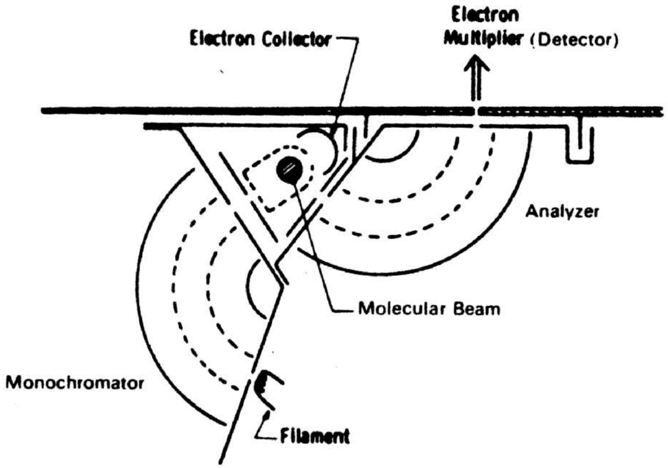
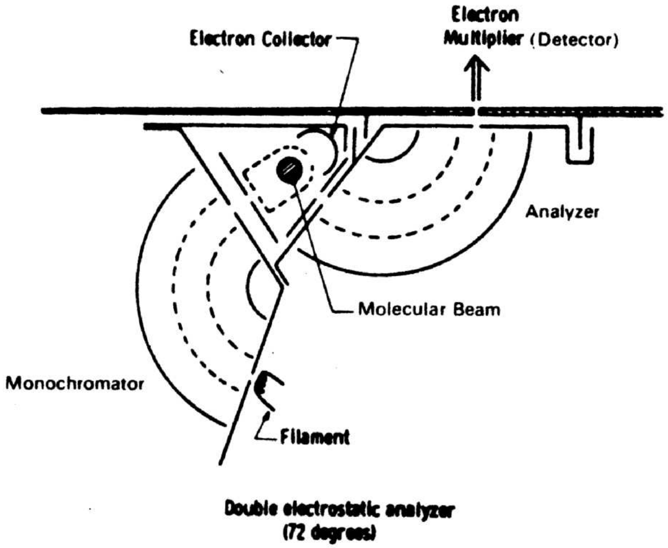
Fun With Carbon Monoxide

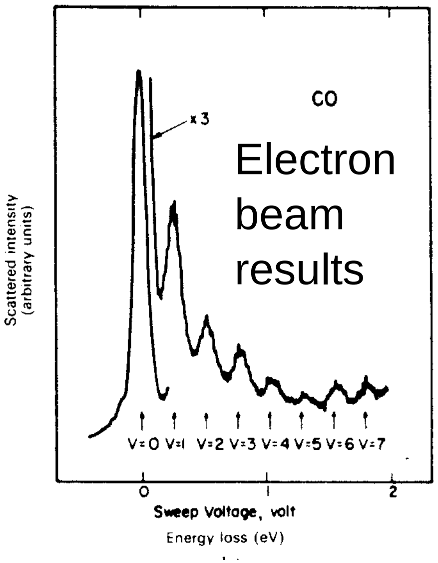


Double electrostatic analyzer
(72 degrees)

Fun With Carbon Monoxide



$\Delta E = 0.25 \pm 0.05 \; eV$



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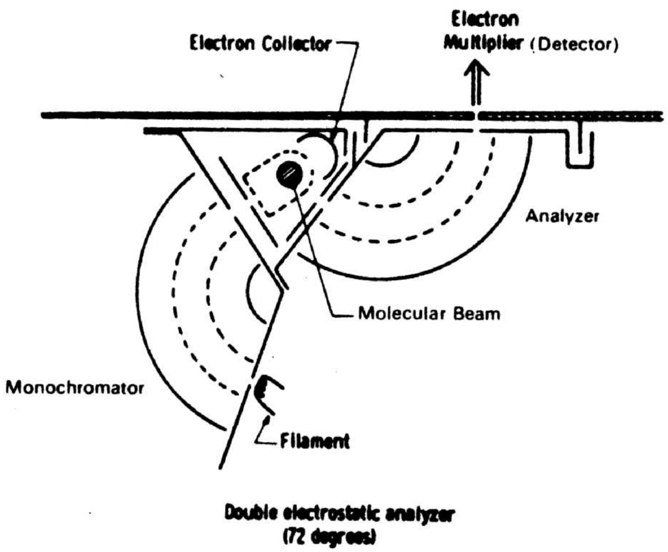

$\longrightarrow$

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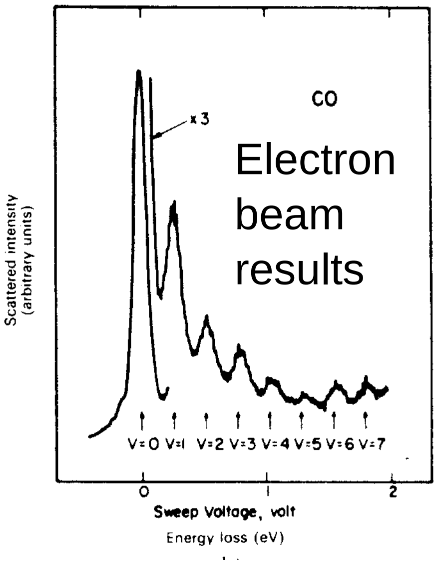

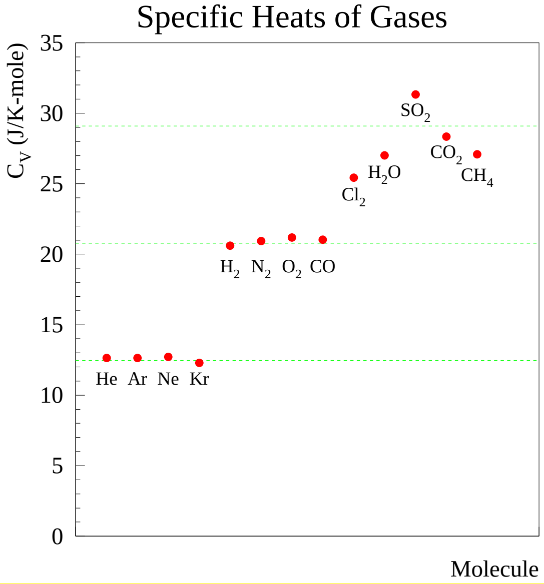

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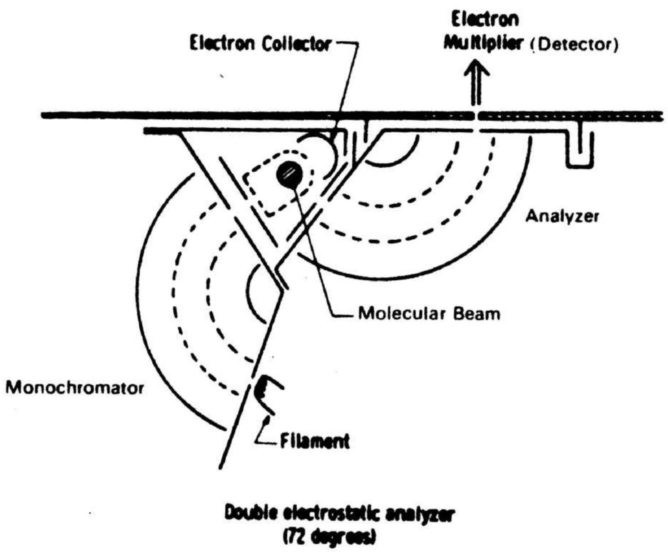

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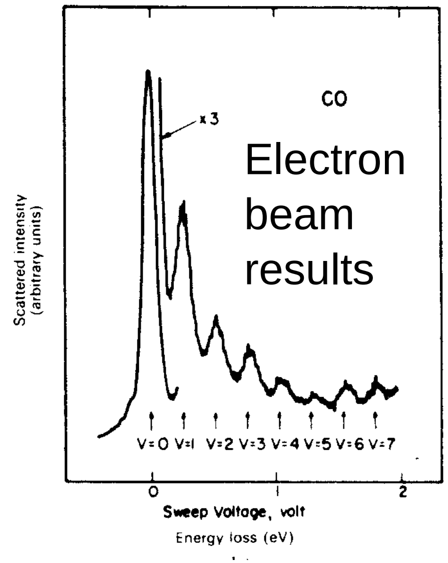
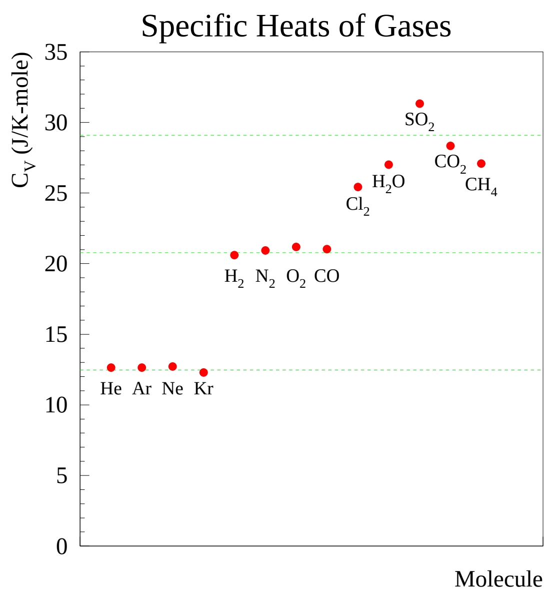
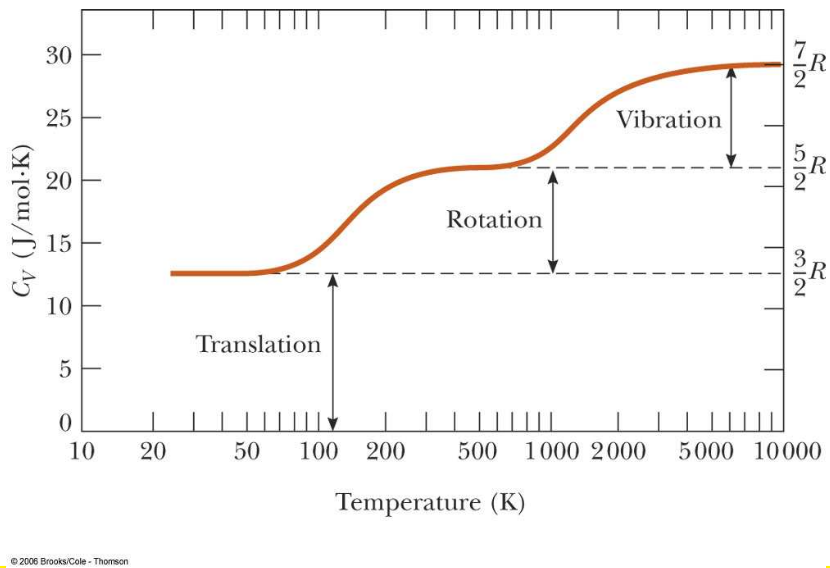
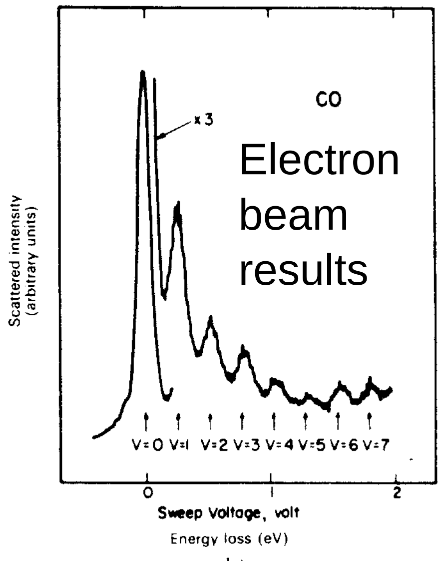






Carbon Monoxide



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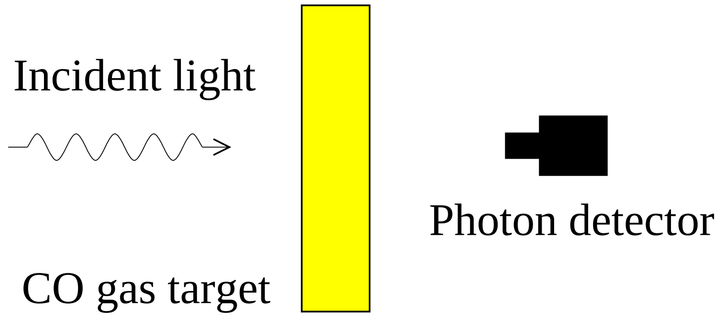
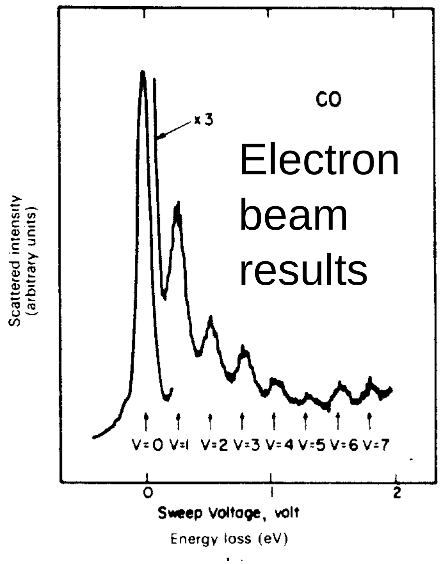
CO Absorption Spectrum



Carbon Monoxide



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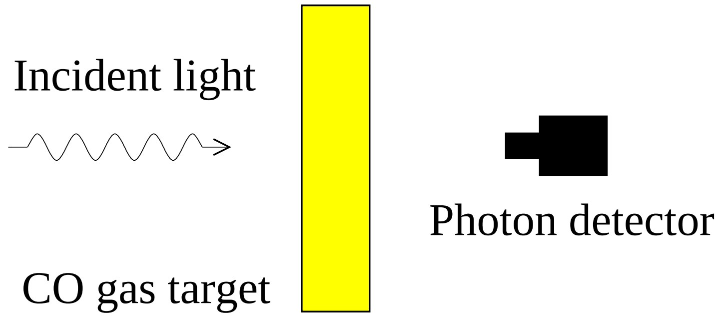
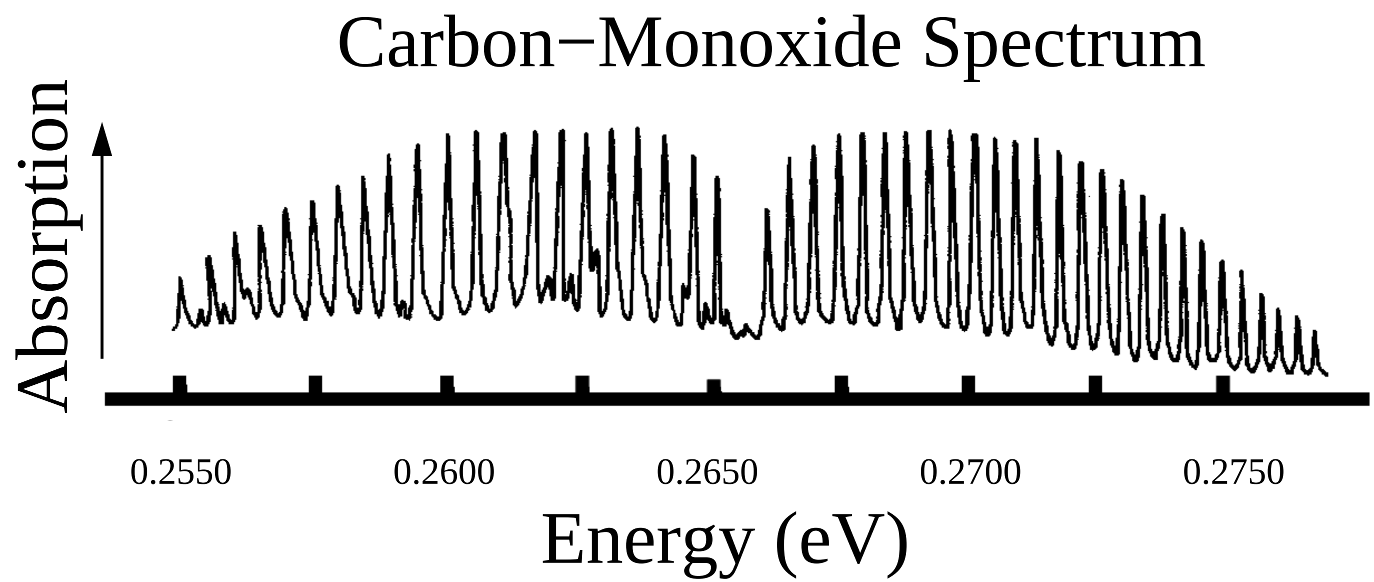


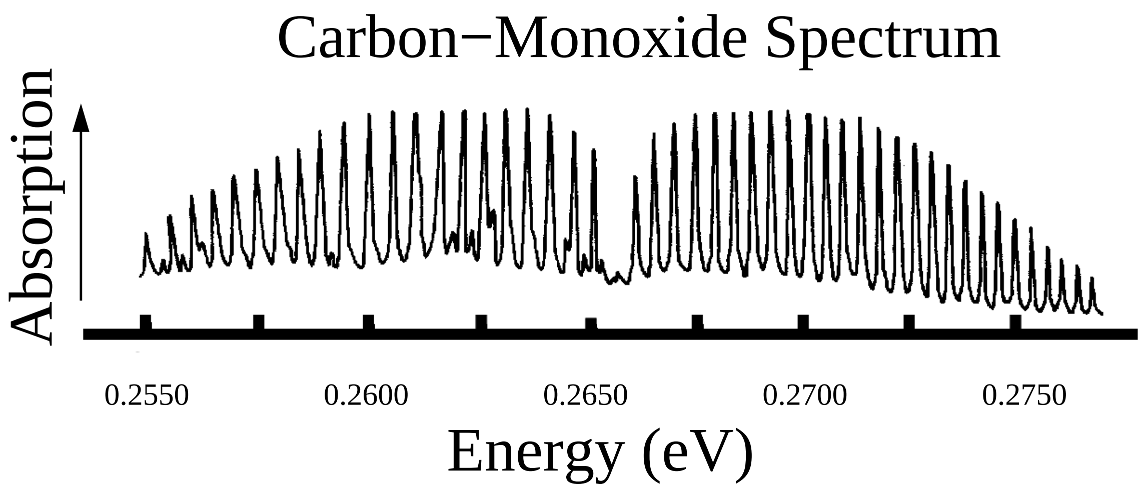


Is Carbon Monoxide A Rigid Rotator?

Excited states of carbon monoxide (CO) can be observed by passing light through a cell containing CO and measuring the absorption spectrum shown below. The molecule can both vibrate and rotate at the same time. The rotational energy states of a rigid rotator are

$$E_l = \frac{\hbar^2}{2I} l(l+1)$$

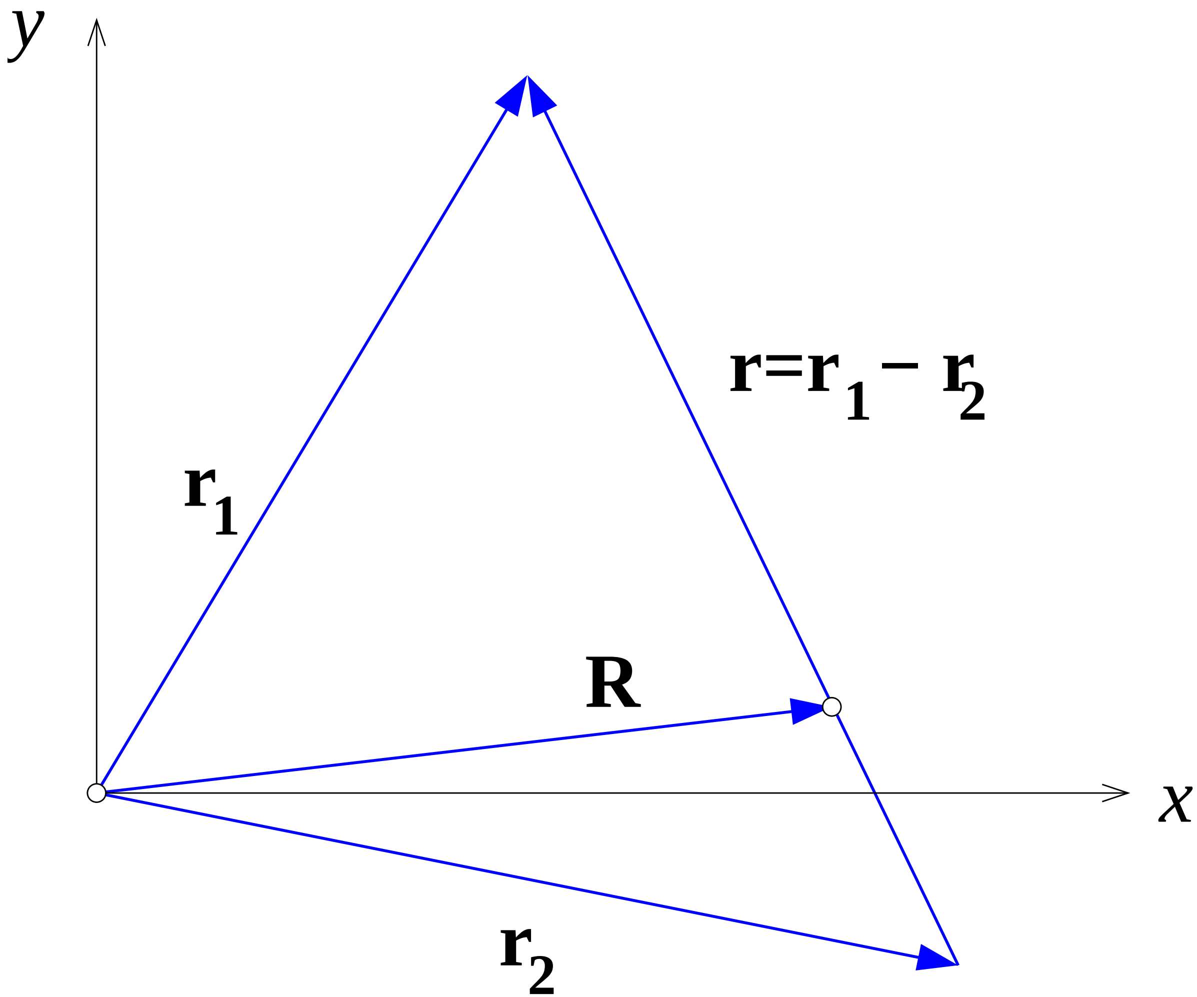
where I is the moment of inertia. The vibrational part of the energy can is described by the harmonic oscillator so $E_n = (n + \frac{1}{2})\hbar\omega_0$ with $\Delta E = \hbar\omega_0 = 0.25 \pm 0.05\ eV$. How does one arrive at the expression above for the rotational energy? Is CO a rigid rotator?



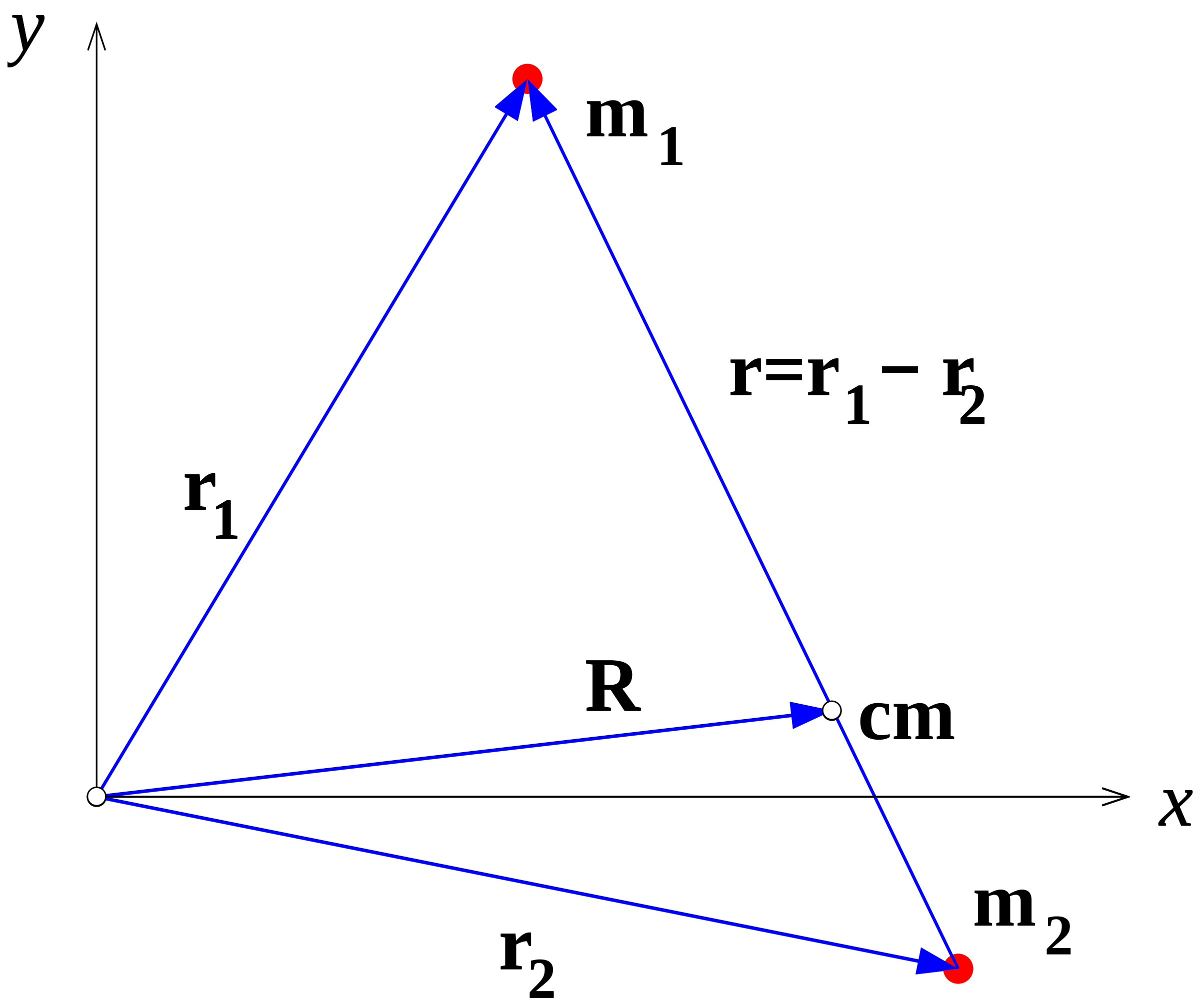
The Plan

1. What is the kinetic and potential energy between the carbon and oxygen atoms in CO in the CM frame in cartesian and spherical coordinates?
2. How do you decompose the kinetic energy into radial and angular parts?
3. What is the Schroedinger equation for the rigid rotator?
4. What is the solution of the rigid rotator Schroedinger equation?

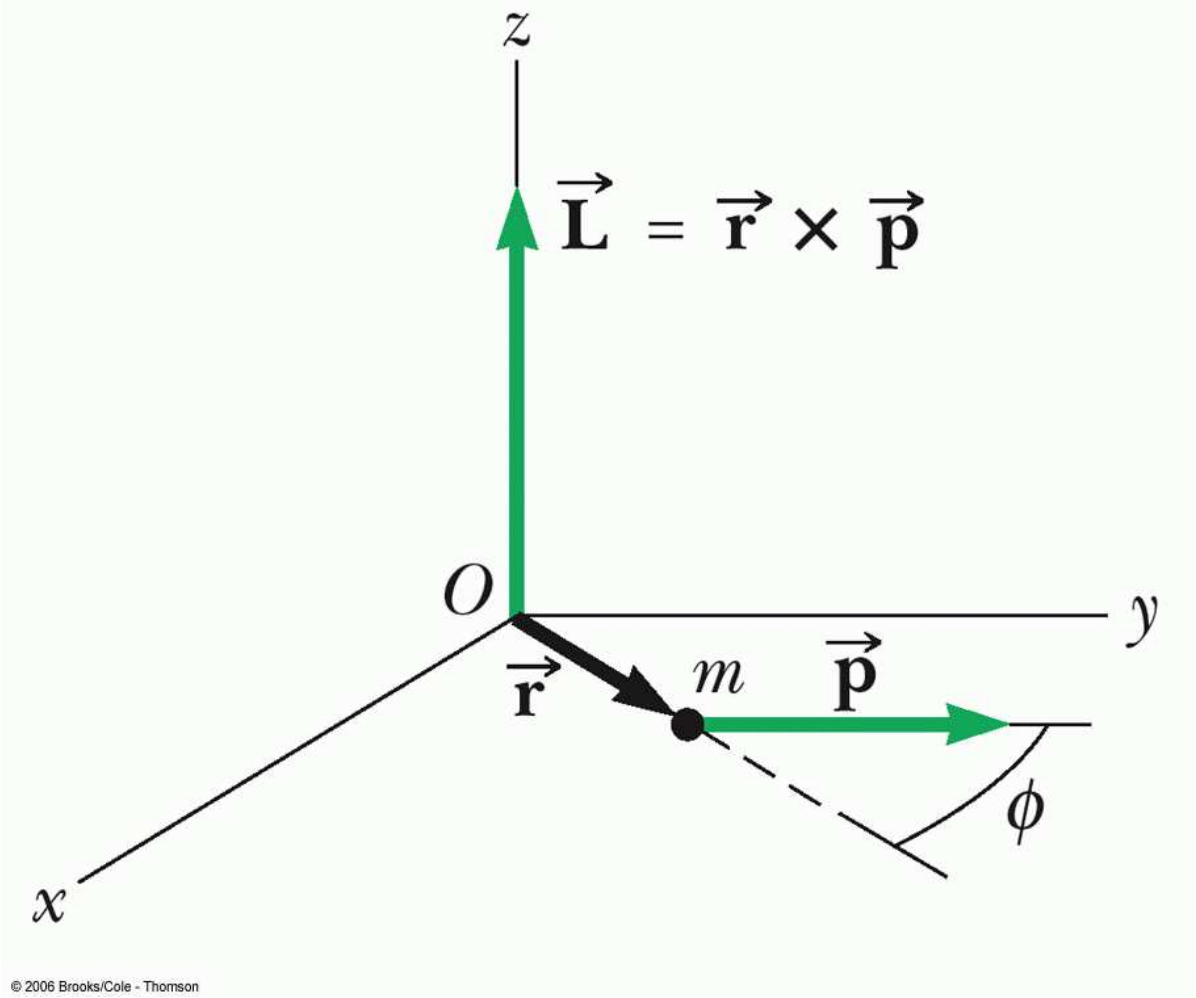
Coordinates



Coordinates



Angular Momentum



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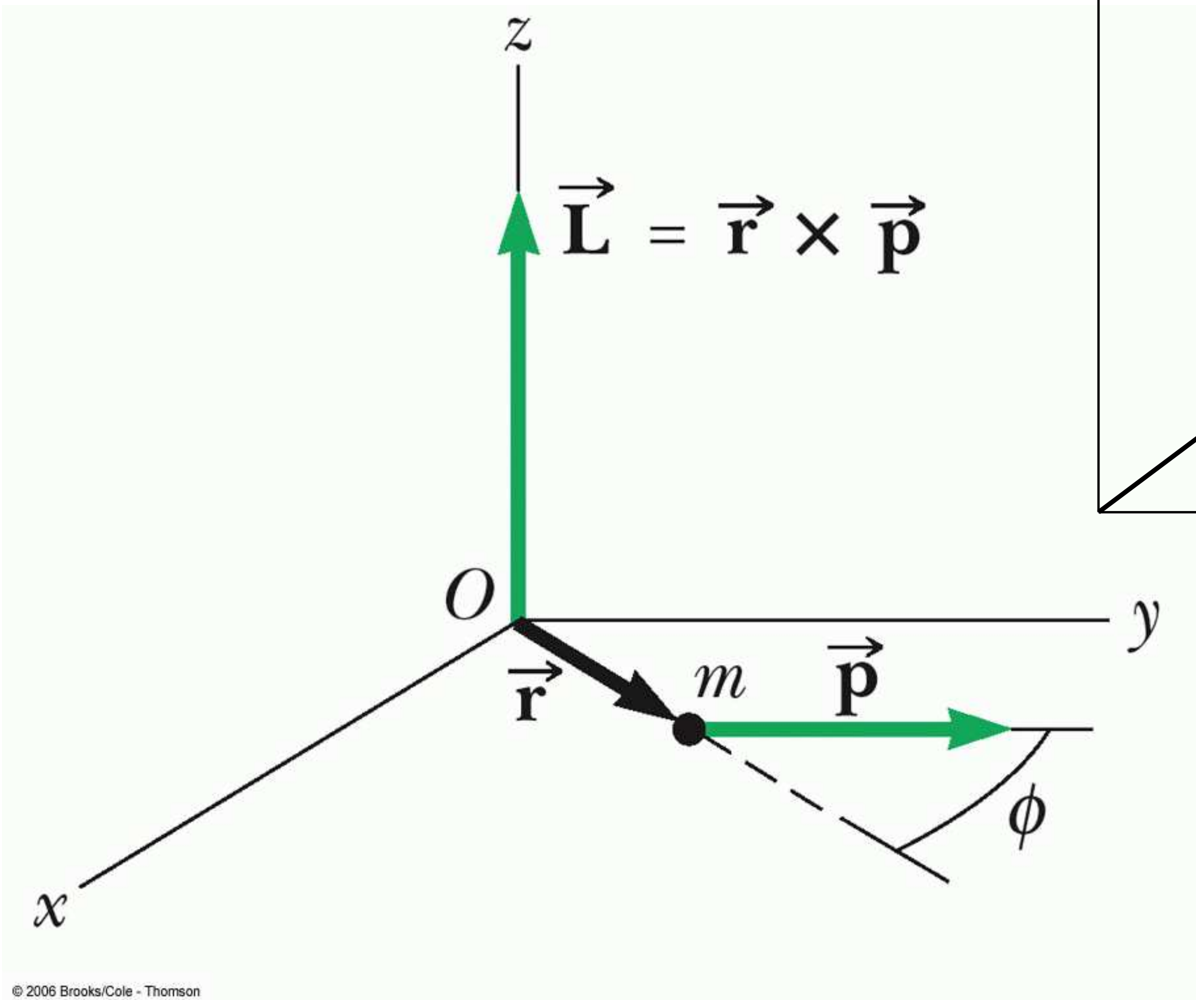
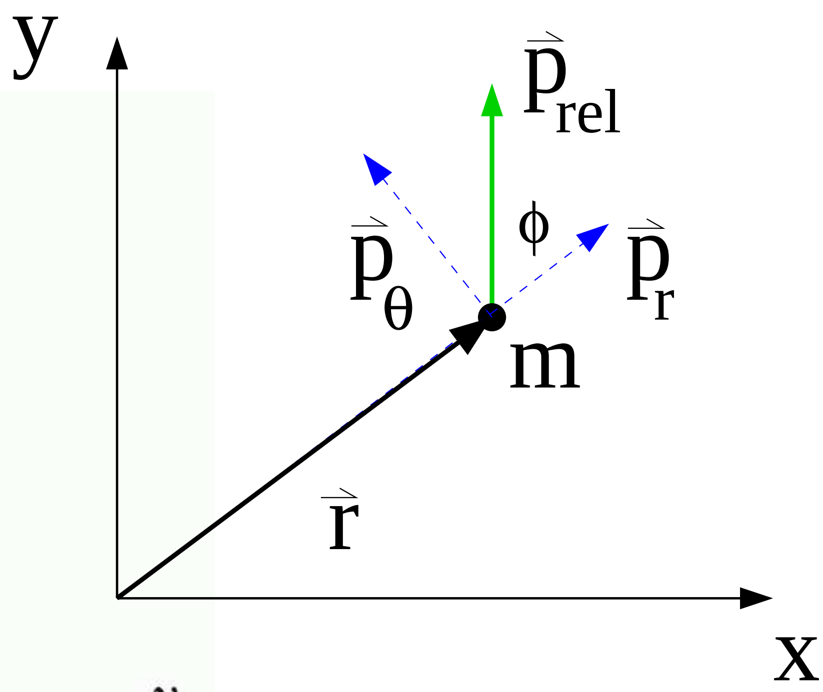
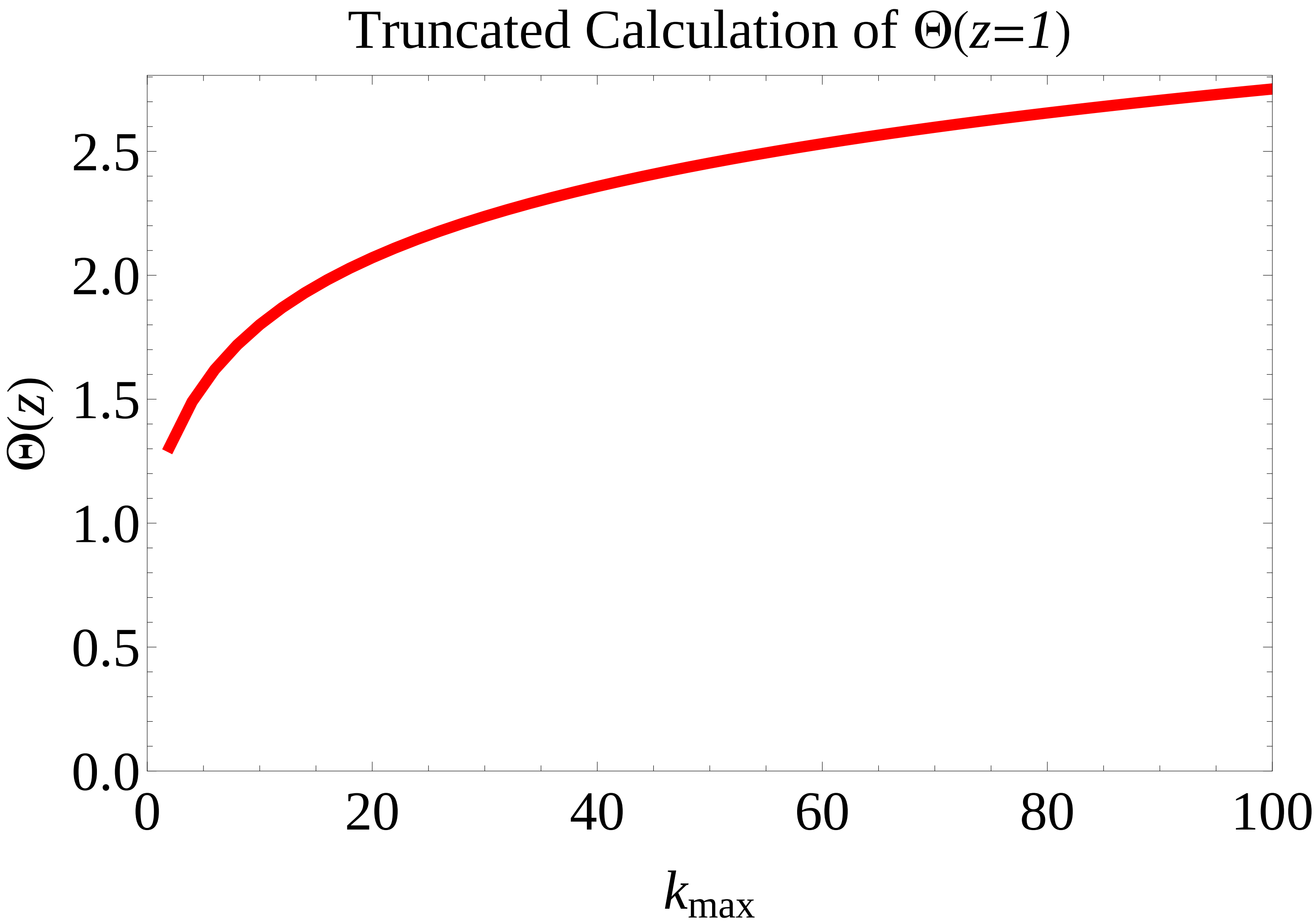




A Convergence Problem



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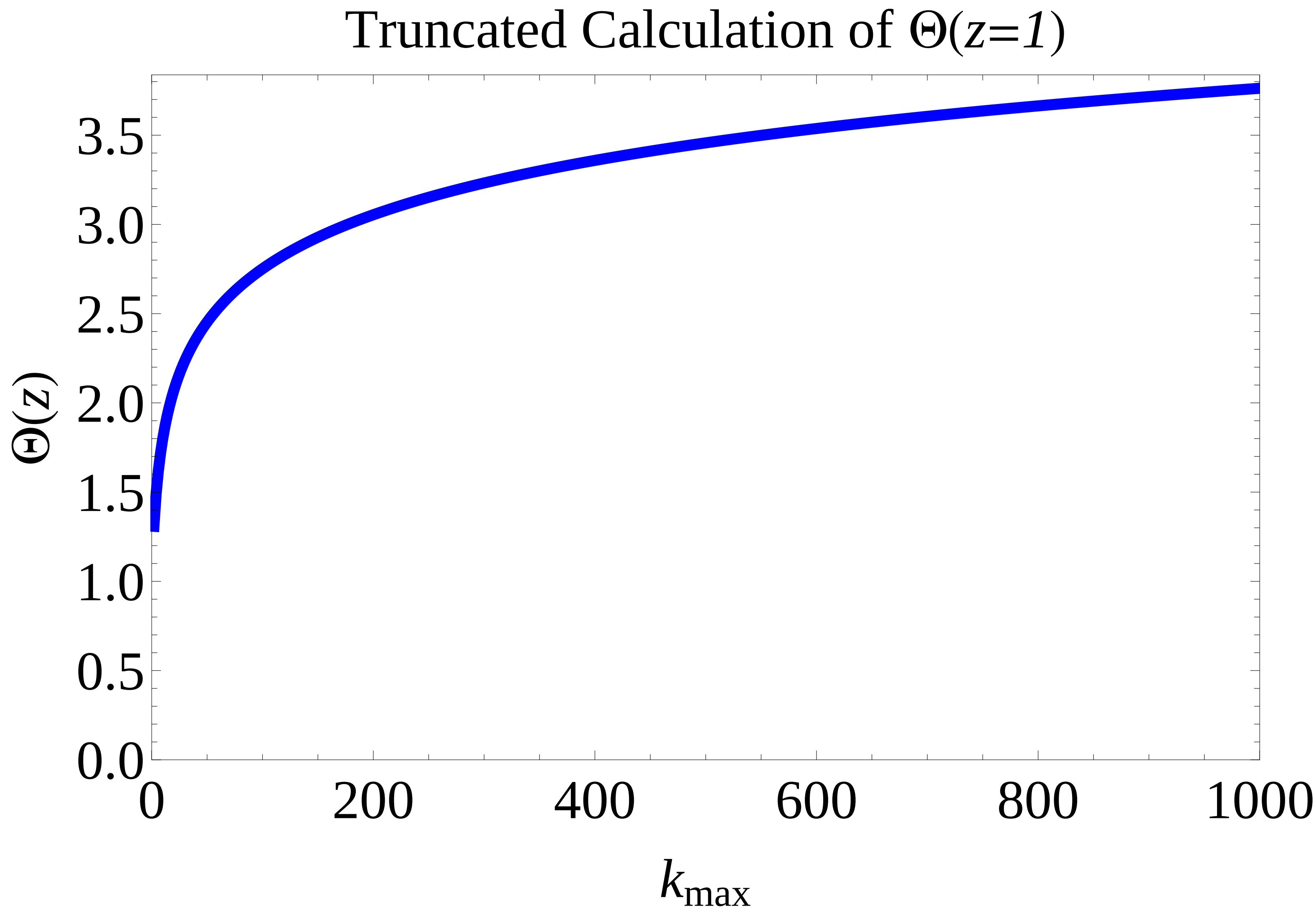

Legendre Polynomials ($m_l = 0$)

$$\Theta(\theta) = P_l(\cos\theta)$$

$$P_0(\cos\theta) = 1$$

$$P_1(\cos\theta) = \cos\theta$$

$$P_2(\cos\theta) = \frac{1}{2}\left(3\cos^2\theta - 1\right)$$

$$P_3(\cos\theta) = \frac{1}{2}\left(5\cos^3\theta - 3\cos\theta\right)$$

Spherical Harmonics ($m_l = m$)

$$\Theta(\theta)\Phi(\phi) = Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}$$

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

$$Y_1^1(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \qquad Y_1^{-1}(\theta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$

$$Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

Summary So Far

$$\frac{p_r^2}{2\mu} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

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

$$m_l = 0, \pm\frac{1}{2}, \pm\frac{2}{2}, \pm\frac{3}{2}, \pm\frac{4}{2}, \pm\frac{5}{2}, \ldots$$

$$\left[-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{m_l^2}{\sin^2\theta}\right]\Theta = A\Theta \qquad A = l(l+1)$$

$$L^2|\phi_s\rangle = \hbar^2 l(l+1)|\phi_s\rangle$$

The Eigenvalues of $\hat{L}^2$ and $\hat{L}_z$

$$\vec{L} = \vec{r} \times \vec{p}$$

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Transformation from Cartesian to spherical coordinates:

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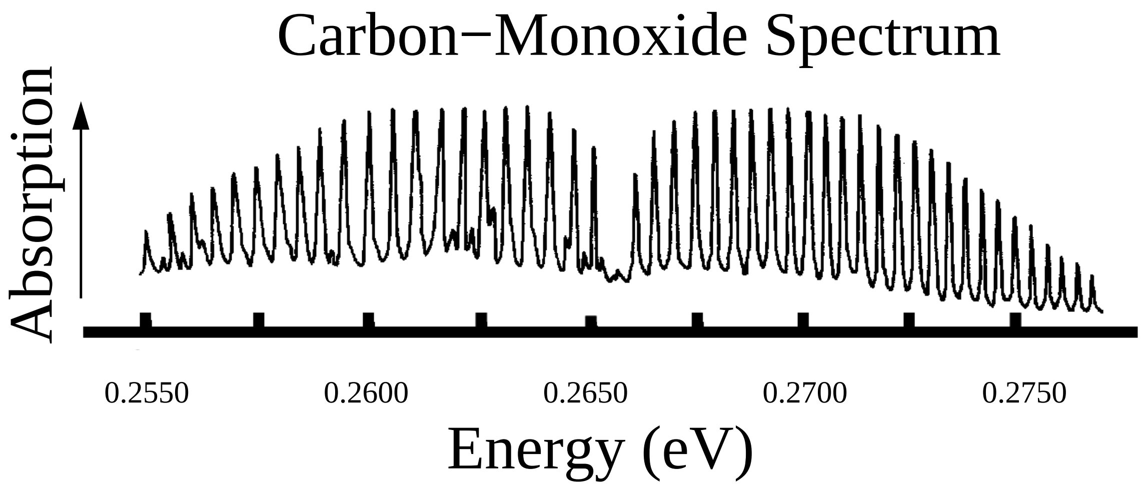

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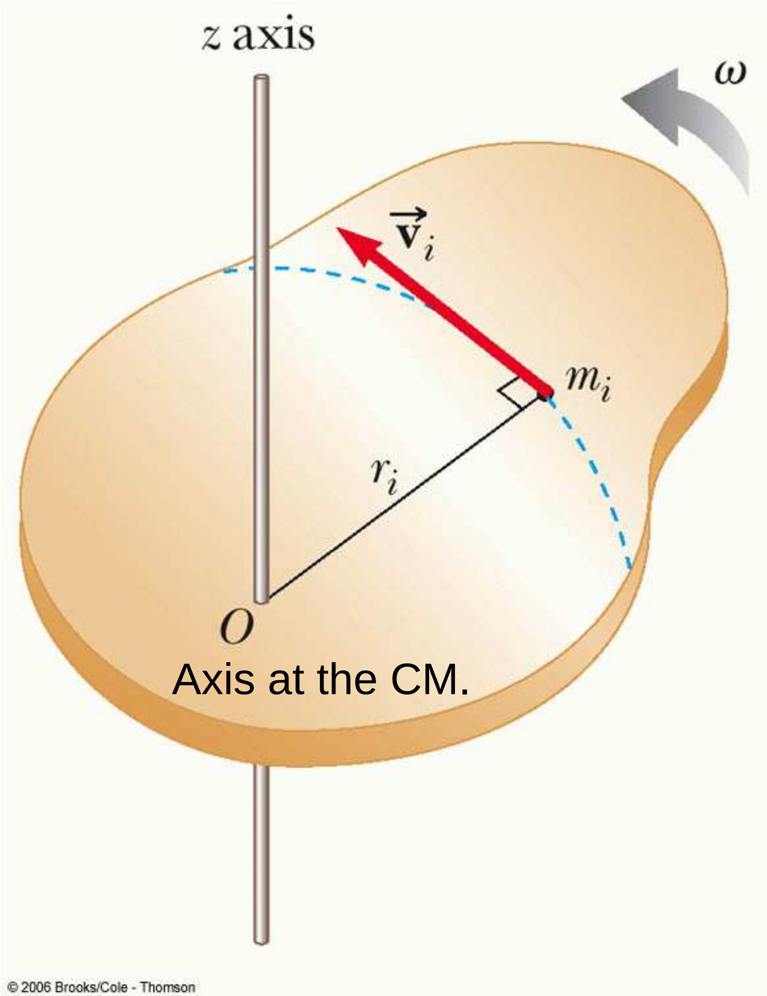
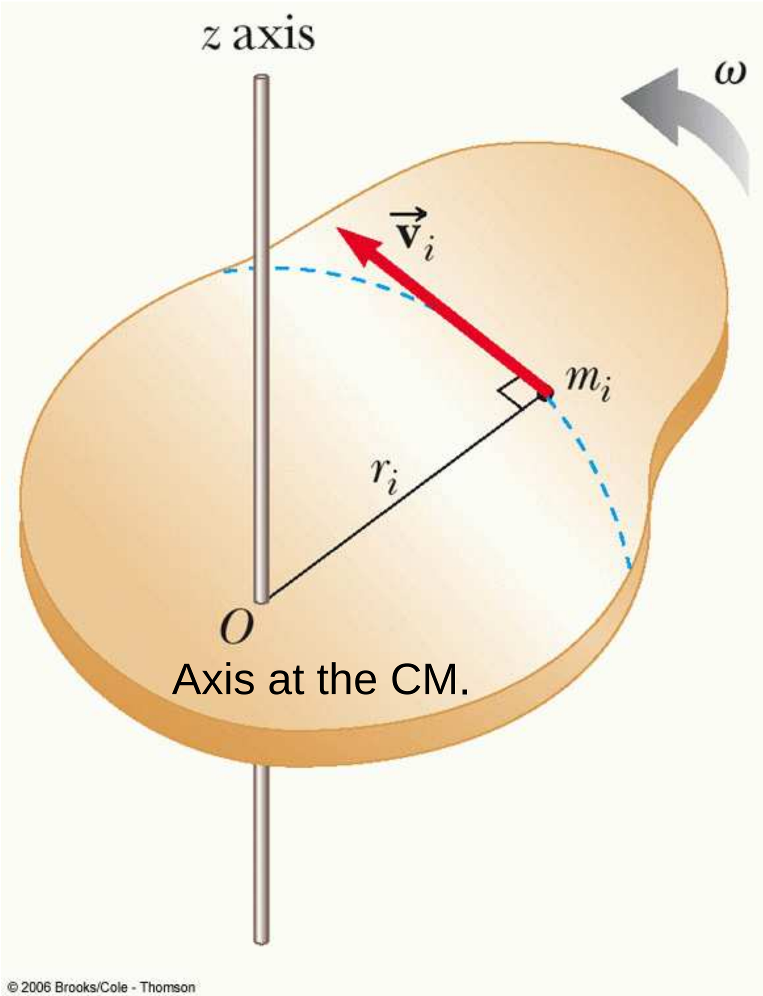
$$L^2|\phi\rangle = \hbar^2 l(l+1)|\phi\rangle \quad L_z|\phi\rangle = \pm m_l\hbar^2|\phi\rangle \quad \Theta(\theta)\Phi(\phi) = Y_{lm}(\theta,\phi)$$

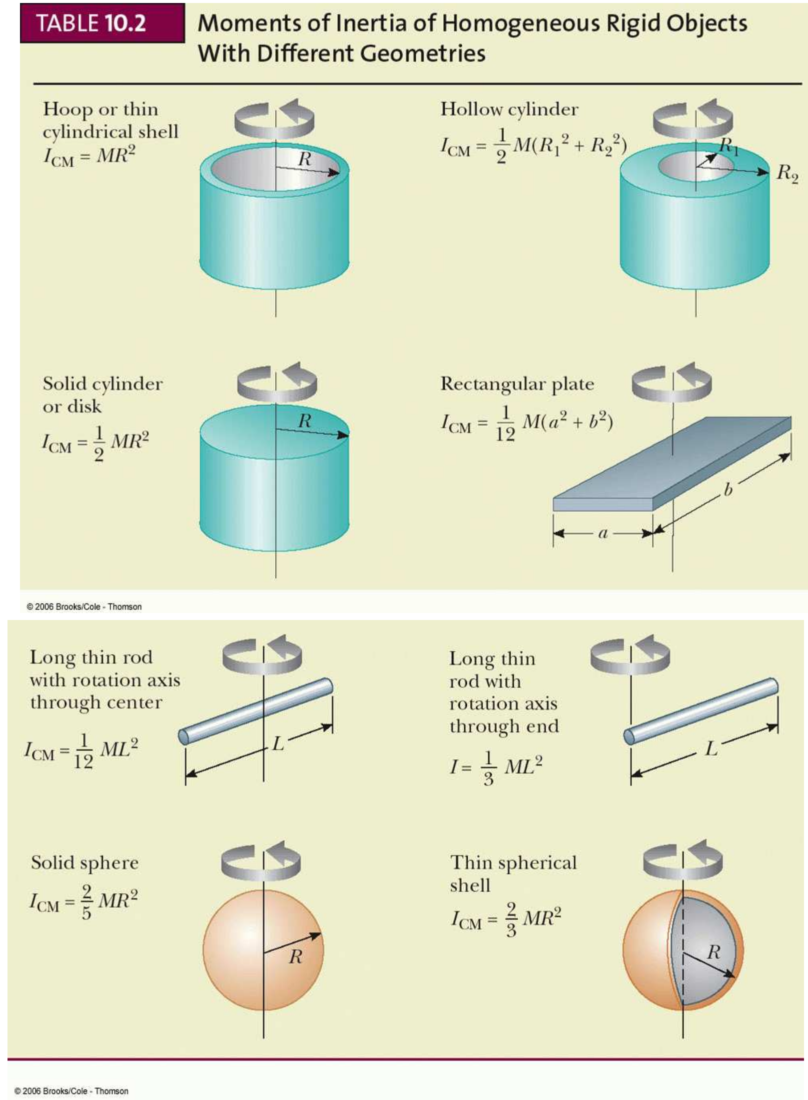
Rotational Kinetic Energy



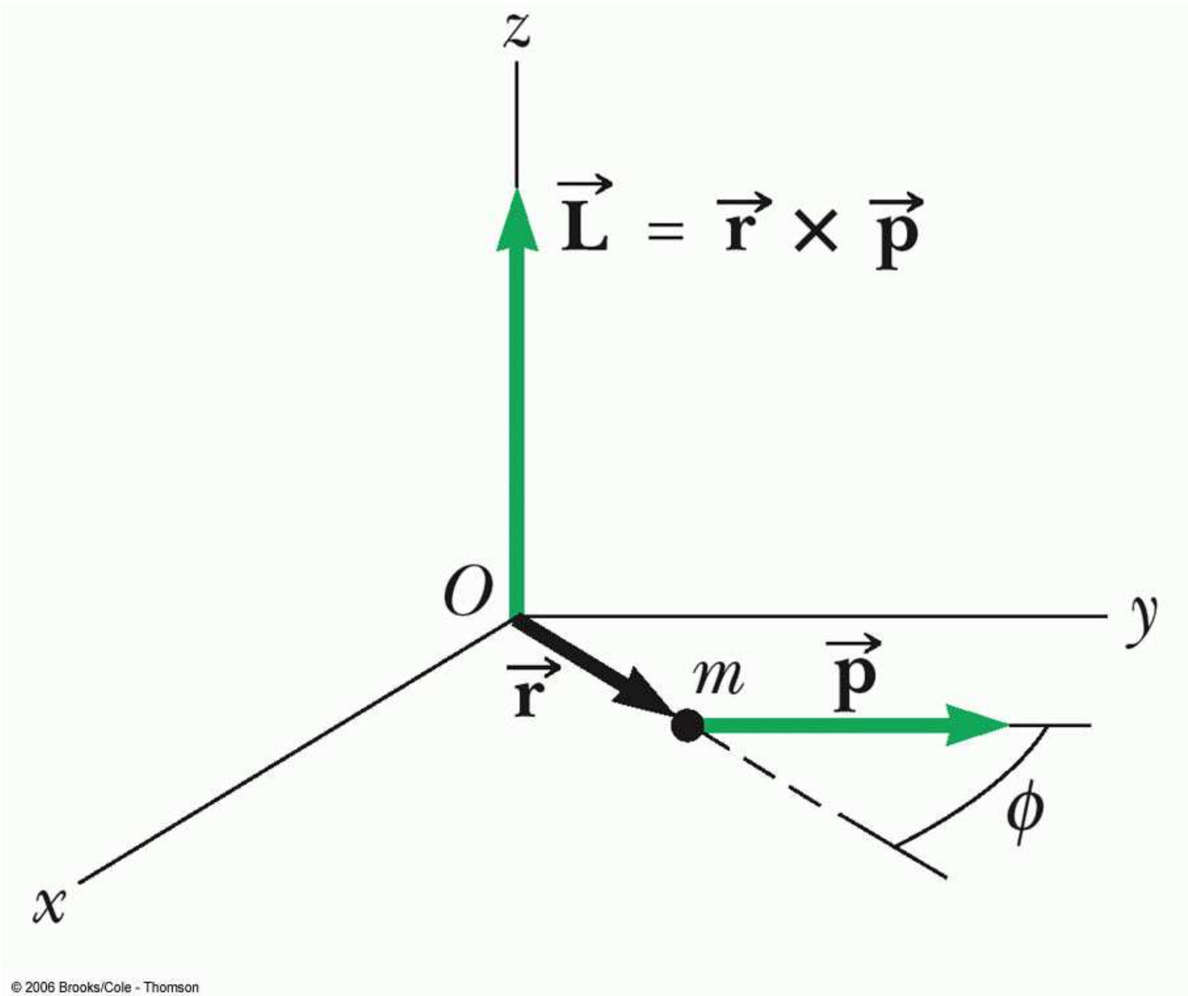
Rotational Kinetic Energy



Axis at the CM.



Angular Momentum



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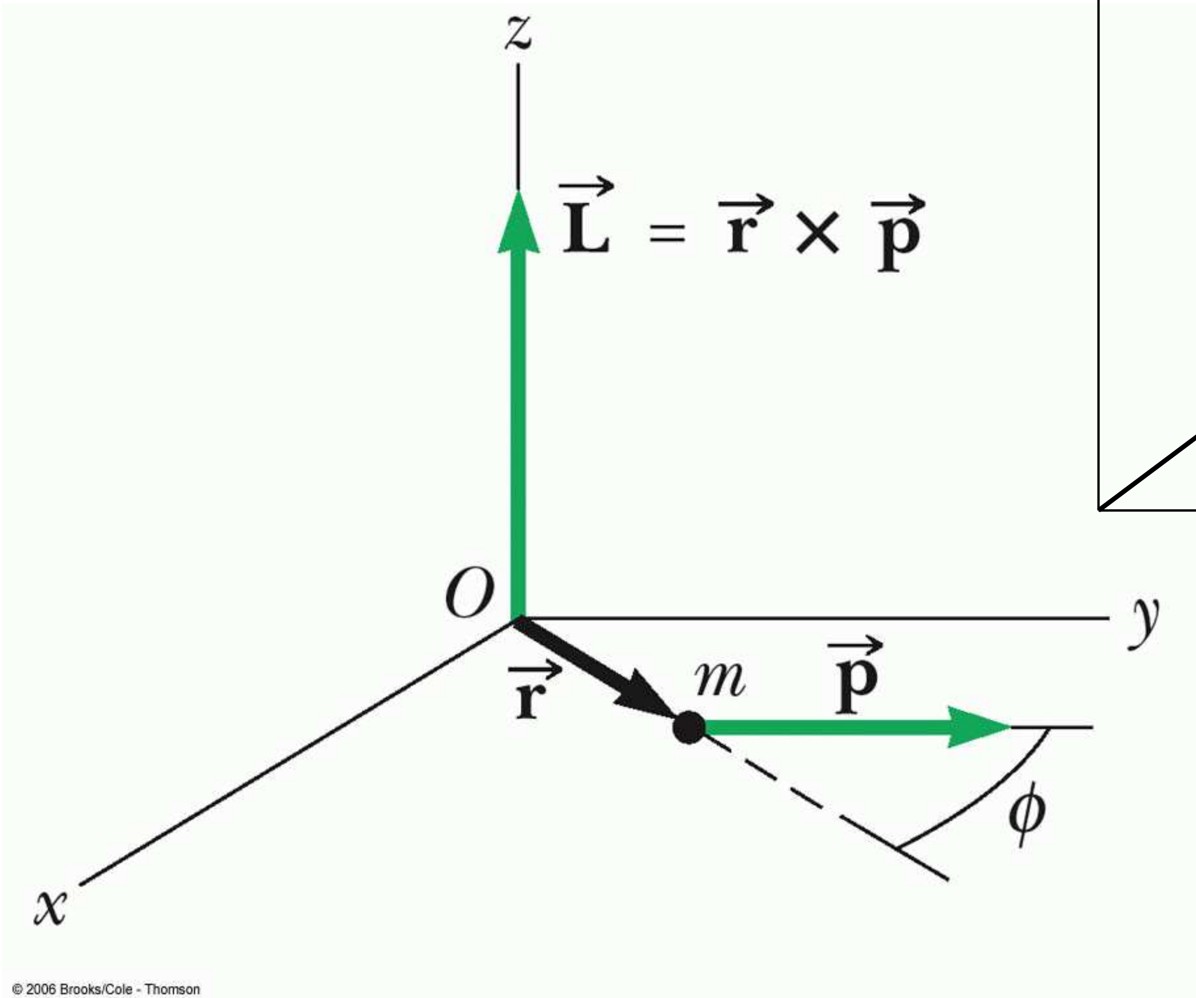
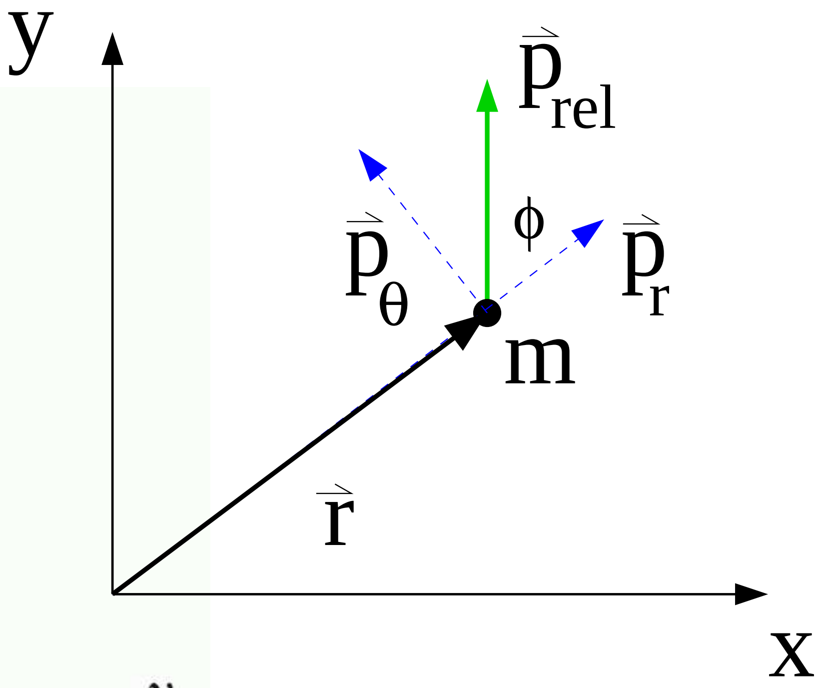
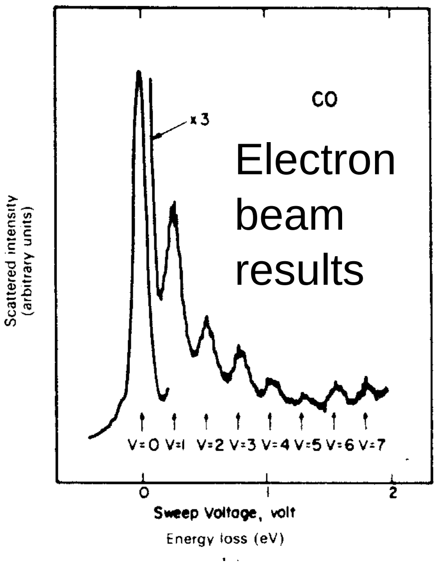




Is CO a Rgid Rotator?



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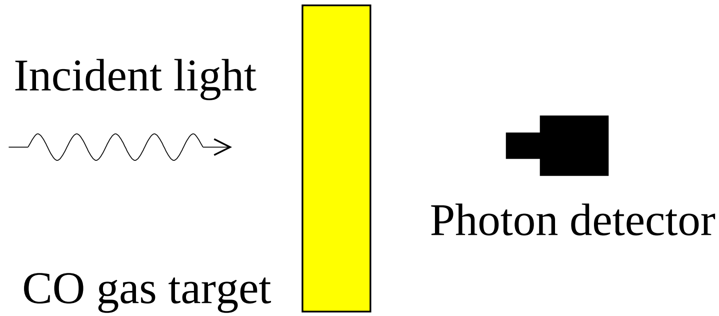
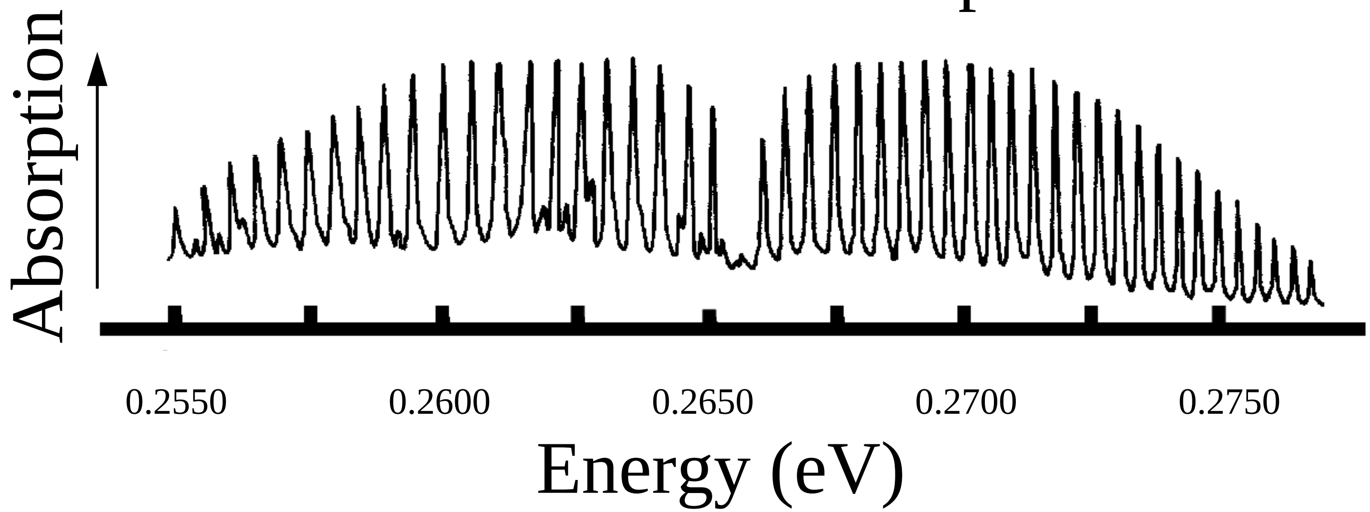
CO Absorption Spectrum



Carbon−Monoxide Spectrum



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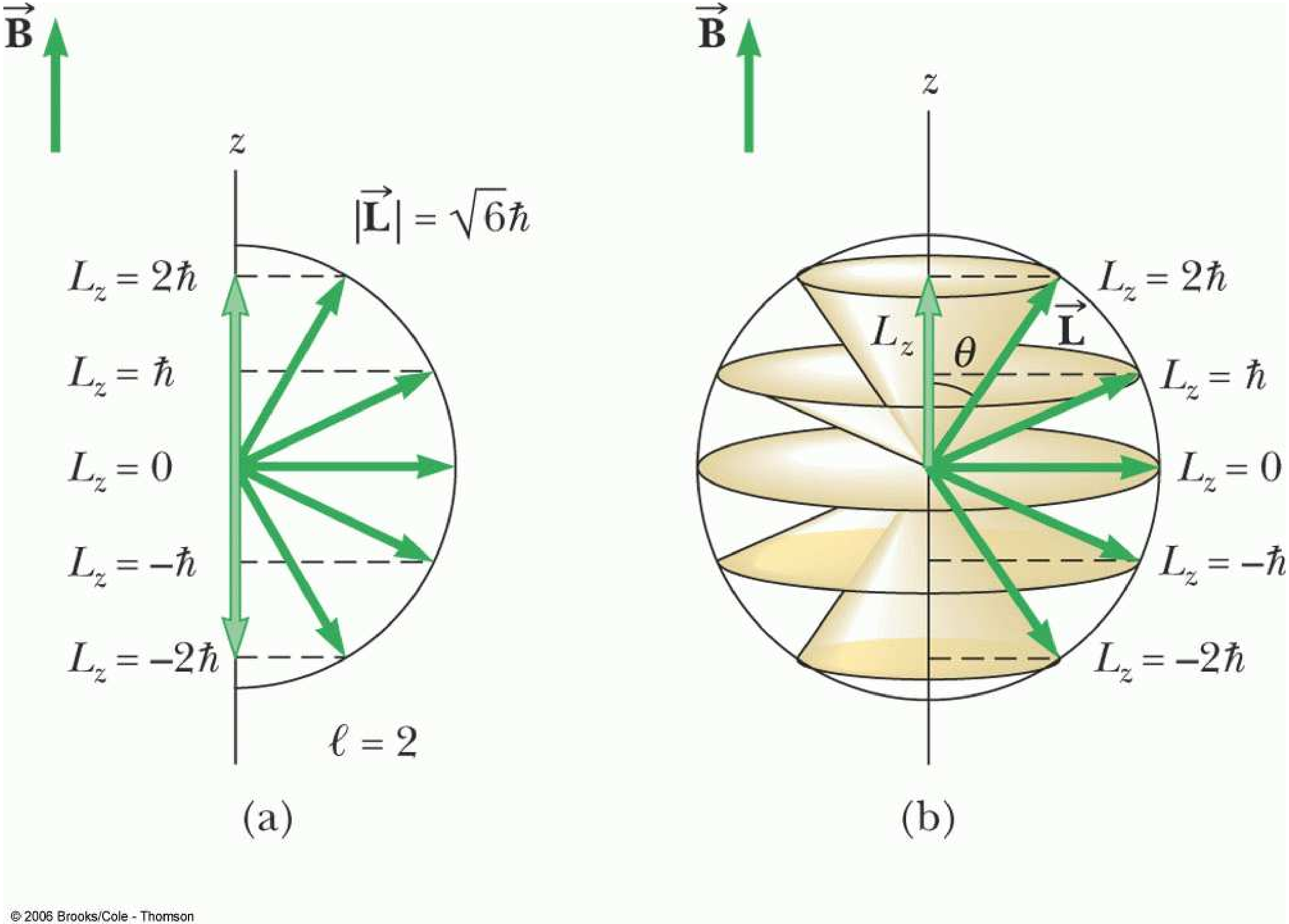
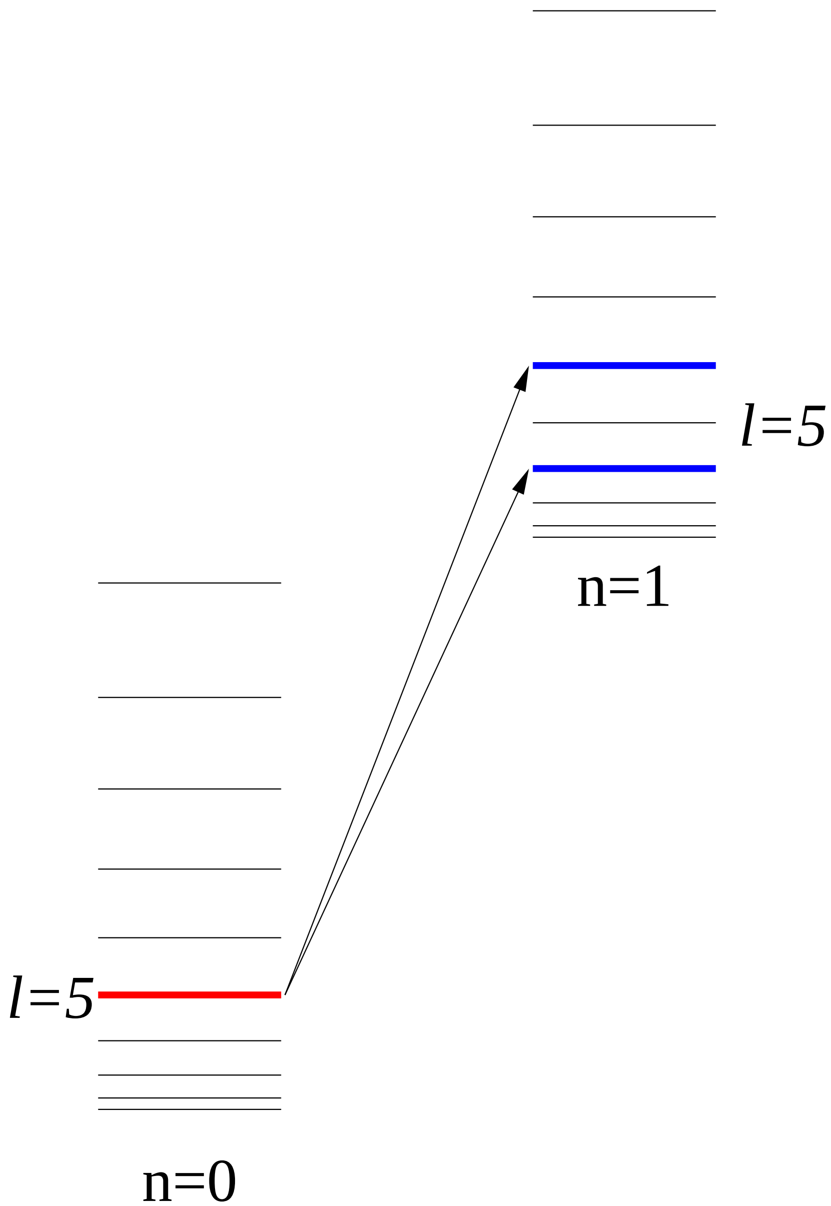


CO Atomic Transitions



Carbon Monoxide Rotation Spectrum