations of the permutations of protons of $(PoH_2)_4$. These permutational orbit structures are shown in Table V for eight protons. The classes 1, 9, 12, 17, and 20 have structures 1^8, 1^44, 1^23^2, 8, and 4^2, and also they correspond to proper or improper rotations of the corresponding orbit foldness. It is interesting to observe that these five classes can be represented by Young Tableau of the five partitions of the integer 4. Thus these conjugacy classes generate new classes upon multiplication by R. All other conjugacy classes of the $\{S_4[S_2]\}^2$ double group double and thus their character values for the double-valued irreducible representations are zero.

The character table of the $\{S_4[S_2]\}^2$ double group is constructed first by obtaining the character table of $S_4[S_2]$ and then finding the double-valued irreducible representations in the double group. The irreducible representations of the $S_4[S_2]$ group, their labels and dimensions are shown in Table VI. These irreducible representations were obtained by constructing unique outer tensor products of four copies of irreducible representations of S_2, then finding the inertia factor groups, and finally multiplying the inertia factor group representations as inner products. The final representation is induced over the whole group.

The actual character values of the single-valued irreducible representations are constructed first by using the combinatorial matrix type generators. We shall consider this for two illustrative examples. First let us consider the E_2 irreducible representation given by $([1^2]\#[1^2]\#[1^2]\#[1^2]) \otimes [2^2]'$. The GCCI of the $[2^2]'$ representation and the various matrix type expressions are

$$P_{S_4}^{[2^2]} = \tfrac{1}{24}[2s_1^4 - 8s_1 s_3 + 6s_2^2],$$

$$T(M)_1 = \frac{1}{2}\left\{\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}\right\},$$

$$T(M)_2 = \frac{1}{2}\left\{\begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}\right\},$$

$$T(M)_3 = \frac{1}{2}\left\{\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}\right\},$$

$$T(M)_4 = \frac{1}{2}\left\{\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}\right\}.$$

Next we replace every s_k in $P_{S_4}^{[2^2]}$ by $T(M)_k$, we obtain

$$\frac{1}{4!2^4}\left\{2\left[\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}\right]^4 - 32\left[\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}\right] \times \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}\right.$$

$$\left. + 24\left[\begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}\right]^2\right\}.$$

The above expression upon simplification of the various terms yields

$$P^{E_2} = \frac{1}{4!2^4}\left\{2\begin{bmatrix} 4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} - 8\begin{bmatrix} 3 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} + 12\begin{bmatrix} 2 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 \end{bmatrix} - 8\begin{bmatrix} 1 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 \end{bmatrix} + 2\begin{bmatrix} 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 \end{bmatrix}\right.$$

$$-32\begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + 32\begin{bmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} + 32\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} - 32\begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 \end{bmatrix} + 24\begin{bmatrix} 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\left. -48\begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} + 24\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \end{bmatrix}\right\}.$$

The string of coefficients $\{2, -8, 12, -8, 2, 0, 0, 0, 0, 0, 0, -32, 32, 32, -32, 0, 0, 24, -48, 24\}$ in the above expression in the order of 20 conjugacy classes in Table V yields the character values times the number of elements in the respective conjugacy classes. Once the orders of the conjugacy classes are factored out we obtain the character string values $\{2, -2, 2, -2, 2, 0, 0, 0, 0, 0, 0, -1, 1, 1, -1, 0, 0, 2, -2, 2\}$ for all 20 conjugacy classes of the wreath product $S_4[S_2]$.

As another example consider the K_2 irreducible representation (eight-dimensional). Since it is given by $([1^2]\#[1^2]\#[1^2]) \otimes [21]'\#([2]\otimes[1])'$ the character generator is given by

$$\frac{1}{4!2^4}\left\{8\left[\begin{bmatrix}1&0&0&0\\0&0&0&0\end{bmatrix}-\begin{bmatrix}0&0&0&0\\1&0&0&0\end{bmatrix}\right]^3-32\begin{bmatrix}0&0&1&0\\0&0&0&0\end{bmatrix}-\begin{bmatrix}0&0&0&0\\0&0&1&0\end{bmatrix}\right\}\left\{\begin{bmatrix}1&0&0&0\\0&0&0&0\end{bmatrix}+\begin{bmatrix}0&0&0&0\\1&0&0&0\end{bmatrix}\right\}.$$

The above expression upon simplification yields

$$P^{K_2}=\frac{1}{4!2^4}\left\{8\begin{bmatrix}4&0&0&0\\0&0&0&0\end{bmatrix}-16\begin{bmatrix}3&0&0&0\\1&0&0&0\end{bmatrix}+16\begin{bmatrix}1&0&0&0\\3&0&0&0\end{bmatrix}-8\begin{bmatrix}0&0&0&0\\4&0&0&0\end{bmatrix}-32\begin{bmatrix}1&0&1&0\\0&0&0&0\end{bmatrix}\right.$$
$$\left.-32\begin{bmatrix}0&0&1&0\\1&0&0&0\end{bmatrix}+32\begin{bmatrix}1&0&0&0\\0&0&1&0\end{bmatrix}+32\begin{bmatrix}0&0&0&0\\1&0&1&0\end{bmatrix}\right\}.$$

From the above expression we infer the coefficient string $\{8,-16,0,16,-8,0,0,0,0,0,-32,-32,32,32,0,0,0,0,0,0\}$ which yields the character value string of $\{8,-4,0,4,-8,0,0,0,0,0,0,-1,-1,1,1,0,0,0,0,0,0\}$.

The double valued irreducible representations are enumerated using the fact that there must be exactly five double-valued irreducible representations since five new conjugacy classes are created. The dimensions of these five irreducible representations must satisfy

$$\ell_1^2+\ell_2^2+\ell_3^2+\ell_4^2+\ell_5^2=384$$

and the only possible solution is $\ell_1=4$, $\ell_2=4$, $\ell_3=8$, $\ell_4=12$, $\ell_5=12$ in the ascending order of dimensionalities. This determines that the dimensions of the doubled-valued irreducible representations of the $\{S_4[S_2]\}^2$ double group should be 4, 4, 8, 12, and 12. We denoted these irreducible representations by G_1', G_2', K', O_1', O_2', where the prime represents that it is a two-valued representation.

The character values of the new double-valued representations are determined by finding the character values of five classes 1, 9, 12, 17, and 20 using the double-valued character formulas. All other classes should have zero character values due to the fact these conjugacy classes double. The character values of classes 9 and 17 are irrational numbers as expected for these higher order rotational operations. Once these character values are generated the remaining character values, which are integral, correspond to classes 12 and 20. Of course the character value of class 1 is the dimension of the irreducible representation of the two-valued representation, which we have already determined. The character values of the five new conjugacy classes in the double group are determined as the character values of the corresponding classes without multiplying by R and then multiplying the value by -1.

Table VII shows the character table of the $\{S_4[S_2]\}^2$ double group as obtained using the repeated application of the above procedure for all 25 irreducible representations. The two-valued representations have primes above the labels to contrast them from the singled-valued irreducible representations. The orthogonality of every row of the character table with every other row was rigorously checked by a computer code that we developed for orthogonality check. It is interesting to note that unlike other lower order groups the

smallest double-valued irreducible representation is four dimensional in the $\{S_4[S_2]\}^2$ double group.

III. NUCLEAR SPIN STATISTICS, SPINOR REPRESENTATIONS, TUNNELING SPLITTINGS OF ROTATIONAL/ROVIBRONIC LEVELS AND OF NONRIGID MOLECULES WITH VERY HEAVY ATOMS

The character tables of the nonrigid groups thus constructed can be used in number of applications such as nuclear spin statistics, correlation of rovibronic levels including half-integral quantum numbers, and in spinor representations. As a first case let us illustrate the use of the table in finding the nuclear spin multiplets. Consider $(PoH_2)_4$ and

TABLE VI. Irreducible representations of the $S_4[S_2]$ group.

Label	Irreducible representation	Dimension
A_1	$([2]\#[2]\#[2]\#[2])\otimes[4]'$	1
T_1	$([2]\#[2]\#[2]\#[2])\otimes[31]'$	3
E_1	$([2]\#[2]\#[2]\#[2])\otimes[2^2]'$	2
T_2	$([2]\#[2]\#[2]\#[2])\otimes[21^2]'$	3
A_2	$([2]\#[2]\#[2]\#[2])\otimes[1^4]'$	1
G_1	$([2]\#[2]\#[2])\otimes[3]'$ $\#([1^2]\otimes[1]'$	4
K_1	$([2]\#[2]\#[2])\otimes[21]'$ $\#([1^2]\otimes[1]'$	8
G_2	$([2]\#[2]\#[2])\otimes[1^3]'$ $\#([1^2]\otimes[1]'$	4
I_1	$([2]\#[2])\otimes[2]'$ $\#([1^2]\#([1^2]\otimes[2]'$	6
I_2	$([2]\#[2])\otimes[2]'$ $\#([1^2]\#([1^2]\otimes[1^2]'$	6
I_3	$([2]\#[2])\otimes[1^2]'$ $\#([1^2]\#([1^2]\otimes[2]'$	6
I_4	$([2]\#[2])\otimes[1^2]'$ $\#([1^2]\#([1^2]\otimes[1^2]'$	6
G_3	$([1^2]\#[1^2]\#[1^2])\otimes[3]'$ $\#([2]\otimes[1]'$	4
K_2	$([1^2]\#[1^2]\#[1^2])\otimes[21]'$ $\#([2]\otimes[1]'$	8
G_4	$([1^2]\#[1^2]\#[1^2])\otimes[1^3]'$ $\#([2]\otimes[1]'$	4
A_3	$([1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[4]'$	1
T_3	$([1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[31]'$	3
E_2	$([1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[2^2]'$	2
T_4	$([1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[21^2]'$	3
A_4	$([1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[1^4]'$	1

TABLE VII. Character table of the $\{S_4[S_2]\}^2$ double group with 25 irreducible reps.

	1^8	$1^6 2$	$1^4 2^2$	$1^2 2^3$	2^4	$1^4 2^2$	$1^2 2^2 2$	2^4	$1^4 4$	$1^2 2 4$	$2^2 4$	$1^2 3^2$	$2 3^2$	$1^2 6$	$2 6$	4^2	8	2^4	$2^2 4$	4^2	$R1^8$	$R1^4 4$	$R4^2$	$R1^2 3^2$	$R8$
		4	6	4	1	12	24	12		24	12		32	32	32	48		12	24						
	1	[8]	[12]	[8]	[2]	[24]	[48]	[24]	12	[48]	[24]	32	[64]	[64]	[64]	[96]	48	[24]	[48]	12	1	12	12	32	48
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	1	-1	-1	1	1	1	1	-1	1	1	-1
A_3	1	-1	1	-1	1	1	-1	1	-1	1	-1	1	-1	-1	1	1	-1	1	-1	1	1	-1	1	1	-1
A_4	1	-1	1	-1	1	-1	1	-1	1	-1	1	1	-1	-1	1	-1	1	1	-1	1	1	1	1	1	1
E_1	2	2	2	2	2	0	0	0	0	0	0	-1	-1	-1	-1	0	0	2	2	2	2	0	2	-1	0
E_2	2	-2	2	-2	2	0	0	0	0	0	0	-1	1	1	-1	0	0	2	-2	2	2	0	2	-1	0
T_1	3	3	3	3	3	1	1	1	1	1	1	0	0	0	0	-1	-1	-1	-1	-1	3	1	-1	0	-1
T_2	3	3	3	3	3	-1	-1	-1	-1	-1	-1	0	0	0	0	1	1	-1	-1	-1	3	-1	-1	0	1
T_3	3	-3	3	-3	3	1	-1	1	-1	1	-1	0	0	0	0	-1	1	-1	1	-1	3	-1	-1	0	1
T_4	3	-3	3	-3	3	-1	1	-1	1	-1	1	0	0	0	0	1	-1	-1	1	-1	3	1	-1	0	-1
G_1	4	2	0	-2	-4	2	0	-2	2	0	-2	1	-1	1	-1	0	0	0	0	0	4	2	0	1	0
G_2	4	2	0	-2	-4	-2	0	2	-2	0	2	1	-1	1	-1	0	0	0	0	0	4	-2	0	1	0
G_3	4	-2	0	2	-4	2	0	-2	-2	0	2	1	1	-1	-1	0	0	0	0	0	4	-2	0	1	0
G_4	4	-2	0	2	-4	-2	0	2	2	0	-2	1	1	-1	-1	0	0	0	0	0	4	2	0	1	0
I_1	6	0	-2	0	6	2	0	2	0	-2	0	0	0	0	0	0	0	2	0	-2	6	0	-2	0	0
I_2	6	0	-2	0	6	0	-2	0	2	0	2	0	0	0	0	0	0	-2	0	2	6	0	2	0	0
I_3	6	0	-2	0	6	0	2	0	-2	0	-2	0	0	0	0	0	0	-2	0	2	6	0	2	0	0
I_4	6	0	-2	0	6	-2	0	-2	0	2	0	0	0	0	0	0	0	2	0	-2	6	0	-2	0	0
K_1	8	4	0	-4	-8	0	0	0	0	0	0	-1	1	-1	1	0	0	0	0	0	8	0	0	-1	0
K_2	8	-4	0	4	-8	0	0	0	0	0	0	-1	-1	1	1	0	0	0	0	0	8	0	0	1	0
G_1'	4	0	0	0	0	0	0	0	$-2\sqrt{2}$	0	0	2	0	0	0	0	$\sqrt{2}$	0	0	2	-4	$2\sqrt{2}$	-2	-2	$-\sqrt{2}$
G_2'	4	0	0	0	0	0	0	0	$2\sqrt{2}$	0	0	2	0	0	0	0	$-\sqrt{2}$	0	0	2	-4	$-2\sqrt{2}$	-2	-2	$\sqrt{2}$
K'	8	0	0	0	0	0	0	0	0	0	0	-2	0	0	0	0	0	0	0	4	-8	0	-4	2	0
O_1'	12	0	0	0	0	0	0	0	$-2\sqrt{2}$	0	0	0	0	0	0	0	$-\sqrt{2}$	0	0	-2	-12	$2\sqrt{2}$	2	0	$\sqrt{2}$
O_2'	12	0	0	0	0	0	0	0	$2\sqrt{2}$	0	0	0	0	0	0	0	$\sqrt{2}$	0	0	-2	-12	$-2\sqrt{2}$	2	0	$-\sqrt{2}$

$(PoD_2)_4$ as examples. Let us represent three m_s functions of the D nucleus by λ, μ, and ν, where these labels represent $m_s = -1$, 0, and +1, respectively. For example, from the character Table VII, we can obtain the GGCI of the representation K_1 as

$$P_G^{K_1} = \tfrac{1}{384}[8s_1^8 + 16s_1^6 s_2 - 16s_1^2 s_2^3 - 8s_2^4 - 32s_1^2 s_3^2 + 32s_2 s_3^2 - 32s_1^2 s_6 + 32s_2 s_6].$$

The ^{3}D nuclear spin generating function is obtained by replacing every s_k in the above expression by $(\lambda^k + \mu^k + \nu^k)$. Thus we obtain

$$P^{K_1} = \tfrac{1}{384}[8(\lambda+\mu+\nu)^8 + 16(\lambda+\mu+\nu)^6(\lambda^2+\mu^2+\nu^2) - 16(\lambda+\mu+\nu)^2(\lambda^2+\mu^2+\nu^2)^3 - 8(\lambda^2+\mu^2+\nu^2)^4$$
$$- 32(\lambda+\mu+\nu)^2(\lambda^3+\mu^3+\nu^3)^2 + 32(\lambda^2+\mu^2+\nu^2)(\lambda^3+\mu^3+\nu^3)^2 - 32(\lambda+\mu+\nu)^2(\lambda^6+\mu^6+\nu^6)$$
$$+ 32(\lambda^2+\mu^2+\nu^2)(\lambda^6+\mu^6+\nu^6)].$$

The coefficient of a typical term $\lambda^i \mu^j \nu^k$ yields the number of ^{3}D nuclear spin functions containing i spin functions with $m_s = -1$, j functions with $m_{s=0}$ and k spin functions with $m_s = +1$ that transform as the K_1 irreducible representation. Once these generating functions are constructed for each of the irreducible representations of the group, then the irreducible representations for the spin functions can be sorted according to their total M_F nuclear spin quantum numbers. The results would be all the spin multiplets and the number of times each spin multiplet would occur in a given irreducible representation. The results thus obtained are shown in Table VIII for both ^{3}D and ^{2}H species.

As seen from Table VIII, the proton species are much fewer compared to the deuterium spin species. By multiplying the spin multiplicity by the frequency of each multiplet and adding the numbers we get the frequencies of the various irreducible representations in the group. Thus

$$\Gamma_H = 15A_1 + A_3 + 6E_1 + 15T_1 + 3T_2 + 10G_1 + G_2 + 3G_3 + 6I_1 + 3I_3 + 8K_1,$$

$$\Gamma_D = 126A_1 + 15A_2 + 15A_3 + 105E_1 + 6E_2 + 210T_1 + 105T_2 + 15T_3 + 3T_4 + 168G_1 + 60G_2 + 60G_3 + 6G_4 + 126I_1 + 63I_2 + 90I_3 + 45I_4 + 210K_1 + 48K_2.$$

In the case of protons, which are fermions, the overall wave function must be antisymmetric and thus the total wave function must transform as A_3 and thus the nuclear spin statistical

TABLE VIII. Nonrigid ^{2}H and ^{3}D nuclear spin species of nonrigid $(PoH_2)_4$ and $(PoD_2)_4$.

Symmetry	^{3}D species	^{2}Proton species
A_1	$^1A_1(4)$, $^5A_1(5)$, $^7A_1(1)$, $^9A_1(4)$, $^{11}A_1(1)$, $^{13}A_1(2)$ $^{17}A_1(1)$	$^1A_1(1)$, $^5A_1(1)$, $^9A_1(1)$
A_2	$^3A_2(1)$ $^5A_2(1)$ $^7A_2(1)$	None
A_3	$^1A_3(1)$ $^5A_3(1)$ $^9A_3(1)$	$^1A_3(1)$
A_4	None	None
E_1	$^1E_1(3)$ $^3E_1(1)$ $^5E_1(5)$ $^7E_1(2)$ $^9E_1(4)$ $^{11}E_1(1)$ $^{13}E_1(1)$	$^1E_1(1)$, $^5E_1(1)$
E_2	$^1E_2(1)$ $^5E_2(1)$	None
T_1	$^1T_1(2)$, $^3T_1(4)$ $^5T_1(7)$, $^7T_1(6)$ $^9T_1(5)$, $^{11}T_1(3)$ $^{13}T_1(2)$, $^{15}T_1(1)$	$^3T_1(1)$, $^5T_1(1)$ $^7T_1(1)$
T_2	$^3T_2(5)$, $^5T_2(3)$ $^7T_2(5)$, $^9T_2(2)$ $^{11}T_2(2)$	$^3T_2(1)$
T_3	$^3T_3(1)$, $^5T_2(1)$,$^7T_2(1)$	None
T_4	$^3T_4(1)$	None
G_1	$^3G_1(6)$, $^5G_1(4)$ $^7G_1(6)$, $^9G_1(3)$ $^{11}G_1(3)$, $^{13}G_1(1)$ $^{15}G_1(1)$	$^3G_1(1)$, $^7G_1(1)$
G_2	$^1G_2(2)$, $^3G_2(2)$, $^5G_2(4)$, $^7G_2(2)$, $^9G_2(2)$	$^1G_2(1)$
G_3	$^3G_3(3)$, $^5G_3(2)$ $^7G_3(3)$, $^9G_3(1)$, $^{11}G_3(1)$	$^3G_3(1)$
G_4	$^1G_4(1)$, $^5G_4(1)$	None
I_1	$^1I_1(4)$, $^3I_1(2)$, $^5I_1(7)$, $^7I_1(3)$, $^9I_1(4)$, $^{11}I_1(1)$ $^{13}I_1(1)$,$^{15}I_1(1)$	$^1I_1(1)$, $^5I_1(1)$
I_2	$^3I_2(4)$, $^5I_2(2)$, $^7I_2(3)$, $^9I_2(1)$, $^{11}I_2(1)$	None
I_3	$^1I_3(1)$, $^3I_3(4)$, $^5I_2(4)$ $^7I_3(4)$, $^9I_3(2)$, $^{11}I_3(1)$	$^3I_3$
I_4	$^1I_4(1)$, $^3I_4(2)$, $^5I_4(3)$ $^7I_5(2)$, $^9I_4(1)$, $^{11}I_5(1)$	None
K_1	$^1K_1(2)$, $^3K_1(7)$, $^5K_1(8)$, $^7K_1(8)$, $^9K_1(5)$, $^{11}K_1(3)$ $^{13}K_1(1)$,	$^3K_1(1)$, $^5K_1(1)$
K_2	$^1K_2(1)$, $^3K_2(3)$, $^5K_2(3)$, $^7K_2(2)$, $^9K_2(1)$	None

TABLE IX. Correlation table for the rovibronic levels of $Tl_2H_4(Tl_2H_4^+)$ for both single- and double-valued representations.

K	Rigid(D_{2d}^2)	Nonrigid($\{S_2[S_2]XI\}^2$)
0	A_1	$A_1^+ + A_1^-$
1	$A_2 + E$	$A_2^+ + A_2^- + E^+ + E^-$
2	$A_1 + B_1 + B_2 + E$	$A_1^+ + A_1^- + B_1^+ + B_1^-$ $+ B_2^+ + B_2^- + E^+ + E^-$
3	$A_2 + B_1 + B_2 + 2E$	$A_2^+ + A_2^- + B_1^+ + B_1^-$ $+ B_2^+ + B_2^- + 2E^+ + 2E^-$
4	$(A_1 + A_2 + B_1 + B_2 + 2E) + D^0$	$A_1^+ + A_1^- + A_2^+ + A_2^-$ $+ B_1^+ + B_1^- + B_2^+ + B_2^-$ $+ 2E^+ + 2E^- + D^0$
n(integer)	$(A_1 + A_2 + B_1 + B_2 + 2E)$ $+ D^{n-4}$	$A_1^+ + A_1^- + A_2^+ + A_2^-$ $+ B_1^+ + B_1^- + B_2^+ + B_2^-$ $+ 2E^+ + 2E^- + D^{n-4}$
1/2	$E_{1/2}$	$E_{1/2}^+ + E_{1/2}^-$
3/2	$E_{1/2} + E_{3/2}$	$E_{1/2}^+ + E_{1/2}^- + E_{3/2}^+ + E_{3/2}^-$
5/2	$E_{1/2} + 2E_{3/2}$	$E_{1/2}^+ + E_{1/2}^-$ $+ 2E_{3/2}^+ + 2E_{3/2}^-$
7/2	$2E_{1/2} + 2E_{3/2}$	$2E_{1/2}^+ + 2E_{1/2}^-$ $+ 2E_{3/2}^+ + 2E_{3/2}^-$
9/2	$2(E_{1/2} + E_{3/2}) + D^{(1/2)}$	$2(E_{1/2}^+ + E_{1/2}^- + E_{3/2}^+ + E_{3/2}^-)$ $+ D^{(1/2)}$
$n+1/2$	$2(E_{1/2} + E_{3/2}) + D^{(n-1/2)}$	$2(E_{1/2}^+ + E_{1/2}^- + E_{3/2}^+ + E_{3/2}^-)$ $+ D^{(n-1/2)}$

the induced representation theory the irreducible representation from the rigid group is correlated into the nonrigid molecular group. We can illustrate this with Tl_2H_4 as the first example. Since the rigid molecule has an equilibrium geometry of D_{2d} we start with the correlation of the rovibronic levels as a function of the total K quantum number. Since the ground electronic state of Tl_2H_4 is a $^1A_1$ state, the overall K values are integral and thus integral quantum number correlations suffice. Table IX shows such a correlation table for both integral and half-integral values of K. As seen from Table IX even in the ground rovibronic state Tl_2H_4 exhibits tunneling splitting into $A_1^+ + A_1^-$ tunneling levels. Excited rovibronic levels show more complex tunneling splittings as demonstrated in Table IX. For all radical species the half-integral correlations are appropriate. For example, removal of an electron from Tl_2H_4 to form $Tl_2H_4^+$ results in a doublet ground electronic state. Thus the group state of $Tl_2H_4^+$ correlates into $E_{1/2}$ representation for the rigid species, which splits into $E_{1/2}^+ + E_{1/2}^-$ tunneling levels. Likewise the excited rovibronic levels follow the pattern in Table IX for half-integral quantum numbers. We have included both half-integral and integral representations in the correlation table for completeness.

IV. CONCLUSION

The spinor double groups of nonrigid molecules that contain heavy atoms and also exhibit large amplitude motions were considered. It was shown that their groups are double groups of wreath product groups. Several examples of double groups of wreath products such as $\{S_2[S_2] \times I\}^2$, $\{S_2[S_3]\}^2$, $\{S_4[S_2]\}^2$, etc., were considered as representatives of nonrigid Tl_2H_4, $Pb_2(CH_3)_6$, $(PoH_2)_4$, etc. It was shown that the conjugacy classes of these groups could be characterized by matrix cycle types. Combinatorial generat-

weights of the rovibronic levels are $A_1(1)$, $A_3(15)$, $E_2(6)$, $T_3(15)$, $T_4(3)$, $G_1(3)$, $G_3(10)$, $G_4(1)$, $I_1(6)$, $I_3(3)$, $K_2(8)$. The nuclear spin statistic weights of the proton species are the same as the frequencies since they are bosons.

The tunneling splittings of the rovibronic levels can be obtained using the double group character table. The overall rovibronic species is the direct product of electronic, vibrational and rotational species. The overall rovibronic species is first correlated in the normal rigid subgroup. Then using

ing functions were considered using the matrix type polynomials. Coefficients in the generating functions were shown to yield the character values of single-valued irreducible representations. The double-valued irreducible representations were obtained by first identifying which conjugacy classes generate new conjugacy classes under the operation R. Then the character values of these classes were systematically obtained. We have derived the character tables of all these double groups that included up to 768 elements. We also presented a few representative applications of the double groups in generating the nuclear spin species of these species and nuclear spin statistical weights. We showed the use of these tables for the correlation of rovibronic levels of nonrigid species into tunneling levels for both integral and half-integral quantum numbers. The tables with double-valued representations are useful for both electronic states with integral and half-integral spin multiplicities for which spin–orbit coupling can mix different electronic states as determined by their symmetries in the double group. We illustrated the construction and application of the correlation table for the rovibronic levels for the Tl_2H_4 case. Construction of the correlation tables for other species can be done as necessary using the character tables, and such applications could be the topic of future studies.

ACKNOWLEDGMENT

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