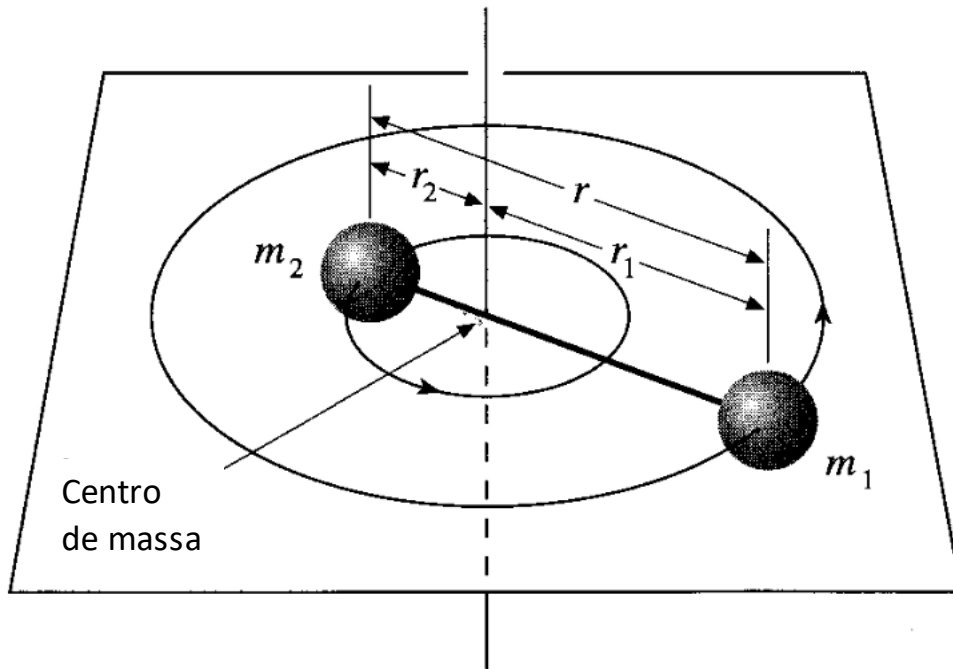


5930300 – Química Quântica

Prof. Dr. Antonio G. S. de Oliveira Filho

Rotor rígido

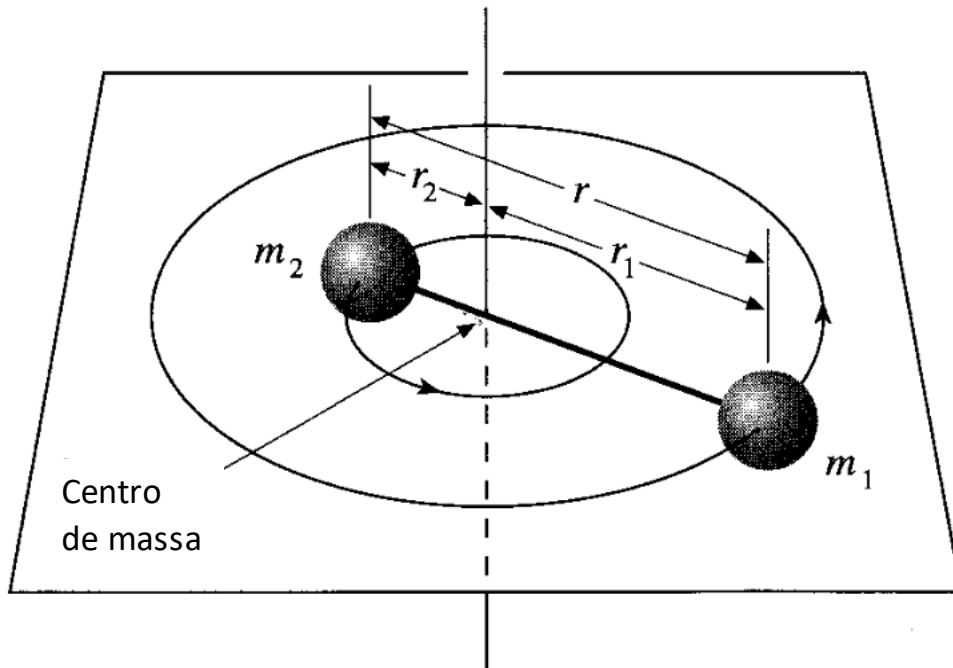
Rotações moleculares



- Massas m_1 e m_2 rodam ao redor do centro de massas.
- r_1 e r_2 : distâncias fixas até o centro de massas.
- ν_{rot} : frequência de rotação.
- Sem ação de forças externas.

Rotor rígido

Rotações moleculares



Velocidades

$$v_1 = 2\pi r_1 \nu_{\text{rot}} = r_1 \omega$$

$$v_2 = 2\pi r_2 \nu_{\text{rot}} = r_2 \omega$$

- $\omega = 2\pi\nu$: frequência angular

Rotor rígado

$$v_1 = r_1\omega$$

$$v_2 = r_2\omega$$

Energia cinética (K)

$$K = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2$$

$$= \frac{1}{2}(m_1r_1^2\omega^2 + m_2r_2^2\omega^2) = \frac{1}{2}(m_1r_1^2 + m_2r_2^2)\omega^2$$

$$= \frac{1}{2}I\omega^2$$

$$I = m_1r_1^2 + m_2r_2^2 = \mu r^2$$

Momento de inércia

$$\mu = \frac{m_1m_2}{m_1 + m_2}$$

Massa reduzida

Rotor rígido

Energia cinética (K)

$$K = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2}$$
$$= \frac{1}{2}I\omega^2$$

Momento angular (L)

$$L = I\omega$$

$$K = \frac{L^2}{2I}$$

$$V(x, y, z) = 0$$

Rotor rígido

$$E = K + V$$

Mecânica clássica



$$\hat{H} = \hat{K} + \hat{V}$$

Mecânica quântica

$$K = \frac{L^2}{2I}$$

$$\hat{K} = \frac{\hbar^2 \nabla^2}{2I} \quad (r \text{ constante})$$

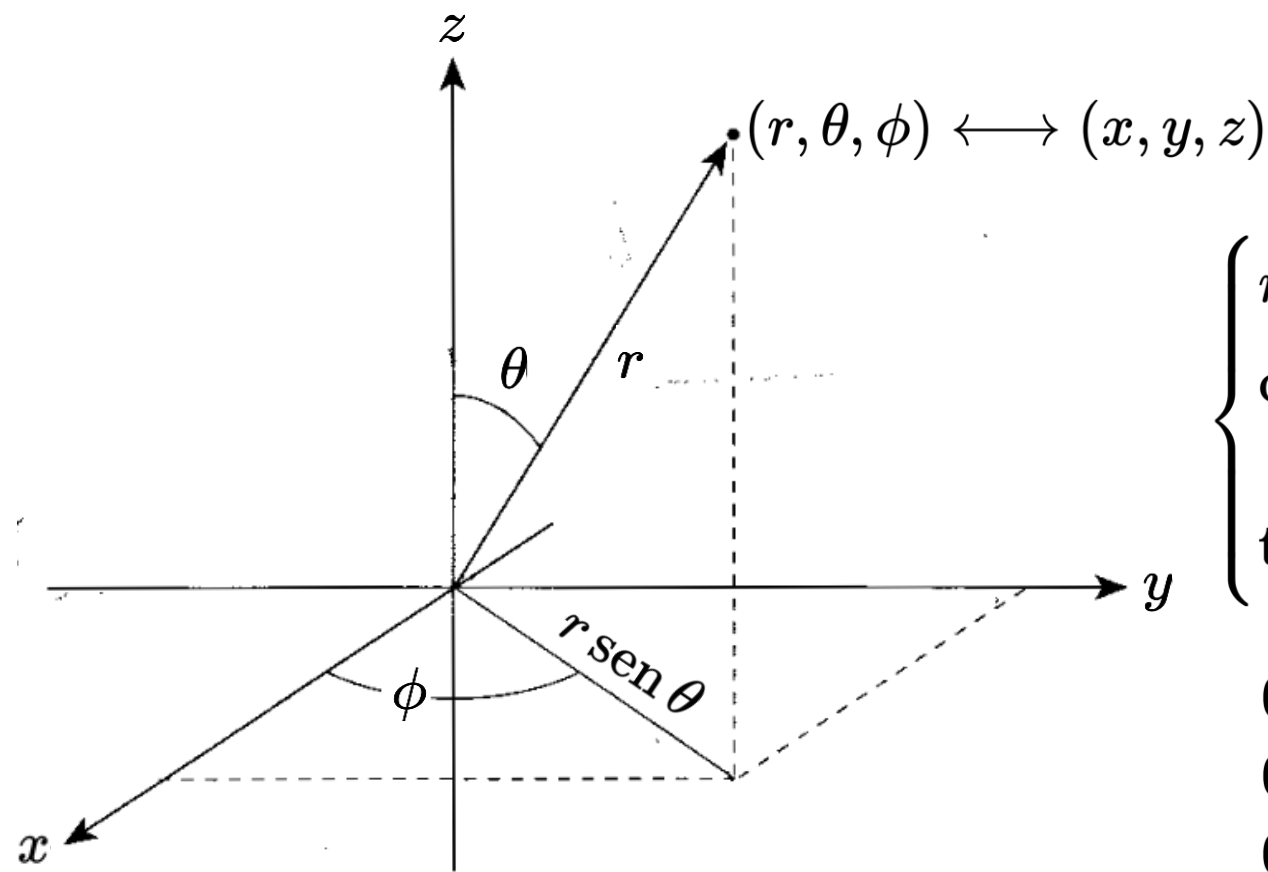
$$V(x, y, z) = 0$$

$$\hat{V} = \hat{O} = 0$$

$$\hat{L}^2 = -\hbar^2 \nabla^2 = -\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

$$\hat{H} = -\frac{\hbar^2}{2I} \nabla^2 = \frac{\hat{L}^2}{2I}$$

Coordenadas esféricas



$$\begin{cases} r = (x^2 + y^2 + z^2)^{1/2} \\ \cos \theta = \frac{z}{(x^2 + y^2 + z^2)^{1/2}} \\ \tan \phi = \frac{y}{x} \end{cases}$$

$$0 \leq r < \infty$$

$$0 \leq \theta \leq \pi$$

$$0 \leq \phi \leq 2\pi$$

$$\begin{cases} x = r \operatorname{sen} \theta \cos \phi & -\infty < x < \infty \\ y = r \operatorname{sen} \theta \operatorname{sen} \phi & -\infty < y < \infty \\ z = r \cos \theta & -\infty < z < \infty \end{cases}$$

Rotor rígido

Operador momento angular

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \begin{cases} x = r \operatorname{sen} \theta \cos \phi \\ y = r \operatorname{sen} \theta \operatorname{sen} \phi \\ z = r \cos \theta \end{cases}$$

Regra da cadeia

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)_{\theta, \phi} + \frac{1}{r^2 \operatorname{sen} \theta} \frac{\partial}{\partial \theta} \left(\operatorname{sen} \theta \frac{\partial}{\partial \theta} \right)_{r, \phi} + \frac{1}{r^2 \operatorname{sen}^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right)_{r, \theta}$$

Para r constante:

$$\nabla^2 = \frac{1}{r^2} \frac{1}{\operatorname{sen} \theta} \frac{\partial}{\partial \theta} \left(\operatorname{sen} \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2} \frac{1}{\operatorname{sen}^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Rotor rígado

Operador momento angular

$$\nabla^2 = \frac{1}{r^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2} \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (\text{para } r \text{ constante})$$

$$\hat{L}^2 = -\hbar^2 \nabla^2 \qquad \hat{H} = \frac{\hat{L}^2}{2I}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right]$$

$$\hat{H} = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right]$$

Rotor rígado

Equação de Schrödinger

$$\hat{H} = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right]$$

$$\hat{H}Y(\theta, \phi) = EY(\theta, \phi)$$

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] Y(\theta, \phi) = EY(\theta, \phi)$$

Rotor rígado

Equação de Schrödinger

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] Y(\theta, \phi) = EY(\theta, \phi)$$

$\times \sin^2 \theta$

$$-\frac{\hbar^2}{2I} \left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \left(\frac{\partial^2}{\partial \phi^2} \right) \right] Y(\theta, \phi) = E \sin^2 \theta Y(\theta, \phi)$$

$$\left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \left(\frac{\partial^2}{\partial \phi^2} \right) \right] Y(\theta, \phi) = -(2IE/\hbar^2) \sin^2 \theta Y(\theta, \phi)$$

$$\beta = \frac{2IE}{\hbar^2}$$

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} + (\beta \sin^2 \theta) Y = 0$$

Rotor rígido

Harmônicos esféricos

$$\text{sen } \theta \frac{\partial}{\partial \theta} \left(\text{sen } \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} + (\beta \text{sen}^2 \theta) Y = 0$$

$$\beta = \frac{2IE}{\hbar^2}$$

Separação de variáveis

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

$$\Phi(\phi) \text{sen } \theta \frac{d}{d\theta} \left(\text{sen } \theta \frac{d\Theta}{d\theta} \right) + \Theta(\theta) \frac{d^2 \Phi}{d\phi^2} + (\beta \text{sen}^2 \theta) \Theta(\theta) \Phi(\phi) = 0$$

$$\div \Theta(\theta)\Phi(\phi)$$

$$\frac{\text{sen } \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\text{sen } \theta \frac{d\Theta}{d\theta} \right) + \beta \text{sen}^2 \theta + \frac{1}{\Phi(\phi)} \frac{d^2 \Phi}{d\phi^2} = 0$$

Rotor rígido

Harmônicos esféricos

$$\underbrace{\frac{\text{sen } \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\text{sen } \theta \frac{d\Theta}{d\theta} \right) + \beta \text{sen}^2 \theta}_{\text{Só depende de } \theta} + \underbrace{\frac{1}{\Phi(\phi)} \frac{d^2\Phi}{d\phi^2}}_{\text{Só depende de } \phi} = 0$$

$$\begin{cases} \frac{\text{sen } \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\text{sen } \theta \frac{d\Theta}{d\theta} \right) + \beta \text{sen}^2 \theta = m^2 \\ \frac{1}{\Phi(\phi)} \frac{d^2\Phi}{d\phi^2} = -m^2 \end{cases}$$

m^2 é uma constante (de separação de variáveis).

Rotor rígado

Harmônicos esféricos

$$\frac{1}{\Phi(\phi)} \frac{d^2\Phi}{d\phi^2} = -m^2$$

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi(\phi)$$

Qual função $\Phi(\phi)$ que derivada duas vezes resulta nela mesma vezes uma constante ao quadrado com o sinal trocado?

Fórmula de Euler

$$e^{ix} = \cos x + i \sin x$$

$$\Phi(\phi) = A_m e^{im\phi}$$

$$\Phi(\phi) = A_{-m} e^{-im\phi}$$

Rotor rígido

Harmônicos esféricos

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi(\phi)$$

$$\Phi(\phi) = A_m e^{im\phi}$$

$$\frac{d(A_m e^{im\phi})}{d\phi} = imA_m e^{im\phi} = im\Phi(\phi)$$

$$\frac{d^2(A_m e^{im\phi})}{d\phi^2} = \frac{d}{d\phi} \frac{d(A_m e^{im\phi})}{d\phi} = (i)^2 m^2 \Phi(\phi)$$

$$\frac{d^2(A_m e^{im\phi})}{d\phi^2} = -m^2 A_m e^{im\phi}$$

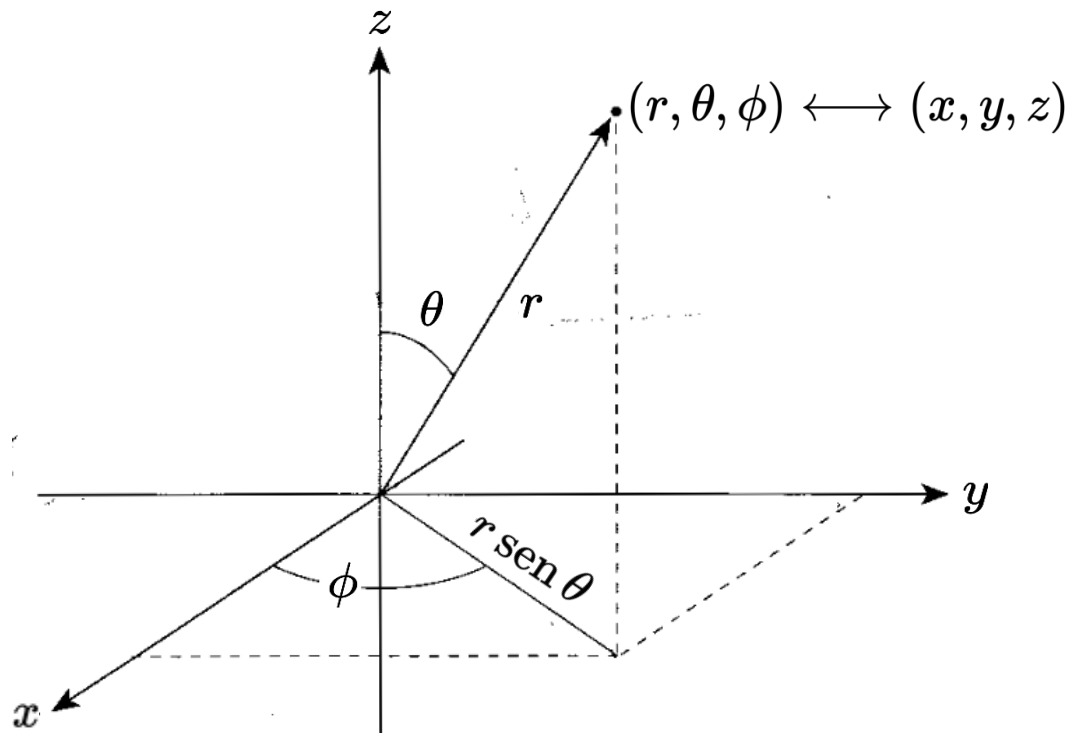
O mesmo pode ser verificado para outra solução.

Rotor rígido

Harmônicos esféricos

$\Phi(\phi) = A_m e^{im\phi}$ deve ser função unívoca de ϕ .

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$



Rotor rígido

Harmônicos esféricos

$$\Phi(\phi) = A_m e^{im\phi}$$

$$\Phi(\phi) = A_{-m} e^{-im\phi}$$

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

$$A_m e^{im(\phi+2\pi)} = A_m e^{im\phi}$$

$$A_{-m} e^{-im(\phi+2\pi)} = A_{-m} e^{-im\phi}$$

$$e^{im(\phi+2\pi)} = e^{im\phi}$$

$$e^{-im(\phi+2\pi)} = e^{-im\phi}$$

$$\frac{e^{im(\phi+2\pi)}}{e^{im\phi}} = 1$$

$$\frac{e^{-im(\phi+2\pi)}}{e^{-im\phi}} = 1$$

$$e^{i2\pi m} = 1$$

$$e^{-i2\pi m} = 1$$

$$e^{\pm i2\pi m} = 1$$

Rotor rígado

Harmônicos esféricos

$$e^{\pm i2\pi m} = 1$$

Fórmula de Euler

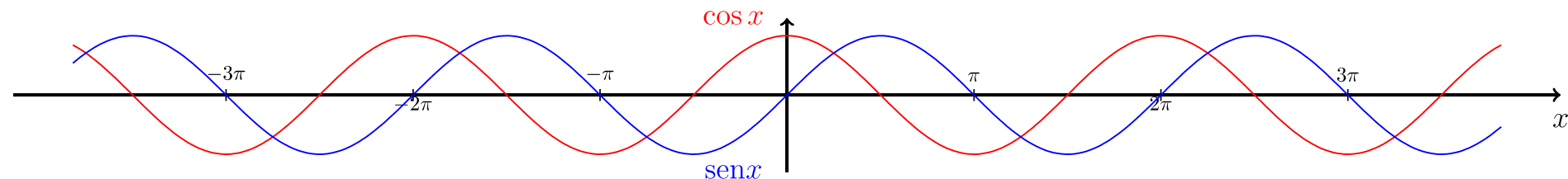
$$e^{ix} = \cos x + i \operatorname{sen} x$$

$$x = 2\pi m$$

$$\cos(2\pi m) \pm i \operatorname{sen}(2\pi m) = 1$$

$$\begin{cases} \operatorname{sen}(2\pi m) = 0 \\ \cos(2\pi m) = 1 \end{cases}$$

$$m = 0, \pm 1, \pm 2, \dots$$



Rotor rígado

Harmônicos esféricos

$$\Phi_m(\phi) = A_m e^{im\phi} \quad m = 0, \pm 1, \pm 2, \dots$$

$\Phi_m(\phi)$ deve ser normalizada.

$$\int_0^{2\pi} \Phi_m^*(\phi) \Phi_m(\phi) d\phi = 1 \quad |A_m|^2 2\pi = 1$$

$$\int_0^{2\pi} A_m^* e^{-im\phi} A_m e^{im\phi} d\phi = 1 \quad A_m = (2\pi)^{-1/2}$$

$$|A_m|^2 \int_0^{2\pi} d\phi = 1$$

$$\Phi_m(\phi) = \frac{1}{(2\pi)^{1/2}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \dots$$

Rotor rígido

Harmônicos esféricos

$$\left\{ \begin{array}{l} \frac{\text{sen } \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\text{sen } \theta \frac{d\Theta}{d\theta} \right) + \beta \text{sen}^2 \theta = m^2 \\ \frac{1}{\Phi(\phi)} \frac{d^2 \Phi}{d\phi^2} = -m^2 \longrightarrow \Phi_m(\phi) = \frac{1}{(2\pi)^{1/2}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \dots \end{array} \right.$$

Equação para $\Theta(\theta)$ não tem coeficientes constantes: difícil de resolver.

$$\Theta(\theta) = \left[\frac{(2l+1)(l-|m|)!}{2(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta)$$

$P_l^{|m|}(x)$: funções associadas de Legendre
(polinômios em $\cos \theta$ e $\text{sen } \theta$).

Condições da solução:

$$\beta = l(l+1)$$

$$l = 0, 1, 2, \dots$$

$$m = 0, \pm 1, \pm 2, \dots, \pm l$$

Rotor rígido

Harmônicos esféricos

$$Y_l^m(\theta, \phi) = \left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos\theta) e^{im\phi}$$

$$l = 0, 1, 2, \dots$$

$$m = 0, \pm 1, \pm 2, \dots, \pm l$$

Notação específica para rotor rígido:

$$l \rightarrow J = 0, 1, 2, \dots$$

$$m \rightarrow M_J = 0, \pm 1, \pm 2, \dots, \pm J$$

$$Y_l^m(\theta, \phi) \rightarrow Y_J^{M_J}(\theta, \phi)$$

Rotor rígado

Harmônicos esféricos

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$$

$$Y_1^1 = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{i\phi}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi}$$

$$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{2i\phi}$$

$$Y_2^1 = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$$

$$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{-i\phi}$$

$$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{-2i\phi}$$

Rotor rígido

Harmônicos esféricos

Autovalores e autofunções

$Y_J^{M_J}(\theta, \phi)$ são autofunções de \hat{L}^2 .

$$\underbrace{\hat{L}^2}_{\text{Operador}} \underbrace{Y_J^{M_J}(\theta, \phi)}_{\text{Autofunção}} = \underbrace{\hbar^2 J(J+1)}_{\text{Autovalor}} \underbrace{Y_J^{M_J}(\theta, \phi)}_{\text{Autofunção}}$$

Os valores possíveis de L^2 são $\hbar^2 J(J+1)$, com $J = 0, 1, 2, \dots$

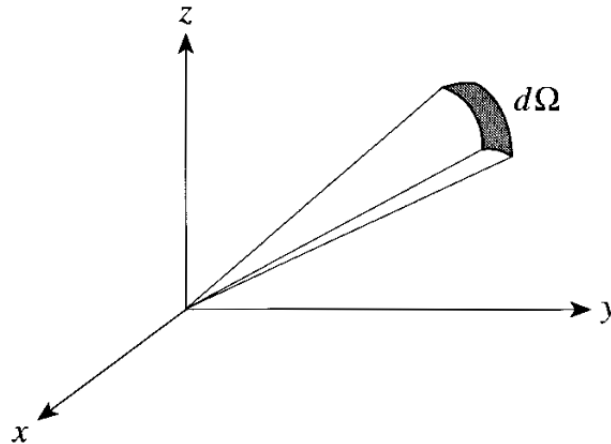
Rotor rígido

Harmônicos esféricos

Ortonormalidade

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_l^m(\theta, \phi)^* Y_n^k(\theta, \phi) = \delta_{ln} \delta_{mk}$$

Note que a integral é sobre uma superfície esférica, cujo elemento diferencial de área é $d\Omega = \sin \theta d\theta d\phi$.



Rotor rígado

Energia

$$\hat{H}Y_J^{M_J}(\theta, \phi) = \frac{\hat{L}^2}{2I}Y_J^{M_J}(\theta, \phi) = EY_J^{M_J}(\theta, \phi)$$

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] Y_J^{M_J}(\theta, \phi) = EY_J^{M_J}(\theta, \phi)$$

$$\beta = \frac{2IE}{\hbar^2} = J(J + 1) \quad J = 0, 1, 2, \dots$$

$$E_J = \frac{\hbar^2}{2I} J(J + 1)$$
$$J = 0, 1, 2, \dots$$

Rotor rígido

Energia

$$E_J = \frac{\hbar^2}{2I} J(J + 1)$$

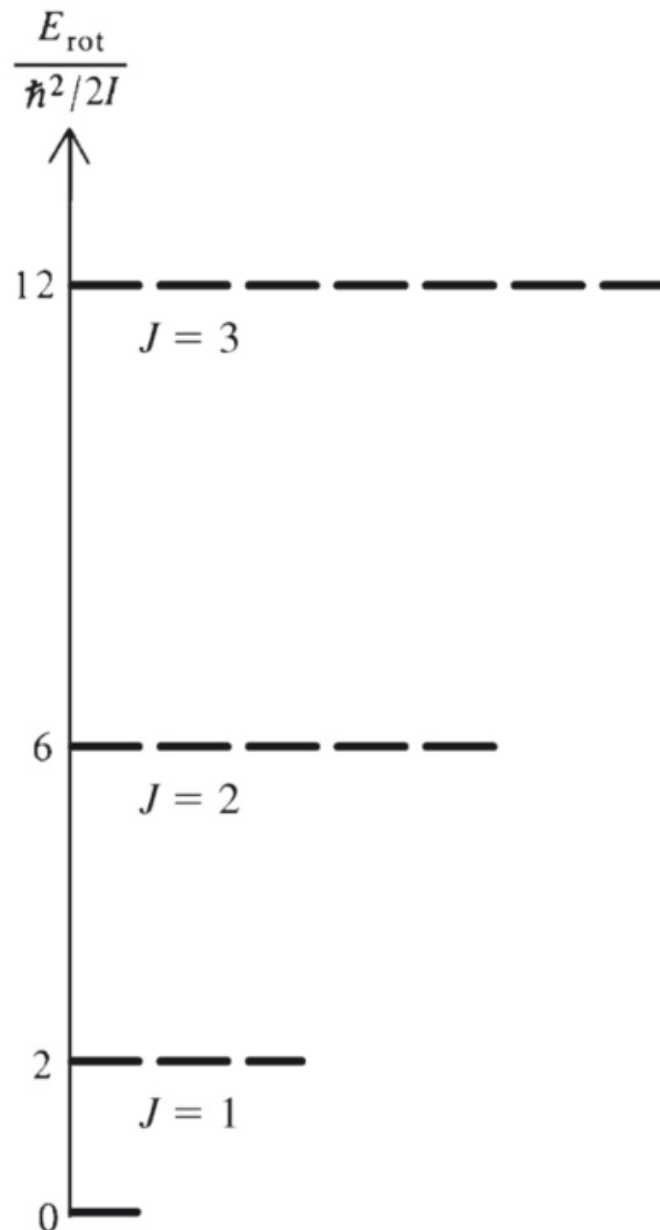
$$J = 0, 1, 2, \dots$$

$$M_J = 0, \pm 1, \pm 2, \dots, \pm J$$

O número quântico M_J não aparece na expressão da energia:

- Estados com mesmo J e diferentes M_J têm a mesma energia, são degenerados.

Degenerescência: $g_J = 2J + 1$



Espectroscopia rotacional

Regra de seleção: $\Delta J = \pm 1$ (Transição observada/permitida)

$$\begin{aligned}\Delta E &= E_{J+1} - E_J \\ &= \frac{\hbar^2}{2I} \{(J+1)(J+2) - J(J+1)\} \\ &= \frac{\hbar^2}{2I} \{\cancel{J^2} + 3J + 2 - \cancel{J^2} - J\} \\ &= \frac{h^2}{8\pi^2 I} \{2J + 2\} = \frac{h^2}{4\pi^2 I} (J + 1)\end{aligned}$$

Espectroscopia rotacional

Regra de seleção: $\Delta J = \pm 1$ (Transição observada/permitida)

$$\Delta E = E_{J+1} - E_J = \frac{h^2}{4\pi^2 I} (J + 1)$$

$$\Delta E = h\nu$$

$$\nu = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I} (J + 1) \quad J = 0, 1, 2, \dots$$

É comum reescrever assim:

$$\nu = 2B(J + 1)$$

$$B = \frac{h}{8\pi^2 I}$$

Constante rotacional (frequência)

Espectroscopia rotacional

$$\nu = 2B(J + 1) \quad J = 0, 1, 2, \dots$$

$$B = \frac{h}{8\pi^2 I}$$

Constante rotacional (frequência)

Em termos do número de onda ($\tilde{\nu}$)

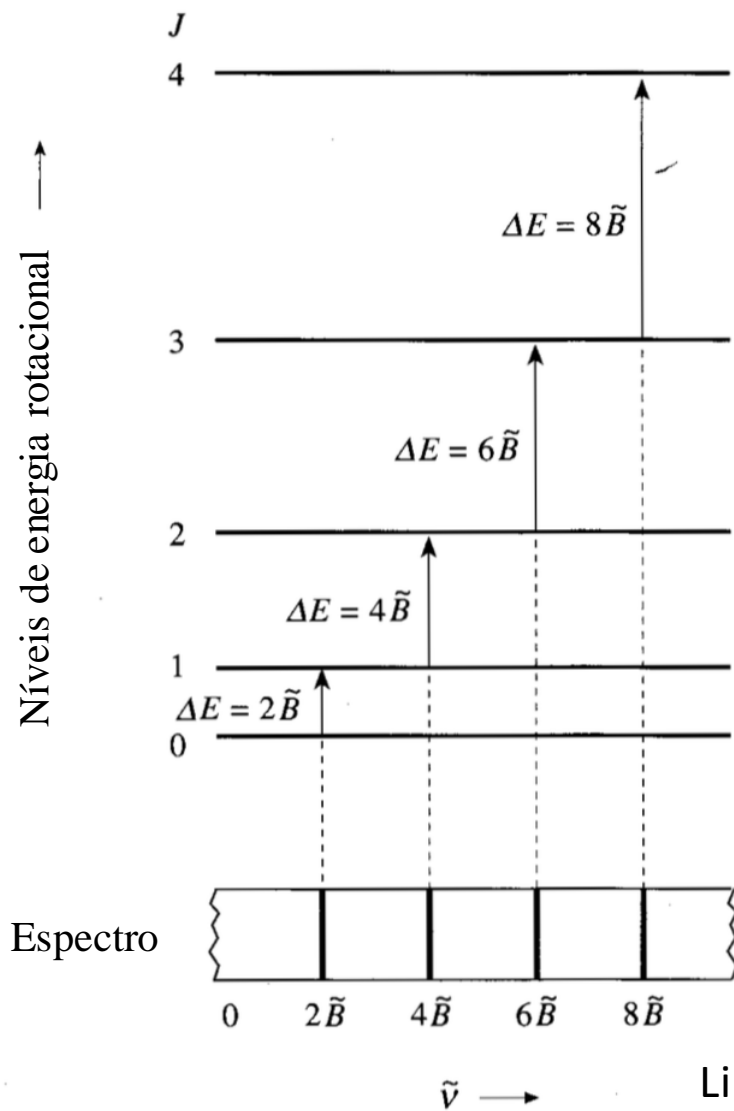
$$\tilde{\nu} = \frac{\nu}{c}$$

$$\tilde{\nu} = 2\tilde{B}(J + 1) \quad J = 0, 1, 2, \dots$$

$$\tilde{B} = \frac{h}{8\pi^2 \tilde{c} I}$$

Constante rotacional (núm. de onda)

Espectroscopia rotacional

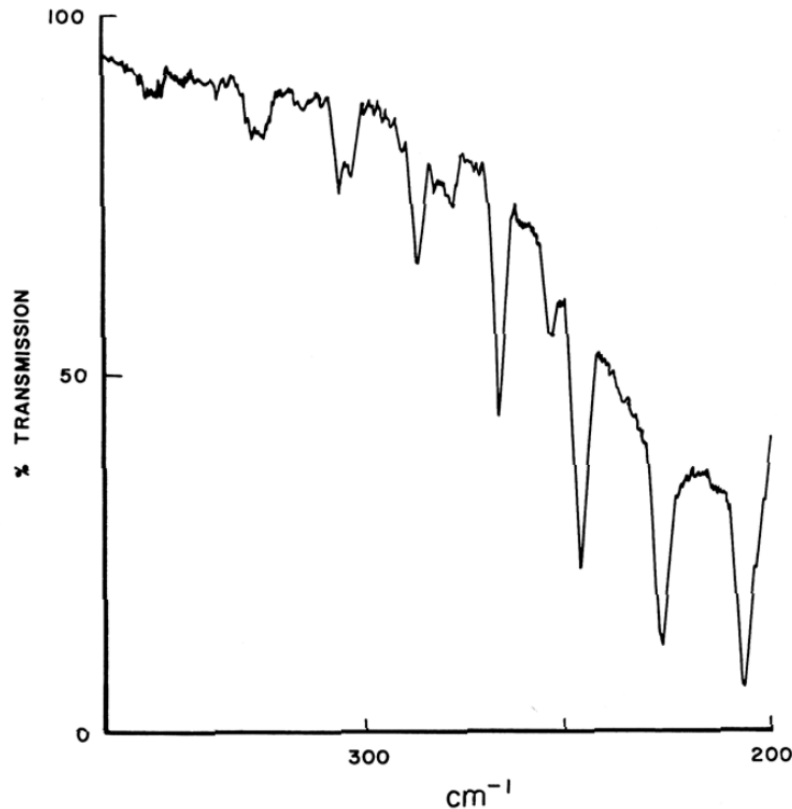


Linhas igualmente espaçadas de $2B$.

Espectroscopia rotacional

Exemplo

O espectro micro-ondas do H^{35}Cl consiste numa série de de linhas igualmente espaçadas de $20,9 \text{ cm}^{-1}$. Determine o comprimento da ligação do H^{35}Cl .



$$2\tilde{B} = 20,9 \text{ cm}^{-1}$$

$$\tilde{B} = \frac{h}{8\pi^2 \tilde{c} I}$$

$$I = \mu R^2$$

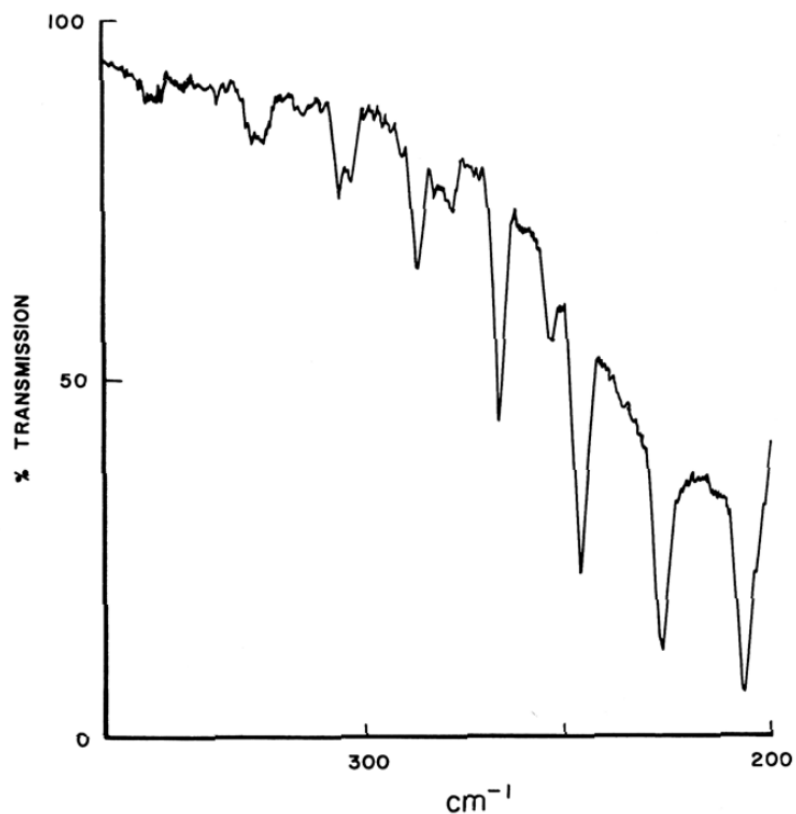
$$2 \times \left(\frac{h}{8\pi^2 \tilde{c} \mu R^2} \right) = 20,9 \text{ cm}^{-1}$$

$$R = \left(\frac{h}{4\pi^2 \mu \tilde{c} (20,9 \text{ cm}^{-1})} \right)^{1/2}$$

Espectroscopia rotacional

Exemplo

O espectro micro-ondas do H^{35}Cl consiste numa série de de linhas igualmente espaçadas de $20,9 \text{ cm}^{-1}$. Determine o comprimento da ligação do H^{35}Cl .



$$R = \left(\frac{h}{4\pi^2 \mu \tilde{c} (20,9 \text{ cm}^{-1})} \right)^{1/2}$$

$$\mu(^1\text{H}^{35}\text{Cl}) = 1,6266 \times 10^{-27} \text{ kg}$$

$$\tilde{c} = 2,99792458 \times 10^{10} \text{ cm s}^{-1}$$

$$h = 6,62607015 \times 10^{-34} \text{ J s}$$

$$R = 1,28 \times 10^{-10} \text{ m}$$

$$R = 1,28 \text{ \AA}$$