

Rotations and vibrations of a molecule

~~KE~~ KE in the COM coordinates Coriolis energy

$$T = \sum_{\alpha} \frac{M_{\alpha}}{2} \vec{V}_{\alpha}^2 + \frac{1}{2} \vec{\omega}^{\dagger} \underline{\Pi} \vec{\omega} + \vec{\omega} \cdot \vec{L}$$

Let's consider the obtained KE as Lagrangian.

Then the generalized momenta are

$$\vec{P}_{\alpha} = \frac{\partial T}{\partial \vec{V}_{\alpha}} = M_{\alpha} \vec{V}_{\alpha} \quad \rightarrow \quad \vec{V}_{\alpha} = \frac{1}{M_{\alpha}} \vec{P}_{\alpha}$$

And the total angular momenta

$$\vec{J} = \frac{\partial T}{\partial \vec{\omega}} = \underline{\Pi} \vec{\omega} + \vec{L} \quad \rightarrow \quad \vec{\omega} = \underline{\Pi}^{-1} (\vec{J} - \vec{L})$$

Using the Legendre transformation

$$\begin{aligned} T_H &= \sum_{i=1}^n \dot{q}^i \frac{\partial \mathcal{L}}{\partial \dot{q}^i} - \mathcal{L} = \\ &= \sum_{\alpha} \vec{V}_{\alpha}^{\dagger} \vec{P}_{\alpha} + \vec{\omega}^{\dagger} \vec{J} - T = \\ &= \sum_{\alpha} \frac{\vec{P}_{\alpha}^2}{2M_{\alpha}} + \underbrace{\frac{1}{2} (\vec{J} - \vec{L})^{\dagger} \underline{\Pi}^{-1} (\vec{J} - \vec{L})}_{\text{Rotational and vibrational motions are coupled}} \end{aligned}$$

Rotational and vibrational motions are coupled

Can be decoupled exactly only if Coriolis energy is 0,

or second option is to consider situation

$$\text{when } \vec{L} = 0$$

(2)

What does it mean to have $\vec{L} = 0$ for a system of particles?

$$L_x = \sum_{\alpha} m_{\alpha} \left(y_{\alpha} \frac{dz_{\alpha}}{dt} - z_{\alpha} \frac{dy_{\alpha}}{dt} \right)$$

$$L_y = \sum_{\alpha} m_{\alpha} \left(z_{\alpha} \frac{dx_{\alpha}}{dt} - x_{\alpha} \frac{dz_{\alpha}}{dt} \right)$$

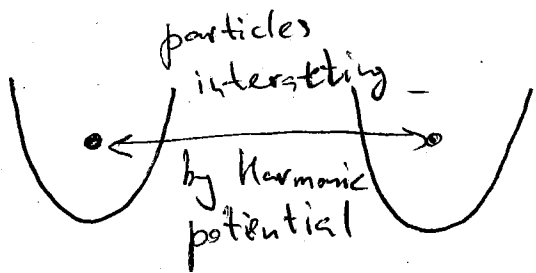
$$L_z = \sum_{\alpha} m_{\alpha} \left(x_{\alpha} \frac{dy_{\alpha}}{dt} - y_{\alpha} \frac{dx_{\alpha}}{dt} \right)$$

As one can see, $\vec{L} = 0$ if all the derivatives are zero \Rightarrow ~~system does not~~ particles do not move,

or alternatively, we can find such values of coefficients $(x_{\alpha}, y_{\alpha}, z_{\alpha})$ that $\vec{L} \approx 0$

Eckart conditions $\vec{L} = \sum_{\alpha} \vec{r}_{\alpha}^0 \times \vec{p}_{\alpha} = 0,$

where \vec{r}_{α}^0 are reference positions of particles



Then every particle can be considered as to be placed in some Harmonic potential.

Therefore Eckart conditions realize in a situation of small vibrations in harmonic potential.

In this case, we can separate vibrational and rotational motions.

Finally, assuming the validity of Eckart conditions, we can write:

$$\hat{H} = \underbrace{\sum_{\alpha} \frac{\vec{p}_{\alpha}^2}{2M_{\alpha}}}_{\text{vibrations}} + \underbrace{\frac{1}{2} \vec{J}^T \underline{I}^{-1} \vec{J}}_{\text{rotations}} + \underbrace{V(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N)}_{\text{PES}}$$

\hat{H}_{rot}

Let's first consider rotations in more details.

We can always choose our coordinate system in such a way that \underline{I} is diagonal,

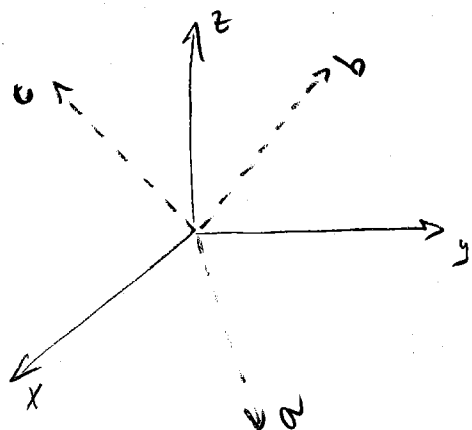
then

$$\hat{H}_{\text{rot}} = \frac{\hbar^2}{2} \left(\frac{1}{I_{aa}} \hat{J}_a^2 + \frac{1}{I_{bb}} \hat{J}_b^2 + \frac{1}{I_{cc}} \hat{J}_c^2 \right)$$

We choose $A(B, C) = \frac{\hbar^2}{4\pi I_{aa} C}$ to convert the resulting energies in cm^{-1}

$$\hat{H}_{\text{rot}} = A \hat{J}_a^2 + B \hat{J}_b^2 + C \hat{J}_c^2$$

a, b, c are orthogonal axis of a coordinate system associated with rotated frame



We need to choose set of good quantum numbers. It is convenient to choose \hat{J}^2 , \hat{J}_z , and \hat{J}_c for characterizing rotations.

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We need to find rotational states in the form of

$$\hat{J}^2 |JKM\rangle = J(J+1) |JKM\rangle$$

$$\hat{J}_z |JKM\rangle = M |JKM\rangle$$

$$\hat{J}_c |JKM\rangle = K |JKM\rangle$$

We first need to prove that $[\hat{J}^2, \hat{H}_{rot}] = 0$
 $\{\hat{J}_z, \hat{J}_c\}$

1) J^2 commutes with any of its projections, so

$$[\hat{J}^2, \hat{J}_{a,b,c}] = 0,$$

therefore it also commutes with $\hat{J}_a^2, \hat{J}_b^2, \hat{J}_c^2,$

$$\text{and thus } [\hat{J}^2, \hat{H}_{rot}] = 0$$

2) Since we rotate our frame with the system,

$$\text{we have } [\hat{J}_z, \hat{J}_c] = 0,$$

$$\text{thus } [\hat{J}_z, \hat{J}_c] = 0$$

3) J_c do not commute with J_a , or J_b ,

thus in general we have

$$[\hat{J}_c, \hat{H}_{rot}] = i(B-A)(\hat{J}_a \hat{J}_b + \hat{J}_b \hat{J}_a),$$

because $[\hat{J}_a, \hat{J}_b] = -i\hbar \hat{J}_c$ etc.

Therefore, only molecules where two axes of inertia are equal can be described by $|JKM\rangle$ functions.

Let's consider some specific molecules.

I) Spherical rotator
 $I_{aa} = I_{bb} = I_{cc}$, then $A = B = C$

$$\hat{H}_{rot} = B (\hat{J}_a^2 + \hat{J}_b^2 + \hat{J}_c^2) = B \hat{J}^2$$

$\hat{H}_{rot} \psi_{rot} = E_{rot} \psi_{rot}$, since \hat{H}_{rot} commutes with J^2, J_z, J_c , we can obtain

$$E_{rot} = B J(J+1)$$

these energy states are degenerate because quantum numbers K and M do not present in E_{rot} . \hat{J}_z and \hat{J}_c both $(2J+1)$ degenerate

total degeneracy is $(2J+1)^2$. Molecules: CH_4, SF_6 etc.

II) Symmetric rotator

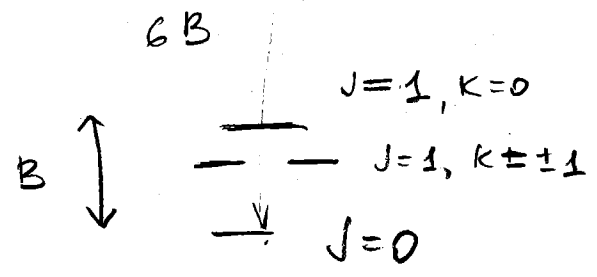
a) $I_{aa} < I_{bb} = I_{cc}$

$$\begin{aligned} \hat{H}_{rot} &= A \hat{J}_a^2 + B (\hat{J}_b^2 + \hat{J}_c^2) = \\ &= B \hat{J}^2 + (A-B) \hat{J}_a^2 \end{aligned}$$

$$\hat{H}_{rot} \chi_{rot} = B J(J+1) + (A-B) K^2$$

M is not contributing and thus energies are $(2J+1)$ -degenerate, and K is with 2 power, so total degeneracy is

$$\begin{matrix} 2(2J+1) & \text{for } K \neq 0 \\ (2J+1) & \text{for } K = 0 \end{matrix} \quad \left. \begin{matrix} \text{---} \uparrow \text{---} \\ \text{---} \end{matrix} \right\} J=2$$



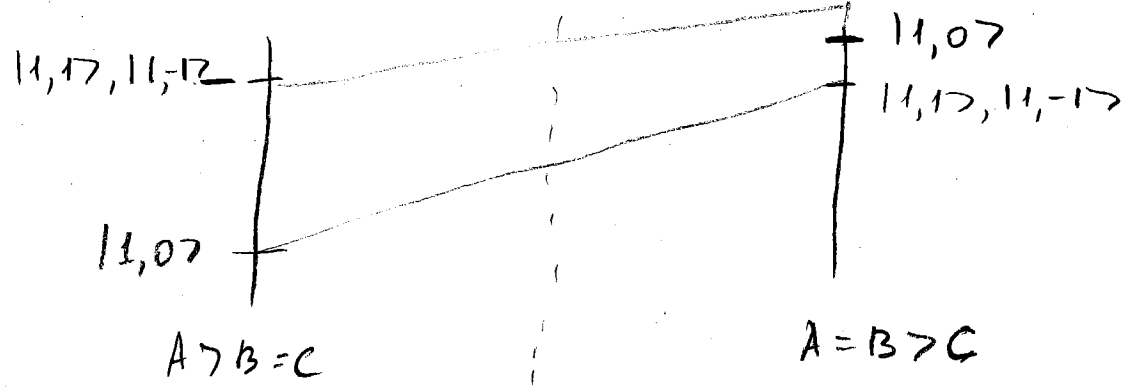
Molecules with symmetries

$C_n, C_{nv}, C_{nh}, D_n, D_{nd}, D_{nh}$ with $n \geq 3$
 NH_3, CH_3Cl etc.

IV) Asymmetric rotor

$$A \neq B \neq C$$

It is convenient to consider two symmetric rotors



and C_i, C_s, S_n

$C_n, C_{nv}, C_{nh}, D_n, D_{nd}, D_{nh}$ with $n=2$,

IV Linear molecules

$$I_{aa} = I_{bb} \quad , \quad I_{cc} = 0$$

$$\hat{H}_{\text{rot}} = B (\hat{J}_a^2 + \hat{J}_b^2) = B (\hat{J}^2)$$

$$E_{\text{rot}} = B J(J+1) \quad \text{with } (2J+1) \text{ degeneracy}$$

For diatomic $I = \mu r^2$, where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{is the reduced mass.}$$

Generally the energy splitting of rotational levels is from few cm^{-1} to few tens of cm^{-1} .

While for electronic states separation is low eV, thus it is thousands of cm^{-1} .

Vibrational motion in molecules

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The Hamiltonian in molecular frame:

$$H = \underbrace{\sum_{\alpha} \frac{\vec{p}_{\alpha}^2}{2M_{\alpha}}}_T + V(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_d, \dots)$$

This Hamiltonian is written in some frame where we assumed that coordinates vectors are orthogonal. This is not necessarily the most convenient coordinates. Because if we add more atoms to the system, we need to reconsider the form of PES etc., so Cartesian coordinates are difficult to formalize.

In general (not necessarily orthogonal) coordinates, the KE can be written as

$$T = \frac{1}{2} \sum_{ij} \frac{a_{ij}}{m_i m_j} p_i p_j, \text{ where we used new coordinates}$$

$$\vec{r}_k = \sum_j c_{kj} \vec{R}_j$$

$$V(\vec{R}_1, \dots, \vec{R}_M) \Rightarrow V(\vec{r}_1, \dots, \vec{r}_M)$$

Let's expand V in Taylor series:

$$V = V^0 + \sum_i \left(\frac{\partial V}{\partial R_i} \right)_0 R_i + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 V}{\partial R_i \partial R_j} \right)_0 R_i R_j + \dots$$

If reference point is chosen in the minima of V ,

$$\text{then } \frac{\partial V}{\partial R_i} \equiv 0, \text{ so } V = V^0 + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 V}{\partial R_i \partial R_j} \right)_0 R_i R_j$$

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Therefore, we have

$$H = \frac{1}{2} \sum_{ij} \frac{a_{ij}}{m_i m_j} p_i p_j + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 V}{\partial R_i \partial R_j} \right)_0 R_i R_j + V_0$$

To simplify the problem, we can find new

orthogonal coordinates, which are obviously

those which diagonalize $\frac{\partial^2 V}{\partial R_i \partial R_j}$ matrix (Hessian) Hess

$$L^T \text{Hess } L = \lambda$$

$$Q = \frac{1}{M} L R$$

Then the Hamiltonian becomes

$$\hat{H}_{\text{vib}} = \sum_i^{3M-6} \left(-\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \lambda_i Q_i^2 \right)$$

Vibrational Hamiltonian

$$\hat{H}_{\text{vib}} \chi_{\text{vib}} = E_{\text{vib}} \chi_{\text{vib}}$$

Importantly, H_{vib} is separable, so each vibrational

mode can be considered separately from each other

$$\chi_{\text{vib}}(Q_1, \dots, Q_{3M-6}) = \prod_{j=1}^{3M-6} \chi_j(Q_j)$$

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial Q_j^2} + \frac{1}{2} \lambda_j Q_j^2 \right) \chi_j(Q_j) = \epsilon_j \chi_j(Q_j)$$

Normal coordinates, normal vibrational modes etc.

Importantly, within a normal mode all nuclei of a molecule vibrate with the same frequency and reach max. amplitude positions (or pass reference) at the same time.

Normal modes are convenient starting point to build more sophisticated models.