Transforming from internal coordinates to Cartesian displacements in the Eckart frame: a Taylor series expansion approach

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In order to describe molecular properties which depend on the instantaneous nuclear geometry, such as the potential energy and electric and magnetic moments, it is advantageous to use geometrically defined (i.e., mass independent) internal coordinates (bond lengths, interatomic distances, valence angles, dihedral angles). In the case of systems possessing a high degree of contortion instability, these coordinates may also be most suitable for describing the rovibrational dynamics (see [1] and references therein). The construction of the corresponding quantum mechanical Hamiltonians has been undertaken in many laboratories (see, e.g., [2–10]) and several of these studies provide theory for a general molecule. However, the use of curvilinear coordinates leads to very complicated expressions for the kinetic energy operator and for larger systems it may become prohibitively difficult to derive this operator. To avoid these problems, it is desirable to reduce the dimensionality of the studied problems by imposing model constraints (i.e., by freezing or constraining internal coordinates). However, it is not straightforward to impose such constraints even when the operator for the corresponding constraint-free task is known (see, e.g., [11,12] and references therein). It is similarly difficult to impose dynamic constraints such as Eckart and Sayvetz conditions (see, e.g., [13]) as shown by the fact that almost all ‘curvilinear’ calculations were performed without such constraints; in these calculations the molecule-fixed axis system is attached directly to the instantaneous configuration of the molecule. Disregarding the dynamic constraints reduces the degree of separability of the vibrational motions from the over-all molecular rotation, thus deteriorating the quality of the vibrational zero-order models. Moreover, it also prevents an accurate determination of the vibrational observables associated with vector and tensor molecular properties (see, e.g., [14]). The curvilinear coordinates also play an important role in the framework of molecular dynamics semiclassical simulations, though these simulations are usually performed in terms of the Cartesian coordinates. For instance [15], a computer simulation of molecular liquids requires that at each simulation step the Eckart geometry be determined from the instantaneous values of the internal coordinates (in order to account for the Coriolis coupling contributions to the correlation functions).

Apparently, the transformation from the internal (curvilinear) coordinates to the constrained Cartesian coordinates in the Eckart frame is of basic importance in a broad area of molecular physics. In general, this transformation leads to the solution of a system of nonlinear equations which can be derived from the imposed constraints and geometrical definitions of the internal coordinates. In principle, these equations may have nonunique solutions. However, if we eliminate large-amplitude motions from the vibrational part of a given dynamical problem, using for instance the Hugen–Bunker–Johns approach [16], we can assume that the vibrational displacements are small enough to allow for an unambiguous solution of the given problem. In the actual solution of the equations one can proceed either numerically or analytically. Though fairly general, the numerical approach [17] is inconvenient from many respects. An analytical solution of the problem in a closed form, on the other hand, appears to be available only in the case of triatomics [18–20]. However, due to the assumption of the ‘infinitesimal’ character of the vibrational displacements, we may seek for solutions...
expressed as Taylor series expansions. In our previous paper on the \(XY_2^+\) molecules [21], we have shown that a cubic expansion leads to fully satisfactory results, even for molecules as light as the deuterated isotopomers of \(H_3\). A very similar procedure has also been used, very successfully, in the case of the MORBID approach of Jensen [22]. The purpose of this paper is to point out the feasibility of extending this procedure to larger molecular systems. Potential prospects of this (computer algebra) approach are illustrated on the planar \(XY_3\) (\(D_3h\)) and \(XY_2^+Y^-\) (\(C_{2v}\)) model systems.

Let us consider a planar \(XY_3\) molecule with \(D_{3h}\) symmetry. The orientation of the molecule-fixed axes of this molecule in its reference (equilibrium) configuration is defined as shown in Fig. 1. All three bond lengths are held fixed at the equilibrium value \(r_e\) and all three (equilibrium) angles are equal to \(\alpha_e = 120^\circ\). The corresponding Cartesian components of the atomic position vectors \(r_i^e\) are

\[
\begin{align*}
    x_1^e &= r_e, \quad y_1^e = 0, \quad z_1^e = 0, \\
    x_2^e &= \frac{1}{2}r_e, \quad y_2^e = \frac{1}{2}\sqrt{3}r_e, \quad z_2^e = 0, \\
    x_3^e &= \frac{1}{2}r_e, \quad y_3^e = -\frac{1}{2}\sqrt{3}r_e, \quad z_3^e = 0, \\
    x_4^e &= 0, \quad y_4^e = 0, \quad z_4^e = 0.
\end{align*}
\]  

(1)

In a displaced configuration we locate the axes with origin at the molecular center of mass so that the Eckart conditions

\[
\sum_i m_i (r_i^e \times \Delta r_i) = 0
\]

(2)

are satisfied (\(m_i\) is the atomic mass of nucleus \(i\)). It can easily be shown that in this case, the Cartesian displacement coordinates satisfy the following constraints:

\[
\begin{align*}
    \Delta x_4 &= \frac{m_y}{m_X} (\Delta x_1 + \Delta x_2 + \Delta x_3), \\
    \Delta y_4 &= \frac{m_y}{m_X} \left( -\sqrt{3}\Delta x_2 + \sqrt{3}\Delta x_3 + 3\Delta y_1 \right), \\
    \Delta z_4 &= -\frac{\sqrt{3}}{3}\Delta y_2, \\
    \Delta z_2 &= \Delta z_3 = \Delta z_1, \\
    \Delta z_4 &= -\frac{3m_y}{m_X} \Delta z_1.
\end{align*}
\]  

(3)

To describe the instantaneous geometry of our molecule it is convenient to use curvilinear coordinates \(S_1, S_2, \ldots, S_5\) expressed in terms of the three bond lengths \(r_{i4}\), the three valence angles \(\alpha_i\), and the distance \(h\) of the atom \(X\) from the plane formed by the three \(Y\) atoms [23]. We define

\[
\begin{align*}
    S_1 &= \Delta r_{14}, \quad S_2 = \Delta r_{24}, \quad S_3 = \Delta r_{34}, \\
    S_4 &= (\Delta x_1 - \Delta x_2 - \Delta x_3)/\sqrt{6}, \\
    S_5 &= (\Delta x_2 - \Delta x_3)/\sqrt{2}, \\
    S_6 &= h,
\end{align*}
\]  

(4)

where

\[
\Delta r_{4i} = |r_{4i}^e| - r_e \quad (i = 1, 2, 3),
\]

\[
\Delta x_i = \arccos(r_{i4}^e/r_{i4}) - \alpha_e \quad (i \neq j \neq k = 1, 2, 3)
\]

and

\[
\frac{D}{\sqrt{A^2 + B^2 + C^2}},
\]

(5)

with

\[
A x + By + Cz + D = \det \begin{bmatrix} x & y & z & 1 \\ (r_{14})_x & (r_{14})_y & (r_{14})_z & 1 \\ (r_{34})_x & (r_{34})_y & (r_{34})_z & 1 \\ (r_{44})_x & (r_{44})_y & (r_{44})_z & 1 \end{bmatrix}.
\]

The nonlinear relations in Eq. (4) can be now inverted with respect to the six independent Cartesian displacements (i.e., \(\Delta x_1, \Delta x_2, \Delta x_3, \Delta y_1, \Delta y_2, \Delta z_1\)) in Eqs. [3], and the main part of our task is thus completed. The problem is simplified by the linear relation \(|\Delta z_1| = m_X/(3m_Y + m_X h)\). To invert, we express the desired Cartesian displacements, \(\Delta \delta_i (\delta = x, y, z)\), as (infinite) Taylor series

\[
\begin{align*}
\Delta \delta_i &= \sum_j C_j^i \delta_j + \frac{1}{2} \sum_{jk} C_{jk}^i \delta_j \delta_k + \frac{1}{6} \sum_{jkl} C_{jkl}^i \delta_j \delta_k \delta_l + \cdots.
\end{align*}
\]  

(6)
substitute these definitions into Eq. (4) and, finally, solve the resulting system of linear equations for the expansion coefficients \( C_{ij} \).

In principle, this “inversion” procedure can be performed numerically. In practice, however, this “numerical” procedure is prone to numerical instabilities. Thus, it is recommendable to proceed symbolically using a computer algebra approach (in this study we rely on MAPLE [24]). Since we consider infinitesimal vibrational displacements, the actual determination of the unknown coefficients can conveniently be carried out recursively, that is, step by step for different orders of the expansion terms. First we neglect all the nonlinear terms and determine the linear coefficients \( C_{ij} \). These are then substituted into our definitions which in turn are used to determine the quadratic coefficients \( C'_{ijk} \). This procedure can be continued to obtain the cubic and higher order expansion coefficients.

The ‘inversion’ procedure described is very robust and straightforward. Nevertheless, as seen in Tables 1–3 (all expansion coefficients missing in the tables are equal to zero), when we increase the accuracy by taking into account terms of higher and higher order, the formal complexity increases. For simple and highly symmetrical systems like the \( XY_3 \) molecule, this is no real problem. For larger and less symmetrical systems, however, the formal complexity makes the suggested procedure rather awkward. To get an insight on this problem, we have performed calculations also for the \( XY^*Y_2 \) system which arises from the \( XY_3 \) system being substituted by an isotope \( Y^* \). Apart from the fact that there are nonzero expansion coefficients, there is an even more dramatic change in the complexity of the problem. This is easily seen from comparing the following examples with their \( XY_3 \) counterparts in Table 2:

\[
\begin{align*}
C(\Delta x_1)_{66} &= -6m_Y M (81m_Y^2 m_Y^2 + 63m_X m_Y m_Y^2, \\
&+ 8m_Y^2 m_Y^2 + 14m_Y^2 m_Y m_Y^2 + 18m_X m_Y^2 m_Y, \\
&+ 5m_Y^2 m_Y^2 + 3m_X m_Y^2) / E, \\
C(\Delta x_2)_{66} &= -3M (-81m_Y^2 m_Y^2 - 8m_Y^2 m_Y, \\
&- 36m_X m_Y m_Y^2 + 45m_Y^2 m_Y^2 - 8m_Y^2 m_Y, \\
&- 32m_X^2 m_Y m_Y^2 + 4m_Y^2 m_Y m_Y, \\
&+ 13m_Y^2 m_Y^2 - m_Y^2 m_Y^2 / E, \\
\end{align*}
\]

where

\[
M = m_X + 2m_Y + m_Y, \\
E = (18m_Y^2 m_Y^2 + 2m_Y m_Y + 9m_Y m_Y^2, \\
+ 18m_Y m_Y m_Y^2 + m_Y^2 m_Y^2 r_Y.
\]

The cubic and higher order expansion coefficients are even more complicated, and so it is not possible to evaluate them economically and present their general form in a meaningful way. However, the calculation, and the presentation of the results, pose no problem if all the involved masses and equilibrium geometry parameters are replaced by numerical values.

The procedure described above for the \( XY_3 \) and \( XY^*Y_2 \) systems can straightforwardly be applied to any mole-

### Table 1

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circular system exhibiting small-amplitude ('infinitesimal') vibrational motions. The procedure can also be adopted to nonrigid systems by removing the large-amplitude motions from the Hamiltonians for the small-amplitude vibration (using, for example, the HBJ approach). Currently, the procedure is applied for constructing effective Hamiltonians describing the intramolecular O–H⋯O proton transfer motion in formimidol and malonaldehyde [25].

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References