Tema 5.-Vibración y Rotación en Mecánica Cuántica

5.1. Oscilador armónico unidimensional

5.2. El rotor rígido

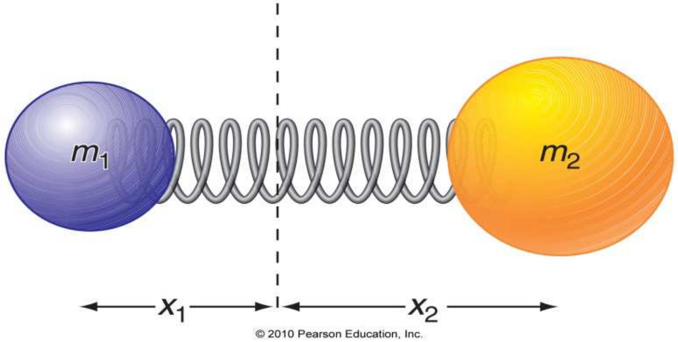
5.3. Cuantización del momento angular

5.4. Funciones propias y valores propios de los operadores de momento
Angular

5.5. Los armónicos esféricos

El oscilador armónico clásico unidimensional

$$F = -kx$$ (Ley de Hooke)



$$F = \mu a = \mu \frac{d^2x}{dt^2} \rightarrow \mu \frac{d^2x}{dt^2} + kx = 0$$

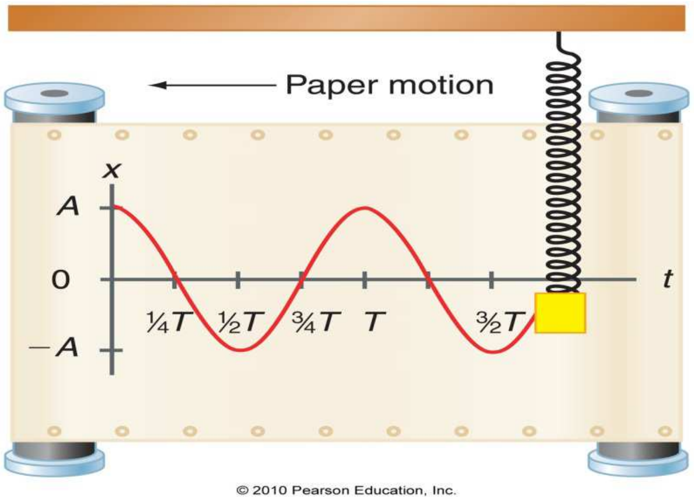
$$x_{cm} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

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

Soluciones de la ecuación diferencial

$$x(t) = c_1 e^{+i\sqrt{(k/\mu)}\,t} + c_2 e^{-i\sqrt{(k/\mu)}\,t}$$

$$x(t) = b_1 \cos\sqrt{\frac{k}{\mu}}t + b_2 \sin\sqrt{\frac{k}{\mu}}t$$



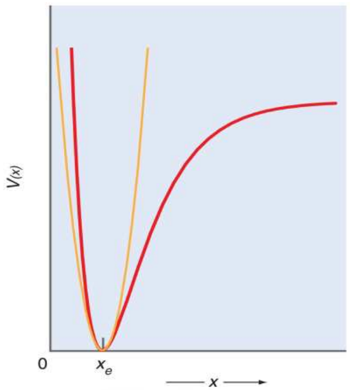
Frecuencia de vibración $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Frecuencia angular $\omega = 2\pi\nu$

$x(t) = A \sin(\omega t + \alpha)$ Ecuación de movimiento

$$E_{potential} = \frac{1}{2}kx^2 \quad \text{and} \quad E_{kinetic} = \frac{1}{2}\mu v^2$$

El oscilador armónico cuántico unidimensional



Energía potencial : $V(x) = \frac{1}{2}kx^2$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_n(x)}{dx^2} + \frac{kx^2}{2}\psi_n(x) = E_n\psi_n(x)$$

$$\psi_n(x) = A_n H_n(\alpha^{1/2}x)e^{-\alpha x^2/2}, \quad \text{for } n = 0, 1, 2, \ldots$$

($\alpha=(k\mu)^{1/2}/\hbar$)

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-(1/2)\alpha x^2}$$

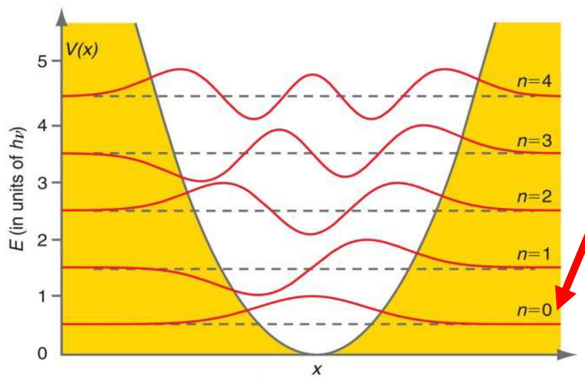
$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-(1/2)\alpha x^2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1)e^{-(1/2)\alpha x^2}$$

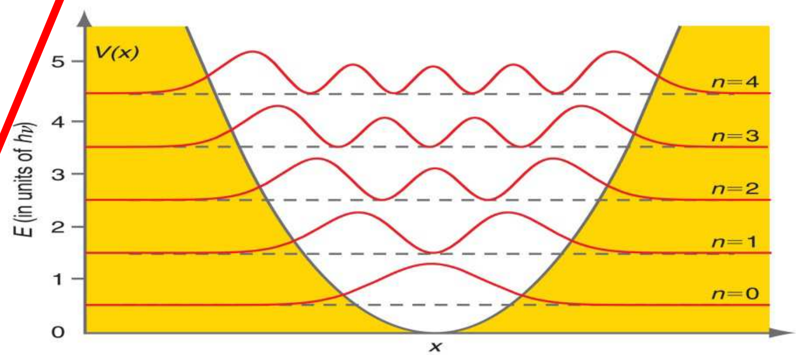
$$\psi_3(x) = \left(\frac{\alpha^3}{9\pi}\right)^{1/4} (2\alpha x^3 - 3x)e^{-(1/2)\alpha x^2}$$

$$E_n = \hbar\sqrt{\frac{k}{\mu}}\left(n + \frac{1}{2}\right) = h\nu\left(n + \frac{1}{2}\right) \quad \text{with } n = 0, 1, 2, 3, \ldots$$

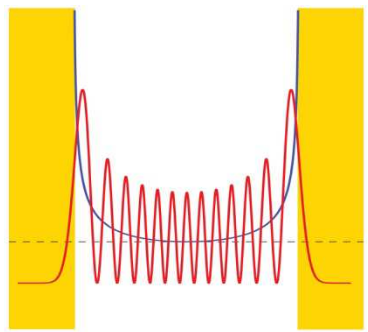
Energía de punto cero $E_o = \frac{1}{2} h\nu$



Funciones de ondas de los primeros estados cuánticos del oscilador armónico unidimensional

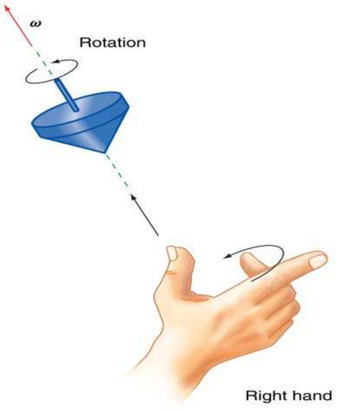


Densidades de probabilidad de los primeros estados cuánticos del oscilador armónico unidimensional



Densidades de probabilidad del duodécimo estados cuántico del oscilador armónico unidimensional

El rotor rígido clásico

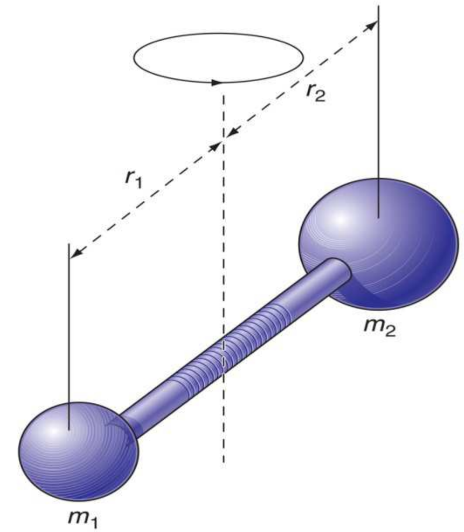


$$|\boldsymbol{\omega}| = \frac{d\theta}{dt}$$

velocidad angular

$$\boldsymbol{\alpha} = \frac{d|\boldsymbol{\omega}|}{dt} = \frac{d^2\theta}{dt^2}$$

aceleración angular



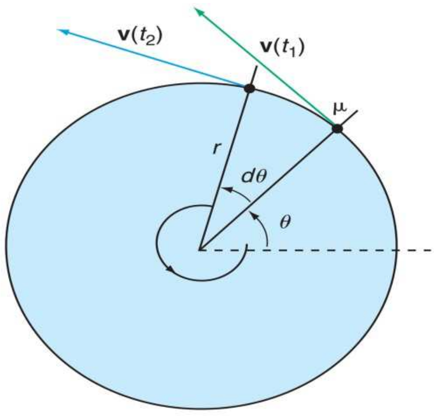
(a)

$$\mathbf{v} = \frac{\Delta \mathbf{s}}{\Delta t} = \frac{\mathbf{r}\Delta\boldsymbol{\theta}}{\Delta t} \quad \text{in the limit as} \quad \Delta t \to 0, \; \mathbf{v} = \frac{\mathbf{r}d\theta}{dt} = r\boldsymbol{\omega}$$

$$E_{kinetic} = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu r^2\omega^2 = \frac{1}{2}I\omega^2$$

momento de inercia

$$E = \frac{p^2}{2\mu} = \frac{l^2}{2\mu r^2} = \frac{l^2}{2I}$$



(b)

momento angular $\mathbf{l} = \mathbf{r} \times \mathbf{p}$

Para un movimiento circular **r** y **p** son perpendiculares

$$l = r \cdot p \cdot \text{sen}\,\theta = r \cdot p$$

Hamiltoniano para una molécula con N átomos excluyendo los grados de libertad electrónicos

$$\hat{H}_{total} = \hat{H}_{trans}(r_{cm}) + \hat{H}_{vib}(\tau_{internal}) + \hat{H}_{rot}(\theta_{cm}, \phi_{cm})$$

$$\psi_{total} = \psi_{trans}(r_{cm})\,\psi_{vib}(\tau_{internal})\,\psi_{rot}(\theta_{cm}, \phi_{cm})$$

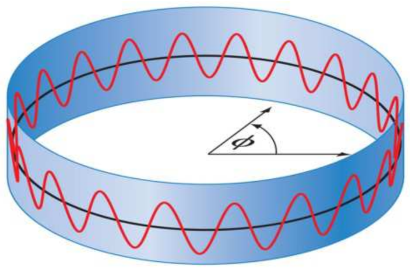
$$E_{total} = E_{trans} + E_{vib} + E_{rot}$$

El rotor rígido bidimensional cuántico

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi(x,y)}{\partial x^2}+\frac{\partial^2\psi(x,y)}{\partial y^2}\right)_{r=r_0} = E\psi(x,y) \xrightarrow{x^2+y^2=r_o^2} -\frac{\hbar^2}{2\mu r_0^2}\frac{d^2\Phi(\phi)}{d\phi^2} = E\Phi(\phi)$$

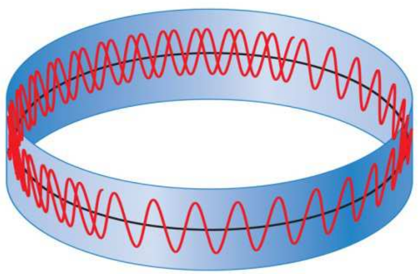
$$\Phi_+(\phi) = A_{+\phi}e^{im_l\phi} \quad \text{and} \quad \Phi_-(\phi) = A_{-\phi}e^{-im_l\phi}$$

si $\Phi(\Phi+2\Pi) = \Phi(\Phi)$



$m_l = \pm$integer

$$\cos 2\pi m_l + i \sin 2\pi m_l = 1 \Rightarrow m_l = 0, \pm 1, \pm 2, \pm 3, \ldots$$



$m_l \neq \pm$integer

$$E_{m_l} = \frac{\hbar^2 m_l^2}{2\mu r_0^2} = \frac{\hbar^2 m_l^2}{2I} \quad \text{for } m_l = 0, \pm 1, \pm 2, \pm 3, \ldots$$

El momento angular también está cuantizado

$$\hat{l}_z\Phi_+(\phi) = \frac{-i\hbar}{\sqrt{2\pi}}\frac{d\,e^{im_l\phi}}{d\phi} = \frac{m_l\hbar}{\sqrt{2\pi}}e^{im_l\phi} = m_l\hbar\,\Phi_+(\phi)$$

$|l_z| = \pm m_l \hbar$

El rotor rígido tridimensional cuántico

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right]=EY(\theta,\phi)$$

Si $\beta = \frac{2\mu r_0^2 E}{\hbar^2}$ ⟹

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

Factorizando la función de ondas

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

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

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\beta\sin^2\theta=m_l^2$$

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

$$\beta = l(l+1),\quad \text{for } l = 0, 1, 2, 3, \ldots \quad \text{and}$$

$$m_l = -l, -(l-1), -(l-2), \ldots, 0, \ldots, (l-2), (l-1), l$$

$$\beta = \frac{2\mu r_0^2 E}{\hbar^2}$$

Armónicos Esféricos

$$Y(\theta,\phi)=Y_l^{m_l}(\theta,\phi)=\Theta_l^{m_l}(\theta)\Phi_{m_l}(\phi)$$

$$E_l = \frac{\hbar^2}{2I}l(l+1),\quad \text{for } l = 0, 1, 2, 3, \ldots$$

$$\hat{H}_{total}\, Y_l^{m_l}(\theta, \phi) = \frac{\hbar^2}{2I} l(l + 1) Y_l^{m_l}(\theta, \phi), \quad \text{for } l = 0, 1, 2, 3, \ldots$$

Degeneración: hay 2*l*+1 valores distintos de m_l que generan armónicos esféricos de misma energía

La cuantización del momento angular

$$\hat{l}^2 Y_l^{m_l}(\theta, \phi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta, \phi)$$

$$\hat{l}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{l}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{l}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Regla de la cadena

$$\hat{l}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{l}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{l}_z = -i\hbar\left(\frac{\partial}{\partial\phi}\right)$$

Las componentes del momento angular no conmutan entre sí

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z$$

$$[\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x$$

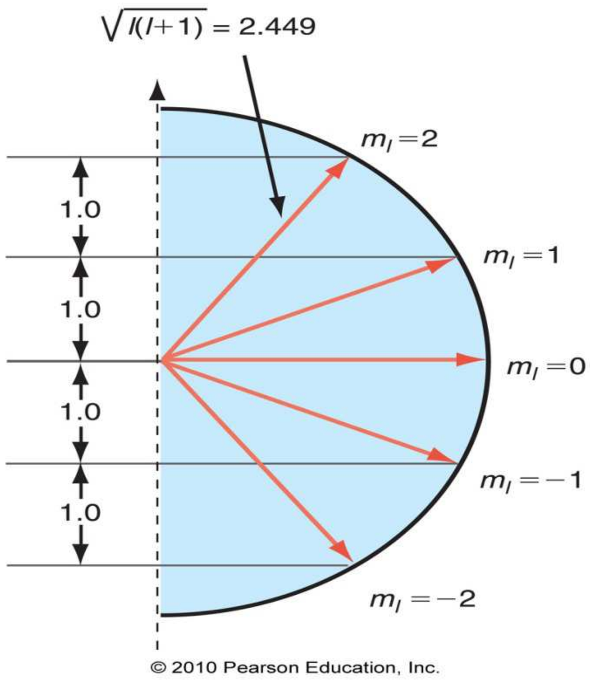
$$[\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y$$

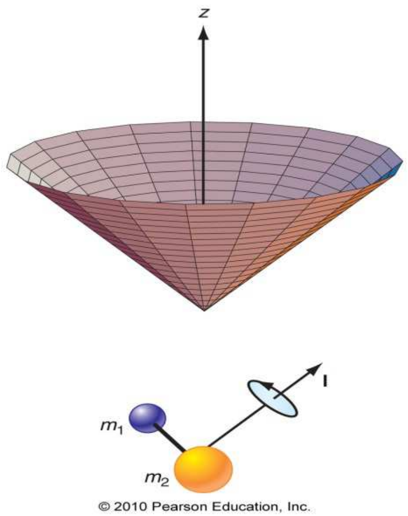
Los armónicos esféricos son funciones propias de la componente *z* del momento angular

$$\hat{l}_z(Y_l^{m_l}(\theta, \phi)) = \Theta(\theta)\left[-i\hbar\frac{\partial}{\partial\phi}\left(\frac{1}{\sqrt{2\pi}}e^{\pm i m_l \phi}\right)\right] = \pm m_l\hbar\Theta(\theta)\Phi(\phi),$$

for $m_l = 0, \pm1, \pm2, \pm3, \ldots, \pm l$

Cuantización Espacial





Orientaciones posibles del momento angular para *l*=2

Orientación del vector momento angular para *l*=2 y m_l=+2

Los Armónicos Esféricos

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

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

$$Y_1^{\pm1}(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$$

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

$$Y_2^{\pm1}(\theta,\phi) = \left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta\, e^{\pm i\phi}$$

$$Y_2^{\pm2}(\theta,\phi) = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$$

$$p_x = \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$$

$$p_y = \frac{1}{\sqrt{2}\,i}(Y_1^1 - Y_1^{-1}) = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$$

$$p_z = Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$d_{z^2} = Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$

$$d_{xz} = \frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1}) = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\cos\phi$$

$$d_{yz} = \frac{1}{\sqrt{2}\,i}(Y_2^1 - Y_2^{-1}) = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin\phi$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2}) = \sqrt{\frac{15}{16\pi}}\sin^2\theta\cos 2\phi$$

$$d_{xy} = \frac{1}{\sqrt{2}\,i}(Y_2^2 - Y_2^{-2}) = \sqrt{\frac{15}{16\pi}}\sin^2\theta\sin 2\phi$$