Lesson 9

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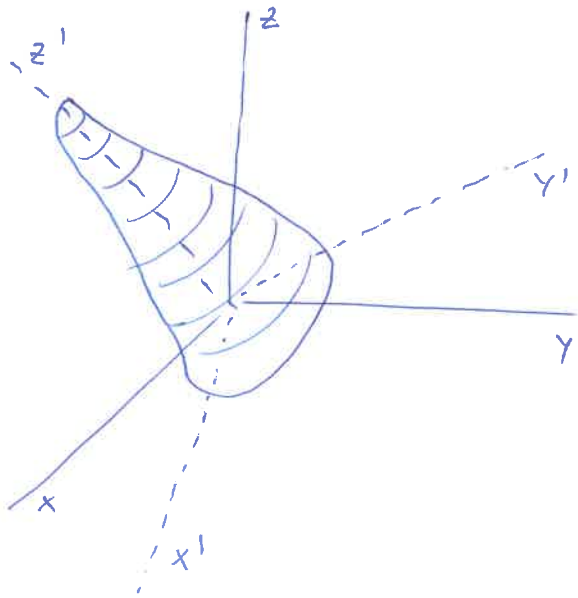
Molecular rotations

- Primed molecular coordinates attached to the molecule
- Principal axes of the momentum inertia tensor
- Kinetic energy $E = \frac{1}{2}\left(\frac{L_{x'}^2}{I_{x'}} + \frac{L_{y'}^2}{I_{y'}} + \frac{L_{z'}^2}{I_{z'}}\right)$



- Quantum Hamiltonian

$$\boxed{\hat{H} = a\hat{L}_{x'}^2 + b\hat{L}_{y'}^2 + c\hat{L}_{z'}^2}$$

a, b, c ... rotational constants of the molecule

$$a = \frac{1}{2I_{x'}} \quad ; \quad b = \frac{1}{2I_{y'}} \quad ; \quad c = \frac{1}{2I_{z'}}$$

1.) Spherical top

$a = b = c = \frac{1}{2I}$

$$\boxed{\hat{H} = a\hat{L}^2}$$

Eigenstates:

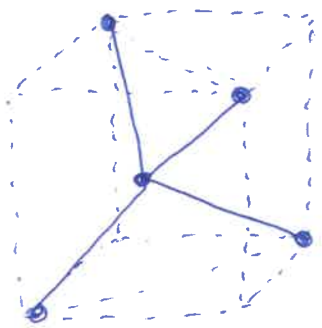
$$\psi^j_{mk}(\alpha,\beta,\gamma) = \sqrt{\frac{2j+1}{8\pi}}\, D^j_{mk}(\alpha,\beta,\gamma)$$

$E_j = a\, j(j+1)$; $j = 0, 1, 2, \ldots$

$(k, m) = -j, -j+1, \ldots 0, \; +j$ ... degeneracy level $= (2j+1)^2$

Similar to diatomic molecules. Differs in the degeneracy level and the degrees of freedom. Diatomics are not rotated around along the axis.

Example   methane CH_4, SF_6 ... high symmetry



2.) Symmetric top $a = b \neq c$ Symmetry C_n for $n \geq 3$

$$\hat{H} = a\hat{L}_{x'}^2 + a\hat{L}_{y'}^2 + c\hat{L}_{z'}^2 + aL_{z'}^2 - aL_{z'}^2$$

$$\boxed{\hat{H} = a\hat{L}^2 + (c-a)L_{z'}^2}$$

Eigenstates: $\psi_{mk}^{j}(\alpha,\beta,\gamma) = \sqrt{\frac{2j+1}{8\pi}}\, D_{mk}^{j}(\alpha,\beta,\gamma)$

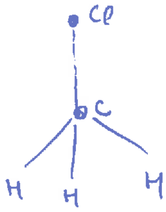
$$\boxed{E_{jk} = a\,j(j+1) + (c-a)k^2}$$

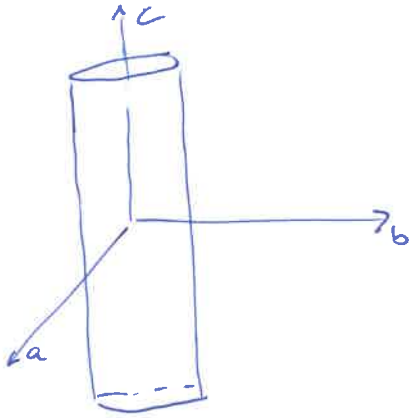
Degeneracy level $= 2(2j+1)$

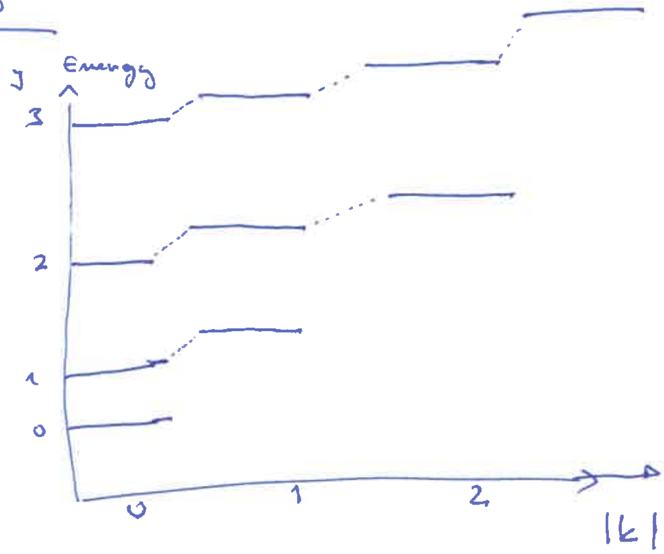
a.) Prolate symmetric top : $c > a = b$

Examples:

CH_3Cl





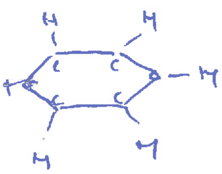


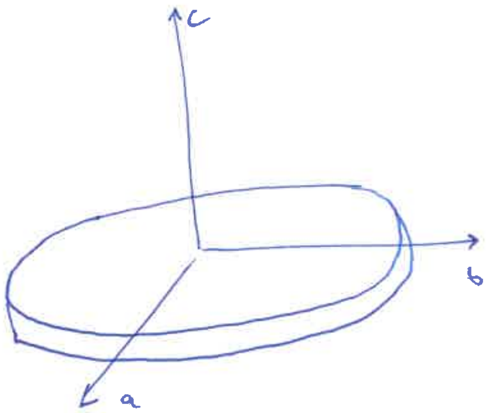
b.) Oblate symmetric top : $c < a = b$

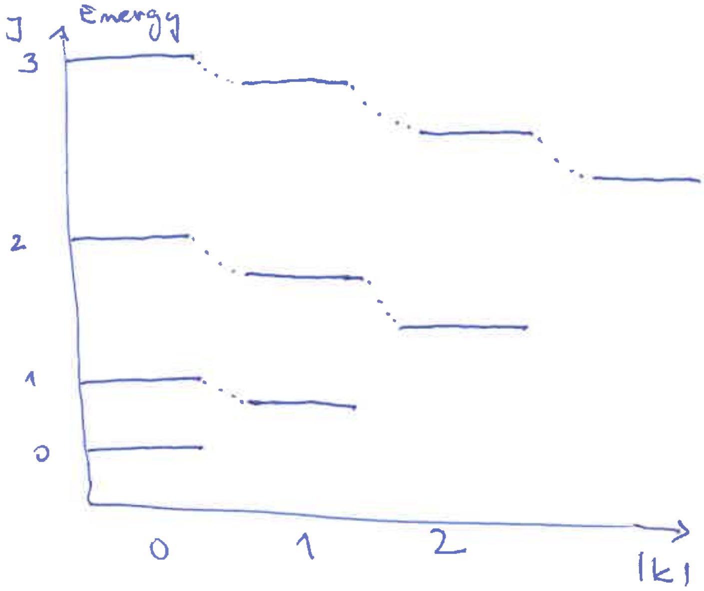
Examples

benzene | amonia

C_6H_6 NH_3







3.) Asymmetric top $a \neq b \neq c$

$D^j_{mk}(\alpha,\beta,\gamma)$ are not the eigenfunctions anymore because $L_{x'}$ and $L_{y'}$ couple D^j_{mk} states through the index "k". ~~Lab. frame~~ - Quantum ~~pre~~ precession. Lab. frame ~~ge~~ quantum numbers (j,m) are still conserved. Eigenstates can be written as:

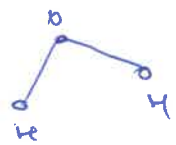
$$|\phi^j_{m\gamma}(\alpha,\beta,\gamma)\rangle = \sum_{k'} c_k |\psi^j_{mk'}\rangle$$

$$\langle\psi^j_{mk}| \qquad (\hat{H} - E)|\phi^j_{m\gamma}\rangle = 0$$

$$\sum_{k'} \langle\psi^j_{mk}| aL_{x'}^2 + bL_{y'}^2 + cL_{z'}^2 |\psi^j_{mk'}\rangle c_{k'} = E c_k$$

Eigenvalue problem in the space with fixed "j". Dimension of the Hamiltonian matrix is $(2j+1) \times (2j+1)$

Examples .. most of the molecules, e.g. H_2O



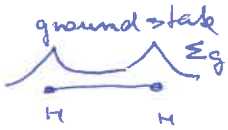
Lesson 9

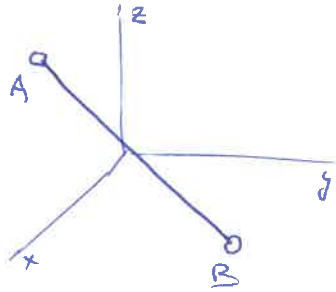
Nuclear spin consideration

On the example of the hydrogen molecule H_2

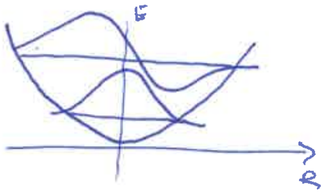
$$\Psi = \Psi_e \cdot \Psi_v \cdot \Psi_r \cdot \Psi_{NS}$$

1.) $P_{AB}\Psi_e = \Psi_e$ ... electronic ground state





2.) $P_{AB}\Psi_v = \Psi_v$ ... vibrational ground state

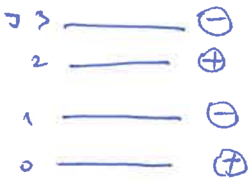


3.) $P_{AB}\Psi_r = ?$

Operation P_{AB} by rotations: $\vartheta \to \pi - \vartheta$; $x = \cos\vartheta \to -x$ $\quad P_l^m(x) = (-1)^{l+m} P_l^m(-x)$

$\varphi \to \pi + \varphi$; $e^{im\varphi} \to (-1)^m e^{im\varphi}$

$$\boxed{P_{AB}\Psi_r = (-1)^l \Psi_r}$$



4.) At the creation of H_2 there are all 4 nuclear-spin configurations $\alpha\alpha$, $\beta\beta$, $\alpha\beta$, $\beta\alpha$ $(\uparrow\uparrow, \downarrow\downarrow, \uparrow\downarrow, \downarrow\uparrow)$. They form states of the total nuclear spin: Triplet configurations:

$(1,1) = \uparrow\uparrow$

$(1,0) = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$

$(1,-1) = \downarrow\downarrow$

$\Big\}$ ortho H_2, $P_{AB}\Psi_{NS} = \Psi_{NS}$

Singlet configuration: $(0,0) = (\uparrow\downarrow - \downarrow\uparrow)$ $\}$ para H_2, $P_{AB}\Psi_{NS} = -\Psi_{NS}$

- ortho H_2 occupies ~~even~~ odd-j rotational levels $j = 1, 3, 5, \ldots$
- para H_2 occupies the even-j rotational levels $j = 0, 2, 4, \ldots$
- At higher temperatures the ratio $\frac{\text{ortho}}{\text{para}} = \frac{3}{1}$
- At low temperatures it is impossible to cool ortho H_2 without a special conversion ortho → para. ~~Both~~ The isomers behave as 2 different gases → anomalous heat capacities of H_2.