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Redundancy Condition and Wilson's Vectors

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Chimica fisica. — *Redundancy Condition and Wilson's Vectors* (*). Nota di MARIANGELA GUSSONI e GIUSEPPE ZERBI, presentata (**) dal Socio G. NATTA.

RIASSUNTO. — Le vibrazioni molecolari sono di solito descritte in termini di « internal displacement coordinates » introdotte da Wilson. A volte, ragioni di simmetria impongono l'uso di un numero di « internal displacement coordinates » maggiore del numero di gradi di libertà della molecola. In questo caso tra le coordinate esistono una o più dipendenze che si chiamano ridondanze.

Le ridondanze sono di solito espresse in letteratura come relazioni del secondo ordine tra le « internal displacement coordinates ». Gli autori mostrano in questo lavoro che nella approssimazione di Wilson le ridondanze hanno sempre una forma lineare e che l'uso di termini del secondo ordine in esse contraddirebbe alla definizione di « internal displacement coordinates ».

In problems of molecular vibrations the more suitable coordinates are the " internal displacement coordinates " ρ_t which are the small changes in the r_t (bond length, bond angles etc.) [1]. In the formalism of the book of Wilson, Decius and Cross they are defined by the two equivalent expressions

$$\rho_t = \sum_{\alpha}^{N} \bar{s}_{t\alpha} \cdot \bar{\xi}_{\alpha} = \sum_{i}^{3N} B_{ti}\, \xi_i \qquad (1)$$

where the sums are extended to the N atoms in the molecule and to their 3 N degrees of freedom; the $\bar{\xi}_{\alpha}$'s are the displacement vectors of the atoms from their equilibrium positions and the $\bar{s}_{t\alpha}$'s are the Wilson's vectors referring to coordinate t and to atom α; ξ_i and B_{ti} are the projections of $\bar{\xi}_{\alpha}$ and $\bar{s}_{t\alpha}$ on the cartesian axes. Normal coordinate calculations are usually performed starting from internal displacement coordinates as defined in eq. (1).

Depending on the geometry of the molecule or on the choice of the force field one may be led to use a number M of coordinates r_t higher than the 3 N–6 vibrational degrees of freedom. In this case the coordinates are related by one or more contraints of the type $\Phi(r_t) = 0$. The relation among the ρ_t is usually expressed [2, 3, 4, 5] as a series espansion in the internal displacements:

$$\sum_{t}^{M} \Phi_t \rho_t + \frac{1}{2} \sum_{tm}^{M} \Phi_{tm} \rho_t \rho_m + \cdots = 0. \qquad (2)$$

Here $\Phi_t = (\partial\Phi/\partial r_t)^{eq}$ and $\Phi_{tm} = (\partial^2\Phi/\partial r_t\, \partial r_m)$ and the sums are extended to all the M internal coordinates. It is usually thought that in the harmonic

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approximation the terms of the first and of the second order in eq. (2) need be considered. Redundancies are then divided into two groups: those for which the Φ_{tm}'s are identically zero (" redundancies exact at the first order " [3]) and those for which the Φ_{tm}'s do not vanish. When the coordinates describing the vibrations of a molecule are related by a redundancy of the second type, the potential energy is usually written with the addition of an extra contribution due to the so called " intramolecular tension " [2, 5]. This contribution does not appear when the redundancy is exact at the first order.

We feel that the distinction of redundancies exact and not exact at the first order is misleading because when the Wilson approximation (defined in eq. (1)) is adopted all the redundancies must be linear. Indeed as far as eq. (1) is accepted for the definition of internal displacements, the sum of the first order terms in eq. (2) vanishes. As a matter of fact it can be easily seen that the exact relation

$$\sum_{t}^{M} \Phi_t \bar{s}_{t\alpha} = 0 \tag{3}$$

is satisfied for each atom α in a molecule whose motion is described by a dependent set of M coordinates related by a constraint $\Phi(r_t) = 0$. As an example let us take the well known XY_4 molecule. In this case the 3 N–6 vibrational degrees of freedom are 9 and the M internal coordinates are 10. Usually the dependence among the coordinates is expressed for this molecule as a second order relation. However, substitution of the appropriate expressions [1] for $\bar{s}_{t\alpha}$ and Φ_t satisfies eq. (3). One then obtains

$$\sum_{t}^{M} \Phi_t \rho_t = \sum_{\alpha}^{N} \bar{\xi}_\alpha \cdot \sum_{t}^{M} \Phi_t \bar{s}_{t\alpha} = 0 \tag{4}$$

which is the first term of eq. (2). This means that the relation among the internal displacement coordinates in the XY_4 molecule is an exact linear relation, at least as long as the Wilson's approximation, namely eq. (1), is used. The geometrical interpretation of this fact is immediate and in the case of the XY_4 molecule becomes particularly evident. If we restrict ourselves to bending coordinates, while each atom vibrates on a portion of a sphere around its equilibrium position, the Wilson's approximation considers the projection of this motion on the tangent plane to the sphere in the equilibrium point. More generally Wilson's method leads to approximate a " curvilinear " surface on which the motion should take place by the plane tangent to it in the equilibrium point. Wilson's vectors are used as a basis to represent the vibration in the internal displacement system. The vibration of each atom is represented in a (3 N–6)–dimensional hyperspace spanned by the Wilson's vectors. When we use a number of basis vectors higher than 3 N–6 one or more *linear* relations must

(1) Expressions for the $\bar{s}_{t\alpha}$'s may be taken from ref. [1]. The values of the Φ_t's may be computed since the geometrical relation $\Phi(r_t) = 0$ is known [4].

exist among them. The use of a quadratic relation such as eq. (2) would mean that while we describe the whole problem on the tangent plane, we constrain the displacements to lay on a curvilinear surface. This is a clear contraddiction. We have shown here the easy example of the XY_4 molecule. A little algebra would show that for all kinds of redundancies an exact first order relation exists among the Wilson's vectors, and therefore among the internal displacement coordinates as defined in eq. (1). These considerations must be extended also to those molecules which have redundancies arising from the use of a particular type of force field, like in the case of the well known Urey Brandley Force Field. Also in this case the relation among the coordinates must be written as a first order expression.

We conclude that, as long as the Wilson's approximation is adopted, all the redundancies among internal displacement coordinates have an exact linear form and no intramolecular tension appears in their Potential Energy. This fact has led us to re-analyse the whole problem of redundancies on a more exact mathematical ground. The results of this investigation, which confirm the thesis of this Note, will be reported elsewhere [6].

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