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ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · NOVEMBER 1985

Impact Factor: 1.6 · DOI: 10.1016/0022-2860(85)87036-8

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Journal of Molecular Structure, 131 (1985) 347—356
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

FORCE CONSTANTS AND MOLECULAR POTENTIAL FUNCTIONS IN REDUNDANT COORDINATES

V. I. PUPYSHEV, S. V. KRASNOSHCHIOKOV and Yu. N. PANCHENKO

Molecular Spectroscopy Laboratory, Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119899 (U.S.S.R.)

(Received 8 May 1985)

ABSTRACT

An analysis is given of problems arising in the theory of molecular vibrations in redundant (dependent) coordinates. Any force constant matrix in redundant coordinates is shown to correspond to the potential function, which is transformed into the exact molecular potential energy function when account is taken of connections between coordinates.

INTRODUCTION

A theoretical interpretation of the experimental data in problems of molecular spectroscopy is frequently carried out using so-called redundant (dependent) sets of internal coordinates, inter-connected by a system of relations which are geometrical in nature. Redundancy of coordinates results in a series of important problems in the theory of molecular vibrations. For example, it is impossible to introduce the force constants as the second derivatives of the energy in the case of redundant coordinates, because the concept of derivative with respect to redundant variables is in general not well defined. In this connection two ways of introducing force constants are accepted in the theory of molecular vibrations which are usually not accurately separated.

In the first case the force constants are defined as the second derivatives of an effective potential function depending on all the coordinates as if they were independent, and coinciding with the molecular energy when account is taken of connections between coordinates. In this case the 'accounting for' connections is carried out after differentiation. The unambiguity of a set of force constants is here associated with the problem of the unambiguity of the effective potential function. The different type of effective potential functions are used in the theory of molecular vibrations. They are based on the specific physical models of the intramolecular interactions, for example, valence-bond model, atom—atom potential model, Urey—Bradley force field and so on [1, 2].

According to another definition of the force constants in redundant

0022-2860/85/$03.30

coordinates, they are effective parameters which are connected with the force constants in independent coordinates in a prescribed way. In the last case the force constants in dependent coordinates are defined ambiguously and it is necessary to have recourse to some conventions in order to determine them from the experimental data [1, 3, 4]. The ambiguity of the force constant determination from the experimental data in independent coordinates is not discussed here.

In this paper an analysis of the problem of the force constant ambiguity in redundant coordinates is given. It is shown that the effective potential function may be constructed for any set of such coordinates. This makes the different definitions equivalent and permits the elimination of a series of problems in the determination of the force constants. The properties of the specific physical models of a force field are not used here, allowing us to hope that development of the suggested approach in the sophisticated quantum mechanical theories of rotation—vibration spectra may be possible.

DEFINITION OF FORCE CONSTANTS

1. Let Q be a set of independent internal coordinates describing the molecular vibrations. In the framework of adiabatic approximation it is possible to introduce the function $E(Q)$ to denote the molecular potential energy surface. For any set of independent coordinates Q (dimension $m = 3N - 6$ for N-atomic nonlinear molecules) it is possible, in principle, to define the $E(Q)$ function as the result of solution of the Schrödinger electronic equation. On the other hand, it is possible to introduce the effective potential function serving as a simulation of $E(Q)$. As a rule, this effective function is given in internal coordinates, the number of which exceeds the number of independent internal coordinates. Without loss of generality it is possible to assume that the set of dependent coordinates P includes, as a subset, the independent variables Q. Therefore, the coordinates from the set P are either the Q coordinates or the q coordinates which, taking account of all the geometrical connections, may be expressed as a function of coordinates Q, i.e. $q = q(Q)$. Thus, $P = (Q, q)$.

The effective potential function $\mathcal{E}(P) = \mathcal{E}(Q, q)$ is given by some additional assumptions and defined by the single condition: the function $\mathcal{E}(P)$, taking into account all the connections for the variables P, must describe $E(Q)$ either in the whole region or definition of variables Q or in selected small regions. Thus

$$\mathcal{E}(P(Q)) = \mathcal{E}(Q, q(Q)) = E(Q). \qquad (1)$$

Many functions of type $\mathcal{E}(P)$ are known [2], which satisfy the equation (1). Consequently, the function $\mathcal{E}(P)$, unlike $E(Q)$, cannot be defined unambiguously without reference to the way in which $\mathcal{E}$ depends on the variables P.

2. Using matrix notation and not distinguishing the coordinate designation and the coordinate set designation it is easy to obtain the derivatives of the potential $E(Q)$ with respect to Q by means of identity (1)

$$\partial E/\partial Q = (\partial \mathcal{E}/\partial P)(\partial P/\partial Q) = (\partial \mathcal{E}/\partial Q) + (\partial \mathcal{E}/\partial q)(\partial q/\partial Q) \text{ and } \partial^2 E/\partial Q^2 =$$

$$= (\partial \mathcal{E}/\partial P)(\partial^2 P/\partial Q^2) + (\partial P/\partial Q) + (\partial^2 \mathcal{E}/\partial F^2)(\partial P/\partial Q) \quad (2)$$

At the extremum, Q_0, of the function $E(Q)$ it is obvious that $\partial E/\partial Q = 0$. However, the partial derivatives $\partial \mathcal{E}/\partial Q$ and $\partial \mathcal{E}/\partial q$, generally speaking, are not equal to zero. The nature of the dependence of $P(Q)$ is given by the connecting conditions (but not by a conceptual agreement as is sometimes considered [1, 3]). Accordingly, the first number of the right hand side of equation (2) is not zero. If $\mathbf{F} = \partial^2 E/\partial Q^2$ is the matrix of force constants in independent coordinates (at Q_0) and the force constant matrix $\mathcal{F}$ in redundant coordinates is defined by the equation

$$\mathcal{F} = \partial^2 \mathcal{E}/\partial P^2 (P(Q_0)) \quad (3)$$

it is clear, from (2), that

$$\mathbf{F} = (\partial \mathcal{E}/\partial P)(\partial^2 P/\partial Q^2) + \mathbf{S}^+ \mathcal{F} \mathbf{S} \quad (4)$$

Here $\mathbf{S} = \partial P/\partial Q$ is a matrix of the form $\begin{pmatrix} \mathbf{I} \\ \mathbf{T} \end{pmatrix}$ ($\mathbf{I}$ is the unit matrix of dimension $m \times m$ and $\mathbf{T} = \partial q/\partial Q\ (q_0)$ [5]).

3. According to the parametric definition of the force constants mentioned above, it can be assumed that

$$\mathbf{F} = \mathbf{S}^+ \mathcal{F} \mathbf{S} \quad (5)$$

Such a definition corresponds to the quadratic form representing the behaviour of $E(Q)$ only in the vicinity of point $Q = Q_0$ with second order accuracy with respect to displacements of Q from Q_0. In addition, the origin of all the coordinates is chosen in such a way that $Q_0 = 0$ and $q(Q_0) = 0$.

Definition (5) seems to be more formal than the definition based on eqns. (1), (3) and (4). Note that in the case of the valence-force model definitions (4) and (5) coincide. In the case of atom—atom potential, for example, they are different: this is connected with peculiarities of the effective potential construction. However, it is shown below that these definitions may be made completely equivalent. The problem of "linear force constants" has been discussed repeatedly [1, 8].

AMBIGUITY OF THE $\mathcal{F}$ MATRIX

1. For the discussion below it is assumed that the matrix $\mathbf{F}$ is defined unambiguously although the calculation of $\mathbf{F}$ from the experimental data encounters a series of principle obstacles [6].

Equation (5) does not define the $\mathbf{F}$ matrix unambiguously, since for any matrix $\mathcal{F}$ satisfying (5) it is possible to produce a matrix $\mathcal{F}'$ defined by the equation

$$\mathcal{F}' = \mathcal{F} + \mathbf{V}$$

such that $\mathbf{F} = \mathbf{S}^+ \mathcal{F}' \mathbf{S}$. Obviously, it is necessary and sufficient that the matrix $\mathbf{V}$ satisfies the equation

$$S^+ V S = 0 \tag{6}$$

This well-known fact is expressed in the clearest form in ref. 7 where the classes of the V matrices satisfying eqn. (6) are considered.

2. It is possible to give another equation of this kind. Let the matrix R be defined as

$$R = S(S^+S)^{-1} S^+ \tag{7}$$

This is possible since the matrix S has full rank. It is quite clear that

$$R = R^+, R^2 = R, RS = S \tag{8}$$

Therefore, R is a self-adjoint operator corresponding to projection onto the linear span of the column-vectors of the S matrix. It is easy to check that condition (6) is equivalent to the following expression

$$RVR = 0 \tag{9}$$

Indeed, eqn. (9) follows from (6) and (7), and vice versa, eqn. (6) may be obtained easily by multiplication of both sides of eqn. (9) by S on the left and by S^+ on the right and applying eqn. (8).

Given an arbitrary real self-adjoint matrix L it is possible to take

$$V = L - RLR \tag{10}$$

This is easy to verify by substitution of (10) into eqn. (9). In general, eqns. (9) and (10) are equivalent.

Note, that one of the $\mathcal{F}$ matrices satisfying eqn. (5) is always known, viz.

$$\mathcal{F}_0 = \begin{pmatrix} F & 0 \\ 0 & 0 \end{pmatrix}$$

The partitioned expression for $\mathcal{F}_0$ corresponds to the subdivision of the P variables into two groups, Q and q. Thus, the solution of (5) is given, in general, by

$$\mathcal{F} = \mathcal{F}_0 + L - RLR \tag{11}$$

where L is an arbitrary self-adjoint matrix. Other examples of numerous expressions for V are given in ref. 7.

3. The problem (5) has another simple solution for $\mathcal{F}$. Since the structure of S is determined (see Section 2 above) it is easy to verify that in the expression

$$\mathcal{F} = \begin{pmatrix} A & B^+ \\ B & C \end{pmatrix} \tag{12}$$

the matrices B and C may be assumed arbitrary. Condition (5) means that

$$S^+\mathcal{F}S = \begin{pmatrix} I \\ T \end{pmatrix}^+ \begin{pmatrix} A & B^+ \\ B & C \end{pmatrix} \begin{pmatrix} I \\ T \end{pmatrix} = A + T^+B + B^+T + T^+CT = F \tag{13}$$

Therefore, for any matrices B and C

$$\mathbf{A} = \mathbf{F} - \mathbf{T}^{+}\mathbf{B} - \mathbf{B}^{+}\mathbf{T} - \mathbf{T}^{+}\mathbf{C}\mathbf{T} \qquad (14)$$

Equation (14), which is equivalent to (5), allows us to vary the force constants $\mathcal{F}$ in redundant coordinates in the most obvious way [1].

4. Let us present a simple example showing the advantage of manipulations using these equations. In ref. 4 the introduction of a uniform canonical force field in redundant coordinates was suggested. The explicit form of the canonical matrices $\mathcal{F}_{can}$ is given below.

In accordance with definition of the matrix T [5] there is dependence between the infinitestimal variations of coordinates δQ and δq thus, $\delta q = \mathbf{T}\,\delta\, Q$ i.e. $-\mathbf{T}\,\delta\, Q + \delta q = 0$. The matrix $\mathbf{J} = (-\mathbf{T}, \mathbf{I})$ defines the coefficients of linear dependence of the coordinate variations. From the definition [4] the canonical force constants satisfy the same equations as the variations given above, i.e. the matrix $\mathcal{F}_{can}$ is defined by the condition $\mathbf{J}\mathcal{F}_{can} = 0$. Using the partitioned expression of $\mathcal{F}$ (see eqn. (12)) and the partitioned form of J we obtain

$$0 = \mathbf{J}\mathcal{F}_{can} = (-\mathbf{T}\,\mathbf{I})\begin{pmatrix}\mathbf{A} & \mathbf{B}^{+}\\ \mathbf{B} & \mathbf{C}\end{pmatrix} = (-\mathbf{T}\mathbf{A} + \mathbf{B}, -\mathbf{T}\mathbf{B}^{+} + \mathbf{C})$$

Thus for the canonical force field the matrices B and C are determined unambiguously from the A matrix by the expressions $\mathbf{B} = \mathbf{T}\mathbf{A}$, $\mathbf{C} = \mathbf{T}\mathbf{B}^{+} = \mathbf{T}\mathbf{A}\mathbf{T}^{+}$. Then eqn. (14), determining the dependence between the matrices A and F, becomes $\mathbf{F} = \mathbf{A} + \mathbf{T}^{+}\mathbf{B} + \mathbf{B}^{+}\mathbf{T} + \mathbf{T}^{+}\mathbf{C}\mathbf{T} = \mathbf{A} + \mathbf{T}^{+}\mathbf{T}\mathbf{A} + \mathbf{A}\mathbf{T}^{+}\mathbf{T} + \mathbf{T}^{+}\mathbf{T}\mathbf{A}\mathbf{T}^{+}\mathbf{T} = (\mathbf{I} + \mathbf{T}^{+}\mathbf{T})\,\mathbf{A}\,(\mathbf{I} + \mathbf{T}^{+}\mathbf{T})$. Hence it appears that for $\mathcal{F}_{can}$ the following expressions are satisfied

$$\mathbf{A} = (\mathbf{I} + \mathbf{T}^{+}\mathbf{T})^{-1}\ \mathbf{F}\ (\mathbf{I} + \mathbf{T}^{+}\mathbf{T})^{-1}$$

$$\mathbf{B} = \mathbf{T}(\mathbf{I} + \mathbf{T}^{+}\mathbf{T})^{-1}\ \mathbf{F}(\mathbf{I} + \mathbf{T}^{+}\mathbf{T})^{-1}$$

$$\mathbf{C} = \mathbf{T}(\mathbf{I} + \mathbf{T}^{+}\mathbf{T})^{-1}\ \mathbf{F}(\mathbf{I} + \mathbf{T}^{+}\mathbf{T})^{-1}\,\mathbf{T}^{+}$$

These expressions in matrix form, taking account of $(\mathbf{I} + \mathbf{T}^{+}\mathbf{T})^{-1} = (\mathbf{S}^{+}\mathbf{S})^{-1}$, have a very simple form using the projection R (see eqn. (7)) $\mathcal{F}_{can} = \mathbf{R}\mathcal{F}\mathbf{R}$. This equation solves completely the problem of determining the canonical force field. The solution of this problem for the particular case where the matrix J has orthogonal rows is given in ref. 4.

CONSTRUCTION OF THE POTENTIAL FUNCTION

1. Before passing to the explicit construction of the function $\mathcal{E}(\mathbf{P})$ for the given matrix $\mathcal{F}$ let us introduce some preliminary considerations. The exact formulation of this statement is given in section 3.

Provided that the function $E(Q)$ is given it is possible to take the function $\mathcal{E}_0(P) = E(Q)$ as an effective potential function. This function satisfies eqn. (1). Note that the derivative of $\mathcal{E}_0(P)$ with respect to P becomes zero at the point Q_0 which is why eqns. (4) and (5) coincide for this function. The force constant matrix $\mathcal{F}_0$ corresponds to the $\mathcal{E}_0(P)$ function, i.e. the matrices B and C are zero.

2. Now we can generalize the construction of section 1 by the "expression of independent variables in terms of dependent ones". Let Y be an arbitrary matrix of the same dimension as $\mathbf{B}^+$. Let the function $X(Q)$ be defined by

$$X(Q) = Q - \mathbf{Y}q(Q) \tag{15}$$

The derivative $\mathbf{X}$ of $X(Q)$ with respect to Q at the point Q_0 satisfies the condition

$$\mathbf{X} + \mathbf{Y}\mathbf{T} = \mathbf{I} \tag{16}$$

since $\partial q/\partial Q = \mathbf{T}$. On introducing the notation $\mathbf{Z}(\mathbf{Y})$ for the matrix $(\mathbf{X}, \mathbf{Y})$ this condition can be expressed as

$$\mathbf{Z}(\mathbf{Y})\mathbf{S} = \mathbf{I}$$

Let us define further the function $\mathcal{E}(\mathbf{Y}, P)$ as

$$\mathcal{E}(\mathbf{Y},P) = E(X(Q) + \mathbf{Y}q) = E(Q + \mathbf{Y}(q - q(Q))).$$

By virtue of definition (15) the function $\mathcal{E}(\mathbf{Y}, P)$ satisfies the condition (1). Besides

$$\partial \mathcal{E}(\mathbf{Y},P)/\partial P = \partial E(X(Q) + Yq)/\partial Q \cdot \mathbf{Z}(\mathbf{Y})$$

This means that the derivative at the point $P(Q_0)$ becomes zero and eqns. (4) and (5) coincide. It is easy to see that the expression (3) defines the force constant matrix $\mathcal{F}_{\mathbf{Y}}$

$$\mathcal{F}_{\mathbf{Y}} = \frac{\partial^2 \mathcal{E}(\mathbf{Y}, P(Q_0))}{\partial P^2} = \mathbf{Z}(\mathbf{Y})^+ \mathbf{F}\, \mathbf{Z}(\mathbf{Y}) = \begin{pmatrix} \mathbf{X}^+\mathbf{F}\mathbf{X} & \mathbf{X}^+\mathbf{F}\mathbf{Y} \\ \mathbf{Y}^+\mathbf{F}\mathbf{X} & \mathbf{Y}^+\mathbf{F}\mathbf{Y} \end{pmatrix} \tag{17}$$

It is clear from (17) and the definition of S that

$$\mathbf{S}^+ \mathcal{F}_{\mathbf{Y}}\, \mathbf{S} = \mathbf{S}^+ \mathbf{Z}(\mathbf{Y})^+ \mathbf{F}\, \mathbf{Z}(\mathbf{Y})\, \mathbf{S} = \mathbf{F} \tag{18}$$

For the matrix $\mathcal{F}_{\mathbf{Y}}$ the blocks $\mathbf{Y}^+\mathbf{F}\mathbf{X}$ and $\mathbf{Y}^+\mathbf{F}\mathbf{Y}$ determine the matrices B and C in expression (12). Unfortunately, not all matrices C, for example, may be expressed in such a form. Indeed, the rank of $\mathbf{Y}^+\mathbf{F}\mathbf{Y}$ does not exceed the rank of Y and the number of "extra" variables q (denoted as n) may be arbitrarily high but the rank of C may be equal to n.

3. Let us formulate the main result of this Section. It consists of the fact that any effective potential function satisfying the matrix $\mathcal{F}$ may be set as a linear combination of the functions $\mathcal{E}(\mathbf{Y}, P)$ with different Y matrices. More precisely, for any matrix $\mathcal{F}$ satisfying (5) (or (14), which is equivalent) there exist numbers α_i and matrices $\mathbf{Y}_i$ ($i = 1, 2 \ldots n + 1$) such that $\sum_{i=1}^{n+1} \alpha_i = 1$ and the function

$$\tilde{\mathcal{E}}(P) = \sum_{i=1}^{n+1} \alpha_i\, \mathcal{E}(\mathbf{Y}_i, P) \tag{19}$$

satisfies condition (1) and has zero derivative with respect to P at the point $P(Q_0)$ with a matrix of second derivatives equal to $\mathscr{F}$ at the same point. The existence of the potential function is mathematically evident and quite trivial. The only important fact is the expression of this function in the form of eqn. (19).

4. Let us prove, first of all, an auxiliary statement, viz. for arbitrary matrices **D** (equal in dimensions to $\mathbf{B}^+$) and **C** (dimensions $n \times n$, $\mathbf{C} = \mathbf{C}^+$) there exist n numbers α_i and matrices $\mathbf{Y}_i$ such that

$$\sum_i \alpha_i \mathbf{Y}_i = \mathbf{D} \text{ and } \sum_i \alpha_i \mathbf{Y}_i^+ \mathbf{F}\, \mathbf{Y}_i = \mathbf{C} \tag{20}$$

In this section we will use Dirac's notations accepted in quantum mechanics, i.e. $|a\rangle$ is a column-vector **a**, $\langle b|$ is a row-vector $\mathbf{b}^+$, and $\langle a|b\rangle$ is the scalar product $\mathbf{a}^+\mathbf{b}$. We suppose also that the **F** matrix is positive definite as is accepted in the theory of small vibrations and that the **C** matrix is non-singular (which can be achieved by an arbitrarily small variation in **C**). Let us require the same for the **D** matrix. Let $\{|l_j\rangle\}$ be a complete orthonormal set of the eigenvectors of **C** and γ_j be the corresponding eigenvalues. Let the vector $\mathbf{D}|l_j\rangle$ be denoted as $|w_j\rangle$. It is easy to check that expression

$$\alpha_j = \langle w_j|\mathbf{F}|w_j\rangle/\gamma_j,\ \mathbf{Y}_j = \alpha_i^{-1}\, |w_j\rangle\, \langle l_j|$$

determines the solution of expression (20). Indeed,

$$\sum_i \alpha_i \mathbf{Y}_i^+ \mathbf{F}\, \mathbf{Y}_i = \sum_i \alpha_i \alpha_i^{-2}\, \langle w_i|\mathbf{F}|w_i\rangle\, |l_i\rangle\, \langle l_i| =$$

$$= \sum_i |l_i\rangle\, \langle l_i|\, \langle w_i|\mathbf{F}|w_i\rangle/\alpha_i = \sum_i |l_i\rangle\, \langle l_i|\gamma_i = \mathbf{C}.$$

Further,

$$\sum \alpha_i \mathbf{Y}_i = \sum_i \alpha_i \alpha_i^{-1}\, |w_i\rangle\, \langle l_i| = \sum_i |w_i\rangle\, \langle l_i| = \mathbf{D} \sum_i |l_i\rangle\, \langle l_i| = \mathbf{D}$$

5. Let us pass to the proof of the statement from Section IV.3 consisting of the proof of the possibility of expressing $\mathscr{F}$ as a linear combination of the $\mathscr{F}_\mathbf{Y}$ matrices (see expression (17)). The coefficients of this combination are defined by the auxiliary construction of the previous section.

Determining the $\mathscr{F}$ matrix means determining its blocks **B** and **C**. Let us set $\mathbf{D} = \mathbf{F}^{-1}\, (\mathbf{B}^+ + \mathbf{T}^+\mathbf{C})$ and determine, using the results of Section 4, the numbers α_i and matrices $\mathbf{Y}_i$ for $i = 1$ to n. Thus

$$\sum_i \alpha_i \mathbf{Y}_i = \mathbf{F}^{-1}\, (\mathbf{B}^+ + \mathbf{T}^+ \sum_i \alpha_i \mathbf{Y}_i^+ \mathbf{F}\, \mathbf{Y}_i)$$

or

$$\sum_i \alpha_i \mathbf{F}\, \mathbf{Y}_i - \mathbf{T}^+ \sum_i \alpha_i \mathbf{Y}_i^+ \mathbf{F}\, \mathbf{Y}_i = \mathbf{B}^+$$

Hence it appears that

$$\sum_i \alpha_i (\mathbf{I} - \mathbf{T}^+ \mathbf{Y}_i^+) \mathbf{F} \mathbf{Y}_i = \mathbf{B}^+$$

Defining the $\mathbf{X}_i$ matrix by the equation $\mathbf{X}_i^+ = \mathbf{I} - \mathbf{T}^+ \mathbf{Y}_i^+$ (cf. (16)) we find that the α_i and the matrices $(\mathbf{Y}_i, \mathbf{X}_i)$ are defined so that

$$\mathbf{C} = \sum_i^n \alpha_i \mathbf{X}_i^+ \mathbf{F} \mathbf{Y}_i, \quad \mathbf{B}^+ = \sum_i^n \alpha_i \mathbf{X}_i \mathbf{F} \mathbf{Y}_i \tag{21}$$

Note that if $\mathbf{Y}_{n+1} = 0$ and

$$\alpha_{n+1} = 1 - \sum_{i=1}^{n} \alpha_i \tag{22}$$

eqn. (21) is satisfied for the extended range $i = 1$ to $n + 1$.

6. Let us consider the properties of the function $\tilde{\mathcal{E}}(P)$ which is defined by the $n + 1$ numbers α_i and the matrices $\mathbf{Y}_i$

$$\tilde{\mathcal{E}}(P) = \sum_{i=1}^{n+1} \alpha_i \mathcal{E}(\mathbf{Y}_i, P)$$

As follows from sections 1 and 2 the introduced function $\tilde{\mathcal{E}}(P)$ (like the functions $\mathcal{E}(\mathbf{Y}_i, P)$), possesses property (1) by virtue of eqn. (22), that is

$$\tilde{\mathcal{E}}(P(Q)) = \sum_{i=1}^{n+1} \alpha_i \mathcal{E}(\mathbf{Y}_i, P(Q)) = (\sum_i \alpha_i) E(Q) = E(Q)$$

Further, at the point $Q = Q_0$ the derivatives of the functions $\mathcal{E}(\mathbf{Y}_i, P)$ and $\tilde{\mathcal{E}}(P)$ with respect to P are zero by definition.

Consider, finally, the second derivatives of $\tilde{\mathcal{E}}(P)$. It is clear that, at the point Q_0

$$\mathcal{F}_1 = \partial^2 \tilde{\mathcal{E}}(P(Q_0))/\partial P^2 = \sum_{i=1}^{n+1} \alpha_i \mathcal{F}_{\mathbf{Y}_i} \tag{23}$$

Since the matrix $\mathcal{F}_{\mathbf{Y}_i}$ satisfies eqn. (18) for all the values i, the analogous equation is satisfied for $\mathcal{F}_1$

$$\mathbf{S}^+ \mathcal{F}_1 \mathbf{S} = \sum_i \alpha_i \mathbf{S}^+ \mathcal{F}_{\mathbf{Y}_i} \mathbf{S} = \sum_i \alpha_i \mathbf{F} = \mathbf{F} \tag{24}$$

But in this instance the comparison of eqns. (23) and (17) with (21) shows that $\mathcal{F}_1$ has the form

$$\mathcal{F}_1 = \begin{pmatrix} \mathbf{A} & \mathbf{B}^+ \\ \mathbf{B} & \mathbf{C} \end{pmatrix}$$

Because condition (24) with eqn. (13) implies the fulfilment of eqn. (14) (the matrix $\mathcal{F}$ given by eqn. (13) is completely determined by blocks **B** and **C**), the matrix $\mathcal{F}_1$ coincides with $\mathcal{F}$. The proof of the statement in section 3 is complete.

CONCLUSION

The results obtained may be summarized.

1. With respect to the use of force constants in redundant coordinates it is possible to describe the multiplicity of all the force constant matrices generating the same solution of the molecular small vibration problem by means of eqn. (11) or eqns. (12) and (14), which are analogues of equations in the fundamental paper by Groner and Günthard [7]. These equations allow us to select the convenient form of expression of the equivalent force constant matrices.

2. For each of the force constant matrices in redundant coordinates there is an effective potential function, the second derivative matrix of which gives the force constants in the equilibrium position. This function may be chosen so that its first derivatives in the equilibrium position are zero, and moreover the effective potential function transforms into the exact one when account is taken of the redundancy of coordinates (see also ref. 8). This result allows us to solve completely the problem of the differentiation of the function with respect to dependent variables, which is incorrect in its formulation. It indicates also the superficiality of the difference between the different definitions of the force constant matrices. The differences mentioned above may be removed by a change of the effective potential function which does not change the physical basis of the problem.

In particular, this allows us to make sense of the following procedure: for the chosen effective potential function $\mathcal{E}(P)$, regardless of the values of its first derivatives at the point $P(Q_0)$, the "dependent" force constants are determined by the equation $\mathcal{F} = \partial^2\mathcal{E}(P)/\partial P^2$. The difference between this equation and eqn. (4) does not affect the description of real molecular vibrations, i.e. the frequencies and the vibrational forms in the independent coordinates. Nevertheless, the parameters of $\mathcal{E}(P)$ as determined from the experimental data when solving the inverse problem will be different in these cases. However, these differences are determined only by the methodological principles, as in the case of construction of the potential curves of diatomic molecules by equations of Dunham or by any other equations.

This statement may be formulated in another way: results of any investigations of molecular force field in redundant coordinates may be interpreted as if they were carried out within the framework of one of the versions of the modified valence-force model.

ACKNOWLEDGEMENT

We are deeply indebted to Dr. R. Gerrard (The University of Sussex, Brighton, U.K.) for reading the manuscript and for his valuable suggestions.

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