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\(^{ijmn}\) 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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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.
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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 $x_j(\alpha)$ and their time derivatives or velocities $v_j(\alpha) = \dot{x}_j(\alpha)$.

$$L = T - V = \frac{1}{2} m \dot{x}_j(\alpha) \dot{x}_j(\alpha) - V(x),$$

where:

$$\dot{x}_j = \frac{dx_j}{dt} = v_j \quad (30.1.1)$$

Greek letters denote particle indices $\alpha = \nu = 1, 2, \ldots, N$ for nuclei or $\alpha = \varepsilon = 1, 2, \ldots, N_e$ for electrons. Cartesian components $x, y, \text{ or } z$ are labeled by indicial letters $i, j, k, \ldots, n$ 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 $x_k(\varepsilon)$ for electrons and $x_k(\nu)$ for nuclei for which the following notation of Fig. 30.1.1 is to be used.

$$x_k(\varepsilon) = r_k(\varepsilon) \quad (30.1.2)$$

$$x_k(\nu) = a_k(\nu) + d_k(\nu) \quad (30.1.3)$$

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 $x_\ell^{\text{B}}$ thru coordinate and velocity vectors.

$$\mathbf{x} = x_\ell \mathbf{e}_\ell = x_\ell^{\text{B}} \mathbf{e}_\ell^{\text{B}} \quad (30.1.4)$$

$$\dot{x} = \dot{x}_\ell \mathbf{e}_\ell = \dot{x}_\ell^{\text{B}} \mathbf{e}_\ell^{\text{B}} + x_\ell \dot{\mathbf{e}}_\ell^{\text{B}} \quad (30.1.5)$$

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

$$\dot{\mathbf{e}}_\ell^{\text{B}} = \omega \times \mathbf{e}_\ell^{\text{B}} = \epsilon_{abc} \omega_a \mathbf{e}_c^{\text{B}} = \epsilon_{abc} \omega_a \mathbf{e}_c^{\text{B}} \quad (30.1.6)$$

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

$$\mathbf{x} = \dot{x}_\ell \mathbf{e}_\ell = \dot{x}_\ell^{\text{B}} \mathbf{e}_\ell^{\text{B}} + x_\ell \dot{\mathbf{e}}_\ell^{\text{B}} = \dot{x}_\ell^{\text{B}} \mathbf{e}_\ell^{\text{B}} + x_\ell \epsilon_{abc} \omega_a \mathbf{e}_c^{\text{B}} = \left(\dot{x}_\ell^{\text{B}} + x_\ell \epsilon_{abc} \omega_a \mathbf{e}_c^{\text{B}}\right) \mathbf{e}_\ell^{\text{B}} \quad (30.1.7)$$
The velocity relation applies to each particle–α in the kinetic term of (30.1.1). (For typographical convenience we delete index overlines. Until otherwise stated, all components are BOD-defined.)

\[
2T = m_\alpha \mathbf{x}(\alpha) \cdot \mathbf{x}(\alpha) = m_\alpha \left[ \dot{x}_k(\alpha) + \epsilon_{ink} \omega_i x_n(\alpha) \right] \left[ \dot{x}_k(\alpha) + \epsilon_{jmk} \omega_j x_m(\alpha) \right]
= m_\alpha \left[ \dot{x}_k(\alpha) \dot{x}_k(\alpha) + 2 \epsilon_{ink} \omega_i x_n(\alpha) \dot{x}_k(\alpha) + \epsilon_{ink} \epsilon_{jmk} \omega_i x_n(\alpha) x_m(\alpha) \omega_j \right]
\]

(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.

\[
2m_\nu \epsilon_{ink} \omega_i x_n(\nu) \dot{x}_k(\nu) = 2m_\nu \epsilon_{ink} \omega_i (a_n(\nu) + d_n(\nu)) \dot{d}_k(\nu)
= 2m_\nu \epsilon_{ink} \omega_i d_n(\nu) \dot{d}_k(\nu)
\]

(30.1.9)

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

\[
m_\alpha \left[ \mathbf{x}(\nu) \times \mathbf{d}(\nu) \right]_i = 0 = m_\nu \epsilon_{ink} a_n(\nu) d_k(\nu)
\]

(30.1.10a)

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

\[
m_\alpha \left[ \mathbf{x}(\nu) \right]_i = 0 = m_\nu x_i(\epsilon) + m_\nu \left( a_i(\nu) + d_i(\nu) \right)
\]

\[
0 \approx m_\nu d_i(\nu)
\]

(30.1.10b) \quad (30.1.10c)

If electronic mass \( m_\epsilon \) 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 $\mathbf{x}(\upsilon)$ and $\mathbf{x}(\epsilon)$ 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 $d_k(\upsilon)$ 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 $\mathbf{a}(\upsilon) \times \mathbf{d}(\upsilon)$ or $\mathbf{a}(\upsilon) \times \mathbf{x}(\upsilon)$ are constrained to zero, no such constraint exists for sums of $\mathbf{x}(\upsilon) \times \dot{\mathbf{x}}(\upsilon)$ or $\mathbf{d}(\upsilon) \times \mathbf{d}(\upsilon)$ 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.

\[
2T = m_v \ddot{d}_k(\upsilon)d_k(\upsilon) + 2m_v \epsilon_{\text{ind}} \omega_i d_k(\upsilon) + I^N_{ij} \dot{\omega}_i \omega_j + m_e \dot{r}_k(\epsilon) \dot{r}_k(\epsilon) + 2m_e \epsilon_{\text{ind}} \omega_i r_k(\epsilon) \dot{r}_k(\epsilon) + I^t_{ij} \dot{\omega}_i \omega_j
\]  

(30.1.11)

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

\[
\epsilon_{\text{ind}} \epsilon_{jmk} \omega_i x_n x_m \omega_j = \omega_i x_n \omega_i - \omega_i x_i \omega_j
\]  

\[
= \omega_i \left[ x_n \delta_{ij} - x_i x_j \right] \omega_j
\]  

(30.1.12)

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

\[
I^N_{mn} = m_v \left[ x_i(\upsilon)x_i(\upsilon) \delta_{mn} - x_m(\upsilon)x_n(\upsilon) \right]
\]  

(30.1.13)

\[
I^t_{mn} = m_e \left[ r_i(\epsilon)r_i(\epsilon) \delta_{mn} - r_m(\epsilon)r_n(\epsilon) \right]
\]  

(30.1.14)

1. Normal mode transformation: Genuine vibrational modes

Cartesian displacements $d_k(\upsilon)$ relate to normal coordinates $\{s_1, s_2, \ldots, s_n\}$ thru linear relations (30.1.15a) to $d_k(\upsilon)$ (summed over $k(\upsilon)$) or vice-versa (30.1.15b) (summed over $n$). Normal $\text{XY}_3$ 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 $\text{XY}_3$ modes in Fig. 30.1.2 that shows the displacements $d_k(\upsilon)$ of a particular $n^{th}$ mode or $n^{th}$ 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.

\[
d_j(\upsilon) = B^{-1}_{j,k(\upsilon)} s_k \quad (30.1.15a)
\]

\[
s_k = B_{k,j(\upsilon)} d_j(\upsilon) \quad (30.1.15b)
\]
(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 ($s_3 = s_{X}^{E_1}, s_5 = s_{Y}^{E_1}$).
2. Non-Genuine modes: Rotation, translation, and tunneling

Non-genuine z-axial rotation mode \( (s_6 = s_6^Z) \) and \( (x,y) \)-translation modes \( (s_6 = s_6^{E1}, s_8 = s_8^{E1}) \) 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” \( (s_9 = s_9^A) \). 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 \( (s_{10} = s_{10}^{E1}, s_{11} = s_{11}^{E1}) \) and a \( z \)-translation \( (s_{12} = s_{12}^{E1}) \), 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

![Diagram](image.png)

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.

\[
m_v \ddot{d}_k (v) \ddot{d}_k (v) = B^{-1}_{k(v),a} m(v) B^{-1}_{k(v),b} \dot{s}_a \dot{s}_b = G^{-1}_{ab} \dot{s}_a \dot{s}_b \tag{30.1.16a}
\]

Here the \( G \)-matrix is an inverse mass matrix defined of \( B^{-1} \)-transformed mass matrix.

\[
G^{-1} = B^{-1T} \times m \times B^{-1}, \quad G = B \times m^{-1} \times B^T \tag{30.1.16b}
\]
The $G$-matrix for $XY_3$ internal $s_a$ coordinates (30.1.15) is diagonal with the following values.

$$
\begin{array}{c|c|c|c|c|c|c|c|c}
  s_a = & s_1 = s_1^A & s_2 = s_2^E & s_3 = s_3^E & s_4 = s_4^E & s_5 = s_5^E & s_6 = s_6^A & s_7 = s_7^E & s_8 = s_8^E \\
  G_{ab} = \delta_{ab} G_{aa} = & \frac{1}{m} & \frac{1}{m} & \frac{1}{m} & \frac{1}{3\mu M} & \frac{1}{3\mu M} & \frac{1}{m} & \frac{1}{m} & \frac{1}{\mu} \\
\end{array}
$$

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

$$G^T = G \quad (30.1.17a) \quad G_{ab} = G_{ba} \quad (30.1.17b)$$

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

$$2m_i \epsilon_{ink} \dot{\omega}_k (\nu) \dot{s}_a (\nu) = 2m_i \epsilon_{ink} \omega_i B^{-1}_{m(\nu),a} B^{-1}_{k(\nu),b} s_a \dot{s}_b
= 2 \xi_{ab} \dot{s}_a \dot{s}_b \quad (30.1.18)$$

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

$$\xi_{ab} = m_i \epsilon_{ink} B^{-1}_{m(\nu),a} B^{-1}_{k(\nu),b} = -\xi_{ba} \quad (30.1.19)$$

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.

$$\xi_{23}^1 = m, \quad \xi_{23}^3 = 0 = \xi_{23}^3, \quad \xi_{45}^3 = 3\mu M = -\xi_{45}^3 \quad (30.1.19\text{ example-a})$$

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

$$\begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \rightarrow \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

and $A_1 \otimes A_2$. $E \otimes E$ applies to genuine modes of $XY_3$, and so (30.1.19) example-a has all vibrational $\xi_{ba}$ components. Coefficients involving rotation-translational motion are as follows.

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

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.

$$L = \frac{1}{2} G_{ab} \dot{s}_a \dot{s}_b + \omega_i \xi_{ab} \dot{s}_a \dot{s}_b + \frac{1}{2} I^N_{ij} \omega_i \omega_j + \frac{1}{2} m_i \dot{r}_i (\nu) \dot{r}_i (\nu) + \omega_i \epsilon_{ink} r_{m(\nu)} (\nu) \dot{r}_n (\nu) + \frac{1}{2} I^F_{ij} \omega_i \omega_j - V(s,r) \quad (30.1.20)$$

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 \( p = \frac{\partial L}{\partial \dot{r}} \). Canonical electronic momentum is

\[
p_{\lambda}(\epsilon) = \frac{\partial L}{\partial \dot{r}_{\lambda}(\epsilon)} = m_e \left[ \dot{r}_{\lambda}(\epsilon) + \epsilon_{\text{ink}} \omega r_{\lambda}(\epsilon) \right]. \quad (30.2.1)
\]

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

Canonical vibrational momentum has an analogous form.

\[
P_v = \frac{\partial T}{\partial \dot{s}_b} = G_{ab}^{\nu} \dot{s}_a + \xi_{ab}^{\nu} \omega_j s_a \quad (30.2.2)
\]

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

\[
J_i = \frac{\partial T}{\partial \omega_j} = I_j^{\nu} \omega_j + \xi_{ij}^{\nu} \dot{s}_a s_a + \frac{m_e}{m} \epsilon_{\text{ink}} r_{\nu}(\epsilon) \dot{r}_i(\epsilon) \quad (30.2.3)
\]

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).

\[
\dot{r}_k(\epsilon) = p_k(\epsilon) / m_e - \epsilon_{\text{ink}} \omega_j r_{\nu}(\epsilon) \quad (30.2.4)
\]

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

\[
\dot{s}_a = P_v G_{\nu a} - \xi_{\nu a}^{\nu} \omega_j s_f \quad (30.2.5a) \quad \dot{s}_b = P_v G_{\nu b} - \omega_j \epsilon_{\text{ink}} s_d \quad (30.2.5b)
\]

Here we define reduced Coriolis \( \xi_{ab}^{\nu} \) zeta-coefficients. (These relate to \( 2^{nd}-\text{kind Christoffel factors.} \)

\[
\xi_{ab}^{\nu} = \xi_{ac}^{\nu} G_{cb} = \epsilon_{\text{ink}} B^{-1} B_{(i(\nu),a)} B_{n(\nu),b} \quad (30.2.5b)
\]

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

\[
1 = \xi_{32}^{3} = -\xi_{23}^{3} = \xi_{45}^{3} = -\xi_{54}^{3} = \xi_{12}^{3} = \ldots \quad (30.2.5c)
\]

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

\[
J_i = I_j^{\nu} \omega_j + \xi_{ab}^{\nu} \left( P_v G_{\nu a} - \omega_j \epsilon_{\text{ink}} s_d \right) + \frac{m_e}{m} \epsilon_{\text{ink}} r_{\nu}(\epsilon) \left( p_k(\epsilon) / m_e - \omega_j \epsilon_{\text{ink}} r_{\nu}(\epsilon) \right) \quad (30.2.6)
\]

Using (30.2.5b) gives another form.

\[
J_i = \left( I_j^{\nu} - \epsilon_{ab}^{\nu} s_d \right) \omega_j + \xi_{ab}^{\nu} P_v + \left( I_j^{\nu} - m_e \epsilon_{\text{ink}} \epsilon_{\text{ink}} r_{\nu}(\epsilon) p_k(\epsilon) \right) \omega_j + \epsilon_{\text{ink}} r_{\nu}(\epsilon) p_k(\epsilon) \quad (30.2.7)
\]

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 \( L^{\text{vib}} \) and electrons \( L^{\text{ele}} \), respectively.

\[
L^{\text{vib}}_i = \epsilon_{ab}^{\nu} s_d P_v \quad (30.2.8a) \quad L^{\text{ele}}_i = \epsilon_{\text{ink}} r_{\nu}(\epsilon) p_k(\epsilon) \quad (30.2.8b)
\]

Electronic angular momentum is a sum over electron label \( \epsilon \) of \( \mathbf{r} \times \mathbf{p} \) terms.
Let bare-rotor-R inertial tensor \( I^R_{mn} \) be the first two terms of the vibrational part (30.2.7).

\[
I^R_{ij} = I^N_{ij} - \sum_{ab} \sum_{db} s^b_d s^d_b
\]

\[
= I^N_{ij} - \left( \varepsilon_{ink} B^{-1}_{m(v),db} B^{-1}_{n(v),db} \right) \left( \varepsilon_{jm} B^{-1}_{p(\lambda),db} B^{-1}_{e(\mu),db} \right) \left( B_{a,p(\lambda)} B_{d,q(\eta)} d_p(\lambda) d_q(\eta) \right)
\]

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 \( s_a = 0 \) for \( a > 5 \). The sums simplify as follows, where (30.1.12-3) are used again.

\[
I^R_{ij} = I^N_{ij} - m_a \varepsilon_{ink} \varepsilon_{jm} \left( \delta_{m,v,p(\lambda)} \delta_{n,v,e(\mu)} d_p(\lambda) d_q(\eta) \right)
\]

\[
= m_v \left[ \varepsilon_{ink} \varepsilon_{jm} x_n(v)x_m(v) - \varepsilon_{ink} \varepsilon_{jm} a_n(v) a_m(v) \right]
\]

The equilibrium-displacement vector sum \((x = a + d)\) of (30.2.6) is then inserted to give a rotor inertia tensor that varies linearly with displacements \( d(v) \) 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 \( I^R_{ij} \) represents the equilibrium inertia with \( d = 0 \).

\[
I^R_{ij} = m_v \varepsilon_{ink} \varepsilon_{jm} \left[ a_n(v) a_m(v) + a_n(v) d_m(v) + d_n(v) a_m(v) \right]
\]

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

\[
J_m = R_m + L^{\text{lib}} + L^{\text{ele}}
\]

(30.2.11a)

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

\[
R_m = I^R_{mn} \omega_n
\]

(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.

\[
H = P \dot{\xi} + p_k(\varepsilon) \dot{r}_k(\varepsilon) + \omega_m J_m - L = T + V
\]

(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.

\[
G_{\text{ab}}^{-1} \dot{s}_a \dot{s}_b = \left( P_c G_{ca} - \xi_c f_c G_{ca} \omega_l s_f \right) G_{ab}^{-1} \left( P_g G_{gb} - \xi_g s_g \omega_j \right)
\]

\[
= G_{bg} P_b P_g - 2 \omega_l \xi_{fg} s_f s_g + \omega_l \xi_{bg} s_g s_f \omega_j \times
\]

(30.2.13a)

The electronic terms give the following.

\[
m \dot{r}_k(\varepsilon) \dot{r}_k(\varepsilon) = m \left( p_k(\varepsilon) / m - \varepsilon_{ink} \omega r_n(\varepsilon) \right) \left( p_k(\varepsilon) / m - \varepsilon_{jm} \omega r_m(\varepsilon) \right)
\]

(30.2.13b)

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

\[
\omega_{\text{ab}} \dot{s}_a \dot{s}_b = \omega_{\text{ab}} s_a P_g - \omega_{\text{ab}} s_a s_d \omega_j \]

(30.2.14a)

\[
\omega_{\text{ab}} \varepsilon_{ink} r_n(\varepsilon) \dot{r}_k(\varepsilon) = \omega_{\text{ab}} r_n(\varepsilon) p_k(\varepsilon) - \omega_{\text{ab}} m \varepsilon_{ink} \varepsilon_{jm} r_n(\varepsilon) r_m(\varepsilon) \omega_j
\]

(30.2.14b)
b. Wilson-Howard-Watson Molecular Hamiltonians

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

$$T = \frac{1}{2} G_{ab} P_a P_b - \omega \xi_{ij} s_j P_i + \frac{1}{2} \omega \xi_{ij} \xi_{ij} s_j s_i \omega_j + \frac{1}{2} I^N \omega_i \omega_j + \omega \xi_{ij} s_j s_i$$

(30.2.15a)

$$+ \frac{1}{2} m \varepsilon_k P_k (\varepsilon) p_k (\varepsilon) - \omega \varepsilon_{ink} r_n (\varepsilon) p_k (\varepsilon) + \frac{1}{2} m \varepsilon_l \varepsilon_{in} \varepsilon_{jnk} r_n (\varepsilon)r_m (\varepsilon) + \frac{1}{2} I' \omega_i \omega_j$$

(30.2.15b)

$$+ \omega \varepsilon_{ink} r_n (\varepsilon) p_k (\varepsilon) - m \varepsilon_l \varepsilon_{ink} \varepsilon_{jnk} r_n (\varepsilon) r_m (\varepsilon) \omega_j$$

(30.2.15c)

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

$$T = \frac{1}{2} \left( I^N_{ij} - \xi_{ij} \xi_{ij} s_j s_i \right) \omega_i \omega_j + \frac{1}{2} G_{ab} P_a P_b + \frac{1}{2} m \varepsilon_k P_k (\varepsilon) p_k (\varepsilon)$$

(30.2.15b)

$$T = \frac{1}{2} I^{R\omega}_{ij} \omega_i \omega_j + \frac{1}{2} G_{ab} P_a P_b + \frac{1}{2} m \varepsilon_k P_k (\varepsilon) p_k (\varepsilon)$$

(30.2.15c)

Finally angular velocity $\omega$ is expressed in terms of nuclear rotor momentum $R$ by inverting (30.2.11b). The classical Wilson-Howard-Watson molecular Hamiltonian follows if we add a potential $V(s,r)$ to $T$.

$$H = T + V(s,r)$$

(30.2.16a)

$$= \frac{1}{2} R \mu^{R\omega}_{ij} R_j + \frac{1}{2} P_a P_a + \frac{1}{2} m \varepsilon_k P_k (\varepsilon) p_k (\varepsilon) + V(s,r)$$

(30.2.16b)

$$= \frac{1}{2} \left( J_i - L^{vib}_i - L^{ele}_i \right) \mu^{R\omega}_{ij} \left( J_j - L^{vib}_j - L^{ele}_j \right) + KE^{vib} + KE^{ele} + V(s,r)$$

(30.2.16c)

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

$$\left( \mu^{R\omega}_{ij} \right)^{-1} = I_{ij} - \xi_{ij} \xi_{ij} s_j s_i$$

(30.2.17a)

$$= I_{ij} + 2m \varepsilon_{ink} \varepsilon_{jnk} a_n (v) d_m (v)$$

(30.2.17b)

$$= m \varepsilon_{ink} \varepsilon_{jnk} \left[ a_n (v) a_m (v) + 2a_n (v) d_m (v) \right]$$

(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.

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

(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 $\frac{1}{2} R^2$ by $\frac{1}{2} \left( J - L \right)^2$ 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 \( J_\sigma = -J_\sigma \) (23.1.20b) adds a (-)sign to that of BOD defined generators \( J_\sigma \) of \( \mathbf{R} \{ \Theta \} = e^{-iJ \cdot \Theta} \) or the standard LAB defined generators \( J_i \) of \( \mathbf{R} \{ \Theta \} = e^{-iJ \cdot \Theta} \).

\[
\begin{align*}
[J_\sigma, J_\tau] &= -i\varepsilon_{abc} J_c \quad (30.2.19a) \\
[J_\sigma, J_\tau] &= +i\varepsilon_{abc} J_c \quad (30.2.19b)
\end{align*}
\]

\( \mathbf{R} \{ \Theta \} \) has the same group multiplication rules as \( \mathbf{R} \{ \Theta \} \) as do \( \mathbf{J} \) and \( \mathbf{J} \) yet the two groups commute. A molecular BOD turning anti-clockwise relative to LAB has positive \( J_z = m > 0 \) but negative \( \bar{J}_z = \bar{n} < 0 \) since BOD sees LAB turning clockwise. The (-) definition \( J_\sigma = -J_\sigma \) 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!).

\[
\left[ L^e \cdot J, L^e \cdot J \right] = i\varepsilon_{ijk} L^e \cdot J \quad (30.2.20)
\]

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.

\[
\frac{1}{2} m_v \delta_j(v) \delta_j(v) = \frac{1}{2} \delta_j(v) \delta_j(v), \quad \text{where:} \quad \delta_j(v) = m_v^{1/2} d_j(v) \tag{30.3.1}
\]

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

\[
\delta_j(v) = [a, j(v)] q_a \quad q_b = [b, k(v)] \delta_j(v) \tag{30.3.2}
\]

The transformation is orthogonal.

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

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

\[
\frac{1}{2} \delta_j(v) \delta_j(v) = \frac{1}{2} q_a q_a \tag{30.3.4}
\]

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

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

A mass-orthogonal Eckart conditioned mode transformation such as \( B^{-1} \) of (30.1.15) 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.

\[
\begin{align*}
\delta_1(1) &\begin{bmatrix} \sqrt{3}/3 & \sqrt{3}/3 & 0 & \sqrt{M}/\sqrt{3\mu} & 0 & 0 & \sqrt{m}/\sqrt{\mu} & 0 \end{bmatrix} q_1 \\
\delta_2(1) &\begin{bmatrix} 0 & 0 & -\sqrt{3}/6 & 0 & \sqrt{M}/3\mu & \sqrt{3}/6 & 0 & \sqrt{m}/\sqrt{\mu} \end{bmatrix} q_2 \\
\delta_1(2) &\begin{bmatrix} -\sqrt{3}/6 & -\sqrt{3}/6 & -1/2 & \sqrt{M}/3\mu & 0 & -1/2 & \sqrt{m}/\sqrt{\mu} & 0 \end{bmatrix} q_3 \\
\delta_2(2) &\begin{bmatrix} 1/2 & -1/2 & \sqrt{3}/6 & 0 & \sqrt{M}/3\mu & -\sqrt{3}/6 & 0 & \sqrt{m}/\sqrt{\mu} \end{bmatrix} q_4 \\
\delta_1(3) &\begin{bmatrix} -\sqrt{3}/6 & -\sqrt{3}/6 & 1/2 & \sqrt{M}/3\mu & 0 & 1/2 & \sqrt{m}/\sqrt{\mu} & 0 \end{bmatrix} q_5 \\
\delta_2(3) &\begin{bmatrix} -1/2 & 1/2 & \sqrt{3}/6 & 0 & \sqrt{M}/3\mu & -\sqrt{3}/6 & 0 & \sqrt{m}/\sqrt{\mu} \end{bmatrix} q_6 \\
\delta_1(4) &\begin{bmatrix} 0 & 0 & 0 & \sqrt{m}/\sqrt{\mu} & 0 & 0 & \sqrt{M}/\sqrt{\mu} & 0 \end{bmatrix} q_7 \\
\delta_2(4) &\begin{bmatrix} 0 & 0 & 0 & 0 & \sqrt{m}/\sqrt{\mu} & 0 & 0 & \sqrt{M}/\sqrt{\mu} \end{bmatrix} q_8 \\
\end{align*}
\tag{30.3.6}
\]

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).

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

For the \( XY_3 \) example we have the following.
This with \((30.3.13)\) is inserted into energy expression \((30.3.11)\) to approximate the effect of momentum.

\[ r_{23}^3 = -1 = -r_{32}^3, \quad r_{24}^3 = 0 = -r_{25}^3, \quad r_{45}^3 = 1 = -r_{54}^3 \] \[ r_{61}^3 = 1 = -r_{32}^3, \quad r_{48}^3 = 0 = r_{75}^3, \quad r_{78}^3 = 1 = -r_{87}^3 \] \[(30.3.9)\]

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 \(\frac{1}{2} k_{ab} \dot{q}_a \dot{q}_b\) 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 \(\frac{1}{2} \omega_b^2 Q_b^2\) as follows.

\[
KE^{\text{vb}} + PE^{\text{vb}} = \frac{1}{2} \dot{q}_a \dot{q}_a + \frac{1}{2} k_{ab} \dot{q}_a \dot{q}_b + \ldots \text{anharmonic } q\text{-terms} \tag{30.3.10a}
\]

\[
= \frac{1}{2} \ddot{Q}_a \dot{Q}_a + \frac{1}{2} \omega_b^2 Q_b^2 + \ldots \text{anharmonic } Q\text{-terms} \tag{30.3.10b}
\]

Examples for XY3 and XY6 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 4th-power \(J^4\), \(J^4\),..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 \(k = ma^2\). The rotor has vibrational kinetic and potential energy \(KE_v\) and \(PE_v\) plus rotational kinetic energy \(RE_J\).

\[
E = KE_v + PE_v + RE_J
\]

\[
= \frac{mr_v^2}{2} + \frac{k}{2} (r-r_0)^2 + \frac{I\omega_r^2}{2} = p_v^2 + \frac{m}{2} \omega_v^2 (r-r_0)^2 + \frac{\mu J^2}{2} \tag{30.3.11}
\]

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

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

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

\[
\frac{\partial}{\partial r} (PE_v + RE_J) = 0 = ma^2 (r-r_0) + \frac{J^2}{2} \frac{\partial \mu}{\partial r} \quad \text{implies:} \quad d = r - r_0 = \frac{J^2}{2ma^2} \frac{\partial \mu}{\partial r} \tag{30.3.13}
\]

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.

\[
\mu \equiv \mu_0 + \frac{\dot{\mu}}{\partial r} (r-r_0) + \ldots = \mu_0 - \frac{\dot{\mu}}{\partial r} \frac{J^2}{2ma^2} \frac{\partial \mu}{\partial r} + \ldots \tag{30.3.14a}
\]

This with \((30.3.13)\) is inserted into energy expression \((30.3.11)\) to approximate the effect of momentum \(J\).
Each normal coordinate has an equilibrium shift. Multi-mass molecular Hamiltonians have vibration normal coordinates:

\[ E = \frac{p_v^2}{2m} + \frac{m}{2} \omega_v^2 (r - r_0)^2 + \frac{\mu J^2}{2} \]

\[ = \frac{p_v^2}{2m} + \frac{m}{2} \omega_v^2 \left( \frac{J^2}{2m \omega_v^2} \frac{\partial \mu}{\partial r} \right)^2 + \frac{\mu J^2}{2} - \frac{\partial \mu}{\partial r} \frac{J^2}{2m \omega_v^2} \frac{\partial \mu}{\partial r} + \ldots \]  

(30.3.14b)

\[ = \frac{p_v^2}{2m} + \frac{J^4}{8m \omega_v^2} \left( \frac{\partial \mu}{\partial r} \right)^2 + \frac{\mu J^2}{2} - \frac{J^4}{4m \omega_v^2} \left( \frac{\partial \mu}{\partial r} \right)^2 + \ldots \]  

(30.3.15)

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

\[ E = \frac{p_v^2}{2m} + \frac{\mu J^2}{2} - \frac{J^4}{8m \omega_v^2} \left( \frac{\partial \mu}{\partial r} \right)^2 + \ldots = \frac{p_v^2}{2m} + \frac{\mu J^2}{2} - \frac{m}{2} \omega_v^2 d^2 + \ldots \]  

(30.3.16)

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 \( r_{\text{min}}=r_0 \) and \( r_{\text{max}}=r_0+2d \).

2. Polyatomic molecular distortion: \( XY_6 \) and \( XY_8 \) examples

Multi-mass molecular Hamiltonians have vibration normal coordinates \( q_\mu \) and BOD momentum \( J_m \).

\[ H = \sum \frac{1}{2} p_\mu p_\mu + \sum \omega_\mu^2 q_\mu q_\mu + \sum J_m J_m \cdot J_m \]  

(30.3.16)

Each normal coordinate has an equilibrium shift \( \delta q_\mu \) like the \( d \) in (30.3.13). Note: \( \frac{\partial}{\partial q} (\mu \mathbf{1}) = \delta q = \omega \mathbf{1} + \mu \mathbf{1} \).

\[ \delta q_\mu = -\frac{1}{2\omega_\mu^2} J_m \frac{\partial \mu}{\partial q_\mu} J_m = -\frac{1}{2\omega_\mu^2} J_m J_m^{-1} \frac{\partial J_m}{\partial q_\mu} J_m^{-1} \]  

(30.3.17)
Inverse inertia is represented by a 3-by-3 matrix $\mu_{\mu\nu} = I_{\mu\nu}^{J}$ inverse to the inertia tensor $I_{\mu\nu}$. The resulting effective Hamiltonian analogous to (30.3.15) involves a $4^\text{th}$-degree $J$-tensor sum over all modes $q_\mu$:

$$H = H_0 - \frac{J^4}{8\omega^2} \sum_{\mu} \frac{\partial J_{\mu\nu}}{\partial q_\mu} \frac{\partial J_{\mu\nu}}{\partial q_\mu} = H_0 - \frac{\omega_\mu \delta q_\mu}{2}$$

where: $H_0 = \frac{1}{2} p_\mu p_\mu + \frac{1}{2} J_{\mu\nu}^{(0)} \mu_{\mu\nu} J_{\mu\nu}^{(0)}$ (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 CsH₈, SF₆, and CF₄, respectively, there is only one linearly independent $4^\text{th}$-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 $r^4$.

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

(30.3.19)

An octahedral (SF₆-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 $H^{0\text{ph}}$, but each RES has an octahedral or cubic shape, respectively, as shown in Fig. 30.3.2(a) and Fig. 30.3.2(b).

$$T^{(4)}(J) = J_1^4 + J_2^4 + J_3^4$$

(30.3.20c)

$$T^{(2,2)}(J) = J_1^2 J_2^2 + J_1^2 J_3^2 + J_2^2 J_3^2$$

(30.3.20d)

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 $-2t_0$ if scalar $t_0$ is adjusted accordingly. Nevertheless, distortion of an octahedral SF₆ molecule described by $T^{(4)}$ is quite different from a $T^{(2,2)}$ distortion of cubic CsH₈ or tetrahedral CF₄.

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 SF₆ 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 SF₆ is least susceptible.

It is vice-versa for cubic CsH₈ or tetrahedral CF₄ 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).
3. Elementary derivation of SF₆ distortion parameters.

Hecht model 4th-rank distortion operator for the SF₆ 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.

\[ H = 10t_{044} \left( J^+ + J^- + \frac{3}{5} J^4 \right) + t_{040} J^4 \]  

(30.3.21)

We now derive the parameters \( t_{040} \) and \( t_{044} \) in terms of SF₆ vibrational mode frequencies.

The distortion Hamiltonian (30.3.18) depends on a sum over genuine modes of the squares \( \delta q^2_{\mu} \) of distortions \( \delta q_{\mu} \) as given by (30.3.17). The key quantity in the distortion expression is the derivative with respect to \( q_{\mu} \) of the inertial tensor \( I_{ij} \) or its inverse \( \mu_{ij} \). Mode tensor derivatives \( \frac{\partial}{\partial q_{ij}} \) are evaluated at the equilibrium positions \( q_{\mu} = 0 \) for the molecule and therefore must be invariant to its molecular symmetry group that is octahedral \( O_h \) for SF₆. Only modes \( q^4_{\mu} \), \( q^6_{\mu} \), \( q^8_{\mu} \), \( q^2_{1\mu} \), \( q^2_{2\mu} \), \( q^2_{3\mu} \), \( q^2_{5\mu} \), and \( q^2_{7\mu} \) that transform like components of an irreducible symmetric 2nd-rank spatial tensor \( \mu_{ij} \) or \( I_{ij} \) may thereby give non-zero \( \frac{\partial}{\partial q_{ij}} \).
Symmetry selection of non-zero $\frac{\partial \nu}{\partial \nu}$ components is the same as selection for non-zero derivatives $\frac{\partial q}{\partial q}$ of Raman polarizability tensors, only Raman-active modes affect inertia to 1st 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.

$$\frac{\partial \mu}{\partial q^A} = \begin{bmatrix} -A/\sqrt{3} & 0 & 0 \\ 0 & -A/\sqrt{3} & 0 \\ 0 & 0 & -A/\sqrt{3} \end{bmatrix}, \quad \frac{\partial \mu}{\partial q^E} = \begin{bmatrix} -E/\sqrt{6} & 0 & 0 \\ 0 & -E/\sqrt{6} & 0 \\ 0 & 0 & 2E/\sqrt{6} \end{bmatrix}, \quad \frac{\partial \mu}{\partial q^T} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & T/\sqrt{2} \\ T/\sqrt{2} & 0 & 0 \end{bmatrix}$$  \hspace{1cm} (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, $q^E_1$), and one $T_{2g}$-mode component (say, $q^{T_{2g}}_3$) on inertia tensor $\mu$.

One must take care to use the mass normalized mode coordinates for the potential form $\frac{1}{2} \omega^2 q^2 \mu$ 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 $q^{A_u}$ mode in Fig. A.2 is $a + q^A/\sqrt{6m}$. (Here $a$ is equilibrium radius.) The $q^E_1$ mode has $a + 2q^E_1/\sqrt{12m}$ for polar atoms and $a - q^E_1/\sqrt{12m}$ for equatorial atoms. The tangential displacements of $T_{2g}$ modes are $q^{T_{2g}}_3/\sqrt{4m}$. The inertia tensor derivative for each mode then follows.

$$\frac{\partial I_{11}}{\partial q^A} = \frac{8am}{\sqrt{6m}}, \quad \frac{\partial I_{11}}{\partial q^E} = \frac{4am}{\sqrt{12m}}, \quad \frac{\partial I_{12}}{\partial q^T} = -\frac{4am}{\sqrt{4m}}.$$  \hspace{1cm} (30.3.23)

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

$$\frac{\partial \mu_1}{\partial q^A} = -\frac{1}{2a^3 \sqrt{6m^3}}, \quad \frac{\partial \mu_1}{\partial q^E} = -\frac{1}{8a^3 \sqrt{3m^3}}, \quad \frac{\partial \mu_2}{\partial q^T} = \frac{1}{8a^3 \sqrt{m^3}}.$$  \hspace{1cm} (30.3.24)

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

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

$$\delta q^A = (A/2a^3 \sqrt{3}) \left(J_x^2 + J_y^2 + J_z^2\right), \quad \delta q^E = (E/2a^3 \sqrt{6}) \left(J_x^2 + J_y^2 + J_z^2\right) \quad \delta q^T = (T/\omega^2 \sqrt{2}) \left(J_x J_y + J_y J_z + J_z J_x\right)$$  \hspace{1cm} (30.3.26)

Combining these yields the total distortion energy from (30.3.16b).
\[ H = H_o - \left( \frac{E^2}{8\omega^2_E} - \frac{T^2}{8\omega^2_F} \right) J_x^6 + J_y^6 + J_z^6 \]  
\[ - \frac{A^2}{24\omega^2_A} + \frac{E^2}{24\omega^2_E} - \frac{T^2}{8\omega^2_F} \]  
\[ J^4 \]  
(30.3.27)

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

\[ 10 t_{044} = \frac{T^2}{8\omega^2_F} - \frac{E^2}{8\omega^2_E} = \frac{1}{256m^3a^6} \left( \frac{1}{\omega^2_T} - \frac{1}{\omega^2_E} \right) = \frac{1}{4I^5} \left( \frac{1}{\omega^2_T} - \frac{1}{\omega^2_E} \right). \]  
(30.3.28)

This should be compared to the measured SF\(_6\) rotational constant \((0.091083 \text{ cm}^{-1})\) in \((\text{mks})\) energy units.

\[ B = \frac{\hbar^2}{2I} = \frac{\hbar^2}{8ma^2} = (0.091083 \text{ cm}^{-1})\hbar(J \cdot \text{sec})c = \frac{m}{100\text{sec}} = 1.811 \times 10^{-24} \text{Joule (30.3.29)} \]

The radius of SF\(_6\) 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 \( J^4 \).

\[ 10 t_{044} = \frac{8h^4}{4(2I)^3} \left( \frac{h^2}{\omega^2_T} - \frac{h^2}{\omega^2_E} \right) = 2B^3 \left( \frac{1}{\epsilon^2_T} - \frac{1}{\epsilon^2_E} \right). \]  
(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 \( (E_g: 644 \text{ cm}^{-1} \text{ or } 1.28 \times 10^{-20} J; \ T_{2g}: 524 \text{ cm}^{-1} \text{ or } 1.04 \times 10^{-20} J) \) and give the anisotropic centrifugal constant.

\[ t_{044} = \frac{B^3}{5} \left( \frac{1}{\epsilon^2_T} - \frac{1}{\epsilon^2_E} \right) = 3.74 \times 10^{-33} \text{ Joule = 5.65 Hz (30.3.30b)} \]

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, \textit{et al.} The tiny value of about \( 56 \text{ Hz} \) for \( 10 t_{044} \) is multiplied by \( J \). 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 \( 1^{st} \) order optical transitions, and these \( v_3 \) and \( v_4 \) 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. \textit{Elementary derivation of SF}_6 \textit{Coriolis parameters}.

Molecular total angular momentum \( J=R+\ell \) and its \( z \)-components \( J_z=R_z+\ell_z \) has integral quantum values \( mh \) but individual rotor \( R_z \) or vibronic \( \ell_z \) may have continuous expectation values \( m\zeta h \) 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 \( v_3 \) and \( v_4 \) of SF\(_6\) can contribute \( 1^{st} \) order vibration angular momentum.

Here we consider Coriolis effects due to vibration angular momentum of \( v_3 \) and \( v_4 \) modes of SF\(_6\) derived in Appendix 30.B. Angular momentum of a Bohr circular orbit can only have integral quanta \( \pm mh \) 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 \( \pm mh \), 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 \( d^a(v) = (d^a_x, d^a_y, d^a_z) \) of nucleus-\( v \) by (30.3.6).
\[ d_j^a(v) = B^{-1}_{j(v),a} = \sqrt{m_v[a, j(v)]} \]

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

\[ \xi_{xy} = -\xi_{yx} = m_v \langle \vec{d}_n(v) \rangle_d \langle \vec{d}_k(v) \rangle_d = m_v \langle | \vec{d}'(v) \times \vec{d}'(v) | \rangle \]
\[ = \varepsilon_{zk} \begin{bmatrix} a, n(v) \end{bmatrix} \begin{bmatrix} b, k(v) \end{bmatrix} = \zeta_{xy} \]

For normalized modes, the \( \xi \) or \( \zeta \) coefficients are equal to the sum over nuclear \( (v) \) 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.

\[ \sum_{v} \sum_{j=1}^{N} m_v [d_j^a(v)]^2 = 1 \]
Appendix 30.A Symmetry defined vibrational normal coordinates

A.1 C_{3v} defined coordinates of Y₃ and XY₃ molecules

The $D_{jk}^{\alpha}$-matrices and $P_{jk}^{\alpha}$-projectors of trigonal symmetry $C_{3v}$ are given in Ch. 15 of Unit 5 and applied to molecular orbitals of a Y₃ 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 $C_3(r,r^2)$.

\[
\begin{align*}
\mathbf{g} &= \begin{pmatrix} 1 & r & r^2 & i_1 & i_2 & i_3 \end{pmatrix} \\
D^A_1 (g) &= \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} \\
D^A_2 (g) &= \begin{pmatrix} 1 & 1 & 1 & -1 & -1 & -1 \end{pmatrix}
\end{align*}
\]

where $\varepsilon_{\pm} = e^{\pm 2\pi i/3}$

Another set (15.1.12) has diagonal $x$-plane reflection $C_2(i_3)$. (They share the same 1-by-1 $D^A_1$ and $D^A_2$.)

\[
\begin{align*}
\mathbf{g} &= \begin{pmatrix} 1 & r & r^2 & i_1 & i_2 & i_3 \end{pmatrix} \\
D^A_1 (g) &= \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} \\
D^A_2 (g) &= \begin{pmatrix} 1 & 1 & 1 & -1 & -1 & -1 \end{pmatrix}
\end{align*}
\]

\[
D^E_{1 2} (g) = \begin{pmatrix} 0 & 1 & -1/2 & \sqrt{3}/2 & -1/2 & \sqrt{3}/2 & -1/2 & -\sqrt{3}/2 & -1/2 & \sqrt{3}/2 \end{pmatrix}
\]

The standard projection formula: $p_{nm}^{\mu} = (\langle \mu | \Sigma_g D_{mn}^{\alpha *}(g) \rangle \mathbf{g}$ repeats the following from (15.1.15).

\[
\begin{align*}
\mathbf{p}_A^1 &= \mathbf{p}_A^1 \mathbf{1} \mathbf{p}_A^1 = (1 + r + r^2 + i_1 + i_2 + i_3)/6 \\
\mathbf{p}_A^2 &= \mathbf{p}_A^2 \mathbf{1} \mathbf{p}_A^2 = (1 + r + r^2 - i_1 - i_2 - i_3)/6 \\
\mathbf{p}_E^{xx} &= \mathbf{p}_E^{xx} \mathbf{1} \mathbf{p}_E^{xx} = (21 - r - r^2 - i_1 - i_2 + 2i_3)/6 \\
\mathbf{p}_E^{yy} &= \mathbf{p}_E^{yy} \mathbf{1} \mathbf{p}_E^{yy} = (21 - r - r^2 + i_1 + i_2 - 2i_3)/6 \\
\mathbf{p}_E^{xy} &= \mathbf{p}_E^{xy} \mathbf{i}_2 \mathbf{p}_E^{xy} = D_{xy}(i_2) \mathbf{p}_E^{xy} = (01 + r + r^2 - i_1 + i_2 - 0i_3)/4 \\
\mathbf{p}_E^{yx} &= \mathbf{p}_E^{yx} \mathbf{i}_2 \mathbf{p}_E^{yx} = D_{yx}(i_2) \mathbf{p}_E^{yx} = (01 + r - r^2 - i_1 + i_2 - 0i_3)/4
\end{align*}
\]

This gives modes for a Y₃ ring of XY₃ in Fig. A.1.1. (The X-atom adds another vector E-doublet.)

\[
\begin{align*}
\left| A_1 \right> &= \left| \mathbf{1} \right| \mathbf{p}_A^1 \sqrt{6} = (1, 1, 1, 1, 1, 1)/\sqrt{6} \\
\left| A_2 \right> &= \left| \mathbf{1} \right| \mathbf{p}_A^2 \sqrt{6} = (1, 1, -1, -1, -1, -1)/\sqrt{6} \\
\left| E_{xx} \right> &= \left| \mathbf{1} \right| \mathbf{p}_E^{xx} \sqrt{3} = (2, -1, -1, -1, 2)/\sqrt{12} \\
\left| E_{yy} \right> &= \left| \mathbf{1} \right| \mathbf{p}_E^{yy} \sqrt{3} = (0, 1, -1, 1, 0)/2 \\
\left| E_{xy} \right> &= \left| \mathbf{1} \right| \mathbf{p}_E^{xy} \sqrt{3} = (0, -1, 1, 1, 0)/2 \\
\left| E_{yx} \right> &= \left| \mathbf{1} \right| \mathbf{p}_E^{yx} \sqrt{3} = (2, -1, -1, 1, -2)/\sqrt{12}
\end{align*}
\]

Model $P_{jk}^{\alpha}$-symmetry configurations in Fig. A.1.1 have LAB-C₂ symmetry-(j=x or y) that is even (x) or odd (y) to LAB x-plane i₃-reflection, and BOD-C₂ symmetry-(k=x or y) to local i₇, i₂, or i₇ BOD planes.

There are $4 = 2^2$ projectors for two-dimensional E-symmetry and one each for $A_1$ and $A_2$ symmetry, making six $P_{jk}^{\alpha}$ in all, and that is the total number of symmetry operators needed here. (Order=3 C₃v=6.)
Fig. 30.A.1. Vibration coordinates for C₃ᵥ symmetric XY₃ molecular model.

(a) XY₃ Symmetry-defined coordinates

(b) Symmetry-projected XY₃ modes
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 1st stage primitive energy form, we seek its analytic eigen-solution using symmetry.

$$ E = \frac{1}{2} m_x \ddot{x}_i (\lambda) \dot{x}_i (\lambda) + \frac{1}{2} k_{\mu \nu} x_j (\mu) x_k (\nu) $$  \hspace{1cm} (A.1.1a)

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

$$ k_{\mu \nu} = -\hat{k}_{\mu \nu} \cdot \hat{x}_j (\mu) k_{\mu \nu} \hat{x}_k (\nu) \hspace{1cm} (A.1.1b) $$

$$ k_{\mu \nu} = -\sum_{\nu} (k_{\mu \nu} \cdot \hat{x}_j (\mu) k_{\mu \nu} \hat{x}_k (\nu)) \hspace{1cm} (A.1.1c) $$

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

The 2nd stage energy form $K_{mn}$ uses mass-orthonormalized $\delta$-displacements $\delta_x = \delta_{x \mu} = x_j (\mu) m_{\mu 1/2}$. For that, each stage needs to have only orthonormal bases and orthogonal or unitary transformation.

$$ E = \frac{1}{2} \delta_x \delta_x + K_{mn} \delta_m \delta_n \hspace{1cm} \text{where:} \hspace{0.5cm} \delta_x = \delta_{x \mu} = x_j (\mu) m_{\mu 1/2} \hspace{1cm} (A.1.2a) $$

$$ K_{mn} = \frac{k_{\mu \nu} y_y}{m_{\mu 1/2} m_{\nu 1/2}} = K_{mn} \hspace{1cm} (A.1.2b) $$

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

The 3rd stage uses symmetry-operator-labeling of $K_{mn}$ bases. XY3 coordinate bases of Fig. A.1.2 are used for $K_{mn}$ in (A.1.3). Y-atom bases $r^m | \hat{y}_x \rangle$ are radial but $r^m | \hat{y}_y \rangle$ are transverse. $K_{mn}$ of (A.1.2b) hook up Y-atom bases $h | \hat{y}_x \rangle$ and $h | \hat{y}_y \rangle$ to each other and to central X-atom bases $| \hat{x}_x \rangle$ and $| \hat{x}_y \rangle$ 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.

$$ \langle A | K | B \rangle = \begin{pmatrix}
| y_x \rangle & r | y_x \rangle & r^2 | y_x \rangle & | y_y \rangle & r | y_y \rangle & r^2 | y_y \rangle & | x_x \rangle & | x_y \rangle \\
| y_x \rangle & 0 & 0 & \sqrt{3} \frac{k}{m} & 0 & \frac{k}{m} & 0 & 0 \\
| y_y \rangle & 0 & 0 & \sqrt{3} \frac{k}{m} & 0 & \frac{k}{m} & 0 & 0 \\
| x_x \rangle & -\frac{j}{\sqrt{m M}} & -\frac{j}{\sqrt{m M}} & 0 & 0 & 0 & 0 & 0 \\
| x_y \rangle & -\frac{j}{\sqrt{m M}} & -\frac{j}{\sqrt{m M}} & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix} \hspace{1cm} (A.1.3) $$

The 4th stage uses symmetry $P^x_{ji}$ projection to reduce $K_{AB} = \langle A | K | B \rangle$ in (A.1.3) above to block diagonal projected forms $K_{AB} = \langle P^x_{ji} A | K | P^x_{ji} B \rangle$ that are derived below in (A.1.4) thru (A.1.10).

Only select rows of matrix $K_{AB} = \langle A | K | B \rangle$ are given in (A.1.3). If $K$ has r-symmetry then a matrix row for a base $r | B \rangle$ that is a rotation $r$ of base $| B \rangle$ is redundant. Also, this choice of basis separates BOD-symmetric-$(k=x)$-radial $| y_x \rangle$ from BOD-antisymmetric-$(k=y)$-transverse $| y_y \rangle$ so that only $P^x_{ji}$ have non-zero projection on $| y_x \rangle$ or
and only $P_{i,j}^\alpha$ have non-zero projection on $|\alpha_i^\gamma\rangle$ or $|\beta_i^\gamma\rangle$. **BOD** label-$k$ of $P_{i,j}^\beta$ has to match the primitive state $|\ell_i^\alpha\rangle$ it projects to get a nonzero projection as shown below.

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

A K-matrix $\langle \alpha_i^X | K | \beta_j^Y \rangle$ has $P_{i,j}^\alpha$ -projected bra $\langle \alpha_i^X |$ and $P_{i,m}^\beta$ -projected ket $|\beta_j^Y\rangle$ with norms $N_i^X$ and $N_m^Y$.

$$\langle \alpha_i^X | = N_i^X \langle \beta_j^Y | = N_j^Y \langle \alpha_i^X | P_{i,j}^\alpha \rangle = \langle \alpha_i^X | P_{i,m}^\beta \rangle (A.1.4a)$$

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

$$P_{x,x}^E \langle \frac{y_1^X}{x} | = (\langle \frac{y_1^X}{x} | + r^1 \langle \frac{y_1^X}{x} | + r^2 \langle \frac{y_1^X}{x} | ) / \sqrt{3} (A.1.5a)$$

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

$$P_{x,y}^E \langle \frac{y_1^X}{x} | = (\frac{r^1 \langle \frac{y_1^X}{x} | - r^2 \langle \frac{y_1^X}{x} | ) / \sqrt{2} (A.1.6a)$$

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

$$P_{x,x}^E \langle X | = | X \rangle (A.1.6e)$$

Symmetry $(Kg=gK)$ and P-rules ($P_{i,j}^\alpha P_{j,m}^\beta = \delta_{i,j} \delta_{\alpha,\beta} P_{i,m}^\alpha$) give $\langle \alpha_i^X | K | \beta_j^Y \rangle$ in terms of $\langle X | K | g \rangle$ in (A.1.3).

$$\langle \alpha_i^X | K | \beta_j^Y \rangle = N_i^X \langle \beta_j^Y | P_{i,m}^\beta \rangle = N_j^Y \langle \alpha_i^X | K P_{\alpha,j}^\alpha \rangle = N_i^X N_j^Y \delta_{\alpha,\beta} \delta_{\beta,j} \langle X | K P_{\alpha,j}^\alpha \rangle$$

(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 $1$-by-$1$ blocks for symmetry irrep species $A_1$ and $A_2$ and a pair of $3$-by-$3$ blocks for vector species $E$.

\[
K = \begin{bmatrix}
\begin{array}{ccc}
A_Y & A_Y & A_Y \\
A_X & A_X & A_X \\
\end{array}
\end{bmatrix}
\]  

(A.1.8)

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

\[
\langle a_Y | k | a_Y \rangle = \sum_h N^X_h \langle k | h | \rangle \langle h | k | \rangle
\]

(A.1.9)

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

\[
\langle A_Y | A_Y \rangle = D_{xx} \alpha_1^*(1) \langle Y | x | Y \rangle + D_{xx} \alpha_1^*(r) \langle Y | x | Y \rangle + D_{xx} \alpha_1^*(r^2) \langle Y | x | Y \rangle
\]

(A.1.10a)

\[
\langle E_Y | E_Y \rangle = \frac{1}{2} \cdot \left( \frac{i}{2} + \frac{3}{4} \right) + \frac{1}{2} \cdot \left( \frac{3}{4} \right) = \frac{i + 3}{4} = \frac{i}{4}
\]

(A.1.10b)

\[
\langle E_Y | E_y \rangle = 0 \cdot (0) + \frac{-1}{2} \cdot \left( \frac{3}{4} \right) + \frac{-1}{2} \cdot \left( \frac{3}{4} \right) = \frac{-3}{4}
\]

(A.1.10c)

Central atom X has ket $| x \rangle$ that is already the irreducible $E_S$ base $| x \rangle = \mathbf{P}_{xx} | x \rangle$ in (A.1.6a).

\[
\langle E_X | E_X \rangle = \langle x | x \rangle = \frac{i}{2}
\]

(A.1.10e)

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

\[
\langle E_y | E_x \rangle = \sqrt{2} \cdot \frac{1}{\sqrt{M}} = \sqrt{2} \cdot \frac{i}{\sqrt{2mM}}
\]

(A.1.10f)

These $C_{3v}$-projected $K$ matrix elements are collected in the form of the $8$-by-$8$ matrix (A.1.8).
Two remaining roots are found by \( 2 \). The first 3-by-3 matrix \( K \) has to be diagonalized. Due to the \( \delta_l \) 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 \( K \) has \( C_{\infty v} \) symmetry.

\[
\begin{pmatrix}
A_{xx} & A_{xy} & A_{xz} \\
A_{yx} & A_{yy} & A_{yz} \\
A_{zx} & A_{zy} & A_{zz}
\end{pmatrix}
\]

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

\[
\begin{pmatrix}
\frac{j}{2} \\
n \frac{k}{2} \\
\frac{j}{2}
\end{pmatrix}
\]

and makes 

\[
\det \begin{pmatrix}
E_{xx} & E_{xy} & E_{xz} \\
E_{yx} & E_{yy} & E_{yz} \\
E_{zx} & E_{zy} & E_{zz}
\end{pmatrix} = 0.
\]

Two remaining roots are found by \( 2 \)-degree solution. Special cases lend consistency checks.

\[
\lambda^{(\pm)} = \frac{1}{4m} \left[ j(2M+3m) + 3k \pm \sqrt{[(2M+3m)^2 - 12j(M+3m)]} \right] \text{ for } j = 0
\]

\[
\left( \frac{0.1k}{2m} \right) \text{ for } k = 0
\]
Problems for Chapter 30

Zeno Redux

23.1.1.