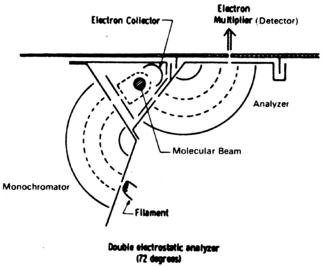
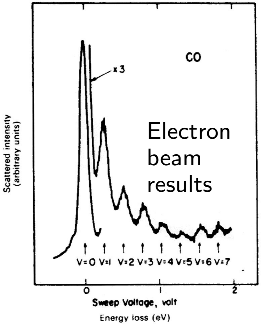
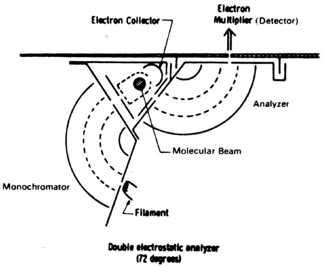


$\longrightarrow$

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



Electron beam results



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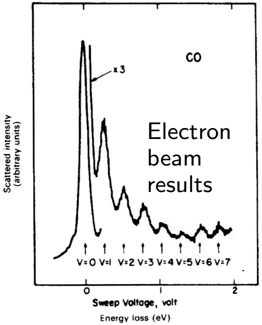
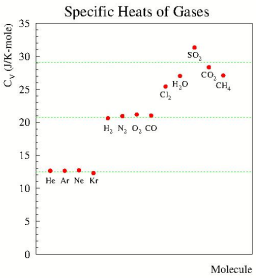
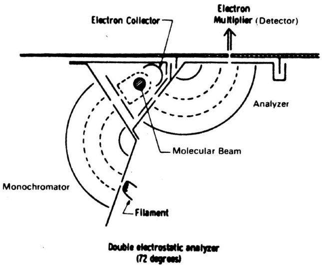
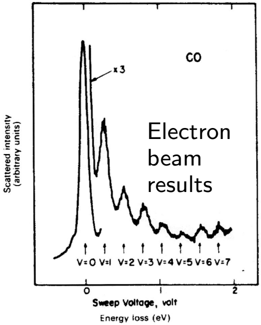


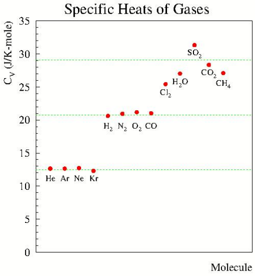


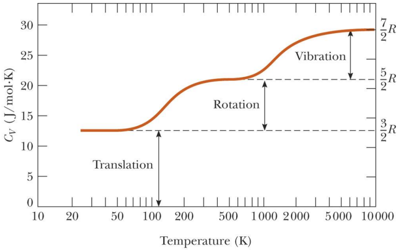
More On Carbon Monoxide 3



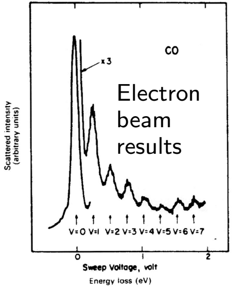
$\Delta E = 0.25 \pm 0.05\ eV$







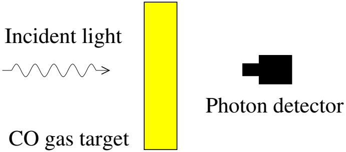
Even More On Carbon Monoxide 4

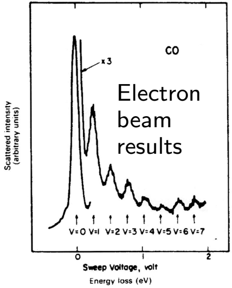


$\longrightarrow$

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

CO Absorption Spectrum

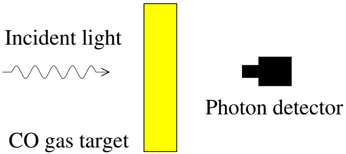




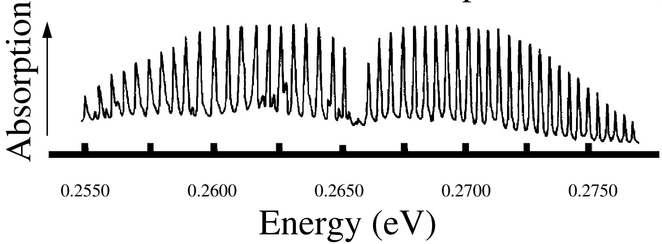
$\rightarrow$

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

CO Absorption Spectrum



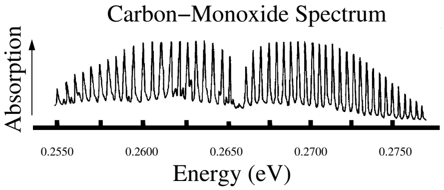
Carbon–Monoxide Spectrum



Excited states of carbon monoxide (CO) can be observed by 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

$$E_\ell = \frac{\hbar^2}{2\mathcal{I}}\ell(\ell+1)$$

where $\mathcal{I}$ is the moment of inertia. The vibrational part of the energy is described by the harmonic oscillator so $E_n = (n + \frac{1}{2})\hbar\omega_0$ with $\Delta E = \hbar\omega_0 = 0.25 \pm 0.05\ eV$ from our previous results. How do you get the expression above for the rotational energy? Is CO a rigid rotator?



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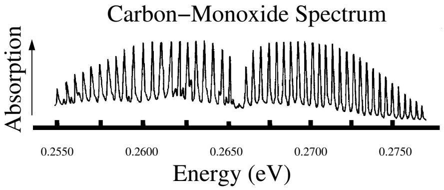
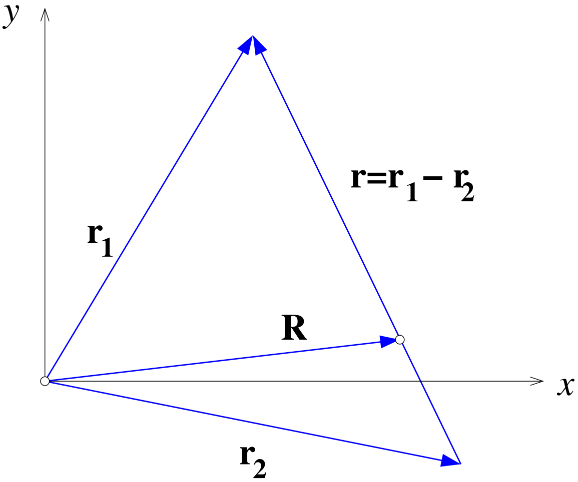
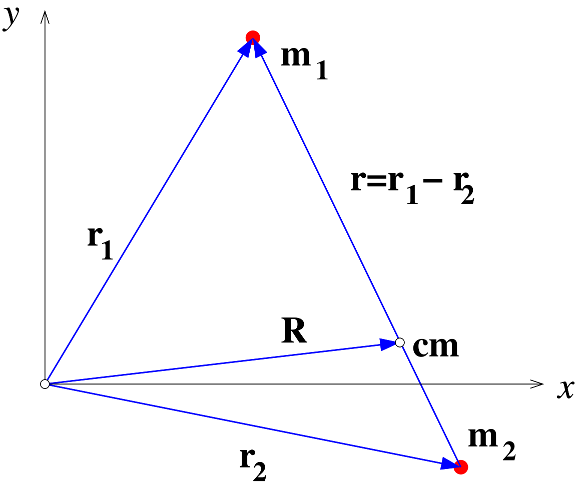
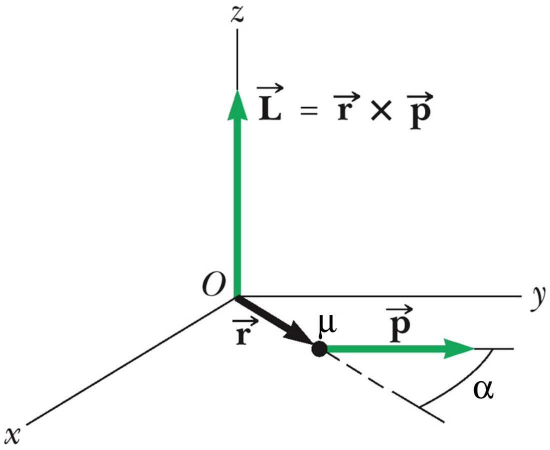
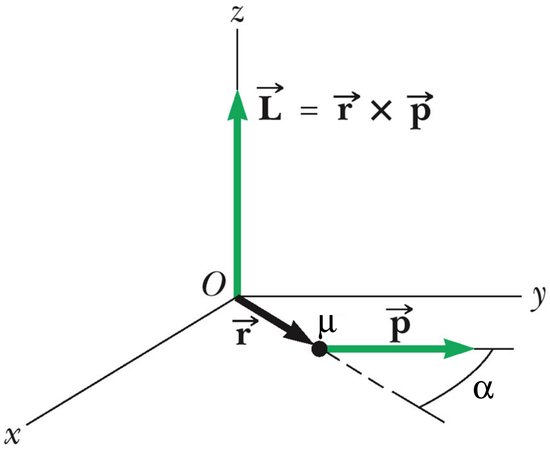


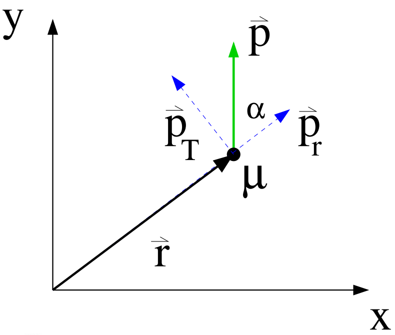
1. What is the kinetic and potential energy between the carbon and oxygen atoms in CO in the CM frame in cartesian and spherical coordinates?
2. How do you decompose the kinetic energy into radial and angular parts?
3. What is the Schroedinger equation for the rigid rotator?
4. What is the solution of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


y
x
r₁
r=r₁ − r₂
R
r₂


y
m 1
r=r 1 − r 2
r 1
R
cm
x
m 2
r 2


z
$\vec{L} = \vec{r} \times \vec{p}$
O
y
$\vec{r}$
μ
$\vec{p}$
α
x


z
$\vec{L} = \vec{r} \times \vec{p}$
O
y
$\vec{r}$
μ
$\vec{p}$
α
x


y
$\vec{p}$
α
$\vec{p}_T$
$\vec{p}_r$
μ
$\vec{r}$
x

The Laplacian

$$\nabla^2\psi = \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi$$

The Laplacian

$$\nabla^2\psi = \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi$$

The Schroedinger Equation in 3D

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V(r)\psi = E\psi$$

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

Steps along the way.

$$+\frac{m_\ell^2}{\sin^2\theta}\Theta - \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = A\Theta$$

Steps along the way.

$$+\frac{m_\ell^2}{\sin^2\theta}\Theta - \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = A\Theta$$

Legendre's Associated Equation

$$(1-z^2)\frac{d^2\Theta}{dz^2} - 2z\frac{d\Theta}{dz} + \left(A - \frac{m_\ell^2}{1-z^2}\right)\Theta = 0 \qquad where \qquad z = \cos\theta$$

Steps along the way.

$$+\frac{m_\ell^2}{\sin^2\theta}\Theta - \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = A\Theta$$

Legendre's Associated Equation

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And its recursion relationship when $m_\ell = 0$

$$a_{k+2} = \frac{k(k+1)-A}{(k+2)(k+1)}a_k$$

We have the recursion relationship when $m_\ell = 0$

$$a_{k+2} = \frac{k(k+1) - A}{(k+2)(k+1)} a_k$$

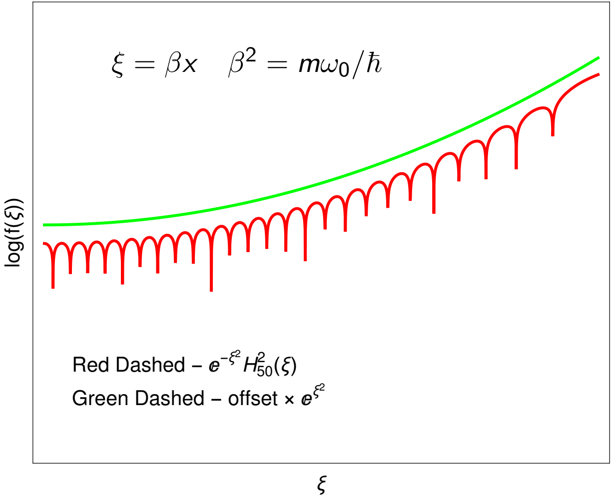
Notice.

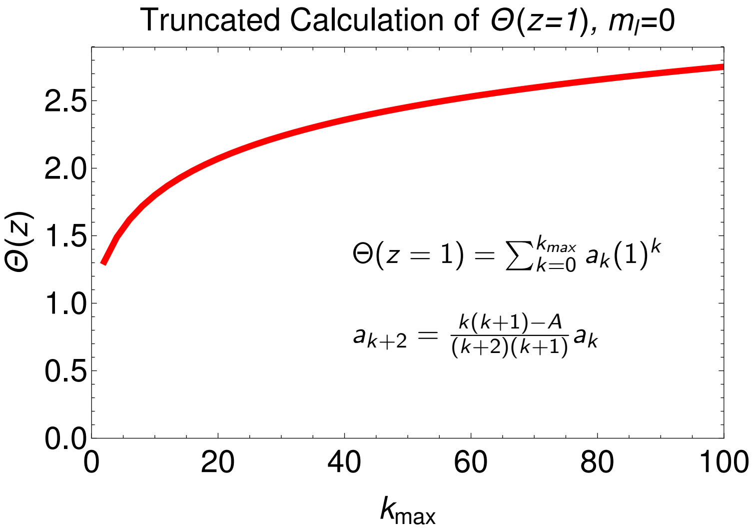
$$\text{Given} \quad a_0 \to a_2 \to a_4 \cdots \quad \text{and given} \quad a_1 \to a_3 \to a_5 \cdots$$

so

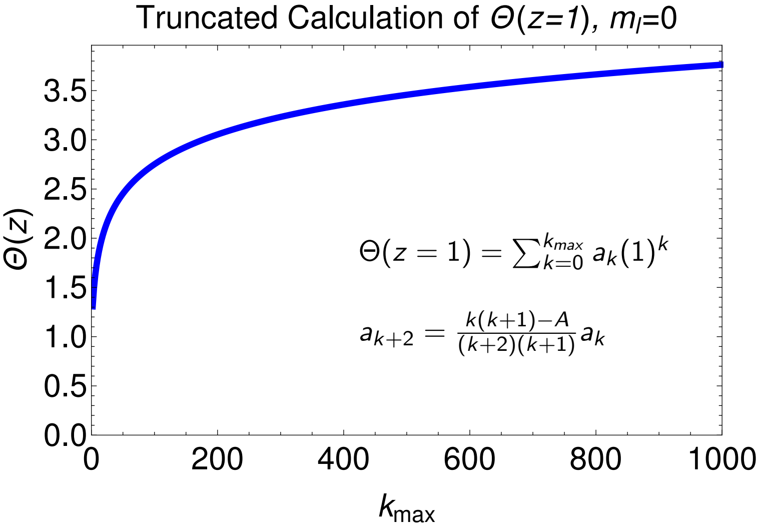
$$\Theta(z) = \sum_{k=0}^{\infty} a_k z^k = \sum_{even}^{\infty} a_k z^k + \sum_{odd}^{\infty} a_k z^k$$

and we choose $a_0 = a_1 = 1$.

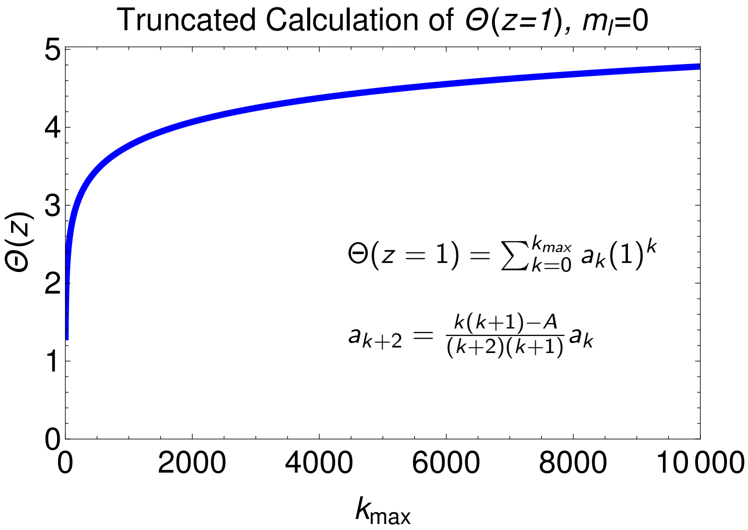

$\xi = \beta x \quad \beta^2 = m\omega_0/\hbar$
log(f(ξ))
ξ
Red Dashed – $e^{-\xi^2} H_{50}^2(\xi)$
Green Dashed – offset × e^{ξ^2}

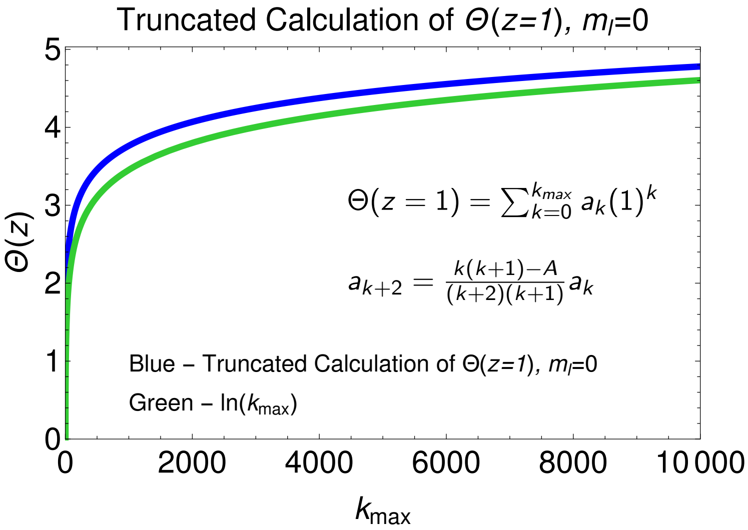

Truncated Calculation of $\Theta(z=1)$, m_l=0
$\Theta(z)$
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
k_{max}
$\Theta(z=1) = \sum_{k=0}^{k_{max}} a_k (1)^k$
$a_{k+2} = \frac{k(k+1)-A}{(k+2)(k+1)} a_k$

Another Convergence Problem



Another Convergence Problem




Truncated Calculation of Θ(z=1), m_l=0
$\Theta(z = 1) = \sum_{k=0}^{k_{max}} a_k (1)^k$
$a_{k+2} = \frac{k(k+1)-A}{(k+2)(k+1)} a_k$
Blue – Truncated Calculation of Θ(z=1), m_l=0
Green – ln(k_{max})
Θ(z)
k_{max}
0
1
2
3
4
5
0
2000
4000
6000
8000
10 000

Legendre Polynomials ($m_\ell = 0$)

$$a_{k+2} = \frac{k(k+1) - A}{(k+2)(k+1)} a_k \qquad m_\ell = 0 \qquad a_0 = a_1 = 1$$

$$\Theta = P_\ell(z) = \sum_{even/odd}^{\ell} a_k z^k \qquad z = \cos\theta$$

First few polynomials.

$$P_0(\cos\theta) = 1 \qquad P_3(\cos\theta) = \tfrac{1}{2}\left(5\cos^3\theta - 3\cos\theta\right)$$

$$P_1(\cos\theta) = \cos\theta \qquad P_4(\cos\theta) = \tfrac{1}{8}\left(35\cos^4\theta - 30\cos^2\theta + 3\right)$$

$$P_2(\cos\theta) = \tfrac{1}{2}\left(3\cos^2\theta - 1\right) \qquad P_5(\cos\theta) = \tfrac{1}{8}\left(63\cos^5\theta - 70\cos^3\theta + 15\cos\theta\right)$$

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

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

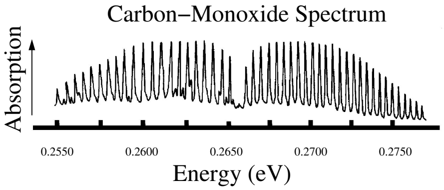
$$Y_1^1(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \qquad Y_1^{-1}(\theta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$

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

Excited states of carbon monoxide (CO) can be observed by 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

$$E_\ell = \frac{\hbar^2}{2\mathcal{I}}\ell(\ell+1)$$

where $\mathcal{I}$ is the moment of inertia. The vibrational part of the energy is described by the harmonic oscillator so $E_n = (n+\frac{1}{2})\hbar\omega_0$ with $\Delta E = \hbar\omega_0 = 0.25 \pm 0.05\ eV$ from our previous results. How do you get the expression above for the rotational energy? Is CO a rigid rotator?



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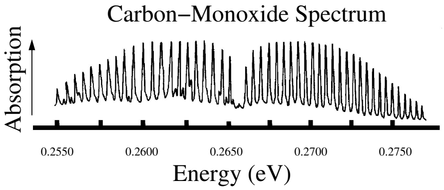


$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi + V(r)\psi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

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

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

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

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

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

The Eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ 29

$$
\begin{aligned}
\vec{L} &= \vec{r} \times \vec{p} \\
&= L_x \hat{i} + L_y \hat{j} + L_z \hat{k}
\end{aligned}
$$

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

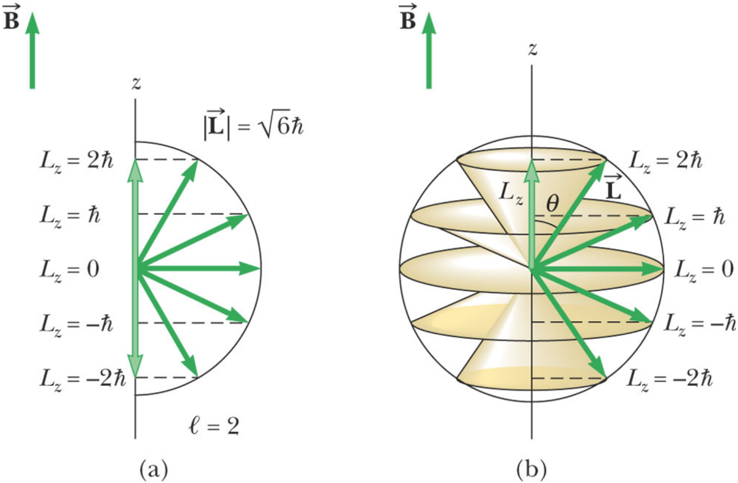
$$\begin{aligned}\vec{L} &= \vec{r} \times \vec{p} \\ &= L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \\ &= (y p_z - z p_y)\,\hat{i} + (z p_x - x p_z)\,\hat{j} + (x p_y - y p_x)\,\hat{k}\end{aligned}$$

$$
\begin{aligned}
\vec{L} &= \vec{r} \times \vec{p} \\
&= L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \\
&= (y p_z - z p_y)\, \hat{i} + (z p_x - x p_z)\, \hat{j} + (x p_y - y p_x)\, \hat{k} \\
&= \frac{\hbar}{i} \left[\left(y \frac{d}{dz} - z \frac{d}{dy} \right) \hat{i} + \left(z \frac{d}{dx} - x \frac{d}{dz} \right) \hat{j} + \left(x \frac{d}{dy} - y \frac{d}{dx} \right) \hat{k} \right]
\end{aligned}
$$

$$\begin{aligned}
\vec{L} &= \vec{r} \times \vec{p} \\
&= L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \\
&= (yp_z - zp_y)\,\hat{i} + (zp_x - xp_z)\,\hat{j} \; + (xp_y - yp_x)\,\hat{k} \\
&= \frac{\hbar}{i}\left[\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\hat{i} + \left(z\frac{d}{dx} - x\frac{d}{dz}\right)\hat{j} \; + \left(x\frac{d}{dy} - y\frac{d}{dx}\right)\hat{k}\right]
\end{aligned}$$

Transformation from Cartesian to spherical coordinates:

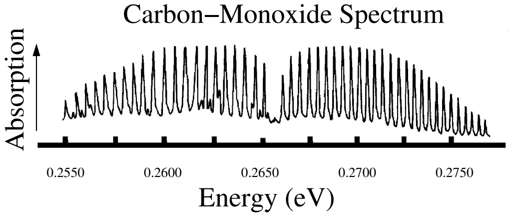
$$\begin{aligned}
x &= r \sin\theta \cos\phi \\
y &= r \sin\theta \sin\phi \\
z &= r \cos\theta
\end{aligned}$$

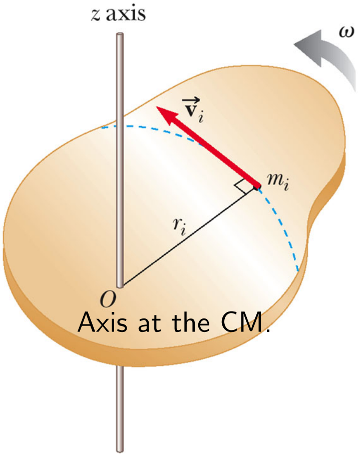

$\vec{B}$
z
$|\vec{L}| = \sqrt{6}\hbar$
$L_z = 2\hbar$
$L_z = \hbar$
$L_z = 0$
$L_z = -\hbar$
$L_z = -2\hbar$
$\ell = 2$
(a)
$\vec{B}$
z
L_z
θ
$\vec{L}$
$L_z = 2\hbar$
$L_z = \hbar$
$L_z = 0$
$L_z = -\hbar$
$L_z = -2\hbar$
(b)

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

$$E_\ell = \frac{\hbar^2}{2\mathcal{I}}\ell(\ell+1)$$

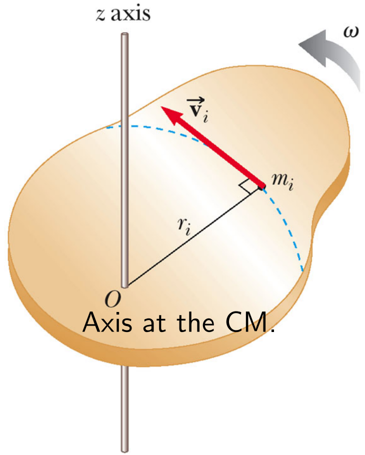
where $\mathcal{I}$ is the moment of inertia. The vibrational part of the energy can is described by the harmonic oscillator so $E_n = (n + \frac{1}{2})\hbar\omega_0$ with $\Delta E = \hbar\omega_0 = 0.25 \pm 0.05\ eV$ from our previous results. How does one obtain the expression above for the rotational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



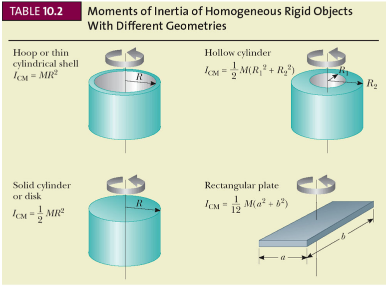


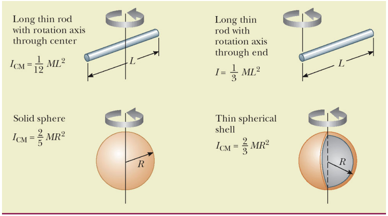
Axis at the CM.

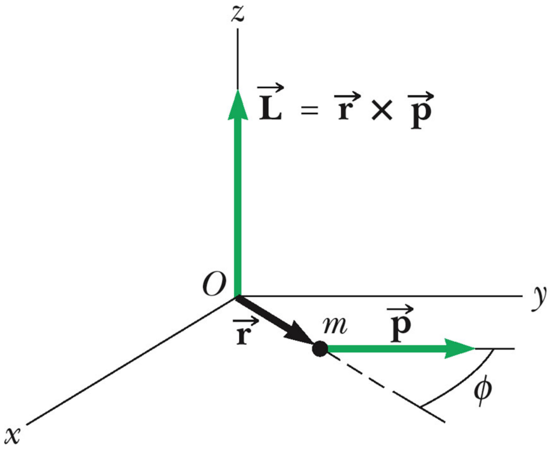
Rotational Kinetic Energy

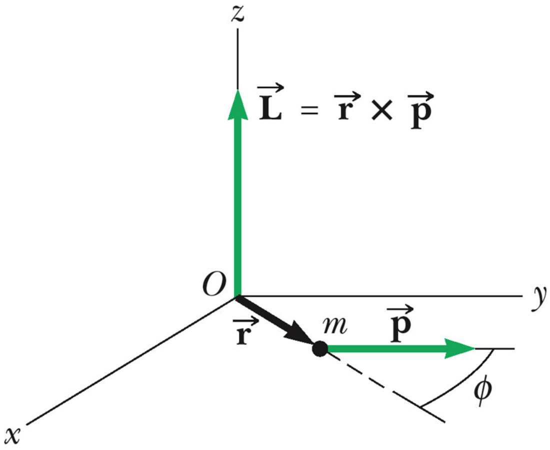


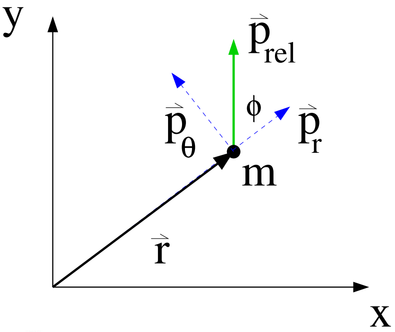
Axis at the CM.






z
$\vec{L} = \vec{r} \times \vec{p}$
O
y
$\vec{r}$
m
$\vec{p}$
ϕ
x


z
$\vec{L} = \vec{r} \times \vec{p}$
O
y
$\vec{r}$
m
$\vec{p}$
ϕ
x


y
$\vec{p}_{rel}$
$\vec{p}_\theta$
ϕ
$\vec{p}_r$
m
$\vec{r}$
x

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 vibrate and rotate at the same time. The rotational energy states of a rigid rotator are

$$E_\ell = \frac{\hbar^2}{2\mathcal{I}}\ell(\ell+1)$$

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

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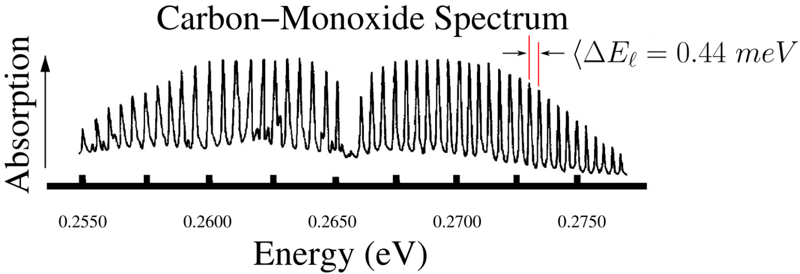
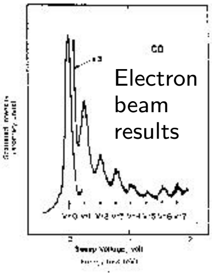
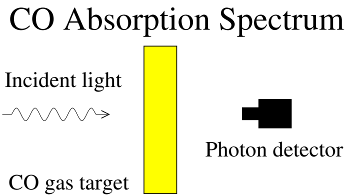
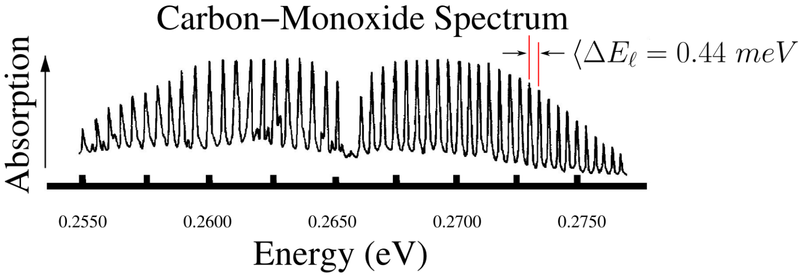


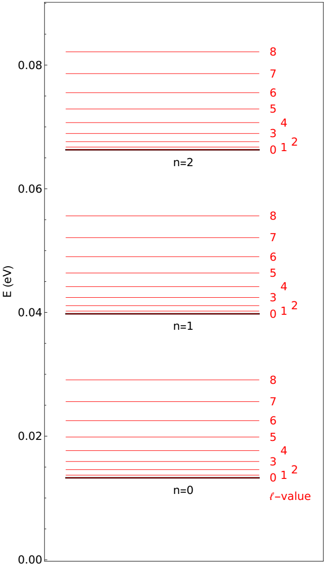


$\longrightarrow$

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



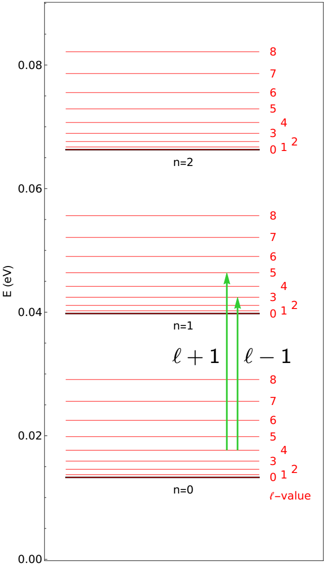




$$E_{nl} = (n + \frac{1}{2})\hbar\omega_0 + \frac{\hbar^2}{2\mathcal{I}}\ell(\ell + 1)$$

$$\Delta E_n = \hbar\omega_0 = 250 \pm 50 \;\; meV$$

$$\Delta E_\ell = \frac{\hbar^2}{\mathcal{I}} = 0.44 \pm 0.07 \;\; meV$$



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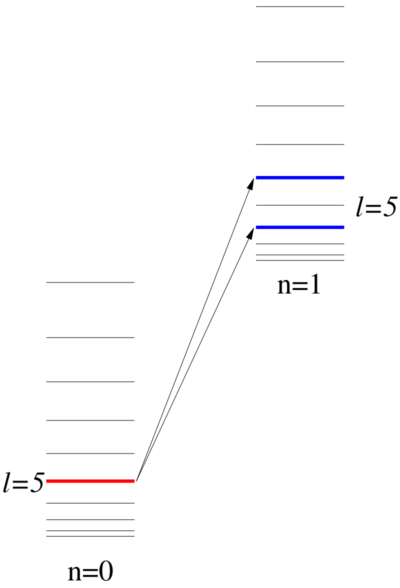
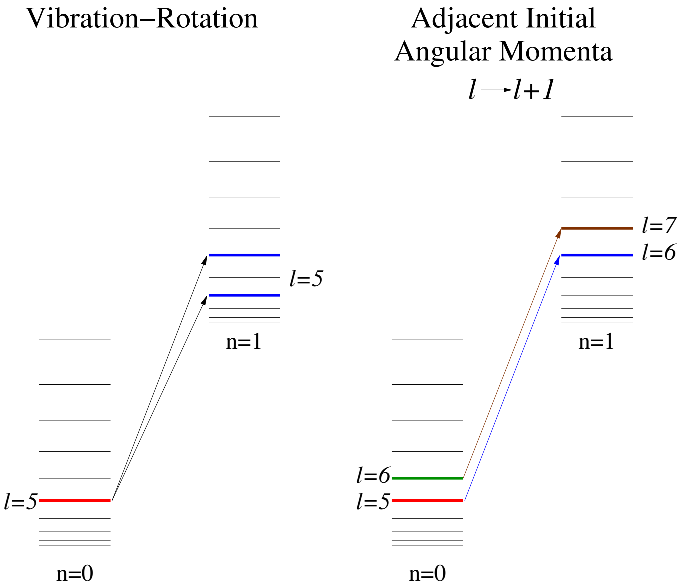
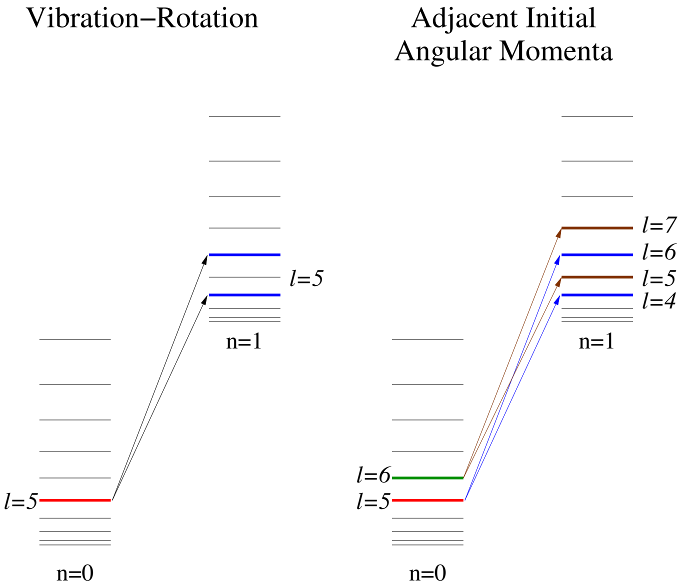
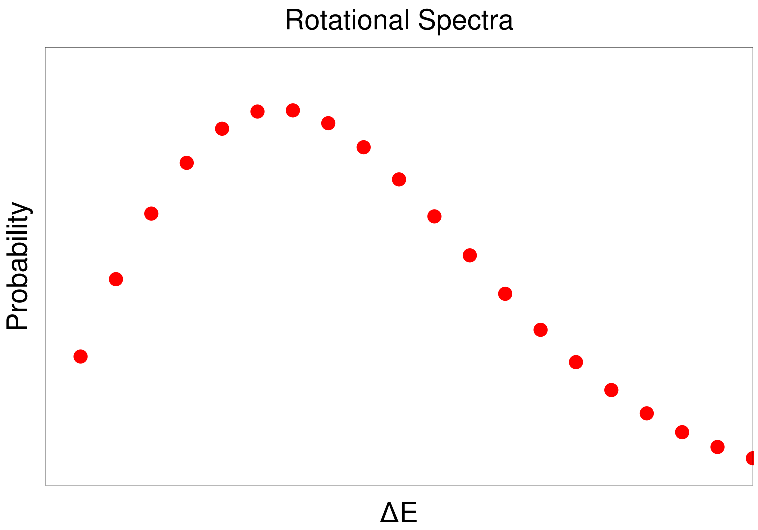


l=5
n=1
l=5
n=0


Vibration–Rotation
l=5
l=5
n=1
n=0
Adjacent Initial
Angular Momenta
l → l+1
l=7
l=6
l=6
l=5
n=1
n=0



Vibration–Rotation
l=5
n=1
l=5
n=0
Adjacent Initial
Angular Momenta
l=7
l=6
l=5
l=4
n=1
l=6
l=5
n=0


Rotational Spectra
Probability
ΔE