und $S_0^{(2)}$ beschrieben. Unter der Voraussetzung, daß das Übergangsmoment $\boldsymbol{\mu}_{ga}^{\text{Lös}}$ ($= \boldsymbol{\mu}_{ga}^*$ in den Veröffentlichungen [10, 27]) des gelösten Moleküls parallel zum Übergangsmoment $\boldsymbol{\mu}_{ga}$ des isolierten Moleküls ist, gelten die folgenden Beziehungen:

$$|\mu_{ga}^{\text{Lös}}|^2 \boldsymbol{R}_0^{(1)} = (|\mu_{ga}^{\text{Lös}}|/|\mu_{ga}|)\, \boldsymbol{R}\,, \qquad (76)$$

$$|\mu_{ga}^{\text{Lös}}|^2 S_0^{(1)} = \text{Sp}\, \boldsymbol{P} + (|\mu_{ga}^{\text{Lös}}|/|\mu_{ga}|)\, \text{Sp}\, \boldsymbol{Q}\,, \qquad (77)$$

wobei Sp die Spur der Tensoren $\boldsymbol{P}$ bzw. $\boldsymbol{Q}$ bedeutet. Äquivalente Größen zu $\boldsymbol{R}_0^{(2)}$ und $S_0^{(2)}$ treten in den Gleichungen, welche die Lösungsmittelabhängigkeit des Übergangsmoments beschreiben, nicht auf, da die Richtung des Reaktionsfeldes immer durch die Dipolmomente $\boldsymbol{\mu}_g$ und $\boldsymbol{\mu}_a$ vorgegeben ist und keine Mittelung über eine Orientierungsverteilung bezüglich der äußeren Feldrichtung durchgeführt werden muß. Aus dem gleichen Grund tritt auch an Stelle der Tensoren $\boldsymbol{P}$ und $\boldsymbol{Q}$ im äußeren Feldeffekt nur deren Mittelwert, die Spur, auf.

Die prinzipiell nach zwei verschiedenen Methoden zugänglichen Größen $\boldsymbol{R}_0^{(1)}$ und $\boldsymbol{R}$ können in günstigen Fällen nach Gl. (76) verglichen werden. Dagegen ist ein Vergleich der Größen $\boldsymbol{P}$ und $\boldsymbol{Q}$ mit aus der äußeren Feldabhängigkeit erhaltenen Größen im allgemeinen nicht möglich, da aus der Lösungsmittelabhängigkeit nur die Werte der Tensoren $\boldsymbol{P}$ und $\boldsymbol{Q}$ in Richtung von $\boldsymbol{F}_{\text{RW}}$ erhalten werden können.

Mein aufrichtiger Dank für die Unterstützung dieser Untersuchungen gilt dem Fonds der Chemischen Industrie.

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Nonlinear Coordinate Transformations for Vibrations of Simple Polyatomic Molecules, Using the Cihla-Pliva Formalism

S. J. Cyvin

Chemistry Department, Oregon State University, Corvallis, Oregon, USA,
and Institute of Physical Chemistry, Technical University of Norway, Trondheim, Norway

(Z. Naturforschg. **21 a**, 1618—1627 [1966]; received 29 April 1966)

Nonlinear coordinate transformations are considered for the molecular vibrations of the bent symmetrical XY_2 and tetrahedral Z_4 models. Algebraic expressions are given for internal coordinates as expanded through cubic terms, using a method due to Cihla and Plíva. The method is compared to other approaches, viz. those of Morino et al. on one hand, and Pariseau et al. on the other. A conclusions is given in favour of the Cihla–Plíva method as regard to a systematic treatment of polyatomic molecules. A similar conclusion applies also to the connected type of calculations where electronic computers are employed.

The study of anharmonic potential functions in polyatomic molecules has attained considerable interest in recent years. Accurate determinations of higher-order force constante have been achieved so far for very few molecules, but this attractive field of research will no doubt be extensively investigated in the future. In this connection it is important to study the *instantaneous* vibrational coordinates, which may be of a general valence-coordinate type. These coordinates are connected with cartesian displacements through *nonlinear* transformations, in contrast to the situation for the usual (linearized) valence coordinates. The latter are the zero-order approximation of the former; it holds for small vibrations. Plíva [1, 2] has evaluated the general valence coordinates for some simple molecular models, viz. bent XY_2 and linear triatomic. Pariseau et al. [3] have described computations for CO_2 involving the nonlinear transformation for general valence coordinates, performed with the aid of electronic-computer programming. The general procedure is outlined for bond stretching and angle bending coordinates. Some years previously Cihla and Plíva [4] have published another general method con-

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[4] Z. Cihla and J. Plíva, Collection Czech. Chem. Commun. **28**, 1232 [1963].

[5] S. R. Polo, J. Chem. Phys. **24**, 1133 [1956].

venient for computer programming, and including out-of-plane bending and torsional coordinates in addition to the above mentioned types.

All the mentioned authors agree that the computational labour is quite formidable and would be impossible without the aid of electronic computers, except for the simplest molecular models. For such models, however, it seems worth while evaluating the algebraic expressions for the nonlinear transformations in question. The subject of the present work is an application of the general method of CIHLA and PLÍVA [4] to some simple models; the results obtained for the bent symmetrical XY_2 model should be consistent with those reported by PLÍVA [1], while the computations for tetrahedral Z_4 have not been done previously. The writer finds the CIHLA–PLÍVA method very interesting and attractive, and he hopes that this paper also will contribute to the explanation of the peculiar formalism of the method.

Transformation Vectors

A general coordinate (q) may be given by a nonlinear transformation, say for instance

$$q = q^0 + A_1 x_1 + A_2 x_2 + A_{11} x_1^2 + A_{12} x_1 x_2 + A_{22} x_2^2, \tag{1}$$

which may be written in matrix notation as

$$q = \mathfrak{A} \cdot \mathfrak{x}^{(2)}, \tag{2}$$

where

$$\mathfrak{A} = [q^0 \;\; A_1 \;\; A_2 \;\; A_{11} \;\; A_{12} \;\; A_{22}], \tag{3}$$

$$\mathfrak{x}^{(2)} = \{1,\; x_1,\; x_2,\; x_1^2,\; x_1 x_2,\; x_2^2\}. \tag{4}$$

According to CIHLA and PLÍVA [4] the vectors in (3) and (4) are referred to as a transformation vector (T-vector) and coordinate vector (X-vector), respectively, the latter being a column matrix. The supersprict $^{(2)}$ in Eq. (4) indicates that the X-vector contains up to quadratic terms.

The T-vector multiplication, say $\mathfrak{A} * \mathfrak{B}$, is of fundamental importance. Assume for the purpose of illustration that $\mathfrak{B}$ simply is defined by

$$r = \mathfrak{B} \cdot \mathfrak{x}^{(1)} = r_0 + B_1 x_1 + B_2 x_2 . \tag{5}$$

The T-vector product in question contains the coefficients of the product $q\,r$, and may be evaluated by means of the elements of the ordinary matrix product $\tilde{\mathfrak{A}} \cdot \mathfrak{B}$. They may be arranged in a rectangular array as follows:

$$\begin{array}{c} \\ q^0 \\ A_1 \\ A_2 \\ A_{11} \\ A_{12} \\ A_{22} \end{array} \begin{array}{c} \begin{array}{ccc} r^0 & B_1 & B_2 \end{array} \\ \left[\begin{array}{ccc} q^0\, r^0 & q^0\, B_1 & q^0\, B_2 \\ A_1\, r^0 & A_1\, B_1 & A_1\, B_2 \\ A_2\, r^0 & A_2\, B_1 & A_2\, B_2 \\ A_{11}\, r^0 & A_{11}\, B_1 & A_{11}\, B_2 \\ A_{12}\, r^0 & A_{12}\, B_1 & A_{12}\, B_2 \\ A_{22}\, r^0 & A_{22}\, B_1 & A_{22}\, B_2 \end{array}\right] \end{array} \quad \begin{array}{c} \\ 0 \\ 1 \\ 2 \\ 11 \\ 12 \\ 22 \end{array} \begin{array}{c} \begin{array}{ccc} 0 & 1 & 2 \end{array} \\ \left[\begin{array}{ccc} 0 & 1 & 2 \\ 1 & 11 & 12 \\ 2 & 12 & 22 \\ 11 & 111 & 112 \\ 12 & 112 & 122 \\ 22 & 122 & 222 \end{array}\right] \end{array}$$

In the resulting T-vector,

$$\mathfrak{C} = \mathfrak{A} * \mathfrak{B}, \tag{6}$$

the elements from the above array should be arranged and added up in accord to the powers of the coordinates in the X-vectors which correspond to $\mathfrak{A}$ and $\mathfrak{B}$. The array of indices shown above is a useful guide for this purpose. In the present example one has to form the product T-vector $\mathfrak{C}$ as

$$\mathfrak{C} = [q^0 r^0 \;\; C_1\, C_2\, C_{11}\, C_{12}\, C_{22}\, C_{111}\, C_{112}\, C_{222}], \tag{7}$$

where

$$C_1 = q^0 B_1 + A_1 r^0, \qquad C_2 = q^0 B_2 + A_2 r^0, \tag{8}$$

$$C_{11} = A_1 B_1 + A_{11} r^0, \quad C_{22} = A_2 B_2 + A_{22} r^0, \quad C_{12} = A_1 B_2 + A_2 B_1 + A_{12} r^0, \tag{9}$$

$$C_{111} = A_{11} B_1, \quad C_{222} = A_{22} B_2, \quad C_{112} = A_{11} B_2 + A_{12} B_1, \quad C_{122} = A_{12} B_2 + A_{22} B_1 . \tag{10}$$

Notice that

$$q\,r = (\mathfrak{A} \cdot \mathfrak{x}^{(2)})\,(\mathfrak{B} \cdot \mathfrak{x}^{(1)}) = \mathfrak{C} \cdot \mathfrak{x}^{(3)}, \tag{11}$$

where

$$\mathfrak{x}^{(3)} = \{1, x_1, x_2, x_1^2, x_1 x_2, x_2^2, x_1^3, x_1^2 x_2, x_1 x_2^2, x_2^3\} . \tag{12}$$

Another important concept is the function of a T-vector $f(\mathfrak{A})$, which is defined on the basis of TAYLOR expansion. For this purpose one defines the auxiliary homogeneous T-vector $\mathfrak{A}'$. With reference to Eq. (3) it is given by

$$\mathfrak{A}' = [0 \;\; A_1 \;\; A_2 \;\; A_{11} \;\; A_{12} \;\; A_{22}], \tag{13}$$

Hence

$$q = q^0 + \mathfrak{A}' \cdot \mathfrak{x}^{(2)}, \quad \text{[cf. Eq. (2)], and also} \quad \mathfrak{A} = q_0\, \mathfrak{I} + \mathfrak{A}', \qquad (14), (15)$$

where $\mathfrak{I}$ is the unit T-vector (of the same dimension as $\mathfrak{A}$). It has the first element equal to unity and all remaining zero. We will have the occasion to use the inverse and square root of a T-vector. The resulting functions are also T-vectors and defined (with reference to $\mathfrak{A}$ above) by

$$(\mathfrak{A})^{-1} = (1/q^0)\,\mathfrak{J} - (1/q^0)^2\,\mathfrak{A}' + (1/q^0)^3\,(\mathfrak{A}')^2 - (1/q^0)^4(\mathfrak{A}')^3 + (1/q^0)^5(\mathfrak{A}')^4 - \dots, \tag{16}$$

$$(\mathfrak{A})^{\frac{1}{2}} = (q^0)^{\frac{1}{2}}\,\mathfrak{J} + \tfrac{1}{2}(1/q^0)^{\frac{1}{2}}\,\mathfrak{A}' - \tfrac{1}{8}(1/q^0)\,(\mathfrak{A}')^2 + \tfrac{1}{16}(1/q^0)_{\frac{5}{2}}(\mathfrak{A}')^3 - \tfrac{5}{128}(1/q^0)_{\frac{7}{2}}(\mathfrak{A}')^4 + \dots\,. \tag{17}$$

Here $(\mathfrak{A}')^2 = \mathfrak{A}' * \mathfrak{A}'$, $(\mathfrak{A}')^3 = \mathfrak{A}' * \mathfrak{A}' * \mathfrak{A}'$, etc.

Molecular Parameters and Coordinates

Let the position vectors referring to the atoms i in the equilibrium position be denoted

$$\boldsymbol{R}_i = \{X_i^{\mathrm{e}}, Y_i^{\mathrm{e}}, Z_i^{\mathrm{e}}\}\,. \tag{18}$$

Cartesian atom displacements are introduced by

$$x_i = X_i - X_i^{\mathrm{e}}, \quad y_i = Y_i - Y_i^{\mathrm{e}}, \quad z_i = Z_i - Z_i^{\mathrm{e}}, \tag{19}$$

or in vector notation

$$\boldsymbol{\rho}_i = \{x_i, y_i, z_i\}\,. \tag{20}$$

Consider now an atom pair $i\,j$. For convenience we think of it as forming a chemical bond; this is however not necessary for the below arguments. The bond vector is introduced by

$$\boldsymbol{D}_{ij} = \Delta\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j\,. \tag{21}$$

It will be convenient to use a single index (say p) for the atom pair in question $(i\,j)$, and we write

$$\boldsymbol{D}_{ij} = \boldsymbol{D}_p = \{D_p^x, D_p^y, D_p^z\}\,, \tag{22}$$

where

$$D_p^x = X_i^{\mathrm{e}} - X_j^{\mathrm{e}}, \; D_p^y = Y_i^{\mathrm{e}} - Y_j^{\mathrm{e}}, \; D_p^z = Z_i^{\mathrm{e}} - Z_j^{\mathrm{e}}.$$

We also introduce the bond displacement vector, which is

$$\boldsymbol{d}_p = \boldsymbol{d}_{ij} = \Delta\boldsymbol{\rho}_{ij} = \boldsymbol{\rho}_i - \boldsymbol{\rho}_j = \{d_p^x, d_p^y, d_p^z\}\,, \tag{23}$$

where

$$d_p^\alpha = \Delta\alpha_{ij} = \alpha_i - \alpha_j \quad \text{for} \quad \alpha = x, y, z\,.$$

The normal coordinates $\boldsymbol{Q}$ are by definition linearized internal coordinates, and one may express the cartesian displacements by

$$x_i = \sum_k a_{ik}^x Q_k\,, \quad y_i = \sum_k a_{ik}^y Q_k\,, \quad z_i = \sum_k a_{ik}^z Q_k\,. \tag{24}$$

The bond displacement vector components (23) are found as the differences of the coefficients from Eq. (24):

$$d_p^\alpha = \sum_k \delta_{pk}^\alpha Q_k\,, \tag{25}$$

where $\delta_{pk}^\alpha = a_{ik}^\alpha - a_{ik}^\alpha$ for $\alpha = x, y, z$. Consider now the expression

$$D_p^\alpha + d_p^\alpha = \mathfrak{D}_p^\alpha \cdot \mathfrak{x}^{(1)}. \tag{26}$$

Here $\mathfrak{x}^{(1)}$ is supposed to be the X-vector [cf. Eq. (4)]

$$\mathfrak{x}^{(1)} = \{1,\ Q_1,\ Q_2, \dots, Q_s\} \tag{27}$$

including the zero-order term and normal coordinates of first degree. In accordance,

$$\mathfrak{D}_p^\alpha = [\mathrm{D}_p^\alpha\, \delta_{p1}^\alpha\, \delta_{p2}^\alpha \cdot \dots \cdot \delta_{ps}^\alpha]\,. \tag{28}$$

As previously, $\alpha = x, y, z$; and s denotes the number of normal coordinates.

Application to General Bond Stretchings

Let d_p be the true (instantaneous) bond stretching for the atom pair p, and D_p^{e} the corresponding equilibrium distance. CHILA and PLÍVA [4] were able to give an expression for this type of coordinate in the elegant form

$$D_p^{\mathrm{e}} + d_p = \mathfrak{U}_p \cdot \mathfrak{x}\,, \tag{29}$$

where

$$\mathfrak{U}_p = \Big[\sum_\alpha (\mathfrak{D}_p^\alpha)^2\Big]^{\frac{1}{2}}, \tag{30}$$

using the notation of the preceding section. Here $(\mathfrak{D}_p^\alpha)^2 = \mathfrak{D}_p^\alpha * \mathfrak{D}_p^\alpha$, and the square root is supposed to be formed according to the above given definitions. $\mathfrak{x}$ is the X-vector for normal coordinates, taken through any desired degree; cf. Eqs. (27), (4). The formula (30) is based on

$$D_p^{\mathrm{e}} + d_p = [(D_p^x + d_p^x)^2 + (D_p^y + d_p^y)^2 + (D_p^z + d_p^z)^2]^{\frac{1}{2}},$$

and is seen in a sense to retain the same form, this being a consequence of using the CIHLA–PLÍVA symbolism.

Application to General Interbond Angle Bendings

Whe shall also use the CIHLA–PLÍVA method for evaluating an angle bending coordinate between two bonds (say p and p') which do not form a straight line in the equilibrium position. Let this coordinate be denoted $\varphi_{pp'}$. If $\Phi_{pp'}$ is the corresponding equilibrium interbond angle, one has [4]

$$\cos(\Phi_{pp'} + \varphi_{pp'}) = \mathfrak{C}_{pp'} \cdot \mathfrak{x} = \cos\Phi_{pp'} + \mathfrak{C}'_{pp'} \cdot \mathfrak{x}\,, \tag{31}$$

where

$$\mathfrak{C}_{pp'} = (\mathfrak{U}_p)^{-1} * (\mathfrak{U}_{p'})^{-1} * \Big[\sum_{\alpha} (\mathfrak{D}_p{}^{\alpha} * \mathfrak{D}_{p'}{}^{\alpha})\Big], \qquad (32)$$

and $\mathfrak{C}'_{pp'}$ is the corresponding homogeneous vector, as defined above. The T-vectors for the individual bonds (p and p') are those in conformance with the previous section. For the angle bending itself one has

$$\varphi_{pp'} = \mathfrak{U}'_{pp'} \cdot \mathfrak{x}\,, \qquad (33)$$

where

$$\begin{aligned}\mathfrak{U}'_{pp'} = &- \frac{1}{\sin \Phi_{pp'}} \mathfrak{C}'_{pp'} - \frac{\cos \Phi_{pp'}}{2 \sin^3 \Phi_{pp'}} (\mathfrak{C}'_{pp'})^2 \\ &- \frac{1+2\cos^2 \Phi_{pp'}}{6 \sin^5 \Phi_{pp'}} (\mathfrak{C}'_{pp'})^3 \\ &- \frac{\cos \Phi_{pp'} (3+2\cos \Phi_{pp'})}{8 \sin^7 \Phi_{pp'}} (\mathfrak{C}'_{pp'})^4 - \ldots \qquad (34)\end{aligned}$$

Treatment of Simple Molecular Models

Introduction

The theory outlined in the preceding sections shall be applied to some simple molecular models. We shall use a set of linearized symmetry coordinates ($\boldsymbol{S}^0$) which are not necessarily the normal coordinates. The coefficients corresponding to δ^{α}_{pk} will then be found as differences between elements of the familiar $\boldsymbol{A}$ matrix ($\boldsymbol{X} = \boldsymbol{A}\,\boldsymbol{S}^0$). It is known that these elements may be expressed in terms of Polo's [5] $\boldsymbol{\rho}^0$ vectors. In order not to confuse our notation [cf. Eq. (20)] we shall identify these vectors by the symbol $\boldsymbol{t}^0$. The connection with the δ^{α}_{pk} coefficients is explicitly

$$\{\delta^x_{pk}, \delta^y_{pk}, \delta^z_{pk}\} = \mathring{\boldsymbol{t}}_{ki} - \mathring{\boldsymbol{t}}_{kj}\ . \qquad (35)$$

Here k refers to the symmetry coordinate, i and j are numbers for atoms, and p indicates as previously the atom pair $(i\,j)$ for which one has taken the differences.

Bent symmetrical XY_2 model

The bent symmetrical XY_2 model is shown in Fig. 1, where the orientation of cartesian axes, numbering of atoms, etc., is explained. The legend includes the chosen linearized symmetry coordinates. The corresponding $\boldsymbol{t}^0$ vectors are given in Table 1.

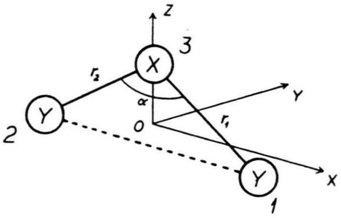

Fig. 1. Bent symmetrical XY_2 molecular model (symmetry C_{2v}). The notation used for instantaneous stretchings and bending are indicated on the figure. Let R denote the equilibrium X–Y distance, and $2\,A$ be the equilibrium YXY angle. If O is the center of gravity, one has

$$Z_3{}^e = 2\,M^{-1}\,m_Y\,R\cos A.$$

$M = m_X + 2\,m_Y$ is the total mass of the molecule. For the principal moments of inertia one has

$$I_y = I_x + I_z = 2\,M^{-1}\,R^2\,m_Y\,(m_X + 2\,m_Y \sin^2 A).$$

Linearized symmetry coordinates:

$$\begin{array}{ll} \text{Species } A_1 & \begin{cases} S_1{}^0 = 2^{-\frac{1}{2}}(r_1{}^0 + r_2{}^0), \\ S_2{}^0 = R\,\alpha^0, \end{cases} \\ \qquad\quad\ B_1 & \ \ S_3{}^0 = 2^{-\frac{1}{2}}(r_1{}^0 - r_2{}^0). \end{array}$$

General bond stretchings

One finds the following $\mathfrak{D}^{\alpha}$ components from Table 1 using Eq. (35), and remembering the definition of $D_p{}^{\alpha}$ [cf. Eq. (22)].

(a) For the atom pair 13, presently identified by the subscript p:

$$\begin{aligned}\{D^x_p, D^y_p, D^z_p\} &= \{R\sin A,\ 0,\ -R\cos A\} \\ \{\delta^x_{p1}, \delta^y_{p1}, \delta^z_{p1}\} &= \{2^{-\frac{1}{2}}\sin A, 0,\ -2^{-\frac{1}{2}}\cos A\}, \\ \{\delta^x_{p2}, \delta^y_{p2}, \delta^z_{p2}\} &= \{\tfrac{1}{2}\cos A,\ 0,\ \tfrac{1}{2}\sin A\}, \\ \{\delta^x_{p3}, \delta^y_{p3}, \delta^z_{p3}\} &= \{2^{\frac{1}{2}}\,m_Y\,I_y^{-1}R^2\sin A,\ 0, \\ &\qquad -2^{\frac{1}{2}}\,m_X\,m_Y\,(M\,I_y)^{-1}\,R^2\cos A\}. \end{aligned} \qquad (36)$$

Atom	$S_1{}^0$	$S_2{}^0$
1	$\{\ 2^{-\frac{1}{2}}\sin A,\ 0,\ -2^{-\frac{1}{2}}M^{-1}m_X\cos A\}$	$\{\ \frac{1}{2}\cos A,\ 0,\ \frac{1}{2}M^{-1}m_X\sin A\}$
2	$\{-2^{-\frac{1}{2}}\sin A,\ 0,\ -2^{-\frac{1}{2}}M^{-1}m_X\cos A\}$	$\{-\frac{1}{2}\cos A,\ 0,\ \frac{1}{2}M^{-1}m_X\sin A\}$
3	$\{\ 0,\ ,\ 0,\ 2^{\frac{1}{2}}M^{-1}m_Y\cos A\}$	$\{\ 0,\ 0,\ -M^{-1}m_Y\sin A\}$

Atom	$S_3{}^0$
1	$\{\ 2^{\frac{1}{2}}(M\,I_y)^{-1}m_X m_Y R^2\sin A,\ 0,\ -2^{\frac{1}{2}}(M\,I_y)^{-1}m_X m_Y R^2\cos A\}$
2	$\{\ 2^{\frac{1}{2}}(M\,I_y)^{-1}m_X m_Y R^2\sin A,\ 0,\ 2^{\frac{1}{2}}(M\,I_y)^{-1}m_X m_Y R^2\cos A\}$
3	$\{-8^{\frac{1}{2}}(M\,I_y)^{-1}m_Y R^2\sin A,\ 0,\ 0\}$

Table 1. $\boldsymbol{t}^0$ vectors for the bent symmetrical XY_2 model.

(b) For the atom pair 23, identified by p':

$$\begin{aligned}
\{D^x_{p'}, D^y_{p'}, D^z_{p'}\} &= \{-R\sin A,\ 0,\ -R\cos A\}\,,\\
\{\delta^x_{p'1}, \delta^y_{p'1}, \delta^z_{p'1}\} &= \{-2^{-\frac{1}{2}}\sin A, 0,\ -2^{-\frac{1}{2}}\cos A\}\,,\\
\{\delta^x_{p'2}, \delta^y_{p'2}, \delta^z_{p'2}\} &= \{-\tfrac{1}{2}\cos A,\ 0,\ \tfrac{1}{2}\sin A\}\,, \qquad (37)\\
\{\delta^x_{p'3}, \delta^y_{p'3}, \delta^z_{p'3}\}&\\
= \{2^{\frac{1}{2}} m_Y I_z^{-1} R^2 \sin A, 0,\ &2^{\frac{1}{2}} m_X m_Y (M I_y)^{-1} R^2 \cos A\}\,.
\end{aligned}$$

The appropriate $\mathfrak{D}^\alpha$ vectors are readily obtained by reading the equations (36) and (37) from top to bottom. In particular, all components of $\mathfrak{D}^y_p$ and $\mathfrak{D}^y_{p'}$ are seen to vanish. The nonvanishing components are also found in Table 2. In order to use Eq. (30) we need to take the squares

$$(\mathfrak{D}^\alpha_p)^2 = \mathfrak{D}^\alpha_p * \mathfrak{D}^\alpha_p = [\,(D^\alpha_p)^2\ \ 2\,\delta^\alpha_{p1}\ \ 2\,\delta^\alpha_{p2}\ \ 2\,\delta^\alpha_{p3}\ \ (\delta^\alpha_{p1})^2\ \ 2\,\delta^\alpha_{p1}\,\delta^\alpha_{p2}\ \ 2\,\delta^\alpha_{p1}\,\delta^\alpha_{p3}\ \ (\delta^\alpha_{p2})^2\ \ 2\,\delta^\alpha_{p2}\,\delta^\alpha_{p3}\ \ (\delta^\alpha_{p3})^2]\,, \qquad (38)$$

and the same for p'. The results are included in Table 2, where also them sum of squares is found. The final step is to take the square root, which presently has been carried through cubic terms. Using Eq. (17) one finds the components as given in Table 3. In accordance, the general stretchings are explicitly given as follows.

$$\left.\begin{matrix} r_1 \\ r_2 \end{matrix}\right\} = 2^{-\frac{1}{2}}(S_1{}^0 \pm S_3{}^0) + \tfrac{1}{8}R^{-1}(S_2{}^0)^2 \pm \tfrac{1}{4}2^{\frac{1}{2}} R^{-1} \varkappa\, S_2{}^0 S_3{}^0 + \tfrac{1}{4}R^{-1}\varkappa^2 (S_3{}^0)^2 - \tfrac{1}{16}2^{\frac{1}{2}} R^{-2}(S_1{}^0 \pm S_3{}^0)\,(S_2{}^0)^2$$
$$\mp \tfrac{1}{4}R^{-2}\varkappa(S_1{}^0 \pm S_3{}^0)\ S_2{}^0 S_3{}^0 - \tfrac{1}{8}2^{\frac{1}{2}} R^{-2}\varkappa^2 (S_1{}^0 \pm S_3{}^0)\,(S_3{}^0)^2 + \dots, \qquad (39)$$

Index	$\mathfrak{D}^x_{p'}, \mathfrak{D}^x_{p'}$	$\mathfrak{D}^z_{p'}, \mathfrak{D}^z_{p'}$	
0	$\pm R\sin A$	$-R\cos A$	
1	$\pm 2^{-\frac{1}{2}}\sin A$	$-2^{-\frac{1}{2}}\cos A$	
2	$\pm\frac{1}{2}\cos A$	$\frac{1}{2}\sin A$	
3	$2^{\frac{1}{2}} m_Y I_y^{-1} R^2 \sin A$	$\mp 2^{\frac{1}{2}} m_X m_Y (M I_y)^{-1} R^2 \cos A$	
Index	$(\mathfrak{D}^x_p)^2, (\mathfrak{D}^x_{p'})^2$	$(\mathfrak{D}^z_p)^2, (\mathfrak{D}^z_{p'})^2$	$\Sigma(\mathfrak{D}^\alpha_p)^2, \Sigma(\mathfrak{D}^\alpha_{p'})^2$
0	$R^2\sin^2 A$	$R^2\cos^2 A$	R^2
1	$2^{\frac{1}{2}} R\sin^2 A$	$2^{\frac{1}{2}} R\cos^2 A$	$2^{\frac{1}{2}} R$
2	$R\sin A\cos A$	$-R\sin A\cos A$	0
3	$\pm 8^{\frac{1}{2}} m_Y I_y^{-1} R^3 \sin^2 A$	$\pm 8^{\frac{1}{2}} m_X m_Y (M I_y)^{-1} R^3 \cos^2 A$	$\pm 2^{\frac{1}{2}} R$
11	$\frac{1}{2}\sin^2 A$	$\frac{1}{2}\cos^2 A$	$\frac{1}{2}$
12	$2^{-\frac{1}{2}}\sin A\cos A$	$-2^{-\frac{1}{2}}\sin A\cos A$	0
13	$\pm 2 m_Y I_y^{-1} R^2 \sin^2 A$	$\pm 2 m_X m_Y (M I_y)^{-1} R^2 \cos^2 A$	± 1
22	$\frac{1}{4}\cos^2 A$	$\frac{1}{4}\sin^2 A$	$\frac{1}{4}$
23	$\pm 2^{\frac{1}{2}} m_Y I_y^{-1} R^2 \sin A\cos A$	$\mp 2^{\frac{1}{2}} m_X m_Y (M I_y)^{-1} R^2 \sin A\cos A$	$\pm 2^{-\frac{1}{2}}\varkappa$
33	$2 m_Y I_y^{-2} R^4 \sin^2 A$	$2(m_X m_Y)^2 (M I_y)^{-2} R^4 \cos^2 A$	$\frac{1}{2}(\varkappa^2+1)$

Table 2. T-vector components in evaluation of general stretchings for the bent symmetrical XY_2 model. Throughout the upper and lower signs apply to p and p', respectively.

Abbreviation: $\varkappa = 4\, m_Y{}^2 (M I_y)^{-1} R^2 \sin A \cos A = m_Y (m_X + 2\, m_Y \sin^2 A)^{-1}, \sin 2\, A$.

Index		$(\frac{1}{2}R^{-1})$	$(-\frac{1}{8}R^{-3})$	$(\frac{1}{16}R^{-5})$	$\mathfrak{U}_p, \mathfrak{U}_p{}'$
0	R				R
1		$2^{\frac{1}{2}} R$			$2^{-\frac{1}{2}}$
3		$\pm 2^{\frac{1}{2}} R$			$\pm 2^{-\frac{1}{2}}$
11		$\frac{1}{2}$	$2R^2$		0
13		± 1	$\pm 4R^2$		0
22		$\frac{1}{4}$	0		$\frac{1}{8}R^{-1}$
23		$\pm 2^{-\frac{1}{2}}\varkappa$	0		$\pm\frac{1}{4}2^{\frac{1}{2}} R^{-1}\varkappa$
33		$\frac{1}{2}(\varkappa^2+1)$	$2R^2$		$\frac{1}{4}R^{-1}\varkappa^2$
111			$2^{\frac{1}{2}} R$	$8^{\frac{1}{2}} R^3$	0
113			$\pm 18^{\frac{1}{2}} R$	$\pm 72^{\frac{1}{2}} R^3$	0
122			$2^{-\frac{1}{2}} R$	0	$-\frac{1}{16}2^{\frac{1}{2}} R^{-2}$
123			$\pm 2R\varkappa$	0	$\mp\frac{1}{4}R^{-2}\varkappa$
133			$2^{\frac{1}{2}} R(\varkappa^2+3)$	$72^{\frac{1}{2}} R^3$	$-\frac{1}{8}2^{\frac{1}{2}} R^{-2}\varkappa^2$
223			$\pm 2^{-\frac{1}{2}} R$	0	$\mp\frac{1}{16}2^{\frac{1}{2}} R^{-2}$
233			$2R\varkappa$	0	$-\frac{1}{4}R^{-2}\varkappa$
333			$\pm 2^{\frac{1}{2}} R(\varkappa^2+1)$	$\pm 8^{\frac{1}{2}} R^3$	$\mp\frac{1}{8}2^{\frac{1}{2}} R^{-2}\varkappa^2$

Table 3. T-vector components in the last step of evaluating general stretchings for the bent symmetrical XY_2 model. See footnote to Table 2.

where the upper and lower signs apply to r_1 and r_2, respectively, and

$$\varkappa = m_Y (m_X + 2\, m_Y \sin^2 A)^{-1} \sin 2\, A\,, \tag{40}$$

The result of Eq. (39) is identical with that of Plíva [1], who has given the equations in terms of linearized valence coordinates. Their connection with the linearized symmetry coordinates is given in the legend of Fig. 1, and Plíva's equations, transscribed to the presently adopted symbols, are given below.

$$r_1 = r_1{}^0 + \tfrac{1}{8} R^{-1} [\varkappa (r_1{}^0 - r_2{}^0) + R\, \alpha^0]^2 \; (1 - R^{-1}\, r_1{}^0 + \dots), \tag{41}$$

$$r_2 = r_2{}^0 + \tfrac{1}{8} R^{-1} [\varkappa (r_1{}^0 - \mathrm{r}_2{}^0) - R\, \alpha^0]^2 \; (1 - R^{-1}\, r_2{}^0 + \dots)\,. \tag{42}$$

General interbond angle bending

The general coordinate $\cos(2\,A + \alpha)$ in the bent symmetrical XY_2 model was evaluated using Eqs. (31), (32) with the $\mathfrak{U}_p$ and $\mathfrak{U}_{p'}$ vectors as given in Table 3. Some intermediate results are listed in Table 4. The components of $\mathfrak{C}'_{pp'}$ are found in the first component column of Table 5. This table shows the last step of the calculations, using Eq. (34). All computations were carried through cubic terms. The final result (for $R\,\alpha$) is accordingly

$$R\,\alpha = S_2{}^0 - 2^{-\frac{1}{2}} R^{-1}\, S_1{}^0\, S_2{}^0 - R^{-1}\, \varkappa (S_3{}^0)^2 + \tfrac{1}{2} R^{-2} [\,(S_1{}^0)^2 + (1 - \varkappa^2)\; (S_3{}^0)^2]\; S_2{}^0 + 2^{\frac{1}{2}} R^{-2}\, \varkappa\, S_1{}^0 (S_3{}^0)^2 - \tfrac{1}{12} R^{-2} (S_2{}^0)^3 + \dots, \tag{43}$$

where $\varkappa$ is the same mass-dependent constant as above; see Eq. (40). Again the result is consistent with that of Plíva [1], who has given the following expression in terms of linearized valence coordinates (cf. legend

Index	$(\mathfrak{U}_p)^{-1}, (\mathfrak{U}_p{}')^{-1}$	$(\mathfrak{U}_p)^{-1} * (\mathfrak{U}_p{}')^{-1}$	$\Sigma(\mathfrak{D}_p^\alpha * \mathfrak{D}_p{}')$
0	R^{-1}	R^{-2}	$R^2 \cos 2\,A$
1	$-2^{-\frac{1}{2}} R^{-2}$	$-2^{\frac{1}{2}} R^{-3}$	$2^{\frac{1}{2}} R \cos 2\,A$
2	0	0	$-R \sin 2\,A$
3	$\mp 2^{-\frac{1}{2}} R^{-2}$	0	0
11	$\frac{1}{2} R^{-3}$	$\frac{3}{2} R^{-4}$	$\frac{1}{2} \cos 2\,A$
12	0	0	$-2^{-\frac{1}{2}} \sin 2\,A$
13	$\pm R^{-3}$	0	0
22	$-\frac{1}{8} R^{-3}$	$-\frac{1}{4} R^{-4}$	$-\frac{1}{4} \cos 2\,A$
23	$\mp \frac{1}{4} 2^{\frac{1}{2}} R^{-3} \varkappa$	0	0
33	$-\frac{1}{4} R^{-3} (\varkappa^2 - 2)$	$-\frac{1}{2} R^{-4} (\varkappa^2 - 1)$	$\frac{1}{2} (\varkappa^2 - 1) \cos 2\,A + \varkappa \sin 2\,A$
111	$-\frac{1}{4} 2^{\frac{1}{2}} R^{-4}$	$-2^{\frac{1}{2}} R^{-5}$	
113	$\mp \frac{3}{4} 2^{\frac{1}{2}} R^{-4}$	0	
122	$\frac{3}{16} 2^{\frac{1}{2}} R^{-4}$	$2^{-\frac{1}{2}} R^{-5}$	
123	$\pm \frac{3}{4} R^{-4} \varkappa$	0	
133	$\frac{3}{8} 2^{\frac{1}{2}} R^{-4} (\varkappa^2 - 2)$	$2^{\frac{1}{2}} R^{-5} (\varkappa^2 - 1)$	
223	$\pm \frac{3}{16} 2^{\frac{1}{2}} R^{-4}$	0	
233	$\frac{3}{4} R^{-4} \varkappa$	$R^{-5} \varkappa$	
333	$\pm \frac{1}{8} 2^{\frac{1}{2}} R^{-4} (\varkappa^2 - 2)$	0	

Table 4. T-vector components in evaluation of general bending for the bent symmetrical XY_2 model. See footnote to Table 2.

Index	$\left(-\dfrac{1}{\sin 2\,A}\right)$	$\left(-\dfrac{\cos 2\,A}{2 \sin^2 2\,A}\right)$	$\left(-\dfrac{1 + 2 \cos^2 2\,A}{6 \sin^5 2\,A}\right)$	$\mathfrak{U}'_{pp'}$
2	$-R^{-1} \sin 2\,A$			R^{-1}
12	$2^{-\frac{1}{2}} R^{-2} \sin 2\,A$			$-2^{-\frac{1}{2}} R^{-2}$
22	$-\frac{1}{2} R^{-2} \cos 2\,A$	$R^{-2} \sin^2 2\,A$		0
33	$R^{-2} \varkappa \sin 2\,A$	0		$-R^{-2} \varkappa$
112	$-\frac{1}{2} R^{-3} \sin 2\,A$	0		$\frac{1}{2} R^{-3}$
122	$2^{-\frac{1}{2}} R^{-3} \cos 2\,A$	$-2^{\frac{1}{2}} R^{-3} \sin^2 2\,A$		0
133	$-2^{\frac{1}{2}} R^{-3} \varkappa \sin 2\,A$	0		$2^{\frac{1}{2}} R^{-3} \varkappa$
222	$\frac{1}{4} R^{-3} \sin 2\,A$	$R^{-3} \sin 2\,A \cos 2\,A$	$-R^{-3} \sin^3 2\,A$	$-\frac{1}{12} R^{-3}$
233	$R^{-3} [\frac{1}{2} (\varkappa^2 - 1) \sin 2\,A + \varkappa \cos 2\,A]$	$-2\, R^{-3} \varkappa \sin^2 2\,A$	0	$\frac{1}{2} R^{-3} (1 - \varkappa^2)$

Table 5. T-vector components in the last step of evaluating the general bending for the bent symmetrical XY_2 model.

Atom	S_1^0	S_2^0	S_3^0
1	$\{\tfrac{1}{12}3^{\frac12}, \tfrac{1}{12}3^{\frac12}, -\tfrac{1}{12}3^{\frac12}\}$	$\{\tfrac{1}{12}6^{\frac12}, \tfrac{1}{12}6^{\frac12}, \tfrac{1}{6}6^{\frac12}\}$	$\{-\tfrac14 2^{\frac12}, \tfrac14 2^{\frac12}, 0\}$
2	$\{-\tfrac{1}{12}3^{\frac12}, \tfrac{1}{12}3^{\frac12}, \tfrac{1}{12}3^{\frac12}\}$	$\{-\tfrac{1}{12}6^{\frac12}, \tfrac{1}{12}6^{\frac12}, -\tfrac{1}{6}6^{\frac12}\}$	$\{\tfrac14 2^{\frac12}, \tfrac14 2^{\frac12}, 0\}$
3	$\{\tfrac{1}{12}3^{\frac12}, -\tfrac{1}{12}3^{\frac12}, \tfrac{1}{12}3^{\frac12}\}$	$\{\tfrac{1}{12}6^{\frac12}, -\tfrac{1}{12}6^{\frac12}, -\tfrac{1}{6}6^{\frac12}\}$	$\{-\tfrac14 2^{\frac12}, -\tfrac14 2^{\frac12}, 0\}$
4	$\{-\tfrac{1}{12}3^{\frac12}, -\tfrac{1}{12}3^{\frac12}, -\tfrac{1}{12}3^{\frac12}\}$	$\{-\tfrac{1}{12}6^{\frac12}, -\tfrac{1}{12}6^{\frac12}, \tfrac{1}{6}6^{\frac12}\}$	$\{\tfrac14 2^{\frac12}, -\tfrac14 2^{\frac12}, 0\}$
Atom	S_4^0	S_5^0	S_6^0
1	$\{0, -\tfrac14, \tfrac14\}$	$\{-\tfrac14, 0, \tfrac14\}$	$\{\tfrac14, \tfrac14, 0\}$
2	$\{0, \tfrac14, \tfrac14\}$	$\{\tfrac14, 0, -\tfrac14\}$	$\{\tfrac14, -\tfrac14, 0\}$
3	$\{0, \tfrac14, -\tfrac14\}$	$\{\tfrac14, 0, \tfrac14\}$	$\{-\tfrac14, \tfrac14, 0\}$
4	$\{0, -\tfrac14, -\tfrac14\}$	$\{-\tfrac14, 0, -\tfrac14\}$	$\{-\tfrac14, -\tfrac14, 0\}$

Table 6. $\boldsymbol{t}^0$ vectors for the tetrahedral Z_4 model.

of Fig. 1).

$$\alpha = \alpha^0 - \tfrac12 R^{-2}[\varkappa(r_1{}^0 - r_2{}^0)^2 + R\,\alpha^0(r_1{}^0 + r_2{}^0)] + \tfrac14 R^{-3}\{2\,\varkappa(r_1{}^0 + r_2{}^0)(r_1{}^0 - r_2{}^0)^2 + R\,\alpha^0\,[2(r_1{}^{02} + r_2{}^{02}) - \varkappa^2(r_1{}^0 - r_2{}^0)^2] - \tfrac13 R^3(\alpha^0)^3\} + \dots \quad (44)$$

Tetrahedral Z_4 model

The molecular model of a regular tetrahedron is shown in Fig. 2, of which the legend includes the chosen linearized symmetry coordinates. The corresponding $\boldsymbol{t}^0$ vectors are given in Table 6.

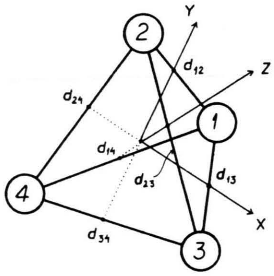

Fig. 2. Tetrahedral Z_4 model (symmetry T_d). The cartesian axes have been chosen along the three two-fold symmetry axes. The instantaneous bond stretching coordinates are indicated on the figure. The equilibrium Z—Z distance is denoted by D (in the text). Linearized symmetry coordinates:

Species A_1 $\quad S_1{}^0 = 6^{-\frac12}(d_{12}{}^0 + d_{13}{}^0 + d_{23}{}^0 + d_{34}{}^0 + d_{24}{}^0 + d_{14}{}^0)$,

$$E \begin{cases} S_2{}^0 = 12^{-\frac12}(2\,d_{23}{}^0 - d_{21}{}^0 - d_{13}{}^0 + 2\,d_{14}{}^0 - d_{34}{}^0 - d_{24}{}^0), \\ S_3{}^0 = \tfrac12(d_{13}{}^0 - d_{12}{}^0 + d_{24}{}^0 - d_{34}{}^0), \end{cases}$$

$$F_2 \begin{cases} S_4{}^0 = 2^{-\frac12}(d_{24}{}^0 - d_{13}{}^0), \\ S_5{}^0 = 2^{-\frac12}(d_{34}{}^0 - d_{12}{}^0), \\ S_6{}^0 = 2^{-\frac12}(d_{14}{}^0 - d_{23}{}^0). \end{cases}$$

It is seen that the symmetry coordinates have been numbered irrespective of the degeneracies in species E (double) and F_2 (triple).

In the following we give the final result for the six general stretchings, without quoting any of the intermediate results.

$$\left.\begin{matrix} d_{24} \\ d_{13} \end{matrix}\right\} = 6^{-\frac12} S_1{}^0 - \tfrac16 3^{\frac12} S_2{}^0 + \tfrac12 S_3{}^0 \pm 2^{-\frac12} S_4{}^0 + \tfrac18 D^{-1}[(3^{\frac12} S_2{}^0 + S_3{}^0)^2 + (S_5{}^0 \pm S_6{}^0)^2] - \tfrac{1}{48}6^{\frac12} D^{-2} S_1{}^0[(3^{\frac12} S_2{}^0 + S_3{}^0)^2 + (S_5{}^0 \pm S_6{}^0)^2] + \tfrac{1}{48} 3^{\frac12} D^{-2}(S_2{}^0 - 3^{\frac12} S_3{}^0)\,(3^{\frac12} S_2{}^0 + S_3{}^0)^2 \mp \tfrac{1}{16} 2^{\frac12} D^{-2}[(3^{\frac12} S_2{}^0 + S_3{}^0)^2 + (S_5{}^0 \pm S_6{}^0)^2]\, S_4{}^0 + \tfrac{1}{48} 3^{\frac12} D^{-2}(S_2{}^0 - 3^{\frac12} S_3{}^0)\,(S_5{}^0 \pm S_6{}^0)^2 + \dots \quad (45)$$

Here the upper and lower signs apply to d_{24} and d_{13}, respectively.

$$\left.\begin{matrix} d_{34} \\ d_{12} \end{matrix}\right\} = 6^{-\frac12} S_1{}^0 - \tfrac16 3^{\frac12} S_2{}^0 - \tfrac12 S_3{}^0 \pm 2^{-\frac12} S_5{}^0 + \tfrac18 D^{-1}[(3^{\frac12} S_2{}^0 - S_3{}^0)^2 + (S_4{}^0 \pm S_6{}^0)^2]\tfrac{1}{48}6^{\frac12} D^{-2} S_1{}^0[(3^{\frac12} S_2{}^0 - S_3{}^0)^2 + (S_4{}^0 \pm S_6{}^0)^2] + \tfrac{1}{48} 3^{\frac12} D^{-2}(S_2{}^0 + 3^{\frac12} S_3{}^0)\,(3^{\frac12} S_2{}^0 - S_3{}^0)^2 \mp \tfrac{1}{16} 2^{\frac12} D^{-2}[(3^{\frac12} S_2{}^0 - S_3{}^0)^2 + (S_4{}^0 \pm S_6{}^0)^2]\, S_5{}^0 + \tfrac{1}{48} 3^{\frac12} D^{-2}(S_2{}^0 + 3^{\frac12} S_3{}^0)\,(S_4{}^0 \pm S_6{}^0)^2 + \dots, \quad (46)$$

where the upper and lower signs apply to d_{34} and d_{12}, respectively

$$\left.\begin{matrix} d_{14} \\ d_{23} \end{matrix}\right\} = 6^{-\frac12} S_1{}^0 + 3^{-\frac12} S_2{}^0 \pm 2^{-\frac12} S_6{}^0 + \tfrac12 D^{-1}(S_3{}^0)^2 + \tfrac18 D^{-1}(S_4{}^0 \pm S_5{}^0)^2 - \tfrac{1}{12} 6^{\frac12} D^{-2} S_1{}^0(S_3{}^0)^2 - \tfrac{1}{48} 6^{\frac12} D^{-2} S_1{}^0(S_4{}^0 \pm S_5{}^0)^2 - \tfrac16 3^{\frac12} D^{-2} S_2{}^0(S_3{}^0)^2 - \tfrac{1}{24} 3^{\frac12} D^{-2} S_2{}^0(S_4{}^0 \pm S_5{}^0)^2 \mp \tfrac14 2^{\frac12} D^{-2}(S_3{}^0)^2 S_6{}^0 \mp \tfrac{1}{16} 2^{\frac12} D^{-2}(S_4{}^0 \pm S_5{}^0)^2 S_6{}^0 + \dots, \quad (47)$$

where the upper and lower signs apply to d_{14} and d_{23}, respectively.

Connection with the Approach of Morino and Hirota

General considerations

Morino and Hirota [6] have already in 1955 given a discussion of instantaneous interatomic distance deviations. Their treatment is based on the (a) parallel and (b) perpendicular displacements which presently shall be identified by the symbols (a) Δz_p, and (b) Δx_p, Δy_p. These coordinates are supposed to be oriented individually for each of the atom pairs (p) in such a way that Δz_p lies along the connecting line of the atoms in their equilibrium position. Special interest is attached to the mean-square values of the mentioned quantities in molecules at thermal equilibrium; they are the mean-square parallel and perpendicular amplitudes. A great deal of work on these quantities has been done, using the approximation of small harmonic vibrations [7–9]. The mean-square perpendicular amplitudes, viz. $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$, have in particular been used for computations of the so-called shrinkage effects in gaseous electron-diffraction measurements of internuclear distances [10–13].

Very little work has been done as to the accurate treatment of anharmonicity for vibrations of polyatomic molecules, but reference should be made to the highly significant work of Kuchitsu and Bartell [14, 15] on methanes, and Morino and Iijima [16] on CO_2 and CS_2; see also Reitan [17]. In one of these papers [14] the formula is given for an instantaneous angle bending as expanded in terms of the parallel and perpendicular displacements, in addition to the known formula for stretchings [6]. Below we reproduce only the formula of the latter case;

$$d_p = \Delta z_p + \tfrac{1}{2}(D_p^{\mathrm{e}})^{-1}[(\Delta x_p)^2 + (\Delta y_p)^2] - \tfrac{1}{2}(D_p^{\mathrm{e}})^{-2}\Delta z_p\,[(\Delta x_p)^2 + (\Delta y_p)^2] + \dots \quad (48)$$

It has been obtained by an expansion of the exact form

$$D_p^{\mathrm{e}} + d_p = [(D_p^{\mathrm{e}} + \Delta z_p)^2 + (\Delta x_p)^2 + (\Delta y_p)^2]^{\frac{1}{2}}. \quad (49)$$

It is the purpose of this section to point out the equivalence of Eq. (49) and the basis of Eqs. (29), (30) in the Cihla–Plíva treatment, viz.

$$D_p^{\mathrm{e}} + d_p = [(D_p^x + d_p^x)^2 + (D_p^y + d_p^y)^2 + (D_p^z + d_p^z)^2]^{\frac{1}{2}}. \quad (50)$$

We need only to consider the connection between the d_p^α coordinates as defined in Eq. (23), and the Δz_p, Δx_p, Δy_p of Eq. (49) above.

Let l_p, m_p and n_p be the unit vectors of the cartesian axes along Δz_p, Δx_p and Δy_p, respectively. Their components are the direction cosines of the bond vector for the atom pair (p) in question. Since l_p is the unit vector along the bond vector itself, one has readily

$$l_p = \boldsymbol{D}_p / D_p^{\mathrm{e}}, \quad (51)$$

using the notation from the preceding sections. The m_p and n_p vectors should be taken as to form a cartesian system along with l_p, but there still remains an ambiguity in their orientation with respect to l_p; this is the subject of an arbitrary choise, usually made to attain best convenience for the special case studied. One has consequently

$$\Delta z_p = \tilde{l}_p \cdot \boldsymbol{d}_p\,, \quad \Delta x_p = \tilde{m}_p \cdot \boldsymbol{d}_p\,, \quad \Delta y_p = \tilde{n}_p \cdot \boldsymbol{d}_p\,. \quad (52)$$

Eqs. (52) may be put into matrix form as

$$\begin{bmatrix} \Delta z_p \\ \Delta x_p \\ \Delta y_p \end{bmatrix} = \mathcal{K}_p \begin{bmatrix} d_p^x \\ d_p^y \\ d_p^z \end{bmatrix}, \quad (53)$$

where
$$\mathcal{K}_p = \begin{bmatrix} l_p^x & l_p^y & l_p^z \\ m_p^x & m_p^y & m_p^z \\ n_p^x & n_p^y & n_p^z \end{bmatrix}. \quad (54)$$

Notice that one also has

$$\mathcal{K}_p \boldsymbol{D}_p = \mathcal{K}_p \begin{bmatrix} D_p^x \\ D_p^y \\ D_p^z \end{bmatrix} = \begin{bmatrix} D_p^{\mathrm{e}} \\ 0 \\ 0 \end{bmatrix}. \quad (55)$$

Application to r_1 in bent symmetrical XY_2

In order to exemplify the above considerations we give here the $\mathcal{K}$ matrix for the $1-3$ atom pair in

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the bent symmetrical XY_2 model treated above. One may write

$$\begin{bmatrix} \Delta \mathrm{z}_{13} \\ \Delta \mathrm{x}_{13} \\ \Delta \mathrm{y}_{13} \end{bmatrix} = \begin{bmatrix} \sin A & 0 & -\cos A \\ -\cos A & 0 & -\sin A \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} \Delta x_{13} \\ \Delta y_{13} \\ \Delta z_{13} \end{bmatrix} \qquad (56)$$

when $\Delta \mathrm{x}_{13}$ and $\Delta \mathrm{y}_{13}$ have been chosen as the appropriate displacements in-plane and perpendicular to the molecular plane, respectively. One may now proceed using Eq. (48), and substituting $\Delta \mathrm{z}_{13}$, $\Delta \mathrm{x}_{13}$, $\Delta \mathrm{y}_{13}$ according to Eq. (56). We shall immediately make use of the fact that $\Delta \mathrm{y}_{13}$ as well as Δy_{13} vanish identically in the present case, and write

$$\begin{aligned} r_1 = {} & d_p{}^x \sin A - d_p{}^z \cos A + \tfrac{1}{2} R^{-1} [(d_p{}^x)^2 \cos^2 A \\ & + 2\, d_p{}^x\, d_p{}^z \sin A \cos A + (d_p{}^z)^2 \sin^2 A] \\ & - \tfrac{1}{2} R^{-2} [(d_p{}^x)^3 \sin A \cos^2 A \\ & + (d_p{}^x)^2\, d_p{}^z \cos A\ (2 \sin^2 A - \cos^2 A) \\ & - d_p{}^x (d_p{}^z)^2 \sin A\ (2 \cos^2 A - \sin^2 A) \\ & - (d_p{}^z)^3 \cos A \sin^2 A] + \dots . \end{aligned} \qquad (57)$$

Here $d_p{}^x = \Delta x_{13}$ and $d_p{}^z = \Delta z_{13}$. These displacements are expressed in terms of the linearized symmetry coordinates (see Fig. 1) as

$$d_p^\alpha = \delta_{p1}^\alpha\, S_1{}^0 + \delta_{p2}^\alpha\, S_2{}^0 + \delta_{p3}^\alpha\, S_3{}^0; \quad \alpha = x, z, \qquad (58)$$

in which the coefficients are given by Eqs. (36). On substituting from (58) into Eq. (57) one obtains the result of Eq. (39) (with upper signs); the actual calculation, however, is rather tedious.

Connection with the Approach of Pariseau et al.

The method of Pariseau et al. [3] for treating instantaneous coordinates is in some sense the most straightforward one, since it makes explicit use of the partial derivatives of the expansion about equilibrium. To take the bond stretching as the simplest example, one obtains from Eq. (50) the following first order partial derivatives at equilibrium

$$b_p{}^\alpha = \partial d_p / \partial d_p{}^\alpha = D_p{}^\alpha / D_p{}^{\mathrm{e}} \quad (\alpha = x, y, z). \qquad (59)$$

For any coordinate such first-order partial derivatives may be identified with the components of the familiar $\boldsymbol{s}$ vectors [18] for the corresponding linearized coordinate. The mentioned investigators [3] have utilized the fact that all higher-order partial derivatives in the expansion may be expressed in terms of the first-order derivatives (59). For the stretching coordinate one has (when omitting the subscript p throughout):

$$\left.\begin{aligned} \partial^2 d / (\partial d^\alpha)^2 &= [1 - (b^\alpha)^2] / D^{\mathrm{e}}, \\ \partial^2 d / \partial d^\alpha\, \partial d^\beta &= - b^\alpha\, b^\beta / D^{\mathrm{e}}, \end{aligned}\right\} \qquad (60)$$

$$\left.\begin{aligned} \partial^3 d / (\partial d^\alpha)^3 &= 3\, b^\alpha [(b^\alpha)^2 - 1] / (D^{\mathrm{e}})^2, \\ \partial^3 d / (\partial d^\alpha)^2\, \partial d^\beta &= b^\beta [3 (b^\alpha)^2 - 1] / (D^{\mathrm{e}})^2, \\ \partial^3 d / \partial d^\alpha\, \partial d^\beta\, \partial d^\gamma &= 3\, b^\alpha\, b^\beta\, b^\gamma / (D^{\mathrm{e}})^2, \end{aligned}\right\} \qquad (61)$$

where α, β, $\gamma = x$, y or z. Pariseau et al. [3] also give the partial derivatives in the case of angle bending; those expressions are however too long and complicated to be reproduced here.

On this place we shall only show the application of Eqs. (59) – (61) to the r_1 stretching in bent XY_2 molecules. The corresponding linearized coordinate is

$$r_1{}^0 = \Delta x_{13} \sin A - \Delta z_{13} \cos A = d_p{}^x \sin A - d_p{}^z \cos A. \qquad (62)$$

This gives us the two nonvanishing first-order partial derivatives (at equilibrium);

$$\begin{aligned} b_p{}^x &= \partial r_1 / \partial d_p{}^x = \partial r_1{}^0 / \partial d_p{}^x = \sin A, \\ b_p{}^z &= \partial r_1 / \partial d_p{}^z = \partial r_1{}^0 / \partial d_p{}^z = -\cos A, \end{aligned} \qquad (63)$$

these results being consistent with Eq. (59) when using the appropriate components from Eqs. (36). Using (63) one obtains from Eqs. (60), (61) the following higher-order partial derivatives.

$$\begin{aligned} \partial^2 r_1 / (\partial d_p{}^x)^2 &= R^{-1} \cos^2 A, \\ \partial^2 r_1 / (\partial d_p{}^z)^2 &= R^{-1} \sin^2 A, \\ \partial^2 r_1 / \partial d_p{}^x\, \partial d_p{}^z &= R^{-1} \sin A \cos A, \end{aligned} \qquad (64)$$

$$\begin{aligned} \partial^3 r_1 / (\partial d_p{}^x)^3 &= -3\, R^{-2} \sin A \cos^2 A, \\ \partial^3 r_1 / (\partial d_p{}^z)^3 &= 3\, R^{-2} \cos A \sin^2 A, \\ \partial^3 r_1 / (\partial d_p{}^x)^2\, \partial d_p{}^z &= \\ & - R^{-2} \cos A (2 \sin^2 A - \cos^2 A), \\ \partial^3 r_1 / \partial d_p{}^x (\partial d_p{}^z)^2 &= R^{-2} \sin A (2 \cos^2 A - \sin^2 A). \end{aligned} \qquad (65)$$

These expressions for the partial derivatives through third order, (63) – (65), are seen to be consistent with Eq. (57)

Conclusion

The Cihla–Plíva [4] method of evaluating general (instantaneous) valence coordinates in terms of linearized symmetry coordinates is found so far to

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[18] E. B. Wilson, Jr., J. Chem. Phys. 9, 76 [1941].

be the most convenient method for systematic calculations. Presently it was successfully applied to the bent symmetrical XY_2 and tetrahedral Z_4 models, for which the computations were carried through cubic terms without too much labour.

The same results could be obtained using the parallel and perpendicular displacements in the approach of MORINO and HIROTA [6]. Although the expansions in terms of these coordinates are very suitable for several purposes, it turns out that the transformation to linearized symmetry coordinates is rather cumbersome; it has been exemplified by considering one of the stretchings (r_1) in the bent symmetrical XY_2 model. The same approach could also be used for the bending coordinate, but would be still more tedious; no details seem worth while reporting in the present work.

In the case of r_1 in bent symmetrical XY_2 also the method of PARISEAU et al. [3] was applied; in this method the partial derivatives of the expansion are evaluated explicitly. Equivalence was shown with the expression in terms of cartesian displacements obtained from the approach according to MORINO and HIROTA [6]. No attempt was made to apply the formulae of PARISEAU et al. [3] for the case of an angle bending; they seem too complicated for systematic evaluation of algebraic expressions.

In cases of less simple molecular models, and computations beyond cubic terms, it seems to be an inevitable conclusion that one must fall back on numerical solutions from electronic-computer calculations. It is not so easily decided which one of the discussed methods is most convenient for computer programming, since the computational labour in that case becomes less important. To the author's opinion, however, the CIHLA–PLÍVA [4] method appears to be the most attractive approach. Moreover, this is so far the only method by which the general out-of-plane bendings and torsional coordinates have been treated.