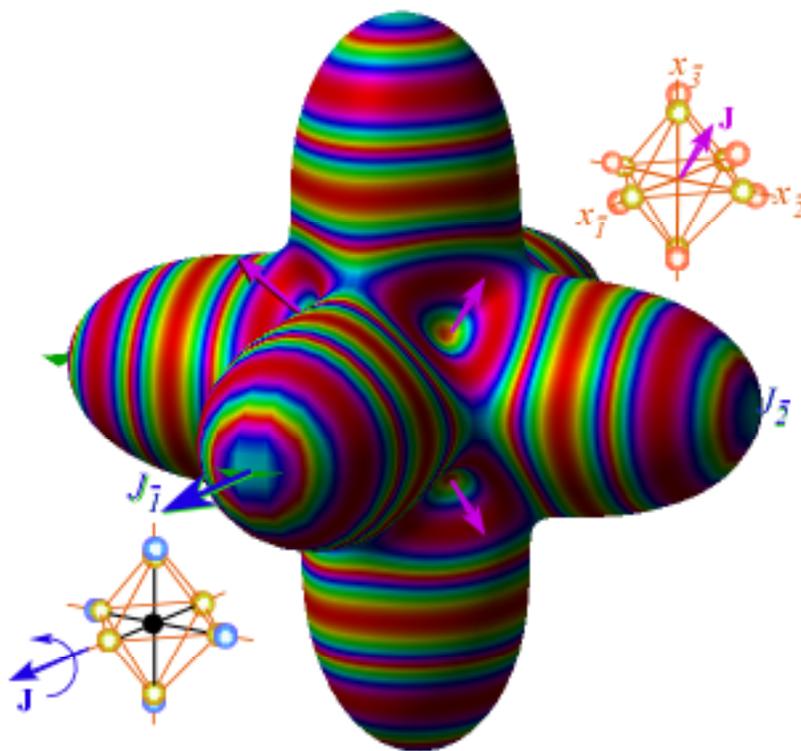


# *Quantum Theory for the Computer Age Unit 10*



## *Molecular Dynamics*

# Unit 10 Molecular Dynamics

Classical and quantum theory of molecular spectroscopy and dynamics is developed using the classical and quantum electrodynamics, vibrational dynamics, rotational dynamics, electronic orbital dynamics and symmetries introduced in Units 5 thru 9. Quantum molecular dynamics (QMD) involves the Born-Oppenheimer Approximation (BOA) and perturbations of it. BOA based QMD attempts to define a molecular body or BOD frame rotating more or less freely in a laboratory or LAB frame with wave functions based on Wigner- $D_{mn}^J$  waves developed in Unit 8 (Ch. 23). QMD states and transitions are characterized by how LAB and BOD perturbations mix BOA bases and ultimately redefine them. Much of modern classical and quantum mechanics as well as their correspondence principles are sorely challenged by these effects.

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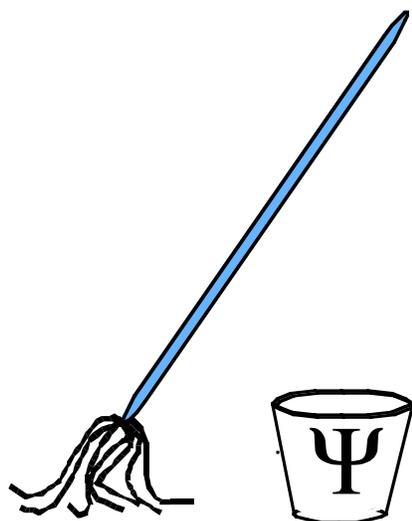
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# Unit 10 Molecular Dynamics



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## Chapter 30

## Molecular Rovibrational

## States and Dynamics

**W. G. Harter**

Quantum molecular dynamics (QMD) shares with quantum electrodynamics (QED) an intrinsic classical prerequisite framework. For QED it is Maxwell-Hamiltonian and Lorentz symmetry. For QMD it is the Wilson-Howard-Watson (WHM) Hamiltonian and rotational symmetry. The WHM Hamiltonian is constructed in a way that introduces a rotational-vibrational-electronic or rovibronic hierarchy in the analysis of rovibrational effects such as Coriolis and centrifugal dynamics. Model molecular systems include  $XY_3$ ,  $XY_6$ , and  $XY_8$  rotational and vibrational structures used to develop more detailed quantum analyses in later chapters.

<b>CHAPTER 30. MOLECULAR ROVIBRATIONAL MECHANICS .....</b>	<b>1</b>
<b>30.1 Classical equations of molecular motion .....</b>	<b>1</b>
a. Lagrangian description of molecular motion.....	1
1. Normal mode transformation: Genuine vibrational modes .....	3
2. Non-Genuine modes: Rotation, translation, and tunneling.....	5
3. Kinetic terms of Lagrangian: Rovibrational Coriolis $\xi$ -coefficients .....	5
<b>30.2 Hamiltonian description of molecular motion .....</b>	<b>7</b>
a. Canonical angular momentum: Coriolis $\zeta$ -coefficients .....	7
1. Legendre-Hamilton-Poincare form.....	8
b. Wilson-Howard-Watson Molecular Hamiltonians .....	9
1. LAB and BOD quantum angular momentum operators .....	10
<b>30.3 Applications of molecular Hamiltonians .....</b>	<b>11</b>
a. Orthonormal mode coordinates. ....	11
b. Centrifugal and Coriolis effects.....	12
1. Elementary spring-mass model .....	12
2. Polyatomic molecular distortion: XY <sub>6</sub> and XY <sub>8</sub> examples .....	13
3. Elementary derivation of SF <sub>6</sub> distortion parameters.....	15
4. Elementary derivation of SF <sub>6</sub> Coriolis parameters. ....	17
<b>Appendix 30.A Symmetry defined vibrational normal coordinates .....</b>	<b>19</b>
A.1 C <sub>3v</sub> defined coordinates of Y <sub>3</sub> and XY <sub>3</sub> molecules .....	19
Vibration matrix and normal mode eigen-solutions .....	21
<b>Problems for Chapter 30.....</b>	<b>26</b>

## Chapter 30. Molecular Rovibrational Mechanics

### 30.1 Classical equations of molecular motion

Some of the most complex and theoretically challenging experiments involve the rotational, vibrational, and electronic motions of polyatomic molecules. In this chapter we will use ideas that have been given in preceding chapters to begin describing molecular *rovibronic* dynamics and spectroscopy. Molecular theory involves rotation and spin states and operators introduced in Ch. 10 and 23, vibrational modes and symmetry of Ch. 15, 20, and 21, electromagnetic transitions of Ch. 22, electronic orbital and tensor operators introduced in Ch. 23, 24 and 25. Quantum molecular dynamics (QMD) has a strong classical Lagrangian and Hamiltonian prerequisite as does quantum electrodynamics (QED) in Ch. 22.

#### a. Lagrangian description of molecular motion

Elementary classical molecular Lagrangians begin with Cartesian nuclear or atomic coordinates  $x_j(\nu)$  and their time derivatives or velocities  $v_j(\nu) = \dot{x}_j(\nu)$ .

$$L = T - V = \frac{1}{2} m \dot{x}_i(\alpha) \dot{x}_i(\alpha) - V(\mathbf{x}), \text{ where: } \dot{x}_j = \frac{dx_j}{dt} = v_j \quad (30.1.1)$$

Greek letters denote particle indices  $\alpha = \nu = 1, 2, \dots, N$  for nuclei or  $\alpha = \varepsilon = 1, 2, \dots, N_e$  for electrons. Cartesian components  $x, y$ , or  $z$  are labeled by indicial letters  $i, j, k, \dots, n$  that range over 1, 2, and 3. A sum over the range of an index, such as  $i$  from 1 to 3 above, is implied if and only if it is repeated within an expression on *one* side of an equation. (We do not sum  $j$  above but repeated  $\alpha$  is summed over  $N+N_e$ .)

Lagrangian  $L$  is to be transformed to a function of the body frame components  $x_{\bar{k}}(\varepsilon)$  for electrons and  $x_{\bar{k}}(\nu)$  for nuclei for which the following notation of Fig. 30.1.1 is to be used.

$$x_{\bar{k}}(\varepsilon) = r_k(\varepsilon) \quad (30.1.2)$$

$$x_{\bar{k}}(\nu) = a_k(\nu) + d_k(\nu) \quad (30.1.3)$$

The  $a_k(\nu)$  are the constant body-fixed nuclear equilibrium positions and  $d_k(\nu)$  are (usually much smaller) vibrational displacements. These quantities are sketched in Fig. 30.1.1(a), and an example involving an  $XY_3$  molecule is shown in Fig. 30.1.1(b). This example and an octahedral  $XY_6$  model in discussions in this unit.

Lab coordinates  $x_\ell$  transform to **BOD** coordinates  $x_{\bar{b}}$  thru coordinate and velocity vectors.

$$\mathbf{x} = x_\ell \mathbf{e}_\ell = x_{\bar{b}} \mathbf{e}_{\bar{b}} \quad (30.1.4)$$

$$\dot{\mathbf{x}} = \dot{x}_\ell \mathbf{e}_\ell + x_\ell \dot{\mathbf{e}}_\ell = \dot{x}_{\bar{b}} \mathbf{e}_{\bar{b}} + x_{\bar{b}} \dot{\mathbf{e}}_{\bar{b}} \quad (30.1.5)$$

Lab unit vectors are assumed fixed  $\dot{\mathbf{e}}_\ell = 0$ , while **BOD** unit vectors rotate at angular velocity  $\bar{\omega}$ .

$$\dot{\mathbf{e}}_{\bar{b}} = \bar{\omega} \times \mathbf{e}_{\bar{b}} = \omega_{\bar{a}} \mathbf{e}_{\bar{a}} \times \mathbf{e}_{\bar{b}} = \varepsilon_{\bar{a}\bar{b}\bar{c}} \omega_{\bar{a}} \mathbf{e}_{\bar{c}} \quad (30.1.6)$$

The antisymmetric Levi-Civita tensor  $\varepsilon_{ijk} = -\varepsilon_{jik} = -\varepsilon_{kji}$  and  $I = \varepsilon_{123}$  gives cross-product (30.1.6) that turns (30.1.5) into a lab-to-**BOD** velocity relation.

$$\dot{\mathbf{x}} = \dot{x}_\ell \mathbf{e}_\ell = \dot{x}_{\bar{b}} \mathbf{e}_{\bar{b}} + x_{\bar{b}} \dot{\mathbf{e}}_{\bar{b}} = \dot{x}_{\bar{b}} \mathbf{e}_{\bar{b}} + x_{\bar{b}} \varepsilon_{\bar{a}\bar{b}\bar{c}} \omega_{\bar{a}} \mathbf{e}_{\bar{c}} = \left( \dot{x}_{\bar{b}} + \varepsilon_{\bar{a}\bar{b}\bar{c}} \omega_{\bar{a}} x_{\bar{c}} \right) \mathbf{e}_{\bar{b}} \quad (30.1.7)$$

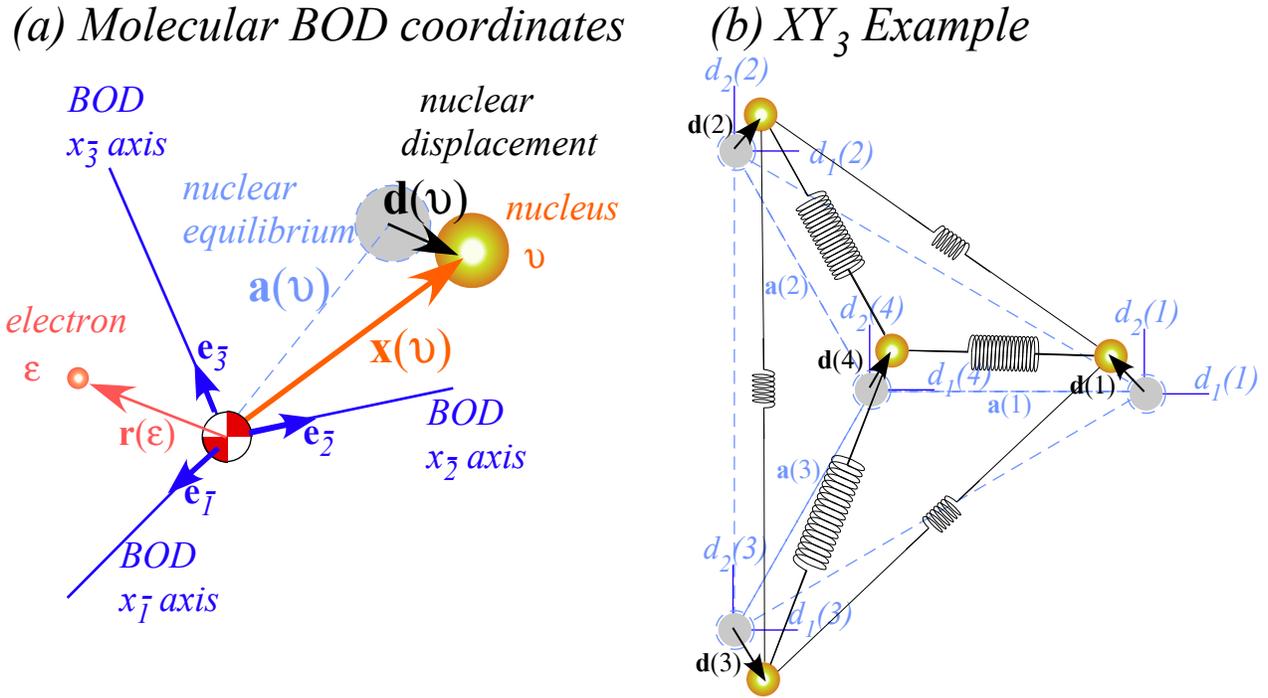


Fig. 30.1.1 Molecular BOD coordinate vectors for classical rovibrational models.

The velocity relation applies to each particle  $\alpha$  in the kinetic term of (30.1.1). (For typographical convenience we delete index overlines. Until otherwise stated, all components are BOD-defined.)

$$\begin{aligned}
 2T &= m_\alpha \mathbf{x}(\alpha) \cdot \dot{\mathbf{x}}(\alpha) = m_\alpha \left[ \dot{x}_k(\alpha) + \varepsilon_{ink} \omega_i x_n(\alpha) \right] \left[ \dot{x}_k(\alpha) + \varepsilon_{jmk} \omega_j x_m(\alpha) \right] \\
 &= m_\alpha \left[ \dot{x}_k(\alpha) \dot{x}_k(\alpha) + 2\varepsilon_{ink} \omega_i x_n(\alpha) \dot{x}_k(\alpha) + \varepsilon_{ink} \varepsilon_{jmk} \omega_i x_n(\alpha) x_m(\alpha) \omega_j \right]
 \end{aligned} \quad (30.1.8)$$

The definitions (30.1.2) of body coordinates may be used to simplify (30.1.7). In particular, the cross-term for nuclear coordinates reduces as follows.

$$\begin{aligned}
 2m_\nu \varepsilon_{ink} \omega_i x_n(\nu) \dot{x}_k(\nu) &= 2m_\nu \varepsilon_{ink} \omega_i (a_n(\nu) + d_n(\nu)) \dot{d}_k(\nu) \\
 &= 2m_\nu \varepsilon_{ink} \omega_i d_n(\nu) \dot{d}_k(\nu)
 \end{aligned} \quad (30.1.9)$$

The last line uses so-called *rotational Eckart conditions*. (Zero total rotation is seen in BOD frame.)

$$m_\alpha [\mathbf{x}(\nu) \times \mathbf{d}(\nu)]_i = 0 = m_\nu \varepsilon_{ink} a_n(\nu) d_k(\nu) \quad (30.1.10a)$$

BOD coordinates are also constrained by *translational Eckart conditions*. (Zero translation in BOD frame.)

$$m_\alpha [\mathbf{x}(\alpha)]_i = 0 = m_e x_i(\varepsilon) + m_\nu (a_i(\nu) + d_i(\nu)) \quad (i = 1, 2, 3) \quad (30.1.10b)$$

$$0 \approx m_\nu d_i(\nu) \quad (i = 1, 2, 3) \quad (30.1.10c)$$

If electronic mass  $m_e$  is negligible, approximate translational Eckart conditions (30.1.10c) may be used.

The translational conditions (30.1.10b) fix the center of total mass (nuclei and electrons) at COM origin of the body frame. Body coordinates  $x(\nu)$  and  $x(\epsilon)$  can only change in such a way that the molecule as a whole does not translate. However, the rotational conditions (30.1.10a), like approximate translation conditions (30.1.10c), involve only the nuclear displacements. The displacements  $d_k(\nu)$  are constrained to change in such a way that no overall rotation of the nuclei occurs in the body frame. Together the Eckart conditions provide six independent constraints on the internal coordinates. The resulting loss of six internal degrees of freedom is supposed to be made up by three overall translational coordinates, and three rotational coordinates such as Euler angles for the nuclear frame. Note that the rotational conditions do not prevent the internal coordinates from having rotational **momentum**. While the mass-weighted sums of  $\mathbf{a}(\nu) \times \dot{\mathbf{d}}(\nu)$  or  $\mathbf{a}(\nu) \times \dot{\mathbf{x}}(\nu)$  are constrained to zero, no such constraint exists for sums of  $\mathbf{x}(\nu) \times \dot{\mathbf{x}}(\nu)$  or  $\mathbf{d}(\nu) \times \dot{\mathbf{d}}(\nu)$  present in (30.1.8). Electrons are treated differently. We do not restrict rotational motion and momentum of the electrons except possibly by (30.1.10b). Their spin is modeled by add-on terms later.

Let us write the kinetic term with nuclear and electronic parts on separate lines.

$$2T = m_\nu \dot{d}_k(\nu) \dot{d}_k(\nu) + 2m_\nu \epsilon_{ink} \omega_i d_n(\nu) \dot{d}_k(\nu) + I_{ij}^N \omega_i \omega_j \\ + m_e \dot{r}_k(\epsilon) \dot{r}_k(\epsilon) + 2m_e \epsilon_{ink} \omega_i r_n(\epsilon) \dot{r}_k(\epsilon) + I_{ij}^e \omega_i \omega_j \quad (30.1.11)$$

The last term in (30.1.7) is rewritten using the tensor identity  $\epsilon_{ink} \epsilon_{jmk} = \delta_{ij} \delta_{mn} - \delta_{im} \delta_{jn}$  to give

$$\epsilon_{ink} \epsilon_{jmk} \omega_i x_n x_m \omega_j = \omega_i x_n x_m \omega_j - \omega_i x_i x_j \omega_j \\ = \omega_i [x_n x_m \delta_{ij} - x_i x_j] \omega_j \quad (30.1.12)$$

The resulting nuclear and electronic inertial tensors are defined as follows:

$$I_{mn}^N = m_\nu [x_\ell(\nu) x_\ell(\nu) \delta_{mn} - x_m(\nu) x_n(\nu)] \quad (30.1.13)$$

$$I_{nm}^e = m_e [r_\ell(\epsilon) r_\ell(\epsilon) \delta_{mn} - r_m(\epsilon) r_n(\epsilon)] \quad (30.1.14)$$

### 1. Normal mode transformation: Genuine vibrational modes

Cartesian displacements  $d_k(\nu)$  relate to **normal coordinates**  $\{s_1, s_2, \dots, s_n\}$  thru linear relations (30.1.15a) to  $d_k(\nu)$  (summed over  $k(\nu)$ ) or vice-versa (30.1.15b) (summed over  $n$ ). Normal  $XY_3$  mode coordinates are found by Ch. 15 symmetry projection (Appendix 30.A) and combined to satisfy Eckart conditions (30.1.10). For example, a  $C_{3v}$  projection (15.3.5) shown in Fig. 15.3.2 helps to label  $XY_3$  modes in Fig. 30.1.2 that shows the displacements  $d_k(\nu)$  of a particular  $n^{\text{th}}$  mode or  $n^{\text{th}}$  column of the  $B^{-1}$  matrix. Only **genuine modes** ( $s_1$  thru  $s_5$ ) satisfy Eckart conditions (30.1.10) by having no rigid  $z$ -rotation or rigid translation. The  $B^{-1}$  and  $B$ -matrix relations also have non-genuine ( $s_5$  thru  $s_8$ ) shown in the next Fig. 30.1.3.

$$d_j(\nu) = B_{j(\nu),n}^{-1} s_n \quad (30.1.15a)$$

$$s_b = B_{b,k(\nu)} d_k(\nu) \quad (30.1.15b)$$

$d_1(1)$	$\frac{\sqrt{3}}{3}$	$\frac{\sqrt{3}}{3}$	$0$	$M$	$0$	$0$	$1$	$0$	$\begin{matrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \\ s_7 \\ s_8 \end{matrix}$	$\frac{\sqrt{3}}{3}$	$0$	$\frac{-\sqrt{3}}{6}$	$\frac{1}{2}$	$\frac{-\sqrt{3}}{6}$	$\frac{-1}{2}$	$0$	$0$	$\begin{matrix} d_1(1) \\ d_2(1) \\ d_1(2) \\ d_2(2) \\ d_1(3) \\ d_2(3) \\ d_1(4) \\ d_2(4) \end{matrix}$	
$d_2(1)$	$0$	$0$	$\frac{\sqrt{3}}{3}$	$0$	$M$	$\frac{\sqrt{3}}{3}$	$0$	$1$		$\frac{\sqrt{3}}{3}$	$0$	$\frac{-\sqrt{3}}{6}$	$\frac{-1}{2}$	$\frac{-\sqrt{3}}{6}$	$\frac{1}{2}$	$0$	$0$		$0$
$d_1(2)$	$\frac{-\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$+\frac{1}{2}$	$M$	$0$	$-\frac{1}{2}$	$1$	$0$		$0$	$\frac{\sqrt{3}}{3}$	$\frac{1}{2}$	$\frac{-\sqrt{3}}{6}$	$\frac{-1}{2}$	$\frac{-\sqrt{3}}{6}$	$0$	$0$		$0$
$d_2(2)$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{-\sqrt{3}}{6}$	$0$	$M$	$\frac{-\sqrt{3}}{6}$	$0$	$1$		$0$	$\frac{1}{3\mu}$	$0$	$\frac{1}{3\mu}$	$0$	$\frac{1}{3\mu}$	$0$	$\frac{-1}{\mu}$		$0$
$d_1(3)$	$\frac{-\sqrt{3}}{6}$	$\frac{-\sqrt{3}}{6}$	$-\frac{1}{2}$	$M$	$0$	$\frac{1}{2}$	$1$	$0$		$0$	$0$	$\frac{m}{\mu}$	$0$	$\frac{m}{\mu}$	$0$	$\frac{M}{\mu}$	$0$		$0$
$d_2(3)$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{-\sqrt{3}}{6}$	$0$	$M$	$\frac{-\sqrt{3}}{6}$	$0$	$1$		$0$	$0$	$\frac{m}{\mu}$	$0$	$\frac{m}{\mu}$	$0$	$\frac{M}{\mu}$	$0$		$0$
$d_1(4)$	$0$	$0$	$0$	$-3m$	$0$	$0$	$0$	$1$		$0$	$0$	$0$	$0$	$0$	$0$	$0$	$0$		$0$
$d_2(4)$	$0$	$0$	$0$	$0$	$-3m$	$0$	$0$	$0$		$1$	$0$	$0$	$0$	$0$	$0$	$0$	$0$		$0$

(a)  $XY_3$  Cartesian displacement coordinates

(b) Genuine  $XY_3$  modes

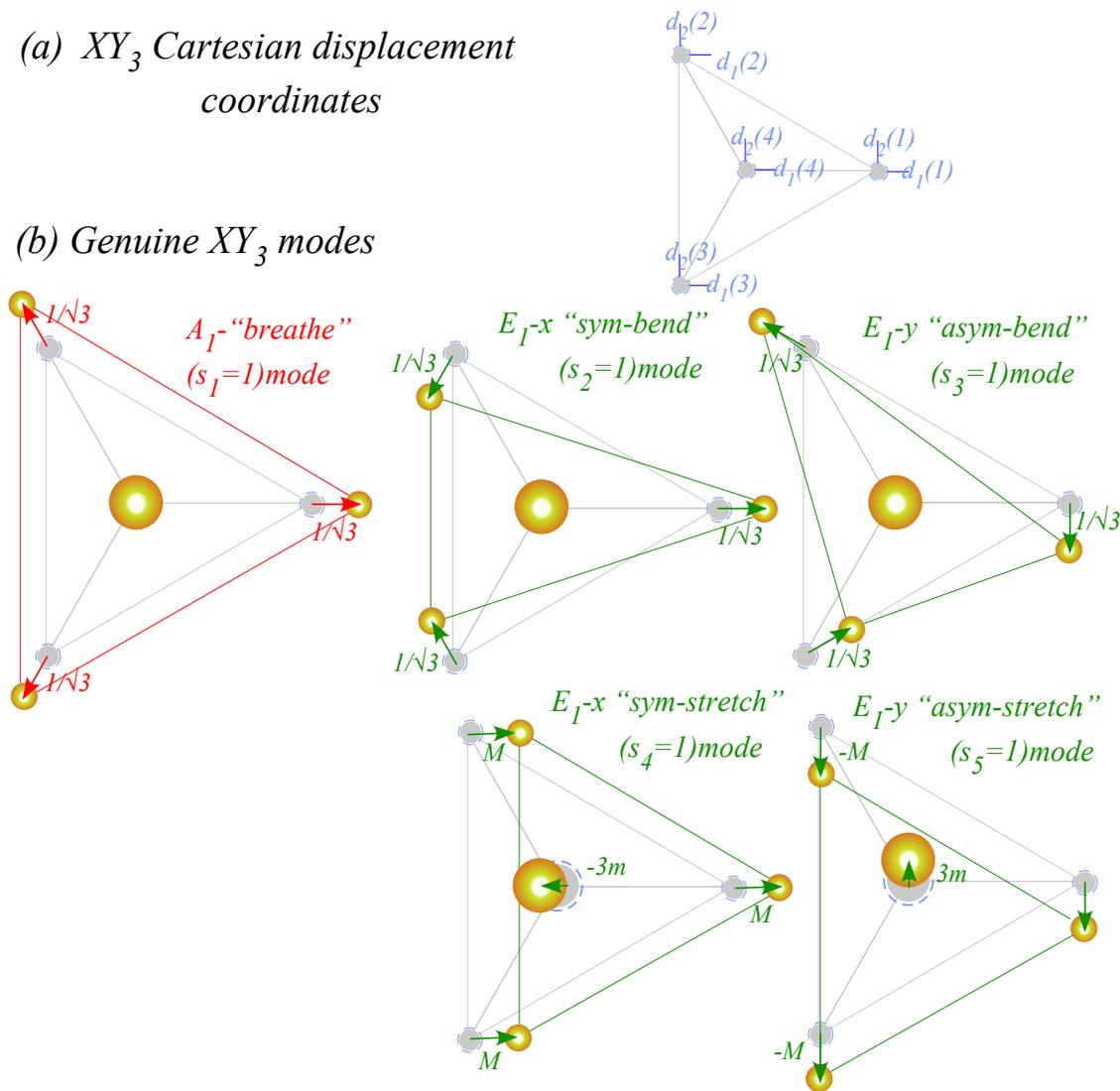


Fig. 30.1.2 Model  $XY_3$  molecule Cartesian and genuine in-plane normal mode coordinates.

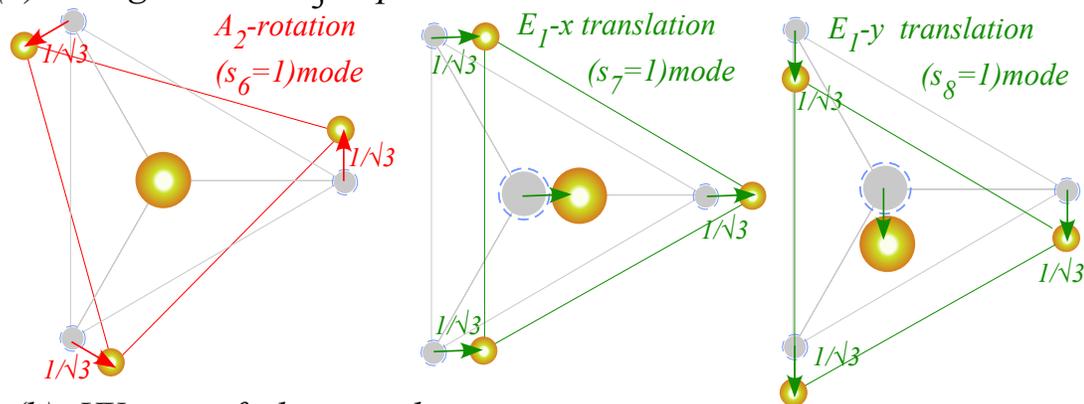
X-mass  $m$ , central Y-mass  $M$ , and total mass  $\mu=M+3m$  determine relative displacements of  $m$  and  $M$  in the stretch modes ( $s_4 = s_x^{E_1}, s_5 = s_y^{E_1}$ ).

2. Non-Genuine modes: Rotation, translation, and tunneling

Non-genuine *z*-axial rotation mode ( $s_6 = s^{A_2}$ ) and (*x,y*)-translation modes ( $s_6 = s_x^{E_1}, s_8 = s_y^{E_1}$ ) are shown in Fig. 30.1.3. Classical Eckart-allowed motion has zero rotation and translation coordinates  $s_6$  through  $s_8$ . Zero frequency motions are purely quantum. A mode is “genuine” if it has non-zero classical frequency.

This  $XY_3$  model has so far ignored four dimensions of out-of-plane *z*-motion. One of these may be a genuine vibration and that is the “inverting umbrella mode” ( $s_9 = s^{A_1}$ ).  $NH_3$   $s_9$  is low frequency (24Ghz) quantum tunneling and so, perhaps, it is non-genuine! The other modes are the two (*x,y*)axial rotations ( $s_{10} = s_x^{E_1}, s_{11} = s_y^{E_1}$ ) and a *z*-translation ( $s_{12} = s^{A_1}$ ), all genuinely non-genuine.  $NH_3$  maser action is due to non-genuine modes. So is most of a genuine 1970-2000 laser renaissance of molecular physics.

(a) Non-genuine  $XY_3$  in-plane modes



(b)  $XY_3$  out-of-plane modes

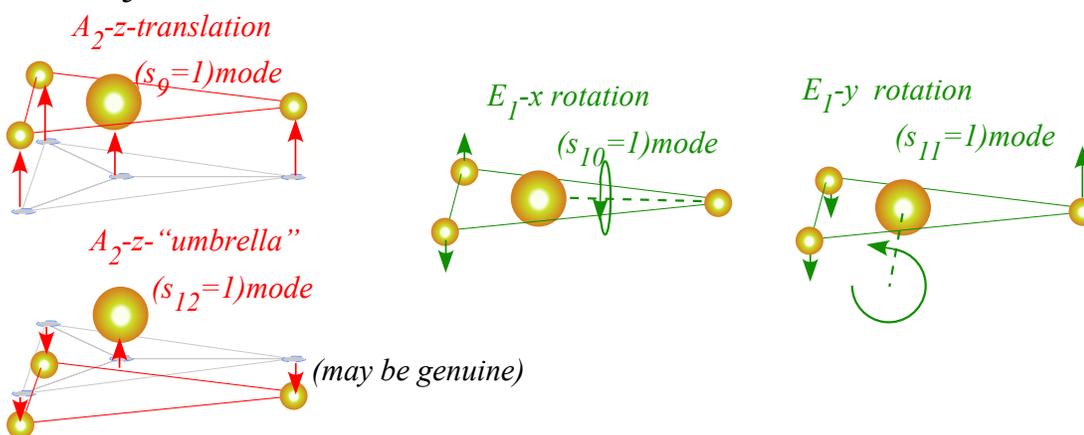


Fig. 30.1.3 Non-genuine  $XY_3$  modes. (a) In-plane translation and rotation (b) Out-of-plane motion.

3. Kinetic terms of Lagrangian: Rovibrational Coriolis  $\xi$ -coefficients

The first kinetic term in (30.1.11) is transformed by substituting (30.1.15b) into the following form.

$$m_\nu \dot{d}_k(\nu) \dot{d}_k(\nu) = B_{k(\nu),a}^{-1} m(\nu) B_{k(\nu),b}^{-1} \dot{s}_a \dot{s}_b = G_{ab}^{-1} \dot{s}_a \dot{s}_b \quad (30.1.16a)$$

Here the *G*-matrix is an inverse mass matrix defined of  $B^{-1}$ -transformed mass matrix.

$$G^{-1} = B^{-1T} \times m \times B^{-1}, \quad G = B \times m^{-1} \times B^T \times \quad (30.1.16b)$$

The  $G$ -matrix for  $XY_3$  internal  $s_a$  coordinates (30.1.15) is diagonal with the following values.

$s_a =$	$s_1 = s^{A_1} Y$	$s_2 = s_x^E Y$	$s_3 = s_y^E Y$	$s_4 = s_x^E XY$	$s_5 = s_x^E XY$	$s_6 = s^{A_2} O$	$s_4 = s_x^E \Rightarrow s_4 = s_y^E \uparrow$
$G_{ab} = \delta_{ab} G_{aa} =$	$\frac{1}{m}$	$\frac{1}{m}$	$\frac{1}{m}$	$\frac{1}{3\mu m M}$	$\frac{1}{3\mu m M}$	$\frac{1}{m}$	$\frac{1}{\mu}$

The  $G$ -matrix is symmetric according to its definition (30.1.16b) but not necessarily diagonal.

$$G^T = G \quad (30.1.17a)$$

$$G_{ab} = G_{ba} \quad (30.1.17b)$$

Substituting of transformation (30.1.15b) into kinetic energy cross term (30.1.11) gives the following.

$$\begin{aligned} 2m_\nu \varepsilon_{ink} \omega_i \dot{d}_n(\nu) \dot{d}_k(\nu) &= 2m_\nu \varepsilon_{ink} \omega_i B_{n(\nu),a}^{-1} B_{k(\nu),b}^{-1} s_a \dot{s}_b \\ &= 2 \quad \xi_{ab}^i \quad s_a \dot{s}_b \end{aligned} \quad (30.1.18)$$

This defines *Coriolis  $\xi_{ab}^i$  xi-coefficients* as follows.

$$\xi_{ab}^i \equiv m_\nu \varepsilon_{ink} B_{n(\nu),a}^{-1} B_{k(\nu),b}^{-1} = -\xi_{ba}^i \quad (30.1.19)$$

Later we see that coefficients  $\xi_{ab}^m$  give the  $m^{\text{th}}$ -BOD-component of angular momentum that two modes  $s_a$  and  $s_b$  can make.  $XY_3$  modes yield two cases with non-zero  $z$  or  $3^{\text{rd}}$ -BOD-component.

$$\xi_{23}^3 = m = -\xi_{32}^3, \quad \xi_{24}^3 = 0 = \xi_{24}^3, \quad \xi_{45}^3 = 3\mu m M = -\xi_{54}^3 \quad (30.1.19)_{\text{example-a}}$$

Angular momentum  $J_3$  transforms like  $C_{3v}$  symmetry  $A_2$ . Products (24.2.40) has  $A_2$  contained in  $E \otimes E$

$(\frac{1}{\sqrt{2}} \begin{vmatrix} E_1 \\ x \end{vmatrix} \begin{vmatrix} E_1 \\ y \end{vmatrix} - \frac{1}{\sqrt{2}} \begin{vmatrix} E_1 \\ y \end{vmatrix} \begin{vmatrix} E_1 \\ x \end{vmatrix})$  and  $A_1 \otimes A_2$ .  $E \otimes E$  applies to genuine modes of  $XY_3$ , and so (30.1.19)<sub>example-a</sub> has all

vibrational  $\xi_{ab}$  components. Coefficients involving rotation-translational motion are as follows.

$$\xi_{16} = m, \quad \xi_{48} = \xi_{75} = 3(M - m), \quad \xi_{78} = \mu \quad (30.1.19b)_{\text{example-b}}$$

Eckart conditions demand  $s_6 = s_7 = s_8 \equiv 0$  so these do not contribute to (30.1.18). From (30.1.1) and (30.1.11) we arrive at the following Lagrangian for an arbitrary set of mode coordinates.

$$\begin{aligned} L &= \frac{1}{2} G_{ab}^{-1} \dot{s}_a \dot{s}_b + \omega_i \xi_{ab}^i s_a \dot{s}_b + \frac{1}{2} I_{ij}^N \omega_i \omega_j \\ &+ \frac{1}{2} m_e \dot{r}_k(\varepsilon) \dot{r}_k(\varepsilon) + \omega_i m_e \varepsilon_{ink} r_n(\varepsilon) \dot{r}_k(\varepsilon) + \frac{1}{2} I_{ij}^e \omega_i \omega_j - V(s, r) \end{aligned} \quad (30.1.20)$$

Potential  $V(s, r)$  includes electrostatic nuclear-nuclear ( $V_{ss}$ ), nuclear-electron ( $V_{sr}$ ), and electron-electron ( $V_{rr}$ ) coupling independent of velocity  $\dot{s}_b$ . The  $V_{ss}$  matrix is diagonal for eigen-modes  $q_a = t_{ab} s_b$ . Spin and orbit interactions may include velocity and spin dependent terms that will be treated later.

## 30.2 Hamiltonian description of molecular motion

A Hamiltonian is a function of coordinates and momentum  $p = \frac{\partial L}{\partial \dot{q}}$ . Canonical *electronic momentum* is

$$p_k(\varepsilon) = \frac{\partial L}{\partial \dot{r}_k(\varepsilon)} = m_e [\dot{r}_k(\varepsilon) + \varepsilon_{ink} \omega_i r_n(\varepsilon)]. \quad (30.2.1)$$

Note that  $\mathbf{p}(\varepsilon)$  has the form  $m_e \mathbf{v}$  where  $\mathbf{v} = \dot{\mathbf{r}}$  (BOD) +  $\boldsymbol{\omega} \times \mathbf{r}$  equals lab measured velocity according to (30.1.6).

Canonical *vibrational momentum* has an analogous form.

$$P_b = \frac{\partial T}{\partial \dot{s}_b} = G_{ab}^{-1} \dot{s}_a + \xi_{ab}^i \omega_i s_a \quad (30.2.2)$$

Canonical *rotational momentum* has both electronic and nuclear parts to be sorted out shortly.

$$J_i = \frac{\partial T}{\partial \omega_i} = I_{ij}^N \omega_j + \zeta_{ab}^i s_a \dot{s}_b + I_{ij}^e \omega_j + m_e \varepsilon_{ink} r_n(\varepsilon) \dot{r}_k(\varepsilon) \quad (30.2.3)$$

### a. Canonical angular momentum: Coriolis $\zeta$ -coefficients

Velocity needs to be expressed in terms of momentum in order to derive a canonical Hamiltonian. The electronic velocity is as follows from (30.2.1).

$$\dot{r}_k(\varepsilon) = p_k(\varepsilon) / m_e - \varepsilon_{ink} \omega_i r_n(\varepsilon) \quad (30.2.4)$$

The vibrational mode velocities are given from (30.2.2) by the following:

$$\dot{s}_a = P_c G_{ca} - \xi_{fc}^i G_{ca} \omega_i s_f \quad (30.2.5a) \quad \dot{s}_b = P_g G_{gb} - \omega_i \zeta_{db}^i s_d \quad (30.2.5b)$$

Here we define *reduced Coriolis  $\zeta_{ab}^i$  zeta-coefficients*. (These relate to *2<sup>nd</sup>-kind Christoffel* factors.)

$$\zeta_{ab}^i \equiv \xi_{ac}^i G_{cb} = \varepsilon_{ink} B_{i(v),a}^{-1} B_{n(v),b} \quad (30.2.5b)$$

Choice of dummy indices have been made to facilitate later substitutions. Note that  $\zeta_{ab}^i \neq -\zeta_{ba}^i$  unless the  $B$ -matrix is orthogonal. Also, note that the reduced coefficients for the  $XY_3$  example are *mass-independent*.

$$1 = \zeta_{32}^3 = -\zeta_{23}^3 = \zeta_{45}^3 = -\zeta_{54}^3, \quad 0 = \zeta_{12}^3 = \dots \quad (30.2.5c)$$

Electronic and vibrational velocity expressions (30.2.4-5) goes into rotational J-momentum (30.2.3).

$$J_i = I_{ij}^N \omega_j + \xi_{ab}^i s_a \left( P_g G_{gb} - \omega_j \zeta_{db}^j s_d \right) + I_{ij}^e \omega_j + m_e \varepsilon_{ink} r_n(\varepsilon) \left( p_k(\varepsilon) / m_e - \omega_j \varepsilon_{jmk} r_m(\varepsilon) \right) \quad (30.2.6)$$

Using (30.2.5b) gives another form.

$$J_i = \left( I_{ij}^N - \xi_{ab}^i \zeta_{db}^j s_a s_d \right) \omega_j + \zeta_{ag}^j s_a P_g + \left( I_{ij}^e - m_e \varepsilon_{ink} \varepsilon_{jmk} r_n(\varepsilon) r_m(\varepsilon) \right) \omega_j + \varepsilon_{ink} r_n(\varepsilon) p_k(\varepsilon) \quad (30.2.7)$$

The first two terms of the electronic contribution cancel according to (30.1.13,14). Two of the other terms represent total angular momenta of vibration  $L^{vib}$  and electrons  $L^{ele}$ , respectively.

$$L_i^{vib} = \zeta_{ab}^i s_a P_b \quad (30.2.8a)$$

$$L_i^{ele} = \varepsilon_{ink} r_n(\varepsilon) p_k(\varepsilon) \quad (30.2.8b)$$

Electronic angular momentum is a sum over electron label  $\varepsilon$  of  $\mathbf{r} \times \mathbf{p}$  terms.

Let bare-rotor- $R$  inertial tensor  $I_{mn}^R$  be the first two terms of the vibrational part (30.2.7).

$$\begin{aligned} I_{ij}^R &\equiv I_{ij}^N - \zeta^i \xi^j s_a s_d \\ &= I_{ij}^N - \left( \varepsilon_{ink} B_{n(v),a}^{-1} m_v B_{k(v),b}^{-1} \right) \left( \varepsilon_{jml} B_{m(\mu),d}^{-1} B_{b,\ell(\mu)} \right) \left( B_{a,p(\lambda)} d_p(\lambda) B_{d,q(\eta)} d_q(\eta) \right) \end{aligned}$$

Generally, the sums are taken over *all* mode indices  $a, b$ , and  $d$  including rotation and translation.

However, terms with  $a > 5$  or  $d > 5$  are zero according to Eckart conditions  $s_a \equiv 0$  for  $a > 5$ . The sums simplify as follows, where (30.1.12-13) are used again.

$$\begin{aligned} I_{ij}^R &= I_{ij}^N - m_v \varepsilon_{ink} \varepsilon_{jml} \delta_{n(v),p(\lambda)} \delta_{k(v),\ell(\mu)} \delta_{m(\mu),q(\eta)} d_p(\lambda) d_q(\eta) \\ &= m_v \left[ \varepsilon_{ink} \varepsilon_{jmk} x_n(v) x_m(v) - \varepsilon_{ink} \varepsilon_{jmk} d_n(v) d_m(v) \right] \end{aligned} \quad (30.2.9)$$

The equilibrium-displacement vector sum ( $\mathbf{x} = \mathbf{a} + \mathbf{d}$ ) of (30.2.6) is then inserted to give a rotor inertia tensor that varies *linearly* with displacements  $\mathbf{d}(v)$  from equilibrium. The rotational Eckart condition (30.1.9) is used to equate the sums of  $a_n d_m$  and  $a_m d_n$ . Here  $I_{ij}^0$  represents the equilibrium inertia with  $d \equiv 0$ .

$$\begin{aligned} I_{ij}^R &= m_v \varepsilon_{ink} \varepsilon_{jmk} \left[ a_n(v) a_m(v) + a_n(v) d_m(v) + d_n(v) a_m(v) \right] \\ &= I_{ij}^0 + 2m_v \varepsilon_{ink} \varepsilon_{jmk} a_n(v) d_m(v) \end{aligned} \quad (30.2.10)$$

Finally, the total angular momentum follows by combining (30.2.7) through (30.2.10).

$$J_m = R_m + L^{vib} + L^{ele} \quad (30.2.11a)$$

Here the electronic and vibrational terms are given by (30.2.8) and the rotor term.

$$R_m = I_{mn}^R \omega_n \quad (30.2.11b)$$

The rotor term varies linearly with normal mode displacements  $d_j(v)$  according to (30.2.10).

### 1. Legendre-Hamilton-Poincare form

The above relations can give the classical Hamiltonian function  $H = \Sigma p \dot{q} - L$  in Poincare form.

$$H = P_b \dot{s}_b + p_k(\varepsilon) \dot{r}_k(\varepsilon) + \omega_m J_m - L = T + V \quad (30.2.12)$$

This is a general result whose verification for this particular case is left as an exercise. Instead, we shall derive  $H$  directly below. First the terms of  $T$  in (30.1.20) that are quadratic in the velocities are converted to the following functions of momentum using (30.2.5) and (30.2.6). Vibrational terms are as follows.

$$\begin{aligned} G_{ab}^{-1} \dot{s}_a \dot{s}_b &= \left( P_c G_{ca} - \xi_{fc}^i G_{ca} \omega_i s_f \right) G_{ab}^{-1} \left( P_g G_{gb} - \zeta_{db}^j s_d \omega_j \right) \\ &= G_{bg} P_b P_g - 2\omega_i \zeta_{fg}^i s_f P_g + \omega_i \xi_{fb}^i \zeta_{db}^j s_f s_d \omega_j \times \end{aligned} \quad (30.2.13a)$$

The electronic terms give the following.

$$\begin{aligned} m_e \dot{r}_k(\varepsilon) \dot{r}_k(\varepsilon) &= m_e \left( p_k(\varepsilon) / m_e - \varepsilon_{ink} \omega_i r_n(\varepsilon) \right) \left( p_k(\varepsilon) / m_e - \varepsilon_{jmk} \omega_j r_m(\varepsilon) \right) \\ &= p_k(\varepsilon) p_k(\varepsilon) / m_e - 2\omega_i \varepsilon_{ink} r_n(\varepsilon) p_k(\varepsilon) + \omega_i m_e \varepsilon_{ink} \varepsilon_{jmk} r_n(\varepsilon) r_m(\varepsilon) \omega_j \end{aligned} \quad (30.2.13b)$$

There is a similarity between the quadratic terms above and the remaining linear velocity terms of  $T$ .

$$\omega_i \xi_{ab}^i s_a \dot{s}_b = \omega_i \zeta_{ag}^i s_a P_g - \omega_i \xi_{ab}^i \zeta_{db}^j s_a s_d \omega_j \quad (30.2.14a)$$

$$\omega_i m_e \varepsilon_{ink} r_n(\varepsilon) \dot{r}_k(\varepsilon) = \omega_i \varepsilon_{ink} r_n(\varepsilon) p_k(\varepsilon) - \omega_i m_e \varepsilon_{ink} \varepsilon_{jmk} r_n(\varepsilon) r_m(\varepsilon) \omega_j \quad (30.2.14b)$$

## b. Wilson-Howard-Watson Molecular Hamiltonians

All kinetic terms are collected to express  $T$  in terms of canonical rovibronic momenta  $\mathbf{R}$ ,  $\mathbf{P}$ , and  $\mathbf{p}$ .

$$\begin{aligned}
 T = & \frac{1}{2} G_{ab} P_a P_b - \omega_i \zeta_{fg}^i s_f P_g + \frac{1}{2} \omega_i \xi_{ab}^i \zeta_{db}^j s_a s_d \omega_j + \frac{1}{2} I_{ij}^N \omega_i \omega_j \\
 & + \omega_i \zeta_{ag}^i s_a P_g - \omega_i \xi_{ab}^i \zeta_{db}^j s_a s_d \omega_j \\
 & + \frac{1}{2} m_e p_k(\epsilon) p_k(\epsilon) - \omega_i \epsilon_{ink} r_n(\epsilon) p_k(\epsilon) + \frac{1}{2} m_e \omega_i \epsilon_{ink} \epsilon_{jmk} r_n(\epsilon) r_m(\epsilon) \omega_j + \frac{1}{2} I_{ij}^e \omega_i \omega_j \\
 & + \omega_i \epsilon_{ink} r_n(\epsilon) p_k(\epsilon) - m_e \omega_i \epsilon_{ink} \epsilon_{jmk} r_n(\epsilon) r_m(\epsilon) \omega_j
 \end{aligned} \tag{30.2.15a}$$

Cancellation simplifies  $T$  particularly for electronic terms. Then rotor inertia matrix (30.2.10) is used.

$$T = \frac{1}{2} \left( I_{ij}^N - \xi_{fb}^i \zeta_{db}^j s_f s_d \right) \omega_i \omega_j + \frac{1}{2} G_{bg} P_b P_g + \frac{1}{2} m_e p_k(\epsilon) p_k(\epsilon) \tag{30.2.15b}$$

$$T = \frac{1}{2} I_{ij}^R \omega_i \omega_j + \frac{1}{2} G_{bg} P_b P_g + \frac{1}{2} m_e p_k(\epsilon) p_k(\epsilon) \tag{30.2.15c}$$

Finally angular velocity  $\omega$  is expressed in terms of nuclear rotor momentum  $\mathbf{R}$  by inverting (30.2.11b).

The classical *Wilson-Howard-Watson molecular Hamiltonian* follows if we add a potential  $V(\mathbf{s}, \mathbf{r})$  to  $T$ .

$$H = T + V(\mathbf{s}, \mathbf{r}) \tag{30.2.16a}$$

$$= \frac{1}{2} R_i \mu_{ij}^R R_j + \frac{1}{2} P_a G_{ab} P_b + \frac{1}{2} m_e p_k(\epsilon) p_k(\epsilon) + V(\mathbf{s}, \mathbf{r}) \tag{30.2.16b}$$

$$= \frac{1}{2} \left( J_i - L_i^{vib} - L_i^{ele} \right) \mu_{ij}^R \left( J_j - L_j^{vib} - L_j^{ele} \right) + KE^{vib} + KE^{el} + V(\mathbf{s}, \mathbf{r}) \tag{30.2.16c}$$

Here the inverse rotor inertia matrix  $\mu_{ij}^R$  is defined in terms of the original inertia tensor  $I_N$  in (30.1.13).

$$\left( \mu_{ij}^R \right)^{-1} = I_{ij}^R = I_{ij}^N - \zeta_{ab}^i \xi_{db}^j s_a s_d \tag{30.2.17a}$$

$$= I_{ij}^0 + 2m_v \epsilon_{ink} \epsilon_{jmk} a_n(\mathbf{v}) d_m(\mathbf{v}) \tag{30.2.17b}$$

$$= m_v \epsilon_{ink} \epsilon_{jmk} \left[ a_n(\mathbf{v}) a_m(\mathbf{v}) + 2a_n(\mathbf{v}) d_m(\mathbf{v}) \right] \tag{30.2.17c}$$

The form (30.2.17c) requires  $(m,n)$ -sums over *all* modes including pure rotation and translation.

For some time the quantum versions of (30.2.16) were thought to be even more complicated. Then, Louck and Watson showed that the quantum molecular Hamiltonian could be written in the same form as the classical Hamiltonian (30.2.16) if one includes a tiny energy shift term.

$$U = -\left( \hbar^2 / 8 \right) \text{Trace } \mu^R. \tag{30.2.18}$$

It is difficult if not impossible to observe  $U$  so we hold off discussing it. Instead we consider dynamics that arise from Hamiltonian (30.2.16) when quantum operators replace the classical canonical variables. However, the underlying LAB to BOD rotational relativity behind the replacement of rotor KE  $\frac{\mu}{2} R^2$  by  $\frac{\mu}{2} (J - L)^2$  in (30.2.16) is anything but trivial. Rather it is analogous to the replacement of KE  $\frac{1}{2m} p^2$  by  $\frac{1}{2m} (p - eA)^2$  in quantum electrodynamics where field is a momentum boost (Recall Sec. 16.)

### 1. LAB and BOD quantum angular momentum operators

A most important point concerns what glues an entire molecule together to allow the concept of a molecular frame. It is assumed that electronic bonding overcomes inter-nuclear repulsion and provides a stable effective adiabatic potential energy that has an approximate quadratic harmonic dependence on the nuclear coordinates  $s_b$ . Such a  $V(s_b)$  is called a *Born Oppenheimer Approximate* (BOA) effective potential and will be discussed at the beginning of Sec. 31.

Commutation of BOD-based momentum operators  $J_{\bar{b}} = -\bar{J}_{\bar{b}}$  (23.1.20b) adds a (-) sign to that of BOD defined generators  $\bar{J}_{\bar{b}}$  of  $\bar{\mathbf{R}}[\bar{\Theta}] = e^{-i\bar{\mathbf{J}} \cdot \bar{\Theta}}$  or the standard LAB defined generators  $J_{\ell}$  of  $\mathbf{R}[\Theta] = e^{-i\mathbf{J} \cdot \Theta}$ .

$$[J_{\bar{a}}, J_{\bar{b}}] = -i\epsilon_{abc} J_{\bar{c}} \quad (30.2.19a) \qquad [\bar{J}_{\bar{a}}, \bar{J}_{\bar{b}}] = +i\epsilon_{abc} \bar{J}_{\bar{c}} \quad (30.2.19b)$$

$\bar{\mathbf{R}}[\bar{\Theta}]$  has the same group multiplication rules as  $\mathbf{R}[\Theta]$  as do  $\bar{\mathbf{J}}$  and  $\mathbf{J}$  yet the two groups commute. A molecular BOD turning anti-clockwise relative to LAB has positive  $\langle \mathbf{J}_z \rangle = m > 0$  but negative  $\langle \bar{\mathbf{J}}_z \rangle = \bar{m} < 0$  since BOD sees LAB turning clockwise. The (-) definition  $J_{\bar{b}} = -\bar{J}_{\bar{b}}$  makes signs come out the same.

The electronic momenta (30.2.8b) satisfy the usual LAB commutation relations as long as the electrons are constricted by BOA to be defined in the BOD frame (that they are holding together!).

$$[L_i^{el}, L_j^{el}] = i\epsilon_{ijk} L_k^{el} \quad (30.2.20)$$

However, the vibrational momenta (30.2.8a) do not necessarily satisfy standard commutation relations. As a result the vibrational momenta can have non-quantized expectation values resulting from an incestuous entanglement of rovibrational modes with the rotor on which the vibrations are based.

### 30.3 Applications of molecular Hamiltonians

Conventional expressions for the molecular inertia matrix such as (30.2.17a) are sums over the genuine vibrational modes, only, and give a different expansion than (30.2.17c). Choosing orthonormal mode variables  $q_a$ , as shown next, gives a unified definition ( $\xi = \zeta$ ) of Coriolis constants.

#### a. Orthonormal mode coordinates.

An orthonormal mode coordinate system is more convenient for quantum purposes. The objective is to simplify the vibrational kinetic terms.

$$\frac{1}{2} m_v \dot{d}_j(v) \dot{d}_j(v) = \frac{1}{2} \dot{\delta}_j(v) \dot{\delta}_j(v), \quad \text{where: } \delta_j(v) = m_v^{\frac{1}{2}} d_j(v) \quad (30.3.1)$$

Mode coordinates  $s_a$  in definition (30.1.15) become an orthonormal set  $q_a$ .

$$\delta_j(v) = [a, j(v)] q_a \quad q_b = [b, k(v)] \delta_k(v) \quad (30.3.2)$$

The transformation is orthogonal.

$$[a, j(v)] [b, j(v)] = \delta_{ab} \quad [a, j(v)] [a, k(\mu)] = \delta_{j(v), k(\mu)} \quad (30.3.3)$$

Orthogonality (30.3.4) means the kinetic term is preserved if the transformation is time independent.

$$\frac{1}{2} \dot{\delta}_j(v) \dot{\delta}_j(v) = \frac{1}{2} \dot{q}_a \dot{q}_a \quad (30.3.4)$$

Comparing (30.1.15) and (30.3.1) relates the two transformations and simplifies preceding quantities.

$$B_{j(v), a}^{-1} = [a, j(v)] / \sqrt{m_v} \quad B_{b, k(v)} = [b, k(v)] \sqrt{m_v} \quad (30.3.5)$$

A mass-orthogonal Eckart conditioned mode transformation such as  $B^{-1}$  of (30.1.15)<sub>x</sub> is easily made into an orthonormal  $[a, j(v)]$  matrix by multiplying row- $j(v)$  of  $B^{-1}$  by  $\sqrt{m_v}$  according to (30.3.5) and then normalizing each column- $s_a$  to give column- $q_a$  of  $[a, j(v)]$  as in the following example.

$$\begin{array}{c} \delta_1(1) \\ \delta_2(1) \\ \delta_1(2) \\ \delta_2(2) \\ \delta_1(3) \\ \delta_2(3) \\ \delta_1(4) \\ \delta_2(4) \end{array} = \begin{array}{c} \left| \begin{array}{cccccccc} \frac{\sqrt{3}}{3} & \frac{\sqrt{3}}{3} & 0 & \sqrt{\frac{M}{3\mu}} & 0 & 0 & \sqrt{\frac{m}{\mu}} & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{3} & 0 & \frac{M}{3\mu} & \frac{\sqrt{3}}{3} & 0 & \sqrt{\frac{m}{\mu}} \\ -\frac{\sqrt{3}}{6} & -\frac{\sqrt{3}}{6} & -\frac{1}{2} & \sqrt{\frac{M}{3\mu}} & 0 & -\frac{1}{2} & \sqrt{\frac{m}{\mu}} & 0 \\ \frac{1}{2} & -\frac{1}{2} & \frac{\sqrt{3}}{6} & 0 & \sqrt{\frac{M}{3\mu}} & -\frac{\sqrt{3}}{6} & 0 & \sqrt{\frac{m}{\mu}} \\ -\frac{\sqrt{3}}{6} & -\frac{\sqrt{3}}{6} & \frac{1}{2} & \sqrt{\frac{M}{3\mu}} & 0 & \frac{1}{2} & \sqrt{\frac{m}{\mu}} & 0 \\ -\frac{1}{2} & \frac{1}{2} & \frac{\sqrt{3}}{6} & 0 & \sqrt{\frac{M}{3\mu}} & -\frac{\sqrt{3}}{6} & 0 & \sqrt{\frac{m}{\mu}} \\ 0 & 0 & 0 & \sqrt{\frac{3m}{\mu}} & 0 & 0 & \sqrt{\frac{M}{\mu}} & 0 \\ 0 & 0 & 0 & 0 & \sqrt{\frac{3m}{\mu}} & 0 & 0 & \sqrt{\frac{M}{\mu}} \end{array} \right| \end{array} \begin{array}{c} q_1 \\ q_2 \\ q_3 \\ q_4 \\ q_5 \\ q_6 \\ q_7 \\ q_8 \end{array} \quad (30.3.6)$$

Each row (or column) of a  $[b, k(v)]$  matrix like (30.3.6) has unit norm and is orthogonal to the others.

Orthonormal coordinates make equal Coriolis coefficients in (30.1.19) and (30.2.6b).

$$\xi_{ab}^i = \varepsilon_{ink} [a, n(v)] [b, k(v)] = -\xi_{ba}^i \quad \text{where: } \xi_{ab}^i = \zeta_{ab}^i = -\zeta_{ba}^i \quad (30.3.8)$$

For the  $XY_3$  example we have the following.

$$\begin{aligned}\zeta_{23}^3 &= -1 = -\zeta_{32}^3, & \zeta_{24}^3 &= 0 = -\zeta_{25}^3, & \zeta_{45}^3 &= 1 = -\zeta_{54}^3 \\ \zeta_{61}^3 &= 1 = -\zeta_{32}^3, & \zeta_{48}^3 &= 0 = \zeta_{75}^3, & \zeta_{78}^3 &= 1 = -\zeta_{87}^3\end{aligned}\quad (30.3.9)$$

So far only the kinetic  $\frac{1}{2}\dot{q}_a\dot{q}_a$  terms (30.3.4) have been simplified. If the electronic bonding forces can be approximated by harmonic potential  $\frac{1}{2}k_{ab}q_aq_b$  then that also needs to be simplified by normal coordinates  $Q_n=q_a$  ( $a|n$ ) that bring the harmonic part of the potential to diagonal form  $\frac{1}{2}\omega_b^2Q_b^2$  as follows.

$$KE^{vib} + PE^{vib} = \frac{1}{2}\dot{q}_a\dot{q}_a + \frac{1}{2}k_{ab}q_aq_b + \dots \text{anharmonic } q\text{-terms} \quad (30.3.10a)$$

$$= \frac{1}{2}\dot{Q}_a\dot{Q}_a + \frac{1}{2}\omega_b^2Q_b^2 + \dots \text{anharmonic } Q\text{-terms} \quad (30.3.10b)$$

Examples for  $XY_3$  and  $XY_6$  vibration modes are given in Appendix 30.A. and used below to derive centrifugal and Coriolis effects for various models including, first of all, a simple rotating spring-mass.

## b. Centrifugal and Coriolis effects

### 1. Elementary spring-mass model

Hamiltonians of 4<sup>th</sup>-power  $J_x^4, J_y^4, \dots$  terms model deformable rotors that change inertia more or less due to centrifugal force. An example in Fig. 30.3.1 is a single rotating mass  $m$  held by a spring  $k = m\omega_v^2$ . The rotor has vibrational kinetic and potential energy  $KE_v$  and  $PE_v$  plus rotational kinetic energy  $RE_J$ .

$$\begin{aligned}E &= KE_v + PE_v + RE_J \\ &= \frac{m\dot{r}^2}{2} + \frac{k}{2}(r-r_0)^2 + \frac{I\dot{\theta}^2}{2} = \frac{p_v^2}{2m} + \frac{m}{2}\omega_v^2(r-r_0)^2 + \frac{\mu J^2}{2}\end{aligned}\quad (30.3.11)$$

Rotational inertia  $I = mr^2 = 1/\mu$ , angular velocity  $\dot{\theta} = \omega_J$ , and momentum  $J = I\dot{\theta} = I\omega_J$  involve radius  $r$  that grows from rest value  $r_0$  until spring force  $F_{spring} = -m\omega_v^2(r-r_0)$  cancels centrifugal force  $F_{centrif} = m\omega_J^2 r$ .

$$F_{spring} + F_{centrif} = 0 = m\omega_J^2 r - m\omega_v^2(r-r_0) \quad \text{implies:} \quad r = r_0 \frac{\omega_v^2}{\omega_v^2 - \omega_J^2} \quad (30.3.12)$$

Centrifugal equilibrium  $r$  blows up as rotation rate  $\omega_J$  nears vibrational frequency  $\omega_v$ . 1<sup>st</sup> derivative of effective potential  $PE_v + RE_J$  in (30.3.11) is zero at equilibrium radius  $r$  or stretch distance  $d = r - r_0$ .

$$\frac{\partial}{\partial r}(PE_v + RE_J) = 0 = m\omega_v^2(r-r_0) + \frac{J^2}{2} \frac{\partial \mu}{\partial r} \quad \text{implies:} \quad d = r - r_0 = \frac{J^2}{2m\omega_v^2} \frac{\partial \mu}{\partial r} \quad (30.3.13)$$

We assume the angular velocity  $\omega_J$  varies inversely with  $r$  so that momentum  $J$  is conserved as it must be since the central spring force exerts no torque.

The inverse inertia  $I = 1/\mu$  is approximated for small stretch ( $d = r - r_0 \ll 1$ ) and (30.3.13) is inserted.

$$\mu \cong \mu_0 + \frac{\partial \mu}{\partial r}(r-r_0) + \dots = \mu_0 - \frac{\partial \mu}{\partial r} \frac{J^2}{2m\omega_v^2} \frac{\partial \mu}{\partial r} + \dots \quad (30.3.14a)$$

This with (30.3.13) is inserted into energy expression (30.3.11) to approximate the effect of momentum  $J$ .

$$\begin{aligned}
 E &= \frac{p_v^2}{2m} + \frac{m}{2} \omega_v^2 (r-r_0)^2 + \frac{\mu J^2}{2} \\
 &= \frac{p_v^2}{2m} + \frac{m}{2} \omega_v^2 \left( \frac{J^2}{2m\omega_v^2} \frac{\partial \mu}{\partial r} \right)^2 + \frac{\mu_0 J^2}{2} - \frac{\partial \mu}{\partial r} \frac{J^2}{2m\omega_v^2} \frac{\partial \mu}{\partial r} \frac{J^2}{2} + \dots \\
 &= \frac{p_v^2}{2m} + \frac{J^4}{8m\omega_v^2} \left( \frac{\partial \mu}{\partial r} \right)^2 + \frac{\mu_0 J^2}{2} - \frac{J^4}{4m\omega_v^2} \left( \frac{\partial \mu}{\partial r} \right)^2 + \dots
 \end{aligned}
 \tag{30.3.14b}$$

This reduces to a simpler form that lends some insight into centrifugal distortion energy.

$$E = \frac{p_v^2}{2m} + \frac{\mu_0 J^2}{2} - \frac{J^4}{8m\omega_v^2} \left( \frac{\partial \mu}{\partial r} \right)^2 + \dots = \frac{p_v^2}{2m} + \frac{\mu_0 J^2}{2} - \frac{m}{2} \omega_v^2 d^2 + \dots
 \tag{30.3.15}$$

The rigid rotor energy is perturbed by a  $J^4/r^6$  term that reduces total energy by just the amount of work needed to stretch the spring by distance  $d$  in (30.3.13). The spring gains  $PE=kd^2/2$  the whole system loses twice that in rotational kinetic energy by expanding to radius  $r=r_0+d$  for a net loss of  $kd^2/2=m\omega_v^2 d^2/2$ .

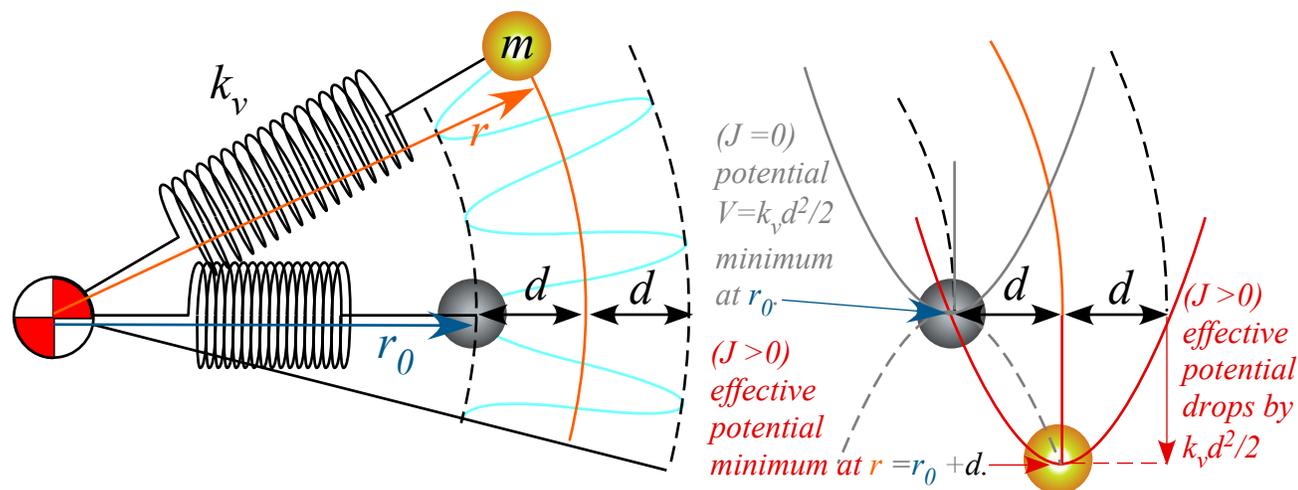


Fig. 30.3.1 Spring-mass model for centrifugal stretch of a model vib-rotor showing effective PE shift.

Imagine a rotor of energy  $E$  is held by a wire at its  $(J=0)$ -radius  $r_0$  but has momentum  $J > 0$  tending to pull it out to radius  $r=r_0+d$ . Cutting the wire changes neither energy  $E$  nor momentum  $J$  but lets mass  $m$  begin vibrating around its new equilibrium of  $r=r_0+d$  with an amplitude  $\pm d$  between  $r_{min}=r_0$  and  $r_{max}=r_0+2d$ .

## 2. Polyatomic molecular distortion: $XY_6$ and $XY_8$ examples

Multi-mass molecular Hamiltonians have vibration normal coordinates  $q_\mu$  and BOD momentum  $J_{\bar{m}}$ .

$$H = \frac{1}{2} p_\mu p_\mu + \frac{1}{2} \omega_\mu^2 q_\mu q_\mu + \frac{1}{2} J_{\bar{m}} \mu_{\bar{m}\bar{n}} J_{\bar{n}}
 \tag{30.3.16}$$

Each normal coordinate has an equilibrium shift  $\delta q_\mu$  like the  $d$  in (30.3.13). Note:  $\frac{\partial}{\partial q} (\mu \cdot \mathbf{I}) = \frac{\partial \mathbf{I}}{\partial q} = \mathbf{0} = \frac{\partial \mu}{\partial q} \cdot \mathbf{I} + \mu \cdot \frac{\partial \mathbf{I}}{\partial q}$ .

$$\delta q_\mu = -\frac{1}{2\omega_\mu^2} J_{\bar{m}} \frac{\partial \mu_{\bar{m}\bar{n}}}{\partial q_\mu} J_{\bar{n}} = -\frac{1}{2\omega_\mu^2} J_{\bar{m}} I_{\bar{m}\bar{n}}^{-1} \frac{\partial I_{\bar{m}\bar{n}}}{\partial q_\mu} I_{\bar{n}\bar{p}}^{-1} J_{\bar{p}}
 \tag{30.3.17}$$

Inverse inertia is represented by a 3-by-3 matrix  $\mu_{\bar{m}\bar{n}} = I_{\bar{m}\bar{n}}^{-1}$  inverse to the inertia tensor  $I_{\bar{m}\bar{n}}$ . The resulting effective Hamiltonian analogous to (30.3.15) involves a 4<sup>th</sup>-degree  $J$ -tensor sum over all modes  $q_\mu$ .

$$H = H_0 - \frac{J_{\bar{k}} J_{\bar{l}} J_{\bar{m}} J_{\bar{n}}}{8\omega_\mu^2} \frac{\partial \mu_{\bar{k}\bar{l}}}{\partial q_\mu} \frac{\partial \mu_{\bar{m}\bar{n}}}{\partial q_\mu} = H_0 - \frac{(\omega_\mu \delta q_\mu)^2}{2} \quad \text{where: } H_0 = \frac{1}{2} p_\mu p_\mu + \frac{1}{2} J_{\bar{m}} \mu_{\bar{m}\bar{n}}^{(0)} J_{\bar{n}} \quad (30.3.18)$$

Mode  $q_\mu$ -sums are discussed below. However, for high symmetry molecules, the allowed  $J$ -tensor forms can be deduced by symmetry alone. For cubic, octahedral, and tetrahedral molecules C<sub>8</sub>H<sub>8</sub>, SF<sub>6</sub>, and CF<sub>4</sub>, respectively, there is only one linearly independent 4<sup>th</sup>-degree  $J$ -tensor or  $(xyz)$ -polynomial. Powers  $J^4$  or  $r^4$  are spherical *scalars* that expand into non-scalar *tensors* linearly dependent on scalar  $r^4$ .

$$r^4 = (r^2)^2 = (x^2 + y^2 + z^2)^2 = (x^4 + y^4 + z^4) + 2(x^2y^2 + x^2z^2 + y^2z^2) \quad (30.3.19)$$

An octahedral (SF<sub>6</sub>-like) molecule uses the first tensor. Cubic or tetrahedral molecules use the other.

$$H^{\text{octahedral}} = H_0 + t_4 (J_1^4 + J_2^4 + J_3^4) \quad (30.3.20a)$$

$$H^{\text{cubic}} = H_0 + t_{22} (J_1^2 J_2^2 + J_1^2 J_3^2 + J_2^2 J_3^2) \quad (30.3.20b)$$

The spherical scalar term  $H_0 = BJ^2 + t_0 J^4$  has  $BJ^2 = B(J_1^2 + J_2^2 + J_3^2)$  of a rigid spherical top  $H^{\text{sph}}$ , but each RES has an octahedral or cubic shape, respectively, as shown in Fig. 30.3.2(a) and Fig. 30.3.2(b).

$$T^{(4)}(J) = J_1^4 + J_2^4 + J_3^4 \quad (30.3.20c)$$

$$= J^4 [\cos^4 \gamma \sin^4 \beta + \sin^4 \gamma \sin^4 \beta + \cos^4 \beta]$$

$$T^{(2,2)}(J) = J_1^2 J_2^2 + J_1^2 J_3^2 + J_2^2 J_3^2 \quad (30.3.20d)$$

$$= J^4 [\cos^2 2\gamma \sin^2 \beta + \sin^2 2\beta]$$

The Hamiltonians (a) and (b) of (30.3.20) and RES (a) and (b) in Fig. 30.3.2 are related in (30.3.19) by a  $\pm$  sign since  $t_{22}$  is just  $-2t_4$  if scalar  $t_0$  is adjusted accordingly. Nevertheless, distortion of an octahedral SF<sub>6</sub> molecule described by  $T^{(4)}$  is quite different from a  $T^{(2,2)}$  distortion of cubic C<sub>8</sub>H<sub>8</sub> or tetrahedral CF<sub>4</sub>.

The octahedral RES has a minimum when the **J** is near one of the eight (111) axes of trigonal (3-fold) symmetry. Whirling about (111) axes has maximum effect on octahedral molecules since they have relatively weak bending bonds that are affected by centrifugal force due to (111) rotation that spreads the six arms of an SF<sub>6</sub> molecule relatively easily. Thus (111) is in a valley in Fig. 30.3.2(a).

However, a rotation about (100), one of six  $(\pm x, \pm y, \pm z)$  axes of tetragonal (4-fold) symmetry, only affects radial bonds normal to these axes, and those stretch very little due to the high radial bond strength. Thus (100) is on one of six octahedral RES peaks in Fig. 30.3.2(a) where SF<sub>6</sub> is least susceptible.

It is *vice-versa* for cubic C<sub>8</sub>H<sub>8</sub> or tetrahedral CF<sub>4</sub> molecules that resist distortion while rotating on any of eight (111)-axes of trigonal (3-fold) symmetry but are susceptible to rotation on any of six  $(\pm 100)$ ,  $(0\pm 10)$ , or  $(00\pm 1)$  tetragonal axes that bend bonds and thus lie in six RES valleys of Fig. 30.3.2(b).

$$(a) H^{\text{Octahedral}} = BJ^2 + t_0 J^4 + t_4 (J_1^4 + J_2^4 + J_3^4)$$

$$(b) H^{\text{Cubic}} = BJ^2 + t_0 J^4 + t_{22} (J_1^2 J_2^2 + J_1^2 J_3^2 + J_2^2 J_3^2)$$

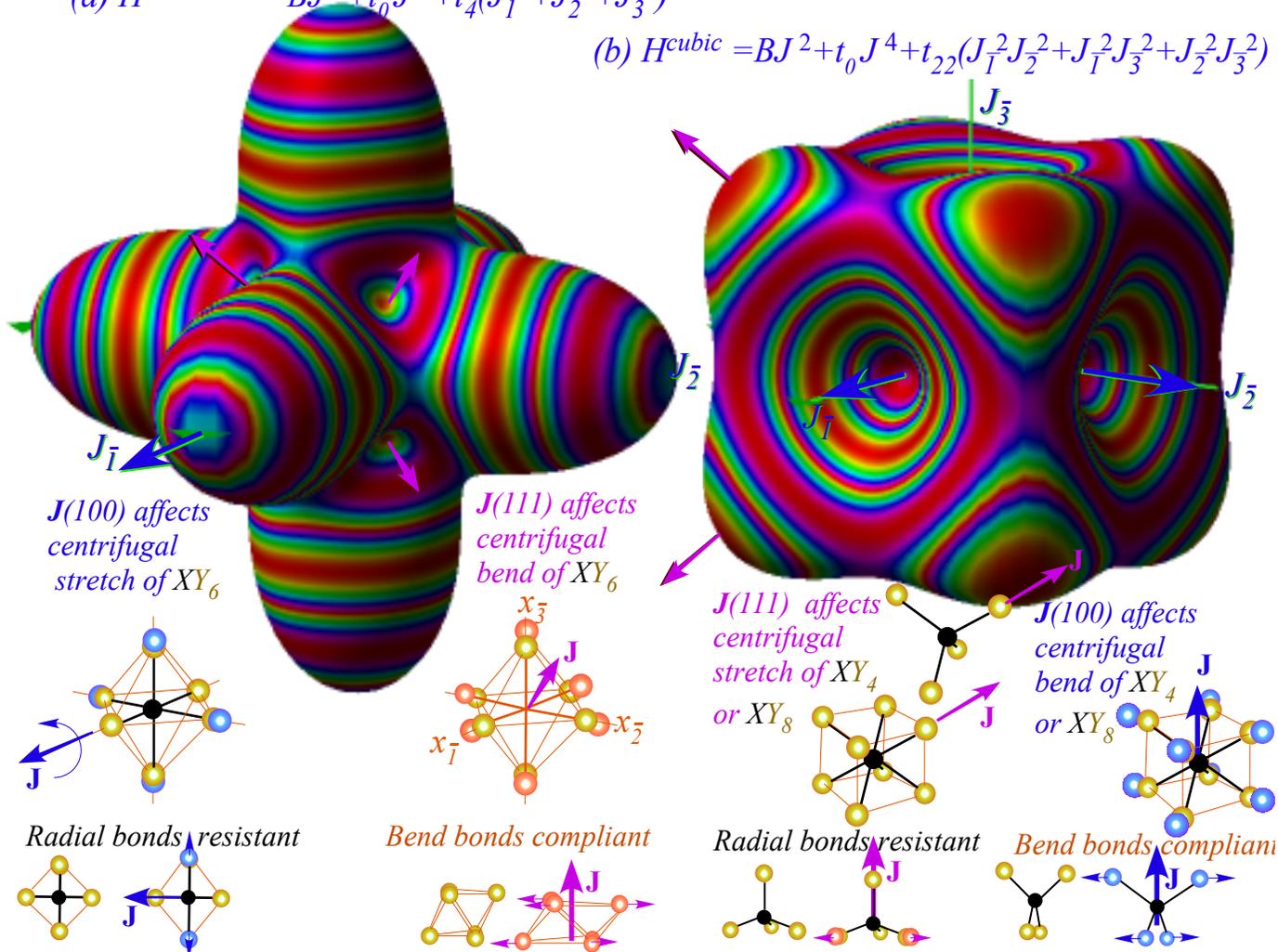


Fig. 30.3.2 Centrifugal 4<sup>th</sup>-degree sphere-top RES. (a) octahedral (*SF*<sub>6</sub>) (b) cubic (*C*<sub>8</sub>*H*<sub>8</sub>) tetrahedral (*CF*<sub>4</sub>)

### 3. Elementary derivation of *SF*<sub>6</sub> distortion parameters.

Hecht model 4<sup>th</sup>-rank distortion operator for the *SF*<sub>6</sub> molecule are discussed in Sec. 25.4 (Recall (25.4.18).) and above. In Hecht's notation the operator and its parameters are written as follows.

$$H = 10t_{044} \left( J_x^4 + J_y^4 + J_z^4 - \frac{3}{5} J^4 \right) + t_{040} J^4 \tag{30.3.21}$$

We now derive the parameters *t*<sub>040</sub> and *t*<sub>044</sub> in terms of *SF*<sub>6</sub> vibrational mode frequencies.

The distortion Hamiltonian (30.3.18) depends on a sum over genuine modes of the squares  $\delta q_\mu^2$  of distortions  $\delta q_\mu$  as given by (30.3.17). The key quantity in the distortion expression is the derivative with respect to *q*<sub>μ</sub> of the inertial tensor *I*<sub>ij</sub> or its inverse μ<sub>ij</sub>. Mode tensor derivatives  $\frac{\partial \mu}{\partial q}$  are evaluated at the equilibrium positions (*q*<sub>μ</sub>=0) for the molecule and therefore must be invariant to its molecular symmetry group that is octahedral *O*<sub>h</sub> for *SF*<sub>6</sub>. Only modes *q*<sup>*A*<sub>g</sub></sup>, *q*<sup>*E*<sub>g</sub></sup>, *q*<sup>*E*<sub>g</sub></sup>, *q*<sup>*T*<sub>2g</sub></sup>, *q*<sup>*T*<sub>2g</sub></sup>, and *q*<sup>*T*<sub>2g</sub></sup> that transform like components of an irreducible symmetric 2<sup>nd</sup>-rank spatial tensor μ<sub>ij</sub> or *I*<sub>ij</sub> may thereby give non-zero  $\frac{\partial \mu}{\partial q}$ .

Symmetry selection of non-zero  $\frac{\partial\mu}{\partial q}$  components is the same as selection for non-zero derivatives  $\frac{\partial\alpha}{\partial q}$  of Raman polarizability tensors, only Raman-active modes affect inertia to 1<sup>st</sup> order. Each component of an allowed  $A_{1g}$ ,  $E_g$ , and  $T_{2g}$  mode shares its coefficient  $A$ ,  $E$ , or  $T$  with others of its kind, as follows.

$$\begin{aligned} \frac{\partial\mu}{\partial q^A} &= \begin{vmatrix} -A/\sqrt{3} & 0 & 0 \\ 0 & -A\sqrt{3} & 0 \\ 0 & 0 & -A/\sqrt{3} \end{vmatrix}, \quad \frac{\partial\mu}{\partial q_1^E} = \begin{vmatrix} -E/\sqrt{6} & 0 & 0 \\ 0 & -E\sqrt{6} & 0 \\ 0 & 0 & 2E/\sqrt{6} \end{vmatrix}, \quad \frac{\partial\mu}{\partial q_1^T} = \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & T/\sqrt{2} \\ 0 & T/\sqrt{2} & 0 \end{vmatrix} \\ \frac{\partial\mu}{\partial q_2^E} &= \begin{vmatrix} E/\sqrt{2} & 0 & 0 \\ 0 & -E\sqrt{2} & 0 \\ 0 & 0 & 0 \end{vmatrix}, \quad \frac{\partial\mu}{\partial q_2^T} = \begin{vmatrix} 0 & 0 & T/\sqrt{2} \\ 0 & 0 & 0 \\ T/\sqrt{2} & 0 & 0 \end{vmatrix} \\ \frac{\partial\mu}{\partial q_3^T} &= \begin{vmatrix} 0 & T/\sqrt{2} & 0 \\ T/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \end{aligned} \quad (30.3.22)$$

Coefficients  $A$ ,  $E$ , and  $T$  are to be evaluated by considering the effect of the  $A_{1g}$ -mode component, one  $E_g$ -mode component (say,  $q_1^{E_g}$ ), and one  $T_{2g}$ -mode component (say,  $q_3^{T_{2g}}$ ) on inertia tensor  $\mu$ .

One must take care to use the mass normalized mode coordinates for the potential form  $\frac{1}{2}\omega_\mu^2 q_\mu^2$  in (30.3.16). The units of  $q$  in (30.3.1) are  $m \cdot \sqrt{kg}$ . The radial coordinate of the F-atoms with mass  $m$  for the  $q^{A_g}$  mode in Fig. A.2 is  $a + q^A / \sqrt{6m}$ . (Here  $a$ ) is equilibrium radius.) The  $q_1^{E_g}$  mode has  $a + 2q_1^{E_g} / \sqrt{12m}$  for polar atoms and  $a - q_1^{E_g} / \sqrt{12m}$  for equatorial atoms. The tangential displacements of  $T_{2g}$  modes are  $q_3^{T_{2g}} / \sqrt{4m}$ . The inertia tensor derivative for each mode then follows.

$$\frac{\partial I_{11}}{\partial q^A} = \frac{8am}{\sqrt{6m}}, \quad \frac{\partial I_{11}}{\partial q_1^E} = \frac{4am}{\sqrt{12m}}, \quad \frac{\partial I_{12}}{\partial q_3^T} = -\frac{4am}{\sqrt{4m}}. \quad (30.3.23)$$

Inertia is  $I_{ij} = \delta_{ij} 4a^2 m$ . The relation  $\mu \cdot \mathbf{I} = \mathbf{1}$  gives the  $\mu$ -derivatives in (30.3.17) by  $\frac{\partial}{\partial q} (\mu \cdot \mathbf{I}) = \mathbf{0} = \frac{\partial\mu}{\partial q} \cdot \mathbf{I} + \mu \cdot \frac{\partial\mathbf{I}}{\partial q}$ .

$$\frac{\partial\mu_{11}}{\partial q^A} = \frac{-1}{2a^3\sqrt{6m^3}}, \quad \frac{\partial\mu_{11}}{\partial q_1^E} = \frac{-1}{8a^3\sqrt{3m^3}}, \quad \frac{\partial\mu_{12}}{\partial q_3^T} = \frac{1}{8a^3\sqrt{m^3}}. \quad (30.3.24)$$

The parameters  $A$ ,  $E$ , and  $T$  in (30.3.22) are then given.

$$A = \left[ 2a^3\sqrt{2m^3} \right]^{-1}, \quad E = \left[ 4a^3\sqrt{2m^3} \right]^{-1}, \quad T = \left[ 4a^3\sqrt{2m^3} \right]^{-1}. \quad (30.3.25)$$

Centrifugal distortion due to angular momentum ( $J_x J_y J_z$ ) is given in terms of  $A$ ,  $E$ , and  $T$  by (30.3.18).

$$\begin{aligned} \delta q^A &= (A / 2\omega_A^2 \sqrt{3}) (J_x^2 + J_y^2 + J_z^2) & \delta q_1^T &= (T / \omega_1^T \sqrt{2}) (J_y J_z) \\ \delta q_1^E &= (E / 2\omega_E^2 \sqrt{6}) (J_x^2 + J_y^2 - 2J_z^2) & \delta q_2^T &= (T / \omega_T^2 \sqrt{2}) (J_x J_z) \\ \delta q_2^E &= (E / 2\omega_E^2 \sqrt{2}) (J_x^2 - J_y^2) & \delta q_3^T &= (T / \omega_T^2 \sqrt{2}) (J_x J_y) \end{aligned} \quad (30.3.26)$$

Combining these yields the total distortion energy from (30.3.16b).

$$H = H_o - \left( \frac{E^2}{8\omega_E^2} - \frac{T^2}{8\omega_T^2} \right) [J_x^4 + J_y^4 + J_z^4] + \left( -\frac{A^2}{24\omega_A^2} + \frac{E^2}{24\omega_E^2} - \frac{T^2}{8\omega_T^2} \right) J^4 \quad (30.3.27)$$

The anisotropic term involves  $E_g$  and  $T_{2g}$  modes only. Combining (30.3.17) and (30.3.19) gives

$${}^{10}t_{044} = \frac{T^2}{8\omega_T^2} - \frac{E^2}{8\omega_E^2} = \frac{1}{256m^3 a^6} \left( \frac{1}{\omega_T^2} - \frac{1}{\omega_E^2} \right) = \frac{1}{4I^3} \left( \frac{1}{\omega_T^2} - \frac{1}{\omega_E^2} \right) \quad (30.3.28)$$

This should be compared to the measured SF<sub>6</sub> rotational constant ( $0.091083 \text{ cm}^{-1}$ ) in (*mks*) energy units.

$$B = \frac{\hbar^2}{2I} = \frac{\hbar^2}{8ma^2} = (0.091083 \text{ cm}^{-1}) \hbar(J \cdot \text{sec}) c \frac{m}{100\text{sec}} = 1.81 \cdot 10^{-24} \text{ Joule} \quad (30.3.29)$$

The radius of SF<sub>6</sub> deduced from this measurement is approximately  $a = 1.58 \times 10^{-10} \text{ m}$ . (Fluorine atomic mass is  $m = 19(1.6 \times 10^{-27} \text{ kg})$ ) The distortion constant has an  $\hbar^4$  scale factor to match  $J^4$ .

$${}^{10}t_{044} = \frac{8\hbar^4}{4(2I)^3} \left( \frac{\hbar^2}{\hbar^2 \omega_T^2} - \frac{\hbar^2}{\hbar^2 \omega_E^2} \right) = 2B^3 \left( \frac{1}{\epsilon_T^2} - \frac{1}{\epsilon_E^2} \right) \quad (30.3.30a)$$

This formula was given first by Berger.

The wavenumber or energy values for the  $E_g$  and  $T_{2g}$  fundamentals, as given in Appendix 30.B, are ( $E_g$ :  $644 \text{ cm}^{-1}$  or  $1.28 \cdot 10^{-20} \text{ J}$ ;  $T_{2g}$ :  $524 \text{ cm}^{-1}$  or  $1.04 \cdot 10^{-20} \text{ J}$ ) and give the anisotropic centrifugal constant.

$$t_{044} = \frac{B^3}{5} \left( \frac{1}{\epsilon_T^2} - \frac{1}{\epsilon_E^2} \right) = 3.74 \cdot 10^{-33} \text{ Joule} = 5.65 \text{ Hz} \quad (30.3.30b)$$

The  $t_{044}$  values deduced from experiment are  $5.7 \pm 0.7 \text{ Hz}$  by Borde and  $5.44 \pm 0.5 \text{ Hz}$  by Patterson and Herlemont, *et al*. The tiny value of about  $56 \text{ Hz}$  for  ${}^{10}t_{044}$  is multiplied by  $J^4$ . Hence, for  $J=100$  this leads to tensor splitting on the order of half a giga-Hertz. We leave as an exercise the calculation of the corresponding centrifugal atomic distortions from (30.3.26).

Spherical tops require dipole  $T_{1u}$  vibrational excitations to get 1<sup>st</sup> order optical transitions, and these  $\nu_3$  and  $\nu_4$  modes around  $615 \text{ cm}^{-1}$  and  $950 \text{ cm}^{-1}$  give much greater centrifugal and Coriolis splitting parametrized by larger and more numerous constants  $B\zeta$ ,  $t_{224}$ , and so forth that fit the spectra.

#### 4. Elementary derivation of SF<sub>6</sub> Coriolis parameters.

Molecular total angular momentum  $J=R+\ell$  and its  $z$ -components  $J_z=R_z+\ell_z$  has integral quantum values  $m\hbar$  but individual rotor  $R_z$  or vibronic  $\ell_z$  may have continuous expectation values  $m\zeta\hbar$  depending on Coriolis coefficients  $\zeta$  that, in turn, vary with the summed areas of classical oscillation paths. Only vector or  $T_{1\{x,y,z\}}$  symmetry modes  $\nu_3$  and  $\nu_4$  of SF<sub>6</sub> can contribute 1<sup>st</sup> order vibration angular momentum.

Here we consider Coriolis effects due to vibration angular momentum of  $\nu_3$  and  $\nu_4$  modes of SF<sub>6</sub> derived in Appendix 30.B. Angular momentum of a Bohr circular orbit can only have integral quanta  $\pm m\hbar$  while a 2D or 3D vibration may have a variety of elliptic polarized orbits noted in Ch. 10. These take various shapes ranging from C-type (circular polarized) oscillation with integral quanta  $\pm m\hbar$ , to A or B-type (linear polarized) oscillation with no angular momentum at all.

It is convenient to use normalized classical mode coordinates  $q^b$ . Setting one to unity ( $q^a = I$ ) and the others to zero gives atomic displacement  $\mathbf{d}^a(\nu) = (d_x^a, d_y^a, d_z^a)$  of nucleus- $\nu$  by (30.3.6).

$$d_j^a(\nu) = B_{j(\nu),a}^{-1} = \sqrt{m_\nu} [a, j(\nu)]$$

A Coriolis coefficient  $\xi_{ab}^i$  from (30.1.19) or  $\zeta_{ab}^i$  from (30.2.5) depends on a pair of modes  $q^a$  and  $q^b$ .

$$\begin{aligned} \xi_{xy}^z &= -\xi_{yx}^z = m_\nu \varepsilon_{znk} d_n^a(\nu) d_k^b(\nu) = m_\nu | \mathbf{d}^x(\nu) \times \mathbf{d}^y(\nu) |_z \\ &= \varepsilon_{znk} [a, n(\nu)] [b, k(\nu)] = \zeta_{xy}^z \end{aligned}$$

For normalized modes, the  $\xi$  or  $\zeta$  coefficients are equal to the sum over nuclear ( $\nu$ ) elliptic path momentum due to  $z$ -rotationally polarized  $z$ -projected vector mode combinations ( $x+iy$ ). Mass normalized coordinates in (30.3.4) are subject to the normalization relations.

$$\sum_{\nu} \sum_{j=1}^3 m_\nu [d_j^a(\nu)]^2 = 1$$

## Appendix 30.A Symmetry defined vibrational normal coordinates

### A.1 C<sub>3v</sub> defined coordinates of Y<sub>3</sub> and XY<sub>3</sub> molecules

The  $D_{jk}^\alpha$ -matrices and  $\mathbf{P}_{jk}^\alpha$ -projectors of trigonal symmetry C<sub>3v</sub> are given in Ch. 15 of Unit 5 and applied to molecular orbitals of a Y<sub>3</sub> structure. The same projections help to analyze of molecular vibrations.

Two sets of  $D_{jk}^E$ -matrices are given. One set (15.1.8) has diagonal 120° rotations C<sub>3</sub>(**r**,**r**<sup>2</sup>).

$$\begin{array}{c}
 \mathbf{g} = \\
 D^{A_1}(\mathbf{g}) = \\
 D^{A_2}(\mathbf{g}) = \\
 D_{e_3 d_3}^{E_1}(\mathbf{g}) =
 \end{array}
 \begin{array}{c}
 \begin{array}{c}
 \mathbf{1} \quad \mathbf{r} \quad \mathbf{r}^2 \quad \mathbf{i}_1 \quad \mathbf{i}_2 \quad \mathbf{i}_3 \\
 \hline
 \begin{array}{cccccc}
 1 & 1 & 1 & 1 & 1 & 1 \\
 1 & 1 & 1 & -1 & -1 & -1 \\
 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} \varepsilon_- & 0 \\ 0 & \varepsilon_+ \end{pmatrix} & \begin{pmatrix} \varepsilon_+ & 0 \\ 0 & \varepsilon_- \end{pmatrix} & \begin{pmatrix} 0 & \varepsilon_+ \\ \varepsilon_- & 0 \end{pmatrix} & \begin{pmatrix} 0 & \varepsilon_- \\ \varepsilon_+ & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}
 \end{array}
 \end{array}
 \end{array}
 \quad \text{where: } \varepsilon_{\pm} = e^{\pm i \frac{2\pi}{3}} \quad (15.1.8)_{\text{repeat}}$$

Another set (15.1.12) has diagonal x-plane reflection C<sub>2</sub>(**i**<sub>3</sub>). (They share the same 1-by-1  $D^{A_1}$  and  $D^{A_2}$ .)

$$\begin{array}{c}
 \mathbf{g} = \\
 D^{A_1}(\mathbf{g}) = \\
 D^{A_2}(\mathbf{g}) = \\
 D_{x_2 y_2}^{E_1}(\mathbf{g}) =
 \end{array}
 \begin{array}{c}
 \begin{array}{c}
 \mathbf{1} \quad \mathbf{r} \quad \mathbf{r}^2 \quad \mathbf{i}_1 \quad \mathbf{i}_2 \quad \mathbf{i}_3 \\
 \hline
 \begin{array}{cccccc}
 1 & 1 & 1 & 1 & 1 & 1 \\
 1 & 1 & 1 & -1 & -1 & -1 \\
 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} & \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} & \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix} & \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix} & \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
 \end{array}
 \end{array}
 \end{array}
 \quad (15.1.12)$$

The standard projection formula:  $\mathbf{P}_{mn}^\mu = (\ell^\mu / \circ G) \sum_g D_{mn}^{\mu*}(g) \mathbf{g}$  repeats the following from (15.1.15).

$$\mathbb{P}^{A_1} = \mathbb{P}^{A_1} \mathbf{1} \mathbb{P}^{A_1} = (\mathbf{1} + \mathbf{r} + \mathbf{r}^2 + \mathbf{i}_1 + \mathbf{i}_2 + \mathbf{i}_3) / 6 \quad (15.2.15a)_{\text{repeat}}$$

$$\mathbb{P}^{A_2} = \mathbb{P}^{A_2} \mathbf{1} \mathbb{P}^{A_2} = (\mathbf{1} + \mathbf{r} + \mathbf{r}^2 - \mathbf{i}_1 - \mathbf{i}_2 - \mathbf{i}_3) / 6 \quad (15.2.15b)_{\text{repeat}}$$

$$\mathbf{P}_{xx}^E = \mathbf{P}_{xx}^E \mathbf{1} \mathbf{P}_{xx}^E = (2\mathbf{1} - \mathbf{r} - \mathbf{r}^2 - \mathbf{i}_1 - \mathbf{i}_2 + 2\mathbf{i}_3) / 6 \quad (15.2.15c)_{\text{repeat}}$$

$$\mathbf{P}_{yy}^E = \mathbf{P}_{yy}^E \mathbf{1} \mathbf{P}_{yy}^E = (2\mathbf{1} - \mathbf{r} - \mathbf{r}^2 + \mathbf{i}_1 + \mathbf{i}_2 - 2\mathbf{i}_3) / 6 \quad (15.2.15d)_{\text{repeat}}$$

$$\mathbf{P}_{xy}^E = \mathbf{P}_{xx}^E \mathbf{i}_2 \mathbf{P}_{yy}^E = D_{xy}^E(\mathbf{i}_2) \mathbf{P}_{xy}^E = (0\mathbf{1} - \mathbf{r} + \mathbf{r}^2 - \mathbf{i}_1 + \mathbf{i}_2 - 0\mathbf{i}_3) / 4 \quad (15.2.15e)_{\text{repeat}}$$

$$\mathbf{P}_{yx}^E = \mathbf{P}_{yy}^E \mathbf{i}_2 \mathbf{P}_{xx}^E = D_{yx}^E(\mathbf{i}_2) \mathbf{P}_{yx}^E = (0\mathbf{1} + \mathbf{r} - \mathbf{r}^2 - \mathbf{i}_1 + \mathbf{i}_2 - 0\mathbf{i}_3) / 4 \quad (15.2.15f)_{\text{repeat}}$$

This gives modes for a Y<sub>3</sub> ring of XY<sub>3</sub> in Fig. A.1.1. (The X-atom adds another vector E-doublet.)

$$\begin{array}{l}
 \langle A_1 | = \langle 1 | \mathbf{P}^{A_1} \sqrt{6} = (1 \quad 1 \quad 1 \quad 1 \quad 1 \quad 1) / \sqrt{6} \\
 \langle A_2 | = \langle 1 | \mathbf{P}^{A_2} \sqrt{6} = (1 \quad 1 \quad 1 \quad -1 \quad -1 \quad -1) / \sqrt{6} \\
 \langle E_{xx} | = \langle 1 | \mathbf{P}_{xx}^E \sqrt{3} = (2 \quad -1 \quad -1 \quad -1 \quad -1 \quad 2) / \sqrt{12} \\
 \langle E_{yx} | = \langle 1 | \mathbf{P}_{xy}^E \sqrt{3} = (0 \quad 1 \quad -1 \quad -1 \quad 1 \quad 0) / 2 \\
 \langle E_{xy} | = \langle 1 | \mathbf{P}_{yx}^E \sqrt{3} = (0 \quad -1 \quad 1 \quad -1 \quad 1 \quad 0) / 2 \\
 \langle E_{yy} | = \langle 1 | \mathbf{P}_{yy}^E \sqrt{3} = (2 \quad -1 \quad -1 \quad 1 \quad 1 \quad -2) / \sqrt{12}
 \end{array}
 \quad
 \begin{array}{l}
 | A_1 \rangle = | A_1 \rangle = | E_{xx} \rangle = | E_{yx} \rangle = | E_{xy} \rangle = | E_{yy} \rangle = \\
 \mathbf{P}^{A_1} | 1 \rangle \sqrt{6} \quad \mathbf{P}^{A_2} | 1 \rangle \sqrt{6} \quad \mathbf{P}_{xx}^E | 1 \rangle \sqrt{3} \quad \mathbf{P}_{yx}^E | 1 \rangle \sqrt{3} \quad \mathbf{P}_{xy}^E | 1 \rangle \sqrt{3} \quad \mathbf{P}_{yy}^E | 1 \rangle \sqrt{3} \\
 = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \frac{1}{\sqrt{6}}, = \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \\ -1 \\ -1 \end{pmatrix} \frac{1}{\sqrt{6}}, = \begin{pmatrix} 2 \\ -1 \\ -1 \\ -1 \\ -1 \\ 2 \end{pmatrix} \frac{1}{\sqrt{12}}, = \begin{pmatrix} 0 \\ 1 \\ -1 \\ -1 \\ 1 \\ 0 \end{pmatrix} \frac{1}{2}, = \begin{pmatrix} 0 \\ -1 \\ 1 \\ -1 \\ 1 \\ 0 \end{pmatrix} \frac{1}{2}, = \begin{pmatrix} 2 \\ -1 \\ -1 \\ 1 \\ 1 \\ -2 \end{pmatrix} \frac{1}{\sqrt{12}}.
 \end{array}$$

Model  $\mathbf{P}_{jk}^\alpha$ -symmetry configurations in Fig. A.1.1 have **LAB**-C<sub>2</sub> symmetry-( $j=x$  or  $y$ ) that is even ( $x$ ) or odd ( $y$ ) to **LAB** x-plane  $\mathbf{i}_3$ -reflection, and **BOD**-C<sub>2</sub> symmetry-( $k=x$  or  $y$ ) to local  $\bar{\mathbf{i}}_1$ ,  $\bar{\mathbf{i}}_2$ , or  $\bar{\mathbf{i}}_3$  **BOD** planes.

There are  $4=2^2$  projectors for two-dimensional E-symmetry and one each for A<sub>1</sub> and A<sub>2</sub> symmetry, making six  $\mathbf{P}_{jk}^\alpha$  in all, and that is the total number of symmetry operators needed here. (Order= $\circ C_{3v}=6$ .)

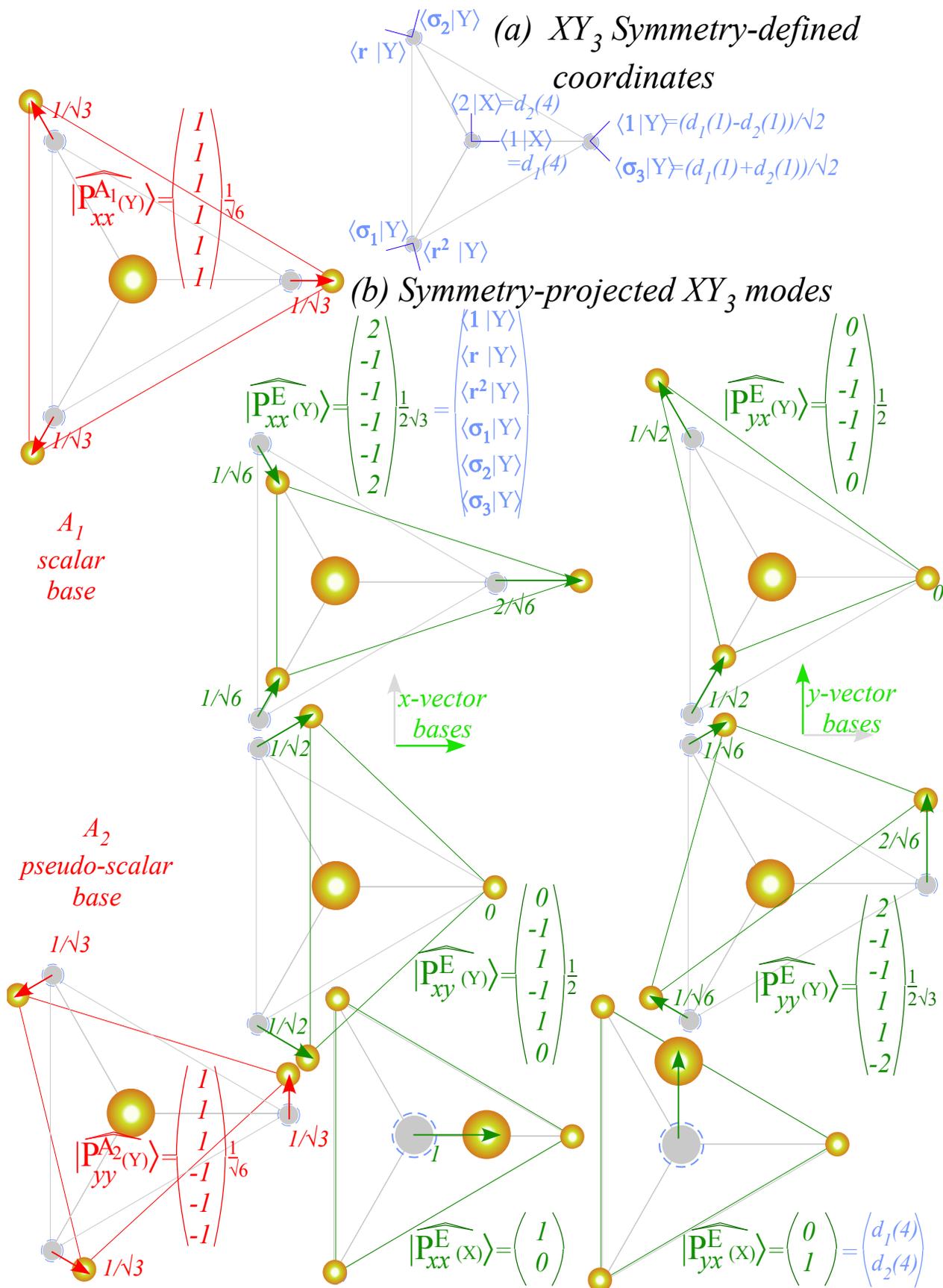


Fig. 30.A.1. Vibration coordinates for  $C_{3v}$  symmetric  $XY_3$  molecular model.

### Vibration matrix and normal mode eigen-solutions

Spring-mass models of symmetric molecular vibration involves a *Hooke matrix*  $K$  that is reduced in stages. From the following 1<sup>st</sup> stage primitive energy form, we seek its analytic eigen-solution using symmetry.

$$E = \frac{1}{2} m \lambda \dot{x}_i(\lambda) \dot{x}_i(\lambda) + \frac{1}{2} k_{\mu_j \nu_k} x_j(\mu) x_k(\nu) \quad (\text{A.1.1a})$$

The 1<sup>st</sup> stage  $k_{\mu_j \nu_k}$  for a coordinate pair  $x_j(\mu)$  and  $x_k(\nu)$  of mass  $m_u$  and  $m_v$  is a sum of each spring constant  $k_{\mu\nu}$  hooking  $m_u$  to  $m_v$  times direction cosine  $\hat{\mathbf{k}}_{\mu\nu} \cdot \hat{\mathbf{x}}_j(\mu)$  and  $\hat{\mathbf{k}}_{\mu\nu} \cdot \hat{\mathbf{x}}_k(\nu)$  of unit  $\hat{\mathbf{k}}_{\mu\nu}$  with  $\hat{\mathbf{x}}_j(\mu)$  and  $\hat{\mathbf{x}}_k(\nu)$ .

$$\begin{aligned} k_{\mu_j \nu_k} &= -[\hat{\mathbf{k}}_{\mu\nu} \cdot \hat{\mathbf{x}}_j(\mu)] k_{\mu\nu} [\hat{\mathbf{k}}_{\mu\nu} \cdot \hat{\mathbf{x}}_k(\nu)] \\ &= -k_{\mu\nu} \cos \angle_{\mu_j}^k \cos \angle_{\nu_k}^k = k_{\nu_k \mu_j} \end{aligned} \quad (\text{A.1.1b})$$

$$\begin{aligned} k_{\mu_j \mu_k} &= -\sum_{\nu} [\hat{\mathbf{k}}_{\mu\nu} \cdot \hat{\mathbf{x}}_j(\mu)] k_{\mu\nu} [\hat{\mathbf{k}}_{\mu\nu} \cdot \hat{\mathbf{x}}_k(\nu)] \\ &= -\sum_{\nu} k_{\mu\nu} \cos \angle_{\mu_j}^k \cos \angle_{\mu_k}^k = k_{\mu_k \mu_j} \end{aligned} \quad (\text{A.1.1c})$$

(A.1.1b) assumes *one* spring  $k_{\mu\nu}$  hooks  $m_u$  to  $m_v$ . Self-energy  $k_{\mu_j \mu_k}$  for  $m_u$  sums over *all*  $k_{\mu\nu}$  hooked to  $m_u$ .

The 2<sup>nd</sup> stage energy form  $K_{mn}$  uses mass-orthonormalized  $\delta$ -displacements  $\delta_\ell = \delta_{j^\mu} = x_j(\mu) m_\mu^{1/2}$ .

$$E = \frac{1}{2} \dot{\delta}_\ell \dot{\delta}_\ell + K_{mn} \delta_m \delta_n \quad \text{where: } \delta_\ell = \delta_{j^\mu} = x_j(\mu) m_\mu^{1/2} \quad (\text{A.1.2a}) \quad K_{mn} = \frac{k_{\mu_j \nu_k}}{m_\mu^{1/2} m_\nu^{1/2}} = K_{nm} \quad (\text{A.1.2b})$$

Next we begin transforming hook matrix  $K_{mn}$  to diagonal form while leaving kinetic form  $\frac{1}{2} \dot{\delta}_\ell \dot{\delta}_\ell$  invariant. For that, each stage needs to have only orthonormal bases and orthogonal or unitary transformation.

The 3<sup>rd</sup> stage uses symmetry-operator-labeling of  $K_{mn}$  bases.  $XY_3$  coordinate bases of Fig. A.1.2 are used for  $K_{mn}$  in (A.1.3). Y-atom bases  $\mathbf{r}^n \left| \begin{smallmatrix} Y_1 \\ x \end{smallmatrix} \right\rangle$  are radial but  $\mathbf{r}^n \left| \begin{smallmatrix} Y_1 \\ y \end{smallmatrix} \right\rangle$  are transverse.  $K_{mn}$  of (A.1.2b) hook up Y-atom bases  $\mathbf{h} \left| \begin{smallmatrix} Y \\ x \end{smallmatrix} \right\rangle$  and  $\mathbf{h} \left| \begin{smallmatrix} Y \\ y \end{smallmatrix} \right\rangle$  to each other and to central X-atom bases  $\left| \begin{smallmatrix} X \\ x \end{smallmatrix} \right\rangle$  and  $\left| \begin{smallmatrix} X \\ y \end{smallmatrix} \right\rangle$  using radial spring constant  $j = k_{XY}$  and peripheral spring constant  $k = k_{YY}$  divided by  $m^{1/2}$  and/or  $M^{1/2}$  according to Fig. A.1.2.

$$\langle A | \mathbf{K} \mathbf{r} | B \rangle = \begin{array}{c|cccc|cc|cc} & \left| \begin{smallmatrix} Y_1 \\ x \end{smallmatrix} \right\rangle & \mathbf{r} \left| \begin{smallmatrix} Y_1 \\ x \end{smallmatrix} \right\rangle & \mathbf{r}^2 \left| \begin{smallmatrix} Y_1 \\ x \end{smallmatrix} \right\rangle & \left| \begin{smallmatrix} Y_1 \\ y \end{smallmatrix} \right\rangle & \mathbf{r} \left| \begin{smallmatrix} Y_1 \\ y \end{smallmatrix} \right\rangle & \mathbf{r}^2 \left| \begin{smallmatrix} Y_1 \\ y \end{smallmatrix} \right\rangle & \left| \begin{smallmatrix} X \\ x \end{smallmatrix} \right\rangle & \left| \begin{smallmatrix} X \\ y \end{smallmatrix} \right\rangle \\ \hline \left\langle \begin{smallmatrix} Y_1 \\ x \end{smallmatrix} \right| & \frac{j}{m} + \frac{3}{2} \frac{k}{m} & \frac{3}{4} \frac{k}{m} & \frac{3}{4} \frac{k}{m} & 0 & \frac{\sqrt{3}}{4} \frac{k}{m} & -\frac{\sqrt{3}}{4} \frac{k}{m} & -\frac{j}{\sqrt{mM}} & 0 \\ \hline \vdots & & & & & & & & \\ \hline \left\langle \begin{smallmatrix} Y_1 \\ x \end{smallmatrix} \right| & 0 & -\frac{\sqrt{3}}{4} \frac{k}{m} & \frac{\sqrt{3}}{4} \frac{k}{m} & \frac{1}{2} \frac{k}{m} & -\frac{1}{4} \frac{k}{m} & -\frac{1}{4} \frac{k}{m} & 0 & 0 \\ \hline \left\langle \begin{smallmatrix} X \\ x \end{smallmatrix} \right| & -\frac{j}{\sqrt{mM}} & -\frac{1}{2} \frac{j}{\sqrt{mM}} & -\frac{1}{2} \frac{j}{\sqrt{mM}} & 0 & 0 & 0 & \frac{3}{2} \frac{j}{M} & 0 \end{array} \quad (\text{A.1.3})$$

The 4<sup>th</sup> stage uses symmetry  $\mathbf{P}_{jx}^\alpha$  projection to reduce  $K_{A,rB} = \langle A | \mathbf{K} \mathbf{r} | B \rangle$  in (A.1.3) above to block diagonal projected forms  $K_{P_k A, P_l B} = \langle \mathbf{P}_{jk}^\alpha A | \mathbf{K} | \mathbf{P}_{jl}^\alpha B \rangle$  that are derived below in (A.1.4) thru (A.1.10).

Only select rows of matrix  $K_{A,rB} = \langle A | \mathbf{K} \mathbf{r} | B \rangle$  are given in (A.1.3). If  $K$  has  $\mathbf{r}$ -symmetry then a matrix row for a base  $\mathbf{r} | B \rangle$  that is a rotation  $\mathbf{r}$  of base  $| B \rangle$  is redundant. Also, this choice of basis separates **BOD**-symmetric- ( $k=x$ )-radial  $\left| \begin{smallmatrix} Y \\ x \end{smallmatrix} \right\rangle$  from **BOD-antisymmetric**- ( $k=y$ )-transverse  $\left| \begin{smallmatrix} Y \\ y \end{smallmatrix} \right\rangle$  so that only  $\mathbf{P}_{jx}^\alpha$  have non-zero projection on  $\left| \begin{smallmatrix} Y \\ x \end{smallmatrix} \right\rangle$  or

$\begin{vmatrix} X \\ x \end{vmatrix}$  and only  $\mathbf{P}_{jy}^\alpha$  have non-zero projection on  $\begin{vmatrix} Y \\ y \end{vmatrix}$  or  $\begin{vmatrix} X \\ x \end{vmatrix}$ . BOD label- $k$  of  $\mathbf{P}_{jk}^\alpha$  has to match the primitive state  $\begin{vmatrix} A \\ k \end{vmatrix}$  it projects to get a nonzero projection as shown below.

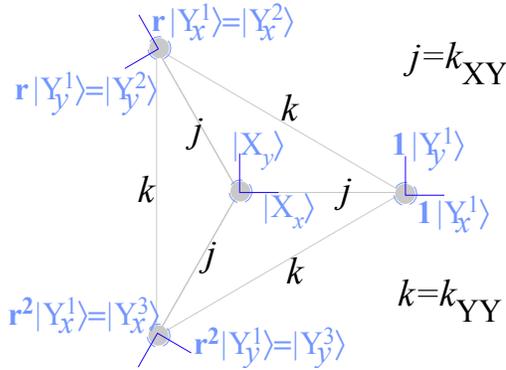


Fig. 30A.1.2 Symmetry labeled radial and angular base vectors

A  $\mathbf{K}$ -matrix  $\langle \begin{smallmatrix} \alpha X \\ jk \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} \beta Y \\ lm \end{smallmatrix} \rangle$  has  $\mathbf{P}_{jk}^\alpha$ -projected bra  $\langle \begin{smallmatrix} \alpha X \\ jk \end{smallmatrix} |$  and  $\mathbf{P}_{lm}^\beta$ -projected ket  $| \begin{smallmatrix} \beta Y \\ lm \end{smallmatrix} \rangle$  with norms  $N_k^X$  and  $N_m^Y$ .

$$\langle \begin{smallmatrix} \alpha X \\ jk \end{smallmatrix} | = N_k^X \langle X | \mathbf{P}_{jk}^{\alpha \dagger} = N_k^X \langle X | \mathbf{P}_{kj}^\alpha \quad (\text{A.1.4a}) \quad | \begin{smallmatrix} \beta Y \\ lm \end{smallmatrix} \rangle = \mathbf{P}_{lm}^\beta | Y \rangle N_m^Y = (\ell^\beta / \circ G) \Sigma_g D_{lm}^\beta(g) \mathbf{g} | Y \rangle N_m^Y \quad (\text{A.1.4b})$$

Scalar  $A_1$  “breathing” ket and pseudo-scalar  $A_2$  “rotation” ket are shown in Fig. A.1.1 (left).

$$\mathbf{P}_{xx}^{A_1} \begin{vmatrix} Y_1 \\ x \end{vmatrix} \sqrt{3} = \left( \begin{vmatrix} Y_1 \\ x \end{vmatrix} + \mathbf{r}^1 \begin{vmatrix} Y_1 \\ x \end{vmatrix} + \mathbf{r}^2 \begin{vmatrix} Y_1 \\ x \end{vmatrix} \right) / \sqrt{3} \quad (\text{A.1.5a}) \quad \mathbf{P}_{yy}^{A_2} \begin{vmatrix} Y_1 \\ y \end{vmatrix} \sqrt{3} = \left( \begin{vmatrix} Y_1 \\ y \end{vmatrix} + \mathbf{r}^1 \begin{vmatrix} Y_1 \\ y \end{vmatrix} + \mathbf{r}^2 \begin{vmatrix} Y_1 \\ y \end{vmatrix} \right) / \sqrt{3} \quad (\text{A.1.5b})$$

Then come  $2^2=4$  vector  $E$ -kets involving peripheral Y-atoms of  $\text{XY}_3$  shown in Fig. A.1.1 (center).

$$\mathbf{P}_{xx}^E \begin{vmatrix} Y_1 \\ x \end{vmatrix} \sqrt{\frac{3}{2}} = \left( 2 \begin{vmatrix} Y_1 \\ x \end{vmatrix} - \mathbf{r}^1 \begin{vmatrix} Y_1 \\ x \end{vmatrix} - \mathbf{r}^2 \begin{vmatrix} Y_1 \\ x \end{vmatrix} \right) \sqrt{\frac{1}{6}} \quad (\text{A.1.6a}) \quad \mathbf{P}_{xy}^E \begin{vmatrix} Y_1 \\ y \end{vmatrix} \sqrt{\frac{3}{2}} = \left( -\mathbf{r}^1 \begin{vmatrix} Y_1 \\ y \end{vmatrix} + \mathbf{r}^2 \begin{vmatrix} Y_1 \\ y \end{vmatrix} \right) \sqrt{\frac{1}{2}} \quad (\text{A.1.6b})$$

$$\mathbf{P}_{yx}^E \begin{vmatrix} Y_1 \\ x \end{vmatrix} \sqrt{\frac{3}{2}} = \left( \mathbf{r}^1 \begin{vmatrix} Y_1 \\ x \end{vmatrix} - \mathbf{r}^2 \begin{vmatrix} Y_1 \\ x \end{vmatrix} \right) \sqrt{\frac{1}{2}} \quad (\text{A.1.6c}) \quad \mathbf{P}_{yy}^E \begin{vmatrix} Y_1 \\ y \end{vmatrix} \sqrt{\frac{3}{2}} = \left( 2 \begin{vmatrix} Y_1 \\ y \end{vmatrix} - \mathbf{r}^1 \begin{vmatrix} Y_1 \\ y \end{vmatrix} - \mathbf{r}^2 \begin{vmatrix} Y_1 \\ y \end{vmatrix} \right) \sqrt{\frac{1}{6}} \quad (\text{A.1.6d})$$

Included also is another pair of vector  $E$ -kets for the central X-atom shown in Fig. A.1.1 (bottom).

$$\mathbf{P}_{xx}^E \begin{vmatrix} X \\ x \end{vmatrix} = \begin{vmatrix} X \\ x \end{vmatrix} \quad (\text{A.1.6e}) \quad \mathbf{P}_{yx}^E \begin{vmatrix} X \\ x \end{vmatrix} = \begin{vmatrix} X \\ y \end{vmatrix} \quad (\text{A.1.6f})$$

Symmetry ( $\mathbf{K}\mathbf{g}=\mathbf{g}\mathbf{K}$ ) and  $\mathbf{P}$ -rules ( $\mathbf{P}_{kj}^\alpha \mathbf{P}_{lm}^\beta = \delta^{\alpha\beta} \delta_{j\ell} \mathbf{P}_{km}^\alpha$ ) give  $\langle \begin{smallmatrix} \alpha X \\ jk \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} \beta Y \\ lm \end{smallmatrix} \rangle$  in terms of  $\langle X | \mathbf{K}\mathbf{g} | Y \rangle$  in (A.1.3).

$$\begin{aligned} \langle \begin{smallmatrix} \alpha X \\ jk \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} \beta Y \\ lm \end{smallmatrix} \rangle &= N_k^X \langle X | \mathbf{P}_{kj}^\alpha \mathbf{K} \mathbf{P}_{lm}^\beta | Y \rangle N_m^Y = N_k^X \langle X | \mathbf{K} \mathbf{P}_{kj}^\alpha \mathbf{P}_{lm}^\beta | Y \rangle N_m^Y = N_k^X N_m^Y \delta^{\alpha\beta} \delta_{j\ell} \langle X | \mathbf{K} \mathbf{P}_{km}^\alpha | Y \rangle \\ &= N_k^X N_m^Y \delta^{\alpha\beta} \delta_{j\ell} (\ell^\alpha / \circ G) \Sigma_g D_{km}^{\alpha*}(g) \langle X | \mathbf{K}\mathbf{g} | Y \rangle \end{aligned} \quad (\text{A.1.7})$$

Mismatch of  $C_{3v}$  symmetry ( $\alpha \neq \beta$ ) or **LAB** index ( $j \neq l$ ) blocks off a  $K$  matrix (A.1.7) into two  $l$ -by- $l$  blocks for symmetry irrep species  $A_1$  and  $A_2$  and a pair of  $3$ -by- $3$  blocks for vector species  $E$ .

$$K = \begin{array}{c|ccc|ccc} \langle \begin{smallmatrix} A_1 Y \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} A_1 Y \\ \text{xx} \end{smallmatrix} \rangle & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \langle \begin{smallmatrix} A_2 Y \\ \text{yy} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} A_2 Y \\ \text{yy} \end{smallmatrix} \rangle & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \langle \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{xy} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} \rangle & \cdot & \cdot & \cdot \\ \cdot & \cdot & \langle \begin{smallmatrix} E Y \\ \text{xy} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{xy} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{xy} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{xy} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} \rangle & \cdot & \cdot & \cdot \\ \cdot & \cdot & \langle \begin{smallmatrix} E X \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E X \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{xy} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E X \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E X \\ \text{xx} \end{smallmatrix} \rangle & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \langle \begin{smallmatrix} E Y \\ \text{yx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{yx} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{yx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{yy} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{yx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E X \\ \text{yx} \end{smallmatrix} \rangle \\ \cdot & \cdot & \cdot & \cdot & \cdot & \langle \begin{smallmatrix} E Y \\ \text{yy} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{yx} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{yy} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{yy} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{yy} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E X \\ \text{yx} \end{smallmatrix} \rangle \\ \cdot & \cdot & \cdot & \cdot & \cdot & \langle \begin{smallmatrix} E X \\ \text{yx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{yx} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E X \\ \text{yx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ \text{yy} \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E X \\ \text{yx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E X \\ \text{yx} \end{smallmatrix} \rangle \end{array} \quad (\text{A.1.8})$$

**BOD**( $k,m$ )-labeled matrix for equal-atom ( $X=Y$ ) is simple since norms  $N_k^X$  cancel group- $g$ -sum terms.

$$\langle \begin{smallmatrix} \alpha Y \\ jk \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} \alpha Y \\ jm \end{smallmatrix} \rangle = \sum_h D_{km}^{\alpha*}(h) \langle \begin{smallmatrix} Y \\ k \end{smallmatrix} | \mathbf{K} \mathbf{h} | \begin{smallmatrix} Y \\ m \end{smallmatrix} \rangle \quad (\text{A.1.9})$$

Also, we sum only a *coset*  $\mathcal{C}_h$  or coordinate-labeling-subset of  $C_{3v}$ . For  $Y$  it is:  $\mathcal{C}_h = \{ \mathbf{h} = \mathbf{1}, \mathbf{r}, \mathbf{r}^2 \}$ .

$$\begin{aligned} \langle \begin{smallmatrix} A_1 Y \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} A_1 Y \\ \text{xx} \end{smallmatrix} \rangle &= D_{xx}^{A_1*}(1) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{1} | \begin{smallmatrix} Y \\ x \end{smallmatrix} \rangle + D_{xx}^{A_1*}(\mathbf{r}) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{r} | \begin{smallmatrix} Y \\ x \end{smallmatrix} \rangle + D_{xx}^{A_1*}(\mathbf{r}^2) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{r}^2 | \begin{smallmatrix} Y \\ x \end{smallmatrix} \rangle \\ &= 1 \cdot \left( \frac{j}{m} + \frac{3}{2} \frac{k}{m} \right) + 1 \cdot \left( \frac{3}{4} \frac{k}{m} \right) + 1 \cdot \left( \frac{3}{4} \frac{k}{m} \right) = \frac{j}{m} + \frac{3k}{m} \end{aligned} \quad (\text{A.1.10a})$$

$$\begin{aligned} \langle \begin{smallmatrix} E Y \\ jx \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ jx \end{smallmatrix} \rangle &= D_{xx}^{E*}(1) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{1} | \begin{smallmatrix} Y \\ x \end{smallmatrix} \rangle + D_{xx}^{E*}(\mathbf{r}) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{r} | \begin{smallmatrix} Y \\ x \end{smallmatrix} \rangle + D_{xx}^{E*}(\mathbf{r}^2) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{r}^2 | \begin{smallmatrix} Y \\ x \end{smallmatrix} \rangle \\ &= 1 \cdot \left( \frac{j}{m} + \frac{3}{2} \frac{k}{m} \right) + \frac{-1}{2} \cdot \left( \frac{3}{4} \frac{k}{m} \right) + \frac{-1}{2} \cdot \left( \frac{3}{4} \frac{k}{m} \right) = \frac{j}{m} + \frac{3}{4} \frac{k}{m} \end{aligned} \quad (\text{A.1.10b})$$

$$\begin{aligned} \langle \begin{smallmatrix} E Y \\ jx \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ jy \end{smallmatrix} \rangle &= D_{xy}^{E*}(1) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{1} | \begin{smallmatrix} Y \\ y \end{smallmatrix} \rangle + D_{xy}^{E*}(\mathbf{r}) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{r} | \begin{smallmatrix} Y \\ y \end{smallmatrix} \rangle + D_{xy}^{E*}(\mathbf{r}^2) \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{r}^2 | \begin{smallmatrix} Y \\ y \end{smallmatrix} \rangle \\ &= 0 \cdot (0) + \frac{-\sqrt{3}}{2} \cdot \left( \frac{\sqrt{3}}{4} \frac{k}{m} \right) + \frac{\sqrt{3}}{2} \cdot \left( -\frac{\sqrt{3}}{4} \frac{k}{m} \right) = -\frac{3}{4} \frac{k}{m} \end{aligned} \quad (\text{A.1.10c})$$

$$\begin{aligned} \langle \begin{smallmatrix} E Y \\ jy \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E Y \\ jy \end{smallmatrix} \rangle &= D_{yy}^{E*}(1) \langle \begin{smallmatrix} Y \\ y \end{smallmatrix} | \mathbf{K} \mathbf{1} | \begin{smallmatrix} Y \\ y \end{smallmatrix} \rangle + D_{yy}^{E*}(\mathbf{r}) \langle \begin{smallmatrix} Y \\ y \end{smallmatrix} | \mathbf{K} \mathbf{r} | \begin{smallmatrix} Y \\ y \end{smallmatrix} \rangle + D_{yy}^{E*}(\mathbf{r}^2) \langle \begin{smallmatrix} Y \\ y \end{smallmatrix} | \mathbf{K} \mathbf{r}^2 | \begin{smallmatrix} Y \\ y \end{smallmatrix} \rangle \\ &= 1 \cdot \left( \frac{1}{2} \frac{k}{m} \right) + \frac{-1}{2} \cdot \left( -\frac{1}{4} \frac{k}{m} \right) + \frac{-1}{2} \cdot \left( -\frac{1}{4} \frac{k}{m} \right) = \frac{3}{4} \frac{k}{m} \end{aligned} \quad (\text{A.1.10d})$$

Central atom  $X$  has ket  $\left| \begin{smallmatrix} X \\ x \end{smallmatrix} \right\rangle$  that is already the irreducible  $E_x$  base  $\left| \begin{smallmatrix} X \\ x \end{smallmatrix} \right\rangle = \mathbf{P}_{xx}^E \left| \begin{smallmatrix} X \\ x \end{smallmatrix} \right\rangle$  in (A.1.6a).

$$\langle \begin{smallmatrix} E X \\ jx \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E X \\ jx \end{smallmatrix} \rangle = \langle \begin{smallmatrix} X \\ x \end{smallmatrix} | \mathbf{K} \mathbf{1} | \begin{smallmatrix} X \\ x \end{smallmatrix} \rangle = \frac{3}{2} \frac{j}{M} \quad (\text{A.1.10e})$$

The remaining two components coupling  $X$  and  $Y$ -atomic coordinates use (A.1.7).

$$\begin{aligned} \langle \begin{smallmatrix} E Y \\ jx \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E X \\ jx \end{smallmatrix} \rangle &= N_x^Y N_x^X \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{1} | \begin{smallmatrix} X \\ x \end{smallmatrix} \rangle & \langle \begin{smallmatrix} E Y \\ \text{xx} \end{smallmatrix} | \mathbf{K} | \begin{smallmatrix} E X \\ \text{xy} \end{smallmatrix} \rangle &= N_x^Y N_y^X \langle \begin{smallmatrix} Y \\ x \end{smallmatrix} | \mathbf{K} \mathbf{1} | \begin{smallmatrix} X \\ y \end{smallmatrix} \rangle \\ &= \sqrt{\frac{3}{2}} \cdot 1 \cdot \left( -\frac{j}{\sqrt{mM}} \right) = -\frac{\sqrt{3}}{\sqrt{2}} \frac{j}{\sqrt{mM}} & & = \sqrt{\frac{3}{2}} \cdot 1 \cdot (0) = 0 \end{aligned} \quad (\text{A.1.10f})$$

These  $C_{3v}$ -projected  $K$  matrix elements are collected in the form of the  $8$ -by- $8$  matrix (A.1.8).

$$\langle \mathbf{P}_{jk}^\alpha A | \mathbf{K} | \mathbf{P}_{j\ell}^\alpha B \rangle = \begin{array}{c|ccc|ccc} \frac{j}{m} + \frac{3k}{m} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \frac{j}{m} + \frac{3k}{4m} & -\frac{3k}{4m} & -\frac{\sqrt{3}}{\sqrt{2}} \frac{j}{\sqrt{mM}} & \cdot & \cdot \\ \cdot & \cdot & -\frac{3k}{4m} & \frac{3k}{4m} & 0 & \cdot & \cdot \\ \cdot & \cdot & -\frac{\sqrt{3}}{\sqrt{2}} \frac{j}{\sqrt{mM}} & 0 & \frac{3}{2} \frac{j}{M} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \frac{j}{m} + \frac{3k}{4m} & -\frac{3k}{4m} & -\frac{\sqrt{3}}{\sqrt{2}} \frac{j}{\sqrt{mM}} \\ \cdot & \cdot & \cdot & \cdot & \cdot & -\frac{3k}{4m} & \frac{3k}{4m} & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & -\frac{\sqrt{3}}{\sqrt{2}} \frac{j}{\sqrt{mM}} & 0 & \frac{3}{2} \frac{j}{M} \end{array} \quad (\text{A.1.10g})$$

Diagonal  $A_1$  and  $A_2$  values are  $(j+3k)/m$  and  $0$ , but  $E$ -type 3-by-3 matrix  $K$  has to be diagonalized. Due to the  $\delta_{j\ell}$  in (A.1.7) the first 3-by-3 matrix for  $(j=\ell=x)$  is identical to the second 3-by-3  $E$ -matrix for  $(j=\ell=y)$ . Thus, all  $E$ -eigenvalues must come in **LAB** 2-fold-degenerate pairs if  $\mathbf{K}$  has  $C_{3v}$  symmetry.

$$\langle K \rangle^{A_1} = \left| \begin{array}{c} |A_1 Y\rangle \\ \frac{j+3k}{m} \end{array} \right|, \quad \langle K \rangle^{A_2} = \left| \begin{array}{c} |A_2 Y\rangle \\ 0 \end{array} \right|, \quad \langle K \rangle^E = \begin{array}{c|cc} |E Y\rangle & |E Y\rangle & |E X\rangle \\ \hline \frac{j}{m} + \frac{3k}{4m} & -\frac{3k}{4m} & -\frac{\sqrt{3}}{\sqrt{2}} \frac{j}{\sqrt{mM}} \\ -\frac{3k}{4m} & \frac{j}{m} + \frac{3k}{4m} & 0 \\ -\frac{\sqrt{3}}{\sqrt{2}} \frac{j}{\sqrt{mM}} & 0 & \frac{3}{2} \frac{j}{M} \end{array} \xrightarrow{j=0} \frac{3k}{4m} \begin{pmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (\text{A.1.10h})$$

$E$ -type eigensolutions for no radial spring ( $j=0$ ) are  $(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}})$  combination of  $Y$ -bases with eigen-value  $3k/2m$

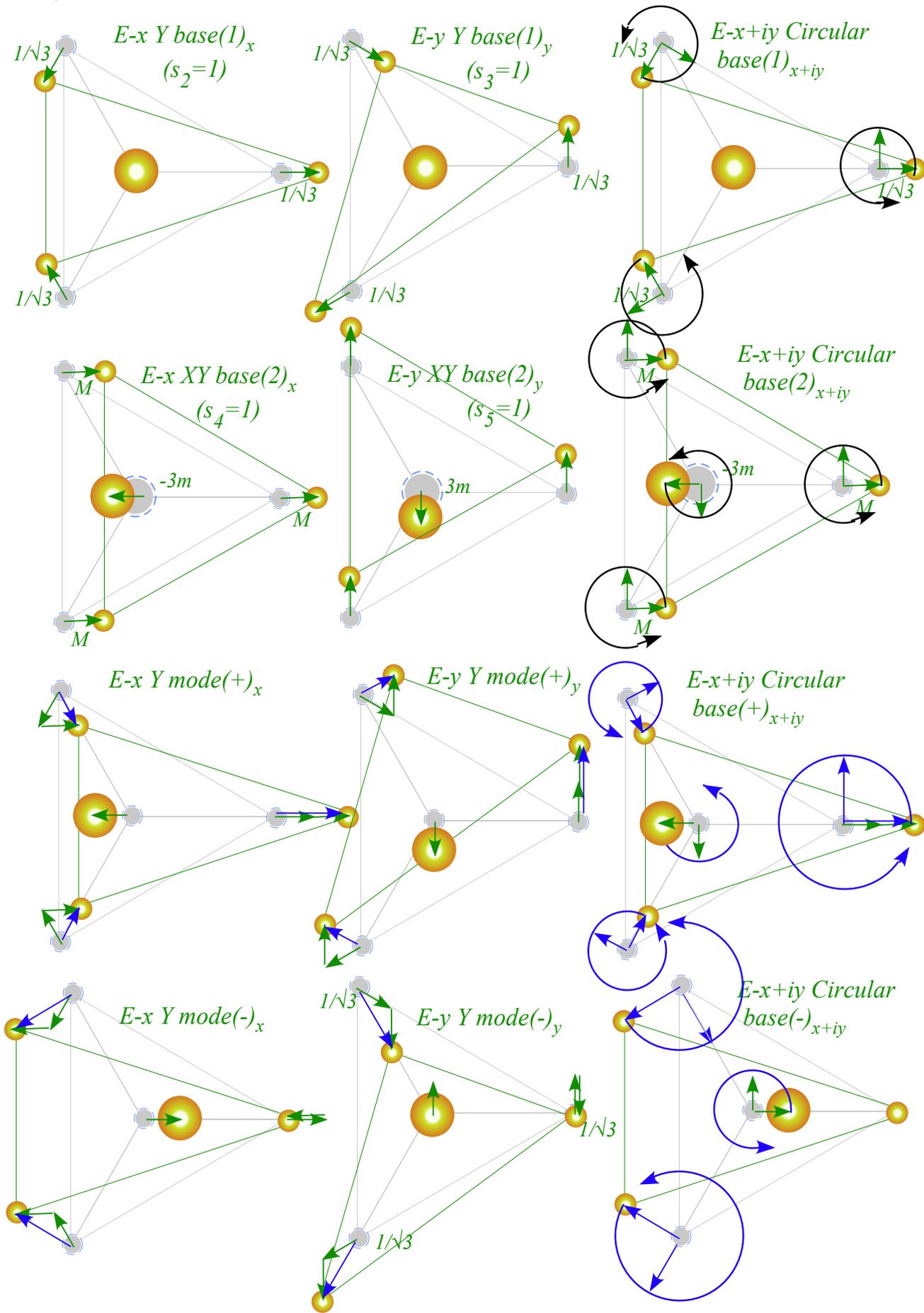
( $\omega^E = \sqrt{3k/2m}$ ) and are genuine  $s_2$  or  $s_3$  modes in Fig. 11.1.2 (top). Orthogonal  $(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}})$   $Y$ -base translations for  $j=0$  have zero frequency as do  $s_4$  or  $s_5$  in Fig. 11.1.2 (bottom) or  $s_7$  or  $s_8$  in Fig. 11.1.3 (top).

The 5<sup>th</sup> and final stage of eigensolution is to diagonalize the 3-by-3  $\langle K \rangle^E$  in (A.1.10g). Its secular equation is of 3<sup>rd</sup>-degree but a translation mode gives a zero root to  $\langle K \rangle^E$  and makes  $\det |\langle K \rangle^E| = 0$ .

$$\begin{aligned} 0 &= -\det \begin{vmatrix} a-\lambda & -b & c \\ -b & b-\lambda & 0 \\ c & 0 & d-\lambda \end{vmatrix} \quad \text{where: } a = \frac{j}{m} + \frac{3k}{4m}, \quad b = \frac{3k}{4m}, \quad c = -\frac{\sqrt{3}}{\sqrt{2}} \frac{j}{\sqrt{mM}}, \quad d = \frac{3}{2} \frac{j}{M}. \\ &= \lambda^3 - [ \text{Trace}_K ] \lambda^2 + [ \Sigma^{2-by-2} \text{minor}_K ] \lambda - {}^{3-by-3} \det_K \\ &= \lambda^3 - [ a+b+d ] \lambda^2 + [ \frac{ab}{bb} + \frac{ac}{cd} + \frac{b^0}{d^0} ] \lambda - \frac{abc}{bb} - d - c \frac{b}{c} \frac{b}{0} \\ &= \lambda^3 - \left[ \frac{j}{m} \left( \frac{2M+3m}{2M} \right) + \frac{3k}{2m} \right] \lambda^2 + \left[ \frac{3k}{4mm} \left( \frac{M+3m}{M} \right) \right] \lambda - 0 \end{aligned} \quad (\text{A.1.11a})$$

Two remaining roots are found by 2<sup>nd</sup>-degree solution. Special cases lend consistency checks.

$$\lambda^{(\pm)} = \frac{1}{4m} \left[ j \left( \frac{2M+3m}{M} \right) + 3k \pm \sqrt{ \left[ j \left( \frac{2M+3m}{M} \right) + 3k \right]^2 - \frac{12jk(M+3m)}{M} } \right] = \begin{cases} \left( 0, \frac{3k}{2m} \right) & \text{for } j=0 \\ \left( 0, \frac{j}{m} + \frac{3}{2} \frac{j}{M} \right) & \text{for } k=0 \end{cases} \quad (\text{A.1.11b})$$



## **Problems for Chapter 30**

*Zeno Redux*

23.1.1.