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Full non-rigid group of di-μ-oxo-bis (tetraamine manganese(II)) as a wreath product

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Abstract

The non-rigid molecule group theory (NRG), in which the dynamical symmetry operations are defined as physical operations, is a new field of chemistry. Balasubramanian computed the NRG of the triple equivalent nitro group rotation in 1,3,5-triamino-2,4,6-trinitrobenzene, and proved that the NRG of this molecule is a group of order 48 (see Chem. Phys. Lett., 398, 15 (2004)). In this work the non-rigid molecule group theory in which the dynamical symmetry operations are defined as physical operations is applied to deduce the character table of the full non-rigid molecule group (f-NRG) of Di μ-oxo-bis(tetraamine manganese(II)).The f-NRG of this molecule is seen to have order 52488 which has 1674 conjugacy classes.

1. Introduction

The mathematical tools of group theory have been used extensively to analyze of the symmetry properties of physical systems. Following Y. G. Smeyers[1,2] and K. Balasubramanian[3,4], the complete set of molecular conversion operations that commute with the nuclear motion operator contains overall rotation operations, describing the molecule rotating as a whole, and intermolecular motion operations, describing molecular moieties moving with respect to the rest of the molecule. Such a set forms a group, which we call the Non-Rigid Group (NRG). Balasubramanian, using the wreath product of groups, computed the character table of non-rigid groups for water pentamer and 1,3,5-triamino-2,4,6-

trinitrobenzene[3,4]. Balasubramanian[3-11] was the first chemist who calculated the non-rigid group of molecules using wreath product formalism. He also computed the character table of non-rigid groups under consideration, using a well-known method for computing the character table of groups which is representable as a wreath product of two groups.

Ashrafi and coauthors computed character tables of the non-rigid groups of some molecules[12-17]. Longuet-Higgins[18] investigated the symmetry groups of nonrigid molecules where changes from one conformation to another can occur easily. In many cases, these symmetry groups are not isomorphic to any of the familiar symmetry groups of rigid molecules, and their character tables are unknown. It is therefore of some interest and importance to develop simple methods of calculating these character tables, which are needed for classification of wave functions, determination of selection rules, and so on.

The method described in the present study is appropriate for molecules that consist of a number of XH_3 groups attached to a rigid framework[19]. An example of this molecule is Di μ-oxo-bis(tetraamine manganese(II)), which is considered in some detail. We first specify the algebraic structure of the full non-rigid group of Di μ-oxo-bis(tetraamine manganese(II)). We will show that the f-NRG of Di μ-oxo-bis(tetraamine manganese(II)) can be represented by the wreath product of some known groups. Then based on the structure of the group we apply a useful programming language, namely GAP[20], and compute the character table of f-NRG of this molecule. Note that we can use GAP to find many properties of the groups. We use [21] for the standard notations and terminology of character theory. The motivation for this study is outlined in [3-17] and the reader is encouraged to consult these papers for background material as well as basic computational techniques.

2. Wreath products

In this section we describe briefly some notation which will be used in the next section. Recall that a function f from a group G into a group K is a homomorphism if for all $x, y \in G$, $(xy)f=(xf)(yf)$. An automorphism of a group G is a bijective homorphism from N on to G. The set of all automorphism of G is a group under the composition operation and denoted by Aut(G).

Let N and H be subgroups of a group G. If N is normal (that is for any $g \in G$ and $x \in N$, $g^{-1}xg \in N$), $G=NH=\{xy \mid x \in N, y \in H\}$, and $N \cap H = \{e\}$, then we say that G is a semidirect product of N by H, denoted by N: H. Note that if H is also a normal subgroup of G, then

$G=N\times H$ is the direct product of N and H. If G= N: H, then each $x\in G$ can be written uniquely as x=nh for some $n\in N$ and $h\in H$, and there is homomorphismφ: $H\longrightarrow$ Aut(N), such that $(h)\varphi=\varphi_h$, where φ_h: $N\longrightarrow N$ is defined by $(n)\varphi_h= h^{-1}n\ h$. We call φ conjugation homomorphism of the semi direct product G and write $G = N :_\varphi H$. We can see that if the homomorphism $\varphi : H\longrightarrow$Aut(N) defined above is trivial, then the semidirect product reduces to the direct product $N\times H$. It is a well-known fact that the homomorphism φ completely determines the semidirect product[22].

Suppose X is a set. The set of all permutations on X, denoted by S_X, is a group which is called the symmetric group on X. In the case that, X = {1, 2, …, n}, we denote S_X by S_n or Sym(n). Let H be group acting on X. This is equivalent to the existence a homomorphism from H into S_X (see [22]). Suppose also that G is a group. The set of all mappings $X\longrightarrow G$ is denoted by G^X, i.e. $G^X = \{f \mid f:X\longrightarrow G\}$. It is clear that $|G^X| = |G|^{|X|}$. We put $G\ Wr_{(X)}H = G^X\times H = \{(f, \pi) \mid f \in G^X, \pi \in H\}$. For $f\in G^X$ and $\pi \in H$, we define an action of H on G^X, by $f^\pi\in G^X$ by $f^\pi=f^\pi(x)=f(x^\pi)$, where $x^\pi=(x)\pi$ is the image of $x\in G$ under the permutation π. It is easy to check that the following law of composition

$$(f , \pi)\ (g ,\sigma) = (fg^\pi , \pi\ \sigma),$$

makes $G\ Wr_{(X)}\ H$ into a group. This group is called the wreath product of G by H with respect to the action of H on X. If the action of H on X is faithful, that is the homomorphism from H into S_X is one to one, then H is a subgroup of S_X and we call H a permutation group on X. In this case $G\ Wr_{(X)}\ H$ is called the standard wreath product of G by H and denoted by $G\wr H$. Note that each function $f\in G^X$ can be identified with its image $(a_1,a_2,\ldots, a_n)$, where $a_i=f(i)$. Therefore G^X can be identified with G, $G\times G\times \ldots \times G=\{(a_1, a_2, \ldots, a_n) \mid a_i \in G\}$, the group of n-tuples of elements of G. Now if $f= (a_1, a_2,\ldots, a_n) \in G^X$ and $\pi \in H$, then

$$f^\pi = (a_{(1)\pi}, a_{(2)\pi},\ldots, a_{(n)\pi}).$$

Hence $G\wr H=G^X\times H = \{(a_1, a_2,\ldots, a_n; \pi) \mid a_i\in G, \pi\in H\}$ and

$$(a_1,a_2,\ldots,a_n; \pi)(b_1,b_2,\ldots, b_n; \sigma)=(a_1b_{(1)\pi},a_2b_{(n)\pi},\ldots, a_n\, b_{(n)\pi},; \pi\sigma)$$

3. Full non-rigid group of Di-μ-oxo-bis(tetraamine manganese(II))

In this section we compute the full non-rigid group of Di-μ-oxo-bis(tetraamine manganese(II)). First of all, we consider the point group of the molecule in the case of a rigid framework. We consider the full non-rigid group W (f-NRG) of this molecule, each equilibrium conformation of which has an ordinary point group symmetry D_{2h}.

In order to characterize full non-rigid of this molecule, we first note that each dynamic symmetry operation of the molecule, considering the rotations of NH_3 groups is composed of two sequential physical symmetry operations. We first have a physical symmetry of framework (as we have to map the NH_3 groups on NH_3 groups).

Before going into the details of the computations of the molecule, we should mention that we consider the speed of rotations of NH_3 groups sufficiently high so that the mean time dynamical symmetry of the molecules makes sense.

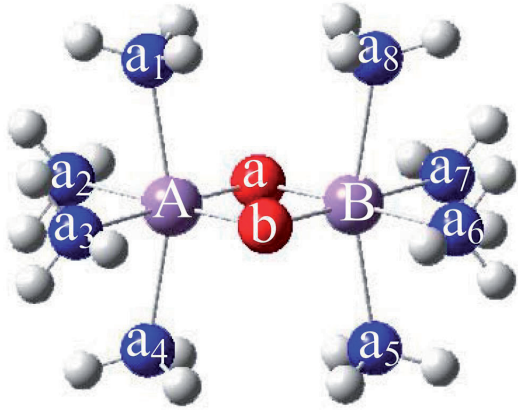

Figure1.The structure of Di-μ-oxo-bis (tetraamine manganese(II))

Now consider symmetry operations of this framework. This operations form an elementary abelian group H of order 8, which is not cyclic so it is isomorphic to $Z_2 \times Z_2 \times Z_2$, where Z_2 is cyclic group of size 2. After accomplishing the first framework symmetry operation we have to map each NH_3 group on itself which forms the group G isomorphic to Z_3, cyclic group of size 3. The number of all such operations is 52488. The composition of such dynamic symmetry operations are described as follows. Let us use the symbols a_1, a_2, a_3, a_4 to indicate nitrogen atoms in the left and a_5, a_6, a_7, a_8 to nitrogen atoms in the right, a and b

to oxygen atoms, A and B to manganese atoms as shown in Figure 1. Now from the symmetry point of view a_i, $1 \leq i \leq 8$, are important and a, b, A, B follow the motion of a_i. Now consider the framework, as shown in Figure 1. Obviously the symmetry group of the framework is generated by the following permutations: $X_1 = (a_1, a_4)(a_5, a_8)$, $X_2 = (a_2, a_3)(a_6, a_7)(a, b)$, $X_3 = (a_1, a_8)(a_2, a_7)(a_3, a_6)(a_4, a_5)(A, B)$.

The permutation X_1 is the reflection (σ_h) with respect to the horizontal plane containing A, B, a, b. X_2 is the reflection with respect to the vertical plane (σ_{v1}) including A, B, a_1, a_4, a_5, a_8. Finally X_3 is the reflection with respect to the vertical plane (σ_{v2}) containing a, b. These operations generate the point group of Di-μ-oxo-bis(tetraamine manganese(II)). This group is abelian and by structure theorem for finitely generated abelian groups we have $H=Z_2\times Z_2\times Z_2$.

Referring to Figure 1, the group of each NH_3 at the eight corners of framework is given in terms of permutations as follows:

$K_1=<(1, 2, 3)>$, $K_2=<(4, 5, 6)>$, $K_3=<(7, 8, 9)>$, $K_4=<(10, 11, 12)>$, $K_5=<(13,14,15)>$, $K_6=<(16,17,18)>$, $K_7=<(19,20,21)>$, $K_8=<(22,23,24)>$.

Therefore the full symmetry group of Di-μ-oxo-bis(tetraamine manganese(II))has the following structure

$$W = (K_1\times K_2 \times \ldots \times K_8): H,$$

where : denotes the semi-direct product. Hence, we can identify every element of W, as a vector $(a_1, a_2, \ldots, a_8; b)$ such that that $a_i \in K_i$ and $b \in H$.

It is clear that H permutes K_i and so W can be written in terms of wreath product

$$W = K \wr H \approx Z_3 \wr (Z_2\times Z_2\times Z_2),$$

where K is the cyclic group of order 3. Note that W has order 52488. We now apply GAP[20] to construct a group which is isomophic to this group as follows

```
x1:=(1, 4)(5, 8);   x2:=(2, 3)(6, 7);   x3:=(1, 8)(2, 7)(3, 6)(4, 5);
H:=Group(x1, x2, x3);   G:=Group((1, 2, 3));
W:=WreathProduct(G, H);
```

By above description it is clear that wreath product of G by H, denoted by W, is the full non-rigid group of this molecule. Minimal generating se of the group W is $\{w_1, w_2, w_3\}$ where

$w_1=(1, 10)(2, 11)(3, 12)(4, 5, 6)(13, 22)(14, 23)(15, 24)(19, 21, 20)$

$w_2=(1, 22, 3, 24, 2, 23)(4, 21)(5, 19)(6, 20)(7, 17, 8, 18, 9, 16)(10, 14, 11, 15, 12, 13)$

w_3=(4, 7, 6, 9, 5, 8)(10, 11, 12)(13, 14, 15)(16, 20, 17, 21, 18, 19)(22, 24, 23).
W has 1674 conjugacy classes and so 1674 irreducible characters. Let
r=(1, 2, 3), =(4, 5, 6), x=(7, 8, 9), y=(10, 11, 12), z=(13, 14, 15), u=(16, 17, 18),
v=(19, 20, 21), w=(22, 23, 24),
k=(1, 22)(2, 23)(3, 24)(4, 19)(5, 20)(6, 21)(7, 16)(8, 17)(9, 18)(10, 13)(11, 14)(12, 15),
m=(4, 7)(5, 8)(6, 9)(16, 19)(17, 20)(18, 21), n=(1,10)(2,11)(3,12)(13,22)(14,23)(15,24).

Let T_1, T_2 and T_3 be the groups generating by the sets {sxuv, ryzw}, {k, m, n} and {sx^2, u^2v, s^2v, ry^2, z^2w, r^2w} respectively. It is easy to check that T_1, T_2 and T_3 are isomorphic to $Z_3\times Z_3$, $Z_2\times Z_2\times Z_2$ and $Z_3\times Z_3\times Z_3\times Z_3\times Z_3\times Z_3$ respectively and $T_1$and T_3 are normal subgroups of W and $T_2 \cap T_3 = 1$. Finally we can see that $W=T_1\times (T_2: T_3)$. So every irreducible character of W is of the form $\varphi\times\gamma$, where $\varphi\in Irr(T_1)$, $\gamma\in Irr(T_2:T_3)$. Recall that $\varphi\times\gamma(ab)=\varphi(a)\gamma(b)$ for all $a\in T_1$ and $b\in T_2:T_3$. Now conjugacy classes of W are of the form (t_1, t_2, t_3) where t_1, t_2 and t_3 are conjugacy classes of T_1, T_2 and T_3 respectively. Using this fact we can compute all of the conjugacy classes and irreducible characters of W. It suffices to find conjugacy classes and irreducible characters of $T_2:T_3$.

Suppose that T_2 = {1, a, b, c, d, e, f, g}. Now we can apply GAP to find the conjugacy classes and character table of the group $T_2:T_3$. Table 1 shows the conjugacy classes, a representative from each class and the order of the conjugacy class. Note the character table of the group T_2: T_3, is very large in size and can be found using GAP. Hence, as explained above, we can find character table of W.

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Table1. Representative and size of the conjugacy classes of T_2: T_3

No	Representative	Size	No	Representative	Size	No	Representative	Size
1	[1, 1]	1	37	$[xy^2z^2uvw^2, 1]$	8	73	$[sx^2yzu^2vw, 1]$	8
2	$[uv^2, 1]$	4	38	$[xy^2z^2u^2w^2, 1]$	8	74	$[sx^2yz^2uv^2, 1]$	8
3	$[zw^2, 1]$	4	39	$[x^2u^2v^2, 1]$	4	75	$[sx^2yz^2u^2v, 1]$	8
4	$[zuv^2w^2, 1]$	8	40	$[x^2zvw^2, 1]$	8	76	$[sx^2y^2z^2w^2, 1]$	8
5	$[yw^2, 1]$	4	41	$[x^2zuw^2, 1]$	8	77	$[sx^2y^2z^2uv^2w^2, 1]$	8
6	$[yuv^2w^2, 1]$	8	42	$[x^2zu^2v^2w^2, 1]$	8	78	$[sx^2y^2z^2u^2vw^2, 1]$	8
7	[yzw, 1]	4	43	$[x^2yu^2v^2w^2, 1]$	8	79	$[s^2x^2zv^2w^2, 1]$	8
8	$[yzuv^2w, 1]$	8	44	$[x^2yzvw, 1]$	8	80	$[s^2x^2zuvw^2, 1]$	4
9	$[yz^2, 1]$	4	45	$[x^2yzuw, 1]$	8	81	$[s^2x^2yzv^2w, 1]$	8
10	$[yz^2uv^2, 1]$	8	46	$[x^2yzu^2v^2w, 1]$	8	82	$[s^2x^2yzuvw, 1]$	4
11	$[y^2uv^2w, 1]$	8	47	$[x^2yz^2u^2v^2, 1]$	8	83	$[s^2x^2y^2z^2v^2w^2, 1]$	8
12	$[y^2zuv^2, 1]$	8	48	$[x^2y^2u^2v^2w, 1]$	8	84	$[s^2x^2y^2z^2uvw^2, 1]$	4
13	$[y^2z^2w^2, 1]$	4	49	$[x^2y^2zu^2v^2, 1]$	8	85	[1, a]	9
14	$[y^2z^2uv^2w^2, 1]$	8	50	$[x^2y^2z^2vw^2, 1]$	8	86	$[zw^2, a]$	36
15	$[xv^2, 1]$	4	51	$[x^2y^2z^2uw^2, 1]$	8	87	$[yw^2, a]$	36
16	[xuv, 1]	4	52	$[x^2y^2z^2u^2v^2w^2, 1]$	8	88	[yzw, a]	36
17	$[xu^2, 1]$	4	53	$[sxu^2v^2, 1]$	2	89	$[yz^2, a]$	36
18	$[xzv^2w^2, 1]$	8	54	$[sxzvw^2, 1]$	8	90	$[y^2z^2w^2, a]$	36
19	$[xzuvw^2, 1]$	8	55	$[sxzu^2v^2w^2, 1]$	4	91	$[su^2, a]$	18
20	$[xzu^2w^2, 1]$	8	56	$[sxyu^2v^2w^2, 1]$	4	92	$[szu^2w^2, a]$	36
21	$[xyv^2w^2, 1]$	8	57	[sxyzvw, 1]	8	93	$[syu^2w^2, a]$	36
22	$[xyuvw^2, 1]$	8	58	$[sxyzu^2v^2w, 1]$	4	94	$[syzu^2w, a]$	36
23	$[xyu^2w^2, 1]$	8	59	$[sxyz^2u^2v^2, 1]$	4	95	$[syz^2u^2, a]$	36
24	$[xyzv^2w, 1]$	8	60	$[sxy^2u^2v^2w, 1]$	4	96	$[sy^2u^2w, a]$	36
25	[xyzuvw, 1]	8	61	$[sxy^2zu^2v^2, 1]$	4	97	$[sy^2zu^2, a]$	36
26	$[xyzu^2w, 1]$	8	62	$[sxy^2z^2vw^2, 1]$	8	98	$[sy^2z^2u^2w^2, a]$	36
27	$[xyz^2v^2, 1]$	8	63	$[sxy^2z^2u^2v^2w^2, 1]$	4	99	$[s^2zuw^2, a]$	36
28	$[xyz^2uv, 1]$	8	64	$[sx^2uv^2, 1]$	2	100	$[s^2yzuw, a]$	36
29	$[xyz^2u^2, 1]$	8	65	$[sx^2u^2v, 1]$	2	101	$[s^2y^2z^2uw^2, a]$	36
30	$[xy^2v^2w, 1]$	8	66	$[sx^2zw^2, 1]$	8	102	$[ryz^2w^2, a]$	2
31	$[xy^2uvw, 1]$	8	67	$[sx^2zuv^2w^2, 1]$	8	103	$[ryz^2uv^2w^2, a]$	4
32	$[xy^2u^2w, 1]$	8	68	$[sx^2zu^2vw^2, 1]$	8	104	$[ry^2zw^2 , a]$	2
33	$[xy^2zv^2, 1]$	8	69	$[sx^2yuv^2w^2, 1]$	8	105	$[ry^2zuv^2w^2, a]$	8
34	$[xy^2zuv, 1]$	8	70	$[sx^2yu^2vw^2, 1]$	8	106	$[ry^2z^2w, a]$	2
35	$[xy^2zu^2, 1]$	8	71	$[sx^2yzw, 1]$	8	107	$[ry^2z^2uv^2w, a]$	8
36	$[xy^2z^2v^2w^2, 1]$	8	72	$[sx^2yzuv^2w, 1]$	8	108	$[rxyz^2v^2w^2, a]$	4

Table1. (Continued)

No	Representative	Size	No	Representative	Size	No	Representative	size
109	$[rxyz^2uvw^2, 1]$	4	135	$[ryz^2w^2, a]$	18	161	$[r^2sxzu^2v^2, b]$	18
110	$[rxyz^2u^2w^2, 1]$	4	136	$[ry^2zw^2, a]$	18	162	$[sx^2uv^2, b]$	18
111	$[rxy^2zv^2w^2, 1]$	8	137	$[ry^2z^2w, a]$	18	163	$[sx^2u^2v, b]$	18
112	$[rxy^2zuvw^2, 1]$	8	138	$[rsyz^2u^2w^2, a]$	18	164	$[rsx^2z^2uv^2, b]$	36
113	$[rxy^2zu^2w^2, 1]$	8	139	$[rsy^2zu^2w^2, a]$	36	165	$[rsx^2z^2u^2v, b]$	36
114	$[rxy^2z^2v^2w, 1]$	8	140	$[rsy^2z^2u^2w, a]$	36	166	[1, c]	81
115	$[rxy^2z^2uvw, 1]$	8	141	$[rs^2yz^2uw^2, a]$	18	167	$[rz^2, c]$	162
116	$[rxy^2z^2u^2w, 1]$	8	142	[1, b]	9	168	$[su^2, c]$	162
117	$[rx^2yz^2vw^2, 1]$	4	143	$[uv^2, b]$	36	169	$[rsz^2u^2, c]$	162
118	$[rx^2yz^2uw^2, 1]$	4	144	$[rz^2, b]$	18	170	$[r^2szu^2, c]$	162
119	$[rx^2yz^2u^2v^2w^2, 1]$	4	145	$[rz^2uv^2, b]$	36	171	[1, d]	81
120	$[rx^2y^2zu^2v^2w^2, 1]$	8	146	$[r^2zuv^2, b]$	36	172	$[sx^2, d]$	162
121	$[rx^2y^2z^2u^2v^2w, 1]$	8	147	$[xv^2, b]$	36	173	$[ry^2, d]$	162
122	$[rsxyz^2vw^2, 1]$	4	148	[xuv, b]	36	174	$[rsx^2y^2, d]$	324
123	$[rsxyz^2u^2v^2w^2, 1]$	2	149	$[xu^2, b]$	36	175	[1, e]	81
124	$[rsxy^2zu^2v^2w^2, 1]$	4	150	$[rxz^2v^2, b]$	36	176	$[s^2x, e]$	162
125	$[rsxy^2z^2u^2v^2w, 1]$	4	151	$[rxz^2uv, b]$	36	177	$[ry^2, e]$	162
126	$[rsx^2yz^2w^2, 1]$	4	152	$[rxz^2u^2, b]$	36	178	$[rs^2xy^2, e]$	324
127	$[rsx^2yz^2uv^2w^2, 1]$	4	153	$[r^2xzv^2, b]$	36	179	[1, f]	81
128	$[rsx^2yz^2u^2vw^2, 1]$	4	154	$[r^2xzuv, b]$	36	180	$[fsx^2, f]$	162
129	$[rsx^2y^2zuv^2w^2, 1]$	4	155	$[r^2xzu^2, b]$	36	181	$[r^2y, f]$	162
130	$[rsx^2y^2zu^2vw^2, 1]$	4	156	$[x^2u^2v^2, b]$	36	182	$[r^2sx^2y, f]$	324
131	$[rsx^2y^2z^2uv^2w, 1]$	4	157	$[rx^2z^2u^2v^2, b]$	36	183	[1, g]	81
132	$[rsx^2y^2z^2u^2vw, 1]$	4	158	$[r^2x^2zu^2v^2, b]$	36	184	$[s^2x, g]$	162
133	$[rs^2x^2yz^2v^2w^2, 1]$	4	159	$[sxu^2v^2, b]$	18	185	$[r^2y, g]$	162
134	$[rs^2x^2yz^2uvw^2, 1]$	2	160	$[rsxz^2u^2v^2, b]$	18	186	$[r^2s^2xy, g]$	324