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A Method for Obtaining the Redundancy Condition among Internal Displacement Coordinates in Molecular Vibrations

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Chimica fisica. — *A Method for Obtaining the Redundancy Condition among Internal Displacement Coordinates in Molecular Vibrations* (*). Nota di MARIANGELA GUSSONI e GIUSEPPE ZERBI, presentata (**) dal Socio G. NATTA.

RIASSUNTO. — Viene proposto un nuovo e semplice metodo per ottenere la relazione di dipendenza per le « internal displacement coordinates ».

Tale metodo sfrutta le singolarità della matrice dell'energia cinetica in coordinate dipendenti ed è facilmente automatizzabile per calcolatori elettronici. Gli altri metodi della lettaratura al contrario esigono un notevole sviluppo algebrico e non sono automatizzabili.

The problem of redundant coordinates is often encountered when the vibration of a molecule is described in terms of the internal coordinates r_t [1]. Symmetry reasons may in fact suggest the use of all the possible internal coordinates of the molecule even if their number is larger than its degrees of freedom. The dependency thus introduced is usually called redundancy.

For sake of clearness we will distinguish the internal coordinates from their small displacements. Bond, bond angles, out of plane and torsional angles are called internal coordinates (r_t). They are independent of the translations and the rotations of the molecule as a whole. Their use would be rather cumbersome, since they are related to the cartesian coordinates by a non–linear relation. However, a drastic simplification has been introduced by Wilson [2]. As long as we are interested only in the small vibrations of the molecule around the equilibrium we may take as coordinates only the small changes in the internal coordinates. We may approximate these changes by means of small linear displacements, which are thus linearly related to the cartesian ones. We call ρ_t the approximated small changes in the internal coordinates (1).

When a set of redundant internal coordinates is adopted, a relation exists among them and may be written explicitly in the form

$$\Phi(r_t) = 0 \qquad (1)$$

Full methods for writing the relation (1) in the case of branching [3, 4, 5] and cyclic [6] redundancies are already described in the literature.

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(1) Wilson calls internal coordinates the internal displacements, but we prefer the present notation to avoid confusion in the following.

The methods however are rather cumbersome and require a differentiation in order to reach the desired relation

$$\Phi(\rho_t) = 0 \tag{2}$$

from eq. (1). Since only the relation (2) among the internal displacement coordinates is of interest to us, we have worked out a method which allows to write it directly for any type of redundancy. The method which we propose has been also automatized for use on computers.

It has been noticed [7] that in the Wilson approximation relation (2) has always the linear form

$$\sum_t^M \Phi_t \rho_t = 0 \tag{3}$$

where the sum is extended to all the M internal coordinates in the molecule and Φ_t are the partial derivatives of $\Phi(r_t)$ taken at the equilibrium. Wilson, Decius and Cross have shown in their book [8] that the existence of a relation like (3) among the internal displacement coordinates is the *sufficient* condition in order that the kinetic energy matrix G expressed in the same system be singular. We shall prove in Appendix I that eq. (3) is also the *necessary* condition for the singularity of the G matrix. We thus know that when a redundancy is present among the coordinates the G matrix is singular and that when the G matrix is singular a redundancy (2) is present among the coordinates.

We will show now the use of the singularity of the G matrix in order to obtain the redundancy relation (2) without knowing its primary form (1).

Let us take a singular G matrix and diagonalize it

$$GD = D\Gamma$$

Here Γ is the transformed G matrix, i.e. the diagonal matrix formed by its eigenvalues and D is the matrix formed by its eigenvectors. The eigenvector D_K belonging to the zero eigenvalue is given by

$$GD_K = 0$$

and may be written in the form [10]

$$D_K = \{G_{k1}, G_{k2}, \cdots, G_{kM}\}$$

where the G_{ki} are the algebraic complements of the elements of the k–th row or column of the G matrix. The singularity of the G matrix yields

$$\sum_t^M g_{kt} G_{kt} = 0 . \tag{4}$$

(2) In the present paper we deal with the case where only one redundancy exists among the coordinates. The generalization to more than one redundancy is obvious.

Comparison of eq. (4) with the equation

$$\sum_{t}^{M} \Phi_t \, g_{kt} = 0$$

resulting from the discussion of Appendix 1, yields

$$G_{kt} = \alpha \Phi_t$$

where α is a constant coefficient.

We may thus conclude that the elements of the eigenvector belonging to the zero eigenvalue are proportional to the coefficients of the redundancy. Therefore it is possible to express the redundancy relation in the form

$$\sum_{t}^{M} G_{kt} \, \rho_t = 0 .$$

When a computer is available the method presented here for finding the coefficients of the redundancy avoids many troublesome calculations. We give in Appendix 2 some typical examples of redundancy relations obtained by a suitable diagonalization of the G matrix by means of a program we have coded for the 7040 IBM macchine.

It may be of interest to mention here that another and similar method to obtain the redundancy relation may be described working only on the B matrix. When the coordinates are dependent through a relation like (3) a relation exists among the rows of the B matrix in the form

$$\sum_{t}^{M} \Phi_t \, b_{tk} = 0 .$$

Since this relation holds for every k, we may form a system of 3 N equations in M unknowns to find the Φ_t coefficients. However, since the B matrix is not symmetrical, difficulties may be found for the solution on computers through diagonalization. The method of the G matrix seems to be more suitable.

APPENDIX 1.—The singularity of the G matrix is not an immediate consequence of the dependence among the coordinates. The proof of this fact needs some considerations which have been made in ref. [8]. Also the proof of the opposite is not immediate. We try to show it here.

If the G matrix described in the ρ–space is singular, a linear combination must exist among its rows (and its columns)

$$\sum_{t}^{M} a_t \, g_{tt'} = 0 . \qquad \text{(A 1.1)}$$

The $g_{tt'}$ are defined as [1]

$$g_{tt'} = \sum_{k}^{3N} \frac{1}{m_k} \, b_{tk} \, b_{t'k}$$

where the sum over k is extended to the 3 N cartesian displacements. The b_{tk} are the coefficients of the linear transformation which relates, in Wilson's approximation, the cartesian displacement coordinates ξ_k and the internal displacement coordinates ρ_t

$$\rho_t = \sum_k^{3N} b_{tk}\,\xi_k .$$

An equivalent relation can be written as

$$\rho_t = \sum_\alpha^{N} \bar{s}_{t\alpha} \cdot \bar{\xi}_\alpha$$

where the $\bar{s}_{t\alpha}$'s are the so-called Wilson vectors and the $\bar{\xi}_\alpha$ are the vector displacements of the atoms from the equilibrium. Substitution of $g_{tt'}$ into eq. (A 1.1) yields

$$\text{(A 1.2)} \qquad \sum_k^{3N} \left\{ \frac{1}{m_k} \sum_t^{M} a_t\, b_{tk} \right\} b_{t'k} = 0 .$$

This equality may be verified by the dependence of the $b_{t'k}$ or by the vanishing of all their coefficients in the sum over k. There are two kinds of dependencies among the $b_{t'k}$, namely the two Eckart conditions.

The first condition [9]

$$\sum_\alpha^{N} \bar{s}_{t'\alpha} = 0$$

can be projected on the cartesian axes $\bar{e}_i$, $\bar{e}_j$, $\bar{e}_k$ yielding

$$\sum_\alpha^{N} \bar{s}_{t'\alpha} \cdot \bar{e}_i = 0$$

$$\sum_\alpha^{N} \bar{s}_{t'\alpha} \cdot \bar{e}_j = 0$$

$$\sum_\alpha^{N} \bar{s}_{t'\alpha} \cdot \bar{e}_k = 0$$

and written as a function of the $b_{t'i}$, which are the projections of the Wilson vectors on the cartesian axes [14]

$$\text{(A 1.3)} \qquad \begin{cases} \sum\limits_{\substack{k \neq 2n \\ k \neq 3n}}^{3N} b_{t'k} = 0 \\ \sum\limits_{\substack{k \neq n \\ k \neq 3n}}^{3N} b_{t'k} = 0 \\ \sum\limits_{\substack{k \neq n \\ k \neq 2n}}^{3N} b_{t'k} = 0 \end{cases} \qquad (n = 1, 2, \cdots, N) .$$

Eq. (A 1.3) coincides with eq. (A 1.2) if and only if

$$\sum_{t}^{N} a_t \, b_{tk} = \lambda m_k$$

where λ is an arbitrary constant. This equation cannot be true because both the coefficients a_t and b_{tk} are determined only by the geometry of the molecule and are completely independent of the masses. The second Eckart condition [9]

$$\sum_{\alpha}^{N} \overline{R}_\alpha \times \bar{s}_{t'\alpha}$$

can be put in the scalar form

$$\text{(A 1.4)} \qquad \left\{ \begin{array}{lll} \sum_{k}^{3N} A_k \, b_{t'k} = 0 & \text{where} \quad A_k = 0 & \text{if} \quad k = 3\alpha - 2 \\ & A_k = -R_{k+1} & k = 3\alpha - 1 \\ & A_k = R_{k-1} & k = 3\alpha \\ \sum_{k}^{3N} A_k \, b_{t'k} = 0 & A_k = -R_{k+2} & k = 3\alpha - 2 \\ & A_k = 0 & k = 3\alpha - 1 \\ & A_k = R_{k-2} & k = 3\alpha \\ \sum_{k}^{3N} A_k \, b_{t'k} = 0 & A_k = -R_{k+1} & k = 3\alpha - 2 \\ & A_k = R_{k-1} & k = 3\alpha - 1 \\ & A_k = 0 & k = 3\alpha \end{array} \right.$$

(α refers to the number of the atoms and R_α^j is the component on the j-th cartesian axis of the equilibrium position vector $\overline{R}_\alpha$ of atom α in the cartesian system). Eq. (A 1.4) coincides with eq. (A 1.2) if and only if

$$\sum_{t}^{M} a_t \, b_{tk} = \lambda A_k \, m_k$$

where λ is an arbitrary constant. This cannot be true for the same reasons discussed in the former case. Thus eq. (A 1.2) is true if and only if

$$\text{(A 1.5)} \qquad \sum_{t}^{M} a_t \, b_{tk} = 0 \, .$$

Since this relation holds for every k, it must also be true that

$$\text{(A 1.6)} \qquad \sum_{t}^{M} a_t \, \rho_t = 0 \, .$$

Therefore the singularity in the G matrix depends on a linear relation among the internal displacement coordinates.

Let us now show that the coefficients a_t in eq. (A 1.6) are the partial derivatives of $\Phi(r_i)$ taken at the equilibrium position like in eq. (3). From

the definition of the internal displacement coordinates through the Wilson vectors [9], it directly follows that the redundancy among internal displacement coordinates may be written in the form

$$\text{(A 1.7)} \qquad \sum_t^M \Phi_t \rho_t = \sum_t^M \left(\frac{\partial \Phi}{\partial r_t}\right)^{eq} \sum_i^{3N} \left(\frac{\partial r_t}{\partial x_i}\right)^{eq} \xi_i = \sum_i^{3N} \left\{ \sum_t^M \left(\frac{\partial \Phi}{\partial r_t} \frac{\partial r_t}{\partial x_i}\right)^{eq} \right\} \xi_i = 0$$

or

$$\text{(A 1.8)} \qquad \sum_i^{3N} \left\{ \sum_t^M \Phi_t \, b_{ti} \right\} \xi_i = 0 \, .$$

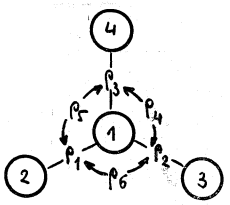
This means that either the ξ_i are dependent or all the coefficients in eq. (A 1.8) vanish. But since the b_{ti} already account for the Eckart conditions among the ξ_i's, eq. (A 1.8) is satisfied if and only if

$$\sum_t^M \Phi_t \, b_{ti} = 0$$

for every i. Comparison of eq. (A 1.8) and (A 1.6) shows that $a_t = \Phi_t$ with exception of an unimportant constant factor.

APPENDIX 2.—We give here three examples which we think most useful in clarifying the results of the method presented in this paper.

1. CH_2O



Geometrical parameters adopted in the computation [11]:

$m_1 = 12.003844$; $m_2 = m_3 = 1.008145$; $m_4 = 16.0$

$r_1^{eq} = r_2^{eq} = 1.09$; $r_3^{eq} = 1.21$

$\alpha_{23}^{eq} = \alpha_{34}^{eq} = \alpha_{24}^{eq} = 120^0$

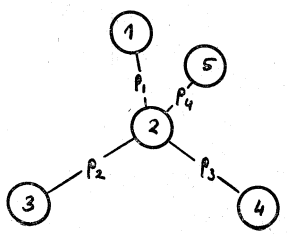
The calculated Φ_t coefficients corresponding to the internal displacement coordinates defined in the figure are

$$\Phi_1 = \Phi_2 = \Phi_3 = 0 \qquad \Phi_4 = \Phi_5 = \Phi_6 = 1/\sqrt{3} \, .$$

The redundancy relation obtained by the method described in refs. [3, 5] is

$$\rho_4 + \rho_5 + \rho_6 = 0 \, .$$

2. CH_4



Geometrical parameters [12]:

$m_1 = m_3 = m_4 = m_5 = 1.008145$; $m_2 = 12.003844$

$r_1^{eq} = r_2^{eq} = r_3^{eq} = r_4^{eq} = 1.09$

$\alpha_{13}^{eq} = \alpha_{14}^{eq} = \alpha_{15}^{eq} = \alpha_{34}^{eq} = \alpha_{35}^{eq} = \alpha_{45}^{eq} = 109^0\,28'$

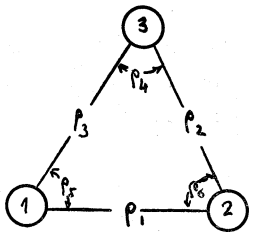
If we number by $5, 6, \cdots, 10$ the coordinates corresponding to the changes in the angles, the calculated coefficients are

$$\Phi_1 = \Phi_2 = \Phi_3 = \Phi_4 = 0 \qquad \Phi_5 = \Phi_6 = \Phi_7 = \Phi_8 = \Phi_9 = \Phi_{10} = 1/\sqrt{6} .$$

The redundancy relation obtained through refs. [3, 5] is

$$\rho_5 + \rho_6 + \rho_7 + \rho_8 + \rho_9 + \rho_{10} = 0 .$$

3. Hypothetical equilateral O_3 molecule (point group D_{2h})



Geometrical parameters (*assumed*):

$m_1 = m_2 = m_3 = 16.0$

$r_1^{eq} = r_2^{eq} = r_3^{eq} = 1.509$

$\alpha_{13}^{eq} = \alpha_{23}^{eq} = \alpha_{12}^{eq} = 60^{\circ}$

The vibrational degrees of freedom in this molecule are three and the internal coordinates chosen are six. We expect three redundancies, divided into A_1' and E' species. The calculated Φ_i's are

Rid. (A_1')	$\Phi_1 = \Phi_2 = \Phi_3 = 0$			$\Phi_4 = \Phi_5 = \Phi_6 = 1/\sqrt{3}$		
Rid. (E')	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6
a)	−0.384	−0.225	0.609	0.334	0.196	−0.530
b)	−0.481	0.573	−0.092	0.419	−0.499	0.080

The corresponding redundancies computed by the method of ref. [6] are

Rid. (A_1')	$\rho_4 + \rho_5 + \rho_6 = 0$					
Rid. (E')	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6
α)	−0.308	−0.308	0.616	0.268	0.268	−0.536
β)	0.754	0	−0.657	−0.657	0.657	0

It is easy to show that

$$0.989\,\alpha - 0.105\,\beta = a$$
$$-0.149\,\alpha - 0.699\,\beta = b .$$

The use of the method presented in this paper may sometimes, as in the case of the O_3 molecule, give nul symmetry coordinates which are not orthogonal to the usual symmetry coordinates written by the standard method. This difficulty may be easily overcome by a suitable change of the other symmetry coordinates. These considerations will be discussed elsewhere [13].

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