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CORIOLIS COUPLING IN POLYATOMIC MOLECULES
WITH PARTLY FROZEN VIBRATIONS

Ara Chutjian

April 1964
CORIOLIS COUPLING IN POLYATOMIC MOLECULES
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Ara Chutjian*

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ABSTRACT

The "Eckart expansion of the normal mode," proposed by Herschbach and Laurie, has been used to derive explicit form for Coriolis coupling constants and first and second order expansion coefficients for the instantaneous moment of inertia tensor. Several examples of "unfrozen" vibrational modes in molecules of $C_{2v}$ and $C_{3v}$ symmetry are treated with the use of Polo's $\rho$-vectors, and the results are given in tabular form.

*National Science Foundation Predoctoral Fellow 1962-64.
List of Symbols Used

\[ \begin{align*}
\rho & \quad \text{Greek rho (lower case)} \\
\zeta & \quad \text{Greek zeta} \\
\delta & \quad \text{Greek delta} \\
\gamma & \quad \text{Greek gamma} \\
\mathcal{L} & \quad \text{Script L} \\
\mathcal{L} & \quad \text{Script S} \\
\epsilon & \quad \text{Greek epsilon} \\
\alpha & \quad \text{Greek alpha} \\
\beta & \quad \text{Greek beta} \\
\theta & \quad \text{Greek theta} \\
\tau & \quad \text{Greek tau} \\
\phi & \quad \text{Greek phi} \\
\psi & \quad \text{Greek psi} \\
\nu & \quad \text{Greek nu} \\
\Sigma & \quad \text{Greek sigma (upper case)}
\end{align*} \]
Table I - Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_i$, $\beta_i$, $\gamma_i$</td>
<td>coordinates of the $i$th atom in the principal axis system, chosen from $x$, $y$, $z$ in cyclic order</td>
</tr>
<tr>
<td>$e_\alpha$, $e_\beta$, $e_\gamma$</td>
<td>unit vectors along axes $\alpha$, $\beta$, $\gamma$</td>
</tr>
<tr>
<td>$I_\alpha$</td>
<td>moment of inertia about $\alpha$th axis</td>
</tr>
<tr>
<td>$Q_s$</td>
<td>normal coordinates</td>
</tr>
<tr>
<td>$\varepsilon_{ik}$</td>
<td>Wilson's $s$-vector on the $i$th atom displaced in the $k$th internal coordinate</td>
</tr>
<tr>
<td>$\xi_{ik}$</td>
<td>Polo's $p$-vector</td>
</tr>
<tr>
<td>$\xi_{st}$</td>
<td>Coriolis coupling constant linking the $s$th and $t$th normal vibrations through rotations about the $\alpha$th axis</td>
</tr>
<tr>
<td>$B$</td>
<td>Coriolis coupling matrix ($3 \times 3N - 6$)</td>
</tr>
<tr>
<td>$S$</td>
<td>internal coordinate matrix ($3N - 6 \times 1$)</td>
</tr>
<tr>
<td>$G$</td>
<td>Wilson's vibrational $G$ matrix ($3N - 6 \times 3N - 6$)</td>
</tr>
<tr>
<td>$L$</td>
<td>transformation matrix between normal and internal coordinates ($3N - 6 \times 3N - 6$)</td>
</tr>
</tbody>
</table>

$L$, $G$, $S$ denote the corresponding quantities for symmetry coordinates.
The calculation of Coriolis coupling constants, moment of inertia corrections, etc., requires a transformation which relates the 3N-6 normal coordinates of the molecule to the 3N cartesian coordinates. In order to specify uniquely the normal vibrations and to minimize the Coriolis coupling terms, six supplementary equations are used, the so-called Eckart conditions (1), (2). These conditions define the molecule-fixed axes in such a way that each normal mode of vibration will cause no net rotation of the axes (giving three equations for rotations about x, y, and z) and will leave the molecular center-of-mass at the origin (giving three more equations for translations along x, y, and z).

The application of these conditions is simplified by the fact that we may take atomic displacements in any direction we wish, as long as we subtract the corresponding rotations and translations of the axes resulting from our arbitrary displacements (3). In the following treatment, the atoms will be moved so as to change one particular normal coordinate by one unit, leaving all other coordinates "frozen". Since a molecule of N atoms in the normal coordinate representation is just an aggregate of 3N-6 "sub-molecules" or independent harmonic oscillators, such "freezing" is allowed, provided we include the effects of translation and rotation for each mode. Also, straightforward symmetry arguments will immediately tell us which modes will be Eckart-corrected, and which of the six Eckart subtractions will have to be applied in each case.
ECKART DISPLACEMENTS

We consider the equilibrium configuration of the atoms to be specified by vectors $\mathbf{r}_1$ with cartesian projections $(\alpha_1^*, \beta_1^*, \gamma_1^*)$. The vibrating atoms will deviate from their equilibrium positions by increments $\rho_1 = (\delta \alpha_1, \delta \beta_1, \delta \gamma_1)$ such that

$$\delta \alpha_1 = \alpha_1 - \alpha_1^*, \text{ etc.}$$

The Eckart conditions state that for an allowed displacement:

$$\sum_{i=1}^{N} m_i \rho_i = 0 \tag{1}$$

$$\sum m_i (r_i^* x \rho_i) = 0 \tag{2}$$

Equation (1) puts the origin of the displaced molecule at the center of the mass; and Eq. (2) requires that the rotation caused by $\rho_1$ will be zero.

The simplest method for evaluating vibrational displacements is to take some arbitrary, convenient displacement of the atoms, calculate the resultant translations and rotations, and subtract these from the arbitrary set. If we denote the arbitrary (uncorrected) set by primes and leave the final unique (corrected) set unprimed, then

$$\delta \alpha_1 = \delta \alpha_1' - \delta \tau_\alpha - (\delta \theta x r_1^*)_\alpha$$

$$= \delta \alpha_1' - \delta \tau_\alpha - (\gamma_1^* \delta \theta \beta_1^* \delta \theta \gamma_1^*) \tag{3}$$

where $\delta \tau_\alpha$ is just the displacement of the center of mass along the $\alpha$th axis given by

$$\delta \tau_\alpha = \sum m_i \delta \alpha_i / M ;$$

and $\delta \theta_\alpha$ is the net rotation about the $\alpha$th axis

$$\delta \theta_\alpha = \Sigma m_i (r_1^* x \rho_1)_\alpha / I_\alpha$$

$$= \Sigma m_i (\beta_1^* \delta \gamma_1' - \gamma_1^* \delta \beta_1') / I_\alpha.$$
Herschbach and Laurie defined the "Eckart expansion of the normal mode" as a set of the \( \delta x_i \) increments which change a particular normal mode one unit, while leaving the other coordinates unaffected ("frozen") \((4)\). From the transformation from internal to normal coordinates

\[
S_k = \sum_{t=1}^{3N-6} L_{kt} Q_t \quad \text{for } k = 1, 2, \ldots, 3N-6
\]

we get, letting \( Q_s = 1 \), and all other \( Q_t = 0 \),

\[
S_k = \sum_t L_{kt} \delta s_t = L_{ks}.
\]

Thus, to obtain the Eckart expansion, we need to find atomic displacements such that this equality will hold. An explicit form can be obtained in terms of the \( \rho \)-vectors introduced by Polo \((5)\), which satisfy

\[
\delta r_{is} = \sum_k \rho_{ik} L_{ks}.
\]

The index \( k \) runs over all the internal coordinates (or symmetry coordinates) in which the \( i \)th atom moves. The form of the \( \rho \)-vector depends on the type of internal coordinate involved (angle bend, bond stretch, torsion, etc.) and its magnitude is such as to change \( S_k \) by one unit leaving all other coordinates unchanged. The properties of the \( \rho \)-vectors and procedures for evaluating them have been fully discussed by Polo \((5)\) and further illustrated in the examples treated by Herschbach and Laurie \((4)\).

The various vibration-rotation parameters are readily evaluated from the Eckart expansion \((4), (6)-(8)) The Coriolis constant linking normal modes \( s \) and \( t \) through rotation about the \( \alpha \)th axis is given by

\[
\zeta_{st} = \sum_{i=1}^{N} m_i (\delta r_{is} \delta r_{it} - \delta r_{it} \delta r_{is})
\]

\((5)\)
The coefficients in the expansion of the instantaneous moment of inertia tensor,

\[ I_{\alpha\beta} = I_{\alpha\beta}^* + \sum_s a_\alpha a_\beta Q_s + \sum_s, t a_\alpha a_\beta Q_s Q_t \]

are given by

\[ a_{\alpha\alpha} = 2\Sigma_{m_i}(\alpha_1^* \delta_1 + \gamma_1^* \delta_{1s} \gamma_{1s}) \]  

(6a)

\[ \alpha_\beta = -\Sigma_{m_i}(\alpha_1^* \delta_1 + \beta_1^* \delta_{1s} \gamma_{1s}) \]  

(6b)

\[ A_{\alpha\alpha} = \Sigma_{m_i} [(\delta_{1s} \gamma_{1s})^2 + (\delta_{1s} \delta_{1s})^2] \]  

(7a)

\[ A_{\alpha\beta} = -\Sigma_{m_i} \delta_{1s} \delta_{1s} \gamma_{1s} \]  

(7b)

Finally, the centrifugal distortion constants are given by (9)

\[ \tau_{\alpha\beta\gamma\delta} = -\Sigma_{i} \frac{1}{\Sigma_{i} \Sigma_{\beta} \Sigma_{\gamma} \Sigma_{\delta}} \cdot \frac{a_{\alpha\beta} \gamma_{\beta} \delta_{\gamma}}{\delta_{\alpha}^2 \sum_{\gamma} \omega_{\gamma}^2 \omega_{\gamma}^2} \]  

(8)

In many examples it is found that the major contributions to the moment of inertia corrections, Cörlolis coupling constants, and rotational distortion coefficients arise from the low-frequency vibrational modes. Thus it is of interest to formulate a method treating a molecular model in which all but one or two of the low-frequency modes are frozen. We shall carry this out for various modes of branched planar WXY₂, tetrahedral WY₂Z₂, and pyramidal XY₃ molecules.

**BRANCHED PLANAR WXY₂ MOLECULES**

**Symmetric Angle Bend**

Figure 1(a) shows the numbering of the coordinates and the atoms. The z-axis is the out-of-plane axis, and the y axis is along the C₂ symmetry axis of the molecule. The ρ vectors are chosen so as to change the 1-2-3 angle \( \varphi (\mathbf{r}) \) by an amount \( \Delta_2 \). From Table II we see that the only Eckart correction
Table II  Symmetry Species of Planar WXY$_2$

Coordinates and Eckart Corrections

<table>
<thead>
<tr>
<th>Specie</th>
<th>Eckart Correction</th>
<th>Mode Number</th>
<th>( \mathcal{J}_k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>( \delta \tau_y )</td>
<td>1</td>
<td>( 2^{-1/2}(s_1+s_2) )</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>( \delta \sigma_y )</td>
<td>2</td>
<td>( 2^{-1/2}(s_5+s_5') )</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>( \delta \tau_x, \delta \theta_z )</td>
<td>3</td>
<td>( s_4 )</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>( \delta \tau_z, \delta \theta_x )</td>
<td>4</td>
<td>( 2^{-1/2}(s_1-s_2) )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>( 2^{-1/2}(s_5-s_5') )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>( s_6 )</td>
</tr>
</tbody>
</table>

\( ^a \) \( R = r_{24}, r = r_{12} = r_{23}; \) the z axis is out of plane, the y axis along the symmetry axis.
for this $A_1$ vibration will involve translation of the center of mass along the symmetry axis, and Eq. (4) gives the set of arbitrary displacements as

$$\delta r'_{ls} = 2^{-1/2} r (e_{21} \times e_\varphi)_{2s}$$

$$\delta r'_{3s} = -2^{-1/2} r (e_{23} \times e_\varphi)_{2s}$$

where $r$ is the 2-1 and 2-3 bond length, and the factor of $2^{-1/2}$ normalizes the change in $x_2 = 2^{-1/2} (S_5 + S'_5)$. Here, $e_{21}$ and $e_{23}$ are unit vectors along the 2-1 and 2-3 bonds respectively, and $e_\varphi = (e_{21} \times e_{23})/\sin \varphi$ is a unit vector along the $z$ axis.

The cartesian projections of these vector displacements are obtained from the dot products

$$\delta x'_{ls} = 2^{-1/2} r L_{2s} (e_{21} \times e_\varphi) \cdot e_x$$

The set of nonvanishing projections generated in this way, for $\alpha = 1/2 \varphi$, are

$$\delta x^{\pm}_{ls} = \mp 2^{-1/2} r L_{2s} \cos \alpha$$

for $i=1$ (upper sign) or $3$ (lower sign), and

$$\delta y'_{ls} = 2^{-1/2} r L_{2s} \sin \alpha$$

for $i=1,3$. The center of mass has moved along the $y$-axis by an amount

$$\delta r_y = 2^{-1/2} r L_{2s} (m/M) \sin \alpha$$

where $m = m_1 + m_3$ is the mass of atoms 1 and 3, and $M$ is the total mass $2m + m_2 + m_4$. The rotational corrections are zero since none of the rotations transform as $A_1$.

After subtracting the center of mass motion from the $y$ coordinates of each of the four atoms, we have the Eckart expansion (10)
\begin{align*}
\delta x_{is} &= \mp 2^{-1/2} r L_{2s} \cos \alpha \quad \text{for } i=1,3,5, \text{(lower sign);} \\
\delta x_{is} &= 0 \quad \text{for } i=2,4; \\
\delta y_{is} &= 2^{-1/2} r L_{2s} (1-2m/M) \sin \alpha \quad \text{for } i=1,3; \\
\delta y_{is} &= -2^{-1/2} r L_{2s} (m/M) \sin \alpha \quad \text{for } i=2,4; \\
\delta z_{is} &= 0 \quad \text{for } i=1,2,3,4,5.
\end{align*}

The moment of inertia corrections given by Eqs. (6) and (7) can be obtained from these corrected displacements and the symmetry relations,

\begin{align*}
y_1^* &= y_3^*, \quad x_1^* = -x_3^*, \quad x_2^* = x_4^* = 0, \quad z_1^* = 0 \quad \text{(for } i=1,2,3,4); \\
\alpha_{xx}^{ss} &= \frac{1}{4m} \delta y_{1s} + 2m_2 (y_2+y_4) \delta y_{2s} \\
\alpha_{yy}^{ss} &= \frac{1}{4m} \delta x_{1s} \\
\alpha_{zz}^{ss} &= \alpha_{xx}^{ss} + \alpha_{yy}^{ss} \\
A_{xx}^{ss} &= 2m (\delta y_{1s})^2 + m_2 (\delta y_{2s})^2 + m_4 (\delta y_{4s})^2 \\
A_{yy}^{ss} &= 2m (\delta x_{1s})^2 \\
A_{zz}^{ss} &= A_{xx}^{ss} + A_{yy}^{ss} = 1
\end{align*}

These results agree with the fact that only the diagonal elements of the moment of inertia tensor, as well as the second order correction coefficients, transform as $A_{1}$. 

From Polo's results, it is readily seen that when all other coordinates of the same symmetry are frozen, the $L_{ss}$ element for the unfrozen coordinate may be obtained from
\[
(L_{ss})^{-2} = \Sigma m_i \rho_{is}^2 - \left[ (a_s^x)^2 + (a_s^y)^2 + (a_s^z)^2 \right] / M
- \left[ (b_s^x)^2 / I_x + (b_s^y)^2 / I_y + (b_s^z)^2 / I_z \right]
\]

where

\[
\Sigma m_i \rho_{is} = \rho_s
\]
\[
\Sigma m_i (r_i \times \rho_{is}) = b_s
\]

In the present case, we set all the \( L_{ks} = 0 \) except the diagonal element

\[
(L_{22})^{-2} = mr^2 \left[ 1 - (2m/M) \sin^2 \alpha \right]
\]

and this relation was used to obtain the result \( A_{22}^{zz} = 1 \).

**Out-of-Plane Bend**

As another example we will change the out-of-plane angle \( \theta \) (\( \theta_s^j \)) of 
\( B_2 \) symmetry shown in Fig. 1(b) by taking \( \rho_{ij} = e \varphi R_i \), and displacing atom
\( i \) by

\[
\delta r_{4t}^i = e \varphi R L_{6t}^i
\]

and leaving \( \delta r_{1t}^i = 0 \) for \( i=1,2,3 \).

The cartesian projections are then \( \delta x_{4t}^i = \delta y_{4t}^i = 0 \), and \( \delta z_{4t}^i = R L_{6t}^i \).

This mode involves a translation along the z-axis by an amount

\[
\delta r_z = R L_{6t}^i m_i / M
\]

and a rotation about the x-axis by an angle

\[
\delta \theta x = R L_{6t}^i m_i y_i / I_x
\]

The final displacements are then

\[
\delta x_{4t}^i = 0 \quad \text{for } i=1,2,3,4;
\]
\[
\delta y_{4t}^i = 0 \quad \text{for } i=1,2,3,4;
\]
\[
\delta z_{4t}^i = -m_i R L_{6t}^i (1/My_i y_i / I_x) \quad \text{for } i=1,2,3
\]
\[ \delta z_{1t} = R_6 (1-m_y^*/M-m_y^*/I_x). \]

The \( B \) elements can be obtained in the same straightforward manner. Thus we find \( B_z = B_y = 0 \), and

\[ B_{xt} = (2m_y^* \delta z_{1t} + m_y^* \delta z_{2t} + m_y^* \delta z_{4t}). \]

The only nonzero first order correction is \( yz \) since only the product \( yz \) transforms as \( B_2 \), and we have

\[ a_t^{yz} = -(2m_y^* \delta z_{1t} + m_y^* \delta z_{2t} + m_y^* \delta z_{4t}). \]

The nonzero second order corrections for this out-of-plane motion take the simple form \( A_{tt}^{xx} = A_{tt}^{yy} = 1 \), as found from Eq. (7a), and

\[ (\mathcal{L}_{6t})^{-2} = m_y^* R^2 \left( 1-m_y^*/M-m_y^*/I_x \right). \]

**Antisymmetric Bond Stretch**

The proper \( \vec{p} \) vectors for this \( B_1 \) mode are shown in Fig. 1(c), and their explicit form is

\[ \vec{p}_1 = -2^{-1/2} e_{21} \]
\[ \vec{p}_3 = 2^{-1/2} e_{23} \]

where the factor of \( 2^{-1/2} \) insures that the displacement of \( \mathcal{L}_4 \) is unity.

The Eckart correction involves a translation along the x-axis of \( \delta y_x = 2^{1/2} \mathcal{L}_{hr} (m/M) \sin \alpha \)
and a rotation about the z-axis by \( \delta \theta_z = 2^{1/2} \mathcal{L}_{hr} (m/I_z) (x^*_1 \cos \alpha - y^*_1 \sin \alpha) \).

The unique displacements for this mode are obtained in the same manner as before, and the results for this mode, as well as those for the symmetric angle bend and out-of-plane bend, are given in a convenient form in Table III.
TABLE III Corrected displacements of atoms in the WXY$_2$ molecule. The rows give the cartesian components of the displacements, and the columns give the atomic numbering.$^a$

<table>
<thead>
<tr>
<th>i=</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{x1}$</td>
<td>$-2^{-1/2} r L_{2s} \cos \alpha$</td>
<td>0</td>
<td>$2^{-1/2} r L_{2s} \cos \alpha$</td>
<td>0</td>
</tr>
<tr>
<td>$\delta_{y1}$</td>
<td>$2^{-1/2} L_{4r} \sin \alpha \left[ 1 - (2m/M) \right]$</td>
<td>$-2^{-1/2} L_{4r} \left( m/M \right) \sin \alpha$</td>
<td>same as 1</td>
<td>$-2^{-1/2} L_{4r} \left( m/M \right) \sin \alpha$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$+2^{-1/2} L_{4r} \left( y_1^*a/I_z \right)$</td>
<td>$+2^{-1/2} L_{4r} \left( y_2^*a/I_z \right)$</td>
<td>$+2^{-1/2} L_{4r} \left( y_4^*a/I_z \right)$</td>
<td></td>
</tr>
<tr>
<td>$B_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\delta_{y2}$</td>
<td>$2^{-1/2} r L_{2s} \sin \alpha \left[ 1 - (2m/M) \right]$</td>
<td>$-2^{-1/2} r L_{2s} \sin \alpha \left( m/M \right)$</td>
<td>same as 1</td>
<td>same as 2</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$2^{-1/2} L_{4r} \cos \alpha - 2^{-1/2} L_{4r} \left( x_1^*a/I_z \right)$</td>
<td>0</td>
<td>$-2^{-1/2} L_{4r} \cos \alpha + 2^{-1/2} L_{4r} \left( x_1^*a/I_z \right)$</td>
<td></td>
</tr>
<tr>
<td>$B_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\delta_{z1}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$B_1$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$-m_4 R L_{6t} \left( 1/M + y_1^<em>y_4^</em>/I_x \right)$</td>
<td>$-m_4 R L_{6t} \left( 1/M + y_2^<em>y_4^</em>/I_x \right)$</td>
<td>same as 1</td>
<td>$R L_{6t} \left( 1-M_{y_1}M_{y_4}^2/I_x \right)$</td>
</tr>
</tbody>
</table>

$^a$ As before, $m=m_1=m_3$, $r_1=r_2=r_3$, $R=r_4$, and $a = m(x_1^* \cos \alpha - y_1^* \sin \alpha)$
Since \( R_z \) transforms as \( B_1 \), we have \( B_{z r} \) as the only non-zero element

\[
B_{z r} = 2m(x_1 \delta y_{1 r}) - m_2 y_2^* \delta x_{2 r} - m_4 y_4^* \delta x_{4 r}.
\]

Also, since the product \( xy \) transforms as \( B_1 \), we obtain only \( a_{r}^{xy} \) as the first order correction, and we have

\[
a_{r}^{xy} = -2m(x_1 \delta y_{1 r}) - m_2 y_2^* \delta x_{2 r}^* m_4 y_4^* \delta x_{4 r}.
\]

For the non-zero second order terms,

\[
\begin{align*}
A_{r r}^{xx} &= 2m (\delta y_{1 r})^2 \\
A_{r r}^{yy} &= 2m (\delta x_{1 r})^2 + m_2 (\delta x_{2 r})^2 + m_4 (\delta x_{4 r})^2 \\
A_{r r}^{zz} &= A_{r r}^{xx} + A_{r r}^{yy} = 1
\end{align*}
\]

the \( \mathcal{L}_{r r} \) element for this coordinate, \((r = 4)\)

\[
(\mathcal{L}_{4 r})^{-2} = m \left\{ 1 - (2m/M) \sin^2 \alpha - (2m/I_z)(x_1^* \cos \alpha + y_1^* \sin \alpha)^2 \right\}
\]

was used in obtaining the last result.

**Coriolis Coupling Constants**

In order for two vibrations to couple via a rotation, the product of the representations of the vibration must transform as one of the rotations. In our case, the \( A_1 \) and \( B_2 \) vibrations couple via \( \xi^{x}_{r s t} \) since \( \Gamma(R_x) = A_1 \times B_2 = B_2 \); the \( A_1 \) and \( B_1 \) via \( \xi^{z}_{s r} \); and the \( B_1 \) and \( B_2 \) via \( \xi^{y}_{s t} \).

From Eq. (5) and Table III we can obtain the non-zero coupling constants:

\[
\begin{align*}
\xi^{x}_{r s t} &= 2m(\delta y_{1 s} \delta z_{1 t}) + m_2 (\delta y_{2 s} \delta z_{2 t}) + m_4 (\delta y_{4 s} \delta z_{4 t}) \\
\xi^{z}_{s r} &= 2m(\delta x_{1 s} \delta y_{1 r}) - m_2 (\delta y_{2 s} \delta x_{2 r}) - m_4 (\delta y_{4 s} \delta x_{4 r}) \\
\xi^{y}_{t r} &= 2m(\delta z_{1 t} \delta x_{1 r}) + m_2 (\delta z_{2 t} \delta x_{2 r}) + m_4 (\delta z_{4 t} \delta x_{4 r})
\end{align*}
\]
Methylene chloride will be chosen as a specific example of a tetrahedral \( WY_2Z_2 \) molecule and the \( \rho \)-vectors for it can, of course, be generalized to other \( WY_2Z_2 \) molecules of \( C_{2v} \) symmetry. The molecular parameters for the vibrational modes can be evaluated as before, and the modes chosen are the three low-frequency vibrations, each in a separate symmetry representation, as shown in Fig. 2: the \( A_1 \) symmetric Cl-Cl angle bend \( (v_4 = 1548 \text{ cm}^{-1}) \), the \( B_2 \) symmetric C-Cl stretch \( (v_9 = 2057 \text{ cm}^{-1}) \), and the \( B_1 \) rocking mode of the \( \text{CH}_2 \) group against the \( \text{CCl}_2 \) plane \( (v_7 = 2673 \text{ cm}^{-1}) \). \(^1\)

**Symmetric Angle Bend**

The symmetry coordinates and Eckart species are given in Table IV. In the \( A_1 \) mode, the chlorines move in the \( yx \) plane with a resultant change in the 1-5-2 angle 2\( \beta \) \( (\phi_4') \) as shown in Fig. 2(a).

If the 5-1 and 5-2 bond lengths are denoted by \( R \), then the appropriate atomic displacement are

\[
\delta r_1' = -\frac{1}{2} R (e_{51} \times e \phi) \phi_{4s}',
\]

\[
\delta r_2' = +\frac{1}{2} R (e_{52} \times e \phi) \phi_{4s}',
\]

where \( e \phi = (e_{51} \times e_{52})/\sin 2\beta \) is a unit vector along the out-of-plane \( x \) axis.

The cartesian projections and the subsequent Eckart corrections can be conveniently obtained by writing the projections of each of the unit vectors as elements of column vectors. Thus

\[
e_{51} = (0, \sin \beta, -\cos \beta) \quad e_{52} = (0, -\sin \beta, -\cos \beta)
\]

\[
e \phi = (1, 0, 0)
\]

\( (10) \)
TABLE IV  Symmetry species of $W_\gamma Z_\gamma$ coordinates and Eckart corrections. $\phi_5$ is torsion between the YWY and ZWZ planes, and $\phi_{10}$ is the redundant coordinate.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Eckart Corr.</th>
<th>Mode No.</th>
<th>$\Delta_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$8\tau_z$</td>
<td>1</td>
<td>$2^{-1/2}(s_3 + s_4)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>$s_{10}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>$2^{-1/2}(s_1 + s_2)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>$s_9$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>$1/2(s_5 + s_6 + s_7 + s_8)$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$8\theta_z$</td>
<td>5</td>
<td>$1/2(s_5 + s_6 - s_7 - s_8)$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$8\tau_x, 8\theta_y$</td>
<td>6</td>
<td>$2^{-1/2}(s_3 - s_4)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>$1/2(s_5 + s_6 - s_7 - s_8)$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$8\tau_y, 8\theta_x$</td>
<td>8</td>
<td>$1/2(s_5 + s_7 - s_6 - s_8)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>$2^{-1/2}(s_1 - s_2)$</td>
</tr>
</tbody>
</table>
Only translations along the symmetry z-axis transform as $A_1$, and this translation is just

$$\delta \tau_z = R \mathcal{L}_4 \left( \frac{m}{M} \right) \sin \beta$$

where $m_1 = m_2 = m$ is the mass of the chlorine atoms, $m_3 = m_4 = m_H$ the mass of the hydrogen atoms, $m_c$ that of the central carbon atom, and $M = 2m + 2m_H + m_c$ the total mass.

The Eckart displacements for this normal mode are summarized in Table V. The displacements in the out-of-plane direction (along the x-axis) are all zero for this in-plane vibration just as in the $A_1$ mode for the WXY$_2$ example. The equilibrium relations for this molecule are $z_1^* = z_2^*$, $z_3^* = z_4^*$; $y_1^* = -y_2^*$, $y_3^* = y_4^*$; $y_5^* = 0$; $x_1^* = x_2^* = x_3^* = 0$, $x_3^* = -x_4^*$.

The elements of the coupling matrix are again all zero since rotations about the x, y, and z axes transform as $B_2$, $B_1$ and $A_2$ respectively, while only the $A_1$ mode is excited.

The initial corrections are relatively simple for this mode, and the non-zero first and second order corrections are

$$a_{ys}^{yy} = 2m z_1^* \delta z_{1s} + 2 \delta z_{3s} \left( 2z_3^* m_H + z_5^* m_c \right)$$

$$a_{zz} = 4 m y_1^* \delta y_{1s}$$

$$a_{xs} = a_{ys}^{yy} + a_{zs}^{zz}$$

$$A_{ss}^{yy} = 2m (\delta z_{1s})^2 + 2m_H (\delta z_{3s})^2 + m_c (\delta z_{5s})^2$$

$$A_{ss}^{zz} = 2m (\delta y_{1s})^2$$

$$A_{ss}^{xx} = A_{ss}^{yy} + A_{ss}^{zz} = 1$$

where the $\mathcal{L}_4$ element derived from the Eckart corrected p vectors is

$$\left( \mathcal{L}_4 \right)^{-2} = \frac{1}{2m} R^2 \left[ 1 - (2m/M) \sin^2 \beta \right].$$
Antisymmetric Bond Stretch

The symmetry coordinate for this mode is \( \mathbf{u}_g = 2^{-1/2}(s_1 - s_2) \), and the \( \mathbf{p} \) vectors for the asymmetric C-Cl stretch are shown in Fig. 2(b). Proper normalization of \( \mathbf{u}_g \) dictates that we divide the \( \mathbf{p} \) vectors on atoms 1 and 2 by \( 2^{1/2} \gamma \), so that

\[
\delta \mathbf{r}'_{1t} = -2^{1/2} e_5 l \mathbf{u}_g \mathbf{r} \\
\delta \mathbf{r}'_{2t} = 2^{-1/2} e_5 \mathbf{u}_g \mathbf{r}
\]

This mode causes a net translation along the \( y \) axis of

\[
\delta \mathbf{r}_y = 2^{1/2} e_5 \mathbf{u}_g (m/M) \sin \beta
\]

and a rotation about the \( x \) axis

\[
\delta \theta_x = 2^{1/2} (m/I_x) e_5 \mathbf{u}_g (y_1^* \cos \beta + z_1^* \sin \beta)
\]

The procedure for obtaining the Eckart expansion is identical to that involved in the \( WXY_2 \) case, and the atomic displacements for this case are given in Table V.

The \( B_2 \) mode couples only with rotations about the \( x \)-axis, and the coupling element is

\[
B_{xt} = 2 \, m y_1^* 8z_{1t} - 2mz_1 8y_{1t} - 2m z_3 8y_{3t} - m c z^* 8y_{5t}
\]

Again proceeding from the definitions in Eqs. (6a) to (7b) and the Eckart displacements, we get

\[
A_{yt} = 2m(y_{1t})^2 + 2m(8y_{3t})^2 + m_c(8y_{5t})^2
\]

\[
A_{tt} = A_{yy} + A_{zz}
\]

\[
A_{yy} = A_{xx} + A_{zz} = 1
\]
The first result follows from the fact that only the yz components of the moment-of-inertia tensor transforms as $B_2$, and the last relation from the vibration's being in the yz plane. The $\mathcal{L}_{99}$ element used in this last result was found to be

$$(\mathcal{L}_{99})^{-2} = m(1-(2m/M) \sin^2 \beta - 2m^2/I_x)$$

where \(a = (y_1^* \cos \beta + z_1^* \sin \beta)\).

**CH$_2$ Rocking Mode**

The coordinate $L_7$ in Fig. 2(c) and Table IV defines the rocking motion of the CH$_2$ group against the CCl$_2$ plane, and is given in terms of the H-C-Cl angles $\epsilon$ (where $\cos \epsilon = e_{51} \cdot e_{53} = -\cos \alpha \cos \beta$)

$$L_7 = \frac{1}{2} (S_5 + S_8 - S_6 - S_7).$$

However, in order to insure that we have a set of independent coordinates, we must eliminate the redundant coordinate $L_{10}$ by setting it equal to zero. (5)

Replacing the combination $-(S_6 + S_7)$ by $S_5 + S_8$, the independent coordinate is $L_7 = S_5 + S_8$.

The appropriate displacement vectors on atom 3 are given by

$$\frac{S_5}{3r} = \frac{1}{2} r (e_{53} \times e_{52})/\cos \psi$$

for a change of one-half unit in $S_5$, and

$$\frac{S_8}{3r} = \frac{1}{2} r (e_{51} \times e_{53})/\cos \psi$$

for a change of one-half unit in $S_8$, where $\cos \psi = e_{52} \cdot (e_{53} \times e_{51})/\sin \epsilon$.

The net displacement of atom 3 will be the sum of these two vectors, and if the appropriate cross and dot products are calculated with the aid of Eqv (10) and the relation $e_{53} = (-\sin \alpha, 0, \cos \alpha)$, we get
\[ \rho_3^{\text{resultant}} = \rho_3^{S_5} + \rho_3^{S_8} = \frac{r \sin \epsilon}{2 \sin \alpha \cos \beta} (\cos \alpha, 0, \sin \alpha) \]

which is a vector in the xz plane.

We can proceed in exactly the same fashion to get the net displacement of atom 4, but a simpler method is just to note that the displacement vector on 4 will be that on 3 rotated through an angle \(2\alpha\) in the xz plane. The appropriate form of the rotation matrix \(R\) is

\[
R = \begin{pmatrix}
\cos 2\alpha & 0 & \sin 2\alpha \\
0 & 1 & 0 \\
-\sin 2\alpha & 0 & \cos 2\alpha
\end{pmatrix}
\]

(11)

and we have that \(\rho_4^{\text{resultant}} = R\rho_3^{\text{resultant}}\), or

\[ \rho_4^{\text{resultant}} = \frac{r \sin \epsilon}{2 \sin \alpha \cos \beta} (\cos \alpha, 0, -\sin \alpha) \]

and the two net displacement vectors differ only in the sign of their \(z\) component.

The Eckart corrections are

\[
\delta x = \frac{r \sin \epsilon}{\sin \alpha \cos \beta} h \frac{m_H}{M} \cos \alpha = 2c \frac{L_x}{I_x} (m_H/M) \cos \alpha
\]

\[
\delta y = \frac{r \sin \epsilon}{\sin \alpha \cos \beta} h \frac{m_H}{I_y} (z_3^* \cos \alpha - x_3^* \sin \alpha)
\]

\[
= 2cdm_H \frac{L_y}{I_y}
\]

where the more convenient notation is

\[
c = \frac{r \sin \epsilon}{2 \sin \alpha \cos \beta}
\]

\[
d = (z_3^* \cos \alpha - x_3^* \sin \alpha)
\]

The sets of displacement for the rocking motion of both hydrogen atoms are shown also in Table V.

For the inertia tensor correction, we see that \(xz\) transforms as \(B_1\), so the term in the first and second order are
\[
\begin{align*}
x^Z_x & = - \left\{ 2m \cdot x_3^* \cdot 3x_1r_3 + 2m \cdot z_3^* \cdot 3x_1r + 2m \cdot z_3^* \cdot 5x_3r + m_c \cdot z_5^* \cdot 5x_3r \right\} \\
A^{xx}_{rr} & = 2m_H (z_3^*)^2 \\
A^{zz}_{rr} & = 2m (5x_3r)^2 + 2m_H (6x_3r)^2 + m_c (8x_5r)^2 \\
A^{yy}_{rr} & = A^{xx}_{rr} + A^{zz}_{rr} = 1
\end{align*}
\]

with the relation
\[
(\mathcal{L}_{88})^{-2} = 2m_H^2 \left\{ 1 - \frac{2m_H}{M} \cos^2 \alpha - \frac{2m_H}{I_y} (z_3^* \cos \alpha - x_3^* \sin \alpha)^2 \right\}.
\]

Coriolis Coupling Constants

From the direct product representations, the \( A_1 \) mode (s) can couple through rotations about the \( y \) axis with the \( B_1 \) mode (r); the \( A_1 \) with the \( B_2 \) (t) through rotations about the \( x \) axis; and the \( B_1 \) with the \( B_2 \) mode via rotations about the \( z \) axis. The non-zero coupling constant will then be
\[
\xi^y_{sr} = 2m (5_1s \cdot 5x_1r) + 2m_H (8_3s \cdot 8x_3r) + m_c (8_5s \cdot 8x_5r),
\]
\[
\xi^y_{st} = 2m (8y_1s \cdot 8x_1t) - 2m_H (8_3s \cdot 8y_3t) - m_c (8_5s \cdot 8y_5t),
\]
\[
\xi^z_{tr} = -2m (8y_1t \cdot 8x_1r) - 2m_H (8y_3t \cdot 8x_3r) - m_c (8y_5t \cdot 8x_5r).
\]

PYRAMIDAL XY_3 MOLECULES

As a further example we examine a degenerate low-frequency mode of a pyramidal XY_3 molecule with C_{3v} symmetry (e.g., NH_3) (12). The column vector notation will be useful here, and the degenerate asymmetric stretch \( \xi \left[ S_4, S_5, S_6 \right] \) which transforms as the \( x \) coordinate of the degenerate pair (see Fig. 3 and Table VI) will be the excited coordinate. Since unit displacements in \( S_4, S_5 \) and \( S_6 \) will cause a total displacement of \( 4/\sqrt{6} \) in \( S_5 \), the \( \rho \) vectors will each be divided by \( 4/\sqrt{6} \) to get the unit displacement in \( S_5 \).
TABLE V. Corrected displacements of atoms in CH₂Cl₂.\(^a\)

<table>
<thead>
<tr>
<th>(\delta x_{11})</th>
<th>(A_1)</th>
<th>(B_1)</th>
<th>(B_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0</td>
<td>(-2c L_7t \cos \alpha (m_H/M))</td>
<td>0</td>
</tr>
<tr>
<td>(2)</td>
<td>0</td>
<td>same as (1)</td>
<td>(-2c L_7t \cos \alpha (1-2m_H/M))</td>
</tr>
<tr>
<td>(3)</td>
<td>0</td>
<td>same as (3)</td>
<td>(-2c L_7t \cos \alpha (m_H/M))</td>
</tr>
<tr>
<td>(4)</td>
<td>0</td>
<td>(-2c L_7t (m_H d z_1^*/l_y))</td>
<td>(-2c L_7t (m_H d z_3^*/l_y))</td>
</tr>
<tr>
<td>(5)</td>
<td>0</td>
<td>(-2c L_7t (m_H d z_5^*/l_y))</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\delta y_{11})</th>
<th>(A_1)</th>
<th>(B_1)</th>
<th>(B_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(\frac{1}{2}R \cdot L_{4s} \cos \beta)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(2)</td>
<td>(\frac{1}{2}R \cdot L_{4s} \cos \beta)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(3)</td>
<td>same as (1)</td>
<td>(2^{1/2} L_{9r} \sin \beta (m/M))</td>
<td>(2^{1/2} L_{9r} \sin \beta (m/M))</td>
</tr>
<tr>
<td>(4)</td>
<td>(2^{-1/2} L_{9r} \sin \beta (-1+2m/M))</td>
<td>(2^{1/2} L_{9r} \sin \beta )</td>
<td>(2^{1/2} L_{9r} \sin \beta )</td>
</tr>
<tr>
<td>(5)</td>
<td>(2^{1/2} L_{9r} (m b z_1^*/l_x))</td>
<td>(2^{1/2} L_{9r} (m b z_3^*/l_x))</td>
<td>(2^{1/2} L_{9r} (m b z_5^*/l_x))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\delta z_{11})</th>
<th>(A_1)</th>
<th>(B_1)</th>
<th>(B_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(\frac{1}{2}R \cdot L_{4s} \sin \beta (1-2m/M))</td>
<td>same as (1)</td>
<td>(-R \cdot L_{4s} \sin \beta (m/M))</td>
</tr>
<tr>
<td>(2)</td>
<td>(\frac{1}{2}R \cdot L_{4s} \sin \beta (1-2m/M))</td>
<td>same as (3)</td>
<td>(\frac{1}{2}R \cdot L_{4s} \sin \beta (m/M))</td>
</tr>
<tr>
<td>(3)</td>
<td>same as (3)</td>
<td>(-R \cdot L_{4s} \sin \beta (m/M))</td>
<td>(-R \cdot L_{4s} \sin \beta (m/M))</td>
</tr>
<tr>
<td>(4)</td>
<td>(2^{-1/2} L_{9r} \cos \beta)</td>
<td>(2^{-1/2} L_{9r} \cos \beta)</td>
<td>0</td>
</tr>
<tr>
<td>(5)</td>
<td>(2^{-1/2} L_{9r} (m b y_1^*/l_x))</td>
<td>(2^{-1/2} L_{9r} (m b y_1^*/l_x))</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) The definitions are \(b = (y_1^* \cos \beta + z_1^* \sin \beta)\); \(c = r \sin e/(2 \sin \alpha \cos \beta)\); \(d = (z_3^* \cos \alpha - x_3^* \sin \alpha)\); \(e\) is the H-C-Cl angle; \(\alpha\) and \(\beta\) are one-half the Cl-C-Cl and H-C-H angles respectively.
Thus,
\[\delta \mathbf{r}_{1s}^i = -2( \gamma^{1/2}/4) e_{41} \mathbf{L}_{4s},\]
\[\delta \mathbf{r}_{2s}^i = ( \gamma^{1/2}/4) e_{42} \mathbf{L}_{4s},\]
\[\delta \mathbf{r}_{3s}^i = ( \gamma^{1/2}/4) e_{43} \mathbf{L}_{4s},\]

where the unit vectors have the projections
\[e_{41} = (\sin \beta, 0, -\cos \beta), \quad e_{42} = R(-120^\circ) e_{41},\]
\[= (-1/2 \sin \beta, -\sqrt{3}/2 \sin \beta, -\cos \beta),\]
\[e_{42} = R(+120^\circ) e_{41} = (-1/2 \sin \beta, \sqrt{3}/2 \sin \beta, -\cos \beta),\]

where \(R(-120^\circ)\) and \(R(+120^\circ)\) are matrices similar to that in Eq. (11) representing rotations of \(-120^\circ\) and \(+120^\circ\) respectively in the \(xy\) plane, and \(\beta\) is the angle between \(e_{41}\) and the negative \(z\) axis as shown in Fig. 3. In terms of the \(XXX\) face angle \(\theta\), we can show that \(\sin^2 \beta = 2(1 - \cos \theta)/9\).

For this member of the degenerate pair, we obtain the corrections
\[\delta x_x = -(3 \sqrt{6}/4) \mathbf{L}_{4s} (m/M) \sin \beta\]
\[\delta \theta_y = \frac{\sqrt{6} \mathbf{L}_{4s} m}{2I_y} \left\{ -\frac{3}{2} z^* \sin \beta - x_1^* \cos \beta + x_2^* \cos \beta \right\},\]

where \(m = m_1 = m_2 = m_3\), and \(z^* = z_1^* = z_2^* = z_3^*\).

The set of displacements are then
\[\delta x_{1s} = + \frac{\sqrt{6}}{2} \mathbf{L}_{4s} \sin \beta(-1 + 3/m) - \frac{\sqrt{6} m z^* \mathbf{L}_{4s}}{2I_y} f\]
\[\delta x_{4s} = \frac{3 \sqrt{6}}{4} \mathbf{L}_{4s} \sin \beta \frac{m}{M} - \sqrt{6} \frac{m z^* \mathbf{L}_{4s}}{2I_y} f\]
### TABLE VI. Symmetry Species of Triangular Pyramidal $XY_2$ Coordinates and Eckart Corrections

<table>
<thead>
<tr>
<th>Species</th>
<th>Eckart Correction</th>
<th>Mode No.</th>
<th>( \mathcal{A}_\text{E} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>( \delta \tau_z )</td>
<td>1</td>
<td>( 3^{-1/2}(s_1+s_2+s_3) )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>( 3^{-1/2}(s_4+s_5+s_6) )</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>( \delta \theta_z )</td>
<td>3</td>
<td>( 2^{-1/2}(s_2-s_3) )</td>
</tr>
<tr>
<td>( E )</td>
<td>( \delta \tau_x \delta \theta_y )</td>
<td>4</td>
<td>( 6^{-1/2}(s_1-s_2-s_3) )</td>
</tr>
<tr>
<td></td>
<td>( \delta \tau_y \delta \theta_x )</td>
<td>5</td>
<td>( 6^{-1/2}(s_4-s_5-s_6) )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>( 2^{-1/2}(s_5-s_6) )</td>
</tr>
</tbody>
</table>
\[ 8x_{2s} = 8x_{1s} = \frac{\sqrt{6}}{3} \mathcal{L}_{4s} \sin \beta (-1 + \frac{6m}{M}) = \frac{\sqrt{6} m z \mathcal{L}_{4s}}{2I}\]

\[ 8y_{2s} = -8y_{3s} = -(3\sqrt{2/3}) \mathcal{L}_{4s} \sin \beta \]

\[ 8y_{1s} = 8y_{4s} = 0 \]

\[ 8z_{1} = \frac{\sqrt{6}}{2} \mathcal{L}_{4s} \cos \beta + \frac{\sqrt{6m x_{1} \mathcal{L}_{4s}}}{2I} \]

\[ 8z_{2} = 8z_{3} = \frac{\sqrt{6}}{4} \mathcal{L}_{4s} \cos \beta + \frac{\sqrt{6m x_{2} \mathcal{L}_{4s}}}{2I} \]

\[ 8z_{4} = 0 \]

where the substitution \( f = (-\frac{3}{2} z \sin \beta - x_{1} \cos \beta + x_{2} \sin \beta) \) has been made.

For the E mode,

\[ B_{ys} = m x_{s} \left[ (\delta x_{1s} + 25x_{2s}) - mx_{1s} \delta z_{1s} - 2mx_{2s} \delta z_{2s} + mz_{s} \delta x_{4s} \right], \]

\[ a_{xx}^{ss} - a_{yy}^{ss} = 8m y_{s}^{2} \delta y_{2s}, \]

\[ a_{xx}^{ss} + a_{yy}^{ss} = 0, \]

\[ a_{xx}^{ss} = -m x_{s} \left[ (\delta x_{1s} + 25x_{2s}) - mx_{1s} \delta z_{1s} - 2mx_{2s} \delta z_{2s} - mz_{s} \delta x_{4s} \right], \]

where use has been made of the relations \( y_{2}^{*} = (\sqrt{3/2}) x_{1}, y_{2} = -y_{3}, x_{2} = x_{3} \).

Also,

\[ A_{xx}^{ss} = -m (\delta x_{1s} \delta z_{1s} + 25x_{2s} \delta z_{2s}), \]

\[ A_{xx}^{ss} = 2m \left[ (\delta y_{2s})^{2} + (\delta z_{2s})^{2} \right] + m (\delta z_{1s})^{2}, \]

\[ A_{yy}^{ss} = 2m \left[ (\delta x_{2s})^{2} + (\delta z_{2s})^{2} \right] + m \left[ (\delta x_{1s})^{2} + (\delta x_{4s})^{2} + (\delta z_{1s})^{2} \right], \]

with the \( \mathcal{L}_{44} \) element given as

\[ (\mathcal{L}_{44})^{2} = \frac{3}{2} m \left[ \frac{3}{2} - \frac{9}{2} \sin^{2} \beta \frac{M}{m} - \frac{m}{I} \frac{3}{2} z \sin \beta + x_{1} \cos \beta + x_{2} \cos \beta \right]. \]
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REFERENCES

10. The elements of the $3 \times 3N-6$ $G$ matrix which give the coupling between this angle bend and overall rotation about the principal axes are obtained from Ref. 4 as

$$ B_{ij} = \Sigma_i m_i [\alpha_i(\partial \beta_i/\partial \theta) - \beta_i(\partial \alpha_i/\partial \theta)]^{*} $$

and are found to vanish identically. The following examples all illustrate the fact that the same species as one of the rotations in order that $G$ have nonzero elements.

12. ibid., p. 110.
FIGURE CAPTIONS

Fig. 1 Displacement vectors and coordinates for planar $\text{WXY}_2$ molecule. $S_3 + S_5 + S_7$, is the redundant coordinate.

Fig. 2 Displacement vectors and internal coordinates for $\text{CH}_2\text{Cl}_2$ molecule. The remaining angles are $S_5 = \chi 1-5-3; S_6 = \chi 2-5-4; S_7 = \chi 1-5-4; \text{and } S_8 = \chi 2-5-3.$

Fig. 3 Displacement vectors and coordinates for $\text{XY}_3$ triangular pyramidal molecule. $S_5$ and $S_6$ are the 1-4-2 and 1-4-3 angles respectively, and $\beta$ is the angle between the $-z$ axis and the 4-1 bond which is taken to lie in the $xz$ plane.
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