

**CHAPTER 4**  
**RIGID-ROTOR MODELS AND ANGULAR MOMENTUM EIGENSTATES**  
**OUTLINE**

**Homework Questions Attached**

<b>SECT</b>	<b>TOPIC</b>
1.	Math Preliminary: Products of Vectors
2.	Rotational Motion in Classical Physics
3.	Angular Momentum in Quantum Mechanics
4.	The 2D Quantum Mechanical Rigid Rotor
5.	The 3D Schrödinger Equation: Spherical Polar Coordinates
6.	The 3D Quantum Mechanical Rigid rotor
7.	Angular Momentum and the Rigid Rotor
8.	Rotational Spectroscopy of Linear Molecules
9.	Application of QM to Molecular Structure: Pyridine
10.	Statistical Thermodynamics: Rotational Contributions to the Thermodynamic Properties of Gases

## Chapter 4 Homework

1. Calculate the scalar product and cross product of the two vectors:

$$\vec{A} = 3\vec{i} - \vec{j} + 2\vec{k} \quad \vec{B} = 2\vec{i} + 4\vec{j} - 3\vec{k}$$

2. Consider a rigid rotor in the state characterized by:  $\psi = Ae^{-2i\phi} \sin^2 \theta$

(a) Verify that  $\psi$  is a solution to the Rigid Rotor Schrödinger Equation (below). What is the eigenvalue (i.e. energy)?

**Note:** You will probably find it useful to use the trigonometric identity,  
 $\sin^2 \theta + \cos^2 \theta = 1 \rightarrow \cos^2 \theta = 1 - \sin^2 \theta$

(b) Calculate the squared angular momentum,  $L^2$ , of the rotor.

(c) Calculate the z-component of angular momentum,  $L_z$ , of the rotor:

3. As discussed in class, the rotational motion of a diatomic molecule chemisorbed on a crystalline surface can be modelled as the rotation of a 2D Rigid Rotor. Consider  $F_2$  adsorbed on a platinum surface. The  $F_2$  bond length is 0.142 nm.

Calculate the frequency (in  $\text{cm}^{-1}$ ) of the rotational transition of an  $F_2$  molecule from the  $m = \pm 2$  level to the  $m = \pm 8$  level.

4. The first two lines the rotational Raman spectrum of  $H^{79}Br$  are found at  $50.2 \text{ cm}^{-1}$  and  $83.7 \text{ cm}^{-1}$ . Calculate the H-Br bond length, in Å.

5. Which of the following molecules will have a rotational microwave absorption spectrum?:  $H_2O$ ,  $H-C\equiv C-H$ ,  $H-C\equiv C-Cl$ , cis-1,2-dichloroethylene, benzene,  $NH_3$ .

6. The first microwave absorption line in  $^{12}C^{16}O$  occurs at  $3.84 \text{ cm}^{-1}$

(a) Calculate the CO bond length.

(b) Predict the frequency (in  $\text{cm}^{-1}$ ) of the 7th. line in the microwave spectrum of CO..

(c) Calculate the ratio of the intensities of the 5th. line to the 2nd line in the spectrum at  $25^\circ\text{C}$

(d) Calculate the the initial state ( $J''$ ) corresponding to the most intense transition in the microwave absorption spectrum of  $^{12}C^{16}O$  at  $25^\circ\text{C}$ .

7. The C≡C and C-H bond lengths in the linear molecule, acetylene (H-C≡C-H) are 1.21 Å and 1.05 Å, respectively
- What are the frequencies of the first two lines in the rotational Raman spectrum?
  - What are the frequencies of the first two lines in the rotational Mookster absorption spectrum, for which the selection rule is  $\Delta J = +3$  ?
  - Calculate the ratio of intensities in the 20th. lowest frequency line to that of the 5th. lowest frequency line in the rotational Raman spectrum at 100 °C.
8. For **two (2)** moles of the non-linear molecule NO<sub>2</sub>(g) at 150 °C, calculate the rotational contributions to the internal energy, enthalpy, constant pressure heat capacity, entropy, Helmholtz energy and Gibbs energy. The Moments of Inertia are:  $I_a = 3.07 \times 10^{-47}$  kg·m<sup>2</sup>,  $I_b = 6.20 \times 10^{-46}$  kg·m<sup>2</sup>,  $I_c = 6.50 \times 10^{-46}$  kg·m<sup>2</sup>. The symmetry number is 2.
9. The molecular rotational partition function of H<sub>2</sub> at 25 °C is  $q^{\text{rot}} = 1.70$ .
- What is  $q^{\text{rot}}$  for D<sub>2</sub> at 25 °C?
  - What is  $q^{\text{rot}}$  for H<sub>2</sub> at 3000 °C?

## DATA

$h = 6.63 \times 10^{-34}$ J·s	$1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$
$\hbar = h/2\pi = 1.05 \times 10^{-34}$ J·s	$1 \text{ \AA} = 10^{-10} \text{ m}$
$c = 3.00 \times 10^8$ m/s = $3.00 \times 10^{10}$ cm/s	$k \cdot N_A = R$
$N_A = 6.02 \times 10^{23}$ mol <sup>-1</sup>	$1 \text{ amu} = 1.66 \times 10^{-27}$ kg
$k = 1.38 \times 10^{-23}$ J/K	$1 \text{ atm.} = 1.013 \times 10^5$ Pa
$R = 8.31$ J/mol-K	$1 \text{ eV} = 1.60 \times 10^{-19}$ J
$R = 8.31$ Pa·m <sup>3</sup> /mol-K	
$m_e = 9.11 \times 10^{-31}$ kg (electron mass)	

### Rigid Rotor Schrödinger Equation:

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

### The $L_z$ Equation:

$$\hat{L}_z \psi = \frac{\hbar}{i} \frac{\partial \psi}{\partial \phi} = m \hbar \psi$$

### Some “Concept Question” Topics

Refer to the PowerPoint presentation for explanations on these topics.

- Significance of angular momentum operator commutation
- Interpretation of  $|L|$  and  $L_z$  for rigid rotor in magnetic field
- Amount of required isotopic data to determine structure of linear molecule
- HOMO and LUMO electron distributions. Relationship to changes in bond lengths in excited electronic states (see, for example, pyridine)
- Equipartition of rotational energy and heat capacity in linear and non-linear molecules

# Chapter 4

## Rigid-Rotor Models and Angular Momentum Eigenstates

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### Outline

- **Math Preliminary: Products of Vectors**
- Rotational Motion in Classical Physics
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**Not Last Topic**

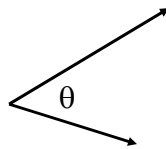
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## Outline (Cont'd.)

- Application of QM to Molecular Structure: Pyridine
- Statistical Thermodynamics: Rotational contributions to the thermodynamic properties of gases

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## Mathematical Preliminary: Products of Vectors



$$\vec{A} = A_x \vec{i} + A_y \vec{j} + A_z \vec{k}$$

$$\vec{B} = B_x \vec{i} + B_y \vec{j} + B_z \vec{k}$$

### Scalar Product (aka Dot Product)

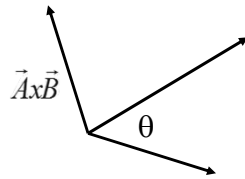
$$\vec{A} \cdot \vec{B} = A_x B_x + A_y B_y + A_z B_z$$

Note that the product is a scalar quantity (i.e. a number)

Magnitude:  $|\vec{A} \cdot \vec{B}| = |\vec{A}| |\vec{B}| \cos(\theta)$

Parallel Vectors:  $|\vec{A} \cdot \vec{B}| = |\vec{A}| |\vec{B}| \cos(0^\circ) = |\vec{A}| |\vec{B}|$

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$$\vec{A} = A_x \vec{i} + A_y \vec{j} + A_z \vec{k}$$

$$\vec{B} = B_x \vec{i} + B_y \vec{j} + B_z \vec{k}$$

### Cross Product

The cross product of two vectors is also a vector.

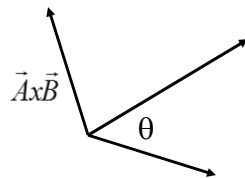
Its direction is perpendicular to both A and B and is given by the “right-hand rule”.

$$\text{Magnitude: } |\vec{A} \times \vec{B}| = |\vec{A}| |\vec{B}| \sin(\theta)$$

$$\text{Parallel Vectors: } |\vec{A} \times \vec{B}| = |\vec{A}| |\vec{B}| \sin(0^\circ) = 0$$

$$\text{Perpendicular Vectors: } |\vec{A} \times \vec{B}| = |\vec{A}| |\vec{B}| \sin(90^\circ) = |\vec{A}| |\vec{B}|$$

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$$\vec{A} = A_x \vec{i} + A_y \vec{j} + A_z \vec{k}$$

$$\vec{B} = B_x \vec{i} + B_y \vec{j} + B_z \vec{k}$$

$$\vec{A} \times \vec{B} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix}$$

$$\vec{A} \times \vec{B} = \vec{i} \begin{vmatrix} A_y & A_z \\ B_y & B_z \end{vmatrix} - \vec{j} \begin{vmatrix} A_x & A_z \\ B_x & B_z \end{vmatrix} + \vec{k} \begin{vmatrix} A_x & A_y \\ B_x & B_y \end{vmatrix} \quad \text{Expansion by Cofactors}$$

$$\vec{A} \times \vec{B} = (A_y B_z - A_z B_y) \vec{i} + (A_z B_x - A_x B_z) \vec{j} + (A_x B_y - A_y B_x) \vec{k}$$

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## Rotational Motion in Classical Physics

### Angular Momentum (L)

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

Magnitude:  $L = rp \sin(\theta)$

Circular Motion:  $L = rp \sin(90^\circ) = rp$

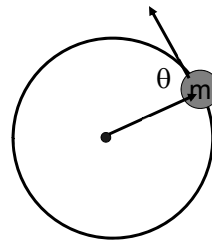
or:  $L = rp = rmv = (mr^2) \left( \frac{v}{r} \right) = (mr^2) \omega$

$$L = I\omega \quad \text{where} \quad I = mr^2 \quad \omega = \frac{v}{r}$$

**Moment of Inertia**      **Angular Frequency**

### Energy

$$E = \frac{p^2}{2m} = \frac{mv^2}{2} = \frac{m(r\omega)^2}{2} = \frac{mr^2\omega^2}{2} = \frac{I\omega^2}{2} \quad \text{or:} \quad E = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$$



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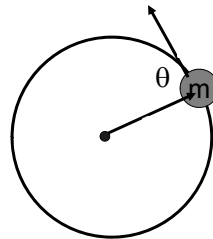


### Comparison of Equations for Linear and Circular Motion

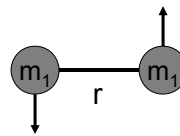
	Linear Motion	Circular Motion	
Mass	$m$	$I = mr^2$	Moment of inertia
Velocity	$v$	$\omega = \frac{v}{r}$	Angular velocity
Momentum	$p = mv$	$L = I\omega$	Angular momentum
Energy	$E = \frac{p^2}{2m}$	$E = \frac{L^2}{2I}$	Energy
or	$E = \frac{mv^2}{2}$	$E = \frac{I\omega^2}{2}$	Energy

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### Modification: Rotation of two masses about Center of Mass



$$I = mr^2$$



$$I = \mu r^2$$

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

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## Angular Momentum in Quantum Mechanics

### Classical Angular Momentum

$$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$$

$$\vec{p} = p_x\vec{i} + p_y\vec{j} + p_z\vec{k}$$

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$\vec{L} = (yp_z - zp_y)\vec{i} + (zp_x - xp_z)\vec{j} + (xp_y - yp_x)\vec{k}$$

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

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## Angular Momentum in Quantum Mechanics

### QM Angular Momentum Operators

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x} = -i\hbar \frac{\partial}{\partial x}$$

$$\hat{p}_y = \frac{\hbar}{i} \frac{\partial}{\partial y} = -i\hbar \frac{\partial}{\partial y}$$

$$\hat{p}_z = \frac{\hbar}{i} \frac{\partial}{\partial z} = -i\hbar \frac{\partial}{\partial z}$$

**Classical**

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

**QM Operator**

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

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

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

$$\hat{L}^2 = \hat{L}_x \bullet \hat{L}_x + \hat{L}_y \bullet \hat{L}_y + \hat{L}_z \bullet \hat{L}_z$$

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### Operator Commutation and Simultaneous Eigenfunctions

It can be shown that:  $[\hat{L}_x, \hat{L}_y] \neq 0$  Do not commute

$[\hat{L}_y, \hat{L}_z] \neq 0$  Do not commute

$[\hat{L}_x, \hat{L}_z] \neq 0$  Do not commute

Because the operators for the individual components do not commute, one **cannot** determine two separate components simultaneously.

i.e. they cannot have simultaneous eigenfunctions.

In contrast, it can be shown that:  $[\hat{L}_z, \hat{L}^2] = 0$  Do commute

Because these operators commute, one **can** determine  $L_z$  and  $L^2$  simultaneously; i.e. they can have simultaneous eigenfunctions.

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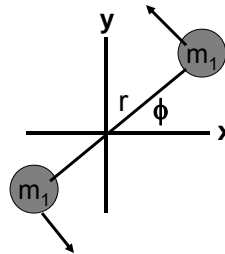
## The 2D Quantum Mechanical Rigid Rotor

Assume that two masses are attached by a rigid rod (i.e. ignore vibrations) at a fixed distance,  $r$ , and are free to rotate about the Center of Mass in their x-y plane.

The angle  $\phi$  represents the angle of rotation relative to the x-axis.

The 2D Schrödinger equation for the relative motion of two masses is:

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi + V\psi = E\psi$$
$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \quad \text{Two Dimensional Laplacian in Cartesian Coordinates}$$
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



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

If one (a) converts the Laplacian to polar coordinates

(b) assumes that the potential energy is constant (arbitrarily 0)

(c) holds r fixed (i.e. neglects derivatives with respect to r)

It can be shown that the Schrödinger Equation for a 2D Rigid Rotor becomes:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial^2\psi}{\partial\phi^2} = E\psi$$

or 
$$-\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\phi^2} = E\psi$$

where  $I = \mu r^2$  is the moment of inertia

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### The Solution

$$-\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\phi^2} = E\psi$$

Assume

$$\psi = Ae^{im\phi}$$

$$\frac{d\psi}{d\phi} = (im)Ae^{im\phi}$$

$$\frac{d^2\psi}{d\phi^2} = (im)^2 Ae^{im\phi}$$

$$\frac{d^2\psi}{d\phi^2} = -m^2\psi$$

$$\frac{\partial^2\psi}{\partial\phi^2} = -\frac{2IE}{\hbar^2}\psi = -\text{Constant} \cdot \psi$$

$$-m^2\psi = -\frac{2IE}{\hbar^2}\psi$$

$$m^2 = \frac{2IE}{\hbar^2} \quad \text{or} \quad E = \frac{\hbar^2 m^2}{2I}$$

Note: So far, m can have any value;  
i.e. there is no energy quantization

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### Application of the Boundary Conditions: Quantization of Energy

$$\psi = Ae^{im\varphi}$$

To be a physically realistic solution, one must have:  $\psi(\varphi + 2\pi) = \psi(\varphi)$

$$\text{Therefore: } Ae^{im\varphi} e^{2\pi mi} = Ae^{im\varphi}$$

$$\text{or } e^{2\pi mi} = 1$$

$$\cos(2\pi m) + i \sin(2\pi m) = 1$$

This is valid only for:  $m = 0, \pm 1, \pm 2, \pm 3, \dots$

Therefore, only certain values for the energy are allowed;  
i.e. the energy is quantized:

$$E = \frac{\hbar^2 m^2}{2I} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots$$

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### Zero Point Energy

$$E = \frac{\hbar^2 m^2}{2I} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots \quad \longrightarrow \quad E_0 = 0$$

There is **no** minimum Zero Point Energy.

One encounters a ZPE only when the particle is bound (e.g. PIB, Harmonic Oscillator, Hydrogen Atom), but not in freely moving systems (e.g. 2D and 3D Rigid Rotor, free particle)

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## Application of the 2D Rigid Rotor

We have solved the 2D Rigid Rotor primarily as a learning exercise, in order to demonstrate the application of angular Boundary Conditions.

However, the model has a real world application, in that it can be used to characterize the rotation of molecules adsorbed on surfaces.

### Example

When an H<sub>2</sub> molecule is chemisorbed on a crystalline surface, its rotation can be approximated as that of a 2D rigid rotor.

The H<sub>2</sub> bond length is 0.74 Å Calculate the frequency (in cm<sup>-1</sup>) of the lowest energy rotational transition of chemisorbed H<sub>2</sub>.

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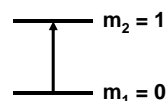
$$E = \frac{\hbar^2 m^2}{2I} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots$$

$$\begin{aligned} r &= 0.74 \text{ \AA} = 0.74 \times 10^{-10} \text{ m} \\ 1 \text{ amu} &= 1.66 \times 10^{-27} \text{ kg} \\ \hbar &= 1.05 \times 10^{-34} \text{ J}\cdot\text{s} \\ h &= 6.63 \times 10^{-34} \text{ J}\cdot\text{s} \\ c &= 3.00 \times 10^{10} \text{ cm/s} \end{aligned}$$

$$\mu = \frac{m_H^2}{m_H + m_H} = \frac{(1 \text{ amu})^2}{1 \text{ amu} + 1 \text{ amu}} = 0.50 \text{ amu} \cdot \frac{1.66 \times 10^{-27} \text{ kg}}{\text{amu}} = 8.30 \times 10^{-28} \text{ kg}$$

$$I = \mu r^2 = (8.30 \times 10^{-28} \text{ kg})(0.74 \times 10^{-10} \text{ m})^2 = 4.55 \times 10^{-48} \text{ kg}\cdot\text{m}^2$$

$$\Delta E = \frac{\hbar^2 m_2^2}{2I} - \frac{\hbar^2 m_1^2}{2I} = \frac{\hbar^2}{2I} \left( \frac{(1.05 \times 10^{-34} \text{ J}\cdot\text{s})^2}{2(4.55 \times 10^{-48} \text{ kg}\cdot\text{m}^2)} \right) = 1.21 \times 10^{-21} \text{ J}$$



$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{1.21 \times 10^{-21} \text{ J}}{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^{10} \text{ cm/s})} = 60.9 \text{ cm}^{-1}$$

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## The Three Dimensional Schrödinger Equation

In Cartesian Coordinates, the 3D Schrödinger Equation is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial y^2} - \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial z^2} + V(x, y, z)\psi = E\psi \quad \psi = \psi(x, y, z)$$

**T(x)      T(y)      T(z)      V(x,y,z)**

The Laplacian in Cartesian Coordinates is:  $\nabla^2 \equiv \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}$

Therefore:  $-\frac{\hbar^2}{2m} \nabla^2 \psi + V(x, y, z) = E\psi$

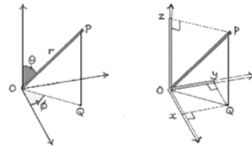
It is sometimes not possible to solve the Schrödinger exactly in Cartesian Coordinates (e.g. the Hydrogen Atom), whereas it **can** be solved in another coordinate system.

The "Rigid Rotor" and the Hydrogen Atom can be solved exactly in Spherical Polar Coordinates.

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## Spherical Polar Coordinates



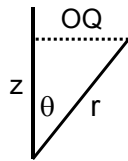
$$OQ = r \sin \theta \text{ so } x = r \sin \theta \cos \phi, y = r \sin \theta \sin \phi \text{ and } z = r \cos \theta$$

To specify a point in space requires three coordinates.  
In the spherical polar coordinate system, they are:

- $r$     $0 \leq r < \infty$    Distance of point from origin (OP)
- $\theta$     $0 \leq \theta < \pi$    Angle of vector (OP) from z-axis
- $\phi$     $0 \leq \phi < 2\pi$    Angle of x-y projection (OQ) from x-axis

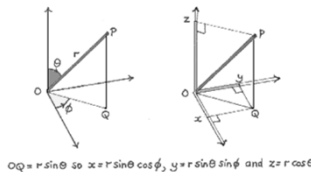
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## Relation of Cartesian to Spherical Polar Coordinates



$$\cos(\theta) = \frac{z}{r}$$

$$z = r \cos(\theta)$$



$$OQ = r \sin \theta \text{ so } x = r \sin \theta \cos \phi, y = r \sin \theta \sin \phi \text{ and } z = r \cos \theta$$

$$OQ = r \sin(\theta)$$

$$\cos(\phi) = \frac{x}{OQ}$$

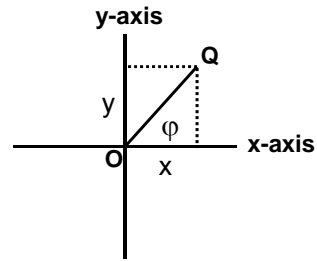
$$x = OQ \cos(\phi)$$

$$x = r \sin(\theta) \cos(\phi)$$

$$\sin(\phi) = \frac{y}{OQ}$$

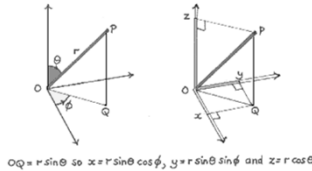
$$y = OQ \sin(\phi)$$

$$y = r \sin(\theta) \sin(\phi)$$



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## The Volume Element in Spherical Polar Coordinates



In Cartesian Coordinates,

the volume element is:  $dV = dx dy dz$

In spherical polar coordinates,

the volume element is:  $dV = dr \bullet r d\theta \bullet r \sin \theta d\phi$

$$dV = dr \bullet r d\theta \bullet r \sin(\theta) d\phi$$

$$dV = r^2 \sin(\theta) dr d\theta d\phi$$

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## The Laplacian in Spherical Polar Coordinates

Cartesian Coordinates:  $\nabla^2 \equiv \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}$

One example of a chain rule formula connecting a derivative with respect to x, y, z to derivatives with respect to r,  $\theta$ ,  $\phi$  is:

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r} \frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta} \frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \phi} \frac{\partial \phi}{\partial x}$$

It may be shown that by repeated application of chain rule formulae of this type (with 2-3 hours of tedious algebra), the Laplacian in spherical polar coordinates is given by:

$$\nabla^2 \equiv \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \phi^2}$$

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## Angular Momentum Operators in Spherical Polar Coordinates

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

↓  
It may be  
shown that

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi} = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$$

$$\hat{L}^2 = \hat{L}_x \cdot \hat{L}_x + \hat{L}_y \cdot \hat{L}_y + \hat{L}_z \cdot \hat{L}_z$$

↓  
It may be  
shown that

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

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## Outline

- Math Preliminary: Products of Vectors
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- Angular Momentum in Quantum Mechanics
- The 2D Quantum Mechanical Rigid Rotor
- The 3D Schrödinger Equation: Spherical Polar Coordinates
- **The 3D Quantum Mechanical Rigid Rotor**
- Angular Momentum and the Rigid Rotor
- Rotational Spectroscopy of Linear Molecules

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## The 3D Quantum Mechanical Rigid Rotor

### 3D Schrödinger Equation for a particle (Sph. Pol. Coords.)

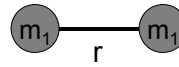
$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(r, \theta, \varphi) \psi = E \psi \quad \psi = \psi(r, \theta, \varphi)$$

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

### Modification: Two masses moving relative to their CM

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

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



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## The Schrödinger Equation in terms of the $\hat{L}^2$ operator

The  $\hat{L}^2$  operator is:  $\hat{L}^2 = -\hbar^2 \left\{ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2} \right\}$

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

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

$$-\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) \right] + \frac{1}{2I} \hat{L}^2 \psi + V \psi = E \psi \quad \text{where } I = \mu r^2$$

↑                    ↑                    ↑  
**Radial KE**    **Rotational KE**    **PE**

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### The Quantum Mechanical Rigid Rotor

~~$$-\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) \right] + \frac{1}{2I} \hat{L}^2 \psi = E\psi$$~~

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

The Rigid Rotor model is used to characterize the rotation of diatomic molecules (and is easily extended to linear polyatomic molecules)

It is assumed that: (1) The distance between atoms ( $r$ ) does not change.

(2) The potential energy is independent of angle [i.e.  $V(\theta, \phi) = \text{Const.} = 0$ ]

Therefore:  $\frac{1}{2I} \hat{L}^2 \psi = E\psi$

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

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### Solution of the Rigid Rotor Schrödinger Equation

We will only outline the method of solution.

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

This equation can be separated into two equations, one containing only  $\theta$  and the second containing only  $\phi$ .

Assume:  $\Psi(\theta, \phi) = \Theta(\theta) \cdot \Phi(\phi)$

↓ Algebra + Separation of Variables

$$\left[ -\frac{\hbar^2}{2I} \frac{1}{\Theta} \sin(\theta) \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial \Theta}{\partial \theta} \right) - E \sin^2(\theta) \right] = C$$

and  $-\frac{\hbar^2}{2I} \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = -C$

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$$\left[ -\frac{\hbar^2}{2I} \frac{1}{\Theta} \sin(\theta) \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial \Theta}{\partial \theta} \right) - E \sin^2(\theta) \right] = C$$

and 
$$-\frac{\hbar^2}{2I} \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \varphi^2} = -C$$

Solution of the  $\Phi$  equation is rather simple.

However, solution of the  $\Theta$  equation most definitely is NOT.

Therefore, we will just present the results for the quantum numbers, energies and wavefunctions that result when the two equations are solved and boundary conditions are applied.

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### The Rigid Rotor Quantum Numbers and Energies

The Quantum Numbers:  $\ell = 0, 1, 2, 3, \dots$

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

Note that because this is a two dimensional problem, there are two quantum numbers.

The Energy:  $E_\ell = \frac{\hbar^2}{2I} \ell(\ell+1)$       $g_\ell = 2\ell+1$

Note that the energy is a function of  $\ell$  only. However, there are  $2\ell + 1$  values of  $m$  for each value of  $\ell$ . Therefore, the degeneracy of the energy level is  $2\ell + 1$

Remember that for a classical Rigid Rotor:  $E = \frac{L^2}{2I}$

Comparing the expressions, one finds for the angular momentum, that:  $L = \sqrt{\ell(\ell+1)} \cdot \hbar$

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### An Alternate Notation

When using the Rigid Rotor molecule to describe the rotational spectra of linear molecules, it is common to denote the two quantum numbers as  $J$  and  $M$ , rather than  $\ell$  and  $m$ .

With this notation, one has:

The Quantum Numbers:  $J = 0, 1, 2, 3, \dots$

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

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

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### The Wavefunctions

When both the  $\Theta$  and  $\Phi$  differential equations have been solved, the resulting wavefunctions are of the form:

$$\psi(\theta, \varphi) = \Theta(\theta) \cdot \Phi(\varphi) = N_{\ell, m} e^{im\varphi} P_{\ell}^{|m|}(\theta)$$

The  $P_{\ell}^{|m|}(\theta)$  are known as the associated Legendre polynomials.

The first few of these functions are given by:

$$\begin{aligned} P_0^0 &= 1 & P_2^0 &= \frac{1}{2}(3\cos^2(\theta) - 1) \\ P_1^0 &= \cos(\theta) & P_2^1 &= \frac{1}{2}\sin(\theta)\cos(\theta) \\ P_1^1 &= \sin(\theta) & P_2^2 &= \sin^2(\theta) \end{aligned}$$

We will defer any visualization of these wavefunctions until we get to Chapter 6: The Hydrogen Atom

$$P_{\ell}^{|m|}(\theta)$$

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## Spherical Harmonics

The product functions of  $\theta$  and  $\phi$  are called "Spherical Harmonics",  $Y_{lm}(\theta, \phi)$ :

$$Y_{lm}(\theta, \phi) = \Theta(\theta) \cdot \Phi(\phi) = N_{lm} e^{im\phi} P_l^{|m|}(\theta)$$

They are the angular solutions to the Schrödinger Equation for any spherically symmetric potential; i.e. one in which  $V(r)$  is independent of the angles  $\theta$  and  $\phi$ .

Some examples are:

$$Y_{11}(\theta, \phi) = N_{11} e^{i\phi} P_1^1(\theta) = N_{11} e^{i\phi} \sin(\theta) \quad Y_{22}(\theta, \phi) = N_{22} e^{2i\phi} P_2^2(\theta) = N_{22} e^{2i\phi} \sin^2(\theta)$$

$$Y_{10}(\theta, \phi) = N_{10} e^{0i\phi} P_1^0(\theta) = N_{10} \cos(\theta) \quad Y_{21}(\theta, \phi) = N_{21} e^{i\phi} P_2^1(\theta) = N_{21} e^{i\phi} \sin(\theta) \cos(\theta)$$

$$Y_{1-1}(\theta, \phi) = N_{1-1} e^{-i\phi} P_1^1(\theta) = N_{1-1} e^{-i\phi} \sin(\theta) \quad Y_{20}(\theta, \phi) = N_{20} e^{0i\phi} P_2^0(\theta) = N_{20} (3 \cos^2(\theta) - 1)$$

$$Y_{2-1}(\theta, \phi) = N_{2-1} e^{-i\phi} P_2^1(\theta) = N_{2-1} e^{-i\phi} \sin(\theta) \cos(\theta)$$

$$Y_{2-2}(\theta, \phi) = N_{2-2} e^{-2i\phi} P_2^2(\theta) = N_{2-2} e^{-2i\phi} \sin^2(\theta)$$

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One of the Spherical Harmonics is:  $Y(\theta, \phi) = Ne^{-i\phi} \sin(\theta)$

Show that this function is an eigenfunction of the Rigid Rotor Hamiltonian and determine the eigenvalue (i.e. the energy).

$$HY = \frac{1}{2I} \hat{L}^2 Y = EY \quad \text{or} \quad -\frac{\hbar^2}{2I} \left[ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2 Y}{\partial \phi^2} \right] = EY$$

$$\frac{\partial Y}{\partial \theta} = Ne^{-i\phi} \cos(\theta)$$

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

$$= Ne^{-i\phi} \left[ 1 - 2\sin^2(\theta) \right]$$

$$\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial Y}{\partial \theta} \right) = \frac{Ne^{-i\phi}}{\sin(\theta)} - 2Ne^{-i\phi} \sin(\theta)$$

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

$$Y(\theta, \varphi) = Ne^{-i\varphi} \sin(\theta)$$

$$\frac{\partial Y}{\partial \varphi} = -iNe^{-i\varphi} \sin(\theta)$$

$$\frac{\partial^2 Y}{\partial \varphi^2} = -Ne^{-i\varphi} \sin(\theta)$$

$$\boxed{\frac{1}{\sin^2(\theta)} \frac{\partial^2 Y}{\partial \varphi^2} = \frac{-Ne^{-i\varphi}}{\sin(\theta)}}$$

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

$$= -\frac{\hbar^2}{2I} \left[ \frac{Ne^{-i\varphi}}{\sin(\theta)} - 2Ne^{-i\varphi} \sin(\theta) - \frac{Ne^{-i\varphi}}{\sin(\theta)} \right]$$

$$= +\frac{\hbar^2}{2I} 2 [Ne^{-i\varphi} \sin(\theta)] = +\frac{\hbar^2}{2I} \cdot 2Y$$

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$$HY = +\frac{\hbar^2}{2I} \cdot 2Y$$

$$\text{Therefore: } E = 2 \frac{\hbar^2}{2I}$$

$$\text{Note: Comparing to: } E_\ell = \frac{\hbar^2}{2I} \ell(\ell+1)$$

$$\text{we see that: } \ell = 1$$

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- Rotational Spectroscopy of Linear Molecules

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## Angular Momentum and the Rigid Rotor

The Spherical Harmonics,  $Y_{lm}(\theta, \phi)$ , are eigenfunctions of the angular momentum operators:

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

The eigenvalues are given by the equations:

$$\hat{L}^2 Y_{lm}(\theta, \phi) = \ell(\ell+1)\hbar^2 Y_{lm}(\theta, \phi)$$
$$\hat{L}_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi)$$

Note: It is straightforward to show that  $\hat{L}^2$  and  $\hat{L}_z$  commute; i.e.  $[\hat{L}^2, \hat{L}_z] = 0$ .

Because of this, it is possible to find simultaneous eigenfunctions of the two operators which are, as shown above, the Spherical Harmonics.

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As discussed earlier, the restrictions on the quantum numbers are given by:

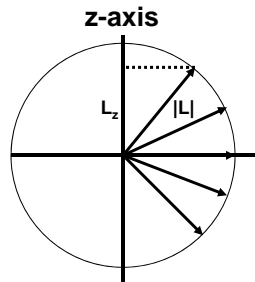
$$\ell = 0, 1, 2, 3, \dots$$

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

Therefore, both the magnitude,  $|L|$ , and the z-component,  $L_z$ , of the angular momentum are quantized to the values:

$$|L| = \sqrt{\ell(\ell+1)\hbar} \quad \ell = 0, 1, 2, 3, \dots$$

$$L_z = m\hbar \quad m = 0, \pm 1, \pm 2, \dots, \pm \ell$$



If a magnetic field is applied, its direction defines the z-axis.

If there is no magnetic field, the z-direction is arbitrary.

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One of the Spherical Harmonics is:  $Y(\theta, \varphi) = Ne^{-i\varphi} \sin(\theta)$

Show that this function is an eigenfunction of  $\hat{L}^2$  and  $\hat{L}_z$  and determine the eigenvalues.

$$\hat{L}^2 = -\hbar^2 \left\{ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2} \right\} \quad \hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$$

We've actually done basically the first part a short while ago.

$$\text{Remember: } HY = \frac{1}{2I} \hat{L}^2 Y = EY = 2 \frac{\hbar^2}{2I} Y$$

$$\text{Therefore: } \hat{L}^2 Y = 2\hbar^2 Y = \ell(\ell+1)\hbar^2 Y \longrightarrow \ell = 1$$

$$\hat{L}_z Y = \frac{\hbar}{i} \frac{\partial Y}{\partial \varphi} = \frac{\hbar}{i} (-i) Ne^{-i\varphi} \sin(\theta) = -\hbar Y = m\hbar Y$$

$$\downarrow$$

$$m = -1$$

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## Preview: The Hydrogen Atom Schrödinger Equation

3D Schrödinger Equation in Spherical Polar Coordinates

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

The Hydrogen atom is an example of a “centrosymmetric” system, which is one in which the potential energy is a function of only  $r$ ,  $V(r)$ .

In this case, the Schrödinger equation can be rearranged to:

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

**Radial Part**

**Angular Part**

Note that the Angular part of the Hydrogen atom Schrödinger equation is the same as Rigid Rotor equation, for which the radial part vanishes.

Therefore, the angular parts of the Hydrogen atom wavefunctions are the same as those of the Rigid Rotor

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## Rotational Spectroscopy of Linear Molecules

### Energy Levels

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

Equivalent Form:  $E_J = \frac{h^2}{8\pi^2 I} J(J+1)$

$$E_J = hc \frac{h}{8\pi^2 Ic} J(J+1)$$

$$E_J = hc\tilde{B}J(J+1)$$

Rotational Constant ( $\text{cm}^{-1}$ ):  $\tilde{B} = \frac{h}{8\pi^2 Ic}$

J	$E_J$	$g_J$
0	0	$g_0=1$
1	$2\tilde{B}$	$g_1=3$
2	$6\tilde{B}$	$g_2=5$
3	$12\tilde{B}$	$g_3=7$
4	$20\tilde{B}$	$g_4=9$

Note: You must use c in cm/s, even when using MKS units.

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## Diatomic versus Linear Polyatomic Molecules

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

In general, for linear molecules, the moment of inertia is given by:

$$I = \sum_{i=1}^N m_i r_i^2$$

N is the number of atoms

$m_i$  is the mass of the atom i

$r_i$  is the distance of atom i from the Center of Mass.

If N=2 (diatomic molecule) the moment of inertia reduces to:

$$I = \mu r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{where } r \text{ is the interatomic distance}$$

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### Selection Rules

#### Absorption (Microwave) Spectroscopy

For a rotating molecule to absorb light, it must have a permanent dipole moment, which changes direction with respect to the electric vector of the light as the molecule rotates.

$$\Delta J = \pm 1 \quad (\Delta J = +1 \text{ for absorption})$$

e.g. HCl, OH (radical) and O=C=S will absorb microwave radiation.

O=C=O and H-C≡C-H will **not** absorb microwave radiation.

#### Rotational Raman Spectroscopy

For a rotating molecule to have a Rotation Raman spectrum, the polarizability with respect to the electric field direction must change as the molecule rotates. All linear molecules have Rotational Raman spectra.

$$\Delta J = \pm 2$$

$\Delta J = +2$ : Excitation (Stokes line)

$\Delta J = -2$ : Deexcitation (Anti-Stokes line)

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### Intensity of Rotational Transitions

The intensity of a transition in the absorption (microwave) or Rotational Raman spectrum is proportional to the number of molecules in the initial state ( $J''$ ); i.e.  $\text{Int.} \propto N_{J''}$

Boltzmann Distribution:  $N_{J''} \propto g_{J''} e^{-\frac{E_{J''}}{kT}}$

$$N_{J''} \propto (2J'' + 1) e^{-\frac{hc\tilde{B}J''(J''+1)}{kT}}$$

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## Rotational Spectra

### Absorption (Microwave) Spectra

$$J'' \rightarrow J'$$

$$\Delta E = E_{J'} - E_{J''}$$

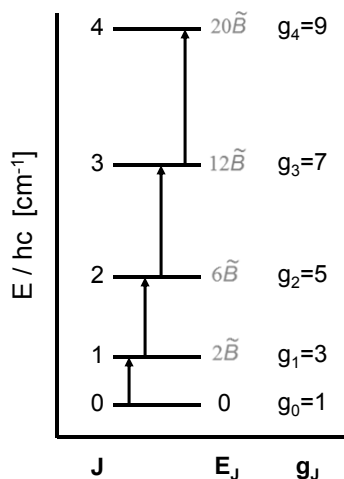
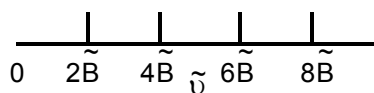
$$\Delta E = hc\tilde{B}J'(J'+1) - hc\tilde{B}J''(J''+1)$$

$$J' = J'' + 1$$

$$\Delta E = hc\tilde{B}(J''+1)(J''+2) - hc\tilde{B}J''(J''+1)$$

$$\Delta E = hc\tilde{B}(2J''+2) \quad J'' = 0, 1, 2, 3, \dots$$

$$\tilde{\nu} = \frac{\Delta E}{hc} = \tilde{B}(2J''+2) \quad J'' = 0, 1, 2, 3, \dots$$



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### Rotational Raman Spectra

$$J'' \rightarrow J'$$

$$\Delta E = E_{J'} - E_{J''}$$

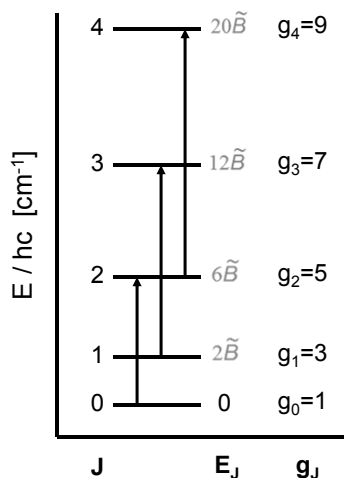
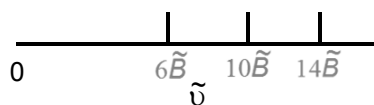
$$\Delta E = hc\tilde{B}J'(J'+1) - hc\tilde{B}J''(J''+1)$$

$$J' = J'' + 2$$

$$\Delta E = hc\tilde{B}(J''+2)(J''+3) - hc\tilde{B}J''(J''+1)$$

$$\Delta E = hc\tilde{B}(4J''+6) \quad J'' = 0, 1, 2, 3, \dots$$

$$\tilde{\nu} = \frac{\Delta E}{hc} = \tilde{B}(4J''+6) \quad J'' = 0, 1, 2, 3, \dots$$



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The HCl bond length is 0.127 nm.

Calculate the spacing between lines in the rotational microwave

absorption spectrum of H-<sup>35</sup>Cl, in cm<sup>-1</sup>.

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{(1 \text{ amu})(35 \text{ amu})}{1 \text{ amu} + 35 \text{ amu}} = 0.972 \text{ amu}$$

$$\mu = 0.972 \text{ amu} \cdot \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 1.61 \times 10^{-27} \text{ kg}$$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = 3.00 \times 10^8 \text{ m/s}$$

$$c = 3.00 \times 10^{10} \text{ cm/s}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$I = \mu r^2 = (1.61 \times 10^{-27} \text{ kg})(0.127 \times 10^{-9} \text{ m})^2 = 2.60 \times 10^{-47} \text{ kg}\cdot\text{m}^2$$

$$\tilde{B} = \frac{h}{8\pi^2 I c} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{8(3.14)^2 (2.60 \times 10^{-47} \text{ kg}\cdot\text{m}^2)(3.00 \times 10^{10} \text{ cm/s})} = 10.78 \text{ cm}^{-1} \approx 10.8 \text{ cm}^{-1}$$

As discussed above, microwave absorption lines occur at  $2\tilde{B}$ ,  $4\tilde{B}$ ,  $6\tilde{B}$ , ...

Therefore, the spacing is  $2\tilde{B}$

$$\text{Spacing} = 2\tilde{B} = 2 \times 10.8 = 21.6 \text{ cm}^{-1}$$

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Calculate the ratio of intensities (at 25°C):  $\frac{I_{3 \rightarrow 4}}{I_{1 \rightarrow 2}}$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

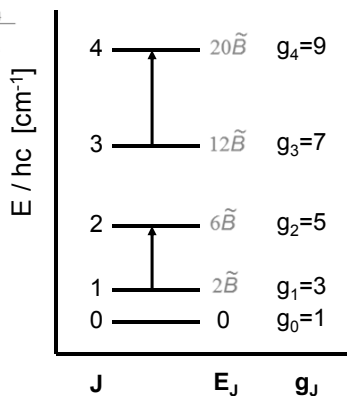
$$c = 3.00 \times 10^{10} \text{ cm/s}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

$$\tilde{B} = 10.8 \text{ cm}^{-1}$$

$$\frac{I_{3 \rightarrow 4}}{I_{1 \rightarrow 2}} = \frac{N_3}{N_1} = \frac{g_3 e^{-E_3/kT}}{g_1 e^{-E_1/kT}} = \frac{7 e^{-12hc\tilde{B}/kT}}{3 e^{-2hc\tilde{B}/kT}} = \frac{7}{3} e^{-10hc\tilde{B}/kT}$$

$$\frac{I_{3 \rightarrow 4}}{I_{1 \rightarrow 2}} = \frac{7}{3} e^{-0.52} \approx 1.4$$



$$\frac{10hc\tilde{B}}{kT} = \frac{10(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^{10} \text{ cm/s})(10.8 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})} = 0.52$$

**Note:** This is equivalent to asking for the ratio of intensities of fourth line to the second line in the rotational microwave spectrum.

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The first 3 Stokes lines in the rotational Raman spectrum of  $^{12}\text{C}^{16}\text{O}_2$  are found at  $2.34\text{ cm}^{-1}$ ,  $3.90\text{ cm}^{-1}$  and  $5.46\text{ cm}^{-1}$ .

Calculate the C=O bond length in  $\text{CO}_2$ , in nm.

$h = 6.63 \times 10^{-34}\text{ J}\cdot\text{s}$   
 $c = 3.00 \times 10^{10}\text{ cm/s}$   
 $k = 1.38 \times 10^{-23}\text{ J/K}$   
 $1\text{ amu} = 1.66 \times 10^{-27}\text{ kg}$

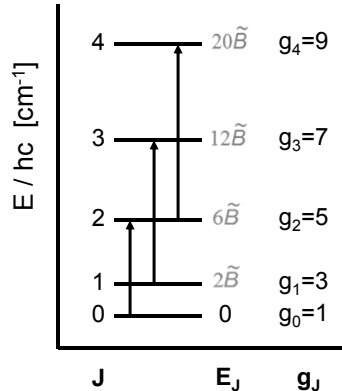
$$2.34\text{ cm}^{-1} = 6\tilde{B} - 0 = 6\tilde{B} \longrightarrow \tilde{B} = 0.39\text{ cm}^{-1}$$

$$3.90\text{ cm}^{-1} = 12\tilde{B} - 2\tilde{B} = 10\tilde{B} \longrightarrow \tilde{B} = 0.39\text{ cm}^{-1}$$

$$5.46\text{ cm}^{-1} = 20\tilde{B} - 6\tilde{B} = 14\tilde{B} \longrightarrow \tilde{B} = 0.39\text{ cm}^{-1}$$

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

$$I = \frac{6.63 \times 10^{-34}\text{ kg}\cdot\text{m}^2/\text{s}}{8(3.14)^2 (0.39\text{ cm}^{-1})(3.00 \times 10^{10}\text{ cm/s})} = 7.18 \times 10^{-46}\text{ kg}\cdot\text{m}^2$$



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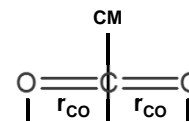
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Calculate the C=O bond length in  $\text{CO}_2$ , in nm.

$h = 6.63 \times 10^{-34}\text{ J}\cdot\text{s}$   
 $c = 3.00 \times 10^{10}\text{ cm/s}$   
 $k = 1.38 \times 10^{-23}\text{ J/K}$   
 $1\text{ amu} = 1.66 \times 10^{-27}\text{ kg}$

$$I = 7.18 \times 10^{-46}\text{ kg}\cdot\text{m}^2$$

$$I = \sum_i m_i r_i^2 = m_o r_{\text{CO}}^2 + m_c (0)^2 + m_o r_{\text{CO}}^2 = 2m_o r_{\text{CO}}^2$$



$$r_{\text{CO}} = \sqrt{\frac{I}{2m_o}}$$

$$m_o = 16\text{ amu} \cdot 1.66 \times 10^{-27}\text{ kg/amu} = 2.66 \times 10^{-26}\text{ kg}$$

$$r_{\text{CO}} = \sqrt{\frac{7.18 \times 10^{-46}\text{ kg}\cdot\text{m}^2}{2 \cdot 2.66 \times 10^{-26}\text{ kg}}} = 1.16 \times 10^{-10}\text{ m} = 0.116\text{ nm} = 1.16\text{ Angstroms}$$

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Calculate the initial state (i.e.  $J''$ ) corresponding to the most intense line in the rotational Raman spectrum of  $^{12}\text{C}^{16}\text{O}_2$  at  $25^\circ\text{C}$ .

Hint: Rather than calculating the intensity of individual transitions, assume that the intensity is a continuous function of  $J''$  and use basic calculus.

$$\begin{aligned} h &= 6.63 \times 10^{-34} \text{ J}\cdot\text{s} \\ c &= 3.00 \times 10^{10} \text{ cm/s} \\ k &= 1.38 \times 10^{-23} \text{ J/K} \\ \tilde{B} &= 0.39 \text{ cm}^{-1} \end{aligned}$$

$$I_{J'' \rightarrow J''+2} \propto N_{J''} \propto (2J''+1) e^{-\frac{J''(J''+1)hc\tilde{B}}{kT}} \propto (2J''+1) e^{-\alpha(J''^2+J'')} \quad \alpha = \frac{hc\tilde{B}}{kT}$$

$N_{J''}$  is at a maximum for  $dN_{J''}/dJ''=0$ .

$$\frac{dN_{J''}}{dJ''} = 0 = (2J''+1) \frac{d}{dJ''} \left( e^{-\alpha(J''^2+J'')} \right) + \left( e^{-\alpha(J''^2+J'')} \right) \frac{d}{dJ''} (2J''+1)$$

$$0 = (2J''+1) \left( e^{-\alpha(J''^2+J'')} \right) (-\alpha)(2J''+1) + \left( e^{-\alpha(J''^2+J'')} \right) \cdot 2$$

$$0 = \left( e^{-\alpha(J''^2+J'')} \right) \left[ -\alpha(2J''+1)^2 + 2 \right]$$

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$$0 = \left( e^{-\alpha(J''^2+J'')} \right) \left[ -\alpha(2J''+1)^2 + 2 \right] \quad \alpha = \frac{hc\tilde{B}}{kT}$$

$$\begin{aligned} h &= 6.63 \times 10^{-34} \text{ J}\cdot\text{s} \\ c &= 3.00 \times 10^{10} \text{ cm/s} \\ k &= 1.38 \times 10^{-23} \text{ J/K} \\ \tilde{B} &= 0.39 \text{ cm}^{-1} \end{aligned}$$

$$\text{Therefore: } \left[ -\alpha(2J''+1)^2 + 2 \right] = 0 \quad \longrightarrow \quad 2J''+1 = \sqrt{\frac{2}{\alpha}}$$

$$2J''+1 = \sqrt{\frac{2(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^{10} \text{ cm/s})(0.39 \text{ cm}^{-1})}} = \sqrt{1060} = 32.6$$

$$J'' = \frac{32.6-1}{2} = 15.8 \approx 16$$

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Consider the linear molecule, H-C≡C-Cl.

There are two major isotopes of chlorine,  $^{35}\text{Cl}$  (~75%) and  $^{37}\text{Cl}$  (~25%). Therefore, one will observe two series of lines in the rotational spectrum, resulting from transitions of H-C≡C- $^{35}\text{Cl}$  and H-C≡C- $^{37}\text{Cl}$ .

Can the structure of H-C≡C-Cl be determined from these two series?

No. There are 3 bond distances to be determined, but only 2 moments of inertia.

What additional information could be used to determine all three bond distances?

The spectrum of D-C≡C $^{35}\text{Cl}$  and D-C≡C $^{37}\text{Cl}$

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### Non-Linear Molecules

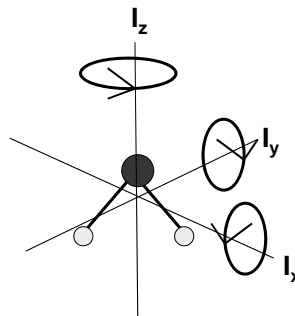
Non-linear molecules will generally have up to 3 independent moments of inertia,  $I_x$ ,  $I_y$ ,  $I_z$ .

The Hamiltonian will depend upon the angular momentum about each of the 3 axes.

$$H = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z}$$

The Schrödinger Equation for non-linear rotors is more difficult to solve, but can be done using somewhat more advanced methods, and the rotational spectra can be analyzed to determine the structure (sometimes requiring isotopic species).

For small to moderate sized molecules (I would guess 10-15 atoms), rotational microwave spectroscopy is the most accurate method for determining molecular structure.



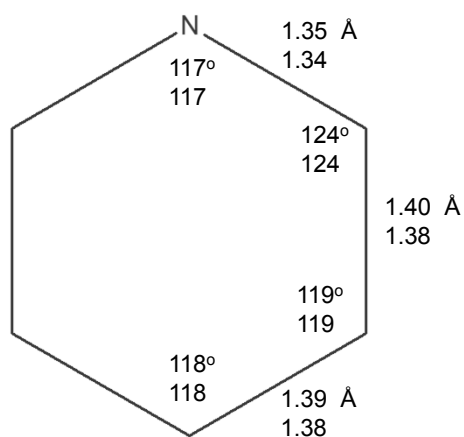
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## Outline (Cont'd.)

- Application of QM to Molecular Structure: Pyridine
- Statistical Thermodynamics: Rotational contributions to the thermodynamic properties of gases

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## The Structure of Pyridine



Calculated: MP2/6-31G(d) – 4 minutes

Experimental: Crystal Structure

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### The Command File for the Structure of Pyridine

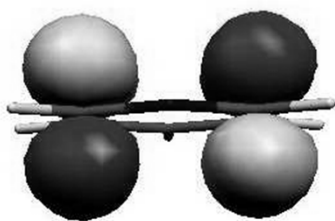
```
#MP2/6-31G(d) opt freq
```

```
Pyridine
```

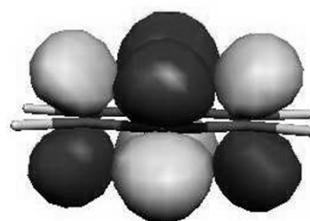
```
0 1
C -1.236603 1.240189 0.000458
C -1.236603 -0.179794 0.000458
C -0.006866 -0.889786 0.000458
C 1.222870 -0.179794 0.000458
C 1.053696 1.280197 0.000458
N -0.104187 1.989731 0.000458
H 1.980804 1.872116 -0.008194
H 2.205566 -0.673935 -0.009628
H -0.006866 -1.989731 -0.009064
H -2.189194 -0.729767 -0.009064
H -2.205551 1.760818 0.009628
```

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### The Frontier Orbitals of Pyridine



**HOMO**



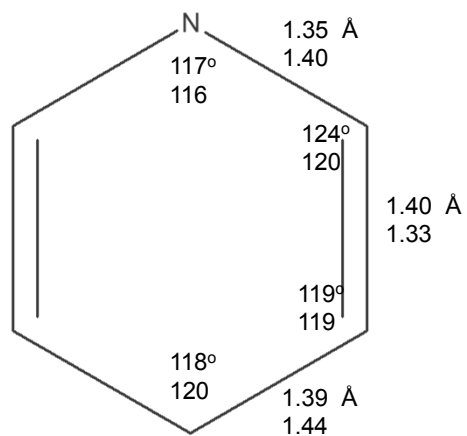
**LUMO**

Calculated: HF/6-31G(d) – <3 minutes

Experimental: Huh???

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### The Structure of Excited State Pyridine



$S_0$ : Calculated: MP2/6-31G(d) – 4 minutes

$T_1$ : Calculated: MP2/6-31G(d) – 11 minutes

Experimental: None

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### Outline (Cont'd.)

- Application of QM to Molecular Structure: Pyridine
- **Statistical Thermodynamics: Rotational contributions to the thermodynamic properties of gases**

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## Statistical Thermodynamics: Rotational Contributions to Thermodynamic Properties of Gases

### A Blast from the Past

$$U = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} \qquad C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N}$$

$$H = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} + kT \left( \frac{\partial \ln Q}{\partial \ln V} \right)_{T,N} \qquad C_P = \left( \frac{\partial H}{\partial T} \right)_{P,N}$$

$$S = k \ln Q + \frac{U}{T}$$

$$A = U - TS = -kT \ln(Q)$$

$$G = H - TS = -kT \ln Q + kT \left( \frac{\partial \ln Q}{\partial \ln V} \right)_{T,N}$$

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### The Rotational Partition Function: Linear Molecules

The Energy:  $\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \qquad g_J = 2J + 1$

The Partition Function:  $q^{\text{rot}} = \sum_{J=0}^{\infty} g_J e^{-\frac{\varepsilon_J}{kT}} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{J(J+1)\hbar^2/2I}{kT}}$

$$q^{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1) \frac{\Theta_R}{T}} \qquad \Theta_R = \frac{\hbar^2}{2Ik}$$

It can be shown that for most molecules at medium to high temperatures:

$$\Delta\varepsilon = \varepsilon_{J+1} - \varepsilon_J \ll kT$$

Thus, the exponent (and hence successive terms in the summation) change very slowly.

Therefore, the summation in  $q^{\text{rot}}$  can be replaced by an integral.

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$$q^{rot} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\frac{\Theta_R}{T}} \quad \Theta_R = \frac{h^2}{8\pi^2 I k}$$

$$q^{rot} = \int_0^{\infty} (2J+1) e^{-J(J+1)\frac{\Theta_R}{T}} dJ$$

This integral can be solved analytically by a simple substitution.

$$u = J(J+1)\frac{\Theta_R}{T} \longrightarrow du = (2J+1)\frac{\Theta_R}{T} dJ$$

$$\text{Therefore: } q^{rot} = \frac{T}{\Theta_R} \int_0^{\infty} e^{-J(J+1)\frac{\Theta_R}{T}} \left[ (2J+1)\frac{\Theta_R}{T} dJ \right] = \frac{T}{\Theta_R} \int_0^{\infty} e^{-u} du$$

$$q^{rot} = \frac{T}{\Theta_R} (-1) [e^{-u}]_0^{\infty} = \frac{T}{\Theta_R} (-1) [0 - 1]$$

$$q^{rot} = \frac{T}{\Theta_R}$$

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$$q^{rot} = \frac{T}{\Theta_R}$$

### A Correction

For homonuclear diatomic molecules, one must account for the fact that rotation by 180° interchanges two equivalent nuclei.

Since the new orientation is indistinguishable from the original one, one must divide by 2 so that indistinguishable orientations are counted once.

For heteronuclear diatomic molecules, rotation by 180° produces a distinguishable orientation. No correction is necessary.

$$q^{rot} = \frac{T}{\sigma \Theta_R} \quad \sigma \text{ is the "symmetry number"}$$

Homonuclear Diatomic Molecule:  $\sigma = 2$

Heteronuclear Diatomic Molecule:  $\sigma = 1$

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### How good is the approximate formula?

$$\text{Exact: } q^{\text{rot}} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1) \frac{\Theta_R}{T}} \quad \text{Approx: } q^{\text{rot}} = \frac{T}{\sigma \Theta_R}$$

$$\text{H}_2: I = 4.61 \times 10^{-48} \text{ kg}\cdot\text{m}^2 \rightarrow \Theta_R = 87.5 \text{ K}$$

$$\text{O}_2: I = 1.92 \times 10^{-46} \text{ kg}\cdot\text{m}^2 \rightarrow \Theta_R = 2.08 \text{ K}$$

Compd.	T	$q^{\text{rot}}(\text{ex})$	$q^{\text{rot}}(\text{app})$	Error
O <sub>2</sub>	298 K	71.8	71.7	0.2%
H <sub>2</sub>	298	1.88	1.70	10%
H <sub>2</sub>	100	0.77	0.57	26%
H <sub>2</sub>	50	0.55	0.29	47%

For molecules like H<sub>2</sub>, HCl, ..., with small moments of inertia, the integral approximation gives poor results, particularly at lower temperatures.

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### The Total Partition Function for N Molecules ( $Q^{\text{rot}}$ )

$$q^{\text{rot}} = \frac{T}{\sigma \Theta_R} \quad \text{and} \quad Q^{\text{rot}} = (q^{\text{rot}})^N$$



$$Q^{\text{rot}} = \left( \frac{T}{\sigma \Theta_R} \right)^N \quad \text{where} \quad \Theta_R = \frac{h^2}{8\pi^2 I k}$$

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### Internal Energy

$$U^{rot} = kT^2 \left( \frac{\partial \ln Q^{rot}}{\partial T} \right)_{V,N} \quad Q^{rot} = \left( \frac{T}{\sigma \Theta_R} \right)^N$$

$$\ln Q^{rot} = \ln \left( \frac{T}{\sigma \Theta_R} \right)^N = N \ln \left( \frac{T}{\sigma \Theta_R} \right) = N [\ln T - \ln(\sigma \Theta_R)]$$

$$\left( \frac{\partial \ln Q^{rot}}{\partial T} \right)_{V,N} = N \frac{d}{dT} [\ln T - \ln(\sigma \Theta_R)] = \frac{N}{T}$$

Therefore:  $U^{rot} = kT^2 \cdot \frac{N}{T} = NkT = nN_A kT$

$$\boxed{U^{rot} = nRT \quad \text{or} \quad \bar{U}^{rot} = RT}$$

This illustrates Equipartition of Rotational Internal Energy.  
 [(1/2)RT per rotation].

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### Enthalpy

$Q^{rot}$  independent of V

$$H^{rot} = kT^2 \left( \frac{\partial \ln Q^{rot}}{\partial T} \right)_{V,N} + kT \left( \frac{\partial \ln Q^{rot}}{\partial \ln V} \right)_{T,N} = U^{rot} + \cancel{kT \left( \frac{\partial \ln Q^{rot}}{\partial \ln V} \right)_{T,N}}$$

$$\boxed{\bar{H}^{rot} = \bar{U}^{rot} = RT}$$

### Heat Capacities

$$\bar{C}_V^{rot} = \frac{C_V^{rot}}{n} = \left( \frac{\partial \bar{U}^{rot}}{\partial T} \right)_{V,N} = R$$

$$\bar{C}_P^{rot} = \frac{C_P^{rot}}{n} = \left( \frac{\partial \bar{H}^{rot}}{\partial T} \right)_{P,N} = R$$

Remember that these results are for Diatomic and Linear Polyatomic Molecules.

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$$\bar{C}_P^{tran} = \frac{5}{2}R \quad \bar{C}_P^{rot} = R$$

Chap. 3

$$\bar{C}_P^{tran} + \bar{C}_P^{rot} = \frac{7}{2}R = \frac{7}{2}(8.314 J / mol \cdot K) = 29.10 J / mol \cdot K$$

Experimental Heat Capacities at 298.15 K

Compd.	C <sub>p</sub> (exp)
H <sub>2</sub>	29.10 J/mol-K
O <sub>2</sub>	29.36
I <sub>2</sub>	36.88

We can see that vibrational (and/or electronic) contributions to C<sub>p</sub> become more important in the heavier diatomic molecules.

We'll discuss this further in Chap. 5

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## Entropy

$$S^{rot} = k \ln Q^{rot} + \frac{U^{rot}}{T} \quad Q^{rot} = \left( \frac{T}{\sigma \Theta_R} \right)^N$$

$$S^{rot} = k \ln \left( \frac{T}{\sigma \Theta_R} \right)^N + \frac{U^{rot}}{T} = Nk \ln \left( \frac{T}{\sigma \Theta_R} \right) + \frac{RT}{T} = nR \ln \left( \frac{T}{\sigma \Theta_R} \right) + R$$

O<sub>2</sub>: r = 1.202 Å = 1.202x10<sup>-10</sup> m (from QM - QCISD/6-311G\*)

$$\mu = \frac{m_O \cdot m_O}{m_O + m_O} = \frac{m_O}{2} = 8.00 \text{ amu} \times 1.66 \times 10^{-27} \text{ kg / amu} = 1.328 \times 10^{-26} \text{ kg}$$

$$I = \mu r^2 = (1.328 \times 10^{-26} \text{ kg}) \cdot (1.202 \times 10^{-10} \text{ m})^2 = 1.92 \times 10^{-46} \text{ kg} \cdot \text{m}^2$$

σ = 2 (Homonuclear Diatomic)

$$\Theta_R = \frac{h^2}{8\pi^2 I k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8 \cdot (3.1416)^2 \cdot 1.92 \times 10^{-46} \text{ kg} \cdot \text{m}^2 \cdot 1.38 \times 10^{-23} \text{ J / K}} = 2.08 \text{ K}$$

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### O<sub>2</sub> (Cont'd)

$$S^{rot} = nR \ln \left( \frac{T}{\sigma \Theta_R} \right) + R \quad \Theta_R = 2.08 K$$

For one mole of O<sub>2</sub> at 298 K:

$$S^{rot} = 1(8.31 J / mol \cdot K) \ln \left( \frac{298 K}{(2)(2.08 K)} \right) + 8.31 J / mol \cdot K$$

$$= 43.8 J / mol \cdot K$$

$$S^{tran} = 151.9 J/mol \cdot K \text{ (from Chap. 3)}$$

$$S^{tran} + S^{rot} = 195.7 J/mol \cdot K$$

$$O_2: S_{mol}(exp) = 205.1 J/mol \cdot K \text{ at } 298.15 K$$

Thus, there is a small, but finite, vibrational (and/or) electronic contribution to the entropy at room temperature.

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### Output from G-98 geom. opt. and frequency calculation on O<sub>2</sub> (at 298 K)

QCISD/6-311G(d)

	E (Thermal) KCAL/MOL	CV CAL/MOL-K	S CAL/MOL-K
TOTAL	3.750	5.023	48.972
ELECTRONIC	0.000	0.000	2.183
TRANSLATIONAL	0.889	2.981	36.321
<b>ROTATIONAL</b>	<b>0.592</b>	<b>1.987</b>	<b>10.459</b>
VIBRATIONAL	2.269	0.055	0.008
	Q	LOG10(Q)	LN(Q)
TOTAL BOT	0.330741D+08	7.519488	17.314260
TOTAL V=0	0.151654D+10	9.180853	21.139696
VIB (BOT)	0.218193D-01	-1.661159	-3.824960
VIB (V=0)	0.100048D+01	0.000207	0.000476
ELECTRONIC	0.300000D+01	0.477121	1.098612
TRANSLATIONAL	0.711178D+07	6.851978	15.777263
ROTATIONAL	0.710472D+02	1.851547	4.263345

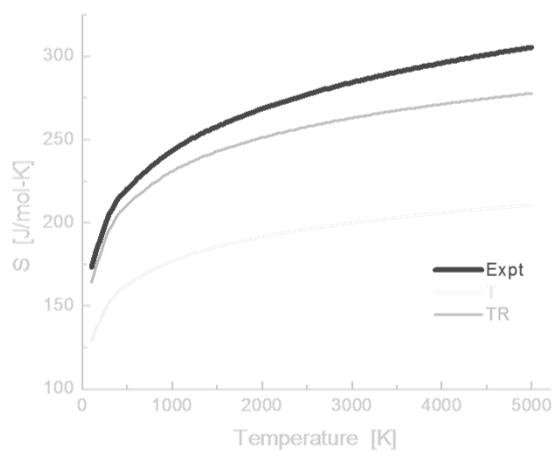
$$\bar{U}^{rot} = \bar{U}_{therm}^{rot} = 0.592 kcal / mol = 2.48 kJ / mol = RT (298 K)$$

$$\bar{C}_V^{rot} = 1.987 cal / mol \cdot K = 8.314 J / mol \cdot K = R$$

$$\bar{S}^{rot} = 10.459 cal / mol \cdot K = 43.8 J / mol \cdot K \text{ (same as our result)}$$

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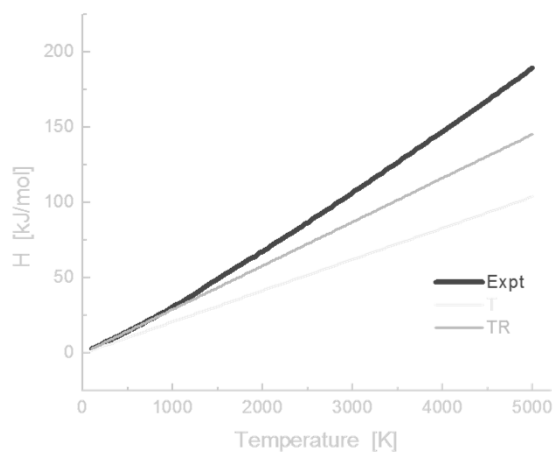
### Translational + Rotational Contributions to O<sub>2</sub> Entropy



Note that the other (vibration and/or electronic) contributions to S are even greater at higher temperature.

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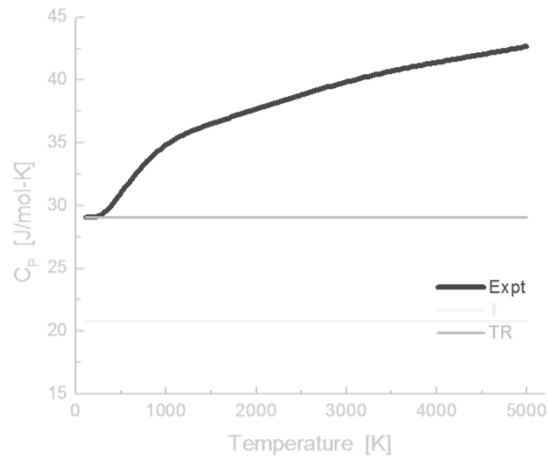
### Translational + Rotational Contributions to O<sub>2</sub> Enthalpy



There are also significant additional contributions to the Enthalpy.

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### Translational + Rotational Contributions to O<sub>2</sub> Heat Capacity



Note that the additional (vibration and/or electronic) contributions to  $C_p$  are not important at room temperature, but very significant at elevated temperatures.

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### Helmholtz and Gibbs Energies

$$A^{rot} = -kT \ln Q^{rot}$$

$$G^{rot} = -kT \ln Q^{rot} + kT \left( \frac{\partial \ln Q^{rot}}{\partial \ln V} \right)_{T,N}$$

~~$Q^{rot}$  independent of  $V$~~

$$A^{rot} = G^{rot} = -kT \ln \left( \frac{T}{\sigma \Theta_R} \right)^N = -NkT \ln \left( \frac{T}{\sigma \Theta_R} \right) = -nRT \ln \left( \frac{T}{\sigma \Theta_R} \right)$$

For O<sub>2</sub> at 298 K:  $\Theta_R = 2.08$  K

$$A^{rot} = G^{rot} = -RT \ln \left( \frac{T}{\sigma \Theta_R} \right) = -(8.314 \text{ J/mol} \cdot \text{K}) \cdot \ln \left( \frac{298 \text{ K}}{2 \cdot 2.08 \text{ K}} \right) = -35.5 \text{ J/mol} \cdot \text{K}$$

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## Non-Linear Polyatomic Molecules

It can be shown that:  $q^{rot} = \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_a \Theta_b \Theta_c} \right)^{1/2}$

$$\Theta_a = \frac{h^2}{8\pi^2 I_a k}$$

$$\Theta_b = \frac{h^2}{8\pi^2 I_b k}$$

$$\Theta_c = \frac{h^2}{8\pi^2 I_c k}$$

The symmetry number is defined as the "number of pure rotational elements (including the identity) in the molecule's point group:

NO<sub>2</sub>:  $\sigma = 2$

NH<sub>3</sub>:  $\sigma = 3$

CH<sub>4</sub>:  $\sigma = 12$

I will always give you the value of  $\sigma$  for non-linear polyatomic molecules.

One can simply use the expression for  $q^{rot}$  above in the same way as for linear molecules to determine the rotational contributions to the thermodynamic properties of non-linear polyatomic molecules (as illustrated in one of the homework problems).

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