THE REDUCTION PROBLEM IN CERTAIN CONTINUOUS GROUPS[+]

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A simple method for the group-theoretical reduc-
tion of representations in problems dealing with
linear molecules is given. Character theory is
used within the framework of a uniquely soluble
system of inhomogeneous linear equations. By this
algebraic technique any cumbersome integrations
can be avoided. Examples for the groups $C_{\infty v}$ and
$D_{\infty h}$ are selected that appear in connection with
fundamental vibrations of linear molecules.

1.   Introduction

Much of the beauty and power of group-theoretical tech-
niques of one kind or another in chemistry is due to a syn-
thesis of rigorous symmetry arguments with quantum-mechanical
ideas and calculations of molecular properties. The quantum
mechanics concerning with the description of a chemical system
can be very complicated, but is is practically always possible
to extract by means of symmetry useful informations without
large numerical calculations. Two main approaches are visible:
from the qualitative view point geometric symmetry operations
(proper and improper rotations, etc.) and their homomorphic
mapping into a group of operators acting in some vector space
are used to predict both the number and kind of system states
together with selection rules for the large body of spectros-
copic and magnetic material, respectively. There is, however,
also a quantitative aspect, not so well known among chemists,
that is dealing with the calculation of matrix elements for
important operators related to observables. We mean the power-
ful Wigner-Eckart theorem[1] which allows by symmetry a factoriza-
tion of families of integrals into products of coupling coef-
ficients (Clebsch-Gordan-,Wigner type, vector addition type,
etc. , tabulated for most cases) and a small number of integrals
(so-called reduced matrix elements) typical for the problem.

The crucial point in each quantum-mechanical treatment is the selection of a sufficiently dimensional physical space for the specific problem under consideration from which the constructions of both the Hamiltonian and overlap matrices follow. The interesting dynamical **variables** (state vectors, energy expectation values, etc.) are found by solving the secular or eigenvalue problem through proper diagonalizations. It is in that area where group theory can be of great use for reduction of the order of these matrices: similarity transformations will generate direct sums of mutually independent matrices[2]. In other words, the symmetry properties of the system define both the size and structure of the corresponding eigenvalue algebra. In the context of this paper we are considering only point group symmetries, i.e. in the case of molecules an interchanging or renumbering of equivalent atoms in the nuclear framework by any rotation , reflection, and combinations therefrom. These symmetry properties are closely related with those of the competent Schrödinger equation due to invariance of the Hamilton operator under the group of symmetry operations for the molecule by commutation. A further observation is concerned with the behavior of the eigenfunctions. It turns out that these functions are basis vectors (in the physical space) for matrix representations of the symmetry group. Furthermore, and this is very important, the so-called irreducibility postulate[3] guarantees that this representation is irreducible under the action of the group (excluding "accidental degeneracy"). It must, however, be clearly understood that this postulate is a consequence of physics, and has nothing to do with group theory[4].

The consequences are heavy: making full use of symmetry means the decomposition of the starting vector space into those invariant (stable) subspaces which are irreducible in relation to the invariance or symmetry group of the Hamiltonian. Before actually dealing with matrices, symmetry-adapted basis vectors, and calculation of matrix elements (i.e. integrals), respectively, important aspects of the problem can be gained by incorporation of character theory for the reduction of the physical representation space. This step is both useful and simple (at least for finite groups) since it is completely independent of

any basis choice. On the other hand, calculations of both matrix elements and selection rules involving certain specific operators are dependent upon the selected bases in one and the same space. The real importance of representation characters for applications of symmetry arguments to physical and chemical problems is established in the fact that every (finite-dimensional) group representation over the field of complex numbers (with the reals forming a subfield) is uniquely determined up to equivalence by the set of ordered numbers that are the traces or characters of the corresponding representation matrices.

The point groups of chemical interest are subgroups of the orthogonal group in a three-dimensional space, $O(3)$, and its subgroup $O^+(3) = SO(3)$ with real unimodular orthogonal transformations. In case of matrices with complex elements one has, respectively, to consider the unitary groups $U(3)$ and $SU(3)$. The representation theory of these groups is well known and a large body of literature exists[5]. The point groups can be divided into the discrete and continuous representatives. Among the latter category the groups $C_{\infty v}$ and $D_{\infty h}$ (in Schönflies notation) are important for linear molecules.

The purpose of this paper is a consideration of the intrinsic difficulties in the reduction of representations for continuous subgroups of $O(3)$ relevant in chemistry. We found it very unappealing to use for these groups (invariant) integration procedures because of their Lie group nature to find the irreducible constitutents of a given representation space. In most cases of practical interest, e.g. in the fields of normal vibration treatment and ligand field theory, only a limited number of stable subspaces is important. Therefore, it seems desirable to look at finite-dimensional algebraic procedures (despite the infinite number of group elements).

The principle of the proposed method is to find a system of nonhomogeneous linear equations with a unique nontrivial solution, i.e., the frequencies of the irreducible parts in the vector space. The heart of the matter is the construction of a suitable coefficient matrix of the system whose elements are the irreducible (simple) characters. Their

selection depends upon both mathematical and physical arguments. Each different problem affords a different set of simple characters. Furthermore, the necessary reducible (compound) character vector is partly dependent upon the coefficient matrix of the system of equations used. In our present approach we concentrate on the groups $C_{\infty v}$ and $D_{\infty h}$, applying the method to some characteristic examples for vibrational analysis.

In Sec.2 we give group-theoretical information on those aspects for continuous groups that are necessary for the structure of $C_{\infty v}$ and $D_{\infty h}$. Sec.3 is devoted to the algebraic reduction procedure for representations of some vector space. These formal arguments will be combined in Sec.4 with physical requirements to solve some typical problems by sample calculations.

2. Group-theoretical remarks

Finite point groups are nowadays an indispensable aid for many branches of both theoretical and experimental chemistry. The character tables are consciously used for reduction of representations and charaterization of state energies and basis functions (e.g., the "orbital business"). On the other hand, point groups of infinite order, like the rotation group of the sphere (important for free atoms and ions), $O(3)$, and the subgroups $SO(3)$, $C_{\infty v}$, and $D_{\infty h}$, respectively, are used more intuitively in chemical applications. This is probably caused by the fact that a simultaneous existence of both the inifinite number of group elements forming a continuum (in a topological sense) and the closure property under the group multiplication law (in an axiomatic sense) is really not very encouraging for the mathematically untrained user of such groups. Looking into the literature, and there is a large body available with all levels of sophistication[6], is in most cases not stimulating enough for the practitioner: he will be forced to fight around with terms and high brow concepts, e.g., continuity in topology, compactness, connectivity, neighborhood of a group element, invariant measures and integrals, etc. In this context we are only dealing with continuous groups that can be derived from the so-called axial (rotation) group as the basic building block. Therefore, great simplifications in the concepts are possible.

Despite excellent treatments of the rotation group[7] it seems
appropriate to give here a short summary of the groups $C_{\infty v}$
and $D_{\infty h}$ in relation to our reduction method.

Let us start out from the simplest continuous point
group, C_∞, that arises from the possible rotations of some
linear molecule (e.g., N_2, HCN, N_3^-, CO_2, diacethylene C_4H_2)
around its main axis where all(!) constitutent atoms are si-
tuated. What are these possible rotations like? Elementary
geometrical drawings will show that in contrast to the finite
cyclic point groups, C_n, the angle of rotation $\phi = 2\pi/n$ ra-
dians can take any value producing thereby unchanged molecu-
lar configurations (i.e. the idea of a symmetry operation).
This means, vice versa, that n is not limited to integer va-
lues, but varies from 1 to ∞. Since the rotation axis is fixed
in space (for convenience we can identify it as the z axis of
a cartesian coordinate system) the rotation angle ϕ defines
unambiguously the element $R(\phi)$. The same is true for $R(\beta)$
where β means an angle again, etc., and there is a non-de-
numerable number of such rotations all defined by their angles
about the same axis. Furthermore, this unique axis makes the
set of all rotations by all (real-valued) angles ϕ, β,...
a closed manifold under the binary operation "followed by"
and clearly a group as a quick glance at the group axioms re-
veals. Here, $R(\phi = 0)$ and $R(-\phi)$ are the identity and the in-
verse, respectively. Lastly, the "parameter" (rotation angle)
ϕ is itself an element of a closed and bounded set of points,
e.g., $0 \leq \phi < 2\pi$. In more technical terms, this is an example
for the concept of compactness. (An extension of the parameter
manifold are the Eulerian angles α, β, γ that define the elements
of the rotation group in the Euclidian 3-space.) It turns out
that the emphasis in the continuous groups is shifted from the
group elements to functional relations between the (finite)
number of parameters whose real values vary continuously with-
in their (bounded) defining regions. One further property is
relevant: let $f(\alpha, \beta, \gamma, ..) = \phi$ be a functional relation to de-
termine the parameter ϕ from the parameters $\alpha, \beta, \gamma, ..$. If the
mapping f is an analytic function in the sense that $f(\alpha, \beta, \gamma, ..)$
can be differentiated any number of times with respect to α

or ß or γ or .., then the corresponding group elements form a Lie group[8].Therefore, in our case the group C_∞ is an example for a one-parameter compact Lie group. In addition the group is abelian since arbitrary rotations about an axis always commute. We now leave the abstract concepts of C_∞ and turn towards its representations.

C_∞ is generated as a point group by the action of the position vector with invariant origin (the "point") in 3-space, e.g., $\vec{r} = (\vec{e}_1,\vec{e}_2,\vec{e}_3)(x,y,z)^T$ in the usual notation. Since the z component of $\vec{r}$ is not affected by the rotations $R_z(\phi)$ about a z axis the natural basis to generate matrix representatives of the group elements is the set of unit vectors, $(\vec{e}_1,\vec{e}_2)$, along both the x and y axis.By trigonometry,we extract (using the active point of view[9]) the matrix representation for $R_z(\phi)$, $\underline{R}_z(\phi)$:

2.1 $\quad \hat{R}_z(\phi) \, (\vec{e}_1,\vec{e}_2) = (\vec{e}_1,\vec{e}_2) \, \underline{R}_z(\phi) \implies \underline{R}_z(\phi) = \begin{pmatrix} \cos\phi, & -\sin\phi \\ \sin\phi, & \cos\phi \end{pmatrix}$.

Due to the cyclic nature of the group $\underline{R}_z(\phi)$ is termed a generator for the matrix group SO(2) isomorphic with C_∞ via Eq.2.1, and the concept of an infinitesimal operator being important in the theory of angular momentum appears in a natural way by making the angle ϕ infinitesimally small but not zero[10]. It is obvious that $\left\{\underline{R}_z(\phi)\right\}$ belongs to a reducible representation (rrep) since C_∞ is abelian and all irreducible representations (ireps) have to be one-dimensional. The reduction is via a basis transformation from the real space of the position vector to the complex (unitary) space of the spherical harmonics, i.e. the functions $\left\{Y_{lm}(\Theta,\phi)\right\}$ well known in mathematical physics. Further considerations of the continuity and periodicity of the functional relations of two angles, e.g., ϕ_1 and ϕ_2

2.2 $\quad f(\phi_1)f(\phi_2) = f(\phi_1 + \phi_2) = f(\phi_2)f(\phi_1)$,

$\qquad f(\phi + 2\pi) = f(\phi)$, $\phi,\phi_1,\phi_2 \in \mathbb{R}$,

show that the only solutions of Eq.2.2 are because of

2.3 $\quad \hat{R}_z(\phi) \, Y_{lm}(\Theta,\phi) = Y_{lm}(\Theta,\phi-\phi) = \exp(-im\phi) \, Y_{lm}(\Theta,\phi)$

in the form of one-dimensional matrices (= characters):

2.4 $\qquad \chi^{(m)}(\phi) = \exp(im\phi)$, with m = 0,±1,±2,±3,....

We end up with a denumerable infinite number of unitary ireps, all one-dimensional, for C_∞ consisting of a non-denumerable infinite number of group elements! This is a striking difference from the finite groups and must have consequences for both the orthogonality relations of the ireps and the reduction procedure of rreps. For the property in Eq.2.4 some references use the symbol for the special unitary group, SU(1), instead of our symbol C_∞. The character table is completely determined by Eq.2.4 where the integer m labels the ireps and is, in physical terms, a so-called "good" quantum number for both state vectors and eigenvalue problems in the mth subspace.

From the chemical point of view the group C_∞ is not very important since all linear molecules have more symmetry than the rotations $\{R_z(\phi)\}$. By inspection, one discovers always an infinite number of reflections σ_v in all mirror planes containing the molecular axis. (σ_v belongs to the category of the "improper" rotations in contrast to the proper or genuine ones.) From abstract group theory it turns out that the appearance of only one symmetry operation σ_v generates by action on the group C_∞[11] a new non-abelian group that is not of the direct product type[11] since σ_v and $R_z(\phi)$ dont commute. A more detailled analysis[12] shows that the new group, named $C_{\infty v}$, is a semi-direct product, i.e. $C_{\infty v} = C_\infty \text{Ⓢ} C_s$ where C_∞ is a normal subgroup, and $C_s = \{E, \sigma_v\}$. To learn the character structure we start from the relations in $C_{\infty v}$, i.e.

2.5 $\qquad R_z(\phi)\ \sigma_v = \sigma_v\ R_z(-\phi)$, and

2.6 $\qquad \sigma_v\ \sigma_v = \sigma_v^2 = E$.

Therefore, the set $\{R_z(\phi), R_z(-\phi)\}$ forms a class (of conjugate group elements) often written $2R_z(\phi)$, whereas the infinite many σ_v are also a class. A proper choice of bases in the sense of Eqs.2.1 and 2.3 will yield the matrix generators

2.7 $\qquad R_z(\phi) = \begin{pmatrix} \exp(-im\phi) & 0 \\ 0 & \exp(im\phi) \end{pmatrix}$, $\sigma_v = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

For $m \neq 0$ the functions $\{Y_{1m}, Y_{1\bar{m}}\}$ with $\bar{m} = -m$ are a natural basis for the 2-dimensional ireps, and there are no higher-dimensional ireps in that group. Besides the trivial irep or

identity rep there must be, as a consequence of Eq.2.6, a second one-dimensional rep in the group with character -1 under the $\{\sigma_v\}$. With these informations the character table in Table 1 is obtained where the entries have the usual meaning.

Table 1. Character table for $C_{\infty v}$. m = 1,2,.... .

$G = C_{\infty v}$	E	$2R_z(\phi)$	$\infty \, \sigma_v$	relevant bases
$\Gamma_1 = A_1 = \sum^+$	1	1	1	$z;\; z^2;\; x^2+y^2;\; Y_{10}$
$\Gamma_2 = A_2 = \sum^-$	1	1	-1	R_z
$\Gamma_m = E_m$	2	$2\cos(m\phi)$	0	for m=1: (R_x,R_y); (x,y); (xz,yz); $(Y_{11},Y_{1\bar{1}})$ for m=2: $(Y_{12},Y_{1\bar{2}})$

For those linear molecules having inversion symmetry too, e.g., N_2, CO_2, N_3^-, a new non-abelian group, named $D_{\infty h}$, arises that can be described in different ways, i.e. as direct product $C_{\infty v} \otimes C_i$, with both $C_{\infty v}$ and $C_i = \{E,i\}$ normal subgroups or, respectively, as a semidirect product $C_\infty \, \textcircled{s} \, C_s \otimes C_i =$ $= C_\infty \, \textcircled{s} \, C_{2h}$, with $C_{2h} = \{E, \sigma_h, C_{2z}, i\}$. We prefer the direct product formalism since the character table of $D_{\infty h}$ originates from those of the parent groups simply as supermatrix $\underline{X}(D_{\infty h})$:

$$2.8 \quad \underline{X}(D_{\infty h}) = \underline{X}(C_{\infty v}) \otimes \underline{X}(C_i) = \begin{pmatrix} \underline{X}(C_{\infty v}) \cdot 1, & \underline{X}(C_{\infty v}) \cdot 1 \\ \underline{X}(C_{\infty v}) \cdot 1, & \underline{X}(C_{\infty v}) \cdot -1 \end{pmatrix} ,$$

where $\underline{X}(C_{\infty v})$ is the character table as matrix taken from Table 1. The numbers in the direct product matrix of Eq.2.8 belong to the (matrix) character table of the point group C_i. There will be no problems in labeling the non-countable infinite number of elements into classes and the discrete infinite number of arising ireps Γ_i in using Eq.2.8 correctly. Let us note here that we use the character tables of $C_{\infty v}$ and $D_{\infty h}$ in a modified matrix form in our reduction method described in the following section.

In concluding this section, we mention that from a topological view point the presence of a discrete subgroup (C_s, C_i, C_{2h}) besides the continuous subgroup C_∞ modifies the somewhat naive conception of Lie groups from above. Since, however, compactness remains we need not go into further details[5,8].

3. The algebraic reduction method

Most applications of symmetry analysis in chemistry are resting upon representation theory. Furthermore, the starting reps are finite-dimensional unitary (or orthogonal) matrices in the case of finite groups. A well-known theorem[5] secures that such rreps can always be reduced uniquely into a direct sum of unitary (or orthogonal) ireps. These ireps are associated with the physically relevant subspaces of the specific problem. Character theory gives a very quick information in that respect. For convenience of the reader we summarize the (well known) relevant expressions for finite groups G: a reduction process due to the theorem cited above for the rrep Γ and the corresponding character system $X^{(\Gamma)}$ implies:

$$3.1 \qquad \Gamma = \sum_{i=1}^{\infty} a_i \; \Gamma_i \implies X^{(\Gamma)}(R) = \sum_{i=1}^{\infty} a_i \; X^{(i)}(R) \; , \; R \in G.$$

The important feature of Eq.3.1 is the uniqueness of the non-negative integers in the set $\{a_i\}$. Specifically, a_i labels the number of times (= frequency or multiplicity) the irep Γ_i is contained in Γ. Of course, the $\{\Gamma_i\}$ is only determined up to equivalence. By means of the famous orthogonality relations for simple characters, the reduction formula follows from Eq.3.1:

$$3.2 \qquad a_i = (1/g) \sum_{R} X^{(\Gamma)}(R) \; X^{(i)}(R)^* \; , \qquad \forall \; R \in G \; ,$$

where the summation is over all (= g) group elements in G. The complex conjugation mark assures the real nature of $\{a_i\}$.

Using this reduction procedure for continuous groups G would imply an infinite sum in Eq.3.2; the way out is a special integration over the defining regions of the parameters (angles) instead of the group elements. The technique of ("invariant") integration involves among other specialities the concept of a "group volume" in the parameter manifold since the order g has no meaning[5,6]. Since our method avoids any integration via a modified form of Eq.3.2, we can leave this cumbersome route.

Fortunately, the continuous groups $G = C_{\infty}$, $C_{\infty v}$, $D_{\infty h}$, and $O(3)$, among others, are characterized by compact parameter spaces. This property causes the validity of some important theorems from finite groups also for these category G. Without

proof[6], we summarize the basic facts for our purposes:

3.3 a) each rep of a compact group is equivalent to a uni-
     tary one;
    b) any rep is completely reducible into finite-dimen-
     sional ireps via the direct sum formalism;
    c) inequivalent ireps are orthogonal.

Due to these properties, Eq.3.1 is taken as the starting point
for the algebraic reduction method in compact groups (later
in the paper applied to $C_{\infty v}$ and $D_{\infty h}$) using (without loss of
generalization) character theory:

    Let us look at Eq.3.1 from the view point of a linear
transformation relating two vector spaces over the same field.
By defining proper bases, we can represent the mapping in
terms of a matrix form which is nothing else but a system of
linear nonhomogeneous equations. The method implies, there-
fore, the selection of both necessary and sufficient equations
(of the type given in the character part of Eq.3.1), i.e.

3.4 $\underline{X}^{(\Gamma)} = \underline{a} \ \underline{X}(G)$,

where the entries have the following meaning:

3.5 $\underline{X}^{(\Gamma)} = \left\{ X^{(\Gamma)}(E), X^{(\Gamma)}(R_2), \ldots, X^{(\Gamma)}(R_r), \ldots \right\}$, for the
               "canonical" $R \in$ compact group G;

   $\underline{a} = \left\{ a_1, a_2, \ldots, a_r, \ldots \right\}$, i.e. the multiplicity vector;

   $\underline{X}(G)$ is the "canonical" part of the character table of G.
The emphasis to the word "canonical" is to remind the user of
the problem under investigation that physical arguments are
responsible for the selection of the character vector $\underline{X}^{(\Gamma)}$
and the interesting part out of the character matrix $\underline{X}(G)$ con-
taining the chemically relevant ireps, respectively. We will
come back to these aspects in the next section.

    Mathematically, we are looking for a unique non-trivial
solution of the unknowns $\left\{ a_i \right\}$ in Eq.3.4, given the transforma-
tion matrix $\underline{X}(G)$ and (row) vector $\underline{X}^{(\Gamma)}$. Again, for convenience
of the reader, we restate the criteria from the theory of
linear equations:

3.6 Theorem. Eq.3.4 has a unique non-trivial solution:

$$\Longleftrightarrow \quad \underline{X}(G)^{-1} \text{ exists } .$$

Therefore, the (row) vector $\underline{a}$ can be obtained from the matrix form $\underline{X}^{(\Gamma)}\underline{X}(G)^{-1}$ or via the theorem of Cramer, for example.

Concluding the mathematical part, we remind the reader of the fact that in the case of finite (point) groups the corresponding character tables intrinsically fulfill Eq.3.6 with rank r = number of classes = number of possible ireps.

4. The method in practice

As cited previously, the method is based upon the balance of the significant symmetry features of the problem with mathematical requirements for a unique solution. We present the procedure and will immediately apply it for the compact groups $C_{\infty v}$ an $D_{\infty h}$ dealing with the calculation of fundamental vibrational species for certain linear molecules. This example is used because most chemists performing infrared and Raman spectroscopic routines will be familiar with it, and the method is, therefore, not hidden behind heavy physical arguments.

The construction and solution of Eq.3.4 will in any case imply a coefficient matrix, i.e. character table $\underline{X}(G)$, of frame

4.1
$$\underline{X}(G) = \begin{pmatrix} 1 & 1 & 1 & \cdots\cdots & 1 \\ 1_2 & \cdot & \cdot & \cdot & \cdot \\ 1_3 & \cdot & \cdot & \cdot & \cdot \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ 1_r & \cdot & \cdot & \cdot & \cdot \end{pmatrix} , \text{ i.e. } X^{(i)}(E) = 1_i ,$$

where both the first row (= identity rep) and column (= dimensions of invariant subspaces realized by ireps of G) are "canonical" informations in view of Eq.3.5. The next step includes the search for the size of $\underline{X}(G)$ by determination of the rank index r due to the theorem Eq.3.6: let r_g be the number of generators for the (compact) group G and let r_i be the number of problem-relevant ireps therein that must be selected by physical and chemical reasoning. In this context we have, contrary

to common usage in group theory, in r_g the identity element E
of G included to have agreement with the information content
of Eq.4.1. The size of $\underline{X}(G)$ is always given by an equal (= r)
number of both lines and columns, i.e.

4.2 $\underline{X}(G) = \text{type}(r,r) = \text{type}(r_i + (r-r_i), r_g + (r-r_g))$.

The recipe depends upon our knowledge of r_i and r_g. Three pos-
sibilities have to be considered:

4.3   Case I   : $r_i = r_g$ (= r), exceptional situation;

        Case II : $r_g < r_i$ (= r), usual situation;

        Case III: $r_i < r_g$ (= r), exceptional situation.

Depending upon the specific situation, one has to select either
$(r-r_g)$ additional group elements or $(r-r_i)$ additional ireps for
completion. The missing simple characters must then be calcu-
lated using standard formulae. These selections for the matrix
$\underline{X}(G)$ are arbitrarily up to the controlling requirement that
the rank remains r for the three cases, i.e. $\det(\underline{X}(G)) \neq 0$.
The final step is the calculation of the compound characters
in the vector $\underline{X}^{(\Gamma)}$ of Eq.3.5 for those group elements that
have finally been selected for $\underline{X}(G)$. With these informations
at hand Eq.3.4 is complete and uniquely soluble for $\{a_i\}$.

        Examples. For illustration purposes we follow along the
usual standard treatments for (elastic) motions of linear mo-
lecules[13]. We are concentrating on characteristic vibrations
(including translations and rotations of molecules as a whole)
in symmetries $C_{\infty v}$ and $D_{\infty h}$. The physically relevant ireps for
translations (T_x, T_y, T_z), rotations $(R_x, R_y$, but R_z is not in-
volved), infrared vibrations (1.rank tensor), and Raman vibra-
tions (2.rank tensor) are collected in Table 2. The g(erade)-
part and u(ngerade)-part of $D_{\infty h}$-ireps is obtained from the
first and second line, respectively, of the supermatrix in
Eq.2.8 with Table 1. For the number and quality of the so-cal-
led fundamental vibrations (= normal modes) the two bottom
lines in Table 2 are appropriate. It is a remarkable feature
that only a few ireps are "canonical" for general vibrations.

Table 2. Canonical ireps for general motions of linear molecules.(Symbols are explained in the text.)

property	$C_{\infty v}$	$D_{\infty h}$ g-part	u-part
T_x, T_y	E_1		E_{1u}
T_z	A_1		A_{1u}
R_x, R_y	E_1	E_{1g}	
R_z			
infrared	A_1, E_1		A_{1u}, E_{1u}
Raman	A_1, E_1, E_2	A_{1g}, E_{1g}, E_{2g}	

It is favorable for the user to have general formulae at hand for the characters of the genuine vibrational part in linear molecules. These data, $X_{vib}^{(\Gamma)}(R)$, are for some typical general group elements (symmetry operations):

4.4 $X_{vib}(E) = 3N - 5$ (for N-atomic linear chain);

$X_{vib}(C_n) = (n_p - 2)(1 + 2\cos \phi) + 1$, $\phi = (2\pi/n)$;

$X_{vib}(\sigma_v) = n_p - 1$; $X_{vib}(C_2') = -n_p + 1$;

$X_{vib}(i) = -3n_p + 1$;

n_p is the number of unmoved atoms under the action of $R \in G$, and the notation C_n will serve instead of the symbol $R_z(\phi)$. Special values for $(1+2\cos \phi)$ are collected in Table 3 for the most useful elements $R \in G$ for $G = C_{\infty v}$, $D_{\infty h}$.

Table 3. Useful characters $(1 + 2\cos \phi)$ for some R.

element R	E	C_2	C_3	C_4	C_6	σ_v	i
$X_{vib}(R)$	3	-1	0	1	2	1	-3

The informations in Eq.4.4 and Table 3 are used for the calculation of the character vector $\underline{X}^{(\Gamma)}$ for the rep Γ_{vib}. Since the vector coordinates are dependent upon $\underline{X}(G)$ we need data for simple characters. These are given, again for convenience, in Table 4 where the calculations are based in parts upon Table 1. Now we are ready for some examples and will treat specific molecules for Cases I and II in Eq.4.3.

Table 4. Selection of simple characters for $\underline{X}(G)$.

column R		E	C_2	C_3	C_4	C_6	σ_v
A_1	$= \sum^+$	1	1	1	1	1	1
A_2	$= \sum^-$	1	1	1	1	1	-1
E_1	$= \Pi$	2	-2	-1	0	1	0
E_2	$= \triangle$	2	2	-1	-2	-1	0
E_3	$= \Phi$	2	-2	2	0	-2	0
E_4		2	2	-1	2	-1	0
E_5		2	-2	-1	0	1	0

for $D_{\infty h}$ -parts:

g: $X(i) = + X(E)$

u: $X(i) = - X(E)$

$X(C_2^!) = X(\sigma_v) X(i)$

Case I - example. For the group $C_{\infty v}$ there are three canonical generators (cf. Sec.2), and three relevant ireps de- termine the vibrational motions (cf. Table 2), i.e. $r_g = r_i = 3$. This means for $\underline{X}(G)$ in any case the structure:

4.5
$$
\begin{array}{c} \\ A_1 \\ E_1 \\ E_2 \end{array}
\begin{array}{ccc} E & C_n & \sigma_v \\ \begin{bmatrix} 1 & 1 & 1 \\ 2 & x_1 & 0 \\ 2 & x_2 & 0 \end{bmatrix} \end{array} = \underline{X}(C_{\infty v}) \, .
$$

In principle we are free in the selection of the rotational generator C_n ($n \neq 1, 1 < n \leqslant \infty$). The only requirement is the non- singularity of $\underline{X}(G)$, cf. the discussion following Eq.4.3. We can take any rotation (around the molecular z-axis) for values of x_1 and x_2 in Eq.4.5 except C_3. The simplest case will be C_4 from Table 4, with $x_1 = 0$ and $x_2 = -2$.

Let us take the specific molecule D-C≡C-H. Since N=4 and $n_p = 4$ for $R = \{E, C_4, \sigma_v\}$ the vector $\underline{X}_{vib}^{(\Gamma)}$ for Eq.3.4 has the coordinates calculated with Eq.4.4 and Table 3:

4.6
$$
\underline{X}_{vib}^{(\Gamma)} = \begin{array}{ccc} E & C_4 & \sigma_v \\ \{ 7 & , & 3 & , & 3 \} \end{array} \, .
$$

Eq.3.4 can now be formulated in terms of three (= r) simul- taneous equations considering Eqs.4.6 and 4.5 using C_4:

4.7
$$
\begin{cases} \begin{array}{ccc} A_1 & E_1 & E_2 \\ 7 = a_1 + 2a_2 + 2a_3 , \\ 3 = a_1 \quad\quad - 2a_3 , \\ 3 = a_1 \quad\quad\quad , \end{array} \end{cases} \longrightarrow (\text{i.e. } X^{(\Gamma)}(E) = \sum_{i=1}^{r} a_i \, l_i)
$$

with the solution $\underline{a} = \{a_1, a_2, a_3\} = \{3, 2, 0\}$. The rrep Γ_{vib} is therefore the direct sum of ireps $3A_1 \oplus 2E_1$. Hence there are three fundamental frequencies of the non-degenerate A_1-type and two double-degenerate ones of the E_1-type for this species. Other $C_{\infty v}$ - molecules can be treated in like manner.

Case II - example. Due to the direct product nature of $D_{\infty h}$ from the parent groups $C_{\infty v}$ and C_i there are four canonical generators, i.e. $\{E, C_n, \sigma_v, i\}$, but vibrational problems afford five ireps (cf. Table 2), i.e. $r_g < r_i$ and we need one additional group element (e.g., a second rotation) for $\underline{X}(G)$. A useful matrix is for instance (with Table 4), where $C_2' = i\,\sigma_v$:

4.8

$$
\begin{array}{c} \\ A_{1g} \\ E_{1g} \\ E_{2g} \\ A_{1u} \\ E_{1u} \end{array}
\begin{array}{ccccc}
E & C_2' & C_4 & \sigma_v & i \\
\left[\begin{array}{ccccc}
1 & 1 & 1 & 1 & 1 \\
2 & 0 & 0 & 0 & 2 \\
2 & 0 & -2 & 0 & 2 \\
1 & -1 & 1 & 1 & -1 \\
2 & 0 & 0 & 0 & -2
\end{array}\right]
\end{array} = \underline{X}(D_{\infty h}) \ .
$$

We consider two molecules, i.e. azide ion N_3^- and diacetylene $H-C\equiv C-C\equiv C-H$. The following data are obtained from Table 3 and Eq.4.4:

4.9

$$
\begin{array}{llccccc}
& E & C_2' & C_4 & \sigma_v & i \\
n_p = & 3 & 1 & 3 & 3 & 1 \\
\underline{X}(\Gamma)_{vib} = & 4 & 0 & 2 & 2 & -2
\end{array} \Bigg\} \text{ for azide ion } (N=N=N) \ ,
$$

$$
\begin{array}{llccccc}
n_p = & 6 & 0 & 6 & 6 & 0 \\
\underline{X}(\Gamma)_{vib} = & 13 & 1 & 5 & 5 & 1
\end{array} \Bigg\} \text{ for diacetylene} \qquad .
$$

The solutions of the two linear equation systems, Eq.3.4, are easily obtained (because of the non-negative integer nature of the multiplicity vector $\underline{a}$). For N_3^- $\underline{a} = \{1, 0, 0, 1, 1\}$ and for diacetylene $\underline{a} = \{3, 2, 0, 2, 2\}$. This determines for both cases the number and quality (irep, degeneracy) of the fundamental vibrations.

With the same method it is of course possible to solve other more elaborated problems in that field, like selection rules for combinations frequencies or overtones that involve direct product characters with special symmetry adaption tech-

niques. Since no new aspects appear for the algebraic method besides an increase of the number of canonical ireps and, consequently, a larger rank of the matrix $\underline{X}(G)$, we dont pursue these applications here.

5.   Conclusions

In this paper we have presented an algebraic reduction method for reducible representations of the compact groups $C_{\infty v}$ and $D_{\infty h}$. This technique based upon character theory avoids the usual integration procedures for continuous groups. The basic idea emerged from the fact that for most applications of both physical and chemical interest only a relatively small number of irreducible representations (ireps) is important (i.e. "canonical"). Closer investigations (in Sec.3) have lead to a much simpler approach of the reduction problem via unique and non-trivial solutions of Eq.3.4 as a matrix form of low order. The choice of the character matrix $\underline{X}(G)$ therein is dependent upon both mathematical and(!) physical criteria. The application for a problem in vibrational analysis of linear molecules shows clearly the simplicity of this method.

Finally, we are considering at present this technique for applications in the groups $O(3), SO(3)$, and certain finite groups of large order.

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