Nonlinearly Dependent Vibrational Coordinates for Polyatomic Harmonic Vibrations

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The recent proposition of Guassoni and Zerbi, that only the linear approximation to a geometric redundancy relation is relevant to the determination of the harmonic vibrations of a system with a redundant coordinate, is shown to be in error.

Guassoni and Zerbi have recently asserted the proposition that it is necessary, in the determination of harmonic molecular vibrations, to neglect terms of order higher than the first in the expansion of the geometric redundancy condition as a Taylor series about the equilibrium configuration. This proposition and the corollary conclusion that the harmonic frequencies of any redundant system are unaffected by the intramolecular tension are in disagreement with previous studies. The purpose of the present note is to re-affirm the correctness of these previous studies by indicating the error underlying the treatment of Guassoni and Zerbi.

If only the first \((n - 1)\) of \(n\) internal vibrational displacement coordinates are independent and form a vibrationally complete set, then a geometric redundancy relation of the form

\[
q_n = \sum_{i=1}^{n-1} a_i q_i + \sum_{i,j} A_{ij} q_i q_j + \frac{1}{2} \sum_{i,j,k} A_{ijk} q_i q_j q_k + \ldots \quad (1)
\]

holds, and the constants \(a_i\), \(A_{ij}\), \(A_{ijk}\), etc. are determined by the equilibrium geometry. The vibrational potential energy (P.E.), regarded as a function of \(n-1\) nonlinearly dependent coordinates \((q_1, \ldots, q_n)\), is generated to any desired degree of exactitude from the Taylor series expansion

\[
V = \sum_{i=1}^{n} f_i q_i + \frac{1}{2} \sum_{i,j} F_{ij} q_i q_j + \frac{1}{3} \sum_{i,j,k} F_{ijk} q_i q_j q_k + \ldots \quad (2)
\]

Equation (2) does not complete the definition of the P.E., and the additional requirement that \(V\) be subject to the redundancy condition, Eq. (1), and have a minimum at \(q_i = 0\) leads to the following expression

\[
\overline{V}(\text{truncated}) = \frac{1}{2} \sum_{i,j} (f_{ij} + f_n A_{ij}) q_i q_j \quad (5)
\]

for the anharmonic P.E.:

\[
\overline{V} = \frac{1}{2} \sum_{i,j} (f_{ij} + f_n A_{ij}) q_i q_j + \frac{1}{2} \sum_{i,j,k} (f_{ijk} + f_n A_{ijk}) q_i q_j q_k + \ldots \quad (3)
\]

with the coefficients \(A_{ij}\), \(A_{ijk}\) vanishing if any of their subscripts equals \(n\), and with

\[
f_n = -f_i/a_i, \quad i = 1, \ldots, (n-1).
\]

The necessary and sufficient condition that \(V\) represent harmonic motion in \((n-1)\) degrees of freedom is that \(V\), when re-expressed in terms of a complete set of \((n-1)\) independent coordinates, should contain only quadratic terms. The validity or invalidity of the proposition of Guassoni and Zerbi depends precisely upon whether or not the application of this necessary and sufficient condition requires that the \(A_{ij}\) be neglected. The straightforward algebraic substitution of Eq. (1) into Eq. (3), followed by application of the above stated condition for harmony, gives as the expression for the P.E. for harmonic vibrations in \((n-1)\) degrees of freedom,

\[
\overline{V} = \frac{1}{2} \sum_{i,j} (f_{ij} + f_n A_{ij}) Q_i Q_j \quad (4a)
\]

with

\[
Q_i = q_i \quad \text{for} \quad i = 1, \ldots, (n-1)
\]

and

\[
Q_n = \frac{1}{n} \sum_{i=1}^{n-1} a_i Q_i \quad (4c)
\]

\[
= q_n - \frac{1}{2} \sum_{i,j} A_{ij} q_i q_j - \ldots \quad (4d)
\]

It is emphasized that the procedure for obtaining Eq. (4) from Eq. (3) does not require neglect of the \(A_{ij}\), \(A_{ijk}\), etc. i.e., does not require neglect of the nonlinearity in the original redundancy condition given by Eq. (1); nor does it require the vanishing of the potential constant \(f_n\) which is associated with the linear term in the original P.E., Eq. (2), and which may be called the intramolecular tension.

It is evident that the P.E. obtained simply by truncating Eq. (3),

\[
\overline{V}(\text{truncated}) = \frac{1}{2} \sum_{i,j} (f_{ij} + f_n A_{ij}) q_i q_j \quad (5)
\]


4 S. Califano and B. Crawford, Z. Elektrochem. 64, 571 [1960].


can not give rise, in view of Eq. (1), to harmonic motion in \((n - 1)\) degrees of freedom unless
\[
A_{ij} = A_{ijk} = \ldots = 0.
\]

If the original redundancy relation is exactly linear so that Eq. (6) is satisfied, then the truncated P.E. is harmonic since Eq. (5) becomes identical to Eq. (4 a) with \(A_{ij} = 0\). Thus a harmonic potential is always consistent with an exactly linear redundancy, but does not require it. The proposition of Gussoni and Zerbi would be valid if Eq. (5) were necessary, instead of Eq. (4), for a harmonic potential in \((n - 1)\) degrees of freedom. Since this is not the case, the proposition of Gussoni and Zerbi is rejected.

For completeness, the proposition of Gussoni and Zerbi is now shown to be unnecessary in the formulation of the harmonic vibrational kinetic energy (K.E.). The anharmonic vibrational K.E. is given by
\[
\text{K.E.} = \frac{1}{2} \sum_{i,j} t_{ij} (q_1, \ldots, q_n) q_i q_j.
\]

Harmonic motion in \((n - 1)\) degrees of freedom is possible if the quadratic form based on a complete set of \((n - 1)\) independent velocities has constant coefficients. The substitution of
\[
q_n = \sum_i a_i q_i + \frac{1}{2} \sum_{i,j} A_{ij} (q_i q_j + q_j q_i) + \ldots,
\]

obtained by differentiation of Eq. (1), into Eq. (7) reveals that harmonic motion in \((n - 1)\) degrees of freedom is consistent, regardless of the neglect or inclusion of the \(A_{ij}, A_{ijk}, \ldots\) in Eq. (8), with a K.E. of the form
\[
\text{K.E.} = \frac{1}{2} \sum_{i,j} T_{ij} \dot{Q}_i \dot{Q}_j
\]
in which the \(T_{ij}\) are constants determined by the equilibrium configuration, and the \(\dot{Q}_i\) are linearized velocities corresponding to the \(Q_i\) of Eq. (4).

The following points are noteworthy:

(a) The introduction of the \(Q_i\) which replace the \(q_i\) simultaneously linearizes the redundancy relation [compare Eqs. (1) and (4 c)] and fulfills the requirements for harmonic motion. The exact redundancy, Eq. (1), is replaced by a linear counterpart, Eq. (4 c), and the equivalence of these two relations is seen from Eq. (4 d).

For the redundant system, the internal coordinates for which the LAGRANGian equations of harmonic motion are to be solved within the WILSON formalism \(^3\) are the coordinates \(Q_1, \ldots, Q_n\) which have the P.E. shown in Eq. (4 a) and which are always linearly coupled, even if the coordinates \(q_1, \ldots, q_n\) are nonlinearly related. Failure to recognize this could lead to the proposition of Gussoni and Zerbi.

(b) In an obvious extension of the present notation to matrix-vector form, the secular equation resulting from the LAGRANGian equations of motion subject to the redundancy, Eq. (1) or Eq. (4 c), is
\[
\tilde{a} (\mathbf{F} + f_n \mathbf{A}) - \omega^2 \mathbf{T}^{-1} \mathbf{a} = 0
\]
from which it follows that a nonzero value of the intramolecular tension \(f_n\) affects the \((n - 1)\) normal frequencies \(\omega\) unless the \(A_{ij}\) vanish.

(c) The cubic and higher order potential constants of Eq. (2) are necessarily not all zero for harmonic vibrations subject to a nonlinear redundancy. In contrast, for harmonic vibrations subject either to no redundancy or to an exactly linear redundancy, all cubic and higher order potential constants of Eq. (2) must vanish.

(d) The WILSON K.E. matrix \(G\) appropriate to harmonic vibrations of a redundant system is always based on a set of linearly coupled coordinates \(Q_i\), so that \(G\) is singular irrespective of the linearity or nonlinearity of the original redundancy relation, Eq. (1), which is expressed in terms of the \(q_i\). It is notable that the matrix \((\mathbf{F} + f_n \mathbf{A})\) is not necessarily singular \(^6\).

(e) The results obtained in this note necessitate rejection of the proposition of Gussoni and Zerbi, but are otherwise not novel, being in full accord with previous studies.

Note added in proof:

The incorrect hypothesis of the necessity, in the harmonic approximation, of ignoring nonlinearity in the redundancy relation is perpetuated in another recent publication \(^10\). That the rows and columns of the redundant \(G\) matrix (based on linearized coordinates designated \(Q\) in the present work) conform to the same linear dependence (resulting in the singularity of \(G\) as do the basis coordinates is well-known \(^3\); and this may be used, as discussed by Gussoni and Zerbi, instead of the TAYLOR series expansion of the primitive geometrical redundancy, to establish the linear approximation to the redundancy relation. However, if the possibility of nonzero intramolecular tension for harmonic vibrations is correctly to be taken into account, the quadratic terms in the redundancy are generally needed and are obtained by the TAYLOR series method, in the course of which the linear terms would first be obtained anyway.

The necessity (referred to in the third example of the second appendix by Gussoni and Zerbi) of constructing symmetry coordinates that are orthogonal not only to one another but also to the linearized redundant symmetry coordinate has been indicated previously \(^11\) and a probable example of the consequence of disregarding this necessity has been cited \(^12\).

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\(^12\) D. E. FREEMAN and G. R. HUNT, Australian J. Chem. 15, 696 [1962].