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PSEUDO-FINITE POINT GROUPS FOR LINEAR MOLECULES

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An attempt is made to find a workable variant of the infinite point groups for linear molecules, using finite-like (sub)groups, specially to avoid operational problems (like integration when dealing with the reduction formula). The new formalism is a descendant of the original, infinite groups. Comments concerning application (limitations and benefits) are made.

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1. Introduction

The *Group formalism* is a wonderful instrument in dealing with the optical spectra of different atomic combinations, like molecules and complexes, in all kind of materials. It tells us how a degenerate spectral term (energy level) splits itself, in a lower symmetry, it chooses elemental wave functions suitable to be combined for subsequent hybridization, establishes selection rules for spectro-optical transitions, etc., all in an elegant and efficient manner [1-5].

This nice construction is very well built and from the viewpoint of the operating rules it is homogeneous, except for the $C_{\infty v}$ and $D_{\infty h}$ groups, concerning the unsymmetrical and symmetrical linear molecules, respectively. The character tables of these two infinite groups are listed together with those of the finite ones in spite of the fact that they are, in some aspects, different. The reason for this association may be the fact that several rules are acting in these two cases the same way as in the first category and that one never uses an infinite number of representations any way. Just a few of the infinite number of representations of the $C_{\infty v}$ and $D_{\infty h}$ groups are of a real practical interest.

Probably the most important deviation of the infinite group's rules, from those of the finite ones, is the way the reduction operation is performed: by integration, instead of summation, leading to complications, among others, when looking for spectral terms splitting or selection rules for the overtones of the degenerate molecular vibrations [6].

We have recently proposed rather simple ways to *avoid* these difficulties, for different specific tasks, in two separate papers [7, 8].

In this paper two new sets of *pseudo-finite (sub)groups* called $C_{nv}^{(\infty)}$ and $D_{nh}^{(\infty)}$ (n=9 and 17) derived directly from the original (infinite) point groups are proposed, instead of the $C_{\infty v}$ and $D_{\infty h}$ respectively, that work like finite groups for a limited number of lower representations (covering most practical cases) ignoring the higher ones. If higher order representations are, nevertheless, necessary, over the chosen ones, the proposed groups can easily be extended, by increasing n, to meet any user's needs. (By increasing n, the number of classes, i.e., representations is increased, see below). We start our construction of the pseudo-finite (sub)groups from the well known infinite groups, $C_{\infty v}$, Table 1 and $D_{\infty h}$, Table 2. The key element we act upon in this enterprise is the rotational operation, C_{∞}^{φ}, by giving φ, i.e. n, just a few finite values, resulting in a limited (finite) number of rotational classes, $2C_n^m$ (m=1, 2, 3, … , n-1), and representations.

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Table 1. The "classic" Character table for unsymmetrical linear molecules.

$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$2C_{\infty}^{2\varphi}$	$2C_{\infty}^{3\varphi}$	…	$\infty\sigma_v$	linear bases	bilinear bases
$A_1 \equiv \Sigma^+$	1	1	1	1	…	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	1	1	…	-1	R_z	
$E_1 \equiv \Pi$	2	$2\cos\varphi$	$2\cos2\varphi$	$2\cos3\varphi$	…	0	$(x, y); (R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	$2\cos2\varphi$	$2\cos4\varphi$	$2\cos6\varphi$	…	0		(x^2-y^2, xy)
$E_3 \equiv \Phi$	2	$2\cos3\varphi$	$2\cos6\varphi$	$2\cos9\varphi$	…	0		
…	…	…	…	…	…	…	…	…

Table 2. The "clasic" Character table for symmetrical linear molecules.

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$2C_{\infty}^{2\varphi}$	...	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	$2S_{\infty}^{2\varphi}$	...	∞C_2	lin.bases	bilin.bases
$A_{1g} \equiv \Sigma_g^+$	1	1	1	...	1	1	1	1	...	1		x^2+y^2, z^2
$A_{2g} \equiv \Sigma_g^-$	1	1	1	...	1	1	1	1	...	-1	R_z	
$E_{1g} \equiv \Pi_g$	2	$2\cos\varphi$	$2\cos2\varphi$	...	0	2	$-2\cos\varphi$	$-2\cos2\varphi$	...	0	(R_x, R_y)	(xz, yz)
$E_{2g} \equiv \Delta_g$	2	$2\cos2\varphi$	$2\cos4\varphi$	...	0	2	$2\cos2\varphi$	$2\cos4\varphi$	...	0		(x^2-y^2, xy)
...	...	...	...	...	...	...	...	...	...	...	...	...
$A_{2u} \equiv \Sigma_u^+$	1	1	1	...	1	-1	-1	-1	...	-1	z	
$A_{1u} \equiv \Sigma_u^-$	1	1	1	...	-1	-1	-1	-1	...	1		
$E_{1u} \equiv \Pi_u$	2	$2\cos\varphi$	$2\cos2\varphi$	...	0	-2	$2\cos\varphi$	$2\cos2\varphi$	...	0	(x, y)	
$E_{2u} \equiv \Delta_u$	2	$2\cos2\varphi$	$2\cos4\varphi$	...	0	2	$-2\cos2\varphi$	$-2\cos4\varphi$	...	0		
...	...	...	...	...	...	...	...	...	...	...	...	...

In other words we make a *choice* for a finite group order *h*. By doing this we selectively subtract finite subgroups (acting as groups) from the infinite groups, containing only the strictly needed information concerning the real linear molecules. There are an unlimited number of such possibilities corresponding to the chosen φ-values, i.e., to the integer n-values. A few, most important, of these possibilities are represented in Table 3, for odd-*n* $C_{nv}^{(\infty)}$, where the characters of the nontrivial E_1 (Π) representation for each φ are given only (the other bi-dimensional representations, in each (sub)group, have the same characters (except for the 120^0 which is a trivial integer), but in different orders (see Tables 5 and 6).

Table 3. Significant rotational E_1 characters for a few fixed φ-values.

10^0 steps→	: . . : . . : . . : . . : . . : . . : . . :
n	$\varphi(^0)$	0	40	80	120	160	180
3	120				-1		
5	72			0.618		-1.618	
7	51.43		1.247		-0.445		-1.802
9	40		1.532	0.347	-1	-1.879	
11	32.73		1.683	0.831	-0.285	-1.310	-1.919
13	27.69		1.771	1.136	0.241	-0.709	-1.497	-1.942
15	24		1.827	1.338	0.618	-0.209	-1	-1.618	-1.956
17	21.18		1.865	1.478	0.891	0.185	-0.547	-1.205	-1.700	-1.966
…	…		…	…	…	…	…	…	…	…

The reason for choosing odd-*n* only, reside in the fact that the new pseudo-finite (sub)groups are, in some important aspects, odd-*n* C_{nv} and D_{nd}, containing the same representations, while the even-*n* C_{nv} and D_{nd} contain also *B* representations that do not exist with the original $C_{\infty v}$ or $D_{\infty h}$ groups. All (sub)groups mentioned in Table 3 obey the four defining phrases for finite point groups, whose limits of applications are gradually moved to higher representations with growing *n*. This can

be seen by using the multiplication table, Table 4, for one of the two chosen and proposed (sub)groups, $C_{9v}^{(\infty)}$ and $C_{17v}^{(\infty)}$ (see Table 5 and 6) considered the most convenient by the dimension/utility relationship, for dealing with the symmetry aspects of the linear unsymmetrical molecules.

Table 4. Multiplication table for the $C_{17v}^{(\infty)}$ -group.

	A_1	A_2	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8
A_1	A_1	A_2	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8
A_2		A_1	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8
E_1			$A_1A_2E_2$	$E_1\ E_3$	$E_2\ E_4$	$E_3\ E_5$	$E_4\ E_6$	$E_5\ E_7$	$E_6\ E_8$	E_7 E_8
E_2				$A_1A_2E_4$	$E_1\ E_5$	$E_2\ E_6$	$E_3\ E_7$	$E_4\ E_8$	E_5 E_8	E_6 E_7
E_3					$A_1A_2E_6$	$E_1\ E_7$	$E_2\ E_8$	E_3 E_8	E_4 E_7	E_5 E_6
E_4						$A_1A_2E_8$	E_1 E_8	E_2 E_7	E_3 E_6	E_4 E_5
E_5							$A_1A_2E_7$	E_1 E_6	E_2 E_5	E_3 E_4
E_6								$A_1A_2E_5$	E_1 E_4	E_2 E_3
E_7									$A_1A_2E_3$	E_1 E_2
E_8										$A_1A_2E_1$

For the linear symmetrical molecules another two (sub)groups, $D_{9h}^{(\infty)}$ and $D_{17h}^{(\infty)}$ (see Tables 7 and 8), are considered. Working with subgroups does not contradict any of the point group's rules. Many problems of the optical spectroscopy are solved with less than a full group of symmetry operations, i.e., in a subgroup's frame.

We will call $C_{nv}^{(\infty)}$ and $D_{nh}^{(\infty)}$, simply groups from now on.

2. Unsymmetrical molecules

In practice, a group with six representations seems, at first, to be (and is, for some simple problems implying lower, practical, spectral terms) enough for a linear molecule: terms higher than E_4 (Γ) are very rarely met. All we have to do, to reach the proposed goal, is give φ, in the $C_{nv}^{(\infty)}$ -group, the proper value. For a six representations character table φ=40^0 is needed (meaning n=9) by transforming the C_{∞}^{φ} operation into C_9^m, (m=1 to 8) the $C_{9v}^{(\infty)}$ group, Table 5, where it is more convenient to use digital characters, instead of the usual cosφ functions in order to have a better visual relationship between the groups of the unsymmetrical and symmetrical molecules (see relations (3) and (3') and Tables 5 and 7 or Tables 6 and 8, respectively).

Table 5. Character table for the proposed low-order groups for unsym. linear molecules.

$C_{9v}^{(\infty)}$	E	$2C_9$	$2C_9^2$	$2C_9^3$	$2C_9^4$	$9\sigma_v$	linear bases	bilinear bases
$A_1 \equiv \Sigma^+$	1	1	1	1	1	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	1	1	1	-1	R_z	
$E_1 \equiv \Pi$	2	1.532	0.347	-1	-1.879	0	(x, y); (R_x, R_y)	(xz, yz)
$E_2 \equiv \Delta$	2	0.347	-1.879	-1	1.532	0		(x^2-y^2, xy)
$E_3 \equiv \Phi$	2	-1	-1	2	-1	0		
$E_4 \equiv \Gamma$	2	-1.879	1.532	-1	0.347	0		

The only problem with the new group is that it is not finite in all aspects. Fortunately this inconvenience affects, as mentioned before, only the mostly unnecessary, higher order, representations. The lower ones (to E_2 (Δ), the first 4 representations out of 6) are behaving, in all

aspects, like in a finite frame, as shown below. (It must be emphasized that different *n* does not mean different groups really, but rather different approximation orders of the same case, in spite of the fact that the characters are different: on common area they give the same results).

Reduction of any binary combination (product) that implies an A (Σ) representation, as one of the factors, for example, is completely valid up to E_4 (Γ) and the new, $C_{9v}^{(\infty)}$ group works entirely like the classic, finite, C_{9v} group.

A problem appears with reduction of some combinations (products) like E_h and E_k, (with h, k>2) representations, however. This behaviour should be expected though, since the rules,

$$E_k \times E_h = E_{k-h} + E_{k+h} \qquad \text{for } k>h \tag{1}$$

and

$$E_k \times E_k = A_1 + A_2 + E_{2k} \tag{2}$$

established with the original, infinite, groups must be obeyed [6], but as can be seen from eq. (2), $E_4 \times E_4$ gives E_8, which does not exist in the proposed table because we decided, for practical reasons, not to use representations over E_4 (Γ). If we want to solve all the problems, to E_4 (in this case), however, then we should construct a table extended to E_8 ($\varphi=2\pi/17$), behaving entirely "finite" to E_4, the $C_{17v}^{(\infty)}$ group, Table 6. Results, to be used in spectroscopy, obtained with Table 6 (n=17) will correspondingly be the same, for lover order representations, with those of the Table 5 (n=9), except that now the table is extended to E_8. Generally speaking, once we have decided the highest k (E_k), obeying "finite" rules, needed in our problem, then we should use $n = 4k + 1$ to construct the necessary group (extended to E_{2k}) that is working as a finite group, all operations giving entirely correct answers, up to E_k and in some specific cases it gives correct answers to as high as E_{2k} (see Table 4).

Excepting the fact that the $C_{nv}^{(\infty)}$ groups are not closed (some products jump out of the table), these groups, limited to E_k, are simply the finite C_{nv} groups, with all the consequences. So, the $C_{17v}^{(\infty)}$ group correctly covers all practical cases to E_4 (Γ) and we will stick to it, as a convenient compromise between the order of the group and the number and variety of the experimentally encountered operations and representations. Of course, $C_{9v}^{(\infty)}$ group can successfully be employed in some simpler, practical cases, as mentioned already.

Table 4 shows the products and the limits of the $C_{17v}^{(\infty)}$ case. "Boxed" figures are not correct in the new frame: they violate eqs. (1) and (2), and should be discarded. A similar table can easily be derived for the $D_{17h}^{(\infty)}$ group, showing the same limitations, to $E_4(\Gamma)$, see below.

The wrong (boxed) results in Table 4 could easily be corrected, however, by observing that any $E_k \times E_j$ product should obey the rule k + j = 2k in each k column. Consequently, E_8 in column E_5 should be E_9; E_7 is E_{10} and similarly in columns E_6, E_7 and E_8. These are correct values in spite of the fact that they are out of the new group. These artificial corrections should be taken only as a formal aspect since there is no need of them in practice. The first approximation is quite enough.

3. Symmetrical molecules

Let us start with the $D_{9h}^{(\infty)}$ group, Table 7, derived directly from $D_{\infty h}$ with $\varphi=40^0$, or from $C_{9v}^{(\infty)}$, Table 5, by using eq. (3'). The $D_{9h}^{(\infty)}$ group (which is not closed, either) is entirely valid, like before, to E_2. Of course, the above are also valid for the n=17, Table 8, to E_4 this time, which can be derived, as for the $D_{9h}^{(\infty)}$ group, directly from $D_{\infty h}$, or from $C_{17v}^{(\infty)}$, Table 6, by using eq. (3').

Table 6. Character table for the proposed high-order group for unsymmetrical linear molecules.

$C_{17v}^{(\infty)}$	E	$2C_{17}$	$2C_{17}^2$	$2C_{17}^3$	$2C_{17}^4$	$2C_{17}^5$	$2C_{17}^6$	$2C_{17}^7$	$2C_{17}^8$	$17\sigma_v$	linear bases	bilin. bases
$A_1 \equiv \Sigma^+$	1	1	1	1	1	1	1	1	1	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	1	1	1	1	1	1	1	-1	R_z	
$E_1 \equiv \Pi$	2	1.865	1.478	0.891	0.185	-0.547	-1.205	-1.700	-1.966	0	$(x, y); (R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	1.478	0.185	-1.205	-1.966	-1.700	-0.547	0.891	1.865	0		(x^2-y^2, xy)
$E_3 \equiv \Phi$	2	0.891	-1.205	-1.966	-0.547	1.478	1.865	0.185	-1.700	0		
$E_4 \equiv \Gamma$	2	0.185	-1.966	-0.547	1.865	0.891	-1.700	-1.205	1.478	0		
$E_5 \equiv X$	2	-0.547	-1.700	1.478	0.891	-1.966	0.185	1.865	-1.205	0		
$E_6 \equiv I$	2	-1.205	-0.547	1.865	-1.700	0.185	1.478	-1.966	0.891	0		
$E_7 \equiv K$	2	-1.700	0.891	0.185	-1.205	1.865	-1.966	1.478	-0.547	0		
$E_8 \equiv \Lambda$	2	-1.966	1.865	-1.700	1.478	-1.205	0.891	-0.547	0.185	0		

Table 7. Character table for the proposed low-order group for symmetrical linear molecules.

$D_{9h}^{(\infty)}$	E	$2C_9$	$2C_9^2$	$2C_9^3$	$2C_9^4$	$9\sigma_v$	i	$2S_{18}^7$	$2S_{18}^5$	$2S_{18}^3$	$2S_{18}$	$9C_2$	lin. bases	bilin. bases
$A_{1g} \equiv \Sigma_g^+$	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, x^2
$A_{2g} \equiv \Sigma_g^-$	1	1	1	1	1	-1	1	1	1	1	1	-1	R_z	
$E_{1g} \equiv \Pi_g$	2	1.532	0.347	-1	-1.879	0	2	1.532	0.347	-1	-1.879	0	(R_x, R_z)	(xz, yz)
$E_{2g} \equiv \Delta_g$	2	0.347	-1.879	-1	1.532	0	2	0.347	-1.879	-1	1.532	0		(x^2-y^2, xy)
$E_{3g} \equiv \Phi_g$	2	-1	-1	2	-1	0	2	-1	-1	2	-1	0		
$E_{4g} \equiv \Gamma_g$	2	-1.879	1.532	-1	0.347	0	2	-1.879	1.532	-1	0.347	0		
$A_{2u} \equiv \Sigma_u^+$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	z	
$A_{1u} \equiv \Sigma_u^-$	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1		
$E_{1u} \equiv \Pi_u$	2	1.532	0.347	-1	-1.879	0	-2	-1.532	-0.347	1	1.879	0	(x, y)	
$E_{2u} \equiv \Delta_u$	2	0.347	-1.879	-1	1.532	0	-2	-0.347	1.879	1	-1.532	0		
$E_{3u} \equiv \Phi_u$	2	-1	-1	2	-1	0	-2	1	1	-2	1	0		
$E_{4u} \equiv \Gamma_u$	2	-1.879	1.532	-1	0.347	0	-2	1.879	-1.532	1	-0.347	0		

Table 8. Character table for the proposed high-order group for symmetrical linear molecules.

$D_{17h}^{(\infty)}$	E	$2C_{17}$	$2C_{17}^2$	$2C_{17}^3$	$2C_{17}^4$	$2C_{17}^5$	$2C_{17}^6$	$2C_{17}^7$	$2C_{17}^8$	$17\sigma_v$	i	$2S_{34}^{15}$	$2S_{34}^{13}$	$2S_{34}^{11}$	$2S_{34}^{9}$	$2S_{34}^{7}$	$2S_{34}^{5}$	$2S_{34}^{3}$	$2S_{34}$	$17C_2$	lin.bases	bilin.bases
$A_{1g}\equiv\Sigma_g^+$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
$A_{2g}\equiv\Sigma_g^-$	1	1	1	1	1	1	1	1	1	-1	1	1	1	1	1	1	1	1	1	-1	R_y	
$E_{1g}\equiv\Pi_g$	2	1.865	1.478	0.891	0.185	-0.547	-1.205	-1.700	-1.966	0	2	1.865	1.478	0.891	0.185	-0.547	-1.205	-1.700	-1.966	0	(R_x, R_z)	(xz, yz)
$E_{2g}\equiv\Delta_g$	2	1.478	0.185	-1.205	-1.966	-1.700	-0.547	0.891	1.865	0	2	1.478	0.185	-1.205	-1.966	-1.700	-0.547	0.891	1.865	0		(x^2-y^2, xy)
$E_{3g}\equiv\Phi_g$	2	0.891	-1.205	-1.966	-0.547	1.478	1.865	0.185	-1.700	0	2	0.891	-1.205	-1.966	-0.547	1.478	1.865	0.185	-1.700	0		
$E_{4g}\equiv\Gamma_g$	2	0.185	-1.966	-0.547	1.865	0.891	-1.700	-1.205	1.478	0	2	0.185	-1.966	-0.547	1.865	0.891	-1.700	-1.205	1.478	0		
$E_{5g}\equiv X_g$	2	-0.547	-1.700	1.478	0.891	-1.966	0.185	1.865	-1.205	0	2	-0.547	-1.700	1.478	0.891	-1.966	0.185	1.865	-1.205	0		
$E_{6g}\equiv I_g$	2	-1.205	-0.547	1.865	-1.700	0.185	1.478	-1.966	0.891	0	2	-1.205	-0.547	1.865	-1.700	0.185	1.478	-1.966	0.891	0		
$E_{7g}\equiv K_g$	2	-1.700	0.891	0.185	-1.205	1.865	-1.966	1.478	-0.547	0	2	-1.700	0.891	0.185	-1.205	1.865	-1.966	1.478	-0.547	0		
$E_{8g}\equiv\Lambda_g$	2	-1.966	1.865	-1.700	1.478	-1.205	0.891	-0.547	0.185	0	2	-1.966	1.865	-1.700	1.478	-1.205	0.891	-0.547	0.185	0		
$A_{2u}\equiv\Sigma_u^+$	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	z	
$A_{1u}\equiv\Sigma_u^-$	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1		
$E_{1u}\equiv\Pi_u$	2	1.865	1.478	0.891	0.185	-0.547	-1.205	-1.700	-1.966	0	-2	-1.865	-1.478	-0.891	-0.185	0.547	1.205	1.700	1.966	0	(x, y)	
$E_{2u}\equiv\Delta_u$	2	1.478	0.185	-1.205	-1.966	-1.700	-0.547	0.891	1.865	0	-2	-1.478	-0.185	1.205	1.966	1.700	0.547	-0.891	-1.865	0		
$E_{3u}\equiv\Phi_u$	2	0.891	-1.205	-1.966	-0.547	1.478	1.865	0.185	-1.700	0	-2	-0.891	1.205	1.966	0.547	-1.478	-1.865	-0.185	1.700	0		
$E_{4u}\equiv\Gamma_u$	2	0.185	-1.966	-0.547	1.865	0.891	-1.700	-1.205	1.478	0	-2	-0.185	1.966	0.547	-1.865	-0.891	1.700	1.205	-1.478	0		
$E_{5u}\equiv X_u$	2	-0.547	-1.700	1.478	0.891	-1.966	0.185	1.865	-1.205	0	-2	0.547	1.700	-1.478	-0.891	1.966	-0.185	-1.865	1.205	0		
$E_{6u}\equiv I_u$	2	-1.205	-0.547	1.865	-1.700	0.185	1.478	-1.966	0.891	0	-2	1.205	0.547	-1.865	1.700	-0.185	-1.478	1.966	-0.891	0		
$E_{7u}\equiv K_u$	2	-1.700	0.891	0.185	-1.205	1.865	-1.966	1.478	-0.547	0	-2	1.700	-0.891	-0.185	1.205	-1.865	1.966	-1.478	0.547	0		
$E_{8u}\equiv\Lambda_u$	2	-1.966	1.865	-1.700	1.478	-1.205	0.891	-0.547	0.185	0	-2	1.966	-1.865	1.700	-1.478	1.205	-0.891	0.547	-0.185	0		

The new groups follow the finite and infinite groups well known rule:

$$C_{\infty v} \times C_i = D_{\infty h} \tag{3}$$

that can be written now as $$C_{nv}^{(\infty)} \times C_i = D_{nh}^{(\infty)} \tag{3'}$$

The digital (instead of cosφ) characters in the new tables are favouring, as mentioned before, an easier test of eq. (3'), and are better complying with the other finite groups (see Tables 7 and 8).

4. Discussion

The new pseudo-finite, $C_{nv}^{(\infty)}$ and $D_{nh}^{(\infty)}$ groups are, to a point, odd-*n* members of the C_{nv} and D_{nd} families, with some minor amendments in the last case: σ_d operation is renamed σ_v (the corresponding bases and characters are the same in the two groups for these operations) and changes position with the C_2 operation in the character table, both for a clear connection with $C_{nv}^{(\infty)}$. In addition, for the same reason, the A_{1u} and A_{2u} representations are interchanging their positions, while the Σ_u^+ and Σ_u^- are preserving their "gerade" order. This way the eq. (3') is clearly illustrated, like with the other finite groups.

There is an apparent supplementary, but harmless, difficulty that is met with the proposed groups for the symmetrical linear molecules: the model (a virtual one) has no horizontal symmetry plane, contrary to reality. This has no damaging effect, however, on the final results in all its applications. In spite of the fact that there is no σ_h, *h* is preserved in the $D_{nh}^{(\infty)}$ group's denomination to account for the real origin of the new group. The same explanation is given for introducing the "(∞)" right superscript.

In both cases, $C_{nv}^{(\infty)}$ and $D_{nh}^{(\infty)}$, the reduction formula,

$$a_i = \frac{1}{h}[\sum_R \chi(R)\chi_i(R)g(R)] \tag{4}$$

is reasonably valid. Here a_i is the number of times the *i*-th irreducible representation, Γ_i (Bethe's symbol) occurs in Γ, χ and χ_i are their characters, $g(R)$ is the number of operations in the class *R*, and *h* is the order of the group. So, the reduction formula operating by integration (needed with the infinite groups),

$$a_i = \int_0^{2\pi} \chi(R)\chi_i(R)dR / \int_0^{2\pi} dR \tag{5}$$

is no longer necessary, thus unifying all point groups as much as the operating rules are concerned, for spectral terms not higher than E_4 (Γ) (in the *n*=17 case).

A point is to be stressed here: using eq. (4), rounding the a_i value is necessary, but this operation is easily done by a PC, eliminating all ambiguity. In fact, this is working well enough even if we use characters with two decimals only, which simplifies the appearance of the newly proposed tables.

The new groups are showing both, the finite and infinite representation symbols.

Following eq. (2), *n* should preferably grow (for practical reasons) in steps of at least 4, from one approximation to another: *n*=5, 9, 13, 17, … , out of which we have chosen 9 and 17, as suitable for practical cases. The other possibilities, 3, 7, 11, 15, … , are inconvenient. They are connected with an odd-number of E_k representations which always leaves one of them unused.

The infinite origin of these groups must be kept in mind, by not taking "ad litteram" all results obtained with these newly proposed pseudo-finite groups for the combinations of higher representations, which could be, sometimes, out of the just proposed character table. These groups should be used in accordance with their clearly mentioned limitations (see Table 4), or, *in extremis*, pass to a higher group.

All properties of the *representations* and of their *characters* of the proposed groups are, with the mentioned restriction (limit to E_k for an E_{2k} table), those met with the classic, finite, groups and they are a consequence of the Orthogonality Theorem:

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'} \tag{6}$$

which can be splitted into three parts in order to be applied to specific conditions [3].

5. Conclusions

We can conclude this paper by saying that the proposed pseudo-finite groups, $C_{nv}^{(\infty)}$ and $D_{nh}^{(\infty)}$, for linear molecules, are good finite-like, adaptable, groups that can be used in relation with our specific needs. In some simple cases, $C_{9v}^{(\infty)}$ and $D_{9h}^{(\infty)}$, are all we need [9]. For energy levels described by wave functions which are bases for E_k with k>2 (Φ, Γ, etc.), like hybrid orbitals, or when dealing with higher order products (describing transitions, for example), however, one has to go to n-values over 9 (in practice, n=17 seems to be satisfactory), i.e., to higher order groups : $C_{17v}^{(\infty)}$ and $D_{17h}^{(\infty)}$. If still higher order representations are to be considered, the corresponding pseudo-finite groups can be deduced, very easily, in the same manner, from the original, $C_{\infty v}$ and $D_{\infty h}$ infinite ones.

The characters of the new pseudo-finite groups are simple numbers, and the operational problems, like reduction of a reducible representation to its irreducible components, are solved much easier in the new frame, like with the real finite groups.

The fact that the new groups are not completely closed is a minor inconsistency with no practical negative effect on their applications.

All point groups used in the optical spectroscopy are thus, operationally, a homogeneous set.

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