

Molecular vibrations and rotations

Prof. dr. Ad van der Avoird

January 28, 2010

Contents

0.1	Books	2
0.2	Introduction	2
0.3	Vibrations of polyatomic molecules (harmonic)	3
0.3.1	Harmonic oscillator in one dimension x	3
0.3.2	Two coupled oscillators	5
0.3.3	Harmonic vibrations of molecules in mass-weighted coordinates	8
0.3.4	Harmonic vibrations of molecules in cartesian (displacement) coordinates	12
0.3.5	Invariance conditions on the matrix F	14
0.3.6	Vibrations in internal coordinates ($3n-6$)	18
0.4	Rotations of rigid (non-linear) molecules	21
0.4.1	Rotation matrices and infinitesimal rotations	22
0.4.2	The rigid rotor in classical mechanics	24
0.4.3	The rigid rotor Hamiltonian	31
0.4.4	The rigid rotor in quantum mechanics	34
0.5	The molecular vibration-rotation Hamiltonian	38
0.5.1	Introduction	38
0.5.2	The (classical) kinetic energy of a semi-rigid molecule	39
0.5.3	Semi-rigid molecules in quantum mechanics	44
0.5.4	Floppy molecules and Van der Waals molecules	46

0.1 Books

1. *Molecular vibrations*, E.B. Wilson, J.C. Decius, and P.C. Cross, McGraw-Hill, New York (1955)
2. *Vibrational states*, S. Califano, Wiley, London (1976)
3. *Molecular Vibrational-Rotational spectra*, D. Papousek and M.R. Aliev, Elsevier, Amsterdam (1982)
4. (*Angular momentum in quantum physics*, L.C. Biedenharn and J.D. Louck, Addison-Wesley, Reading (1981))

0.2 Introduction

Nuclear motion — Born-Oppenheimer approximation, second step

For n nuclei with coordinates $\underline{r}_k, k = 1, \dots, n$ the Schrödinger equation for the nuclear motion problem is given by:

$$\hat{H}(\underline{r}_1, \dots, \underline{r}_n)\Psi(\underline{r}_1, \dots, \underline{r}_n) = E\Psi(\underline{r}_1, \dots, \underline{r}_n) \quad (1)$$

with the Hamiltonian \hat{H} consisting of the kinetic and potential energy operators:

$$\hat{H}(\underline{r}_1, \dots, \underline{r}_n) = \hat{T}(\underline{r}_1, \dots, \underline{r}_n) + \hat{V}(\underline{r}_1, \dots, \underline{r}_n). \quad (2)$$

The potential energy $V(\underline{r}_1, \dots, \underline{r}_n)$ can be obtained from the electronic Schrödinger equation (Born-Oppenheimer approximation, first step). It is an energy eigenvalue of the electronic Hamiltonian with coordinates of the nuclei fixed at $\underline{r}_k, k = 1, \dots, n$. Variation of the nuclear coordinates \underline{r}_k yields the potential energy surface $V(\underline{r}_1, \dots, \underline{r}_n)$.

Solution of the nuclear motion Schrödinger equation for molecules
→ translations, rotations, vibrations

Spectroscopy: microwave, submillimeter, IR / Raman

0 – 30 cm^{-1}	rotations
100 – 5000 cm^{-1}	vibrations

Lasers → very high resolution (in principle)
(7 significant digits)

Doppler and collision broadening occurring in the gas phase are avoided in molecular beams (“supersonic nozzle beams”: very low T)

Globally:

rotational spectrum → molecular structure

vibrational spectrum → intramolecular forces (“force field”) associated with chemical bonds

spectra of van der Waals molecules → intermolecular (noncovalent) forces

0.3 Vibrations of polyatomic molecules (harmonic)

0.3.1 Harmonic oscillator in one dimension x

Momentum operator, in atomic units ($\hbar = 1$):

$$\hat{p}_x = \frac{1}{i} \frac{d}{dx} \quad (3)$$

The Hamiltonian of a harmonic oscillator is:

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} f \hat{x}^2 = -\frac{1}{2m} \frac{d^2}{dx^2} + \frac{1}{2} f \hat{x}^2, \quad (4)$$

where $f = \frac{d^2V}{dx^2}$ is the force constant. It is assumed that $\frac{dV}{dx} = 0$ (potential minimum) and that higher than second derivatives of V can be neglected.

It is convenient to introduce mass-weighted coordinates:

$$q = \sqrt{m}x \quad (5)$$

$$\hat{p} = \frac{1}{i\sqrt{m}} \frac{d}{dx} = \frac{1}{i} \frac{d}{dq} \quad (6)$$

and write:

$$\boxed{\hat{H} = \frac{1}{2} \hat{p}^2 + \frac{1}{2} \lambda \hat{q}^2} \quad (7)$$

where $\lambda = \frac{f}{m}$

The frequency of the harmonic oscillator is $\omega_0 = \sqrt{\lambda}$.

$$\text{Eigenvalues are the energies} \quad E_v = \omega_0 \left(v + \frac{1}{2} \right) \quad v = 0, 1, 2, \dots \quad (8)$$

$$\text{Eigenfunctions are} \quad \Psi_v(q) = H_v(\sqrt{\omega_0} q) \exp\left(-\frac{1}{2} \omega_0 q^2\right), \quad (9)$$

where H_v are Hermite polynomials.

0.3.2 Two coupled oscillators

Example 1:

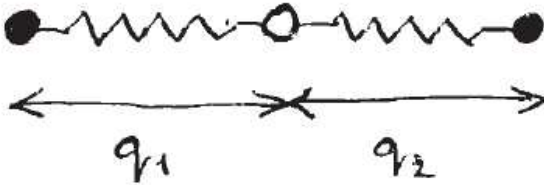


Figure 1: Linear CO₂ with two internal coordinates.

Example 2:

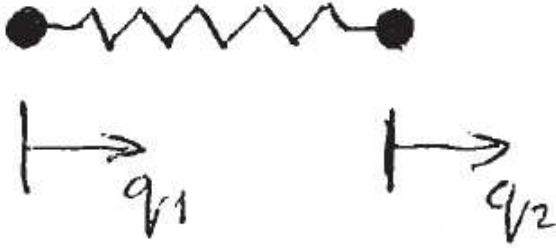


Figure 2: Diatomic molecule in laboratory coordinates.

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + \frac{1}{2}f_{11} \hat{q}_1^2 + \frac{1}{2}f_{22} \hat{q}_2^2 + f_{12} \hat{q}_1 \hat{q}_2 \quad (10)$$

Let us assume symmetry, so that $m_1 = m_2 = m$ and $f_{11} = f_{22}$. Define new coordinates:

$$Q_1 = (q_1 + q_2)/\sqrt{2} \quad q_1 = (Q_1 + Q_2)/\sqrt{2} \quad (11)$$

$$Q_2 = (q_1 - q_2)/\sqrt{2} \quad q_2 = (Q_1 - Q_2)/\sqrt{2} \quad (12)$$

The associated momentum operators are:

$$\hat{P}_1 = \frac{1}{i} \frac{\partial}{\partial Q_1} = \frac{1}{i} \left[\frac{\partial q_1}{\partial Q_1} \frac{\partial}{\partial q_1} + \frac{\partial q_2}{\partial Q_1} \frac{\partial}{\partial q_2} \right] = (\hat{p}_1 + \hat{p}_2)/\sqrt{2} \quad (13)$$

$$\hat{P}_2 = \frac{1}{i} \frac{\partial}{\partial Q_2} = (\hat{p}_1 - \hat{p}_2)/\sqrt{2} \quad (14)$$

Hence:

$$\hat{p}_1 = \frac{1}{i} \frac{\partial}{\partial q_1} = \frac{1}{i} \left[\frac{\partial Q_1}{\partial q_1} \frac{\partial}{\partial Q_1} + \frac{\partial Q_2}{\partial q_1} \frac{\partial}{\partial Q_2} \right] = (\hat{P}_1 + \hat{P}_2) / \sqrt{2} \quad (15)$$

$$\hat{p}_2 = \frac{1}{i} \frac{\partial}{\partial q_2} = (\hat{P}_1 - \hat{P}_2) / \sqrt{2} \quad (16)$$

Substitution of these new coordinates gives:

$$\begin{aligned} \hat{H} &= \frac{1}{4m} \left[(\hat{P}_1 + \hat{P}_2)^2 + (\hat{P}_1 - \hat{P}_2)^2 \right] + \frac{1}{4} f_{11} (\hat{Q}_1 + \hat{Q}_2)^2 + \\ &+ \frac{1}{2} f_{12} (\hat{Q}_1 + \hat{Q}_2) (\hat{Q}_1 - \hat{Q}_2) + \frac{1}{4} f_{22} (\hat{Q}_1 - \hat{Q}_2)^2 \end{aligned} \quad (17)$$

$$\begin{aligned} &= \frac{1}{2m} (\hat{P}_1^2 + \hat{P}_2^2) + \frac{1}{4} (f_{11} + f_{22} + 2f_{12}) \hat{Q}_1^2 + \\ &+ \frac{1}{4} (f_{11} + f_{22} - 2f_{12}) \hat{Q}_2^2 + \frac{1}{2} (f_{11} - f_{22}) \hat{Q}_1 \hat{Q}_2 \end{aligned} \quad (18)$$

The last term vanishes because $f_{11} = f_{22}$ and we get:

$$\hat{H} = \frac{1}{2m} \hat{P}_1^2 + \frac{1}{2} (f_{11} + f_{12}) \hat{Q}_1^2 + \frac{1}{2m} \hat{P}_2^2 + \frac{1}{2} (f_{11} - f_{12}) \hat{Q}_2^2 = \hat{H}_1 + \hat{H}_2. \quad (19)$$

As one can see, our system separates into two uncoupled oscillators, with:

$$\text{coordinates} \quad Q_1 = (q_1 + q_2) / \sqrt{2} \quad Q_2 = (q_1 - q_2) / \sqrt{2} \quad (20)$$

$$\text{frequencies} \quad \omega_1 = \left(\frac{f_{11} + f_{12}}{m} \right)^{1/2} \quad \omega_2 = \left(\frac{f_{11} - f_{12}}{m} \right)^{1/2} \quad (21)$$

The energy of the system is:

$$E = E_{v_1} + E_{v_2} = \omega_1 \left(v_1 + \frac{1}{2} \right) + \omega_2 \left(v_2 + \frac{1}{2} \right) \quad (22)$$

Example 1: CO₂

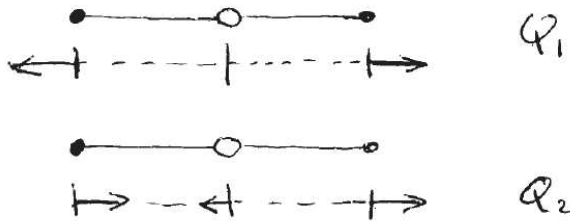


Figure 3: Q_1 and Q_2 for CO₂.

$$Q_1 = (q_1 + q_2)/\sqrt{2} \text{ — symmetric stretch vibration}$$

$$Q_2 = (q_1 - q_2)/\sqrt{2} \text{ — asymmetric stretch vibration}$$

Q_1 and Q_2 are called “normal mode” coordinates

Example 2: Diatomic molecule

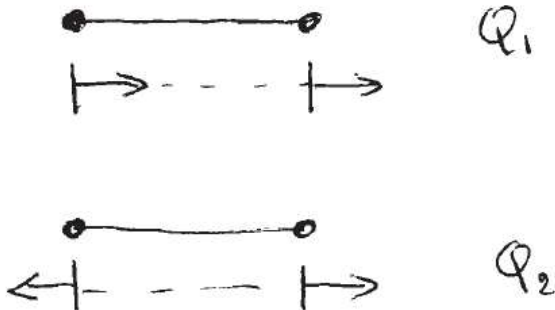


Figure 4: Q_1 and Q_2 for a diatomic molecule.

$$Q_1 = (q_1 + q_2)/\sqrt{2} \text{ — overall translation (center of mass motion)}$$

$$Q_2 = (q_1 - q_2)/\sqrt{2} \text{ — stretch vibration (relative motion)}$$

In Example 2 the molecule (center of mass) freely moves in space, the energy does **not** depend on Q_1 , and we get $\omega_1 = 0$. This corresponds to the **invariance condition**:

$$f_{11} + f_{12} (= f_{12} + f_{22}) = 0. \quad (23)$$

For the stretch vibration $Q_2 = (q_1 - q_2)/\sqrt{2}$ we find:

$$\omega_2 = \left(\frac{f_{11} - f_{12}}{m} \right)^{1/2} = \left(\frac{2f_{11}}{m} \right)^{1/2} = \left(\frac{f_{11}}{\mu} \right)^{1/2}, \quad (24)$$

where $\mu = \frac{m}{2}$ is the reduced mass.

Conclusion:

Both examples show that the simple transformation $Q_{1,2} = (q_1 \pm q_2)/\sqrt{2}$ separates the potential energy, while the kinetic energy remains separated. As a result we get two uncoupled harmonic oscillators.

0.3.3 Harmonic vibrations of molecules in mass-weighted coordinates

Coordinates of atoms:

$$\underline{r}_k = \underline{a}_k + \underline{d}_k \quad (k = 1, \dots, n) \quad (25)$$

where \underline{a}_k denotes equilibrium positions and \underline{d}_k stands for displacements. The components of the coordinates are:

$$\begin{pmatrix} x_k \\ y_k \\ z_k \end{pmatrix} = \begin{pmatrix} a_{kx} \\ a_{ky} \\ a_{kz} \end{pmatrix} + \begin{pmatrix} d_{kx} \\ d_{ky} \\ d_{kz} \end{pmatrix} \quad (26)$$

Altogether:

$$r_{k\alpha} = a_{k\alpha} + d_{k\alpha} \quad k = 1, \dots, n; \quad \alpha = 1, 2, 3(x, y, z) \quad (27)$$

$$r_i = a_i + d_i \quad i = 1, \dots, 3n \quad (28)$$

Atomic masses: m_k , $k = 1, \dots, n$, or m_i , $i = 1, \dots, 3n$

$$\begin{pmatrix} m_1 = m_2 = m_3 \\ m_4 = m_5 = m_6 \\ \text{etc.} \end{pmatrix}$$

Mass-weighted coordinates (for displacements):

$$q_i = \sqrt{m_i} d_i \quad (29)$$

Kinetic energy

Classical expression:

$$T = \frac{1}{2} \sum_i m_i \dot{d}_i^2 = \frac{1}{2} \sum_i \dot{q}_i^2 = \frac{1}{2} \sum_i p_i^2 \quad (30)$$

Quantum expression:

$$\hat{T} = \frac{1}{2} \sum_i \hat{p}_i^2 = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial q_i^2} \quad (31)$$

Potential energy:

$$V = V_0 + \sum_i \left(\frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots \quad (32)$$

$$= V_0 + \sum_i f_i q_i + \frac{1}{2} \sum_i \sum_j f_{ij} q_i q_j + \dots \quad (33)$$

Forces in equilibrium position are equal to zero:

$$f_i = \left(\frac{\partial V}{\partial q_i} \right)_0 = 0 \quad \text{for all } i = 1, \dots, 3n \quad (34)$$

V_0 is a constant (we will omit it). We use the harmonic approximation:

$$V = \frac{1}{2} \sum_{i,j} f_{ij} q_i q_j \quad (35)$$

Matrix - vector notation:

$$\underline{q} = \begin{pmatrix} q_1 \\ \vdots \\ q_i \\ \vdots \\ q_{3n} \end{pmatrix} \quad \underline{p} = \begin{pmatrix} p_1 \\ \vdots \\ p_i \\ \vdots \\ p_{3n} \end{pmatrix} \quad \underline{\underline{f}} = \begin{pmatrix} f_{11} & \dots & f_{1,3n} \\ \vdots & \ddots & \vdots \\ f_{3n,1} & \dots & f_{3n,3n} \end{pmatrix} \quad (36)$$

We use column-vectors, $\underline{\underline{f}}$ is the force constant matrix. Now the Hamiltonian may be written:

$$\boxed{H = \frac{1}{2} \underline{p}^T \underline{p} + \frac{1}{2} \underline{q}^T \underline{\underline{f}} \underline{q}} \quad (37)$$

We transform the coordinates as follows:

$$\underline{Q} = \underline{\underline{L}}^{-1} \underline{q} \quad \underline{q} = \underline{\underline{L}} \underline{Q} \quad (38)$$

For the momenta we get:

$$\underline{P} = \underline{\underline{L}}^T \underline{p} \quad \underline{p} = (\underline{\underline{L}}^T)^{-1} \underline{P} \quad (39)$$

Proof (comment by PG): we know that $q_k = L_{km}Q_m$. For coordinate Q_j the conjugate momentum is (we use the Einstein's summation convention and the chain rule)

$$\begin{aligned}\hat{P}_j &= \frac{1}{i} \frac{\partial}{\partial Q_j} = \frac{1}{i} \frac{\partial q_k}{\partial Q_j} \frac{\partial}{\partial q_k} = \frac{1}{i} \frac{\partial}{\partial Q_j} (L_{km}Q_m) \frac{\partial}{\partial q_k} = \\ &= \frac{1}{i} L_{km} \delta_{jm} \frac{\partial}{\partial q_k} = \frac{1}{i} L_{kj} \frac{\partial}{\partial q_k} = L_{kj} \hat{P}_k = (\underline{\underline{L}}^T)_{jk} \hat{P}_k\end{aligned}\quad (40)$$

Substitution of the new coordinates and momenta into H yields:

$$H = \frac{1}{2} \underline{\underline{P}}^T \underline{\underline{L}}^{-1} (\underline{\underline{L}}^{-1})^T \underline{\underline{P}} + \frac{1}{2} \underline{\underline{Q}}^T \underline{\underline{L}}^T \underline{\underline{f}} \underline{\underline{L}} \underline{\underline{Q}} \quad (41)$$

Let us choose $\underline{\underline{L}}$ such that it is real and:

$$\underline{\underline{L}}^{-1} (\underline{\underline{L}}^{-1})^T = \underline{\underline{E}} \quad (42)$$

Where $\underline{\underline{E}}$ is the identity matrix. Taking the inverse, it follows that:

$$\underline{\underline{L}}^T \underline{\underline{L}} = \underline{\underline{E}} \quad (43)$$

And for non-singular $\underline{\underline{L}}$ it also follows that:

$$\underline{\underline{L}}^T = \underline{\underline{L}}^{-1} \quad (44)$$

which means that $\underline{\underline{L}}$ is an **orthogonal** (and unitary, since it is real) matrix. We may further choose $\underline{\underline{L}}$ such that:

$$\underline{\underline{L}}^T \underline{\underline{f}} \underline{\underline{L}} = \underline{\underline{\Lambda}} \quad (45)$$

where $\underline{\underline{\Lambda}} = \begin{pmatrix} \lambda_1 & & 0 \\ & \ddots & \\ 0 & & \lambda_{3n} \end{pmatrix}$ is a **diagonal** matrix. Multiplying by $\underline{\underline{L}}$ gives

$$\boxed{\underline{\underline{f}} \underline{\underline{L}} = \underline{\underline{L}} \underline{\underline{\Lambda}}} \quad (46)$$

For i^{th} column of $\underline{\underline{L}}$, denoted by $\underline{\underline{L}}_i$, we have:

$$\underline{\underline{f}} \underline{\underline{L}}_i = \underline{\underline{L}}_i \lambda_i \quad (47)$$

which shows that $\underline{\underline{L}}_i$ is an eigenvector of $\underline{\underline{f}}$ with the eigenvalue λ_i . Thus to find $\underline{\underline{L}}$ we have to diagonalize $\underline{\underline{f}}$, i.e., to find eigenvectors and eigenvalues of $\underline{\underline{f}}$.

Substitution of these results into H yields:

$$H = \frac{1}{2} \underline{P}^T \underline{P} + \frac{1}{2} \underline{Q}^T \underline{\Lambda} \underline{Q} = \frac{1}{2} \sum_i P_i^2 + \frac{1}{2} \sum_i \lambda_i Q_i^2 = \frac{1}{2} \sum_i [P_i^2 + \lambda_i Q_i^2] \quad (48)$$

In other words the transformation $\underline{q} \rightarrow \underline{Q}$, $\underline{p} \rightarrow \underline{P}$ gave us $3n$ uncoupled harmonic oscillators. The frequencies are

$$\omega_i = \sqrt{\lambda_i} \quad (49)$$

The Q_i are called “normal coordinates”:

$$Q_i = \sum_j (\underline{L}^{-1})_{ij} q_j = \sum_j L_{ji} q_j \quad (50)$$

or:

$$\underline{Q} = \underline{L}^{-1} \underline{q} = \underline{L}^T \underline{q} \quad (51)$$

We used mass-weighted coordinates $q_i = \sqrt{m_i} d_i$, and we can write:

$$\underline{q} = \underline{M}^{1/2} \underline{d} \quad \text{with} \quad \underline{M} = \begin{pmatrix} m_1 & & & 0 \\ & m_2 & & \\ & & \ddots & \\ 0 & & & m_{3n} \end{pmatrix} \quad (52)$$

$\underline{M}^{1/2}$ has $m_i^{1/2}$ on the diagonal. The normal coordinates are then given in terms of atomic displacements by:

$$\boxed{\underline{Q} = \underline{L}^T \underline{M}^{1/2} \underline{d}} \quad (53)$$

Example: H_2O normal modes.

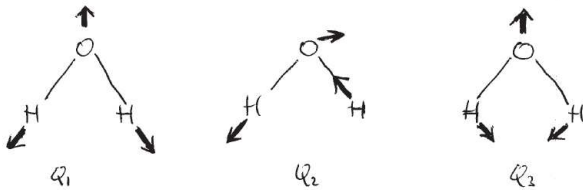


Figure 5: Normal modes of water molecule.

- Q_1 — symmetric stretch vibration

- Q_2 — asymmetric stretch vibration
- Q_3 — bending vibration
- + 3 overall translations (frequencies = 0)
- + 3 overall rotations (frequencies = 0)

0.3.4 Harmonic vibrations of molecules in cartesian (displacement) coordinates

\underline{d} — coordinates, $\underline{\underline{F}}$ — force constants

$$F_{ij} = \left(\frac{\partial^2 V}{\partial d_i \partial d_j} \right)_0 = m_i^{1/2} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 m_j^{1/2} = m_i^{1/2} f_{ij} m_j^{1/2} \quad (54)$$

$$\underline{\underline{F}} = \underline{\underline{M}}^{1/2} \underline{\underline{f}} \underline{\underline{M}}^{1/2} \quad \underline{\underline{f}} = \underline{\underline{M}}^{-1/2} \underline{\underline{F}} \underline{\underline{M}}^{-1/2} \quad (55)$$

The Hamiltonian of the system in simple cartesian coordinates (\underline{d} and \underline{p}_d , $p_{d,i} = \frac{1}{i} \frac{\partial}{\partial d_i} = \frac{1}{i} m_i^{1/2} \frac{\partial}{\partial q_i}$) is:

$$H = \frac{1}{2} \underline{p}_d^T \underline{\underline{M}}^{-1} \underline{p}_d + \frac{1}{2} \underline{d}^T \underline{\underline{F}} \underline{d} = \sum_i \frac{(p_d)_i^2}{2m_i} + \frac{1}{2} \sum_{i,j} F_{ij} d_i d_j \quad (56)$$

To uncouple H we return to normal coordinates \underline{Q} :

$$\underline{Q} = \underline{\underline{\mathcal{L}}}^{-1} \underline{d} \quad \underline{d} = \underline{\underline{\mathcal{L}}} \underline{Q} \quad (57)$$

$$\underline{p}_d = (\underline{\underline{\mathcal{L}}}^T)^{-1} \underline{P} \quad (58)$$

Applying this to H :

$$H = \frac{1}{2} \underline{P}^T \underline{\underline{\mathcal{L}}}^{-1} \underline{\underline{M}}^{-1} (\underline{\underline{\mathcal{L}}}^{-1})^T \underline{P} + \frac{1}{2} \underline{Q}^T \underline{\underline{\mathcal{L}}}^T \underline{\underline{F}} \underline{\underline{\mathcal{L}}} \underline{Q} \quad (59)$$

which becomes:

$$H = \frac{1}{2} \underline{P}^T \underline{P} + \frac{1}{2} \underline{Q}^T \underline{\underline{\Lambda}} \underline{Q} \quad (60)$$

if:

$$\underline{\underline{\mathcal{L}}}^T \underline{\underline{M}} \underline{\underline{\mathcal{L}}} = \underline{\underline{E}} \quad (61)$$

and

$$\underline{\underline{\mathcal{L}}}^T \underline{\underline{F}} \underline{\underline{\mathcal{L}}} = \underline{\underline{\Lambda}} \quad (62)$$

From the last equation we get:

$$\underline{\underline{F}} \underline{\underline{\mathcal{L}}} = (\underline{\underline{\mathcal{L}}}^T)^{-1} \underline{\underline{\Lambda}} \quad (63)$$

Substituting the previous one gives:

$$\boxed{\underline{\underline{F}} \underline{\underline{\mathcal{L}}} = \underline{\underline{M}} \underline{\underline{\mathcal{L}}} \underline{\underline{\Lambda}}} \quad (64)$$

so $\underline{\underline{\mathcal{L}}}$ must satisfy a generalized eigenvalue problem of $\underline{\underline{F}}$ with $\underline{\underline{M}}$ as the metric (or “overlap”) matrix.

From the equation $\underline{\underline{F}} = \underline{\underline{M}}^{1/2} \underline{\underline{f}} \underline{\underline{M}}^{1/2}$ follows directly the relation between the eigenvectors $\underline{\underline{L}}$ and $\underline{\underline{\mathcal{L}}}$:

$$\underline{\underline{\mathcal{L}}} = \underline{\underline{M}}^{-1/2} \underline{\underline{L}} \quad \underline{\underline{L}} = \underline{\underline{M}}^{1/2} \underline{\underline{\mathcal{L}}} \quad (65)$$

(It can be also easily seen from $\underline{\underline{q}} = \underline{\underline{L}} \underline{\underline{Q}}$, $\underline{\underline{d}} = \underline{\underline{\mathcal{L}}} \underline{\underline{Q}}$ and $\underline{\underline{q}} = \underline{\underline{M}}^{1/2} \underline{\underline{d}}$.)

Because $\underline{\underline{L}}^{-1} = \underline{\underline{L}}^T$ we have:

$$\underline{\underline{\mathcal{L}}}^{-1} = \underline{\underline{\mathcal{L}}}^T \underline{\underline{M}} \quad (66)$$

and the normal coordinates are given in terms of atomic displacements by:

$$\underline{\underline{Q}} = \underline{\underline{\mathcal{L}}}^{-1} \underline{\underline{d}} = \underline{\underline{\mathcal{L}}}^T \underline{\underline{M}} \underline{\underline{d}} \quad (67)$$

or:

$$Q_i = \underline{\underline{\mathcal{L}}}_i^T \underline{\underline{M}} \underline{\underline{d}} = \sum_i \mathcal{L}_{ji} m_j d_j \quad (68)$$

where $\underline{\underline{\mathcal{L}}}_i$ is the i^{th} column of $\underline{\underline{\mathcal{L}}}$.

Remember:

- the index i runs over eigenvalues λ_i and the associated normal coordinates Q_i
- the index $j = k\alpha$, $k = 1, \dots, n$, $\alpha = 1, 2, 3$ (x, y, z)

Thus

$$\boxed{Q_i = \sum_k \sum_\alpha \mathcal{L}_{k\alpha, i} m_k d_{k\alpha}} \quad (69)$$

0.3.5 Invariance conditions on the matrix $\underline{\underline{F}}$

We will now derive invariance conditions which show that **six** eigenvalues λ_i of the matrix $\underline{\underline{F}}$ are equal to zero. The associated normal coordinates correspond to overall **translations** and **rotations** of the whole molecule.

$$\begin{aligned} V &= V_0 + \sum_i \left(\frac{\partial V}{\partial d_i} \right)_0 d_i + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 V}{\partial d_i \partial d_j} \right)_0 d_i d_j = \\ &= V_0 + \sum_{k=1}^n \sum_{\alpha=1,2,3} \underbrace{\left(\frac{\partial V}{\partial d_{k\alpha}} \right)_0}_{=0} d_{k\alpha} + \frac{1}{2} \sum_{k,l=1}^n \sum_{\alpha,\beta} F_{k\alpha,l\beta} d_{k\alpha} d_{l\beta} \end{aligned} \quad (70)$$

The force acting on atom k in the direction $\alpha = x, y, z$ is:

$$\frac{\partial V}{\partial d_i} = \frac{\partial V}{\partial d_{k\alpha}} = \underbrace{\left(\frac{\partial V}{\partial d_{k\alpha}} \right)_0}_{=0} + \sum_{l=1}^n \sum_{\beta} F_{k\alpha,l\beta} d_{l\beta} \quad (71)$$

Translational invariance: this force should not change if we move all atoms by the same distance: $d_{l\beta} = \delta_\beta$ for $l = 1, \dots, n$, hence

$$0 = \sum_{l=1}^n \sum_{\beta} F_{k\alpha,l\beta} \delta_\beta = \sum_{\beta} \delta_\beta \sum_{l=1}^n F_{k\alpha,l\beta} \quad (72)$$

As this should apply to any $\underline{\delta}$ we must require that

$$\boxed{\sum_{l=1}^n F_{k\alpha,l\beta} = 0} \quad (73)$$

for all $k = 1, \dots, n; \alpha = 1, 2, 3; \beta = 1, 2, 3(x, y, z)$

This is the first set of invariance conditions. Note that summation here is over l , with fixed k, α and β . Different k, α and β give different conditions, so indeed we have here a **set** of invariance conditions.

Equation (64) ($\underline{\underline{F}} \underline{\underline{\mathcal{L}}} = \underline{\underline{M}} \underline{\underline{\mathcal{L}}} \underline{\underline{\Lambda}}$) written in components is:

$$\sum_j F_{ij} \mathcal{L}_{jr} = \sum_j m_i \mathcal{L}_{ij} \Lambda_{jr} = m_i \mathcal{L}_{ir} \lambda_r \quad (74)$$

The matrix elements \mathcal{L}_{jr} for $j = 1, \dots, 3n$ form the r^{th} column of $\underline{\underline{\mathcal{L}}}$ i.e. the r^{th} eigenvector $\underline{\underline{\mathcal{L}}}_r$

$$\begin{matrix} i = (k, \alpha) \\ j = (l, \beta) \end{matrix} \sum_{l=1}^n \sum_{\beta} F_{k\alpha,l\beta} \mathcal{L}_{l\beta,r} = m_k \mathcal{L}_{k\alpha,r} \lambda_r \quad (75)$$

Now suppose that

$$\mathcal{L}_{l\beta,r} = \begin{cases} 1 & \text{for all } l = 1, \dots, n \text{ and for } \beta = 1 \\ 0 & \text{for } \beta = 2, 3 \end{cases} \quad (76)$$

It follows immediately from the invariance condition, eq. (73) that the left hand side of equation (75) equals 0. Thus also the right hand side must be equal to 0 and, since not all components of $\underline{\mathcal{L}}_r$ are equal to zero, λ_r must be equal to zero. So we have found one eigenvalue $\lambda_r = 0$ and the associated eigenvector $\underline{\mathcal{L}}_r$ with components = 1 for $\beta = 1$ and = 0 for $\beta = 2, 3$. Similarly we find two more eigenvalues $\lambda_{r'} = \lambda_{r''} = 0$ with eigenvectors $\underline{\mathcal{L}}_{r'}$ and $\underline{\mathcal{L}}_{r''}$ that have components in the directions $\beta = 2$ and $\beta = 3$. Let us call these three eigenvalues:

$$\boxed{\lambda_1 = \lambda_2 = \lambda_3 = 0} \quad (77)$$

The associated normal coordinates are:

$$Q_r = \sum_{k\alpha} \mathcal{L}_{k\alpha,r} m_k d_{k\alpha} \quad (78)$$

Substituting the conditions for $\underline{\mathcal{L}}_r$ into this general formula leads to:

$$\begin{aligned} Q_1 &= \sum_{k=1}^n m_k d_{k1} \\ Q_2 &= \sum_{k=1}^n m_k d_{k2} \\ Q_3 &= \sum_{k=1}^n m_k d_{k3} \end{aligned} \quad (79)$$

This can be written in a more compact way:

$$\boxed{\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \sum_{k=1}^n m_k \underline{d}_k} \quad (80)$$

These are the normal coordinates for the overall translations of the molecule ($\lambda_1 = \lambda_2 = \lambda_3 = 0$). In fact, they are the coordinates of the center of mass of the molecule.

Rotational invariance

We will now see how all the atoms move when we rotate the whole molecule and we will again require that the forces on the atoms do not change during this movement.

We rotate the molecule around the axis \underline{e}_γ , $\gamma = 1, 2, 3 (= x, y, z)$ over an angle $\Delta\varphi_\gamma$. For very small (infinitesimal) rotations it turns out that a vector \underline{r}_0 changes as follows:

$$\underline{r} = \underline{r}_0 + \Delta\varphi_\gamma \underline{e}_\gamma \times \underline{r}_0 \quad (81)$$

(This will be demonstrated in chapter 3.) Atom k has equilibrium position \underline{a}_k . After the rotation of the molecule its position becomes

$$\underline{r}_k = \underline{a}_k + \underline{d}_k = \underline{a}_k + \Delta\varphi_\gamma \underline{e}_\gamma \times \underline{a}_k \quad (82)$$

Thus the displacement of the k^{th} atom is:

$$\underline{d}_k = \Delta\varphi_\gamma \underline{e}_\gamma \times \underline{a}_k \quad (83)$$

The force acting on atom k in the direction α was zero when the atom was in its equilibrium position, and it must still be zero after we rotated the whole molecule (because the relative positions of the atoms did not change):

$$0 = \left(\frac{\partial V}{\partial d_{k\alpha}} \right) = \sum_l \sum_\beta F_{k\alpha, l\beta} d_{l\beta} \quad (84)$$

After substituting $d_{l\beta}$:

$$0 = \sum_{l=1}^n \sum_\beta F_{k\alpha, l\beta} \Delta\varphi_\gamma (\underline{e}_\gamma \times \underline{a}_l)_\beta \quad (85)$$

As this should apply to any $\Delta\varphi_\gamma$ for $\gamma = 1, 2$ and 3 we must require that the following invariance conditions are fulfilled:

$$\boxed{\sum_{\beta=1,2,3} \sum_{l=1}^n F_{k\alpha, l\beta} (\underline{e}_\gamma \times \underline{a}_l)_\beta = 0} \quad (86)$$

for $k = 1, \dots, n, \alpha = 1, 2, 3, \gamma = 1, 2, 3 (= x, y, z)$

It follows that the vector $\underline{\mathcal{L}}_r$ with components $\mathcal{L}_{k\alpha, r} = (\underline{e}_\gamma \times \underline{a}_k)_\alpha$ is an eigenvector of $\underline{\underline{F}}$ with eigenvalue $\lambda_r = 0$. There are three such vectors: $\gamma = 1, 2, 3$. Let us label these eigenvectors with $r = 4, 5, 6$. Associated normal coordinates are:

$$Q_{\gamma+3} = \sum_{k=1}^n \sum_{\alpha=1,2,3} m_k (\underline{e}_\gamma \times \underline{a}_k)_\alpha d_{k\alpha} = \sum_{k=1}^n m_k (\underline{e}_\gamma \times \underline{a}_k) \cdot \underline{d}_k \quad (87)$$

The vector product satisfies the relation:

$$(\underline{a} \times \underline{b}) \cdot \underline{c} = \underline{a} \cdot (\underline{b} \times \underline{c}) \quad (88)$$

Using this relation we get:

$$Q_{\gamma+3} = \sum_{k=1}^n m_k \underline{e}_\gamma \cdot (\underline{a}_k \times \underline{d}_k) \quad (89)$$

The vectors \underline{e}_1 , \underline{e}_2 and \underline{e}_3 are unit vectors along the axes of the Cartesian coordinate system:

$$\underline{e}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \underline{e}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \underline{e}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (90)$$

As a result we have:

$$\begin{pmatrix} Q_4 \\ Q_5 \\ Q_6 \end{pmatrix} = \sum_{k=1}^n m_k \underline{a}_k \times \underline{d}_k \quad (91)$$

These are the normal coordinates of **overall rotations** of the molecule. The associated eigenvalues are $\lambda_4 = \lambda_5 = \lambda_6 = 0$.

So far we have found six normal coordinates of the molecule (Q_1, \dots, Q_6), that correspond with eigenvalues $\lambda_1 = \dots = \lambda_6 = 0$. The remaining normal coordinates Q_i

$$Q_i = \sum_k \sum_\alpha m_k \mathcal{L}_{k\alpha,i} d_{k\alpha} = \underline{\mathcal{L}}_i^T \underline{M} \underline{d} \quad (92)$$

must be found as the eigenvectors of the matrix \underline{F} , with “overlap matrix” \underline{M} . For these eigenvectors we have:

$$\underline{\mathcal{L}}_i^T \underline{M} \underline{\mathcal{L}}_j = \underline{E} \quad (93)$$

where \underline{E} is the unit matrix. Thus

$$\underline{\mathcal{L}}_i^T \underline{M} \underline{\mathcal{L}}_j = \delta_{ij} \quad (94)$$

The coordinates Q_1, Q_2, Q_3 describe the **translations** of (the center of mass of) the molecule, the coordinates Q_4, Q_5, Q_6 describe the overall **rotations**, the remaining Q_i are the $(3n - 6)$ “real” vibrations. We want to separate these “real” vibrations from the rotations and translations. This can be achieved by using a “molecule-fixed” coordinate system that rotates and

translates with the molecule. Such a system is defined by requiring that at every moment the following conditions are satisfied:

$$\begin{cases} \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \sum_{k=1}^n m_k \underline{d}_k = 0 \\ \begin{pmatrix} Q_4 \\ Q_5 \\ Q_6 \end{pmatrix} = \sum_{k=1}^n m_k \underline{a}_k \times \underline{d}_k = 0 \end{cases} \quad (95)$$

These are the so-called **Eckhart conditions**. (Compare to equations (80) and (91).) Setting Q_1, Q_2, Q_3 equal to zero implies that the origin of the molecule-fixed coordinate system is the center of mass of the molecule. Setting Q_4, Q_5, Q_6 equal to zero minimizes the coupling between rotations and vibrations. The latter coupling cannot be completely removed, however, in contrast with the coupling between vibrations and translations. All of this will be explained below.

0.3.6 Vibrations in internal coordinates ($3n-6$)

1. Bond lengths r_{kl}
2. Bending angles Θ_{kln}
3. Out-of-plane wagging Θ_{klmn}
4. Torsion angles τ_{klmn}



Figure 6: Example: Internal coordinates of water molecule ($s_1 = \Delta r_{kl}$, $s_2 = \Delta r_{km}$, $s_3 = \Delta \Theta_{klm}$).

The Cartesian coordinates \underline{r}_k are functions of the internal coordinates, and this also applies to the displacements \underline{d}_k . There are $3n$ Cartesian coordinates \underline{d}_k , for $k = 1, \dots, n$, but $3n - 6$ internal coordinates \underline{s} . Besides the internal coordinates \underline{s} , there are also 3 coordinates that describe the position of the molecule in space (actually the position of the center of mass) and 3 angle coordinates that describe the orientation of the molecule.

The force constants F_{ij} of the molecule in Cartesian coordinates have little physical meaning. Rather, we know the force constants related to bond lengths, bond angles, etc. — the internal coordinates \underline{s} — these force constants form the matrix $\underline{\mathcal{F}}$:

$$\mathcal{F}_{ij} = \left(\frac{\partial^2 V}{\partial s_i \partial s_j} \right) \quad (96)$$

The harmonic approximation of the potential in the internal coordinates \underline{s} is:

$$V = \frac{1}{2} \underline{s}^T \underline{\mathcal{F}} \underline{s} \quad (97)$$

We need to write also the kinetic energy in terms of the internal coordinates \underline{s} . To achieve this, we first define the transformation

$$\underline{s} = \underline{\underline{B}} \underline{d} \quad (98)$$

- \underline{d} is a column vector of length $3n$
- \underline{s} is a column vector of length $3n - 6$
- $\underline{\underline{B}}$ is a matrix of dimension $(3n - 6) \times (3n)$

If \underline{s} is a small (infinitesimal) change of the internal coordinates, and \underline{d} is a small change of the Cartesian displacements, then:

$$B_{ij} = \frac{\partial s_i}{\partial d_j} \quad (99)$$

Example H₂O - see Figure 6:

$$s_1 = \Delta r_{kl} \quad (100)$$

$$r_{kl} = [(x_k - x_l)^2 + (y_k - y_l)^2 + (z_k - z_l)^2]^{1/2} \quad (101)$$

$$\frac{\partial s_1}{\partial x_k} = \frac{1}{2} [\dots]^{-1/2} \cdot 2(x_k - x_l) = \frac{x_k - x_l}{r_{kl}} \quad (102)$$

$$\frac{\partial s_1}{\partial x_l} = \frac{x_l - x_k}{r_{kl}} = -\frac{\partial s_1}{\partial x_k} \quad (103)$$

These elements, together with derivatives with respect to y_k, y_l, z_k and z_l , form the 1st row of the matrix $\underline{\underline{B}}$. The remaining elements of this row are equal to zero.

$$s_3 = \Delta\Theta_{klm} \quad (104)$$

$$\cos \Theta_{klm} = \frac{\underline{r}_{kl} \cdot \underline{r}_{km}}{r_{kl}r_{km}} \quad (105)$$

Differentiation would give us the elements of the third row of the $\underline{\underline{B}}$ matrix. In a similar way we compute all the elements of the matrix.

For the usual types of coordinates 1 — 4 you can find the derivatives in the books of Wilson, Decius, and Cross and of Califano. All derivatives must be calculated for the equilibrium structure of the molecule.

$\underline{\underline{B}}$ is not a square matrix, so $\underline{\underline{B}}^{-1}$ is not defined. The remedy is to add to \underline{s} the 6 coordinates Q_1, \dots, Q_6 of translation and rotation of the whole molecule. These also are (already presented) linear combinations of \underline{d} (see section E). After adding these 6 rows $\underline{\underline{B}}$ becomes a square and non-singular matrix, so it is possible to write:

$$\underline{d} = \underline{\underline{B}}^{-1} \underline{s} \quad (106)$$

For the momenta \underline{p}_s , conjugate to \underline{s} we have:

$$\underline{p}_s = (\underline{\underline{B}}^{-1})^T \underline{p}_d \quad \underline{p}_d = \underline{\underline{B}}^T \underline{p}_s \quad (107)$$

Now we can write the Hamiltonian of the molecule as follows:

$$\begin{aligned} H = T + V &= \frac{1}{2} \underline{p}_d^T \underline{\underline{M}}^{-1} \underline{p}_d + \frac{1}{2} \underline{d}^T \underline{\underline{F}} \underline{d} = \\ &= \frac{1}{2} \underline{p}_s^T \underline{\underline{B}} \underline{\underline{M}}^{-1} \underline{\underline{B}}^T \underline{p}_s + \frac{1}{2} \underline{s}^T \underline{\underline{\mathcal{F}}} \underline{s} \end{aligned} \quad (108)$$

where

$$\underline{\underline{\mathcal{F}}} = (\underline{\underline{B}}^{-1})^T \underline{\underline{F}} \underline{\underline{B}}^{-1}. \quad (109)$$

We define the matrix $\underline{\underline{\mathcal{G}}}$:

$$\underline{\underline{\mathcal{G}}} = \underline{\underline{B}} \underline{\underline{M}}^{-1} \underline{\underline{B}}^T. \quad (110)$$

Then we can write

$$H = \frac{1}{2} \underline{p}_s^T \underline{\underline{\mathcal{G}}} \underline{p}_s + \frac{1}{2} \underline{s}^T \underline{\underline{\mathcal{F}}} \underline{s} \quad (111)$$

We want to uncouple the Hamiltonian:

$$H = \frac{1}{2} \sum_i (P_i^2 + \lambda_i Q_i^2) = \frac{1}{2} \underline{P}^T \underline{P} + \frac{1}{2} \underline{Q}^T \underline{\underline{\Lambda}} \underline{Q} \quad (112)$$

To do this we must return to the normal coordinates. We use the transformation:

$$\underline{s} = \underline{\mathcal{L}}' Q \quad (113)$$

Through an analogy to what we have already seen, we derive conditions:

$$(\underline{\mathcal{L}}')^T \underline{\mathcal{G}}^{-1} \underline{\mathcal{L}}' = \underline{E} \quad (114)$$

$$(\underline{\mathcal{L}}')^T \underline{\mathcal{F}} \underline{\mathcal{L}}' = \underline{\Lambda} \quad (115)$$

$$(116)$$

We can combine these two equations into one:

$$\underline{\mathcal{F}} \underline{\mathcal{L}}' = \left(\underline{\mathcal{L}}'^T \right)^{-1} \underline{\Lambda} = \underline{\mathcal{G}}^{-1} \underline{\mathcal{L}}' \underline{\Lambda} \quad (117)$$

This is a generalised eigenvalue problem of the matrix $\underline{\mathcal{F}}$ with “overlap matrix” $\underline{\mathcal{G}}^{-1}$. As we can see, $\underline{\mathcal{G}}^{-1}$ is indeed symmetric:

$$\underline{\mathcal{G}}^{-1} = \left(\underline{B}^{-1} \right)^T \underline{M} \underline{B}^{-1} \quad (118)$$

After multiplying equation (117) by $\underline{\mathcal{G}}$ from the left side:

$$\boxed{\begin{aligned} \underline{\mathcal{G}} \underline{\mathcal{F}} \underline{\mathcal{L}}' &= \underline{\mathcal{L}}' \underline{\Lambda} \\ \underline{\mathcal{G}} \underline{\mathcal{F}} \underline{\mathcal{L}}'_i &= \underline{\mathcal{L}}'_i \lambda_i \end{aligned}} \quad (119)$$

This is the eigenvalue problem of the matrix $\underline{\mathcal{G}} \underline{\mathcal{F}}$. This method is called “**Wilson’s GF matrix method**”.

The dimension of this method is $3n - 6$, as we can omit the 6 rows associated with Q_i in \underline{B} (we don’t need \underline{B}^{-1} in $\underline{\mathcal{G}} = \underline{B} \underline{M}^{-1} \underline{B}^T$) and we define $\underline{\mathcal{F}}$ as $\mathcal{F}_{ij} = \left(\frac{\partial^2 V}{\partial s_i \partial s_j} \right)$. The internal coordinates do not change when the whole molecule is translated or rotated. That is, the Eckart conditions are automatically taken into account.

0.4 Rotations of rigid (non-linear) molecules

See also: Paul Wormer, Courses and teaching material

<http://www.theochem.ru.nl/pwormer/teachmat.html>

The rigid rotor in classical and quantum mechanics

0.4.1 Rotation matrices and infinitesimal rotations

Choose a coordinate frame that “rotates with the molecule” — such a frame is called a **body-fixed (BF) frame**. So the orientation of the molecule is defined by the orientation of the BF frame relative to the **laboratory = space fixed (SF) frame**.

Hence, the orientation of the molecule, i.e., the orientation of the BF axes, with respect to the SF frame is described by a 3×3 matrix of direction cosines: the rotation matrix $\underline{\underline{C}}$.

Any orientation (rotation) can be described by three Euler angles φ, ϑ, χ :

rotate around the z -axis over $\varphi \rightarrow x', y', z'$ axes (z' axis = z axis)

rotate around the y' -axis over $\vartheta \rightarrow x'', y'', z''$ axes (y'' axis = y' axis)

rotate around the z'' -axis over χ

The corresponding rotation matrices (containing direction cosines) are:

$$\underline{\underline{C}}_z(\varphi) = \begin{pmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \underline{\underline{C}}_{y'}(\vartheta) = \begin{pmatrix} \cos \vartheta & 0 & \sin \vartheta \\ 0 & 1 & 0 \\ -\sin \vartheta & 0 & \cos \vartheta \end{pmatrix} \quad (120)$$

For rotations around the x -axis we have:

$$\underline{\underline{C}}_x(\alpha) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & -\sin \alpha \\ 0 & \sin \alpha & \cos \alpha \end{pmatrix} \quad (121)$$

The Euler (three-angle) rotation matrix is:

$$\underline{\underline{C}}(\varphi, \vartheta, \chi) = \underline{\underline{C}}_{z''}(\chi)\underline{\underline{C}}_{y'}(\vartheta)\underline{\underline{C}}_z(\varphi), \quad (122)$$

which can also be written as (prove this!):

$$\underline{\underline{C}}(\varphi, \vartheta, \chi) = \underline{\underline{C}}_z(\varphi)\underline{\underline{C}}_{y'}(\vartheta)\underline{\underline{C}}_x(\chi) \quad (123)$$

We define the so-called Lie derivatives or **infinitesimal rotations** $\underline{\underline{J}}_x, \underline{\underline{J}}_y, \underline{\underline{J}}_z$:

$$\underline{\underline{J}}_z = \left(\frac{d\underline{\underline{C}}_z(\varphi)}{d\varphi} \right)_{\varphi=0} = \begin{pmatrix} -\sin \varphi & -\cos \varphi & 0 \\ \cos \varphi & -\sin \varphi & 0 \\ 0 & 0 & 0 \end{pmatrix}_{\varphi=0} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (124)$$

$$\underline{\underline{J}}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \quad \underline{\underline{J}}_y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}$$

Any vector can be decomposed as:

$$\underline{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = x\underline{e}_1 + y\underline{e}_2 + z\underline{e}_3 \quad (125)$$

in term of unit vectors:

$$\underline{e}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \underline{e}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \underline{e}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (126)$$

The infinitesimal rotations of the vector \underline{r} are:

$$\begin{aligned} \underline{\underline{J}}_x \underline{r} &= \begin{pmatrix} 0 \\ -z \\ y \end{pmatrix} = \underline{e}_1 \times \underline{r} \\ \underline{\underline{J}}_y \underline{r} &= \begin{pmatrix} z \\ 0 \\ -x \end{pmatrix} = \underline{e}_2 \times \underline{r} \\ \underline{\underline{J}}_z \underline{r} &= \begin{pmatrix} -y \\ x \\ 0 \end{pmatrix} = \underline{e}_3 \times \underline{r} \end{aligned} \quad (127)$$

Any infinitesimal rotation $\underline{\omega} = \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$ can be described as

$$\begin{aligned} \underline{\underline{J}}_{\underline{\omega}} &= \omega_x \underline{\underline{J}}_x + \omega_y \underline{\underline{J}}_y + \omega_z \underline{\underline{J}}_z = \\ &= \begin{pmatrix} 0 & -\omega_z & \omega_y \\ \omega_z & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \end{pmatrix} = \underline{\underline{\Omega}} \end{aligned} \quad (128)$$

— this is the most arbitrary antisymmetric 3×3 matrix (any 3×3 antisymmetric matrix can be written in this way).

It is easy to verify that

$$\boxed{\underline{\underline{J}}_{\underline{\omega}} \underline{r} = \underline{\underline{\Omega}} \underline{r} = \underline{\omega} \times \underline{r}} \quad (129)$$

Furthermore, it follows that:

$$\frac{d\underline{\underline{C}}_z(\varphi)}{d\varphi} = \begin{pmatrix} -\sin \varphi & -\cos \varphi & 0 \\ \cos \varphi & -\sin \varphi & 0 \\ 0 & 0 & 0 \end{pmatrix} = \underline{\underline{J}}_z \underline{\underline{C}}_z(\varphi) = \underline{\underline{C}}_z(\varphi) \underline{\underline{J}}_z \quad (130)$$

0.4.2 The rigid rotor in classical mechanics

A set of particles (atoms) has the coordinates $\underline{r}_k(t)$ in the laboratory (SF) frame. Their masses are m_k .

The position vector of the center of mass is:

$$\underline{R}(t) = M^{-1} \sum_{k=1}^n m_k \underline{r}_k(t) \quad (131)$$

with M denoting the total mass, $M = \sum_k m_k$.

In a coordinate frame which moves with $\underline{R}(t)$, but has axes parallel to the axes of the laboratory (SF) frame, the atoms have coordinates:

$$\underline{\rho}_k(t) = \underline{r}_k(t) - \underline{R}(t) \quad (132)$$

It follows that:

$$\boxed{\sum_k m_k \underline{\rho}_k(t) = \underline{0} \quad \text{at each time } t} \quad (133)$$

(prove this). In other words: the position vector of the center of mass is $\underline{0}$ in the center of mass frame.

We assume that the particles (atoms) belong to a moving rigid body (molecule). We define a rotating (BF) coordinate frame so that any time t :

$$\underline{\rho}_k(t) = \underline{\underline{C}}(\varphi(t), \vartheta(t), \chi(t)) \underline{a}_k \quad (134)$$

The vectors \underline{a}_k are the constant position vectors of the atoms in the BF coordinate frame that rotates with the molecule. The angles $\varphi(t)$, $\vartheta(t)$, $\chi(t)$ are the Euler angles describing the orientation of the BF frame with respect to the SF frame at time t .

Finally, we can write:

$$\boxed{\underline{r}_k(t) = \underline{R}(t) + \underline{\underline{C}}(\varphi(t), \vartheta(t), \chi(t)) \underline{a}_k} \quad (135)$$

with

- $\underline{r}_k(t)$ — coordinates of atom k in the laboratory (SF) frame
- $\underline{R}(t)$ — coordinates of the center of mass in the laboratory (SF) frame
- $\underline{\underline{C}}(\varphi(t), \vartheta(t), \chi(t))$ — rotation matrix containing direction cosines of the rotating BF axes in the laboratory (SF) frame

· \underline{a}_k — constant position vector of atom k in BF coordinates

The velocities of the atoms are:

$$\underline{v}_k(t) = \frac{\partial \underline{r}_k(t)}{\partial t} = \dot{\underline{r}}_k(t) \quad (136)$$

$$\begin{aligned} \dot{\underline{r}}_k(t) &= \dot{\underline{R}}(t) + \underline{\underline{C}}(\varphi(t), \vartheta(t), \chi(t)) \underline{a}_k \\ &= \dot{\underline{R}}(t) + \underline{\underline{C}}(\varphi, \vartheta, \chi) \underline{\underline{C}}^{-1}(\varphi, \vartheta, \chi) \underline{\rho}_k(t) \end{aligned} \quad (137)$$

Rotation matrices are orthogonal:

$$\boxed{\underline{\underline{C}}^{-1} = \underline{\underline{C}}^T} \quad (138)$$

Theorem: The matrix $\underline{\underline{C}} \underline{\underline{C}}^{-1} = \underline{\underline{C}} \underline{\underline{C}}^T$ is an antisymmetric matrix.

Proof:

$$\begin{aligned} \underline{\underline{C}} \underline{\underline{C}}^T &= \underline{\underline{E}} \quad \text{identity matrix} \\ \underline{\underline{C}} \underline{\underline{C}}^T + \underline{\underline{C}} \underline{\underline{C}}^T &= \underline{\underline{0}} \end{aligned} \quad (139)$$

Hence

$$\underline{\underline{C}} \underline{\underline{C}}^T = -\underline{\underline{C}} \underline{\underline{C}}^T = -\left(\underline{\underline{C}} \underline{\underline{C}}^T\right)^T \quad (140)$$

Let us assume that:

$$\boxed{\underline{\underline{C}} \underline{\underline{C}}^T = \underline{\underline{\Omega}} = \begin{pmatrix} 0 & -\omega_z & \omega_y \\ \omega_z & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \end{pmatrix}} \quad (141)$$

Theorem:

The relation between the angular velocity $\underline{\omega}$ and the time derivatives

$\underline{\dot{q}} = \begin{pmatrix} \dot{\varphi} \\ \dot{\vartheta} \\ \dot{\chi} \end{pmatrix} = \frac{\partial}{\partial t} \begin{pmatrix} \varphi \\ \vartheta \\ \chi \end{pmatrix}$ of the Euler angles is given by:

$$\boxed{\underline{\omega} = \underline{\underline{U}} \begin{pmatrix} \dot{\varphi} \\ \dot{\vartheta} \\ \dot{\chi} \end{pmatrix} = \underline{\underline{U}} \underline{\dot{q}}} \quad (142)$$

with

$$\boxed{\underline{\underline{U}} = \begin{pmatrix} 0 & -\sin \varphi & \cos \varphi \sin \vartheta \\ 0 & \cos \varphi & \sin \varphi \sin \vartheta \\ 1 & 0 & \cos \vartheta \end{pmatrix}} \quad (143)$$

Proof:

$$\begin{aligned}\underline{\dot{C}}(\varphi, \vartheta, \chi) &= \underline{\dot{C}}_z(\varphi)\underline{C}_y(\vartheta)\underline{C}_z(\chi) \\ &+ \underline{C}_z(\varphi)\underline{\dot{C}}_y(\vartheta)\underline{C}_z(\chi) + \underline{C}_z(\varphi)\underline{C}_y(\vartheta)\underline{\dot{C}}_z(\chi)\end{aligned}\quad (144)$$

$$\underline{\dot{C}}_z(\varphi) = \frac{\partial}{\partial t}\underline{C}_z(\varphi) = \frac{\partial \underline{C}_z(\varphi)}{\partial \varphi} \frac{\partial \varphi}{\partial t} = \underline{J}_z \underline{C}_z(\varphi) \dot{\varphi} \quad (145)$$

$$\begin{aligned}\underline{\Omega} &= \underline{\dot{C}} \underline{C}^T = \underline{J}_z \left[\underline{C}_z(\varphi) \underline{C}_y(\vartheta) \underline{C}_z(\chi) \underline{C}_z^T(\chi) \underline{C}_y^T(\vartheta) \underline{C}_z^T(\varphi) \right] \dot{\varphi} \\ &+ \underline{C}_z(\varphi) \underline{J}_y \left[\underline{C}_y(\vartheta) \underline{C}_z(\chi) \underline{C}_z^T(\chi) \underline{C}_y^T(\vartheta) \right] \underline{C}_z^T(\varphi) \dot{\vartheta} \\ &+ \underline{C}_z(\varphi) \underline{C}_y(\vartheta) \underline{J}_z \left[\underline{C}_z(\chi) \underline{C}_z^T(\chi) \right] \underline{C}_y^T(\vartheta) \underline{C}_z^T(\varphi) \dot{\chi}\end{aligned}\quad (146)$$

Each “box” yields the identity matrix \underline{E} (because rotation matrices are orthogonal), so we have:

$$\underline{\Omega} = \underline{J}_z \dot{\varphi} + \underline{C}_z(\varphi) \underline{J}_y \underline{C}_z^T(\varphi) \dot{\vartheta} + \underline{C}_z(\varphi) \underline{C}_y(\vartheta) \underline{J}_z \underline{C}_y^T(\vartheta) \underline{C}_z^T(\varphi) \dot{\chi} \quad (147)$$

Substitution of eq. (120) for the matrices \underline{C}_z and \underline{C}_y and eq. (124) for \underline{J}_z and \underline{J}_y , and using the relation in eq. (128) between $\underline{\Omega}$ and $\underline{\omega}$ proves eqs. (142) and (143).

As a result we can express the velocities of the atoms as:

$$\begin{aligned}\dot{\underline{r}}_k(t) &= \dot{\underline{R}}(t) + \underline{\dot{C}} \underline{C}^T \underline{\rho}_k(t) \\ &= \dot{\underline{R}}(t) + \underline{\Omega} \underline{\rho}_k(t)\end{aligned}\quad (148)$$

One may remember that multiplication of the vector $\underline{\rho}_k(t)$ by the antisymmetric matrix $\underline{\Omega}$ can be replaced by taking the vector product $\underline{\omega} \times \underline{\rho}_k(t)$:

$$\dot{\underline{r}}_k(t) = \dot{\underline{R}}(t) + \underline{\omega} \times \underline{\rho}_k(t) \quad (149)$$

Because $\underline{\rho}_k(t)$ is the velocity of atom k in a coordinate frame that moves with the center of mass, but **does not rotate**, it follows that $\underline{\omega}$ is the angular velocity in the laboratory (SF) frame

$$\underline{\omega}^{SF} = \underline{\omega} \quad (150)$$

We may further write

$$\begin{aligned}
\dot{\underline{r}}_k(t) &= \dot{\underline{R}}(t) + \underline{\omega} \times \underline{\rho}_k(t) \\
&= \dot{\underline{R}}(t) + \underline{\underline{C}} \underline{\underline{C}}^{-1} \left(\underline{\omega} \times \underline{\rho}_k(t) \right) \\
&= \dot{\underline{R}}(t) + \underline{\underline{C}} \left[\left(\underline{\underline{C}}^{-1} \underline{\omega} \right) \times \left(\underline{\underline{C}}^{-1} \underline{\rho}_k(t) \right) \right]
\end{aligned} \tag{151}$$

The last line follows from the properties of the vector product under rotation:

$$\underline{\underline{C}} (\underline{a} \times \underline{b}) = (\underline{\underline{C}} \underline{a}) \times (\underline{\underline{C}} \underline{b}).$$

Here we can substitute $\underline{a}_k = \underline{\underline{C}}^{-1} \underline{\rho}_k(t)$ and we get:

$$\boxed{\dot{\underline{r}}_k(t) = \dot{\underline{R}}(t) + \underline{\underline{C}} \left(\underline{\omega}^{BF} \times \underline{a}_k \right)} \tag{152}$$

The angular velocity with respect to the rotating (BF) frame is:

$$\underline{\omega}^{BF} = \underline{\underline{C}}^{-1} \underline{\omega} = \underline{\underline{C}}^{-1} \underline{\omega}^{SF} = \underline{\underline{C}}^{-1} \underline{\underline{U}} \begin{pmatrix} \dot{\varphi} \\ \dot{\vartheta} \\ \dot{\chi} \end{pmatrix} = \underline{\underline{V}} \begin{pmatrix} \dot{\varphi} \\ \dot{\vartheta} \\ \dot{\chi} \end{pmatrix} \tag{153}$$

with

$$\boxed{\underline{\underline{V}} = \underline{\underline{C}}^{-1} \underline{\underline{U}} = \begin{pmatrix} -\sin \vartheta \cos \chi & \sin \chi & 0 \\ \sin \vartheta \sin \chi & \cos \chi & 0 \\ \cos \vartheta & 0 & 1 \end{pmatrix}} \tag{154}$$

This can be easily shown, if one remembers eq. (143):

$$\begin{aligned}
\underline{\underline{V}} &= \underline{\underline{C}}^{-1} \underline{\underline{U}} = \underline{\underline{C}}_z^T(\chi) \underline{\underline{C}}_y^T(\vartheta) \underline{\underline{C}}_z^T(\varphi) \begin{pmatrix} 0 & -\sin \varphi & \cos \varphi \sin \vartheta \\ 0 & \cos \varphi & \sin \varphi \sin \vartheta \\ 1 & 0 & \cos \vartheta \end{pmatrix} = \\
&= \underline{\underline{C}}_z^T(\chi) \underline{\underline{C}}_y^T(\vartheta) \underline{\underline{C}}_z^T(\varphi) \left(\underline{e}_3, \underline{\underline{C}}_z(\varphi) \underline{e}_2, \underline{\underline{C}}_z(\varphi) \underline{\underline{C}}_y(\vartheta) \underline{e}_3 \right) = \\
&= \left(\underline{\underline{C}}_z^T(\chi) \underline{\underline{C}}_y^T(\vartheta) \underline{e}_3, \underline{\underline{C}}_z^T(\chi) \underline{e}_2, \underline{e}_3 \right) = \begin{pmatrix} -\sin \vartheta \cos \chi & \sin \chi & 0 \\ \sin \vartheta \sin \chi & \cos \chi & 0 \\ \cos \vartheta & 0 & 1 \end{pmatrix}
\end{aligned} \tag{155}$$

We have now expressed the velocities of the atoms $\dot{\underline{r}}_k$ in terms of the velocity of the center of mass $\dot{\underline{R}}$ and the angular velocity $\underline{\omega}^{SF}$, or $\underline{\omega}^{BF}$, or $\underline{\dot{q}} = \begin{pmatrix} \dot{\varphi} \\ \dot{\vartheta} \\ \dot{\chi} \end{pmatrix}$.

We want to derive the expression for the kinetic energy, but first we define:

$$\underline{\rho}_k(t) = \begin{pmatrix} x_k(t) \\ y_k(t) \\ z_k(t) \end{pmatrix} \rightarrow \underline{\underline{X}}_k(t) = \begin{pmatrix} 0 & -z_k(t) & y_k(t) \\ z_k(t) & 0 & -x_k(t) \\ -y_k(t) & x_k(t) & 0 \end{pmatrix} \quad (156)$$

— an antisymmetric matrix with the cartesian (SF) coordinates of atom k . We define a similar matrix for the BF frame:

$$\underline{a}_k = \begin{pmatrix} a_{kx} \\ a_{ky} \\ a_{kz} \end{pmatrix} \rightarrow \underline{\underline{A}}_k = \begin{pmatrix} 0 & -a_{kz} & a_{ky} \\ a_{kz} & 0 & -a_{kx} \\ -a_{ky} & a_{kx} & 0 \end{pmatrix} \quad (157)$$

When we consider the elements of the product matrix $\underline{\underline{X}}_k^T \underline{\underline{X}}_k$:

$$\begin{aligned} \left(\underline{\underline{X}}_k^T \underline{\underline{X}}_k \right)_{11} &= y_k^2 + z_k^2 = (x_k^2 + y_k^2 + z_k^2) - x_k^2 \\ \left(\underline{\underline{X}}_k^T \underline{\underline{X}}_k \right)_{12} &= -x_k y_k \end{aligned} \quad (158)$$

we see that the matrix

$$\underline{\underline{I}}^{SF}(t) = \sum_k m_k \underline{\underline{X}}_k^T(t) \underline{\underline{X}}_k(t) \quad (159)$$

is the inertia tensor of the molecule in the laboratory frame. Similarly, we see that:

$$\underline{\underline{I}}^{BF} = \sum_k m_k \underline{\underline{A}}_k^T \underline{\underline{A}}_k \quad (160)$$

is the inertia tensor in the BF frame. It is obvious that $\underline{\underline{I}}^{BF}$ is constant in time.

The kinetic energy

$$T = \frac{1}{2} \sum_k m_k v_k^2 = \frac{1}{2} \sum_k m_k \dot{\underline{r}}_k \cdot \dot{\underline{r}}_k = \frac{1}{2} \sum_k m_k \dot{\underline{r}}_k^T \dot{\underline{r}}_k \quad (161)$$

can be written in different ways.

In the laboratory (SF) frame we get:

$$T = \frac{1}{2} \sum_k m_k \dot{\underline{R}}^T \dot{\underline{R}} + \sum_k m_k \dot{\underline{R}}^T \left(\underline{\omega} \times \underline{\rho}_k \right) + \frac{1}{2} \sum_k m_k \left(\underline{\omega} \times \underline{\rho}_k \right)^T \left(\underline{\omega} \times \underline{\rho}_k \right) \quad (162)$$

The second term vanishes, because

$$\sum_k m_k \dot{\underline{R}}^T (\underline{\omega} \times \underline{\rho}_k) = \dot{\underline{R}}^T \left(\underline{\omega} \times \sum_k m_k \underline{\rho}_k \right) = \dot{\underline{R}}^T (\underline{\omega} \times \underline{0}) = \underline{0} \quad (163)$$

see eq. (133). We may further write that:

$$\underline{\underline{Q}} \underline{\rho}_k = \underline{\omega} \times \underline{\rho}_k = -\underline{\rho}_k \times \underline{\omega} = -\underline{\underline{X}}_k \underline{\omega} \quad (164)$$

and the result becomes:

$$T = \frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}} + \frac{1}{2} \underline{\omega}^T \left(\sum_k m_k \underline{\underline{X}}_k^T \underline{\underline{X}}_k \right) \underline{\omega} \quad (165)$$

$$\boxed{T = \frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}} + \frac{1}{2} \underline{\omega}^T \underline{\underline{I}}^{SF} \underline{\omega}} \quad (166)$$

The first term corresponds to the translation of the center of mass, the second to the rotation. As we see, there is an **exact** separation between translation and rotation.

In the BF frame we obtain (also here the cross term vanishes):

$$\begin{aligned} T &= \frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}} + \frac{1}{2} \sum_k m_k (\underline{\omega}^{BF} \times \underline{a}_k)^T \underline{\underline{C}}^T \underline{\underline{C}} (\underline{\omega}^{BF} \times \underline{a}_k) \\ &= \frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}} + \frac{1}{2} (\underline{\omega}^{BF})^T \left(\sum_k m_k \underline{\underline{A}}_k^T \underline{\underline{A}}_k \right) \underline{\omega}^{BF} \end{aligned} \quad (167)$$

$$\boxed{T = \frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}} + \frac{1}{2} (\underline{\omega}^{BF})^T \underline{\underline{I}}^{BF} \underline{\omega}^{BF}} \quad (168)$$

Let us now express the kinetic energy in terms of the Euler angles $\underline{q} = \begin{pmatrix} \varphi \\ \vartheta \\ \chi \end{pmatrix}$.

To this end we must substitute:

$$\begin{aligned} \underline{\omega}^{SF} &= \underline{\omega} &= \underline{\underline{U}} \dot{\underline{q}} \\ \underline{\omega}^{BF} &= \underline{\underline{C}}^{-1} \underline{\underline{U}} \dot{\underline{q}} &= \underline{\underline{V}} \dot{\underline{q}} \end{aligned} \quad (169)$$

Ater this substitution we get:

$$\boxed{\begin{aligned} T &= \frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}} + \frac{1}{2} \dot{\underline{q}}^T \underline{\underline{U}}^T \underline{\underline{I}}^{SF} \underline{\underline{U}} \dot{\underline{q}} \\ T &= \frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}} + \frac{1}{2} \dot{\underline{q}}^T \underline{\underline{V}}^T \underline{\underline{I}}^{BF} \underline{\underline{V}} \dot{\underline{q}} \end{aligned}} \quad (170)$$

which we can also write as

$$\boxed{T = \frac{1}{2}M\dot{\underline{R}}^T\dot{\underline{R}} + \frac{1}{2}\dot{\underline{q}}^T\underline{\underline{g}}\dot{\underline{q}}} \quad (171)$$

where

$$\boxed{\underline{\underline{g}} = \underline{\underline{U}}^T \underline{\underline{I}}^{SF} \underline{\underline{U}} = \underline{\underline{V}}^T \underline{\underline{I}}^{BF} \underline{\underline{V}}} \quad (172)$$

is the metric matrix (metric tensor — “overlap matrix”) belonging to the Euler angles \underline{q}

(N.B. we have seen this previously, in Wilson’s GF method, where instead of \underline{q} we used internal coordinates \underline{s} . The matrix $\underline{\underline{G}}$, defined there, is the inverse of the metric tensor, $\underline{\underline{G}}^{-1} = \underline{\underline{g}}_s$. Of course, $\underline{\underline{g}}$ and $\underline{\underline{g}}_s$ are different matrices, but they play a similar role.)

Finally, we present an expression for the kinetic energy in terms of angular momenta

$$\underline{J} = \sum_k \underline{J}_k = \sum_k m_k \underline{r}_k \times \dot{\underline{r}}_k \quad (173)$$

In SF coordinates:

$$\begin{aligned} \underline{r}_k &= \underline{R} + \underline{\rho}_k \\ \dot{\underline{r}}_k &= \dot{\underline{R}} + \underline{\omega} \times \underline{\rho}_k \end{aligned} \quad (174)$$

$$\begin{aligned} \underline{J} &= \sum_k m_k \underline{R} \times \dot{\underline{R}} + \sum_k m_k \underline{\rho}_k \times \dot{\underline{R}} \\ &+ \sum_k m_k \underline{R} \times (\underline{\omega} \times \underline{\rho}_k) + \sum_k m_k \underline{\rho}_k \times (\underline{\omega} \times \underline{\rho}_k) \end{aligned} \quad (175)$$

Because $\sum_k m_k \underline{\rho}_k = \underline{0}$, the second and the third term vanish. The fourth term can be rewritten as follows

$$\begin{aligned} \sum_k m_k \underline{\rho}_k \times (\underline{\omega} \times \underline{\rho}_k) &= - \sum_k m_k \underline{\rho}_k \times (\underline{\rho}_k \times \underline{\omega}) = \\ &= - \sum_k m_k \underline{X}_k \left(\underline{X}_k \underline{\omega} \right) = \sum_k m_k \underline{X}_k^T \underline{X}_k \underline{\omega} = \underline{\underline{I}}^{SF} \underline{\omega} \end{aligned} \quad (176)$$

so that we get

$$\boxed{\underline{J} = M\underline{R} \times \dot{\underline{R}} + \underline{\underline{I}}^{SF} \underline{\omega}} \quad (177)$$

In this equation $\underline{J}_{CM} = M\underline{R} \times \dot{\underline{R}}$ is the angular momentum due to the center of mass motion, and $\underline{\underline{I}}^{SF} \underline{\omega}$ is the rotational angular momentum.

In BF coordinates:

$$\begin{aligned}
\underline{r}_k &= \underline{R} + \underline{C} \underline{a}_k \\
\dot{\underline{r}}_k &= \dot{\underline{R}} + \underline{C} (\underline{\omega}^{BF} \times \underline{a}_k) \\
\underline{J} &= \underline{J}_{CM} + \underline{C} \underline{I}^{BF} \underline{\omega}^{BF}
\end{aligned} \tag{178}$$

Summarizing:

$\underline{J} = \underline{J}_{CM} + \underline{J}_{rot}^{SF}$	$\underline{J}_{rot}^{SF} = \underline{I}^{SF} \underline{\omega}^{SF}$	(179)
$\underline{J} = \underline{J}_{CM} + \underline{C} \underline{J}_{rot}^{BF}$	$\underline{J}_{rot}^{BF} = \underline{I}^{BF} \underline{\omega}^{BF}$	

Apart from the term related to the motion of the center of mass, we then get for the kinetic energy:

$$\begin{aligned}
T &= \frac{1}{2} (\underline{J}^{SF})^T (\underline{I}^{SF})^{-1} \underline{J}^{SF} \\
T &= \frac{1}{2} (\underline{J}^{BF})^T (\underline{I}^{BF})^{-1} \underline{J}^{BF}
\end{aligned} \tag{180}$$

0.4.3 The rigid rotor Hamiltonian

To go from classical mechanics to quantum mechanics, we must first write the classical kinetic energy in terms of the **coordinates** \underline{q} and **conjugated momenta** \underline{p} .

In classical mechanics, if q_i are the (possibly curvilinear) coordinates, then the conjugated momenta are defined as:

$$\boxed{p_i = \frac{\partial T}{\partial \dot{q}_i}} \tag{181}$$

In cartesian coordinates, $\underline{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$, the expression for the kinetic energy is:

$$T = \frac{1}{2} m v^2 = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

This is consistent with eq. (181), because $p_x = \frac{\partial T}{\partial \dot{x}} = m\dot{x}$, etc., and $\underline{p} = m\dot{\underline{r}} = m\underline{v}$.

Let us now apply this to the **Euler angles** $\underline{q} = \begin{pmatrix} \varphi \\ \vartheta \\ \chi \end{pmatrix}$, and first derive the conjugated momenta \underline{p} . We return to eq. (171):

$$T = \frac{1}{2} \dot{\underline{q}}^T \underline{g} \dot{\underline{q}} = \frac{1}{2} \sum_{i,j} g_{ij} \dot{q}_i \dot{q}_j \tag{182}$$

with the metric tensor given by $\underline{\underline{g}} = \underline{\underline{U}}^T \underline{\underline{I}}^{SF} \underline{\underline{U}} = \underline{\underline{V}}^T \underline{\underline{I}}^{BF} \underline{\underline{V}}$, see eq. (172). The momenta are:

$$p_i = \frac{\partial T}{\partial \dot{q}_i} = \sum_j g_{ij} \dot{q}_j \quad \underline{\underline{p}} = \underline{\underline{g}} \underline{\underline{\dot{q}}} \quad \underline{\underline{\dot{q}}} = \underline{\underline{g}}^{-1} \underline{\underline{p}} \quad (183)$$

and the classical Hamiltonian for the kinetic energy is:

$$T = \frac{1}{2} \underline{\underline{p}}^T \left(\underline{\underline{g}}^{-1} \right)^T \underline{\underline{g}} \underline{\underline{p}} = \frac{1}{2} \underline{\underline{p}}^T \left(\underline{\underline{g}}^{-1} \right)^T \underline{\underline{p}} \quad (184)$$

$$\boxed{T = \frac{1}{2} \underline{\underline{p}}^T \underline{\underline{g}}^{-1} \underline{\underline{p}}} \quad (185)$$

According to the postulates of quantum mechanics, the momentum operators conjugated to a set of (curvilinear) coordinates q_i are:

$$\boxed{p_i = \frac{\hbar}{i} \frac{\partial}{\partial q_i}} \quad (186)$$

The quantum mechanical momentum operators conjugated to the Euler angles are:

$$\underline{\underline{p}} = \frac{\hbar}{i} \begin{pmatrix} \partial/\partial\varphi \\ \partial/\partial\vartheta \\ \partial/\partial\chi \end{pmatrix} \quad (187)$$

From here on, we will use atomic units with $\hbar = 1$.

We want to quantize equation (185). But we must be careful, because the matrices $\underline{\underline{U}}$ and $\underline{\underline{V}}$ are functions of φ , ϑ , χ , and so is the matrix $\underline{\underline{g}}$. So, $\underline{\underline{p}}$ does not commute with $\underline{\underline{g}}^{-1}$.

B. Podolski [*Quantum-mechanically correct form of Hamiltonian function for conservative system*, Phys. Rev., **32**, 812 (1928)]:

We cannot simply replace the classical momenta in eq. (185) by operators, but we have to use the general formula for the Laplace operator

$$\Delta = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (188)$$

in curvilinear coordinates q . This yields:

$$\boxed{T = \frac{1}{2} g^{-1/2} \underline{\underline{p}}^T g^{1/2} \underline{\underline{g}}^{-1} \underline{\underline{p}}} \quad (189)$$

where $g = \det(\underline{\underline{g}})$.

We see that, if $\underline{\underline{g}}$ did not depend on $\underline{\underline{q}}$, then g would commute with $\underline{\underline{p}}$ and we would have the simpler expression: $T = \frac{1}{2}\underline{\underline{p}}^T \underline{\underline{g}}^{-1} \underline{\underline{p}}$.

The expression for $\underline{\underline{g}}$ is known in terms of the Euler angles, $\underline{\underline{g}} = \underline{\underline{V}}^T \underline{\underline{I}}^{BF} \underline{\underline{V}}$, (Euler angles appear in $\underline{\underline{V}}$, $\underline{\underline{I}}^{BF}$ is constant for a rigid rotor). So, we can derive an explicit quantum mechanical formula for T . We start by calculating

$$g = \det(\underline{\underline{g}}) = \det(\underline{\underline{V}}^T \underline{\underline{I}}^{BF} \underline{\underline{V}}) = (\det \underline{\underline{V}})^2 \det \underline{\underline{I}}^{BF} = \sin^2 \vartheta I_1 I_2 I_3 \quad (190)$$

I_1, I_2, I_3 are the so-called principal moments of inertia — the eigenvalues of $\underline{\underline{I}}^{BF}$. We can then write:

$$T = -\frac{\hbar^2}{2 \sin \vartheta} \left(\frac{\partial}{\partial \varphi}, \frac{\partial}{\partial \vartheta}, \frac{\partial}{\partial \chi} \right) \sin \vartheta \underline{\underline{V}}^{-1} (\underline{\underline{I}}^{BF})^{-1} (\underline{\underline{V}}^T)^{-1} \begin{pmatrix} \partial/\partial \varphi \\ \partial/\partial \vartheta \\ \partial/\partial \chi \end{pmatrix} \quad (191)$$

Further we should plug in the explicit formula for $\underline{\underline{V}}$, eq. (154). It appears that the result can simply be written in terms of the angular momenta $\underline{\underline{J}}^{SF}$ or $\underline{\underline{I}}^{BF}$, but we must first quantize these.

In classical mechanics:

$$\begin{aligned} \underline{\underline{J}}^{SF} &= \underline{\underline{I}}^{SF} \underline{\underline{\omega}} = \underline{\underline{I}}^{SF} \underline{\underline{U}} \dot{\underline{\underline{q}}} \\ \dot{\underline{\underline{q}}} &= \underline{\underline{g}}^{-1} \underline{\underline{p}} = \underline{\underline{U}}^{-1} (\underline{\underline{I}}^{SF})^{-1} (\underline{\underline{U}}^T)^{-1} \underline{\underline{p}} \end{aligned} \quad (192)$$

Combining these two equations gives:

$$\underline{\underline{J}}^{SF} = (\underline{\underline{U}}^T)^{-1} \underline{\underline{p}} \quad (193)$$

After inverting $\underline{\underline{U}}^T$ and substituting $\underline{\underline{p}} = \frac{1}{i} \begin{pmatrix} \partial/\partial \varphi \\ \partial/\partial \vartheta \\ \partial/\partial \chi \end{pmatrix}$ we derive the expressions for $\underline{\underline{J}}^{SF}$ in terms of the Euler angles:

$$\boxed{\begin{aligned} \underline{\underline{J}}_x^{SF} &= i \left(\cos \varphi \cot \vartheta \frac{\partial}{\partial \varphi} + \sin \varphi \frac{\partial}{\partial \vartheta} - \frac{\cos \varphi}{\sin \vartheta} \frac{\partial}{\partial \chi} \right) \\ \underline{\underline{J}}_y^{SF} &= i \left(\sin \varphi \cot \vartheta \frac{\partial}{\partial \varphi} - \cos \varphi \frac{\partial}{\partial \vartheta} - \frac{\sin \varphi}{\sin \vartheta} \frac{\partial}{\partial \chi} \right) \\ \underline{\underline{J}}_z^{SF} &= i \left(-\frac{\partial}{\partial \varphi} \right) \end{aligned}} \quad (194)$$

Analogously, we find

$$\underline{J}^{BF} = (\underline{V}^T)^{-1} \underline{p} = \underline{C}^{-1} (\underline{U}^T)^{-1} \underline{p} = \underline{C}^T \underline{J}^{SF} \quad (195)$$

After a similar elaboration we get:

$$\boxed{\begin{aligned} \underline{J}_x^{BF} &= i \left(\frac{\cos \chi}{\sin \vartheta} \frac{\partial}{\partial \varphi} - \sin \chi \frac{\partial}{\partial \vartheta} - \cot \vartheta \cos \chi \frac{\partial}{\partial \chi} \right) \\ \underline{J}_y^{BF} &= i \left(-\frac{\sin \chi}{\sin \vartheta} \frac{\partial}{\partial \varphi} - \cos \chi \frac{\partial}{\partial \vartheta} + \cot \vartheta \sin \chi \frac{\partial}{\partial \chi} \right) \\ \underline{J}_z^{BF} &= i \left(-\frac{\partial}{\partial \chi} \right) \end{aligned}} \quad (196)$$

Now we know that

$$\underline{J}^{BF} = (\underline{V}^T)^{-1} \underline{p} = (\underline{V}^T)^{-1} \begin{pmatrix} \partial/\partial\varphi \\ \partial/\partial\vartheta \\ \partial/\partial\chi \end{pmatrix} \quad (197)$$

and we can also show (via substitution and differentiation) that

$$\frac{-i\hbar}{\sin \vartheta} \left(\frac{\partial}{\partial \varphi}, \frac{\partial}{\partial \vartheta}, \frac{\partial}{\partial \chi} \right) \sin \vartheta \underline{V}^{-1} = (J_x^{BF}, J_y^{BF}, J_z^{BF}) = (\underline{J}^{BF})^T \quad (198)$$

When we apply this to equation (191), we get simple **quantum mechanical** expressions for the kinetic energy:

$$\boxed{T = \frac{1}{2} (\underline{J}^{BF})^T (\underline{I}^{BF})^{-1} \underline{J}^{BF}} \quad (199)$$

and similarly

$$\boxed{T = \frac{1}{2} (\underline{J}^{SF})^T (\underline{I}^{SF})^{-1} \underline{J}^{SF}} \quad (200)$$

These are the **exact** quantum mechanical expressions in which the operators \underline{J}^{BF} and \underline{J}^{SF} are known. It appears that in terms of the angular momenta, the classical and quantum mechanical expressions are the same! To some extent this is a coincidence.

0.4.4 The rigid rotor in quantum mechanics

It is simpler to work in the BF frame, because (in contrast with \underline{I}^{SF} , which depends on the Euler angles) \underline{I}^{BF} is a constant matrix

$$\underline{I}^{BF} = \sum_k m_k \underline{A}_k^T \underline{A}_k$$

depending on the constant position vectors \underline{a}_k . It is a symmetric 3×3 matrix, so we can easily diagonalise it and its eigenvalues are real. It is customary to choose a rotating coordinate frame that makes $\underline{\underline{I}}^{BF}$ diagonal

$$\underline{\underline{I}}^{BF} = \begin{pmatrix} I_1 & 0 & 0 \\ 0 & I_2 & 0 \\ 0 & 0 & I_3 \end{pmatrix} \quad (\underline{\underline{I}}^{BF})^{-1} = \begin{pmatrix} I_1^{-1} & 0 & 0 \\ 0 & I_2^{-1} & 0 \\ 0 & 0 & I_3^{-1} \end{pmatrix} \quad (201)$$

and define the rotational constants:

$$\boxed{A = \frac{1}{2I_1} \quad B = \frac{1}{2I_2} \quad C = \frac{1}{2I_3}} \quad (202)$$

Then, we obtain the well known kinetic energy expression:

$$\boxed{T = A (J_x^{BF})^2 + B (J_y^{BF})^2 + C (J_z^{BF})^2} \quad (203)$$

The components of $\underline{\underline{J}}^{SF}$ satisfy the following commutation relations:

$$\boxed{[J_x^{SF}, J_y^{SF}] = i\hbar J_z^{SF}} \quad (204)$$

(with cyclic permutations of the indices x, y, z). The components of the BF angular momentum operators, $\underline{\underline{J}}^{BF}$, obey **anomalous** commutation relations:

$$\boxed{[J_x^{BF}, J_y^{BF}] = -i\hbar J_z^{BF}} \quad (205)$$

(cyclic permutations of the indices x, y, z are allowed; pay attention to the minus sign!)

Since $\underline{\underline{J}}^{SF} = \underline{\underline{C}} \underline{\underline{J}}^{BF}$ and $\underline{\underline{C}}^T \underline{\underline{C}} = \underline{\underline{E}}$ it follows that

$$(\underline{\underline{J}}^{SF})^2 = (\underline{\underline{J}}^{SF})^T \underline{\underline{J}}^{SF} = (\underline{\underline{J}}^{BF})^T \underline{\underline{C}}^T \underline{\underline{C}} \underline{\underline{J}}^{BF} = (\underline{\underline{J}}^{BF})^2 = J^2 \quad (206)$$

All components of $\underline{\underline{J}}^{SF}$ commute with $(J^{SF})^2$ and, similarly, all components of $\underline{\underline{J}}^{BF}$ commute with $(J^{BF})^2$.

Furthermore, $J_z^{SF} = -i \frac{\partial}{\partial \varphi}$ commutes with $J_z^{BF} = -i \frac{\partial}{\partial \chi}$. So, we have a set of commuting operators:

$$\boxed{J^2, J_z^{SF}, J_z^{BF}} \quad (207)$$

The question is: are these operators constants of the motion, i.e., do they commute with the Hamiltonian?

$$T = A (J_x^{BF})^2 + B (J_y^{BF})^2 + C (J_z^{BF})^2$$

The answer is:

- J^2 commutes with T , because it commutes with J_x^{BF} , J_y^{BF} , and J_z^{BF} .
- J_z^{SF} also commutes with T , because $J_z^{SF} = -i\frac{\partial}{\partial\varphi}$ and the operators J_x^{BF} , J_y^{BF} do not contain φ (they contain only $\frac{\partial}{\partial\varphi}$)
- J_z^{BF} does not commute with T , because it does not commute with $(J_x^{BF})^2$, and $(J_y^{BF})^2$

Let us now consider some special cases.

Symmetric top

$$A = B \neq C$$

- prolate $A = B < C$ (like a cigar)
- oblate $A = B > C$ (like a pancake)

Examples of a symmetric top: benzene, NH_3 (we will use the notation $\underline{J} \equiv \underline{J}^{BF}$)

$$H = T = A(J_x^2 + J_y^2) + CJ_z^2 = AJ^2 + (C - A)J_z^2 \quad (208)$$

This Hamiltonian does commute with $J_z = J_z^{BF}$. Hence, there are three constants of the motion in this case, and three quantum numbers: j , k , and m .

$H j, k, m\rangle =$	$E_{j,k} j, k, m\rangle$	
$J^2 j, k, m\rangle =$	$j(j+1) j, k, m\rangle$	
$J_z^{BF} j, k, m\rangle =$	$k j, k, m\rangle$	$-j \leq k \leq j$
$J_z^{SF} j, k, m\rangle =$	$m j, k, m\rangle$	$-j \leq m \leq j$

(209)

The energy eigenvalues are

$$E_{j,k} = Aj(j+1) + (C - A)k^2 \quad (210)$$

The energy does not depend on the quantum number m , so it is $(2j+1)$ -fold degenerate.

Since T commutes with J_z^{BF} , the eigenfunctions of T have to be also eigenfunctions of $J_z^{BF} = -i\frac{\partial}{\partial\chi}$, with eigenvalue k . So, they contain a factor

$\exp(ik\chi)$. Similarly, they have to be eigenfunctions of $J_z^{SF} = -i\frac{\partial}{\partial\varphi}$, with eigenvalue m , which yields the factor $\exp(im\varphi)$. Thus, they can be written as:

$$|j, k, m\rangle = \Psi_{j,k,m}(\varphi, \vartheta, \chi) = \exp(im\varphi)d_{mk}^{(j)}(\vartheta) \exp(ik\chi) = D_{mk}^{(j)}(\varphi, \vartheta, \chi)^* \quad (211)$$

The functions $D_{mk}^{(j)}(\varphi, \vartheta, \chi)$ are called Wigner rotation matrices. The functions $d_{mk}^{(j)}(\vartheta)$, which are called Wigner (small) d -matrices, are the solutions of a differential equation in $\cos\vartheta$; they can be obtained by means of recursion relations.

Spherical top

$A = B = C$, examples: CH_4 , SF_6

$$H = T = AJ^2 \quad (212)$$

$$E_j = Aj(j+1) \quad (213)$$

The energy does not depend on the quantum numbers k and m , so it is $(2j+1)^2$ -fold degenerate.

The eigenfunctions of the spherical top Hamiltonian are the same functions $D_{km}^{(j)}(\varphi, \vartheta, \chi)^*$

Asymmetric top

The three rotational constants are different, $A > B > C$. J_z^{BF} is not a constant of the motion, thus k is not a good quantum number. But j and m remain good quantum numbers.

The eigenfunctions of H can be written as:

$$\Psi_{j,m,i}(\varphi, \vartheta, \chi) = \sum_{k=-j}^j D_{mk}^{(j)}(\varphi, \vartheta, \chi)^* c_{ki} \quad (214)$$

The coefficients c_{ki} follow from diagonalization of the matrix of the Hamiltonian H in the basis of Wigner D -functions, $D_{km}^{(j)}(\varphi, \vartheta, \chi)^*$, for fixed j and m , and $k = -j, \dots, j$. The dimension of this matrix is $2j+1$.

The matrix elements can be easily derived by writing T in terms of raising (or step-up) and lowering (or step-down) operators:

$$J_{\pm}^{BF} = J_x^{BF} \mp iJ_y^{BF} \quad (215)$$

These operators act on the basis functions as:

$$J_{\pm}^{BF} |j, k, m\rangle = [j(j+1) \pm k(k \pm 1)]^{1/2} |j, k \pm 1, m\rangle \quad (216)$$

Note the interchange of the + and – signs in the definition of these operators, eq. (215), which is due to the **anomalous** commutation relations between the components of \underline{J}^{BF} . The alternative is not to interchange the + and – signs in the definition of the operators, but then the interchange occurs in eq. (216).

For more details we refer to Paul Wormer’s lecture notes, mentioned at the beginning of this section, and to the textbooks on angular momentum theory listed in these notes.

0.5 The molecular vibration-rotation Hamiltonian

0.5.1 Introduction

In Chapter 2 we discussed pure vibrations (in the harmonic approximation), in Chapter 3 pure rotations. Now we will consider the vibrations and rotations of molecules simultaneously.

The question is: how do we define the rotating (BF) axes in a vibrating molecule? Or: how can we separate vibrations and rotations? The answer to the latter question is that we cannot do this exactly. By a suitable choice of the rotating axes we can minimize the coupling between vibrations and rotations, however.

Our task is then to:

1. Derive the Hamiltonian for which the rot-vib coupling is minimal.
2. Find the approximations needed to arrive at a harmonic oscillator model for the vibrations and a rigid rotor model for the rotations.

A lot of attention has been given to these issues, by Eckhart, Sayvetz, Van Vleck, Wigner & Hirschfelder, Wilson & Howard, Darling & Dennison, Watson, and others.

0.5.2 The (classical) kinetic energy of a semi-rigid molecule

The word semi-rigid implies that the vibrations involve only small displacements of the atoms from their equilibrium positions in the molecule.

To derive the classical expression for the kinetic energy T we write the $3n$ cartesian coordinates $\underline{r}_k(t)$ of the atoms with respect to a laboratory (SF) frame in terms of:

- 3 coordinates $\underline{R}(t)$ — the origin of the moving BF frame
- 3 Euler angles φ, ϑ, χ — the orientation of the rotating BF frame axes
- $3n - 6$ internal coordinates — bond lengths, angles between bonds, etc.

by means of the equation:

$$\underline{r}_k(t) = \underline{R}(t) + \underline{C}(\varphi(t), \vartheta(t), \chi(t)) \underline{a}_k(t) \quad (217)$$

Because of the vibrations, also the $\underline{a}_k(t)$ depend on t now. However, they are not internal coordinates, but ($3n$, not $3n - 6$) cartesian coordinates of the atoms with respect to the rotating frame. The atomic velocities are:

$$\begin{aligned} \dot{\underline{r}}_k &= \dot{\underline{R}}(t) + \dot{\underline{C}}(\varphi, \vartheta, \chi) \underline{a}_k + \underline{C} \dot{\underline{a}}_k \\ &= \dot{\underline{R}}(t) + \underline{C}(\underline{\omega}^{BF} \times \underline{a}_k) + \underline{C} \dot{\underline{a}}_k \end{aligned} \quad (218)$$

When comparing this to the previously derived equations, we see an extra term $\underline{C} \dot{\underline{a}}_k$, because $\underline{a}_k(t)$ depends on time. First, let us choose $\underline{R}(t)$ as the position of the center of mass:

$$\underline{R}(t) = M^{-1} \sum_k m_k \underline{r}_k(t) \quad (219)$$

Then, it follows that at each time t

$$\sum_k m_k \underline{a}_k(t) = \underline{0} \quad (220)$$

so, it is also true that

$$\sum_k m_k \dot{\underline{a}}_k(t) = \underline{0} \quad (221)$$

The kinetic energy can be written as

$$\begin{aligned}
T &= \frac{1}{2} \sum_k m_k \dot{\underline{r}}_k^T \dot{\underline{r}}_k = \\
&= \frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}} + \sum_k m_k \dot{\underline{R}}^T \underline{\underline{C}} (\underline{\omega}^{BF} \times \underline{a}_k) + \\
&+ \sum_k m_k \dot{\underline{R}}^T \underline{\underline{C}} \dot{\underline{a}}_k + \frac{1}{2} \sum_k m_k (\underline{\omega}^{BF} \times \underline{a}_k)^T (\underline{\omega}^{BF} \times \underline{a}_k) + \\
&+ \sum_k m_k (\underline{\omega}^{BF} \times \underline{a}_k)^T \dot{\underline{a}}_k + \frac{1}{2} \sum_k m_k \dot{\underline{a}}_k^T \dot{\underline{a}}_k
\end{aligned} \tag{222}$$

We have used here that $\underline{\underline{C}}^T \underline{\underline{C}} = \underline{\underline{E}}$ ($\underline{\underline{C}}$ is an orthogonal matrix). The second and third term vanish, because of the translational conditions for \underline{a}_k and $\dot{\underline{a}}_k$, eqs. (220) and (221):

$$\begin{aligned}
\sum_k m_k \dot{\underline{R}}^T \underline{\underline{C}} (\underline{\omega}^{BF} \times \underline{a}_k) &= \dot{\underline{R}}^T \underline{\underline{C}} \left(\underline{\omega}^{BF} \times \sum_k m_k \underline{a}_k \right) = \\
&= \dot{\underline{R}}^T \underline{\underline{C}} (\underline{\omega}^{BF} \times \underline{0}) = \underline{0}
\end{aligned} \tag{223}$$

$$\sum_k m_k \dot{\underline{R}}^T \underline{\underline{C}} \dot{\underline{a}}_k = \dot{\underline{R}}^T \underline{\underline{C}} \left(\sum_k m_k \dot{\underline{a}}_k \right) = \dot{\underline{R}}^T \underline{\underline{C}} \underline{0} = \underline{0} \tag{224}$$

So, there is an exact separation between the translations in the kinetic energy and the rotations and vibrations. Because of this separation, we can now “forget” about the term $\frac{1}{2} M \dot{\underline{R}}^T \dot{\underline{R}}$ that corresponds to the kinetic energy of the (center-of-mass) translation, as it does not interfere with the rotations and vibrations.

The fourth term was already elaborated in Chapter 3, where we wrote it in terms of the inertia tensor $\underline{\underline{I}}^{BF}$. It contains the coordinates $\underline{a}_k(t)$ and is now time-dependent (because of the vibrations).

The fifth term is the rotation-vibration coupling. We will also rewrite this term, with the aid of the relation $(\underline{a} \times \underline{b}) \cdot \underline{c} = \underline{a} \cdot (\underline{b} \times \underline{c})$. The result is:

$$T = \underbrace{\frac{1}{2} (\underline{\omega}^{BF})^T \underline{\underline{I}}^{BF} \underline{\omega}^{BF}}_{\text{rotation}} + \underbrace{\sum_k m_k (\underline{\omega}^{BF})^T (\underline{a}_k \times \dot{\underline{a}}_k)}_{\text{rot-vib coupling}} + \underbrace{\frac{1}{2} \sum_k m_k \dot{\underline{a}}_k^T \dot{\underline{a}}_k}_{\text{vibration}} \tag{225}$$

We cannot eliminate the rot-vib coupling term but we can minimize it, by an appropriate choice of the rotating axes.

Eckart's first attempt (1934)

At each time t , choose the principal axes of the inertia tensor $\underline{\underline{I}}^{BF}(t)$ as the rotating axes, i.e., choose a BF coordinate frame, that makes $\underline{\underline{I}}^{BF}$ diagonal. The principal moments of inertia I_1 , I_2 and I_3 are the eigenvalues of $\underline{\underline{I}}^{BF}$.

This led to the so-called Eckart paradox: the inclusion of the rotation-vibration coupling (with the aid of first order perturbation theory) yields a kinetic energy term that has the same form, $AJ_x^2 + BJ_y^2 + CJ_z^2$, as the rigid rotor Hamiltonian. The constants, however, are given by expressions such as $A = \frac{I_1}{2(I_2 - I_3)^2}$, instead of $\frac{1}{2I_1}$, as for the rigid rotor. This is a paradox, because one expects that in the limit of zero amplitude vibrations T should be precisely the rigid rotor kinetic energy. It was shown later by Van Vleck that the inclusion of second order terms restores the correct expressions.

A derivation of this result was given by F. Jørgensen in his thesis.

Eckart's second attempt (1935)

Let us assume an equilibrium structure of the molecule with atomic positions $\underline{a}_k(0)$ and small displacements $\underline{d}_k(t)$

$$\begin{aligned}\underline{a}_k(t) &= \underline{a}_k(0) + \underline{d}_k(t) \\ \dot{\underline{a}}_k(t) &= \dot{\underline{d}}_k(t) \quad \text{since } \underline{a}_k(0) \text{ is constant.}\end{aligned}\tag{226}$$

It is obvious that, if $\underline{d}_k(t) = \underline{0}$, we may choose the axes of the rotating frame as the principal axes of $\underline{\underline{I}}^{BF}$. But how do we choose the frame when $\underline{d}_k(t) \neq \underline{0}$?

Eckart (1935): choose the rotating frame such that the vibrational displacements at each time t satisfy the Eckart conditions (see Chapter 2):

$$\begin{aligned}\text{a) } \sum_k m_k \underline{d}_k(t) &= \underline{0} \\ \text{b) } \sum_k m_k \underline{a}_k(0) \times \underline{d}_k(t) &= \underline{0}\end{aligned}\tag{227}$$

The three conditions a) follow directly from putting the origin of the coordinate system at the center of mass, which implies that:

$$\underline{0} = \sum_k m_k \underline{a}_k(t) = \underbrace{\sum_k m_k \underline{a}_k(0)}_{=\underline{0}} + \underbrace{\sum_k m_k \underline{d}_k(t)}_{=\underline{0}}\tag{228}$$

The first, time-independent, term in the above equation equals $\underline{0}$, because we assumed that $\underline{d}_k(0) = \underline{0}$. Then, it follows that also the second term must be equal to zero at all times t . We knew this already: the translations separate exactly from both the rotations and vibrations.

The three conditions b) give the best possible separation of rotations and vibrations, because:

$$\begin{aligned} T_{\text{rot-vib}} &= (\underline{\omega}^{BF})^T \sum_k m_k \underline{a}_k(t) \times \dot{\underline{a}}_k(t) && \text{Coriolis coupling} \\ &= (\underline{\omega}^{BF})^T \sum_k m_k \underline{a}_k(0) \times \dot{\underline{d}}_k(t) + (\underline{\omega}^{BF})^T \sum_k m_k \underline{d}_k(t) \times \dot{\underline{d}}_k(t) \end{aligned} \quad (229)$$

The first term, which is linear in the vibrational displacements \underline{d}_k , equals $\underline{0}$ because of (the time derivative of) conditions b). The second term that is quadratic in \underline{d}_k remains. This term is (the time derivative of) the minimum value of $\sum_k m_k \underline{a}_k^T \underline{a}_k$. One can see this by looking at the change in $\sum_k m_k \underline{a}_k^T \underline{a}_k$ under an infinitesimally small rotation $\Delta \underline{\omega}$, which is equal to $-2 \sum_k m_k \Delta \underline{\omega}^T (\underline{a}_k(0) \times \underline{a}_k(t))$.

The conditions b) implicitly fix the directions of the axes of the rotating (BF) frame. The orientation of this frame relative to the laboratory (SF) frame is determined by the rotation matrix $\underline{C}(\varphi, \vartheta, \chi)$. An explicit formula for $\underline{C}(\varphi, \vartheta, \chi)$ can be derived directly from the conditions b).

Write b) as:

$$\underline{0} = \sum_k m_k \underline{a}_k(0) \times \underline{d}_k(t) = \sum_k m_k \underline{a}_k(0) \times \underline{a}_k(t) \quad (230)$$

which holds because $\underline{a}_k(0) \times \underline{a}_k(0) = \underline{0}$. Recall that

$$\underline{r}_k(t) = \underline{R}(t) + \underline{C} \underline{a}_k(t) \quad (231)$$

or

$$\underline{a}_k(t) = \underline{C}^T [\underline{r}_k(t) - \underline{R}(t)] \quad (232)$$

Combined with b) this gives:

$$\underline{0} = \sum_k m_k \underline{a}_k(0) \times \underline{C}^T [\underline{r}_k(t) - \underline{R}(t)] \quad (233)$$

This equation, written in components, is

$$\begin{aligned} 0 &= \sum_k \sum_{\gamma} m_k a_{k\alpha}(0) C_{\beta\gamma}^T [r_{k\gamma}(t) - R_{\gamma}(t)] \\ &\quad - \sum_k \sum_{\gamma} m_k a_{k\beta}(0) C_{\alpha\gamma}^T [r_{k\gamma}(t) - R_{\gamma}(t)] \end{aligned} \quad (234)$$

Now we define a matrix $\underline{\underline{Y}}$ with components:

$$Y_{\alpha\beta}(t) = \sum_k m_k [r_{k\alpha}(t) - R_\alpha(t)] a_{k\beta}(0) \quad (235)$$

or, in matrix notation

$$\underline{\underline{Y}}(t) = \sum_k m_k [\underline{\underline{r}}_k(t) - \underline{\underline{R}}(t)] \otimes \underline{\underline{a}}_k(0) \quad (236)$$

where \otimes defines the outer (or tensor) product of two vectors. We find that:

$$\sum_\gamma (C_{\gamma\beta} Y_{\gamma\alpha} - C_{\gamma\alpha} Y_{\gamma\beta}) = 0 \quad (237)$$

or, in matrix form

$$\underline{\underline{Y}}^T \underline{\underline{C}} = \underline{\underline{C}}^T \underline{\underline{Y}} \quad (238)$$

$\underline{\underline{C}}$ is orthogonal, $\underline{\underline{C}}^T = \underline{\underline{C}}^{-1}$, so:

$$\underline{\underline{Y}}^T = \underline{\underline{C}}^T \underline{\underline{Y}} \underline{\underline{C}}^T \quad (239)$$

$$\underline{\underline{Y}}^T \underline{\underline{Y}} = \underline{\underline{C}}^T \underline{\underline{Y}} \underline{\underline{C}}^T \underline{\underline{Y}} = (\underline{\underline{C}}^T \underline{\underline{Y}})^2 \quad (240)$$

$\underline{\underline{Y}}^T \underline{\underline{Y}}$ is symmetric and positive-definite, so $(\underline{\underline{Y}}^T \underline{\underline{Y}})^{1/2}$ is well defined, and we can write:

$$(\underline{\underline{Y}}^T \underline{\underline{Y}})^{1/2} = \underline{\underline{C}}^T \underline{\underline{Y}} \quad (241)$$

So we get:

$$\underline{\underline{C}} = \underline{\underline{Y}} (\underline{\underline{Y}}^T \underline{\underline{Y}})^{-1/2} \quad (242)$$

This equation gives the rotation matrix $\underline{\underline{C}}$, which defines the orientation of the body-fixed frame, in terms of the matrix $\underline{\underline{Y}}(t)$. The matrix $\underline{\underline{Y}}(t)$ contains the equilibrium positions $\underline{\underline{a}}_k(0)$ of the atoms in the molecule, but also depends on their instantaneous positions $\underline{\underline{r}}_k(t) - \underline{\underline{R}}(t) = \underline{\underline{\rho}}_k(t)$ relative to the space fixed frame (with the origin at the center of mass). So, at each time t , we can determine the BF frame that satisfies the Eckart conditions b) by computing the matrix $\underline{\underline{C}}$.

The result of applying the Eckart conditions is that:

$$T = \frac{1}{2} (\underline{\underline{\omega}}^{BF})^T \underline{\underline{I}}^{BF} \underline{\underline{\omega}}^{BF} + (\underline{\underline{\omega}}^{BF})^T \sum_k m_k \underline{\underline{d}}_k \times \underline{\underline{d}}_k + \frac{1}{2} \sum_k m_k \underline{\underline{d}}_k^T \underline{\underline{d}}_k \quad (243)$$

Let us assume now that the $3n$ displacements $\underline{\underline{d}}_k$ that satisfy the six Eckart conditions depend on $3n - 6$ internal coordinates, namely by:

$$\underline{\underline{d}} = \underline{\underline{\mathcal{L}}} \underline{\underline{Q}} = \underline{\underline{M}}^{-1/2} \underline{\underline{L}} \underline{\underline{Q}} \quad (244)$$

(see Chapter 2). The first six Q_i are zero because of the Eckart conditions (see Section 3.5). The other Q_i are the normal coordinates of vibration, which in turn depend on $3n - 6$ internal coordinates \underline{s} (bond lengths, angles) as $\underline{Q} = (\underline{\mathcal{L}}')^{-1} \underline{s}$. Substitution of these results into the kinetic energy, while remembering that $\underline{L}^T = \underline{L}^{-1}$, yields:

$$T = \frac{1}{2} (\underline{\omega}^{BF})^T \underline{I}^{BF} \underline{\omega}^{BF} + \sum_{\alpha} \omega_{\alpha}^{BF} \underline{Q}^T \underline{\zeta}^{\alpha} \dot{\underline{Q}} + \frac{1}{2} \dot{\underline{Q}}^T \dot{\underline{Q}} \quad (245)$$

The matrices $\underline{\zeta}^{\alpha}$ are antisymmetric Coriolis coupling matrices, with elements defined as:

$$\zeta_{ij}^{\alpha} = -\zeta_{ji}^{\alpha} = \sum_k \sum_{\beta, \gamma=1}^3 m_k \epsilon_{\alpha\beta\gamma} L_{k\beta,i} L_{k\gamma,j} \quad (246)$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol which is +1 if (α, β, γ) is an even permutation of (1,2,3), -1 if it is an odd permutation, and 0 if two or three of its subscripts are equal. The result in eq. (245) is the classical kinetic energy, in terms of the rotations $\underline{\omega}^{BF}$ and the normal coordinates of vibration \underline{Q} .

0.5.3 Semi-rigid molecules in quantum mechanics

Before we can quantize the rotational-vibrational Hamiltonian T , we first have to switch to conjugate momenta also for the vibrations. The vibrational momenta P_i conjugated with the normal coordinates are:

$$P_i = \frac{\partial T}{\partial \dot{Q}_i} = \dot{Q}_i - \sum_j \sum_{\alpha} \omega_{\alpha}^{BF} \zeta_{ij}^{\alpha} Q_j \quad (247)$$

The vibrational angular momentum $\underline{\Pi}$ is defined as:

$$\Pi_{\alpha} = \underline{Q}^T \underline{\zeta}^{\alpha} \underline{P} \quad (248)$$

and the components of the total angular momentum are defined as:

$$J_{\alpha}^{BF} = \frac{\partial T}{\partial \omega_{\alpha}} = (\underline{I}^{BF} \underline{\omega}^{BF})_{\alpha} + \underline{Q}^T \underline{\zeta}^{\alpha} \dot{\underline{Q}} \quad (249)$$

Substituting these expressions into the classical expression for the kinetic energy of a semi-rigid molecule (eq. 245), we obtain:

$$T = \frac{1}{2} (\underline{J}^{BF} - \underline{\Pi})^T \underline{\mu} (\underline{J}^{BF} - \underline{\Pi}) + \frac{1}{2} \underline{P}^T \underline{P} \quad (250)$$

where

$$\underline{\underline{\mu}} = (\underline{\underline{I}}')^{-1} \quad (251)$$

and the components of $\underline{\underline{I}}'$ — the effective inertia tensor — are

$$I'_{\alpha\beta} = I_{\alpha\beta}^{BF} + \underline{Q}^T \underline{\underline{\zeta}}^\alpha \underline{\underline{\zeta}}^\beta \underline{Q} \quad (252)$$

The effective inertia tensor depends both indirectly, through \underline{J}^{BF} , and directly on the vibrational coordinates Q_i . Note that equation (250) is not quantum mechanical, it is just a classical expression in terms of conjugate momenta.

The quantum expression is then, according to Podolski

$$T = \frac{1}{2} \mu^{1/2} (\underline{J}^{BF} - \underline{\underline{\Pi}})^T \underline{\underline{\mu}}^{-1/2} (\underline{J}^{BF} - \underline{\underline{\Pi}}) + \frac{1}{2} \mu^{1/2} \underline{P}^T \underline{\underline{\mu}}^{-1/2} \underline{P} \quad (253)$$

with $\mu = \det(\underline{\underline{\mu}})$ and the vibrational linear and angular momentum operators \underline{P} and $\underline{\underline{\Pi}}$ given by:

$$P_i = \frac{\hbar}{i} \frac{\partial}{\partial Q_i} \quad (254)$$

$$\Pi_\alpha = \underline{Q}^T \underline{\underline{\zeta}}^\alpha \underline{P} \quad (255)$$

The total angular momentum operator \underline{J}^{BF} was already defined in eq. (196).

The total Hamiltonian is

$$H = T + V \quad (256)$$

The potential V depends only on the internal coordinates, it describes the so-called molecular force field.

This ‘‘Eckart’’ Hamiltonian was obtained by Wilson and Howard in 1936, [E.B. Wilson and J.B. Howard, *The Vibration-Rotation Energy Levels of Polyatomic Molecules I. Mathematical Theory of Semirigid Asymmetrical Top Molecules*, J. Chem. Phys. **4**, 260-268 (1936)] who followed the procedure described above, and it was further refined by Darling and Dennison in 1940 [B.T. Darling and D.M. Dennison, *The water vapor molecule*, Phys. Rev. **57**, 128-139 (1940)]. It remained the standard until 1968, when Watson [J.K.G. Watson, *Simplification of the molecular vibration-rotation Hamiltonian*, Mol. Phys. **15**, 479-490 (1968)] was able to simplify it drastically by commuting the determinant of the metric tensor through the derivatives. The ro-vibrational Hamiltonian obtained by Watson, often referred to as the ‘‘Watson Hamiltonian’’, is

$$H = \frac{1}{2} (\underline{J}^{BF} - \underline{\underline{\Pi}})^T \underline{\underline{\mu}}^{-1} (\underline{J}^{BF} - \underline{\underline{\Pi}}) + \frac{1}{2} \underline{P}^T \underline{P} + U + V \quad (257)$$

The potential-like term U is the “Watson term”

$$U = -\frac{1}{8} \sum_{\alpha=1}^3 \mu_{\alpha\alpha} \quad (258)$$

It is proportional to the trace of the effective reciprocal inertia tensor and depends only on the internal coordinates, not on the momenta.

The next question of interest is how to arrive at the harmonic oscillator + rigid rotor model? Three approximations must be made:

1. Assume that the effective inertia tensor $\underline{\underline{I}}'$ is constant, i.e., does not depend on the internal coordinates \underline{Q} . Then $\underline{\underline{\mu}}$ commutes with $\underline{\underline{\Pi}}$ and the terms quadratic in $\underline{\underline{\Pi}}$ vanish. Also, replace $\underline{\underline{I}}'$ with $\underline{\underline{I}}^{BF}(0)$, i.e., by the inertia tensor of the equilibrium structure. This implies a neglect of distortions of the structure by centrifugal forces.
2. Neglect Coriolis interactions, i.e., the cross terms between the total angular momentum \underline{J}^{BF} and the vibration angular momentum $\underline{\underline{\Pi}}$.
3. Neglect anharmonic terms in the potential V , i.e., terms with higher than quadratic dependence on the vibrational coordinates \underline{Q} .

After these three approximations we get the rigid rotor + harmonic oscillator Hamiltonian:

$$\begin{aligned} H &= T + V = \\ &= \frac{1}{2} (\underline{J}^{BF})^T (\underline{\underline{I}}^{BF}(0))^{-1} \underline{J}^{BF} + \frac{1}{2} \underline{P}^T \underline{P} + \frac{1}{2} \underline{Q}^T \underline{\underline{\Lambda}} \underline{Q} = \\ &= \underbrace{\frac{1}{2} \sum_{\alpha,\beta} J_{\alpha}^{BF} [I^{-1}(0)]_{\alpha\beta} J_{\beta}^{BF}}_{\text{rotations}} + \underbrace{\frac{1}{2} \sum_i [P_i^2 + \lambda_i Q_i^2]}_{\text{harmonic vibrations}} \end{aligned} \quad (259)$$

The Coriolis and anharmonic terms that were neglected are sometimes taken into account by means of perturbation theory.

0.5.4 Floppy molecules and Van der Waals molecules

The Eckart and Watson Hamiltonians were derived with the assumption that the vibrations of the molecule involve only small displacements of the atoms, with respect to a well-defined equilibrium structure. There are also many examples where this assumption is not valid, they are called floppy molecules (or molecular complexes).

Floppy molecules

These are molecules where some vibrations have large amplitudes.

Examples:

- internal rotation in ethane, $\text{CH}_3\text{—CH}_3$
- inversion-tunneling in ammonia, NH_3

A generalization of the Eckart approach was given by Sayvetz: in essence, he treated the “floppy” internal coordinates in the same way as Eckart treated the external coordinates. This imposes additional (Eckart-Sayvetz) conditions on the remaining internal coordinates.

Van der Waals molecules

These are weakly bound complexes of “normal” molecules. The molecules are held together by noncovalent forces: hydrogen bonding or Van der Waals (dispersion) forces.

All intermolecular coordinates are “floppy” in this case. The “Van der Waals vibrations” against the weak intermolecular bonds have large amplitudes and much lower frequencies than the intramolecular vibrations. Except for the mode that involves the stretch of the intermolecular bond length, they are more like (hindered) internal rotations, rather than small-amplitude vibrations. The potential V is strongly anharmonic and often shows multiple equivalent global (and local) minima, instead of a single equilibrium structure. The barriers between these minima are relatively low and the complex can quantum mechanically tunnel through these barriers, which gives rise to additional splittings of the rotation-vibration levels. These splittings can be observed in spectra, especially if these are measured with high resolution.

Also here one can define a rotating (BF) frame and transform the coordinates from the SF to the BF frame. Coriolis coupling between the internal and overall rotations is usually quite important, however. The potential V is simpler in BF coordinates, because it only depends on the internal coordinates.

Symmetry

In semi-rigid molecules one can use the point group symmetry of the equilibrium structure to simplify the calculation of the (normal mode) vibrations and to derive selection rules. In “floppy” molecules or complexes one may apply the permutation-inversion symmetry group, which is based on the fact that the atomic nuclei are bosons or fermions. Not all permutations of identical nuclei are “feasible”, however, because some permutations may interconvert structures that are separated by high energy barriers. Only those permutation-inversion operations are called feasible that interconvert structures separated by small barriers, and give rise to observable level splittings due to tunneling through these barriers.

The only permutations of identical nuclei that are feasible for semi-rigid molecules correspond to the overall rotations of the whole molecule. The permutation-inversion group is isomorphic to the point group of the equilibrium structure in this case. For “floppy” molecules it contains additional feasible permutation-inversion operations corresponding to tunneling between different, but equivalent, equilibrium structures (minima in the potential surface).

For more information, see for example:

P. R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy*, NRC Research Press, Ottawa, Second edition (1998).

Acknowledgement

I am very grateful to Piotr Gniewek, for his excellent contributions to the preparation of these lecture notes.