

## **COURSE DESCRIPTION**

**TITLE:** Spectroscopy

**Course Code:**

**CREDITS:** 2

**TYPE-WHEN:** Monsoon 2020-21

**FACULTY NAME:** Dr. Marimuthu Krishnan

**PRE-REQUISITE:** None for UG3-CND students. Non-CND students interested in taking this course as an elective must have secured at least B- grade in Science-I.

**OBJECTIVE:** The objective of this course is to understand the basic principles and applications of different spectroscopic techniques commonly used in natural sciences.

### **COURSE TOPICS:**

- **Introduction:** Classical mechanical description of spectroscopy, quantum mechanics and energy quantization, energy-level diagram, energy spectrum: electronic states, vibrational states, rotational states, excitation and relaxation, absorption and emission of electromagnetic waves by materials
- **Atomic Spectra:** Spectral series of hydrogen and alkali atoms, selection rules, L-S coupling, many-electron atoms, isotope shift, hyperfine splitting of spectral lines
- **Molecular Spectra:** Electronic spectra of diatomic and polyatomic molecules, Born-Oppenheimer approximation, Franck-Condon principle, absorption and emission spectra, fluorescence and phosphorescence, Jablonsky diagram, effect of solvation of electronic spectra, rotational spectrum of a diatomic molecule using a rigid rotator model, energy levels and spectrum of a non-rigid diatomic molecule, effect of isotopic substitution on rotational spectra, vibrational spectrum of a diatomic molecule using the harmonic and anharmonic oscillator models. vibrational-rotational coupling in a diatomic molecule, molecular spectra of chain molecules
- **Raman and Infrared Spectroscopy:** Classical and quantum theory of Raman effect, normal vibrations of CO<sub>2</sub> and H<sub>2</sub>O molecules, vibrational and rotational Raman spectra, basic concept of infrared spectroscopy, interpretation of Raman and IR

- spectra, identification of Raman-active and/or IR-active modes based on symmetry arguments
- Introduction to Nuclear Magnetic Resonance (NMR), and Electron Spin Resonance (ESR) spectroscopy

**PREFERRED TEXTBOOKS:**

1. Physical Chemistry - P. W. Atkins
2. Fundamentals of Molecular Spectroscopy - C. N. Banwell
3. Spectra of Diatomic Molecules - Herzberg
4. Atomic Spectra & Atomic Structure - Gerhard Herzberg
5. Molecular Spectroscopy - G. M. Barrow
6. Molecules and Radiation: An Introduction to Modern Molecular Spectroscopy - J. I. Steinfeld
7. Physical Chemistry - A Molecular Approach - D. A. McQuarrie and J. D. Simon

**GRADING:**

Quiz - 25%

Final exam – 40%

Assignments – 35%

**OUTCOME:** The students will be able to apply these concepts and techniques to their research problems.

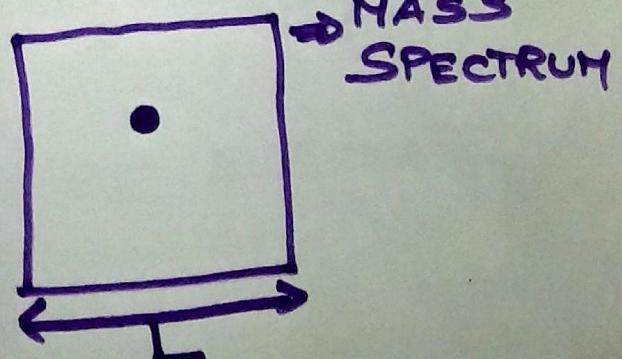
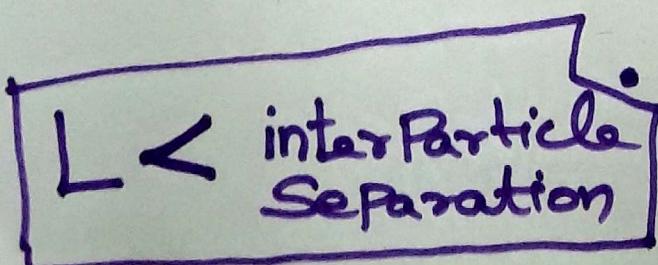
# SPECTROSCOPY

## KNOWN FACTS :-

- ① ATOMS ARE MADE OF ELECTRONS, PROTONS, NEUTRONS
- ② NUCLEUS + ELECTRONS  
    ↓                  ↓  
    CENTER            (ORBITS)  
• REVOLVE AROUND  
• CLOUD OF ELECTRONS  
• ORBITALS
- ③ ATOMS CAN BOND WITH OTHER ATOMS  $\rightarrow$  MOLECULES  
• DIFFERENT TYPES OF BONDS  
 $\text{---} \times \text{---} \times \text{---}$

## PROBLEM-I :-

- CONSIDER  $N$  IDENTICAL PARTICLES (ATOMS)
- ~~DILUTE~~ DILUTE THE SYSTEM



## → POSSIBLE QUESTIONS

- ① WHAT IS THE MASS OF THE ATOM?
- ② IS THE ATOM STATIC OR DYNAMIC?

STATIC ÷

- CLASSICALLY POSSIBLE
- QUANTUM MECHANICS?
- WHERE IS IT LOCATED?  
(ELECTRON MICROSCOPY;  
CRYSTAL STRUCTURE;  
X-RAY DIFFRACTION;)

DYNAMIC ÷

→ HOW FAST DOES IT MOVE?

(FROM TEMPERATURE;

$\langle \text{KINETIC ENERGY} \rangle \Rightarrow \text{TEMPERATURE}$ :

$t_1 \rightarrow \text{TIME RESOLUTION}$

$t_1$

$t_2$

SPEED CAN BE ESTIMATED!

③ HOW ARE THE ELECTRONS  
DISTRIBUTED IN THE ATOM?

三

WILL IT CHANGE WITH  
THE POSITION OF THE ATOM?

④ WHAT IS THE SIZE OF THE ATOM?

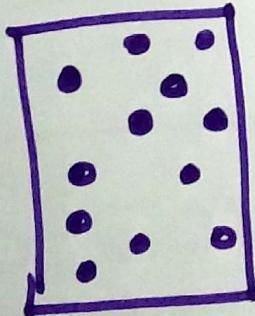
## SIZE OF THE NUCLEUS?

```

graph LR
    SIZE[SIZE] --> CLASSICAL[CLASSICAL]
    SIZE --> QM[QM]
    CLASSICAL -- "(van der WALL RADIUS)" --> CLASSICAL

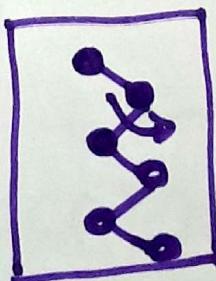
```

# INCREASE COMPLEXITY?



# N PARTICLE SYSTEM

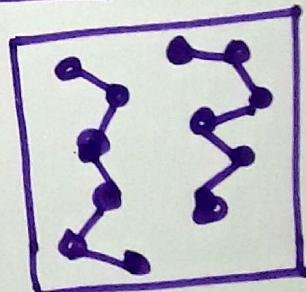
## ⇒ ATOMIC INTERACTIONS



# SINGLE MOLECULE ⇒ BONDS

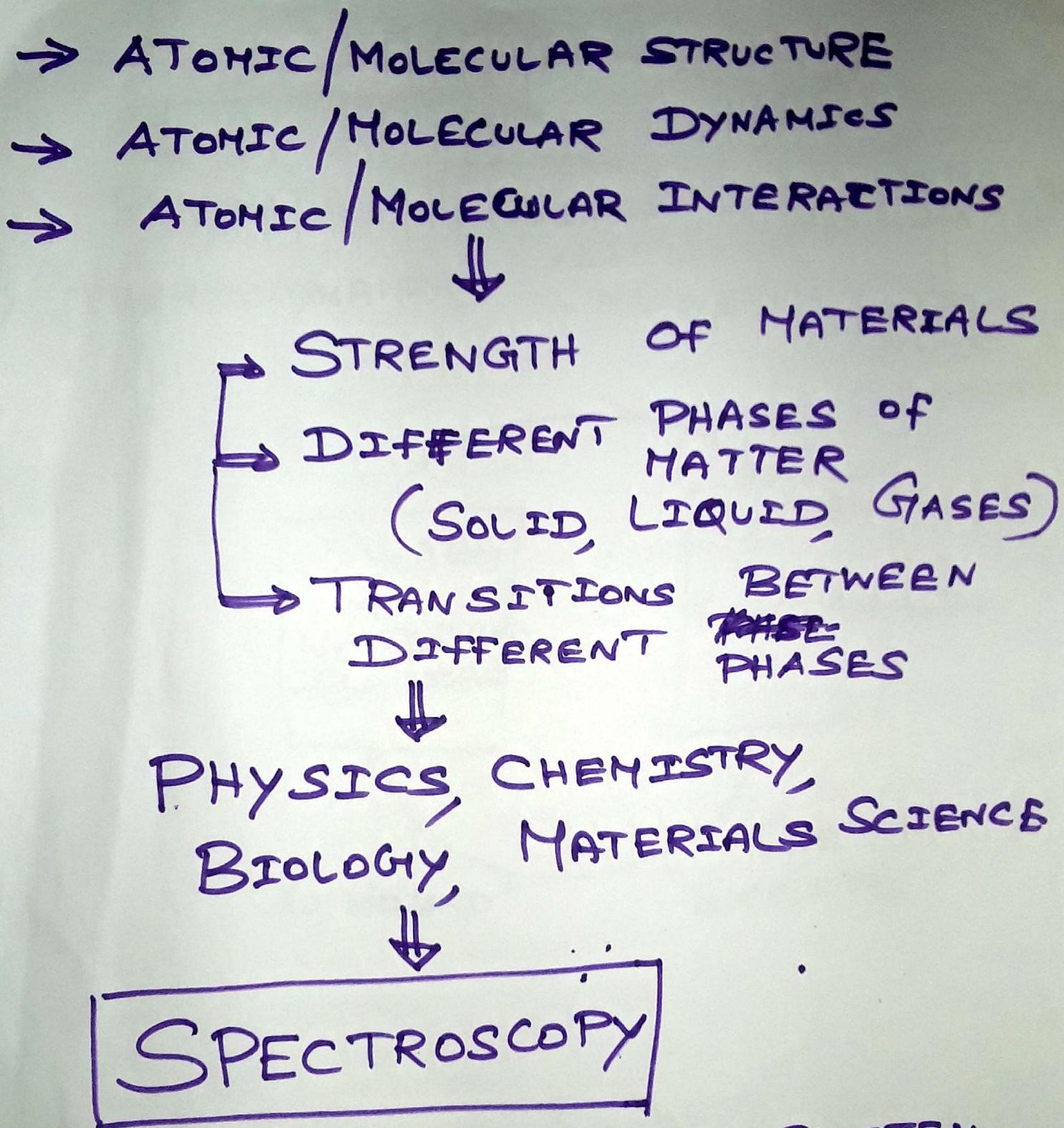
## → STRENGTHS

## RELATIVE MOTION OF ATOMS



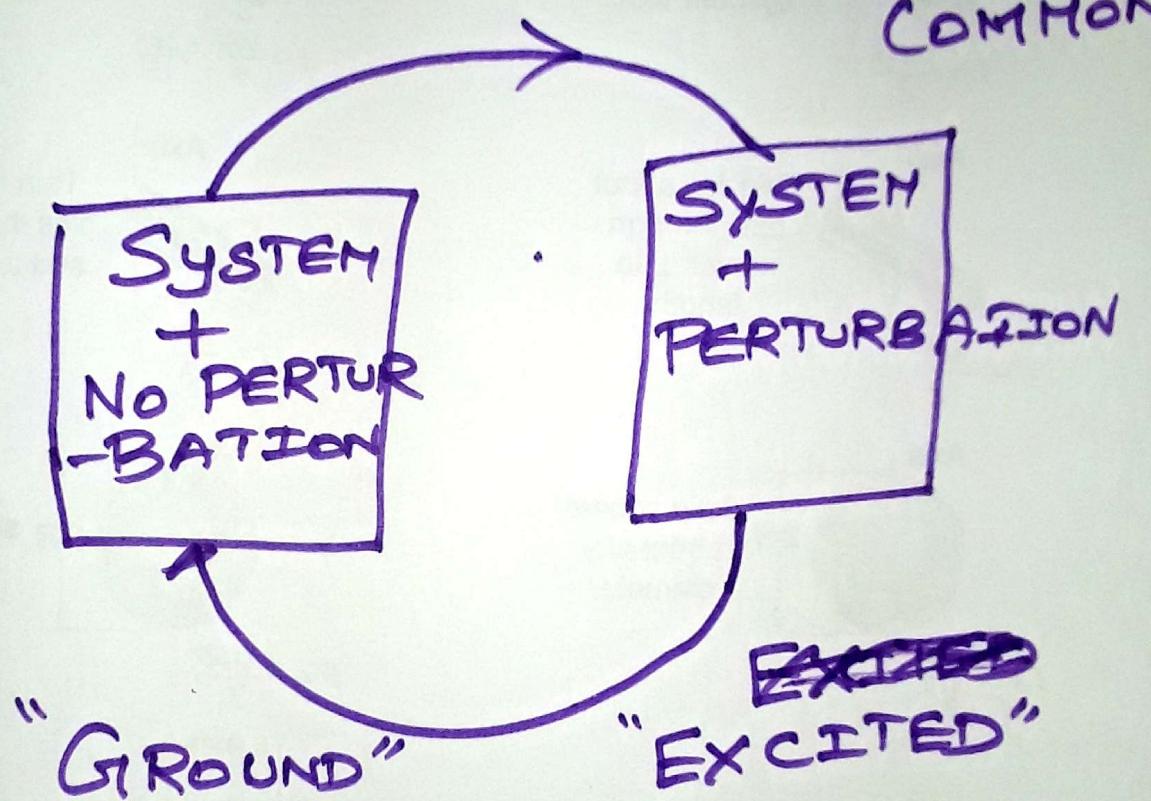
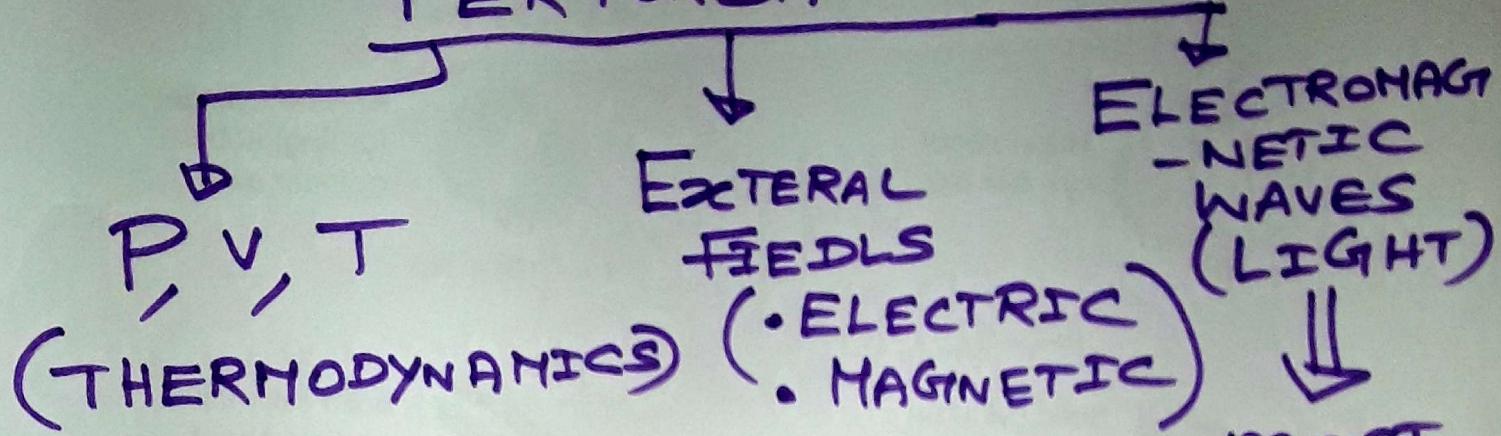
N MOLECULES  
⇒ MOLECULAR  
INTERACTION - NS

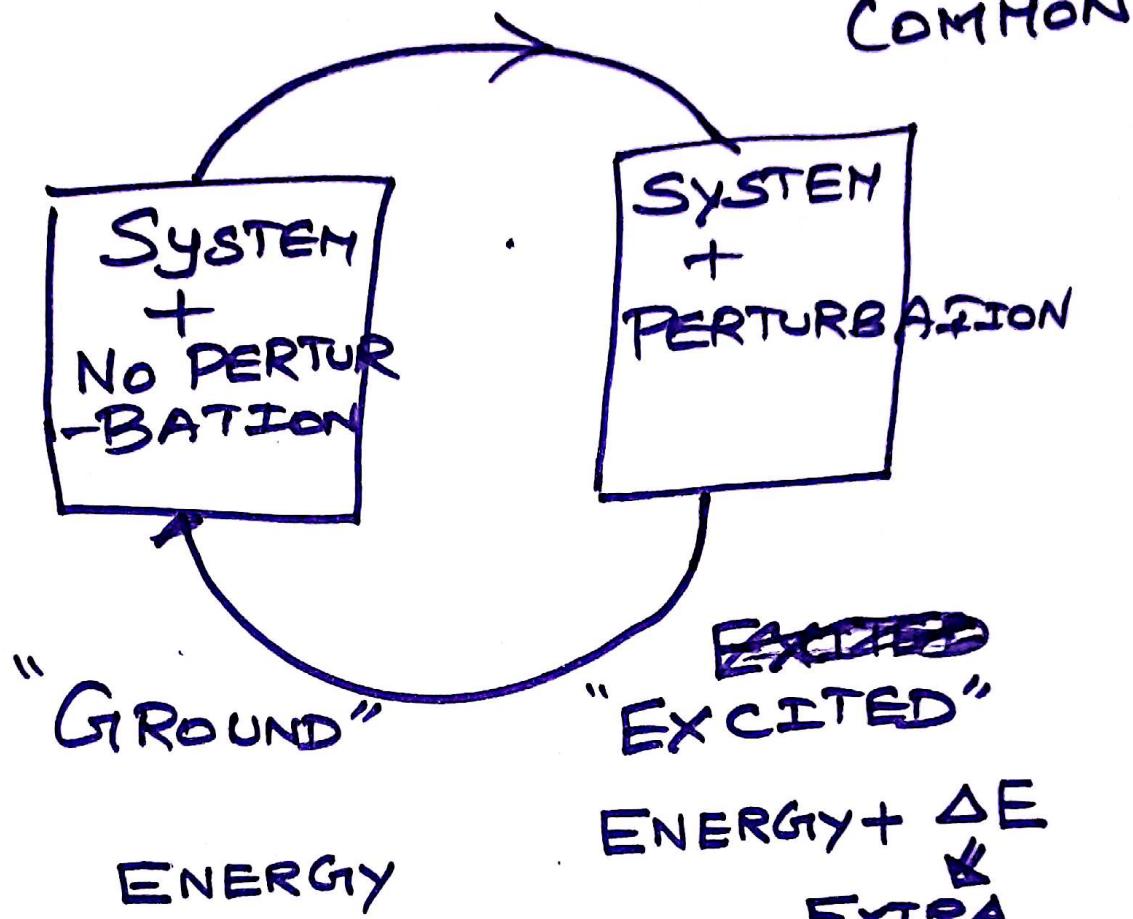
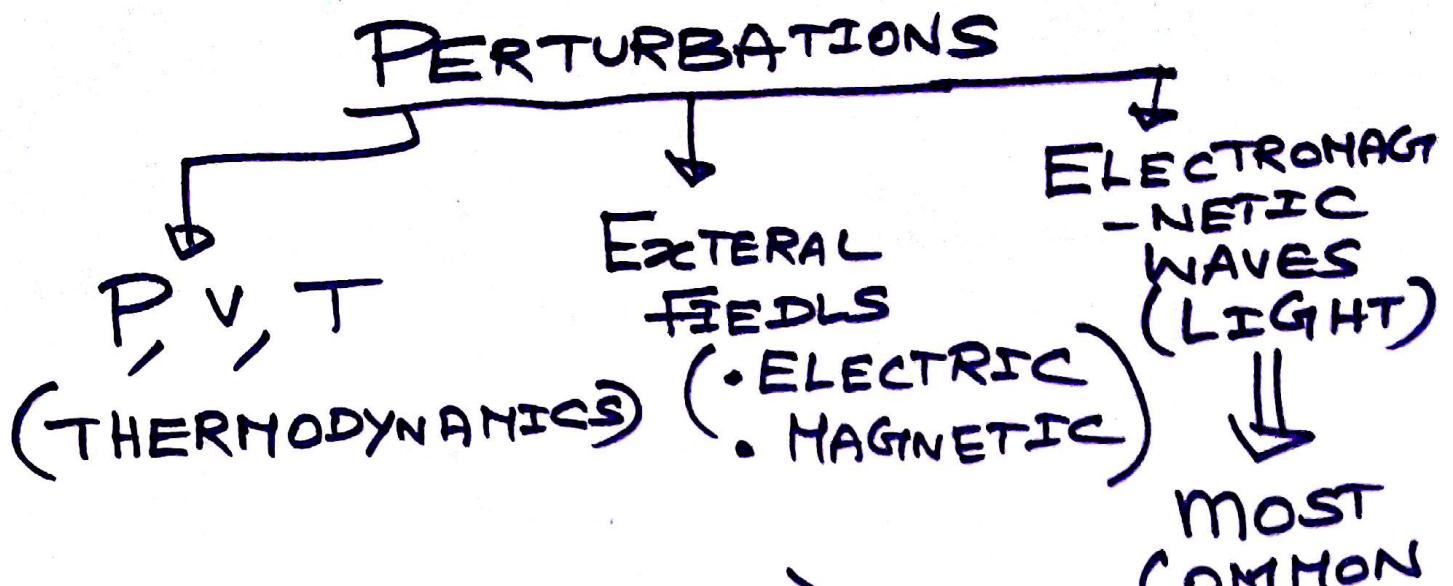
- BOND VIBRATION
- BEND VIBRATION
- TORSIONAL MOTION
- TRANSLATION
- ROTATION



TO UNDERSTAND THE SYSTEM,  
YOU MUST DISTURB / PERTURB  
IT ! ↗ STUDY HOW THE  
SYSTEM RESPONDS TO  
THE PERTURBATION !

# PERTURBATIONS





HAMILTONIAN:  $H_0$

SMALL PERTURBATION

$$\Delta H \rightarrow 0$$

LARGE PERTURBATION

$$\Delta H \gg 0$$

$$H_0 + \Delta H$$



$$H_0 + H_p$$



$$H_p = \Delta H$$

PERTURBATIVE PART OF THE HAMILTONIAN

# MANY-BODY SYSTEMS

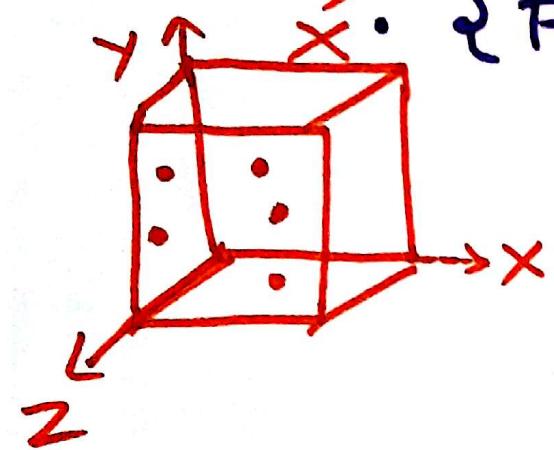
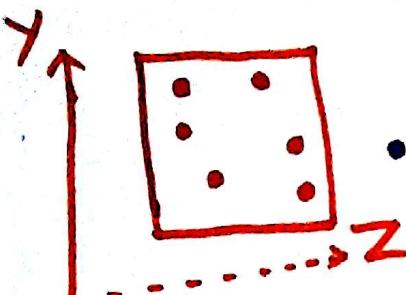
## → THERMODYNAMICS

- $P, V, T, n$ ; HERE  $n \Rightarrow$  NUMBER OF MOLES
- FIXED  $n$ ;  $P = f(V, T)$   
    ↓  
    EQUATION OF STATE
- ALL PROPERTIES CAN BE EXPRESSED AS FUNCTIONS OF  $P, V, T, n$
- THE CONCEPTS OF ATOMS, MOLECULES, ELECTRONS ETC... ARE NOT NEEDED
- DIFFERENT ENERGY FUNCTIONS:
  - HEAT
  - WORK
  - ENTHALPY
  - INTERNAL ENERGY
  - ENTROPY
  - HELMHOLTZ FREE ENERGY
  - GIBBS FREE ENERGY
  - CHEMICAL POTENTIAL

# MANY-BODY SYSTEMS

## ⇒ CLASSICAL STATISTICAL MECHANICS:

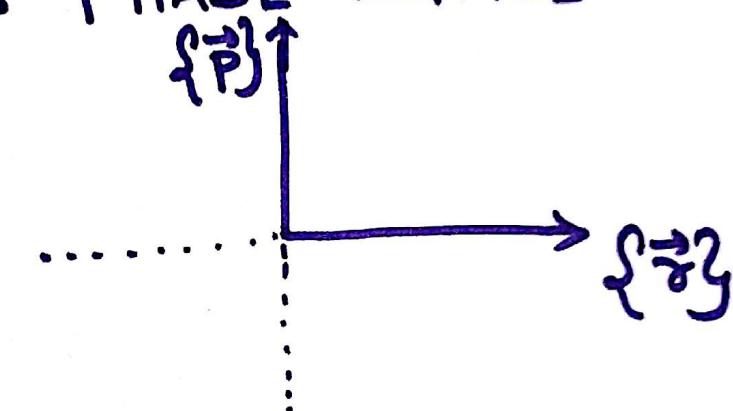
- SYSTEM CONSISTS OF N PARTICLES



- $\{\vec{r}\} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  SET OF POSITIONS

- $\{\vec{p}\} = (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$  SET OF MOMENTA

- PHASE SPACE



- DEFINE HAMILTONIAN

TOTAL ENERGY OF THE SYSTEM →

$$H(\{\vec{r}\}, \{\vec{p}\}) = U(\{\vec{r}\}) + K(\{\vec{p}\})$$

POTENTIAL ENERGY

KINETIC ENERGY

INTERATOMIC  
INTERACTIONS

Thermal Energy



- $U(\{\vec{r}\})$  DEFINES THE POTENTIAL ENERGY SURFACE

- SOLVE HAMILTON'S EQUATIONS OF MOTION TO UNDERSTAND HOW  $\{\vec{r}\}$  AND  $\{\vec{P}\}$  VARY WITH TIME.  
(DYNAMICS)

**FORCE ON ATOM  $i$**

$$\frac{d\vec{P}_i}{dt} = -\frac{\partial H}{\partial \vec{r}_i} = -\frac{\partial U}{\partial \vec{r}_i}$$

HERE  $\frac{\partial}{\partial \vec{r}_i} = \left( \frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right)$

GRADIENT

$$\frac{d\vec{r}_i}{dt} = \frac{\partial H}{\partial \vec{P}_i}; \quad ; \quad ;$$

- INITIAL CONDITIONS:

AT TIME  $t=0$ :

$$\{\vec{r}(t=0)\}, \quad \{\vec{P}(t=0)\}$$

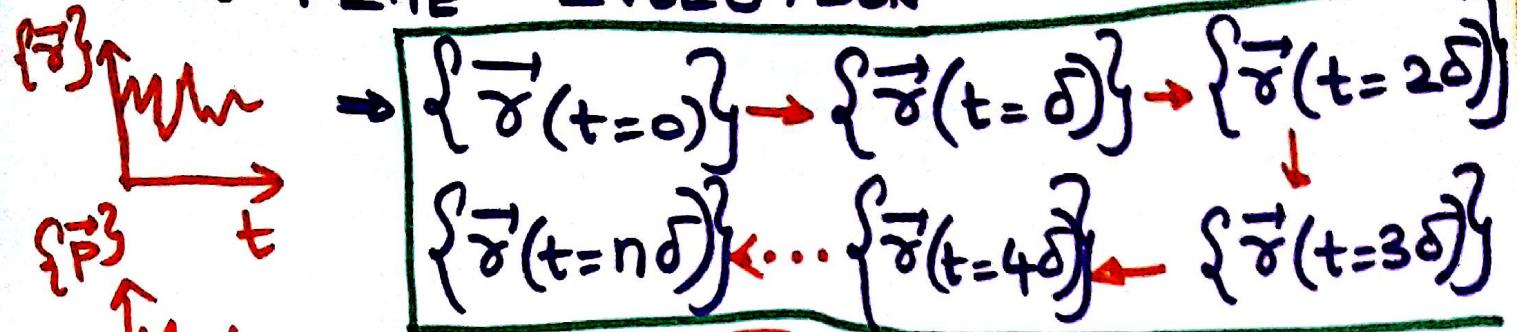
↓

X-RAY DIFFRACTION      NMR      RANDOM

↓

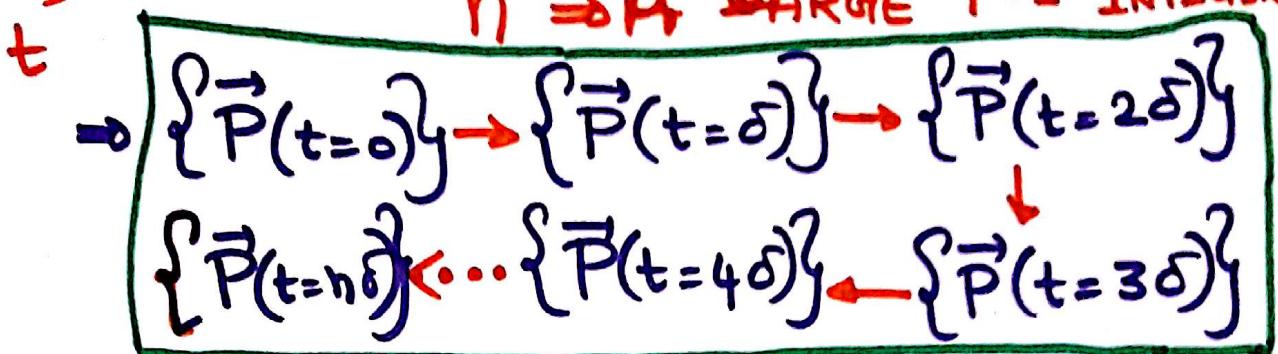
MAXWELL-BOLTZMANN DISTRIBUTION

## • TIME EVOLUTION

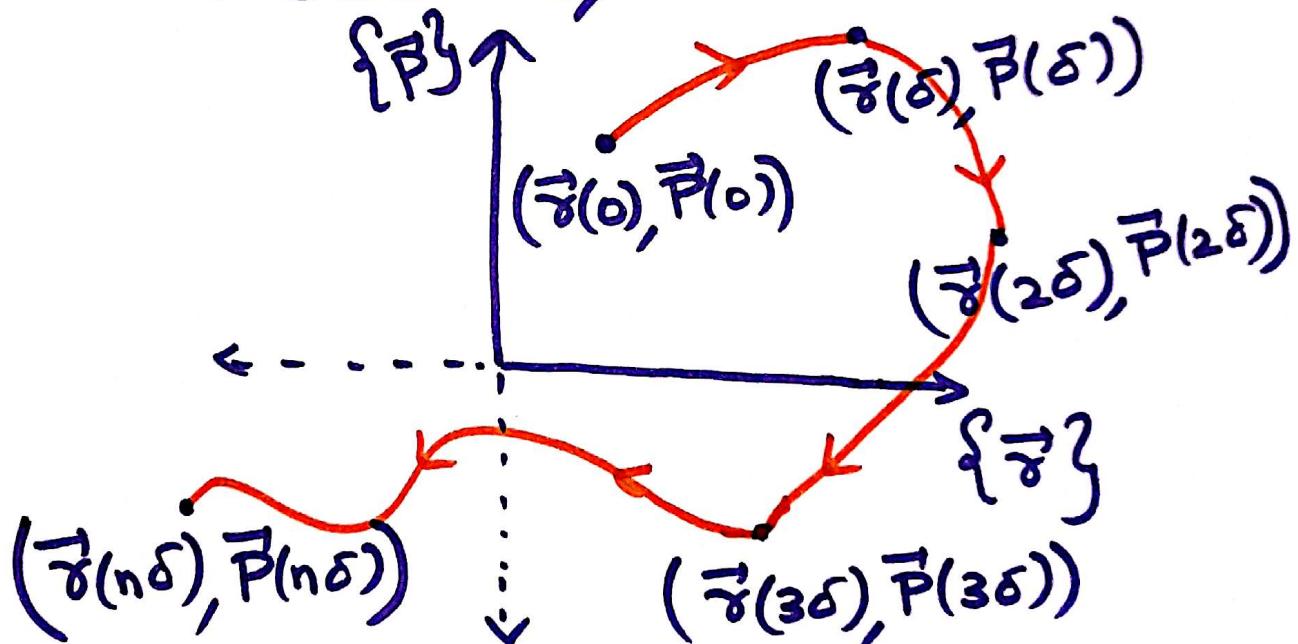


HERE  $\delta \Rightarrow$  TIME STEP

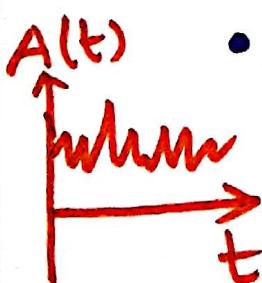
$n \Rightarrow$  A LARGE +VE INTEGER



## • TRAJECTORY ON PHASE SPACE



- ALL PROPERTIES CAN BE WRITTEN AS FUNCTIONS OF  $\{\vec{r}\}$  AND  $\{\vec{P}\}$



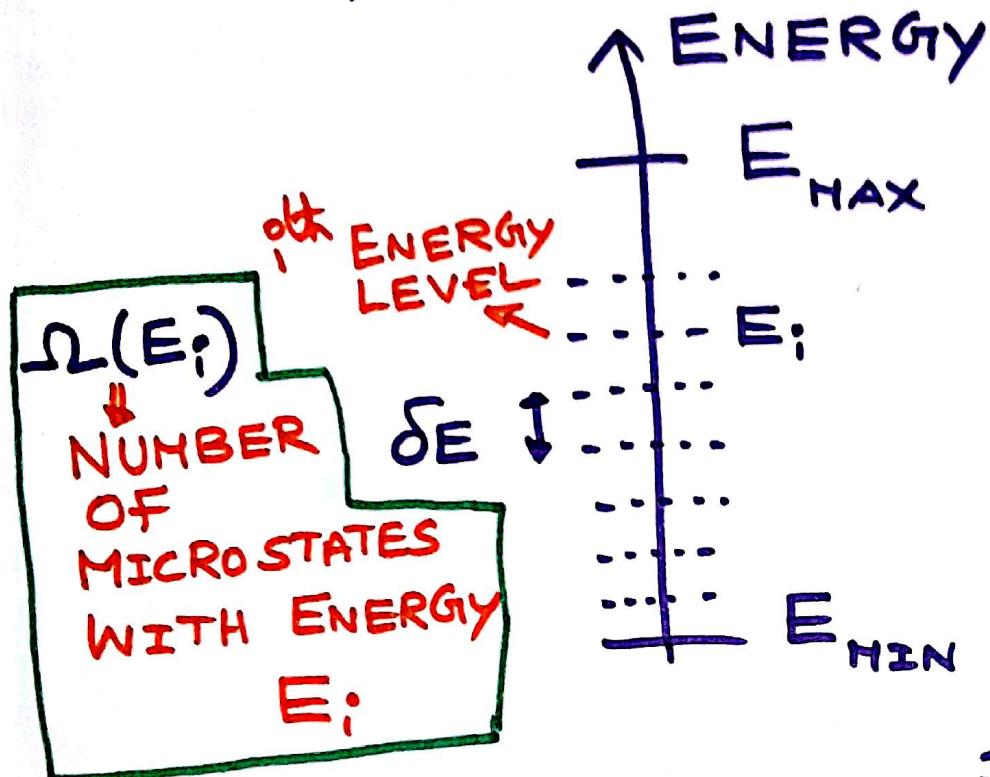
$$A(t) = A(\{\vec{r}(t)\}, \{\vec{P}(t)\})$$

TIME EVOLUTION of "A" CAN BE STUDIED

# ENERGY-LEVEL DIAGRAM

$E_{\text{MIN}} \rightarrow \text{LOWEST ENERGY OF THE SYSTEM}$

$E_{\text{MAX}} \rightarrow \text{HIGHEST ENERGY}$



$\delta E \rightarrow 0; \delta E = 0$   
CONTINUOUS ENERGY SPECTRUM (CLASSICAL SYSTEMS)

$\delta E \neq 0$   
DISCRETE ENERGY LEVELS  
(QUANTUM SYSTEMS)

WHAT IF SOME EXTRA ENERGY  $E_p$  IS ADDED TO THE SYSTEM ?

$E_{\text{MAX}} - E_{\text{MIN}}$  CAN VARY

SYSTEM CAN TRANSIT BETWEEN DIFFERENT ENERGY LEVELS

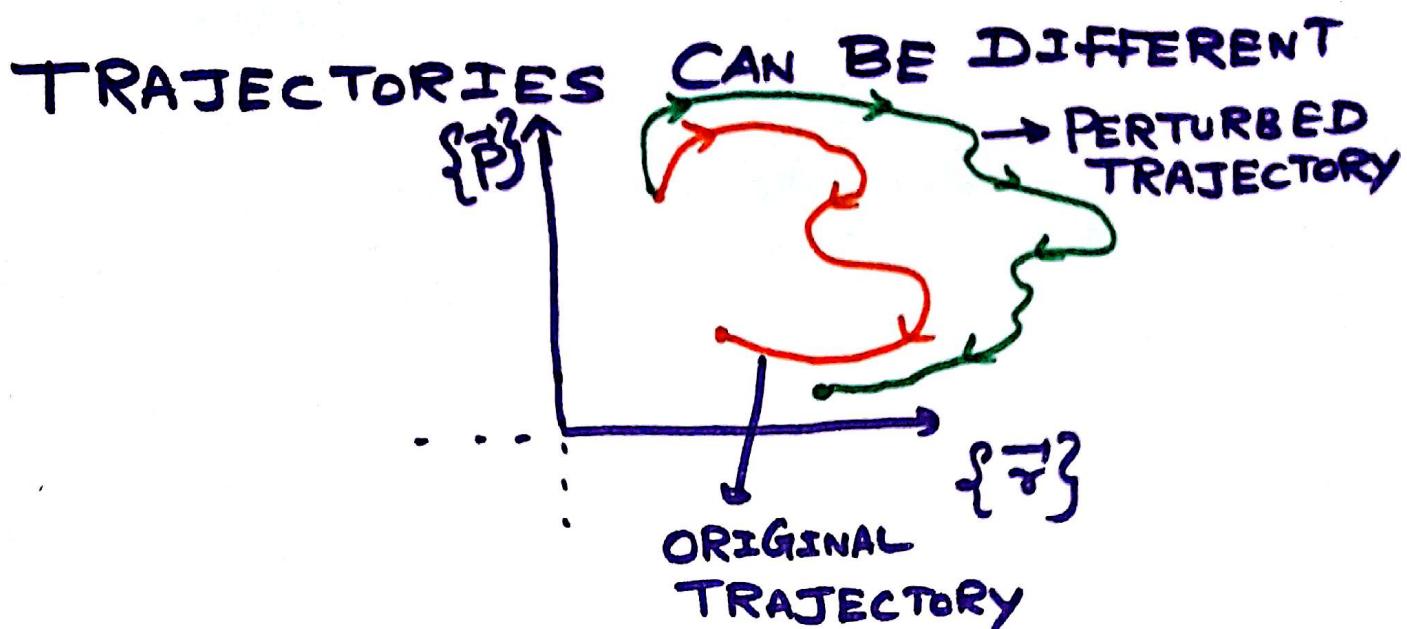
COMPARE ORIGINAL AND PERTURBED SYSTEMS

# COMPARE ORIGINAL AND PERTURBED SYSTEMS

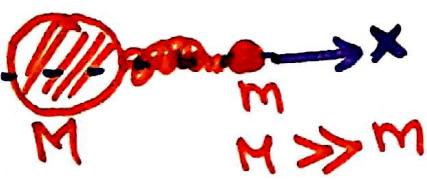
ORIGINAL SYSTEM:

$$H_0(\{\vec{r}\}, \{\vec{p}\})$$

PERTURBED SYSTEM:  $H_0(\{\vec{r}\}, \{\vec{p}\}) + H_p$



EXAMPLE: ONE-DIMENSIONAL SIMPLE HARMONIC OSCILLATOR (CLASSICAL)



REDUCED MASS

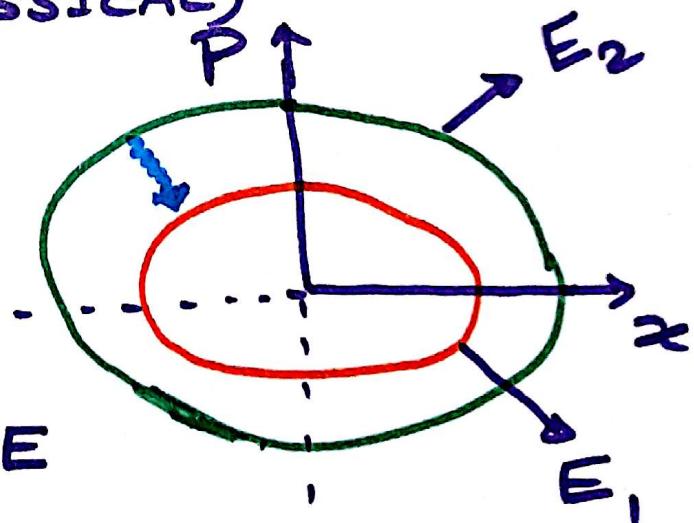
$$\mu = \frac{Mm}{M+m} \approx m$$

$$H_0(x, p) = \frac{p^2}{2\mu} + \frac{1}{2} kx^2 = E$$

SET  $H_0 = E$  INITIALLY

$$\frac{x^2}{(\sqrt{\frac{2E}{k}})^2} + \frac{p^2}{(\sqrt{2mE})^2} = 1$$

ELLIPSE

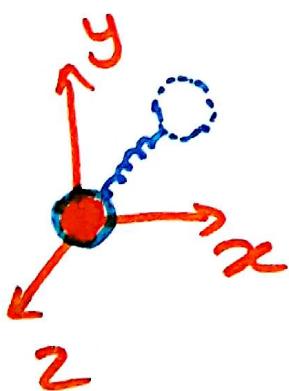
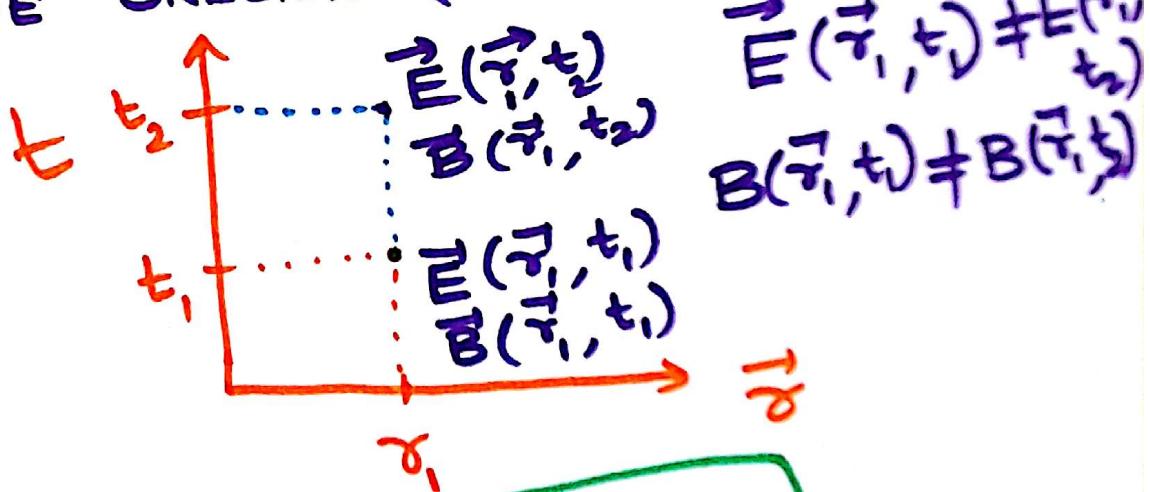


$$E_2 = E_1 + E_p$$

# A CLASSICAL DESCRIPTION OF SPECTROSCOPY

- SYSTEM COMPOSED OF CHARGED PARTICLES
- CHARGES ARE BOUND TO THE ATOMS/MOLECULES IN THE SYSTEM
- CONSIDER A SINGLE CHARGE & LOCATED AT THE ORIGIN; MASS  $m$   
 $\langle \vec{r} \rangle = (0, 0, 0)$
- TURN ON AN ELECTROMAGNETIC WAVE OF FREQUENCY  $\omega$

- CHARGE WILL OSCILLATE AROUND THE ORIGIN (HARMONIC OSCILLATOR)



$$U_{\text{HAR}}(\vec{r}, t) = \frac{1}{2} K \vec{r} \cdot \vec{r}$$

IGNORE THE EFFECT OF THE MAGNETIC FIELD (Not a moving charge)

## • DIPOLE MOMENT OF THE SYSTEM

$$\vec{\mu} = Q \vec{r}$$

FOR A SYSTEM OF DISCRETE CHARGES :

$$\vec{\mu} = \sum_{i=1}^N Q_i \vec{r}_i$$

## • INTERACTION ENERGY OF THE CHARGE WITH THE ELECTRIC FIELD

$$U_{\text{EXT}}(\vec{r}, t) = -\vec{\mu} \cdot \vec{E}(\vec{r}, t)$$

AT A GIVEN TIME, MAGNITUDE OF  $\vec{E}$  IS CONSTANT WITHIN THE VICINITY OF THE CHARGE.  
(ONLY TIME DEPENDENCE)

## • EQUATION OF MOTION

$$m \frac{d^2 \vec{r}}{dt^2} = -K \vec{r} - b \frac{d\vec{r}}{dt} + F_0 \cos \omega t$$

HARMONIC RESTORING FORCE

POSITIVE DAMPING FORCE EXTERNAL FORCE DUE TO LIGHT

NOTE:  $\vec{E}(\vec{r}, t) = \vec{E}_0(\vec{r}) \cos \omega t$

$$F_0 = \frac{d\vec{r}}{dt} \cdot \vec{E}_0 \quad (\vec{E}_0 \text{ DOESN'T CHANGE WITH } x, y, z)$$

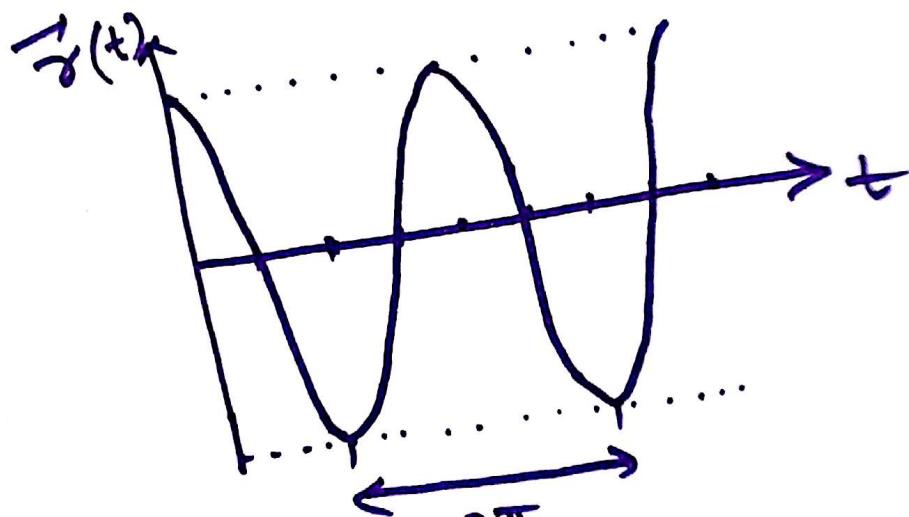
- $$\frac{d^2\vec{\gamma}}{dt^2} + 2\Gamma \frac{d\vec{\gamma}}{dt} + \omega_0^2 \vec{\gamma} = \frac{F_0}{m} \cos \omega t$$

HERE  $\Gamma = \frac{b}{2m}$  (DAMPING COEFFICIENT)

$$\omega_0 = \sqrt{\frac{k}{m}}$$
 (NATURAL FREQUENCY OF THE OSCILLATOR)

### DRIVEN HARMONIC OSCILLATOR

- CASE I:  $\Gamma = 0 \rightarrow$  NO DAMPING FORCE  
 $F_0 = 0 \rightarrow$  NO LIGHT



$$\vec{r}(t) = A \sin(\omega_0 t) + B \cos(\omega_0 t)$$

$$\vec{r}(t) = \vec{r}_0 e^{-i\omega_0 t}$$

• CASE II :  $\Gamma \neq 0$  DAMPING FORCE

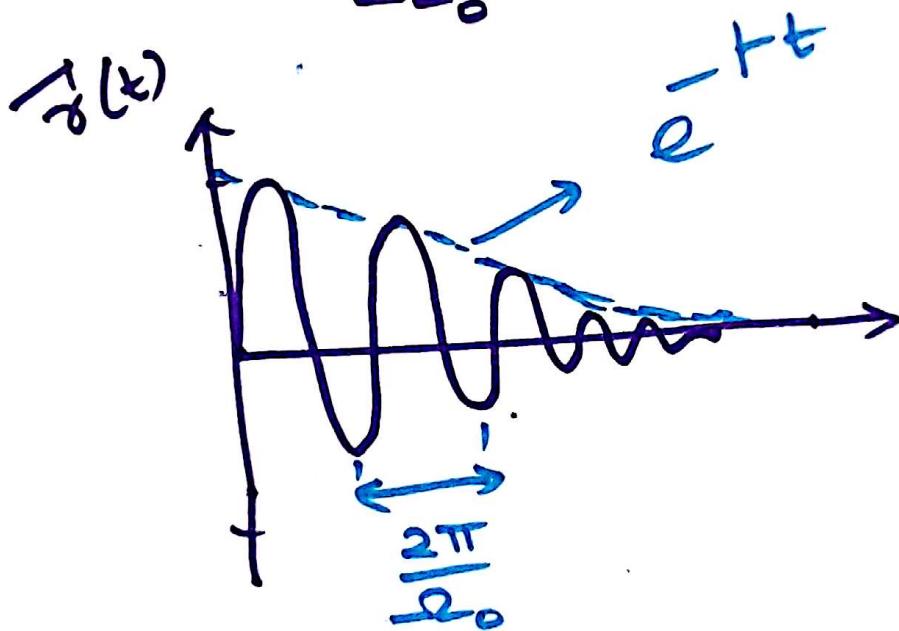
$f_0 = 0 \Rightarrow$  NO LIGHT

$$\vec{\gamma}(t) = \vec{\gamma}_0 e^{-i\Omega_0 t} e^{-\Gamma t}$$

REDUCED FREQUENCY  $\Leftrightarrow \Omega_0 = \sqrt{\omega_0^2 - \Gamma^2}$

WEAK DAMPING :  $\Gamma \rightarrow 0$

$$\Omega_0 \approx \omega_0$$

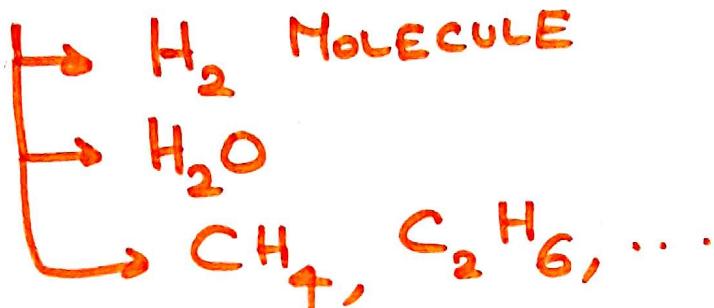


• CASE III :  $\Gamma \neq 0$   
 $f_0 \neq 0$

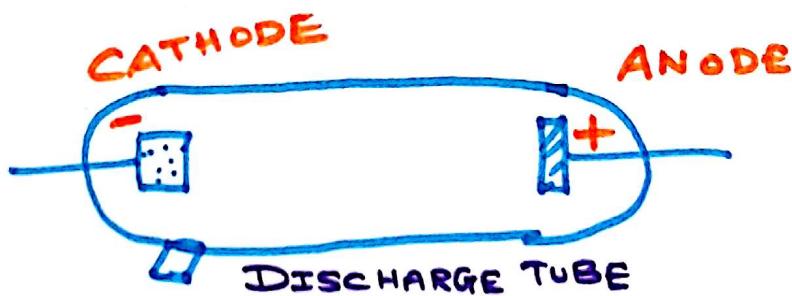
WHEN  $\omega = \omega_0$ ; RESONANCE

# ATOMIC SPECTRA

- SIMPLEST ATOM: HYDROGEN ATOM
- HOW DO WE OBTAIN THE LINE SPECTRA OF HYDROGEN ATOMS?

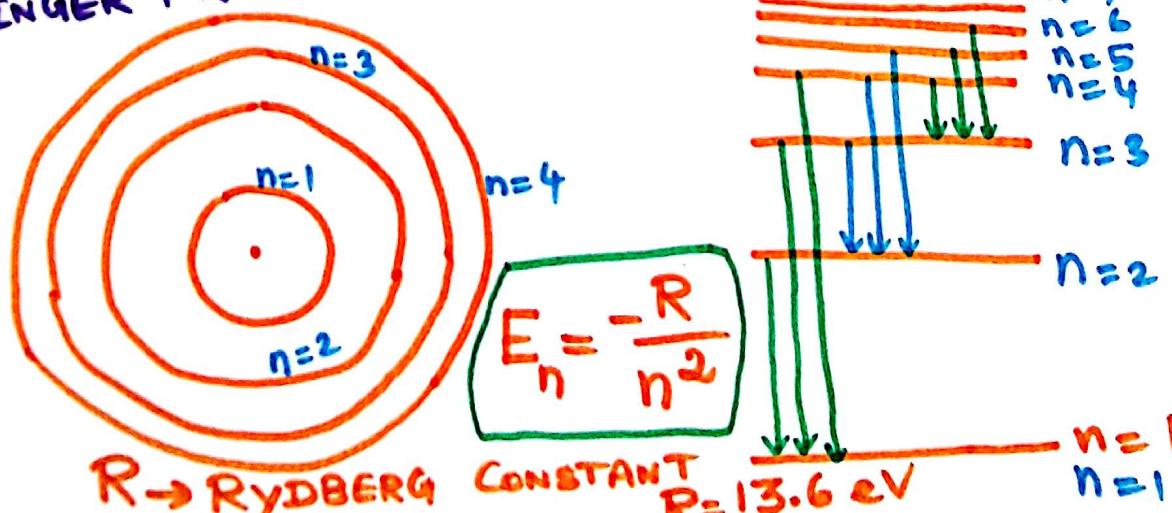


- DISSOCIATION OF H<sub>2</sub> MOLECULE



- BOHR'S MODEL OF THE HYDROGEN ATOM

FINGER PRINT OF HYDROGEN

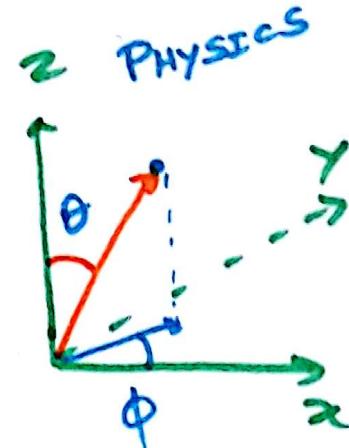
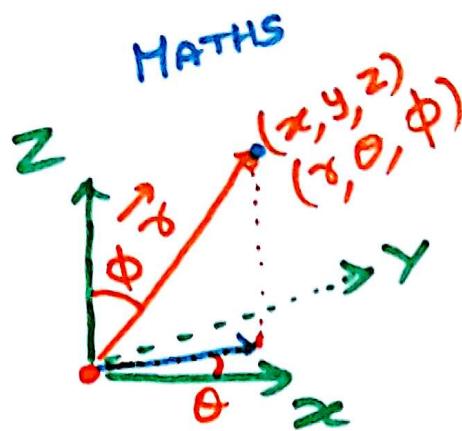


n=1  $\Rightarrow$  LYMAN (ULTRAVIOLET)  
 n=2  $\Rightarrow$  BALMER (VISIBLE)  
 n=3  $\Rightarrow$  PASCHEN (NEAR INFRARED)

n=4  $\Rightarrow$  BRACKETT (FAR IR)  
 n=5  $\Rightarrow$  PFUND (FAR IR)

# QUANTUM MECHANICS OF HYDROGEN ATOM

$$\begin{aligned}0 &\leq \theta \leq 2\pi \\0 &\leq \phi \leq \pi \\0 &\leq r \leq \infty\end{aligned}$$



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

$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta \\0 &\leq \phi \leq 2\pi \\0 &\leq \theta \leq \pi\end{aligned}$$

→ WAVE FUNCTION  $\Psi(x, y, z)$

OR  $\Psi(r, \theta, \phi)$

→ PROBABILITY DENSITY AT  $\vec{r}$

$$\Psi^*(x, y, z) \Psi(x, y, z)$$

(OR)

$$\Psi^*(r, \theta, \phi) \Psi(r, \theta, \phi)$$

→ PROBABILITY OF FINDING THE ELECTRON  
IN AN INFINITESIMAL VOLUME

$$\Psi^*(x, y, z) \Psi(x, y, z) dx dy dz$$

(OR)

$$\Psi^*(r, \theta, \phi) \Psi(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi$$

• CONSTRUCT THE HAMILTONIAN

→ KINETIC ENERGY OPERATOR

$$\frac{-\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]$$

(OR)

PHYSICS CONVENTION

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

→ POTENTIAL ENERGY  $\frac{-e^2}{4\pi\epsilon_0 r}$

• SOLVE THE SCHRODINGER EQUATION

$$H_0 \Psi(x, y, z) = E \Psi(x, y, z)$$

(OR)

$$H_0 \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

• SOLUTION:

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

RADIAL PART

ANGULAR PART

\* SPHERICAL HARMONICS

## • QUANTUM NUMBERS

$n \rightarrow$  PRINCIPAL QUANTUM NUMBER

$l \rightarrow$  ORBITAL OR AZIMUTHAL QUANTUM NUMBER

$m \rightarrow$  MAGNETIC QUANTUM NUMBER

$s \rightarrow$  SPIN

$\Rightarrow$  ALLOWED VALUES:

$$n = 1, 2, 3, \dots$$

$$l = 0, 1, 2, \dots, n-1$$

$$m = -l, -l+1, -l+2, \dots, 0, \dots, l-1, l$$

$$s = \pm \frac{1}{2}$$

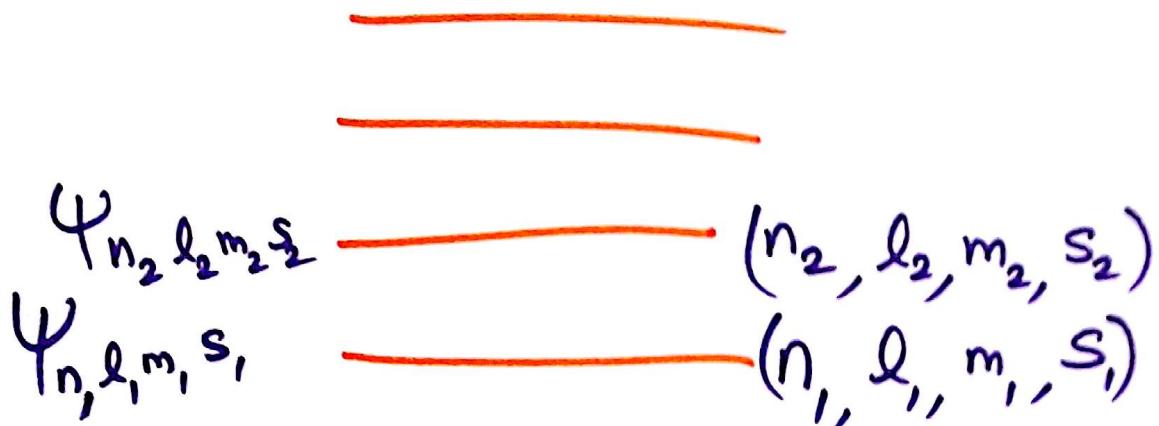
$\Rightarrow n$  GOVERNS THE ENERGY AND SIZE OF THE ORBITAL

$l$  GOVERNS THE SHAPE OF THE ORBITAL AND THE ELECTRONIC ANGULAR MOMENTUM

$m$  GOVERNS THE DIRECTION OF THE ORBITALS AND THE BEHAVIOUR OF ELECTRON IN A MAGNETIC FIELD

$s$  GOVERNS THE AXIAL ANGULAR MOMENTUM OF THE ELECTRON.

- STATES ARE DEFINED BY THESE QUANTUM NUMBERS

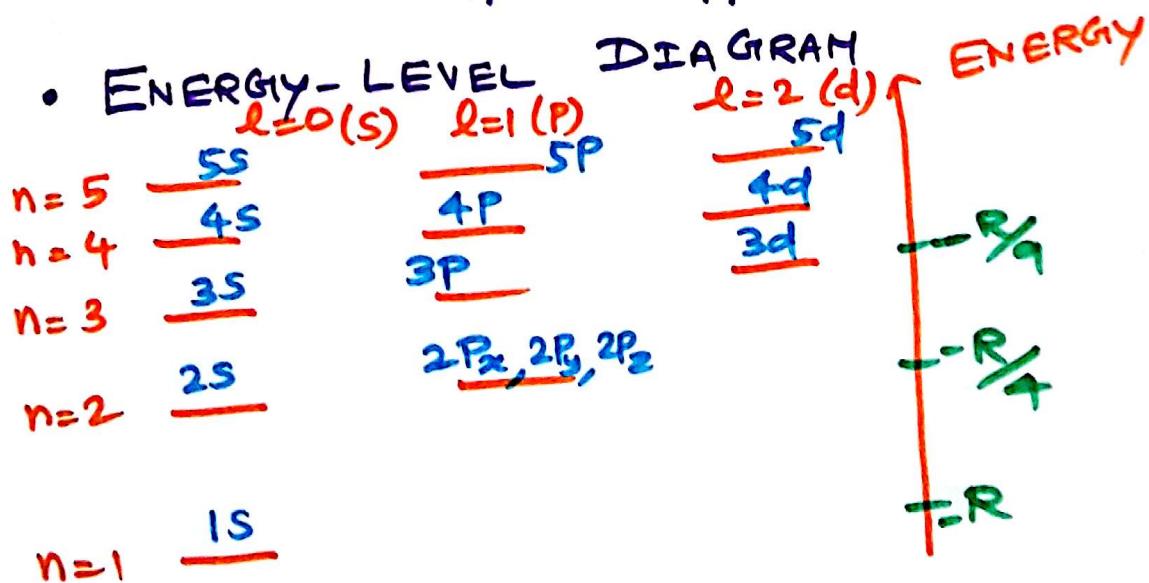


- ENERGIES OF ATOMIC ORBITALS

→ CALCULATE THE ENERGIES OF 1S, 2S, 2P<sub>x</sub>, 2P<sub>y</sub>, 2P<sub>z</sub>, 3S, 3P<sub>x</sub>, 3P<sub>y</sub>, 3P<sub>z</sub>, and 3d

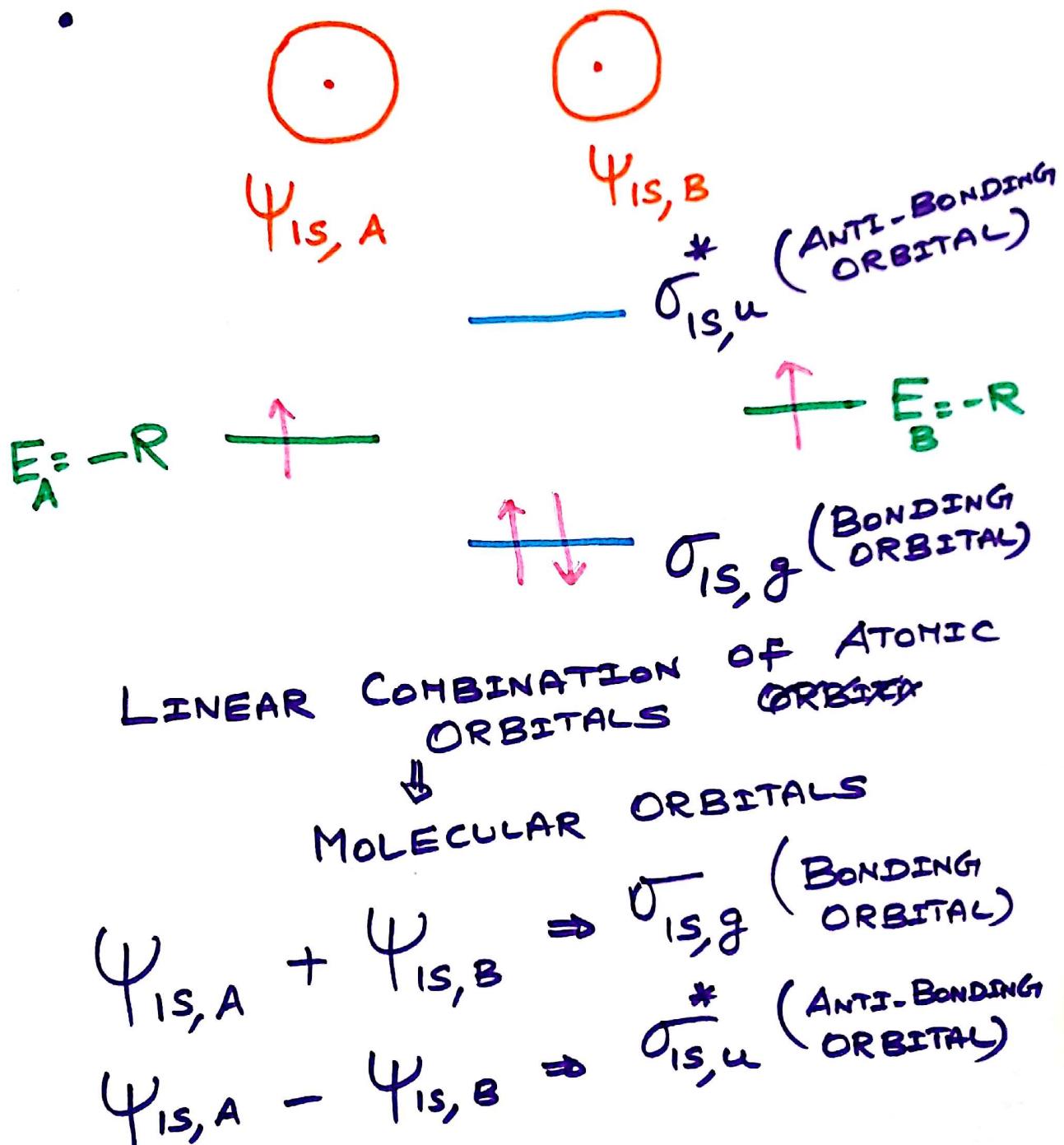
DEGENERATE                                    DEGENERATE

$$\rightarrow E_n = -\frac{R}{n^2}$$



## HYDROGEN MOLECULE

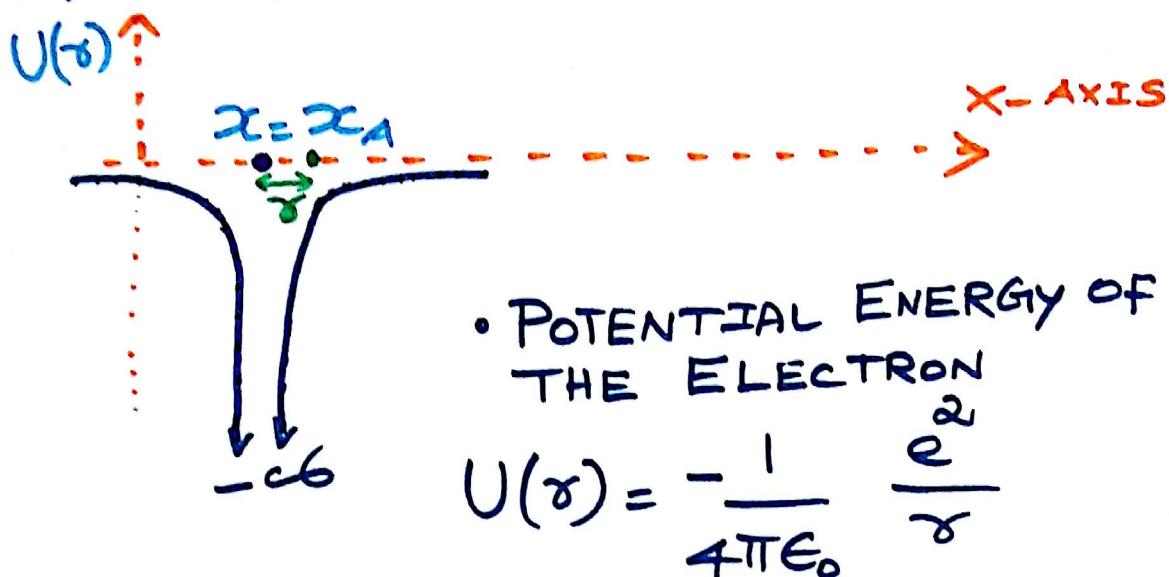
- CONSIDER TWO HYDROGEN ATOMS IN THEIR RESPECTIVE GROUND STATES (1S ORBITALS)



CLASS WORK

# ATOM → MOLECULE → SOLID

- HYDROGEN ATOM



- POTENTIAL ENERGY OF THE ELECTRON

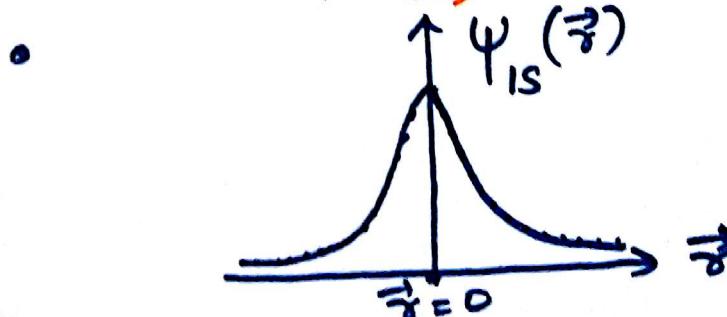
$$U(\gamma) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{\gamma}$$

- $U(\gamma)$  IS LESS THAN OR EQUAL TO ZERO ALWAYS (ATTRACTIVE FORCE)
- As  $\gamma \rightarrow 0$ ,  $U(\gamma) \rightarrow -\infty$
- VISUALIZE THIS ENERGY IN 3D SPACE
- GROUND STATE WAVE FUNCTION

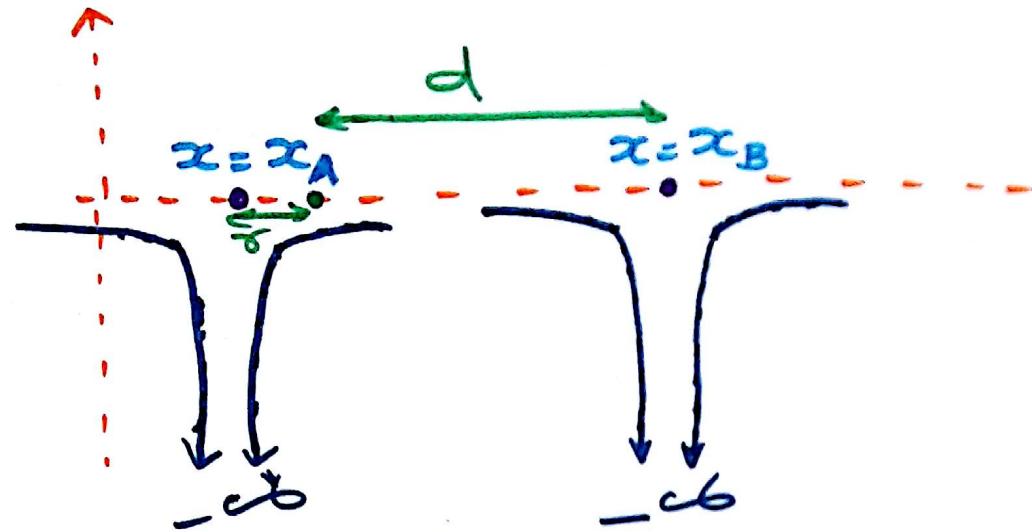
**ASSUME**  
 $\gamma_A = 0$

$$\psi_{1s}(\vec{\gamma}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\gamma/a_0}$$

↳ ALWAYS POSITIVE REGARDLESS OF  $x, y, z$  VALUES



- AN ELECTRON BETWEEN TWO ATOMS



- POTENTIAL ENERGY OF THE ELECTRON

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} + \Delta U(d)$$

WE KNOW :-

- $\Delta U(d) = 0$  WHEN  $d$  IS LARGE
- WHEN  $d \rightarrow 0$  OR WHEN  $d$  IS SMALL, INTER ATOMIC INTERACTIONS BECOME IMPORTANT

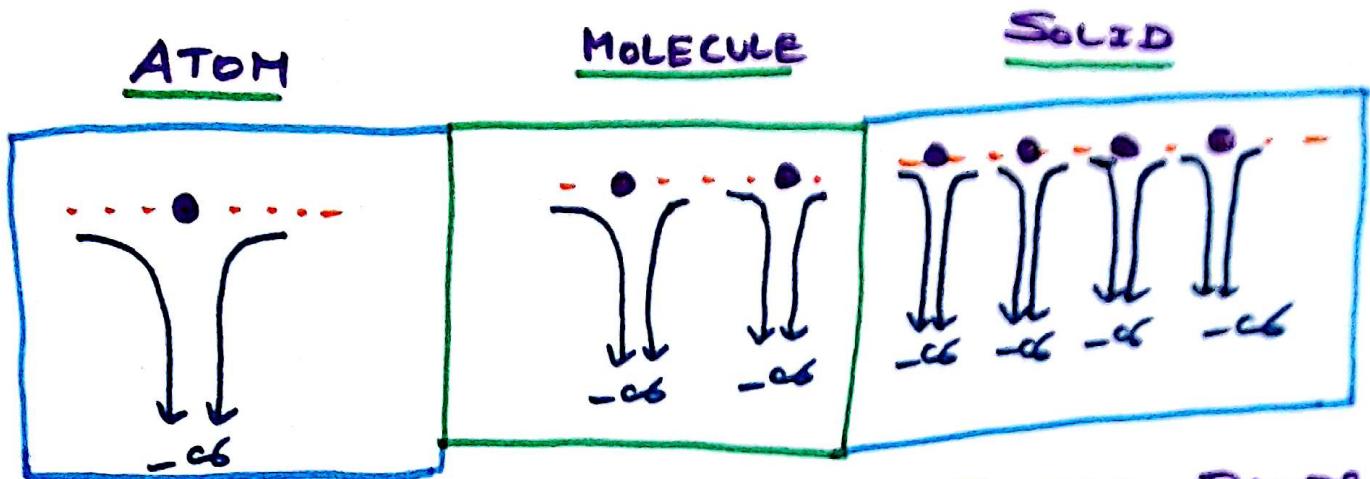
PERTURBATION DUE TO THE INTERACTION OF THE ELECTRON WITH THE NEIGHBORING ATOM

ELECTRON-ELECTRON  
ELECTRON-NUCLEUS

- $\Delta U(d) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{d}$  (ELECTRON-ELECTRON REPULSION IGNORED)

- As you DECREASE  $d$ , THE BARRIER BETWEEN THE ATOMS DECREASES.

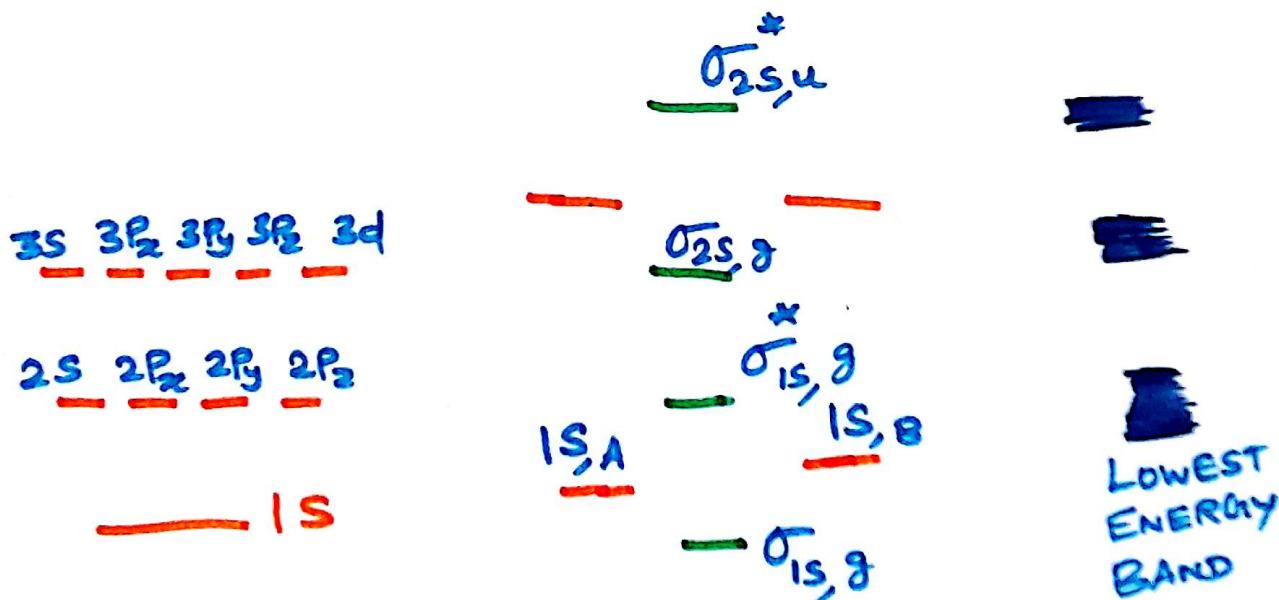
PLOT  $U(x) = -\frac{1}{4\pi\epsilon_0} e^2 \left[ \frac{1}{|x|} + \frac{1}{|x+d|} \right]$



- ATOMIC ORBITALS
- ENERGY LEVELS

- MOLECULAR ORBITALS
- ENERGY LEVELS

- ENERGY BANDS
- ENERGY LEVELS



# HYDROGEN MOLECULE

- LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

$$\Psi_M(\vec{r}) = C_A \Psi_A(\vec{r}) + C_B \Psi_B(\vec{r})$$

↓ CONSTANT      ↗ CONSTANT  
 ATOMIC ORBITAL OF ATOM A      ATOMIC ORBITAL OF ATOM B

- HAMILTONIAN

$$\hat{H} = \left( -\frac{\hbar^2 \nabla^2}{2m} + U_A(\vec{r}) \right) + \Delta U(d)$$

$\hat{H}_{o,A} \Psi_A(\vec{r}) = E_{IS,A} \Psi_A(\vec{r})$   
 $\hat{H}_{o,B} \Psi_B(\vec{r}) = E_{IS,B} \Psi_B(\vec{r})$

$$+ \left( -\frac{\hbar^2 \nabla^2}{2m} + U_B(\vec{r}) \right)$$

$$\hat{H} = \underbrace{\hat{H}_{o,A}}_{\substack{\text{HAMILTONIAN} \\ \text{OF ISOLATED A}}} + \underbrace{\hat{H}_{o,B}}_{\substack{\text{HAMILTONIAN} \\ \text{OF ISOLATED B}}} + \Delta U(d) \xrightarrow{\text{PERTURBATION}}$$

$$\hat{H} \Psi_M(\vec{r}) = E_M \Psi_M(\vec{r})$$

$$\hat{H} (C_A \Psi_A(\vec{r}) + C_B \Psi_B(\vec{r})) = E_M \Psi_M(\vec{r})$$

$\times \Psi_A^*(\vec{r})$  AND INTEGRATE ON BOTH SIDES AND USE THE FOLLOWING

$$\int_{-\infty}^{\infty} \Psi_A^*(\vec{r}) \hat{H} \Psi_A(\vec{r}) d\vec{r} \approx E_{IS,A}$$

$$\int_{-\infty}^{\infty} \Psi_A^*(\vec{r}) \hat{H} \Psi_B(\vec{r}) d\vec{r} \approx -V$$

$$\Rightarrow C_A E_{IS,A} - C_B V = E_M C_A$$

III<sup>by</sup>  $\times \Psi_B^*(\vec{r})$  AND INTEGRATE

$$-V C_A + E_{IS,B} C_B = E_M C_B$$

$$(E_{IS,A} - E_H) C_A - V C_B = 0$$

$$-V C_A + (E_{IS,B} - E_H) C_B = 0$$

SOLUTION :

$$\begin{pmatrix} C_A \\ C_B \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Anti-Bond

$$\begin{pmatrix} C_A \\ C_B \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Bond

$$\begin{vmatrix} E_{IS,A} - E_H & -V \\ -V & E_{IS,B} - E_H \end{vmatrix} = 0$$

Anti-Bonding

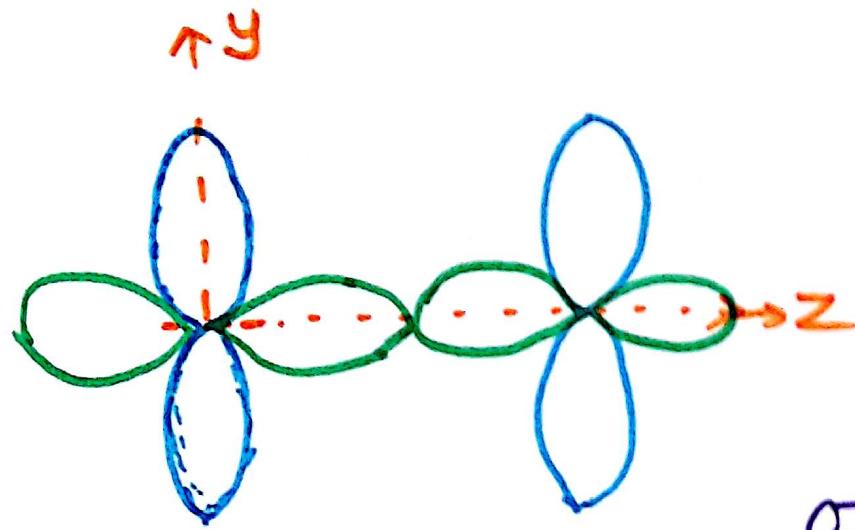
$$E_M = E_{IS} \pm V$$

BONDING

$$E_H = E_{IS} + V$$

$$E_H = E_{IS} - V$$

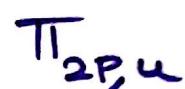
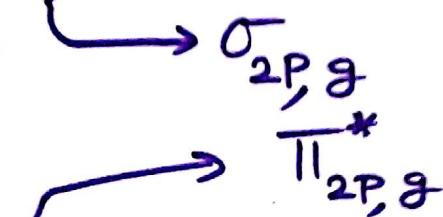
# • OVERLAP OF P ORBITALS



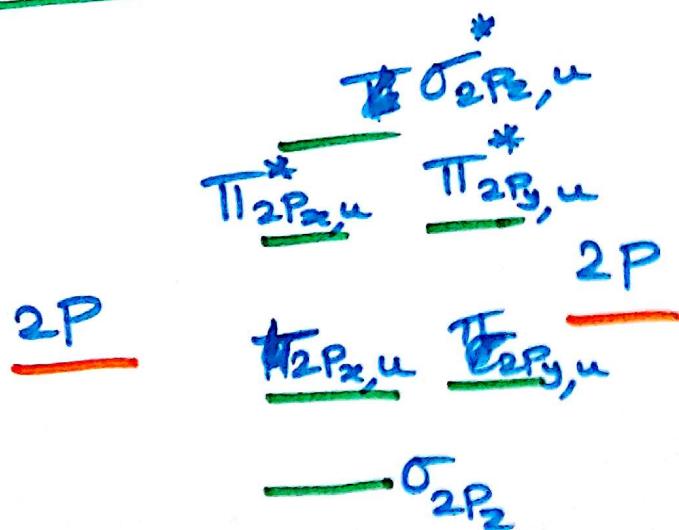
$$2P_{z,A} \oplus 2P_{z,B}$$



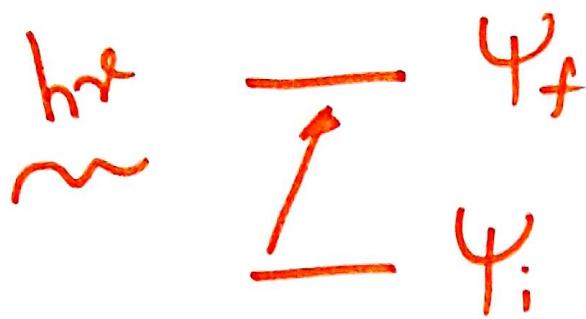
$$2P_{y,A} \oplus 2P_{y,B}$$



$E_{\sigma_{2P_z}} < E_{\pi_{2P,z}} = E_{\pi_{2P,y}} < E_{\pi_{2P,z}^*} = E_{\pi_{2P,y}^*} < E_{\sigma_{2P_g}^*}$



## TRANSITION PROBABILITY



$\hat{V}(\vec{r}, t) \Rightarrow$  TIME-DEPENDENT PERTURBATION

TRANSITION PROBABILITY

$$T_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 e(E)$$

$$T_{i \rightarrow f} \propto \left| \langle \psi_f | \hat{\mu} | \psi_i \rangle \right|^2$$

TRANSITION DIPOLE MOMENT  
INTEGRAL

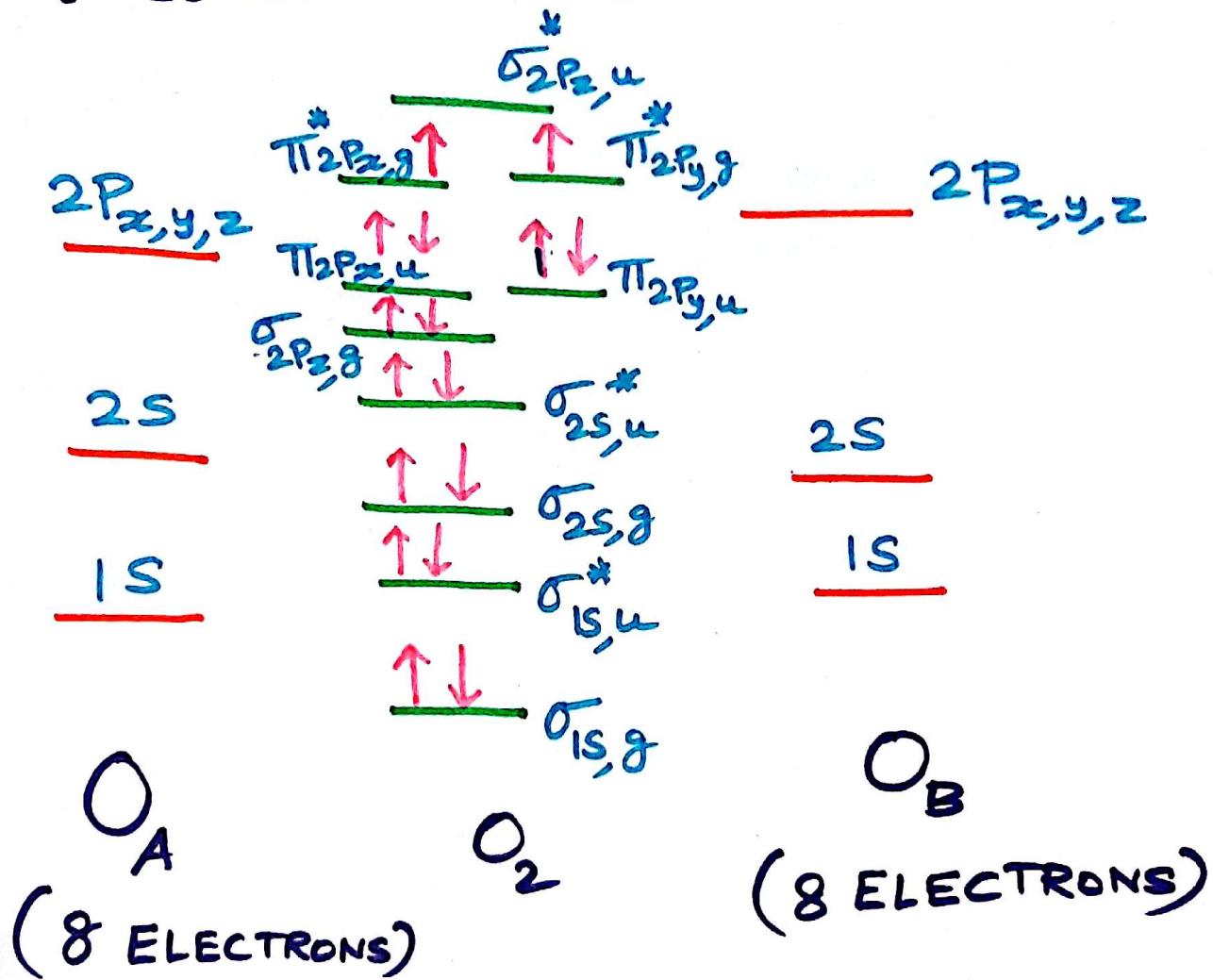
$T_{i \rightarrow f} = 0$  : TRANSITION IS FORBIDDEN

$T_{i \rightarrow f} \neq 0$  : TRANSITION IS ALLOWED

SELECTION RULES

# HOW DO WE DISTRIBUTE ELECTRONS IN MOLECULAR ORBITALS/LEVELS?

- CONSIDER  $O_2$  MOLECULE

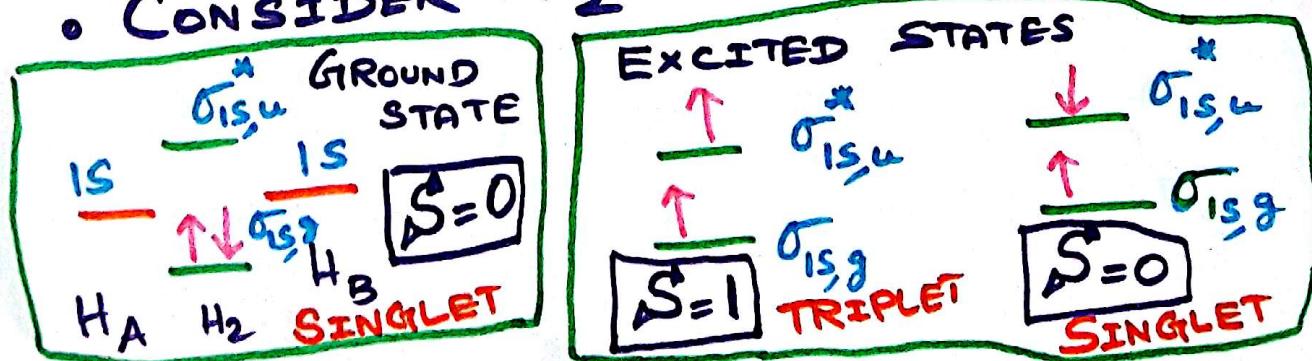


HOMO: HIGHEST OCCUPIED MOLECULAR ORBITAL

LUMO: LOWEST UNOCCUPIED MOLECULAR ORBITAL.

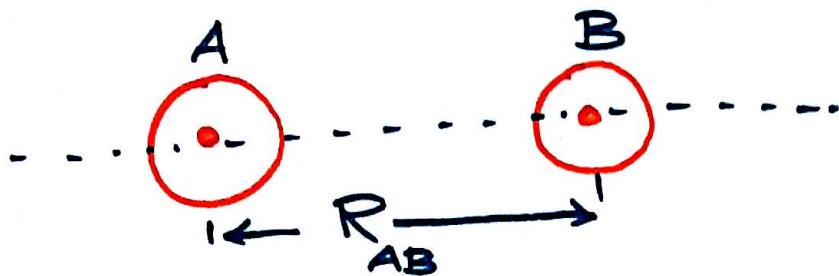
SPIN MULTIPlicity =  $2S+1$        $S \rightarrow$  TOTAL SPIN

- CONSIDER  $H_2$  MOLECULE:



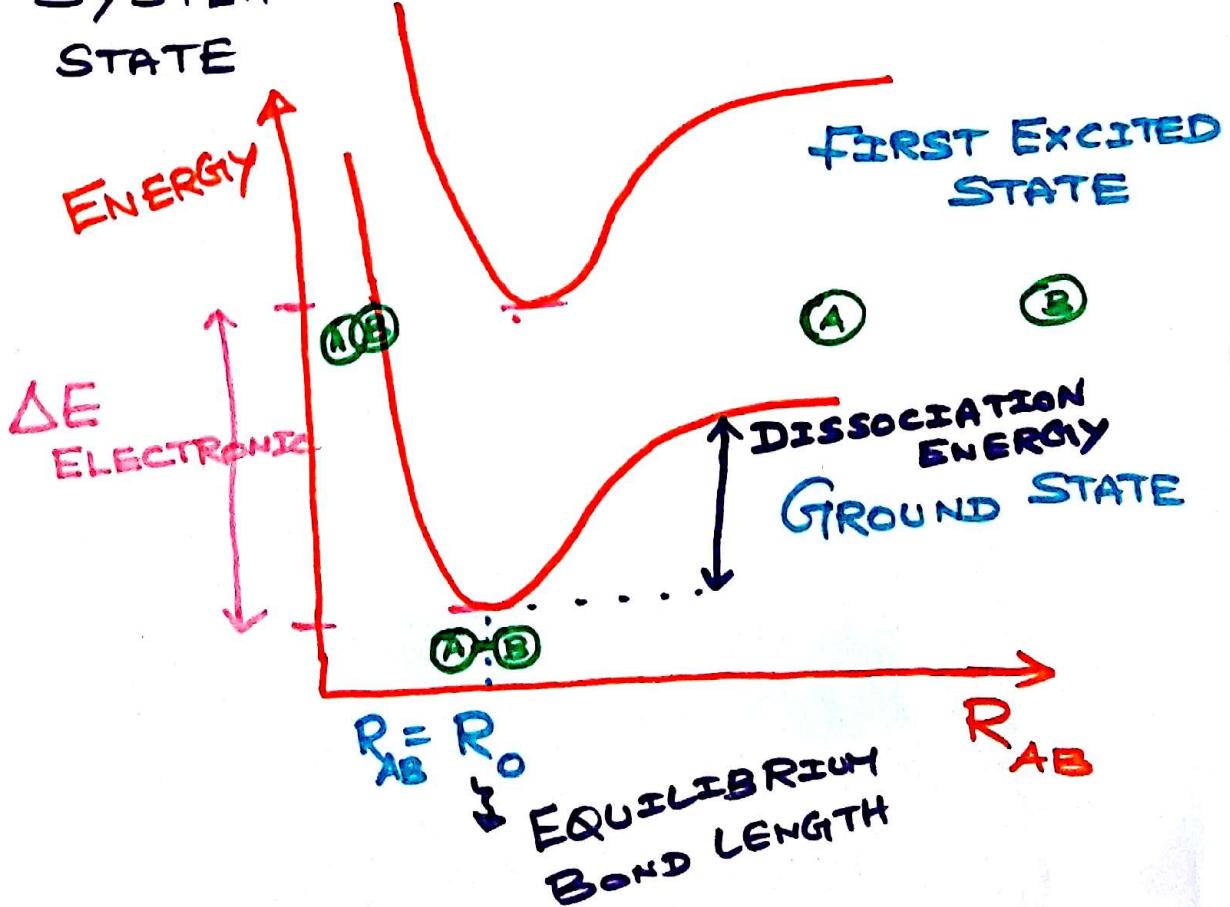
# ELECTRONIC ENERGY SURFACES

- CONSIDER A DIATOMIC MOLECULE

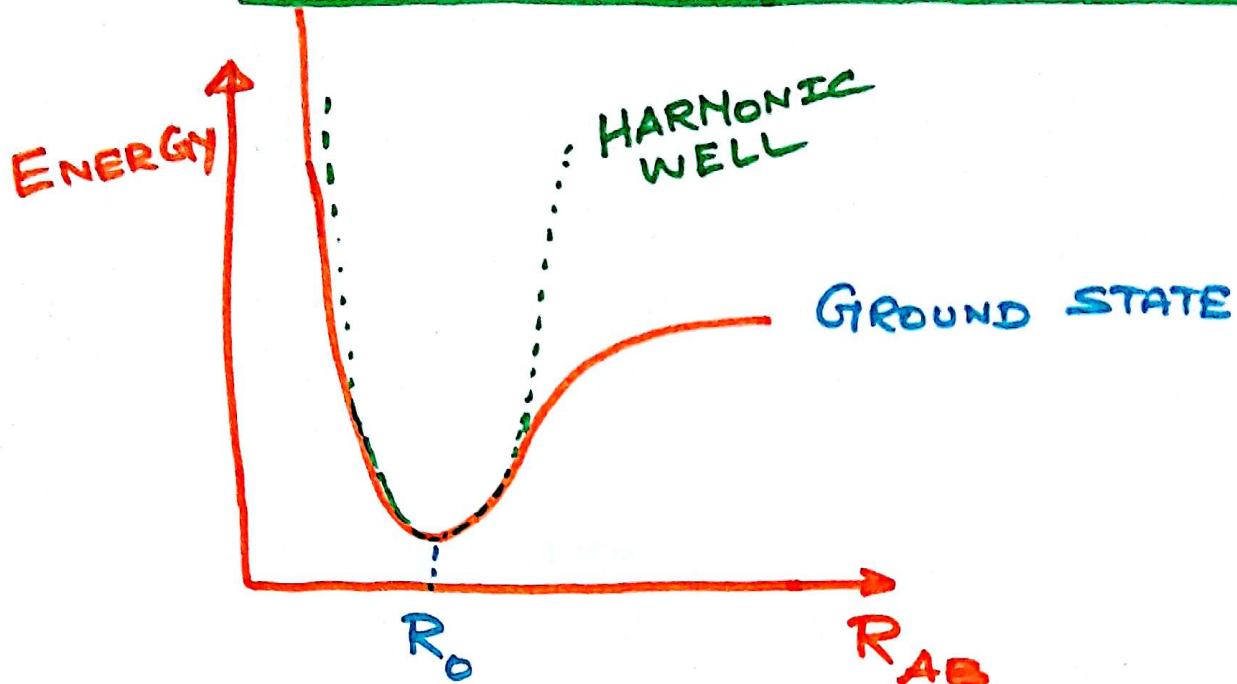


- $R_{AB} \Rightarrow$  INTER NUCLEAR DISTANCE

- VARY  $R_{AB}$ , BUT ENSURE THAT THE SYSTEM IS ALWAYS IN ITS GROUND STATE



# VIBRATIONAL SPECTROSCOPY



- CONSIDER THE GROUND STATE OF A DIATOMIC MOLECULE
- INITIAL CONDITION:  $R_{AB} = R_0$
- SUPPLY EXTERNAL PERTURBATION ENERGY  $\Delta V$  TO THE MOLECULE

$$\Delta V \ll \Delta E$$

ELECTRONIC

- SMALL AMPLITUDE OSCILLATIONS VIBRATIONS ABOUT THE ENERGY MINIMUM.  $\Rightarrow$  SIMPLE HARMONIC MOTION

$$U(x) = \frac{1}{2} k x^2$$

# VIBRATIONAL SPECTROSCOPY

- LET  $U(R_{AB})$  DENOTES THE ENERGY SURFACE
- EXPAND  $U(R_{AB})$  ABOUT  $R_0$

$$U(R_{AB}) = U(R_0) + \frac{1}{1!} \left. \frac{dU}{dR_{AB}} \right|_{R_0} (R_{AB} - R_0)$$

DIFFERENT FROM  $U(x_1, y_1, z_1, x_2, y_2, z_2)$

$$+ \frac{1}{2!} \left. \frac{d^2U}{dR_{AB}^2} \right|_{R_0} (R_{AB} - R_0)^2$$

$$+ \frac{1}{3!} \left. \frac{d^3U}{dR_{AB}^3} \right|_{R_0} (R_{AB} - R_0)^3 + \dots$$

- SMALL AMPLITUDE OSCILLATION

$$|R_{AB} - R_0| \rightarrow 0$$

$\Rightarrow$  IGNORE HIGHER-ORDER TERMS  
 $\Rightarrow$  USE  $\left. \frac{dU}{dR_{AB}} \right|_{R_0} = 0$

$\Rightarrow$  SET  $U(R_0) = 0$

HARMONIC APPROXIMATION LIKE SPRING CONSTANT

$$U(R_{AB}) \approx \frac{1}{2} \left. \frac{d^2U}{dR_{AB}^2} \right|_{R_0} (R_{AB} - R_0)^2$$

$$U(x) = \frac{1}{2} k x^2$$

# VIBRATIONAL SPECTROSCOPY

- USE QUANTUM HARMONIC OSCILLATOR MODEL

$$H\psi = E\psi$$

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi = E\psi$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{ REDUCED MASS}$$

- ENERGY OF THE OSCILLATOR

$$E_v = (v + \frac{1}{2})\hbar\omega ; \quad \omega = \sqrt{\frac{k}{\mu}}$$

$\vdots$

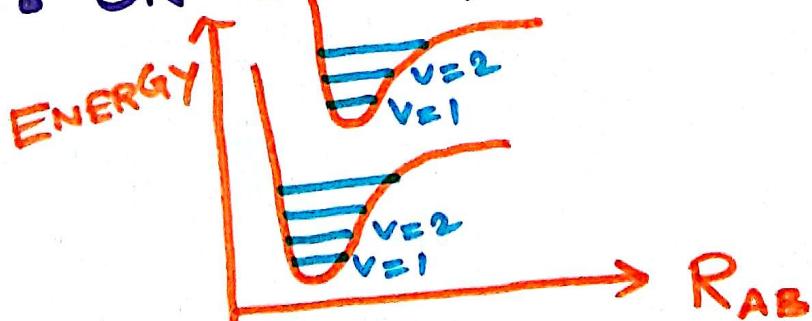
$v=4$	$\frac{9}{2}\hbar\omega$
$v=3$	$\frac{7}{2}\hbar\omega$
$v=2$	$\frac{5}{2}\hbar\omega$
$v=1$	$\frac{3}{2}\hbar\omega$
$v=0$	$\hbar\omega$

$v=0, 1, 2, \dots$   
vibrational quantum number

$\hbar\omega \{$

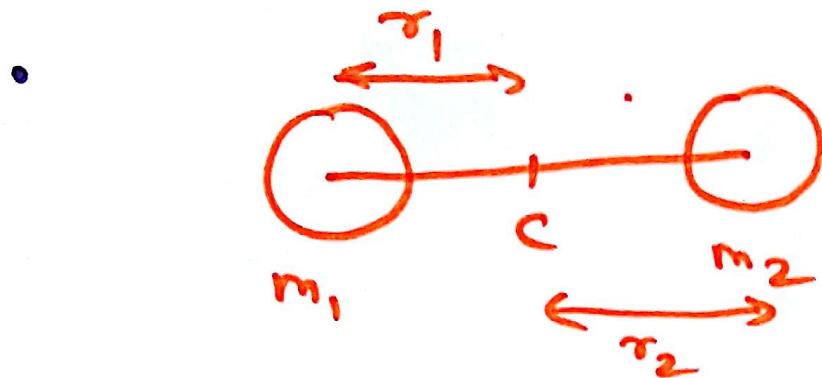
$$\hbar\omega \ll \Delta E_{\text{ELECTRONIC}}$$

- ON ENERGY SURFACE



# ROTATIONAL SPECTROSCOPY

## • RIGID DIATOMIC MOLECULE



$$\rightarrow \text{MOMENT OF INERTIA : } I = m_1 r_1^2 + m_2 r_2^2$$

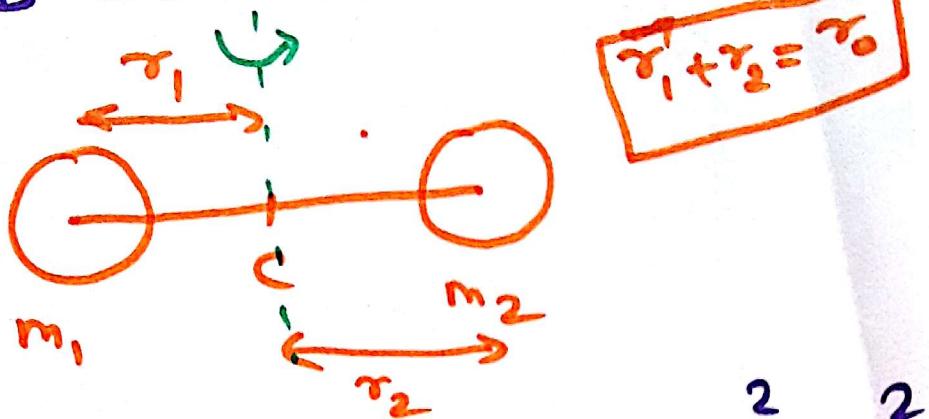
## → ROTATIONAL ENERGY

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

$\downarrow J = 0, 1, 2, \dots$   
ROTATIONAL QUANTUM NUMBER

# ROTATIONAL SPECTROSCOPY

- RIGID DIATOMIC MOLECULE



→ MOMENT OF INERTIA :  $I = m_1 r_1^2 + m_2 r_2^2$

→ ROTATIONAL ENERGY

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

$J = 0, 1, 2, \dots$   
ROTATIONAL QUANTUM NUMBER

• WE KNOW THAT

$$m_1 \gamma_1 = m_2 \gamma_2 = m_2 (\gamma_0 - \gamma_1)$$

$$\Rightarrow I = (m_1 \gamma_1) \gamma_1 + (m_2 \gamma_2) \gamma_2$$

$$\gamma_1 = \frac{m_2 \gamma_0}{m_1 + m_2}$$

$$= m_2 \gamma_2 \gamma_1 + m_1 \gamma_1 \gamma_2$$

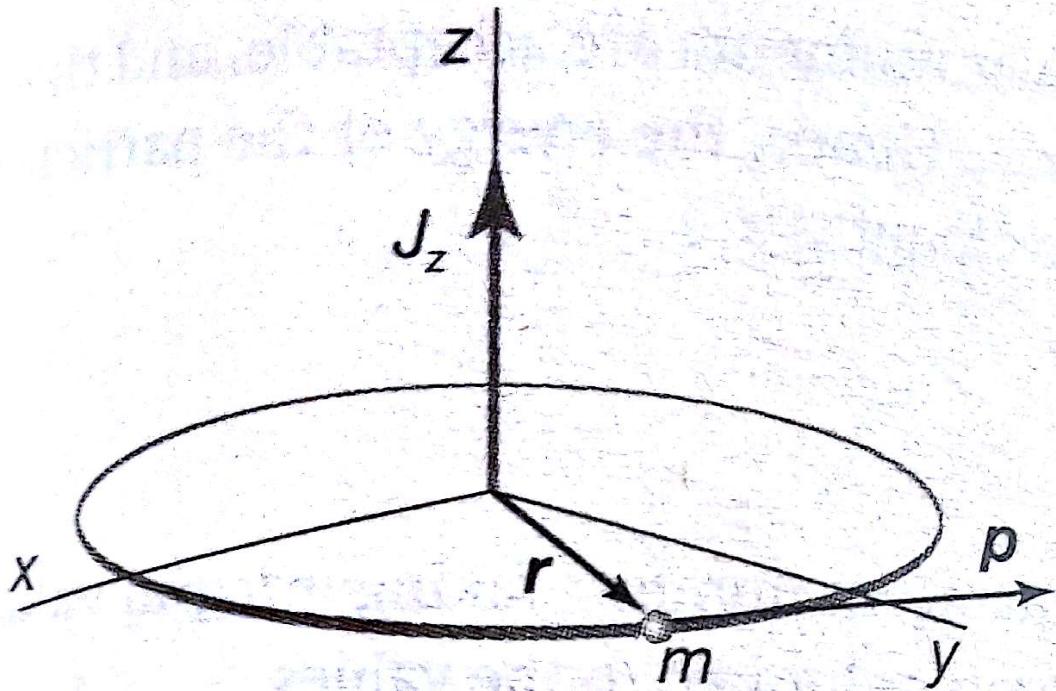
$$\gamma_2 = \frac{m_1 \gamma_0}{m_1 + m_2}$$

$$I = \gamma_1 \gamma_2 (m_1 + m_2)$$

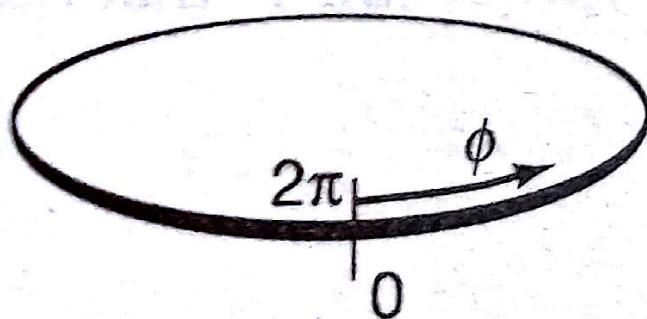


$$I = \left( \frac{m_1 m_2}{m_1 + m_2} \right) \gamma_0^2 = \mu \gamma_0^2$$

REduced MASS



**12.23** The angular momentum of a particle of mass  $m$  on a circular path of radius  $r$  in the  $xy$ -plane is represented by a vector  $J$  with the single nonzero component  $J_z$  of magnitude  $pr$  perpendicular to the plane.



The hamiltonian for a particle of mass  $m$  in a plane (with  $V = 0$ ) is the same as that given in eqn 16:

$$H = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$

and the Schrödinger equation is  $H\psi = E\psi$ , with the wavefunction a function of the angle  $\phi$ . It is always a good idea to use coordinates that reflect the full symmetry of the system, so we introduce the coordinates  $r$  and  $\phi$  (Fig. 12.26), where  $x = r \cos \phi$  and  $y = r \sin \phi$ . By standard manipulations (see *Further reading*) we can write

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \quad (12.5)$$

5. The value  $m_1 = 0$  corresponds to  $\lambda = \infty$ ; a 'wave' of infinite wavelength has a constant height at all values of  $\phi$ . See *Further information 1*.

However, because the radius of the path is fixed, the derivative with respect to  $r$  can be discarded. The hamiltonian then becomes

$$H = -\frac{\hbar^2}{2mr^2} \frac{d^2}{d\phi^2}$$

The moment of inertia  $I = mr^2$  has appeared automatically, so  $H$  may be written

$$H = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} \quad (12.52)$$

and the Schrödinger equation is

$$\frac{d^2\psi}{d\phi^2} = -\frac{2IE}{\hbar^2}\psi \quad (12.53)$$

The normalized general solutions of the equation are

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} \quad m_l = \pm \frac{(2IE)^{1/2}}{\hbar}$$

The quantity  $m_l$  is just a dimensionless number at this stage.

We now select the acceptable solutions from among these general solutions by imposing the condition that the wavefunction should be single-valued. That is, the wavefunction  $\psi$  must satisfy a **cyclic boundary condition**, and match at points separated by a complete revolution:  $\psi(\phi + 2\pi) = \psi(\phi)$ . On substituting the general wavefunction into this condition, we find

$$\psi_{m_l}(\phi + 2\pi) = \frac{e^{im_l(\phi+2\pi)}}{(2\pi)^{1/2}} = \frac{e^{im_l\phi} e^{2\pi im_l}}{(2\pi)^{1/2}} = \psi_{m_l}(\phi) e^{2\pi im_l}$$

As  $e^{i\pi} = -1$ , this relation is equivalent to

$$\psi_{m_l}(\phi + 2\pi) = (-1)^{2m_l} \psi(\phi) \quad (12.54)$$

Because we require  $(-1)^{2m_l} = 1$ ,  $2m_l$  must be a positive or a negative even integer (including 0), and therefore  $m_l$  must be an integer:  $m_l = 0, \pm 1, \pm 2, \dots$ .

In the discussion of translational motion in one dimension, we saw that the opposite signs in the wavefunctions  $e^{ikx}$  and  $e^{-ikx}$  correspond to opposite directions of travel, and that the linear momentum is given by the eigenvalue of the linear momentum operator. The same conclusions can be drawn here, but now we need the eigenvalues of the angular momentum operator. In classical mechanics the orbital angular momentum  $l_z$  about the z-axis is defined as<sup>7</sup>

$$l_z = xp_y - yp_x \quad [12.55]$$

where  $p_x$  is the component of linear motion parallel to the x-axis and  $p_y$  is the component parallel to the y-axis. The operators for the two linear momentum components are given in eqn 11.32, so the operator for angular momentum about the z-axis, which we denote  $l_z$ , is

$$l_z = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (12.56)$$

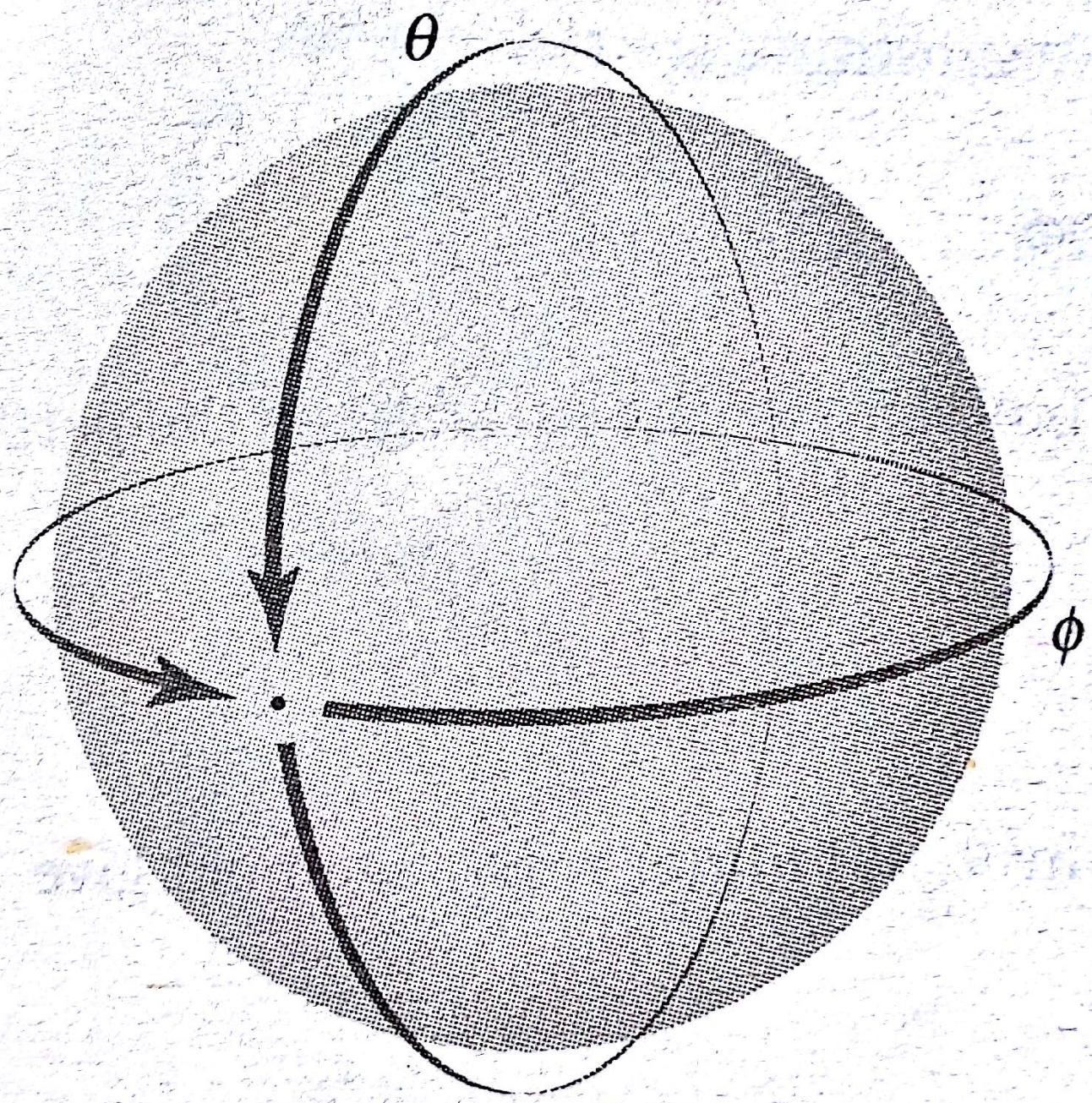
When expressed in terms of the coordinates  $r$  and  $\phi$ , by standard manipulations this equation becomes

$$l_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad (12.57)$$

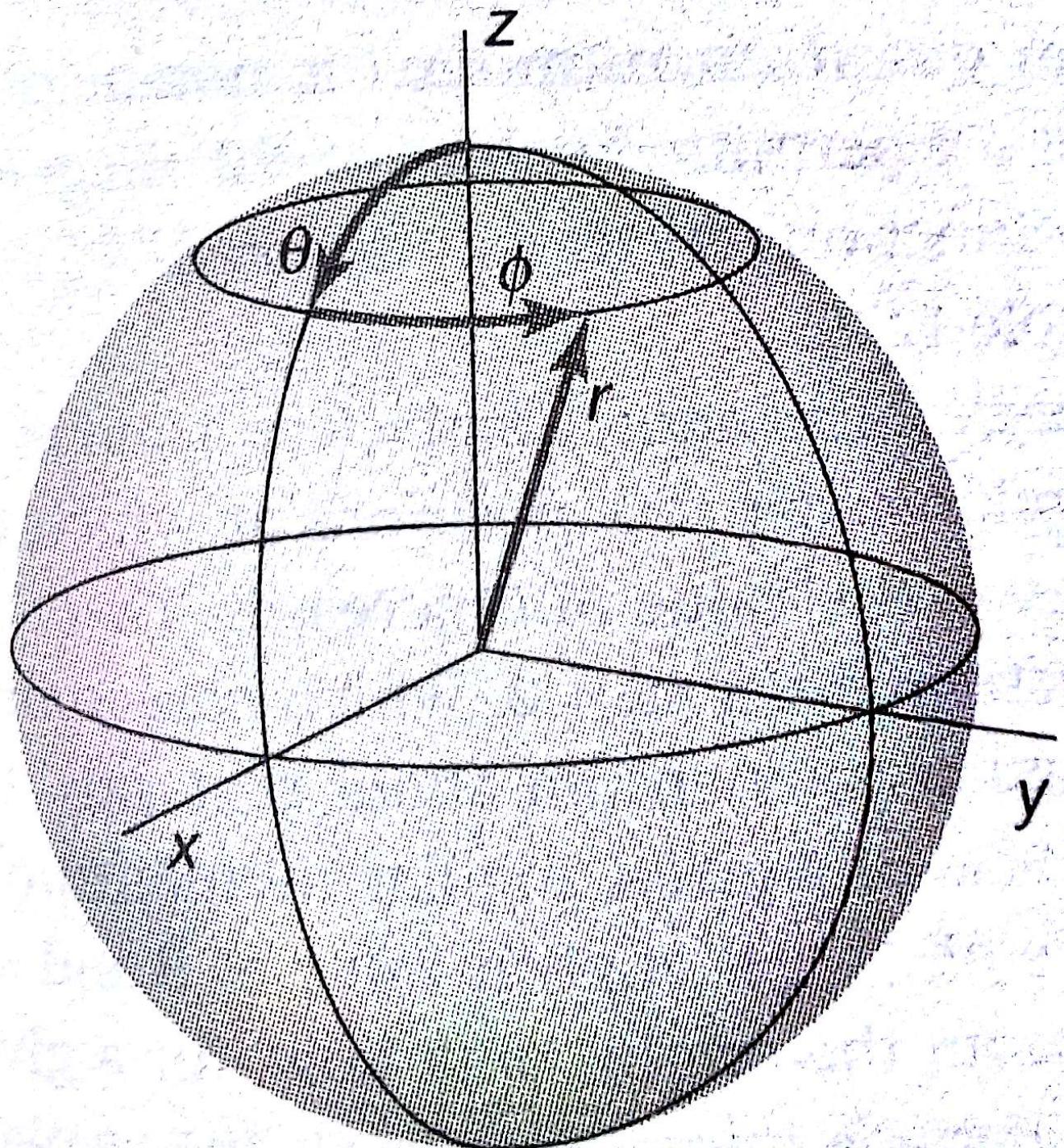
With the angular momentum operator available, we can test the wavefunction in eqn 50. Disregarding the normalization constant, we find

$$l_z \psi_{m_l} = \frac{\hbar}{i} \frac{d\psi_{m_l}}{d\phi} = im_l \frac{\hbar}{i} e^{im_l \phi} = m_l \hbar \psi_{m_l} \quad (12.58)$$

That is,  $\psi_{m_l}$  is an eigenfunction of  $l_z$ , and corresponds to an angular momentum  $m_l \hbar$ . When  $m_l$  is positive, the angular momentum is positive (clockwise when seen from below); when  $m_l$  is negative, the angular momentum is negative (counterclockwise when seen from below). These features are the origin of the vector representation of angular momentum, in which the magnitude is represented by the length of a vector and the direction of motion by its orientation (Fig. 12.28).



**12.30** The wavefunction of a particle on the surface of a sphere must satisfy two cyclic boundary conditions; this requirement leads to two quantum numbers for its state of angular momentum.



**12.31** Spherical polar coordinates. For a particle confined to the surface of a sphere, only the colatitude,  $\theta$ , and the azimuth,  $\phi$ , can change.

## 12.7 Rotation in three dimensions: the particle on a sphere

We now consider a particle of mass  $m$  that is free to move anywhere on the surface of a sphere of radius  $r$ . We shall need the results of this calculation when we come to describe the states of electrons in atoms (Chapter 13) and of rotating molecules (Chapter 16). The requirement that the wavefunction should match as a path is traced over the poles as well as round the equator of the sphere surrounding the central point introduces a second cyclic boundary condition and therefore a second quantum number (Fig. 12.30).

### (a) The Schrödinger equation

The hamiltonian for motion in three dimensions (Table 11.1) is

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (12.59)$$

The symbol  $\nabla^2$  is a convenient abbreviation for the sum of the three second derivatives; it is called the **laplacian**, and read either ‘del squared’ or ‘nabla squared’. For the particle confined to a spherical surface,  $V=0$  wherever it is free to travel, and the radius  $r$  is a constant. The wavefunction is therefore a function of the **colatitude**,  $\theta$ , and the **azimuth**,  $\phi$  (Fig. 12.31), and we write it  $\psi(\theta, \phi)$ . The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi \quad (12.60)$$

As shown in the following *Justification*, this partial differential equation can be simplified by the separation of variables procedure by expressing the wavefunction (for constant  $r$ ) as the product

$$\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi) \quad (12.61)$$

where  $\Theta$  is a function only of  $\theta$  and  $\Phi$  is a function only of  $\phi$ .

## JUSTIFICATION 12.0

The laplacian in spherical polar coordinates is (see *Further reading*)

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{2}{r^2} \Lambda^2 \quad (12.6)$$

where the **legendrian**,  $\Lambda^2$ , is

$$\Lambda^2 = \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \quad (12.6)$$

Because  $r$  is constant, we can discard the part of the laplacian that involves differentiation with respect to  $r$ , and so write the Schrödinger equation as

$$\frac{1}{r^2} \Lambda^2 \psi = -\frac{2mE}{\hbar^2} \psi$$

or, because  $I = mr^2$ , as

$$\Lambda^2 \psi = -\varepsilon \psi \quad \varepsilon = \frac{2IE}{\hbar^2}$$

To verify that this expression is separable, we substitute  $\psi = \Theta\Phi$ :

$$\frac{1}{\sin^2\theta} \frac{\partial^2(\Theta\Phi)}{\partial\phi^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial(\Theta\Phi)}{\partial\theta} = -\varepsilon\Theta\Phi$$

We now use the fact that  $\Theta$  and  $\Phi$  are each functions of one variable, so the partial derivatives become complete derivatives:

$$\frac{\Theta}{\sin^2\theta} \frac{d^2\Phi}{d\phi^2} + \frac{\Phi}{\sin\theta} \frac{d}{d\theta} \sin\theta \frac{d\Theta}{d\theta} = -\varepsilon\Theta\Phi$$

Division through by  $\Theta\Phi$ , multiplication by  $\sin^2\theta$ , and minor rearrangement give

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \sin\theta \frac{d\Theta}{d\theta} + \varepsilon \sin^2\theta = 0$$

The first term on the left depends only on  $\phi$  and the remaining two terms depend only on  $\theta$ . We met a similar situation when discussing a particle on a rectangular surface (*Justification 12.2*) and, by the same argument, the complete equation can be separated. Thus, if we set the first term equal to the numerical constant  $-m_l^2$  (a constant clearly chosen with an eye to the future), the separated equations are

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m_l^2 \quad \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \sin\theta \frac{d\Theta}{d\theta} + \varepsilon \sin^2\theta = m_l^2$$

The first of these two equations is the same as in *Justification 12.4*, so it has the same solutions (eqn 50). The second is much more complicated to solve, but the solutions are tabulated as the *associated Legendre functions*. The cyclic boundary conditions on  $\theta$  result in the introduction of a second quantum number,  $l$ , which identifies the acceptable solutions. The presence of the quantum number  $m_l$  in the second equation implies, as we see below, that the range of acceptable values of  $m_l$  is restricted by the value of  $l$ .

be separated. Thus, if we set the first term equal to the numerical constant  $-m_l^2$  (a constant clearly chosen with an eye to the future), the separated equations are

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m_l^2 \quad \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \sin \theta \frac{d\Theta}{d\theta} + \epsilon \sin^2 \theta = m_l^2$$

The first of these two equations is the same as in Justification 12.4, so it has the same solutions (eqn 50). The second is much more complicated to solve, but the solutions are tabulated as the *associated Legendre functions*. The cyclic boundary conditions on  $\theta$  result in the introduction of a second quantum number,  $l$ , which identifies the acceptable solutions. The presence of the quantum number  $m_l$  in the second equation implies, as we see below, that the range of acceptable values of  $m_l$  is restricted by the value of  $l$ .

---

As indicated in Justification 12.6, solution of the Schrödinger equation shows that the acceptable wavefunctions are specified by two quantum numbers  $l$  and  $m_l$  which are restricted to the values

$$l = 0, 1, 2, \dots \quad m_l = l, l-1, \dots, -l \quad (12.64)$$

Note that the **orbital angular momentum quantum number**  $l$  is non-negative and that, for a given value of  $l$ , there are  $2l + 1$  permitted values of the **magnetic quantum number**,  $m_l$ . The normalized wavefunctions are usually denoted  $Y_{l,m_l}(\theta, \phi)$  and are called the **spherical harmonics** (Table 12.3).

Figure 12.32 is a representation of the spherical harmonics for  $l = 0$  to  $4$  and  $m_l = 0$  which emphasizes how the number of angular nodes (the positions at which the wavefunction passes through zero) increases as the value of  $l$  increases. There are no angular nodes around the  $z$ -axis for functions with  $m_l = 0$ , which corresponds to there being no component of orbital angular momentum about that axis. Figure 12.33 shows the distribution of the particle of a given angular momentum in more detail. In this representation, the value of  $|Y_{l,m_l}|^2$  at each value of  $\theta$  and  $\phi$  is proportional to the distance of the surface from the origin. Note how, for a given value of  $l$ , the most probable location of the particle migrates towards the  $xy$ -plane as the value of  $|m_l|$  increases.<sup>8</sup>

8. The real and imaginary components of the  $\phi$  component of the wavefunctions,  $e^{im_l\phi} = \cos m_l \phi + i \sin m_l \phi$ , each have  $|m_l|$  angular nodes, but these nodes are not seen when we plot the probability density, because  $|e^{im_l\phi}|^2 = 1$ .

**Table 12.3** The spherical harmonics  $Y_{l,m_l}(\theta, \phi)$

$l$	$m_l$	$Y_{l,m_l}$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
	$\pm 1$	$\mp \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	$\pm 1$	$\mp \left(\frac{15}{8\pi}\right)^{1/2} \cos\theta \sin\theta e^{\pm i\phi}$
	$\pm 2$	$\mp \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
	$\pm 1$	$\mp \left(\frac{21}{64\pi}\right)^{1/2} (5\cos^2\theta - 1)\sin\theta e^{\pm i\phi}$
	$\pm 2$	$\left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta e^{\pm 2i\phi}$
$\pm 3$		$\mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

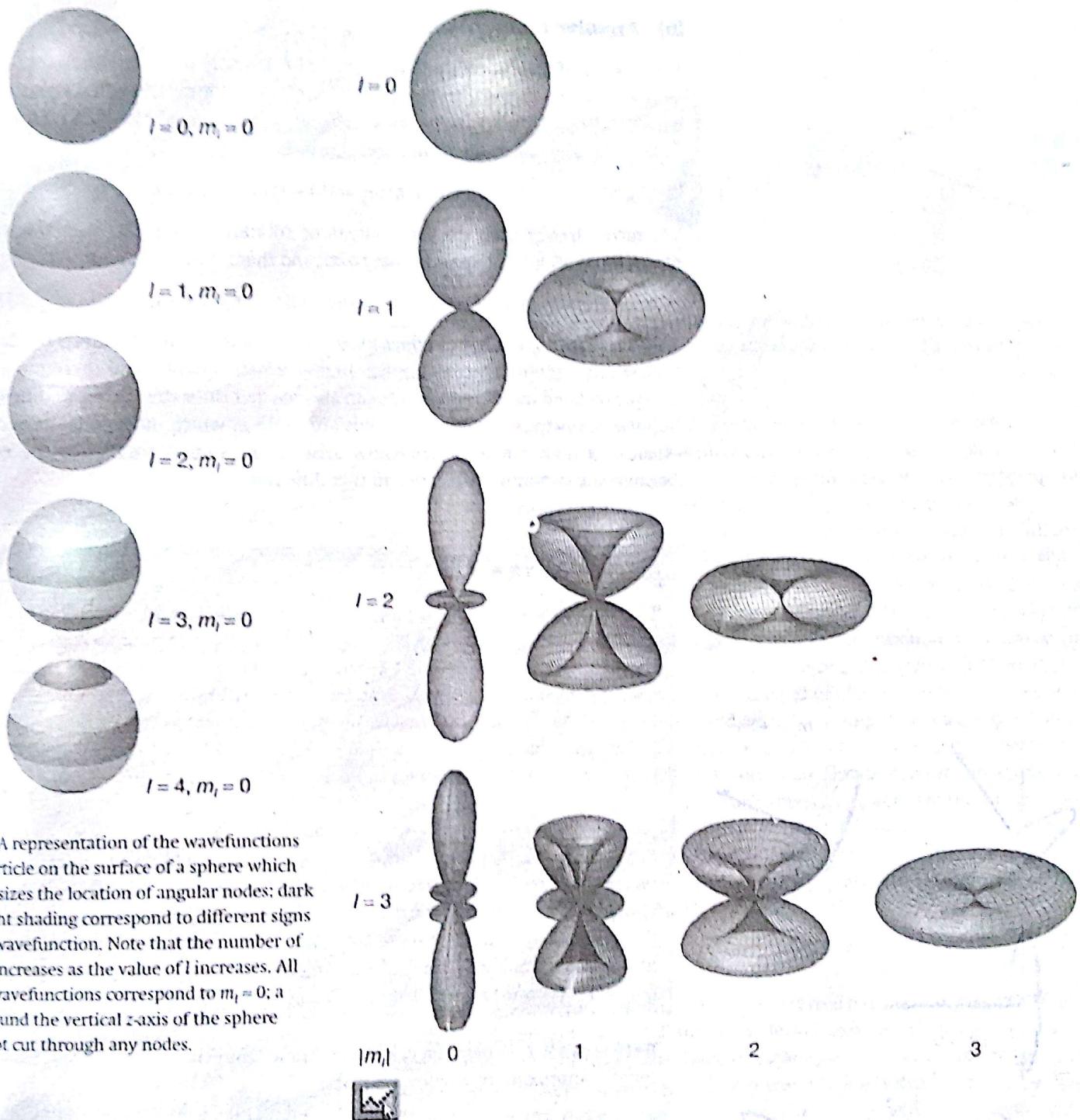
The spherical harmonics are orthogonal and normalized in the following sense:

$$\int_0^\pi \int_0^{2\pi} Y_{l',m'_l}(\theta, \phi)^* Y_{l,m_l}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{l'l} \delta_{m'_l m_l}$$

An important 'triple integral' is

$$\int_0^\pi \int_0^{2\pi} Y_{l'',m''_l}(\theta, \phi)^* Y_{l',m'_l}(\theta, \phi) Y_{l,m_l}(\theta, \phi) \sin \theta d\theta d\phi$$

= 0 unless  $m''_l = m'_l + m_l$  and  $l'', l'$ , and  $l$  can form a triangle.



**12.32** A representation of the wavefunctions of a particle on the surface of a sphere which emphasizes the location of angular nodes; dark and light shading correspond to different signs of the wavefunction. Note that the number of nodes increases as the value of  $l$  increases. All these wavefunctions correspond to  $m_l = 0$ ; a path round the vertical  $z$ -axis of the sphere does not cut through any nodes.



**12.33** A more complete representation of the wavefunctions for  $l = 0, 1, 2$ , and  $3$ . The distance of a point on the surface from the origin is proportional to the square modulus of the amplitude of the wavefunction at that point.

It also follows from the solution of the Schrödinger equation that the energy  $E$  of the particle is restricted to the values

$$E = \frac{\hbar^2}{2l} l(l+1) \quad l = 0, 1, 2, \dots \quad (12.65)$$

We see that the energy is quantized, and that it is independent of  $m_l$ . Because there are  $2l+1$  different wavefunctions (one for each value of  $m_l$ ) that correspond to the same energy, it follows that a level with quantum number  $l$  is  $(2l+1)$ -fold degenerate.

## (b) Angular momentum

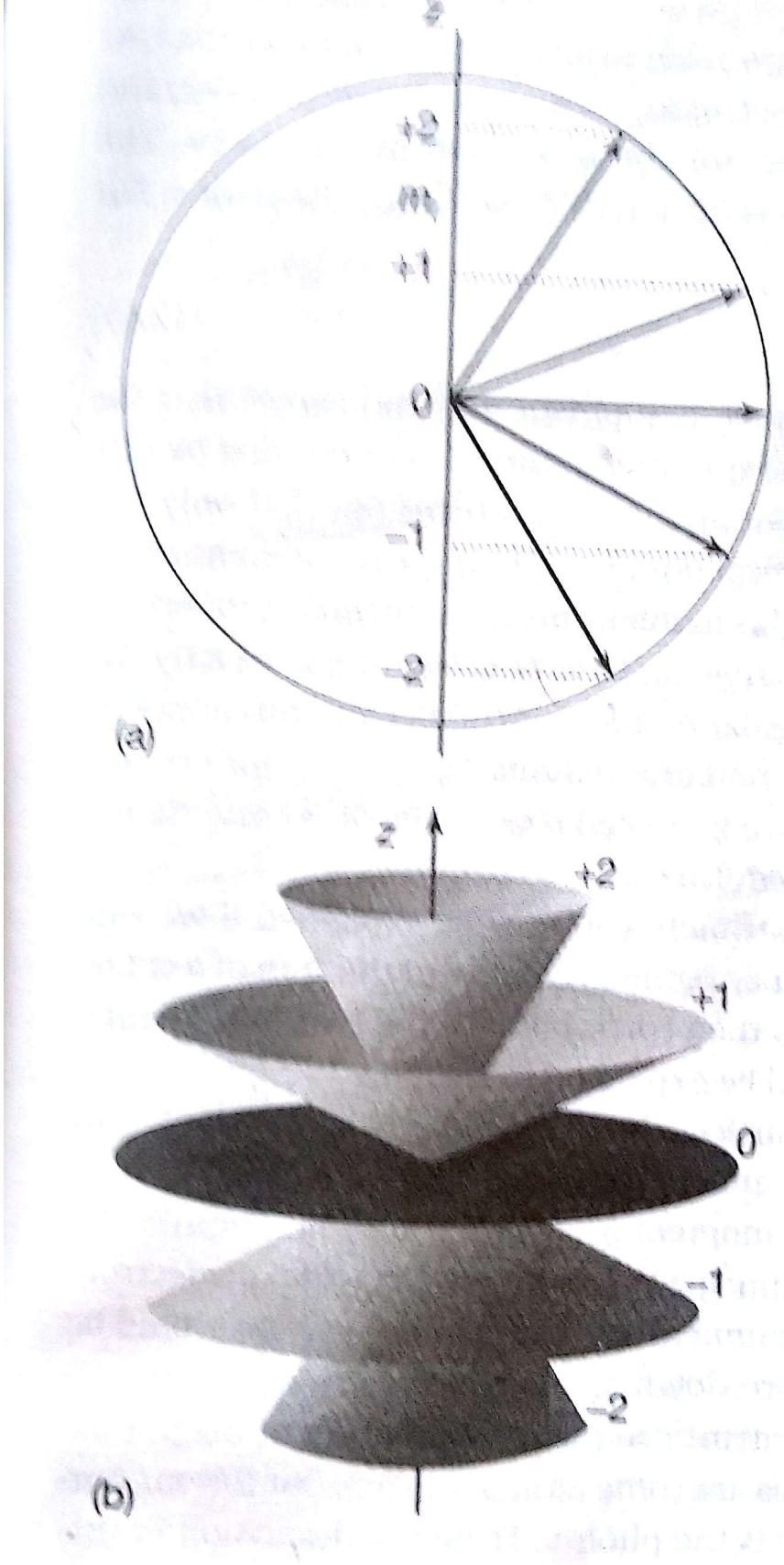
The energy of a rotating particle is related classically to its angular momentum  $J$  by  $E = J^2/2I$  (see *Further information 2*). Therefore, by comparing this equation with eqn 65, we can deduce that, because the energy is quantized, then so too is the magnitude of the angular momentum, and confined to the values

$$\text{Magnitude of angular momentum} = \{l(l+1)\}^{1/2}\hbar \quad l = 0, 1, 2, \dots \quad (12.66a)$$

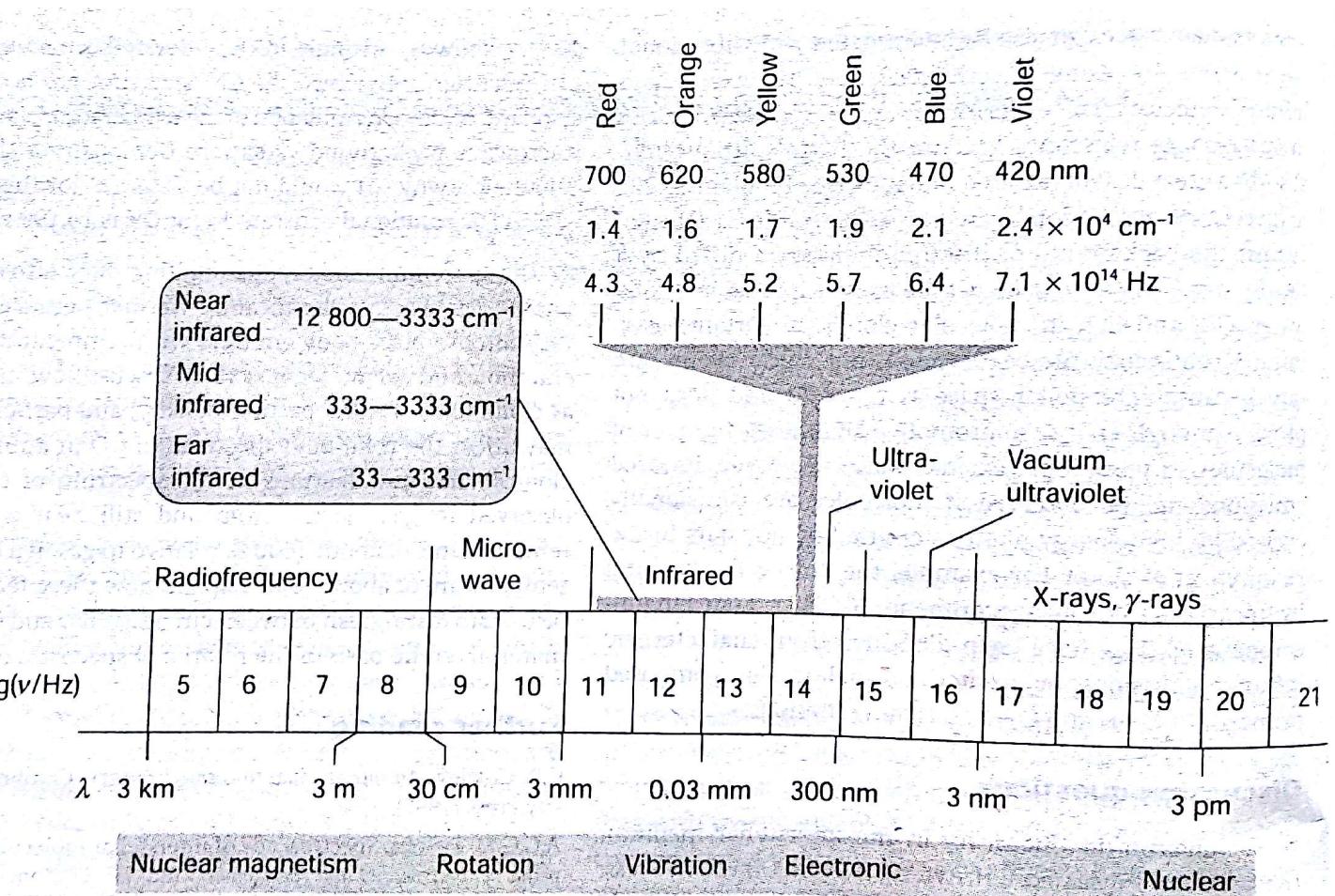
We have already seen (in the context of rotation in a plane) that the angular momentum about the  $z$ -axis is quantized, and that it has the values

$$\text{z-component of angular momentum} = m_l\hbar \quad m_l = l, l-1, \dots, -l \quad (12.66b)$$

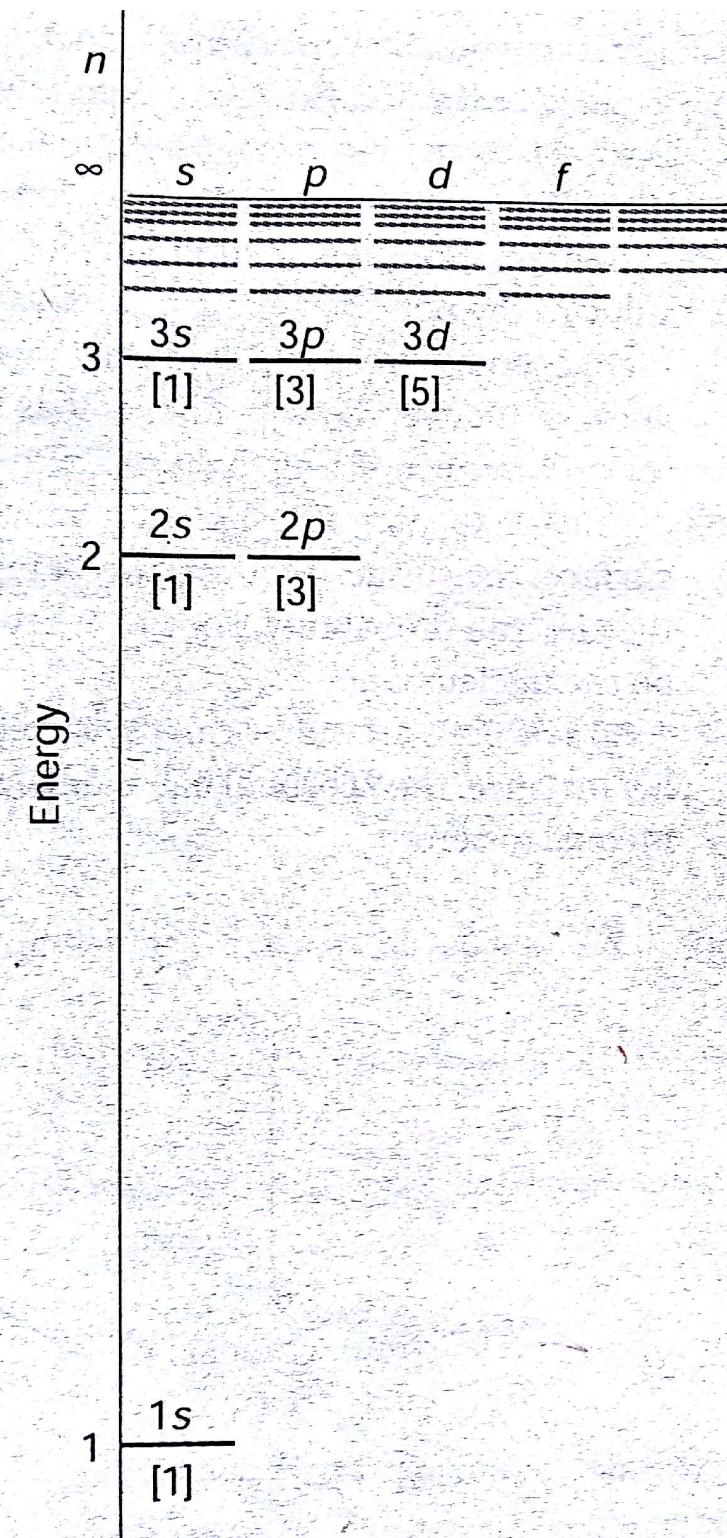
The fact that the number of nodes in  $\psi_{l,m_l}(\theta, \phi)$  increases with  $l$  reflects the fact that higher angular momentum implies higher kinetic energy, and therefore a more sharply buckled wavefunction. We can also see that the states corresponding to high angular momentum around the  $z$ -axis are those in which most nodal lines cut the equator: a high kinetic energy now arises from motion parallel to the equator because the curvature is greatest in that direction.



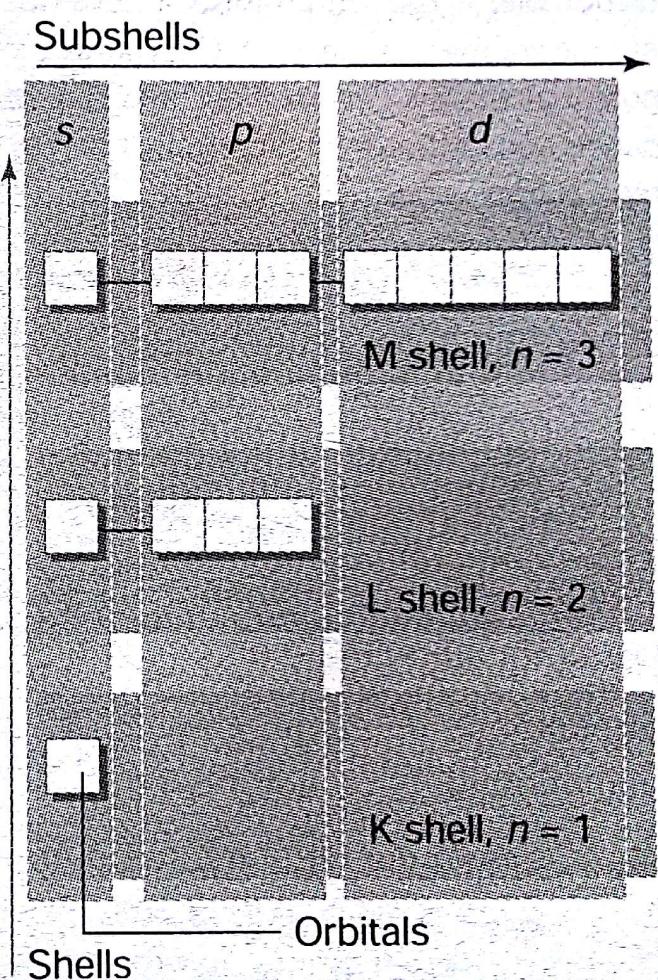
**12.36** (a) A summary of Fig. 12.34. However, because the azimuthal angle of the vector around the  $\hat{z}$ -axis is indeterminate, a better representation is as in (b), where each vector lies at an unspecified azimuthal angle on its cone.



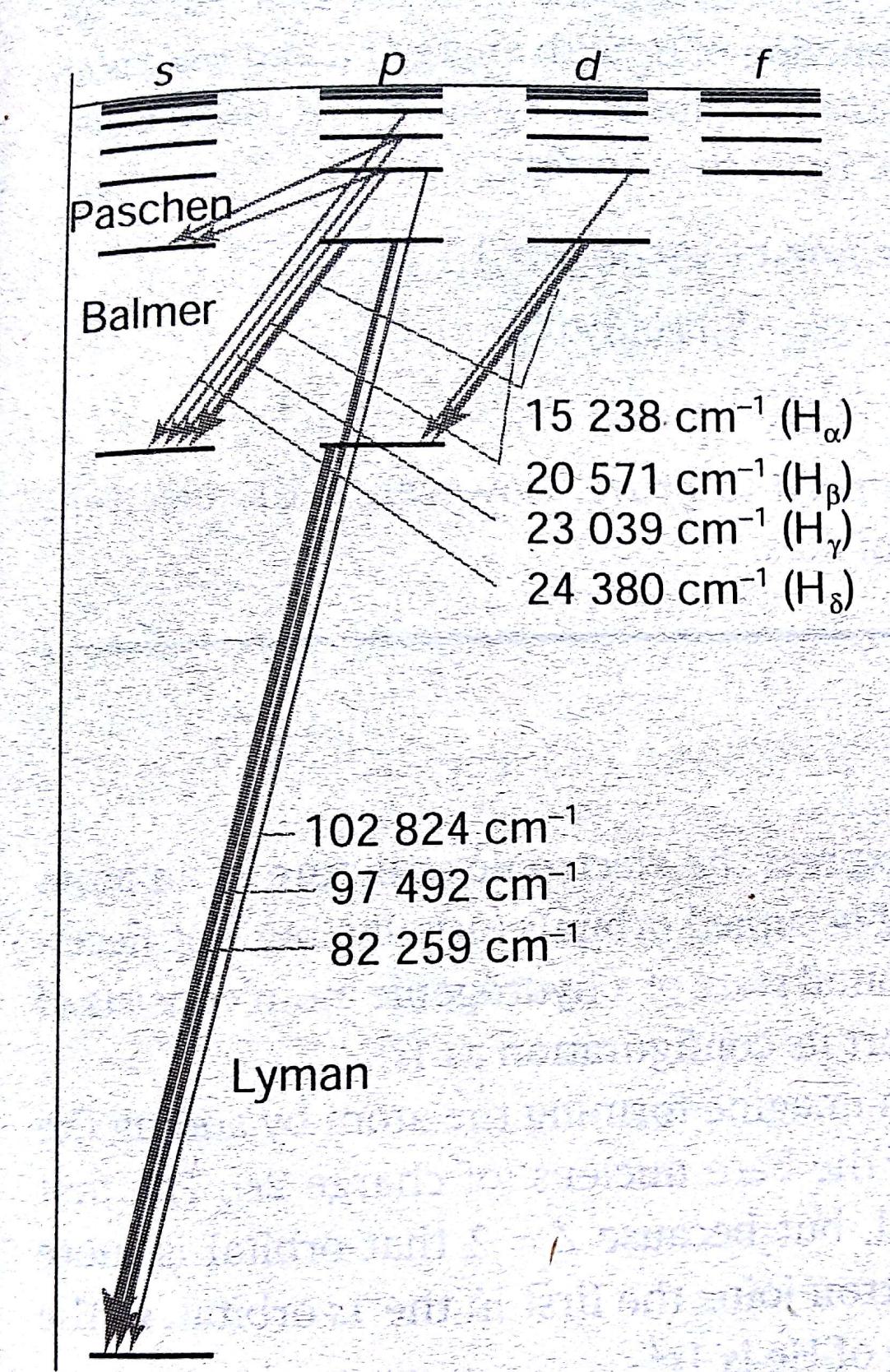
**16.1** The electromagnetic spectrum and the classification of the spectral regions. The band at the bottom of the illustration indicates the types of transitions that absorb or emit in the various regions. ('Nuclear magnetism' refers to the types of transitions discussed in Chapter 18; 'nuclear' refers to transitions within the nucleus.)



**13.8** The energy levels of the hydrogen atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. In hydrogenic atoms, all orbitals of a given shell have the same energy .



**13.9** The organization of orbitals (white squares) into subshells (characterized by  $l$ ) and shells (characterized by  $n$ ).



**13.19** A Grotrian diagram that summarizes the appearance and analysis of the spectrum of atomic hydrogen. The thicker the line, the more intense the transition.

We saw in Section 12.10 that the rate of transition between two states is proportional to the square of the transition dipole moment,  $\mu_{fi}$ , between the initial and final states, where

$$\mu_{fi} = \langle f | \mu | i \rangle \quad [13.28]$$

and  $\mu$  is the electric dipole moment operator. For a one-electron atom  $\mu$  is multiplication by  $-e\mathbf{r}$  with components  $\mu_x = -ex$ ,  $\mu_y = -ey$ , and  $\mu_z = -ez$ . If the transition dipole moment is zero, the transition is forbidden; the transition is allowed if the transition moment is nonzero. Physically, the transition dipole moment is a measure of the dipolar ‘kick’ that the electron gives to or receives from the electromagnetic field.

To evaluate a transition dipole moment, we consider each component in turn. For example, for the z-component,

$$\mu_{z,fi} = -e \langle f | z | i \rangle = -e \int \psi_f^* z \psi_i d\tau \quad (13.29)$$

To evaluate the integral, we note from Table 12.3 that  $z = (4\pi/3)^{1/2}rY_{1,0}$ , so

$$\int \psi_f^* z \psi_i d\tau = \left(\frac{4\pi}{3}\right)^{1/2} \int_0^\infty R_{n_f, l_f} r R_{n_i, l_i} r^2 dr \int_0^\pi \int_0^{2\pi} Y_{l_f, m_{l_f}}^* Y_{1,0} Y_{l_i, m_{l_i}} \sin \theta d\theta d\phi$$

It follows from the properties of the spherical harmonics (Section 12.7) that the integral

$$\int_0^\pi \int_0^{2\pi} Y_{l_f, m_{l_f}}^* Y_{1,0} Y_{l_i, m_{l_i}} \sin \theta d\theta d\phi$$

is zero unless  $l_f = l_i \pm 1$  and  $m_{l_f} = m_{l_i} + m$ . Because  $m = 0$  in the present case, the angular integral, and hence the  $z$ -component of the transition dipole moment, is zero unless  $\Delta l = \pm 1$  and  $\Delta m_l = 0$ , which is a part of the set of selection rules. The same procedure, but considering the  $x$ - and  $y$ -components, results in the complete set of rules.

### Illustration 13.3

To identify the orbitals to which a  $4d$  electron may make radiative transitions, we first identify the value of  $l$  and then apply the selection rule for this quantum number. Because  $l = 2$ , the final orbital must have  $l = 1$  or  $3$ . Thus, an electron may make a transition from a  $4d$  orbital to any  $np$  orbital (subject to  $\Delta m_l = 0, \pm 1$ ) and to any  $nf$  orbital (subject to the same rule). However, it cannot undergo a transition to any other orbital, so a transition to any  $ns$  orbital or to another  $nd$  orbital is forbidden.

**Self-test 13.6** To what orbitals may a  $4s$ -electron make radiative transitions?  
[to  $np$  orbitals only]

# TIME DEPENDENT PERTURBATION THEORY

- CONSIDER TWO QUANTUM STATES  $i$  AND  $f$
- IN THE ABSENCE OF LIGHT (AT  $t=0$ )

$$\Psi_i^D(\vec{r}, t=0) \quad D \rightarrow \text{DARK}$$

$$\Psi_f^D(\vec{r}, t=0)$$

HAMILTONIAN

$$\hat{H} = \hat{H}_0$$

TIME EVOLUTION OF  $\Psi_i^D$  AND  $\Psi_f^D$

$$\Psi_i^D(\vec{r}, t) = \Psi_i^D(\vec{r}, 0) e^{-i E_i t / \hbar}$$

$$\Psi_f^D(\vec{r}, t) = \Psi_f^D(\vec{r}, 0) e^{-i E_f t / \hbar}$$

- IN THE PRESENCE OF LIGHT

$$\text{HAMILTONIAN} \quad \hat{H} = \hat{H}_0 + \hat{H}^{(1)}$$

$$\Psi^B(\vec{r}, t) = C_i \Psi_i^D(\vec{r}, t) + C_f \Psi_f^D(\vec{r}, t)$$

$$\text{AT } t=0: \quad C_i = 1; \quad C_f = 0$$

$C_i$  AND  $C_f$  DEPEND ON TIME

$C_i^2 \rightarrow$  PROBABILITY OF FINDING THE SYSTEM IN STATE  $i$  (at a given time)

$C_f^2 \rightarrow$  PROBABILITY OF FINDING THE SYSTEM IN STATE  $f$

$$C_i^2 + C_f^2 = 1$$

CORRELATED

$$\hat{H}^{(1)} = -\vec{\mu} \cdot \vec{E} \xrightarrow{\text{DIPOLE MOMENT}} \text{ELECTRIC FIELD}$$

$$= -\mu_x E_x - \mu_y E_y - \mu_z E_z$$

CONSIDER A POLARIZED LIGHT  
( $E_x = E_y = 0; E_z \neq 0$ )

$$\hat{H}^{(1)} = -\mu_z E_z$$

$$= -\mu_z (2E_z^0 \cos(2\pi x t))$$

$$= -\mu_z (E_z^0 (e^{-i2\pi x t} + e^{i2\pi x t}))$$

$$\cdot (\hat{H}_0 + \hat{H}^{(1)}) (c_i \Psi_i^D(\vec{r}, t) + c_f \Psi_f^D(\vec{r}, t))$$

$$= -\frac{\hbar}{i} \frac{\partial}{\partial t} (c_i \Psi_i^D(\vec{r}, t) + c_f \Psi_f^D(\vec{r}, t))$$

~~$$\cdot c_i \hat{H}_0 \Psi_i^D(\vec{r}, t) + c_f \hat{H}_0 \Psi_f^D(\vec{r}, t)$$~~

$$+ c_i \hat{H}^{(1)} \Psi_i^D(\vec{r}, t) + c_f \hat{H}^{(1)} \Psi_f^D(\vec{r}, t)$$

$$= -\frac{\hbar}{i} \left[ c_i \frac{\partial \Psi_i^D(\vec{r}, t)}{\partial t} + c_f \frac{\partial \Psi_f^D(\vec{r}, t)}{\partial t} \right]$$

$$+ \Psi_i^D(\vec{r}, t) \frac{\partial c_i}{\partial t} + \Psi_f^D(\vec{r}, t) \frac{\partial c_f}{\partial t}$$

$$\cdot c_i \hat{H}^{(1)} \Psi_i^D(\vec{r}, t) + c_f \hat{H}^{(1)} \Psi_f^D(\vec{r}, t)$$

$$= -\frac{\hbar}{i} \left[ \Psi_i^D(\vec{r}, t) \frac{\partial c_i}{\partial t} + \Psi_f^D(\vec{r}, t) \frac{\partial c_f}{\partial t} \right]$$

$\times \Psi_f^{D^*}(\vec{r}, t)$  AND INTEGRATE AND USE  
THE FACT  $\int_{\vec{r}} \Psi_f^{D^*}(\vec{r}, t) \Psi_i^D(\vec{r}, t) d\vec{r} = 0$   
 $= 1; i=f$

$$\Rightarrow C_i \int_{\vec{r}} \Psi_f^{D^*}(\vec{r}, t) H^{(1)} \Psi_i^D(\vec{r}, t) d\vec{r} + C_f \int_{\vec{r}} \Psi_f^{D^*}(\vec{r}, t) H^{(1)} \Psi_f^D(\vec{r}, t) d\vec{r} = -\frac{i}{\hbar} \frac{\partial C_f}{\partial t}$$

$\Rightarrow$  APPROXIMATION: SMALL PERTURBATION  
(FIRST- ORDER)

$$C_i \rightarrow 1 ; C_f \rightarrow 0$$

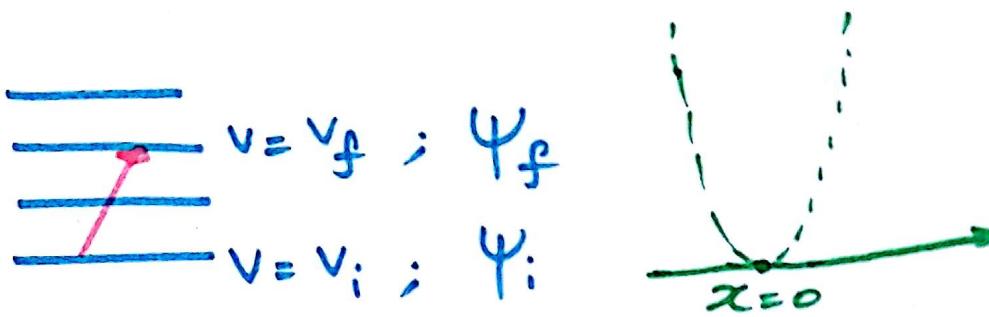
$$\frac{\partial C_f}{\partial t} \approx -\frac{i}{\hbar} \int_{\vec{r}} \Psi_f^{D^*}(\vec{r}, t) H^{(1)} \Psi_i^D(\vec{r}, t) d\vec{r}$$

$$\frac{\partial C_f}{\partial t} = \frac{-i}{\hbar} e^{+i \frac{(E_f - E_i)}{\hbar} t} \int_{\vec{r}} \Psi_f^{D^*}(\vec{r}, 0) H^{(1)} \Psi_i^D(\vec{r}, 0) d\vec{r}$$

RATE OF CHANGE OF PROBABILITY  
INTEGRATE: TIME EVOLUTION OF  $C_f$   
IF  $\frac{\partial C_f}{\partial t} = 0 \Rightarrow$  NO CHANGE IN  $C_f$   
NO TRANSITION  
 $C_f^2 \Rightarrow$  PROBABILITY  
 $H^{(1)} \Rightarrow$  TRANSITION DIPOLE  
MOMENT INTEGRAL

$\Rightarrow$  SUBSTITUTE

## SELECTION RULES FOR VIBRATIONAL TRANSITIONS



# TRANSITION DIPOLE MOMENT INTEGRAL

$$I_{i \rightarrow f} = \int \psi_f^*(\vec{r}) \hat{\mu} \psi_i(\vec{r}) d\vec{r}$$

# $\gamma$ DIPOLE MOMENT OF AN N-PARTICLE SYSTEM

$$E = \sum_{i=1}^N Q_i \frac{1}{r_i}$$

CHARGE

POSITION

$$\mu(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \approx \mu(\vec{r}_{1,0}, \vec{r}_{2,0}, \dots, \vec{r}_{N,0}) + (\vec{\nabla}_{3N} \mu) \cdot \vec{\Delta r}_{3N} + \dots$$

( IGNORE HIGHER-ORDER TERMS )

**HERE**

$E(\vec{r}_{1,0}, \vec{r}_{2,0}, \dots, \vec{r}_{N,0}) \Rightarrow$  EQUILIBRIUM CONFIGURATION (ENERGY-MINIMUM CONFIGURATION)

$\mu(\vec{\sigma}_{1,0}, \vec{\sigma}_{2,0}, \dots, \vec{\sigma}_{N,0}) \rightarrow$  PERMANENT DIPOLE MOMENT  
 (MAY OR MAY NOT BE EQUAL TO ZERO)

$$\nabla_{\vec{m}^2} = \left( \frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \dots, \frac{\partial}{\partial x_n} \right)$$

$$\Delta_{3^n} = \left( \frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \dots, \frac{\partial}{\partial x_n} \right)$$

FOR A DIATOMIC MOLECULE

$$x = R_{AB} - R_0$$

$$\mu(x) = \mu(x=0) + \left. \frac{d\mu}{dx} \right|_{x=0} x + \dots$$

$$I_{i \rightarrow f} = \int_x \Psi_f^*(x) \left[ \mu(x=0) + \left. \frac{d\mu}{dx} \right|_{x=0} x \right] \Psi_i(x) dx$$

$$= \mu(x=0) \int_x \Psi_f^*(x) \Psi_i(x) dx + \left. \frac{d\mu}{dx} \right|_{x=0} \int_x \Psi_f^*(x) x \Psi_i(x) dx$$

0 ( $\Psi_f$  AND  $\Psi_i$  ARE  
ORTHOGONAL)

$$I_{i \rightarrow f} \approx \boxed{\left. \frac{d\mu}{dx} \right|_{x=0}} \quad \boxed{\int_x \Psi_f^*(x) x \Psi_i(x) dx}$$

FOR  $I_{i \rightarrow f} \neq 0$ ;

$$\boxed{\left. \frac{d\mu}{dx} \right|_{x=0} \neq 0} \quad \text{SELECTION RULE 1}$$

$$\boxed{\int_x \Psi_f^*(x) x \Psi_i(x) dx \neq 0} \quad \text{SELECTION RULE 2}$$

$$\text{CONSIDER} \quad \int_x \Psi_f^*(x) \approx \Psi_i(x) dx$$

RECALL: FOR AN ONE-DIMENSIONAL QUANTUM HARMONIC OSCILLATOR

$$\Psi_v(x) = N_v H_v(q) e^{-\frac{q^2}{2}}$$

HERE  $N_v = \left( \frac{1}{\alpha \pi^{1/2} 2^v v!} \right)^{1/2}$

$$\alpha = \left( \frac{\hbar}{m\omega} \right)^{1/2} \quad q = \frac{x}{\alpha} \quad ; \quad \alpha = \left( \frac{\hbar^2}{mk} \right)^{1/4}$$

$H_v(q) \rightarrow \text{HERMITE POLYNOMIAL}$

RECURRENCE OR RECURSION RELATION:

$$H_{v+1}(q) = 2q H_v(q) - 2v H_{v-1}(q)$$

$$\Rightarrow q H_v(q) = \frac{H_{v+1}(q) + 2v H_{v-1}(q)}{2}$$

$$\times N_v e^{-q^2/2} \text{ ON BOTH SIDES}$$

$$q \Psi_v(x) = \frac{\left( \frac{N_v}{N_{v+1}} \right) \Psi_{v+1}(x) + 2v \left( \frac{N_v}{N_{v-1}} \right) \Psi_{v-1}(x)}{2}$$

$$\approx \Psi_v(x) = \left( \frac{\alpha}{2} \right) \left[ \frac{N_v}{N_{v+1}} \Psi_{v+1}(x) + 2v \left( \frac{N_v}{N_{v-1}} \right) \Psi_{v-1}(x) \right]$$

$$\int_x \Psi_{v_f}^*(x) \propto \Psi_{v_i}(x) dx$$

$$= \int_x \Psi_{v_f}^*(x) \left(\frac{\alpha}{2}\right) \left[ \frac{N_{v_i}}{N_{v_{i+1}}} \Psi_{v_{i+1}}(x) + 2v_i \left(\frac{N_{v_i}}{N_{v_{i-1}}}\right) \Psi_{v_{i-1}}(x) \right] dx$$

$$= \left(\frac{\alpha}{2}\right) \frac{N_{v_i}}{N_{v_{i+1}}} \int_x \Psi_{v_f}^*(x) \Psi_{v_{i+1}}(x) dx$$

$$+ \left(\frac{\alpha}{2}\right) \left(\frac{2v_i N_{v_i}}{N_{v_{i-1}}}\right) \int_x \Psi_{v_f}^*(x) \Psi_{v_{i-1}}(x) dx$$

FIRST INTEGRAL

~~$\int_x \Psi_{v_f}^*(x) \Psi_{v_{i+1}}(x) dx \neq 0$~~

ONLY WHEN  $v_f = v_i + 1$

SECOND INTEGRAL

$$\Rightarrow \Delta v = v_f - v_i = +1$$

$$\int_x \Psi_{v_f}^*(x) \Psi_{v_{i-1}}(x) dx \neq 0$$

ONLY WHEN  $v_f = v_i - 1$

$$\Rightarrow \Delta v = v_f - v_i = -1$$

SELECTION RULE 2 :

$$\Delta v = \pm 1$$

## HERMITE POLYNOMIALS

$$\frac{d^2 H_v(y)}{dy^2} - 2y \frac{dH_v(y)}{dy} + 2v H_v(y) = 0$$

THE SOLUTIONS OF THIS DIFFERENTIAL EQUATION ARE HERMITE POLYNOMIALS

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$

## USING LADDER OPERATORS:

$$Q = \left( \frac{m\omega}{\hbar} \right)^{\frac{1}{2}} z$$

LADDER UP OPERATOR  $b^+ = \frac{1}{\sqrt{2}} \left( \frac{d}{dz} + Q \right)$

$$b^+ \Psi_v(z) = C_+ \Psi_{v+1}(z)$$

LADDER DOWN OPERATOR  $b^- = \frac{1}{\sqrt{2}} \left( \frac{d}{dz} - Q \right)$

$$b^- \Psi_v(z) = C_- \Psi_{v-1}(z)$$

$$Q = \frac{b^+ + b^-}{\sqrt{2}}$$

$$\Rightarrow z = \sqrt{\frac{\hbar}{m\omega}} \left( \frac{b^+ + b^-}{\sqrt{2}} \right)$$

$$z \Psi_{v_i}(z) = \sqrt{\frac{\hbar}{m\omega}} \left( \frac{b^+ \Psi_{v_i}(z) + b^- \Psi_{v_i}(z)}{\sqrt{2}} \right)$$

$$= \sqrt{\frac{\hbar}{m\omega}} \left( \frac{C_{+v_i} \Psi_{v_i+1}(z) + C_{-v_i} \Psi_{v_i-1}(z)}{\sqrt{2}} \right)$$

$$\int \Psi_{v_f}^*(z) z \Psi_{v_i}(z) dz$$

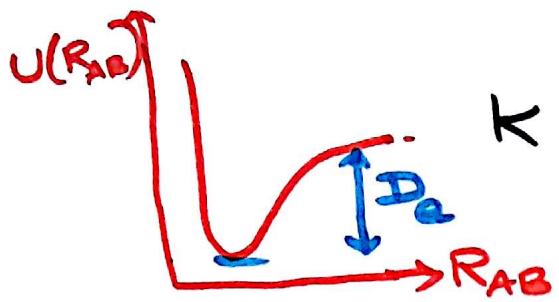
$$= B \int_z \Psi_{v_f}^*(z) \Psi_{v_i+1}(z) dz$$

$$+ D \int_z \Psi_{v_f}^*(z) \Psi_{v_i-1}(z) dz$$

$$\Rightarrow \Delta V = V_f - V_i = \pm 1$$

## ANHARMONICITY

- HARMONIC POTENTIAL  $U(R_{AB}) = \frac{1}{2} K (R_{AB} - R_0)^2$



$$K = \left. \frac{d^2 U(R_{AB})}{d R_{AB}^2} \right|_{R_{AB}=R_0}$$

$$\frac{1}{2} K x^2$$

$$x = R_{AB} - R_0$$

$$R_{AB} = R_0$$

- ANHARMONIC POTENTIAL (OR) MORSE POTENTIAL

$$U(R_{AB}) = D_e \left[ 1 - e^{-\alpha(R_{AB} - R_0)} \right]^2$$

$x = R_{AB} - R_0$

$$= D_e \left[ 1 - \left( 1 - \alpha x + \frac{\alpha^2 x^2}{2} - \frac{1}{6} \alpha^3 x^3 + \dots \right) \right]^2$$

$x \rightarrow 0$ ; IGNORE HIGHER ORDER TERMS

$$U(R_{AB}) \approx D_e \frac{\alpha^2 x^2}{2} \quad K = 2D_e \alpha^2$$

HARMONIC FORM

WHAT IF  $x$  IS LARGE!

$$U(R_{AB}) \approx D_e \left[ \left( \alpha x - \frac{\alpha^2 x^2}{2} \right)^2 \right]$$

PERTURBATION  
TO HARMONIC  
POTENTIAL

$$= D_e \left( \alpha^2 x^2 + \frac{\alpha^4 x^4}{4} - 2(\alpha x) \left( \frac{\alpha^2 x^2}{2} \right) \right)$$

$$= \frac{1}{2} (2D_e \alpha^2) x^2 - \alpha^3 x^3 + \frac{\alpha^4 x^4}{4} - \dots$$

HARMONIC

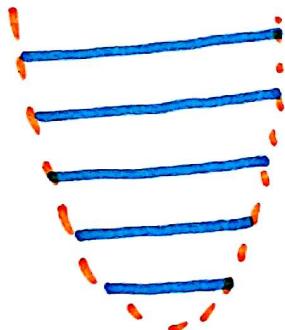
ANHARMONIC

$$E_v^{\text{HARMONIC}} = (v + \frac{1}{2}) \hbar\omega$$

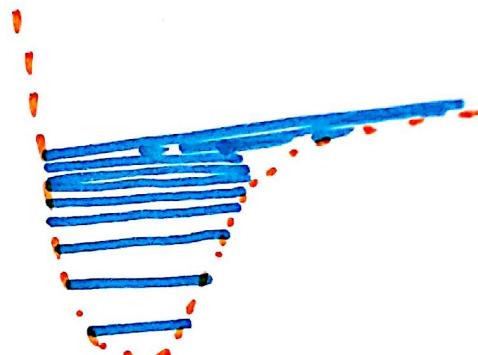
$$E_v^{\text{ANHARMONIC}} = (v + \frac{1}{2}) \hbar\omega - (v + \frac{1}{2})^2 \hbar\omega X_e$$

ANHARMONICITY  
CONSTANT  
(POSITIVE)

$$E_v^{\text{GENERAL}} = (v + \frac{1}{2}) \hbar\omega - (v + \frac{1}{2})^2 \hbar\omega X_e + (v + \frac{1}{2})^3 \hbar\omega T_e + \dots$$



HARMONIC  
ENERGY LEVELS  
ARE EQUALLY  
SPACED



ANHARMONIC  
SPACING BETWEEN  
SUCCESSIVE LEVELS  
DECREASES WITH  
INCREASING  $v$   
(EFFECT OF ANHARMONICITY  
INCREASES WITH  $v$ )

SELECTION RULES CHANGE:  
 $|\Delta v| > 1 \Rightarrow$  ARE ALSO ALLOWED  
(WEAK)

$$\begin{aligned} v=0 &\rightarrow v=1 \\ v=0 &\rightarrow v=2 \\ v=0 &\rightarrow v=3 \end{aligned}$$

FUNDAMENTAL  
FIRST OVERTONE  
SECOND OVERTONE