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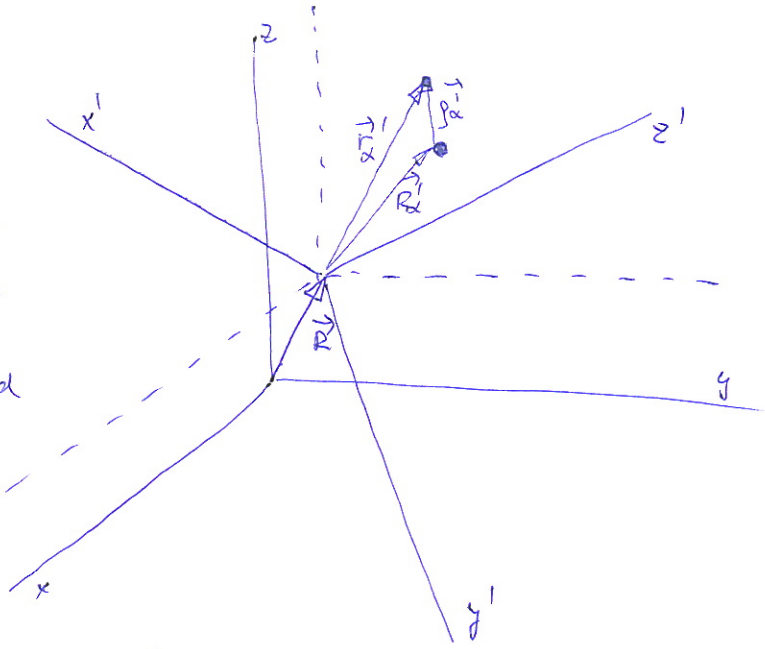
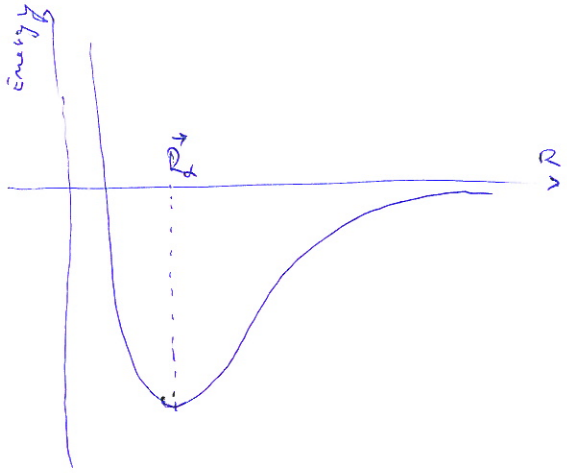
Separation of molecular translations, rotations, and vibrations.

- Classical mechanics (CM)



- $\vec{r}_\alpha^{\,\prime}$ ... equilibrium positions of the nuclei in the primed frame of reference
- $\vec{r}_\alpha^{\,\prime}$ ... nuclear position vectors in the primed frame
- $\vec{\rho}_\alpha = \vec{r}_\alpha^{\,\prime} - \vec{R}_\alpha^{\,\prime}$ ... nuclear displacements
- $\vec{v}_\alpha^{\,\prime} = \dot{\vec{r}}_\alpha^{\,\prime}$ .... local velocity of the nuclei α.



Total (unprimed) velocity is

$$\vec{v}_\alpha = \dot{\vec{R}} + \vec{\omega} \times \vec{r}_\alpha^{\,\prime} + \vec{v}_\alpha^{\,\prime}$$

(Every rotation of the primed system can be expressed as a single rotation around a fixed axis)

Total kinetic energy T

$$2T = \sum_\alpha^M m_\alpha v_\alpha^2 = \sum_\alpha m_\alpha \dot{R}^2 + \sum_\alpha m_\alpha (\vec{\omega} \times \vec{r}_\alpha^{\,\prime}) \cdot (\vec{\omega} \times \vec{r}_\alpha^{\,\prime}) + \sum_\alpha m_\alpha v_\alpha^{\prime 2} + 2\dot{\vec{R}} \cdot \vec{\omega} \times \sum_\alpha m_\alpha \vec{r}_\alpha^{\,\prime}$$

$$+ 2\dot{\vec{R}} \cdot \sum_\alpha m_\alpha \vec{v}_\alpha^{\,\prime} + 2 \sum_\alpha m_\alpha (\vec{\omega} \times \vec{r}_\alpha^{\,\prime}) \cdot \vec{v}_\alpha^{\,\prime}$$

$$2\vec{\omega} \cdot \sum_\alpha m_\alpha \vec{r}_\alpha^{\,\prime} \times \vec{v}_\alpha^{\,\prime}$$

$$\varepsilon_{ijk}\, \omega_j\, r'_{\alpha k}\, v'_{\alpha i} = \varepsilon_{jki}\, \omega_j\, r'_{\alpha k}\, v'_{\alpha i} = \vec{\omega} \cdot (\vec{r}_\alpha^{\,\prime} \times \vec{v}_\alpha^{\,\prime})$$

Choice for the degrees of freedom of M particles

- Center of mass vector $\vec{R}$ (origin of the primed frame) .... 3 degrees
- Euler angles of the primed frame's orientation ..... 3 degrees (2 for linear system)
- Cartesian coordinates of all the particles in the primed frame ..... 3M degrees

$\Rightarrow$ We have $3M+6$ coordinates $\Rightarrow$ they are not independent $\Rightarrow$ There must be 6 conditions to be satisfied by this set of $3M+6$ coordinates

First 3 conditions

$$\sum_\alpha m_\alpha \vec{r}'_\alpha = 0 \quad (A)$$

define the position of the center of mass in the primed system

Initial positions $\Rightarrow$ $\sum_\alpha m_\alpha \vec{R}'_\alpha = 0 = \sum_\alpha m_\alpha \vec{\rho}'_\alpha$ (relative forces)

Remaining 3 conditions

should define the orientation of the primed system. Goal is to define the orientation in such a way, in which molecule does not rotate in the primed system $\Rightarrow$ Not trivial if we imagine simultaneous vibrational motions of M particles

our choice gives zero angular momentum of the equilibrium positions:

$$\sum_\alpha m_\alpha \vec{R}'_\alpha \times \vec{v}'_\alpha = 0 \quad (B)$$

Two terms in the kinetic energy $2T$ (4th and fifth) will disappear due to the first 3 conditions:

(B) applied here ↓

$$2T = \dot{R}^2 \sum_\alpha m_\alpha + \sum_\alpha m_\alpha (\vec{\omega}\times\vec{r}'_\alpha).(\vec{\omega}\times\vec{r}'_\alpha) + \sum_\alpha m_\alpha v'^2_\alpha + 2\vec{\omega}.\sum_\alpha m_\alpha (\vec{\rho}'_\alpha \times \vec{v}'_\alpha)$$

$2T_t$ — translational energy, constant in zero external field

$2T_r$ — rotational energy

$2T_v$ — "vibrational energy"

$2T_c$ — coriolis energy coupling rotations and vibrations, 1-10% of T_r for H_2, HD

Rotational term

$$\sum_\alpha m_\alpha (\varepsilon_{ijk}\omega_j r'_{\alpha k} \varepsilon_{ilm}\omega_l r'_{\alpha m}) = \sum_\alpha m_\alpha (\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl})\omega_j r'_{\alpha k}\omega_l r'_{\alpha m}$$

$$= \sum_\alpha m_\alpha \omega_j^2 r'^2_\alpha - \sum_\alpha m_\alpha \omega_j r'_{\alpha j} r'_{\alpha k}\omega_k = \sum_{jk}\omega_j I_{jk}\omega_k$$

where

$$I_{jk} = \sum_\alpha m_\alpha (r'^2_\alpha \delta_{jk} - r'_{\alpha j} r'_{\alpha k})$$

Instantaneous tensor of inertia

- **Approximation**: for small displacements $\vec{\rho}'_\alpha = \vec{r}'_\alpha - \vec{R}'_\alpha$ we can compute I_{jk} using equilibrium positions $\vec{R}'_\alpha$ instead of $\vec{r}'_\alpha$.

- **Choice**: We choose the orientation of the primed coordinate system along the principal axes of I_{jk} => diagonal tensor of inertia

$$\vec{L} = I\vec{\omega} \Rightarrow 2T_r = \omega_{x'}^2 I_{x'x'} + \omega_{y'}^2 I_{y'y'} + \omega_{z'}^2 I_{z'z'}$$

$$2T_r = \frac{L_{x'}^2}{I_{x'x'}} + \frac{L_{y'}^2}{I_{y'y'}} + \frac{L_{z'}^2}{I_{z'z'}}$$

Rotational Hamiltonian in QM will depend only on the Euler angles and becomes separable

Quantum mechanics (QM)

$$2H_N = 2T_t(\vec{R}) + 2T_r(\alpha,\beta,\gamma) + 2T_v(\vec{r}'_\alpha) + 2V(\vec{r}'_\alpha) + 2T_c(\vec{r}'_\alpha,\alpha,\beta,\gamma)$$

3 — 3 — 3N — Perturbation theory

Vibrational term

$$2T_v = \sum_\alpha m_\alpha v_\alpha'^2 \quad ; \quad \vec{v}_\alpha' = \dot{\vec{r}}_\alpha' = \dot{\vec{\rho}}_\alpha \text{, because } \dot{\vec{R}}_\alpha = 0$$

$$2T_v = \sum_\alpha m_\alpha \dot{\vec{\rho}}_\alpha'^2$$

Rescaled coordinates $q_i = \sqrt{m_{(i-1)/3+1}}\ \rho'_{(i-1)/3+1,\,[(i-1)\%3]+1}$

$$\{\rho'_{ik}\}_{i=1,k=1}^{M,3} \longrightarrow \{q_i\}_{i=1}^{3M}$$

$q_1 = \sqrt{m_1}\,\rho_{1x}$, $q_2 = \sqrt{m_1}\,\rho_{1y}$, $q_3 = \sqrt{m_1}\,\rho_{1z}$

$q_4 = \sqrt{m_2}\,\rho_{2x}$, ...

$$2T_v = \sum_{i=1}^{3M} \dot{q}_i^2$$

Because $\vec{R}_\alpha'$ are fixed, we can express $V(\vec{r}_\alpha')$ as

$$V(\vec{R}_\alpha, q_i) \equiv V(q_i)$$

Vibrational Hamiltonian

$$2H_v = \sum_{i=1}^{3M} \dot{q}_i^2 + 2V(q_i)$$

Harmonic aproximation (aproximation of small displacements)

$$2V(q_i) = 2V(0) + 2\sum_{i=1}^{3M} \frac{\partial V}{\partial q_i}\Big|_0 q_i + \sum_{i,j=1}^{3M} 2\frac{\partial^2 V}{\partial q_i \partial q_j}\Big|_0 q_i q_j + \dots$$

$$\frac{\partial^2 V}{\partial q_i \partial q_j}\Big|_0 = f_{ij}$$

$$2H_v = \sum_i \dot{q}_i^2 + \sum_{i,j} f_{ij} q_i q_j$$

matrix of force constants
more often Hessian matrix

In matrix form: $2H_v = \dot{q}^+ q + q^+ f q$

f ... real, symmetric → Hermitian

Λ ... diagonal $\{\lambda\}_i$. We introduce

L ... unitary

$$f = L \Lambda L^+$$

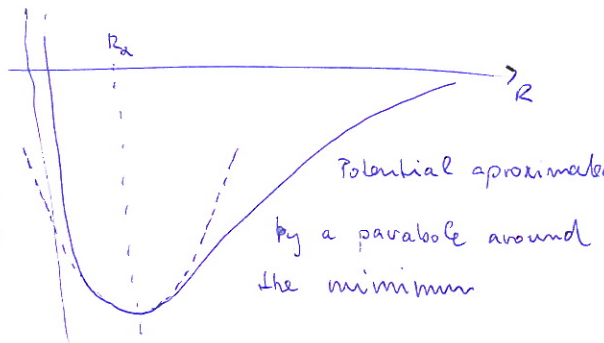
$$Q = L^+ q$$

$$q = L Q$$

$$2H_v = \dot{Q}^+ L^+ L \dot{Q} + Q^+ L^+ f L Q$$

$$2H_v = \dot{Q}^+ \dot{Q} + Q^+ \Lambda Q = \sum_{\nu=1}^{3M} \dot{Q}_\nu^2 + \sum_{\nu=1}^{3M} \lambda_i Q_i^2$$

Q_ν are normal modes



Potential aproximated by a parabole around the minimum

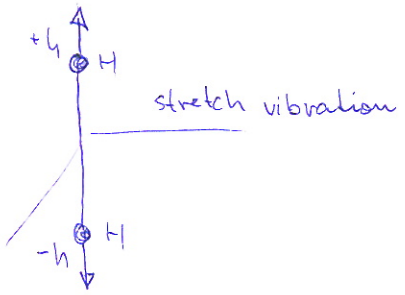
Decomposition to $3M$ harmonic oscilators

$$E_{vn} = \sqrt{\lambda_\nu}\,(n + 1/2)$$

- Visualisation of normal modes Q_v $\qquad Q = L^+ q$

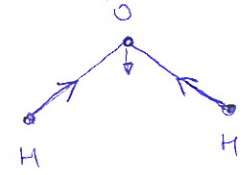
L^+ defines combinations of weighted cartesian displacements q

Examples: H_2 : $Q_6 = \begin{pmatrix} 0 \\ 0 \\ +h \\ 0 \\ 0 \\ -h \end{pmatrix}$ $\begin{matrix} \} \alpha = 1 \\ \\ \\ \\ \} \alpha = 2 \end{matrix}$

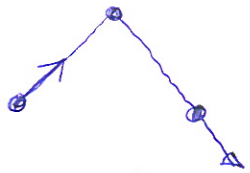


stretch vibration

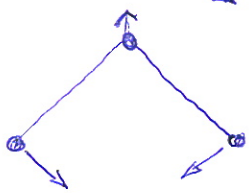
2.) H_2O



A.) symmetric stretch mode



b.) asymmetric stretch mode



c.) bending mode

(6 redundant)

- Zero frequency vibrations : Problem : We still have $3M$ vibrations and they contribute (wrongly) to the total energy of H_N. What is their contributions and how they look like?

$2H_v = \dot{q}^+ \dot{q} + q^+ f q$ Unitary change $q \to t = Uq \Rightarrow 2H_v = \dot{t}^+ U U^+ t + t^+ \underbrace{U f U^+}_{\bar{f}} t$ $\quad q = U^+ t$

$2H_v = \dot{t}^+ \dot{t} + t^+ \bar{f} t$ $\quad \bar{f} = U f U^+$ (spectrum of f does not change by unitary transf.)

We define:

1.) $t_1 = N_1 \sum_{\alpha=1}^{M} \sqrt{m_\alpha}\, q_{\alpha x}$

2.) $t_2 = N_2 \sum_{\alpha=1}^{M} \sqrt{m_\alpha}\, q_{\alpha y}$

3.) $t_3 = N_3 \sum_{\alpha=1}^{M} \sqrt{m_\alpha}\, q_{\alpha z}$

4) $t_4 = N_4 \sum_{\alpha=1}^{M} \sqrt{m_\alpha} \left(R'_{\alpha y} q_{\alpha z} - R'_{\alpha z} q_{\alpha y} \right)$

5.) $t_5 = N_5 \sum_{\alpha=1}^{M} \sqrt{m_\alpha} \left(R'_{\alpha z} q_{\alpha x} - R'_{\alpha x} q_{\alpha z} \right)$

6.) $t_6 = N_6 \sum_{\alpha=1}^{M} \sqrt{m_\alpha} \left(R'_{\alpha x} q_{\alpha y} - R'_{\alpha y} q_{\alpha x} \right)$

$$U = \begin{array}{c|cccccc} N_1 & \sqrt{m_1} & 0 & 0 & \cdots & \sqrt{m_M} & 0 & 0 \\ N_2 & 0 & \sqrt{m_1} & 0 & \cdots & 0 & \sqrt{m_M} & 0 \\ N_3 & 0 & 0 & \sqrt{m_1} & \cdots & 0 & 0 & \sqrt{m_M} \\ N_4 & 0 & -\sqrt{m_1} R'_{1z} & \sqrt{m_1} R'_{1y} & \cdots & 0 & -\sqrt{m_M} R'_{Mz} & \sqrt{m_M} R'_{My} \\ N_5 & \sqrt{m_1} R'_{1z} & 0 & -\sqrt{m_1} R'_{1x} & \cdots & \sqrt{m_M} R'_{Mz} & 0 & -\sqrt{m_M} R'_{Mx} \\ N_6 & -\sqrt{m_1} R'_{1y} & \sqrt{m_1} R'_{1x} & 0 & \cdots & -\sqrt{m_M} R'_{My} & \sqrt{m_M} R'_{Mx} & 0 \end{array}$$

arbitrary unitary extension

- What is the meaning of $t_1, t_2 \dots t_6$ coordinates ?

Let's translate the molecule by h in direction of x-axis:

$q_{\alpha x} \xrightarrow{h_x} q_{\alpha x} + \sqrt{m_\alpha}\, h$

$q_{\alpha y} \xrightarrow{h_x} q_{\alpha y}$

$q_{\alpha z} \xrightarrow{h_x} q_{\alpha z}$

$t_{\nu x_1} \longrightarrow t_1 + N_1 h \sum_{\alpha=1}^{M} m_\alpha$

$t_{\nu>1} \longrightarrow$?

$$t_{\nu>1} \longrightarrow \sum_{\mu=1}^{3M} u_{\nu\mu} q_\mu = \sum_{\alpha=1}^{M} u_{\nu,\alpha x}(q_{\alpha x} + \sqrt{m_\alpha} h) + u_{\nu,\alpha y} q_{\alpha y} + u_{\nu,\alpha z} q_{\alpha z}$$

$$= t_\nu + h \sum_{\alpha=1}^{M} u_{\nu,\alpha x} \sqrt{m_\alpha} = t_{\nu>1} \quad \text{for } \nu > 1$$

Unitarity of U requires: $\sum_\alpha \sqrt{m_\alpha}\, u_{\nu,\alpha x} = 0$

(first row orthonormal to the other rows)

After the h_x translation $t_1 \to t_1 + N_1 h \sum_{\alpha=1}^{M} m_\alpha$; $t_{\nu>1} \to t_{\nu>1}$ => t_1 represents translation

Prove for $t_4, t_5, t_6 \dots$ represent rotations

- Hessian $\bar{f}_{\mu\nu}$ in coordinates t_ν

Potential energy $V(\{t_\nu\}_1^{3M})$ does not depend on translations or rotations of the system.

Let's do h_x translation $\quad t_1 \longrightarrow t_1 + \delta t_1$

$t_{\nu>1} \to t_{\nu>1}$

$$2V = \sum_{\mu,\nu}' t_\mu \bar{f}_{\mu\nu} t_\nu \xrightarrow{h_x} \sum_{\substack{\mu\neq 1 \\ \nu\neq 1}} t_\mu \bar{f}_{\mu\nu} t_\nu + \sum_{\nu\neq 1} (t_1+\delta t_1)\bar{f}_{1\nu} t_\nu + \sum_{\mu\neq 1} t_\mu \bar{f}_{\mu 1}(t_1+\delta t_1) + \bar{f}_{11}(t_1+\delta t_1)^2$$

$$0 = 2\sum_{\nu} \delta t_1 \bar{f}_{1\nu} t_\nu + \bar{f}_{11}(\delta t_1)^2$$ must be valid for any displacement t_ν, $\nu = 1 \dots 3M$ and any translation δt_1

$\Rightarrow \bar{f}_{1\nu} = 0$; $\nu = 1 \dots 3M$

$f_{\mu\nu} =$

$$\begin{pmatrix} \ddots & & 0 \\ & \ddots & \\ 0 & & \begin{matrix} \bar{f}_{77} & \bar{f}_{78} & \bar{f}_{79} \dots \\ \bar{f}_{87} & \bar{f}_{88} & \bar{f}_{89} \dots \\ \bar{f}_{97} & \dots & \dots \\ \vdots & & \end{matrix} \end{pmatrix}$$

Block-diagonal matrix with 6 zero eigenvalues

=> 6 zero-frequency vibrations give zero energy to the nuclear Hamiltonian => Redundant coordinates (5-6) do not contribute to the energy of H_N