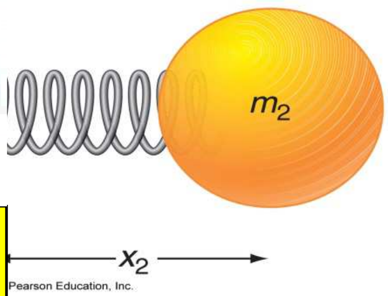
bración y Rotación en Mecánica Cuántica

- r armónico unidimensional
- ígido
- ción del momento angular
- s propias y valores propios de los operadores de momento
- nicos esféricos

El oscilador armónico clásico unidimensional

$-k\,x$ (Ley de Hooke)



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

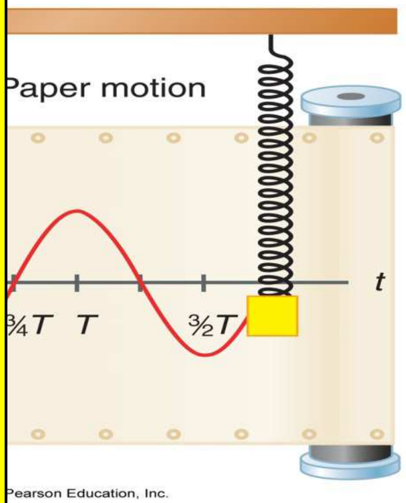
$x_1 + m_2x_2$ / $n_1 + m_2$

$n_1 m_2$ / $+ m_2$

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

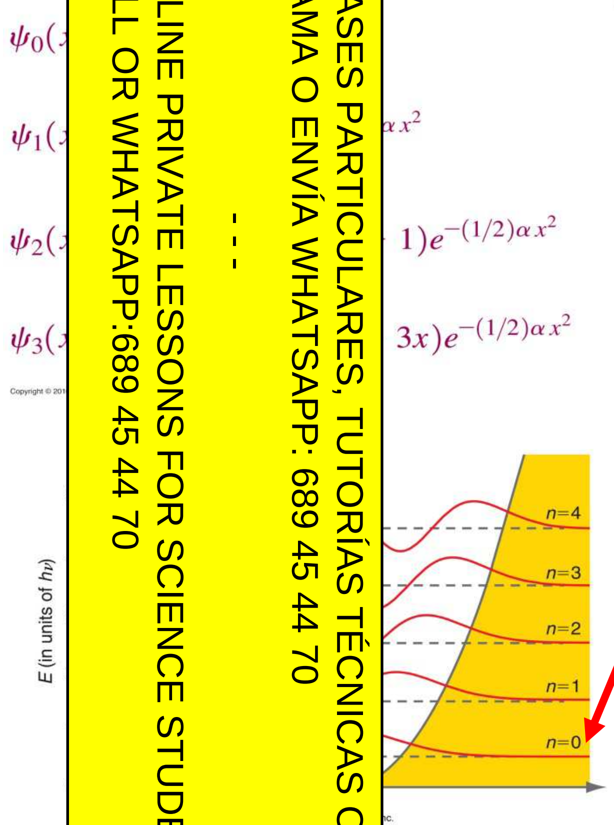
$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_n(x)}{dx^2} + \frac{kx^2}{2}\psi_n(x) = E_n\psi_n(x)$$

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

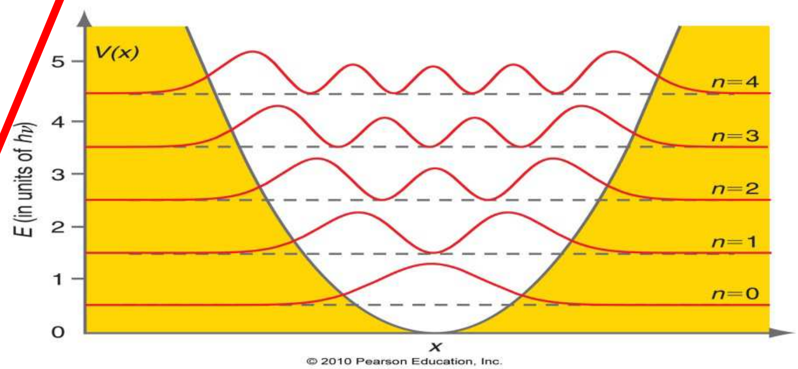
$(\alpha=(k\mu)^{1/2}/\hbar)$

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

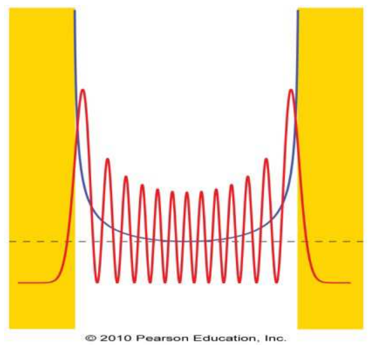
Energía de punto cero $E_o = \frac{1}{2}\, h\nu$



Func... los prim...icos del c... unidimensional



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



Densidades de probabilidad del duodécimo estados cuántico del oscilador armónico unidimensional

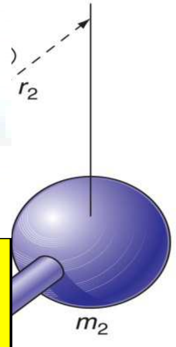
El rotor rígido clásico

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

velocidad angular

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

aceleración angular



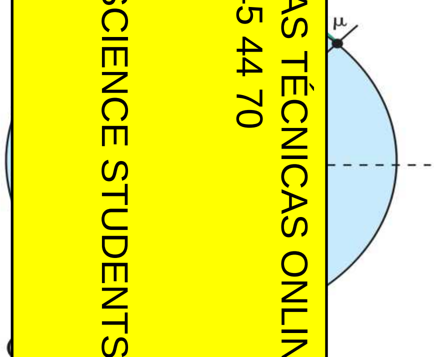
$$\mathbf{v} = \frac{\Delta \mathbf{s}}{\Delta t} = \frac{\mathbf{r}\Delta\boldsymbol{\theta}}{\Delta t} \quad \text{in the limit as} \quad \Delta t \to 0,\ \mathbf{v} = \frac{\mathbf{r}d\theta}{dt} = r\boldsymbol{\omega}$$

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

momento de inercia

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

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



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

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

miltoniano para una molécula con N átomos
cluyendo los grados de libertad electrónicos

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

ducation, Inc.

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

ducation, Inc.

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

El rotor rígido bidimensional cuántico

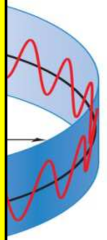
$$-\frac{1}{2}\ldots\frac{\partial^2\psi(x,y)}{\partial y^2}\Bigg)_{r=r_0} = E\psi(x,y)$$

$x^2+y^2=r_o^{\,2}$

$$-\frac{\hbar^2}{2\mu r_0^2}\frac{d^2\Phi(\phi)}{d\phi^2} = E\Phi(\phi)$$

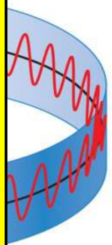
$$\Phi_+(\phi) = A_{+\phi}e^{im_l\phi} \quad \text{and} \quad \Phi_-(\phi) = A_{-\phi}e^{-im_l\phi}$$

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



$$\cos 2\pi m_l + i\sin 2\pi m_l = 1$$

$m_l = 0, \pm1, \pm2, \pm3, \ldots$



$$E_{m_l} = \frac{\hbar^2 m_l^2}{2\mu r_0^2} = \frac{\hbar^2 m_l^2}{2I} \quad \text{for } m_l = 0, \pm1, \pm2, \pm3, \ldots$$

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

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

... función de ondas

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

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

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

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

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

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

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

...cos Esféricos

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

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

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

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

La cuantización del momento angular

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

$$\hat{l}_x \cdots - z\frac{\partial}{\partial y}\Big)$$

$$\hat{l}_y \cdots - x\frac{\partial}{\partial z}\Big)$$

$$\hat{l}_z \cdots - y\frac{\partial}{\partial x}\Big)$$

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 … momento angu… entre sí

$$\cdots i\hbar\hat{l}_z$$

$$\cdots i\hbar\hat{l}_x$$

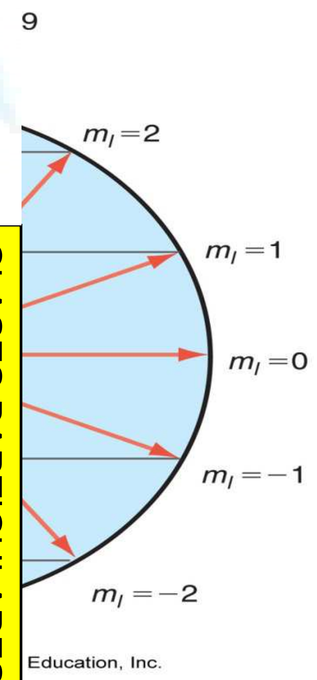
$$\cdots i\hbar\hat{l}_y$$

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

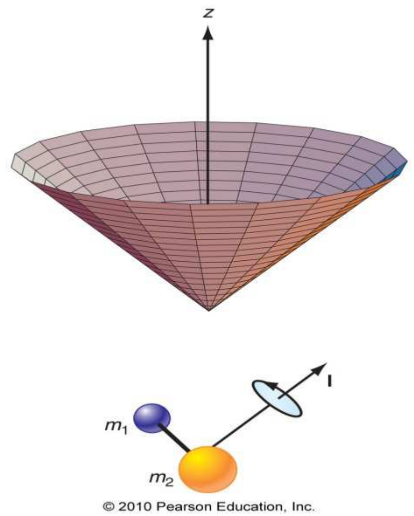
$$\hat{l}_z(Y_l^{m_l}(\theta,\phi)) = \Theta(\theta)\left[-i\hbar\frac{\partial}{\partial\phi}\left(\frac{1}{\sqrt{2\pi}}e^{\pm i m_l\phi}\right)\right] = \pm m_l\hbar\Theta(\theta)\Phi(\phi),$$

for $m_l = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l$

Cuantización Espacial



Orie … del momento angular para l=2



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

Los Armónicos Esféricos

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

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

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

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

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

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

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

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

$\ldots\cos\theta$

$Y \ldots n\,\theta\, e^{\pm i\phi}$

$Y \ldots (3\cos^2\theta - 1)$

$Y \ldots n\,\theta\cos\theta\, e^{\pm i\phi}$

$Y \ldots \sin^2\theta\, e^{\pm 2i\phi}$