

## 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  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.

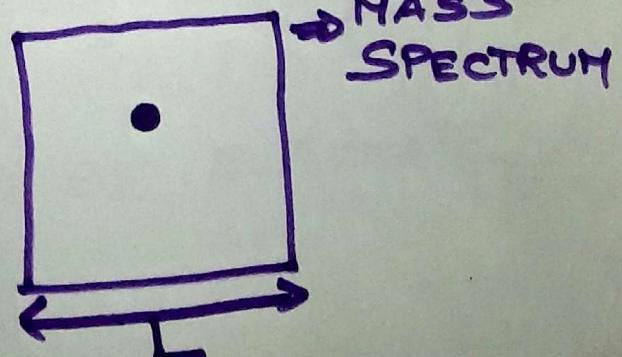
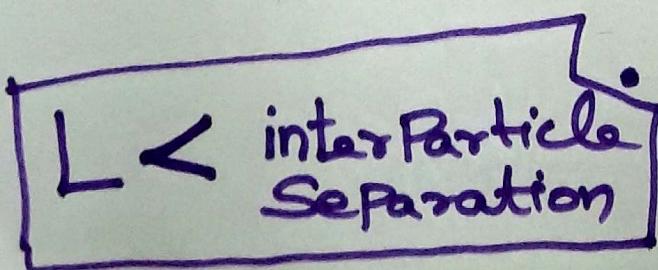
# SPECTROSCOPY

## KNOWN FACTS :-

- ① ATOMS ARE MADE OF ELECTRONS, PROTONS, NEUTRONS
- ② NUCLEUS + ELECTRONS  
    ↓                    ↓  
    CENTER              (CORBITS)
  - REVOLVE AROUND
  - CLOUD OF ELECTRONS
  - ORBITALS
- ③ ATOMS CAN BOND WITH OTHER ATOMS  $\rightarrow$  MOLECULES
  - DIFFERENT TYPES OF BONDS  
    —    x    —    x    —

## 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;

$\langle$  KINETIC ENERGY  $\rangle \Rightarrow$  TEMPERATURE;

$\bullet \Rightarrow$  TIME RESOLUTION

$t_1$

$t_2$

SPEED  $\downarrow$  CAN BE ESTIMATED!

③ HOW ARE THE ELECTRONS  
DISTRIBUTED IN THE ATOM?



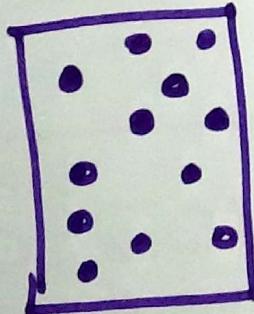
WILL IT CHANGE WITH  
THE POSITION OF THE ATOM?

④ WHAT IS THE SIZE OF THE  
ATOM?

SIZE OF THE NUCLEUS?

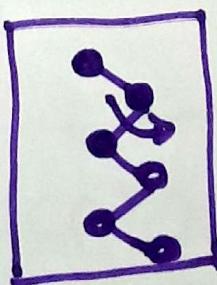
SIZE → CLASSICAL (van der  
WALL RADIUS)  
SIZE → QM

INCREASE COMPLEXITY:



N PARTICLE  
SYSTEM

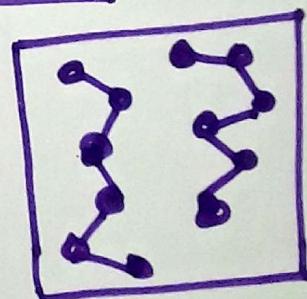
⇒ ATOMIC  
INTERACTIONS



SINGLE  
MOLECULE  
⇒ BONDS

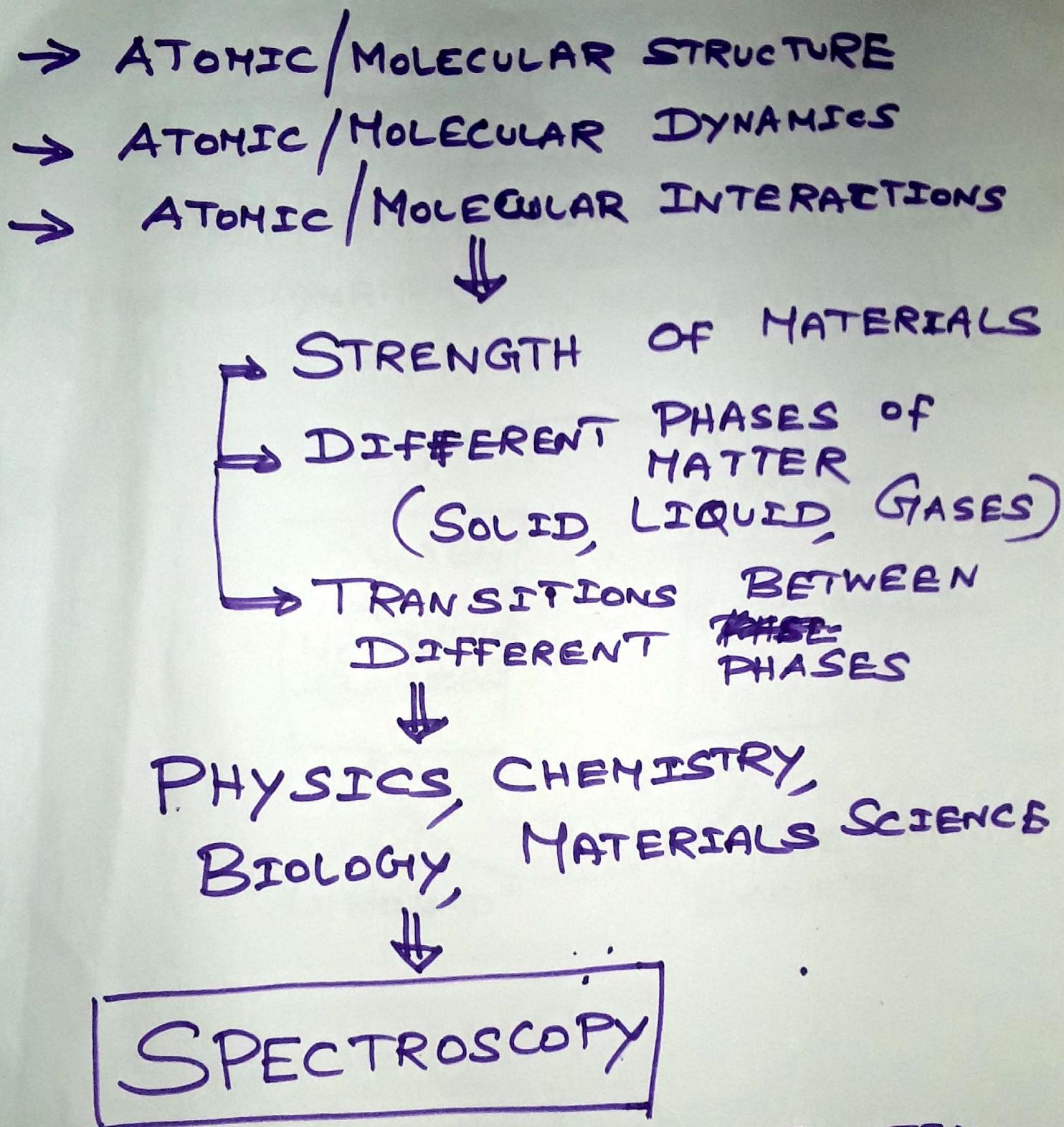
⇒ STRENGTHS

⇒ RELATIVE  
MOTION OF ATOMS



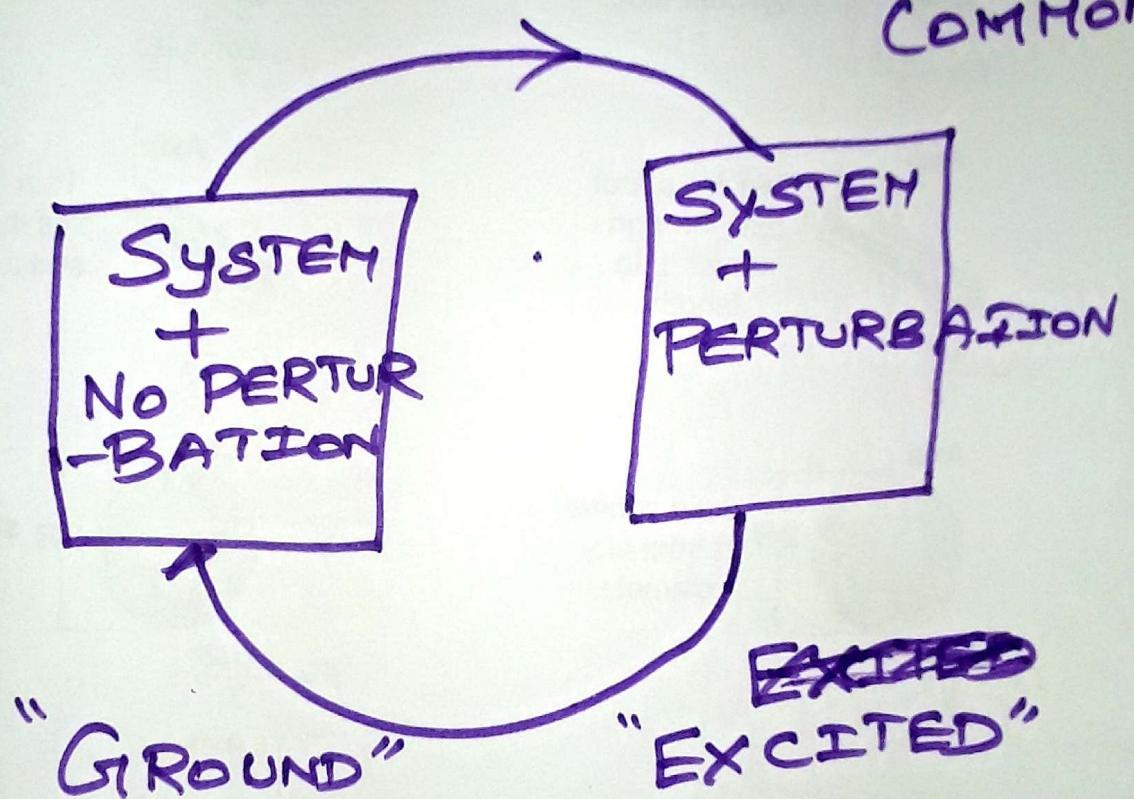
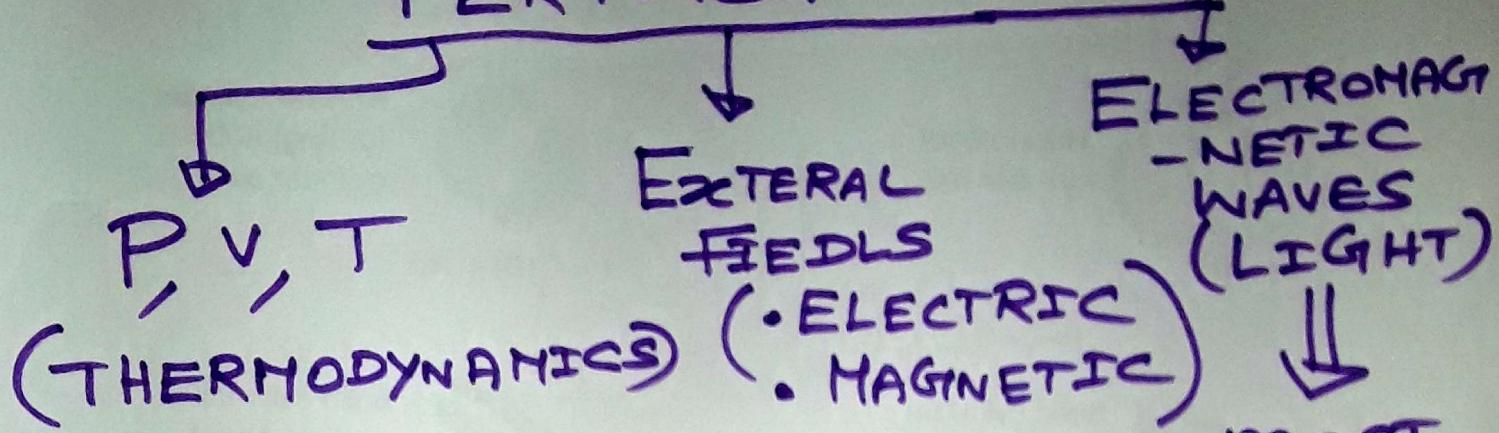
N MOLECULES  
⇒ MOLECULAR  
INTERACTION - NS

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

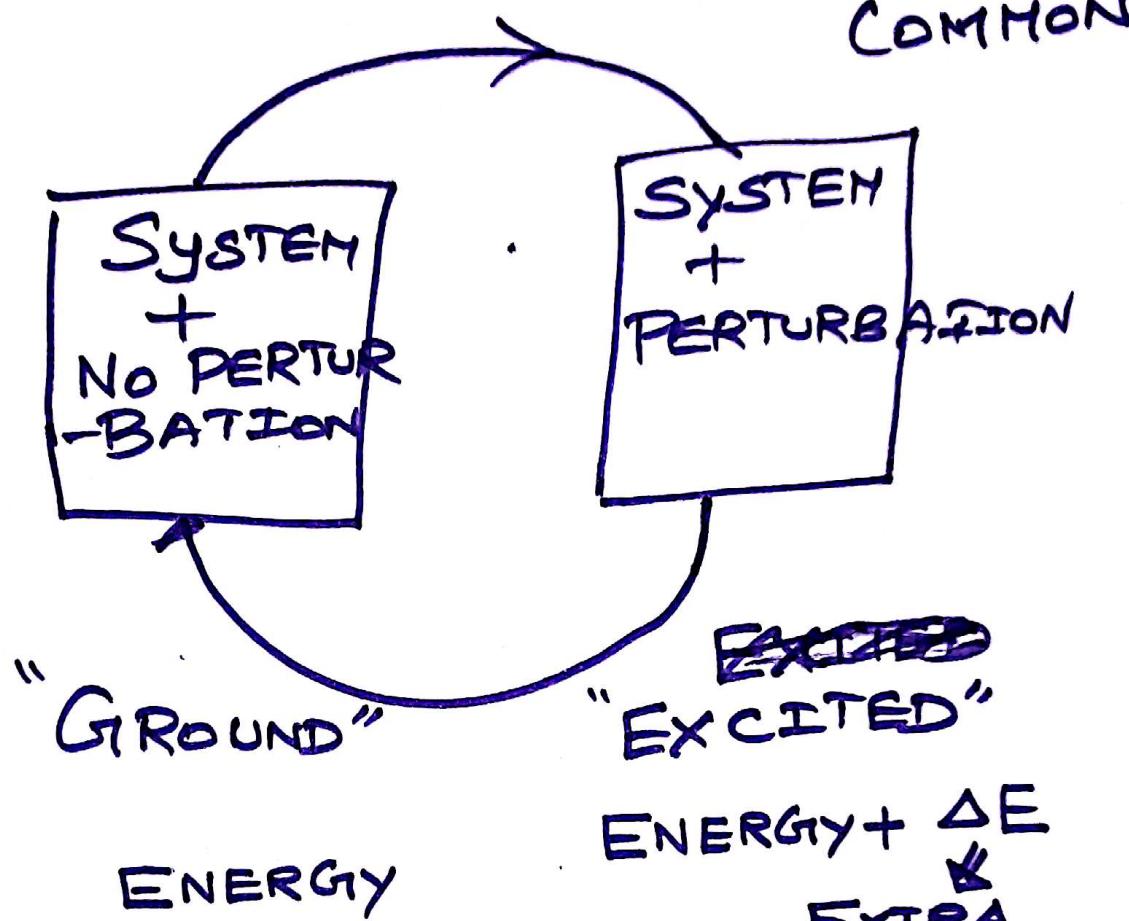
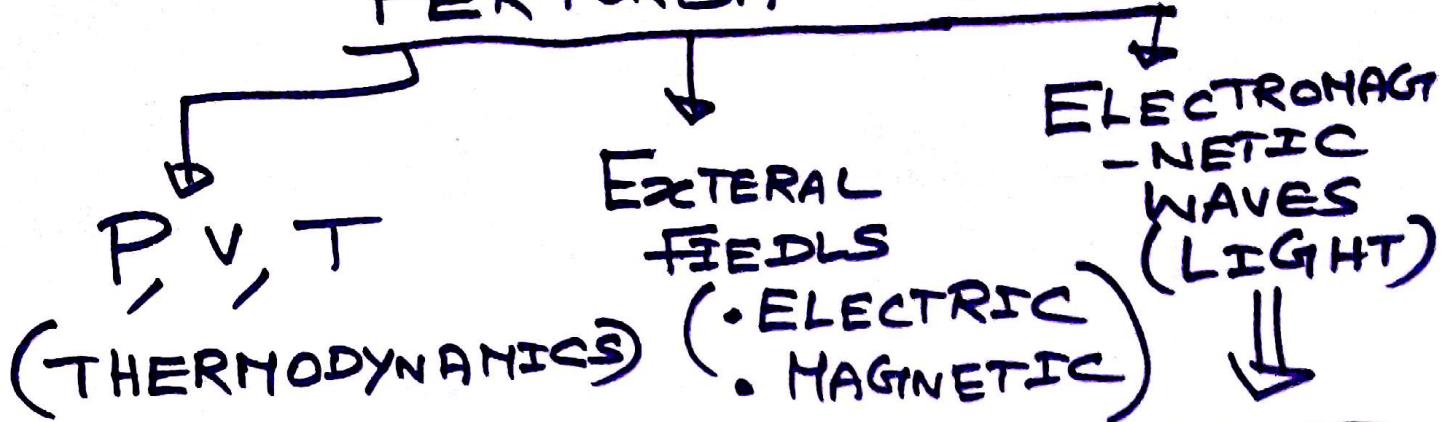


TO UNDERSTAND THE SYSTEM,  
YOU MUST DISTURB/ PERTURB  
IT! ↗ STUDY HOW THE  
SYSTEM RESPONDS TO  
THE PERTURBATION!

# PERTURBATIONS



# PERTURBATIONS



HAMILTONIAN:

$$H_0$$

SMALL PERTURBATION

$$\Delta H \rightarrow 0$$

LARGE PERTURBATION

$$\Delta H \gg 0$$

$$H_0 + \Delta H$$

$$H_p = \Delta H$$

$$H_0 + H_p$$

PERTURBATIVE PART OF THE HAMILTONIAN

# MANY-BODY SYSTEMS

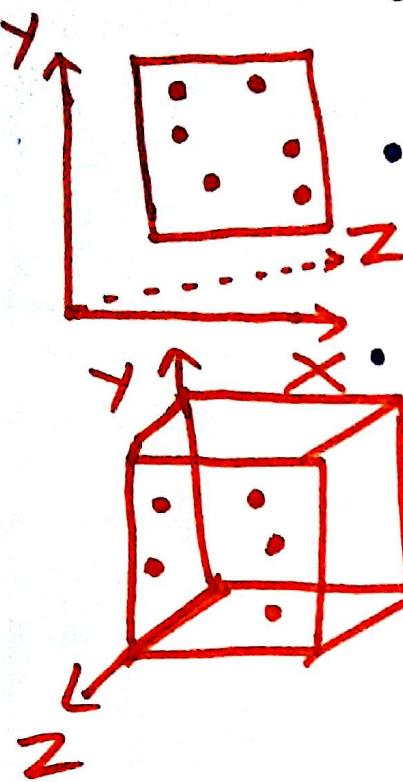
## → THERMODYNAMICS

- $P, V, T, n$ ; 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



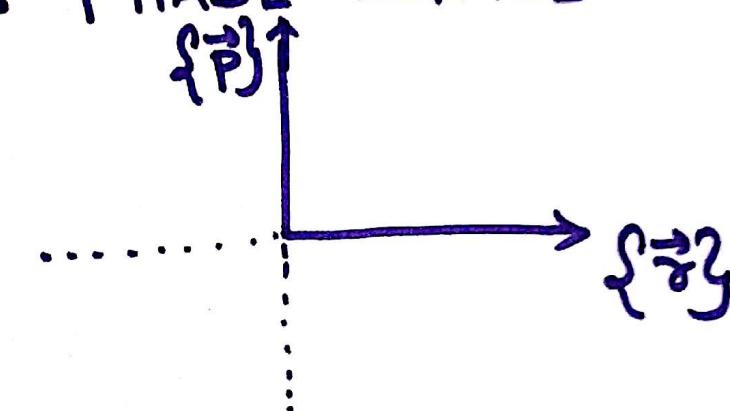
$$\{\vec{r}\} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

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:

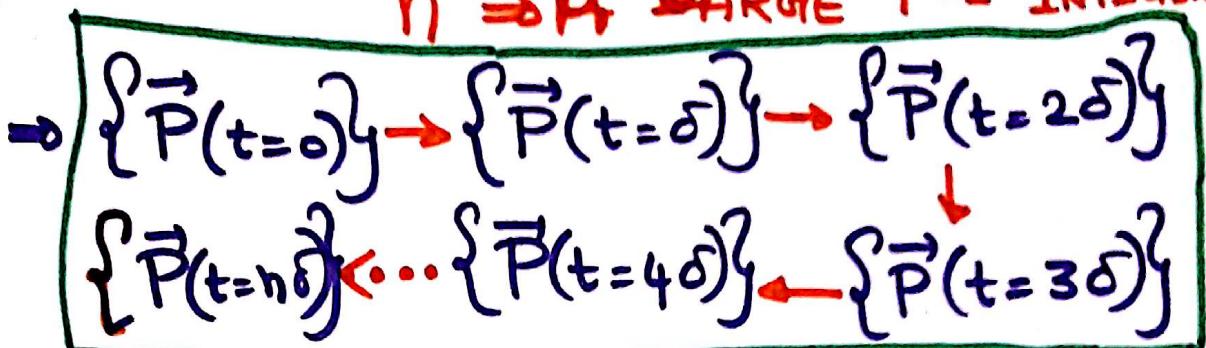
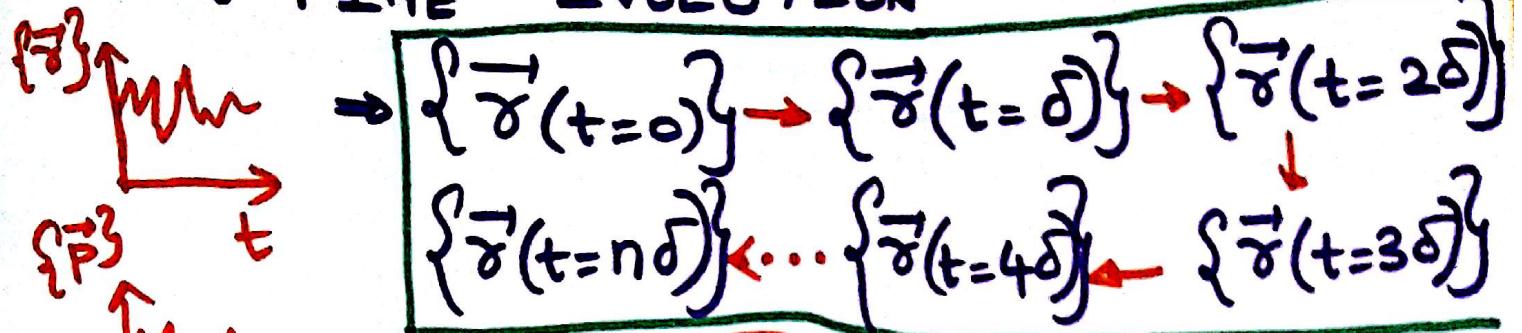
AT TIME  $t=0$ :

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

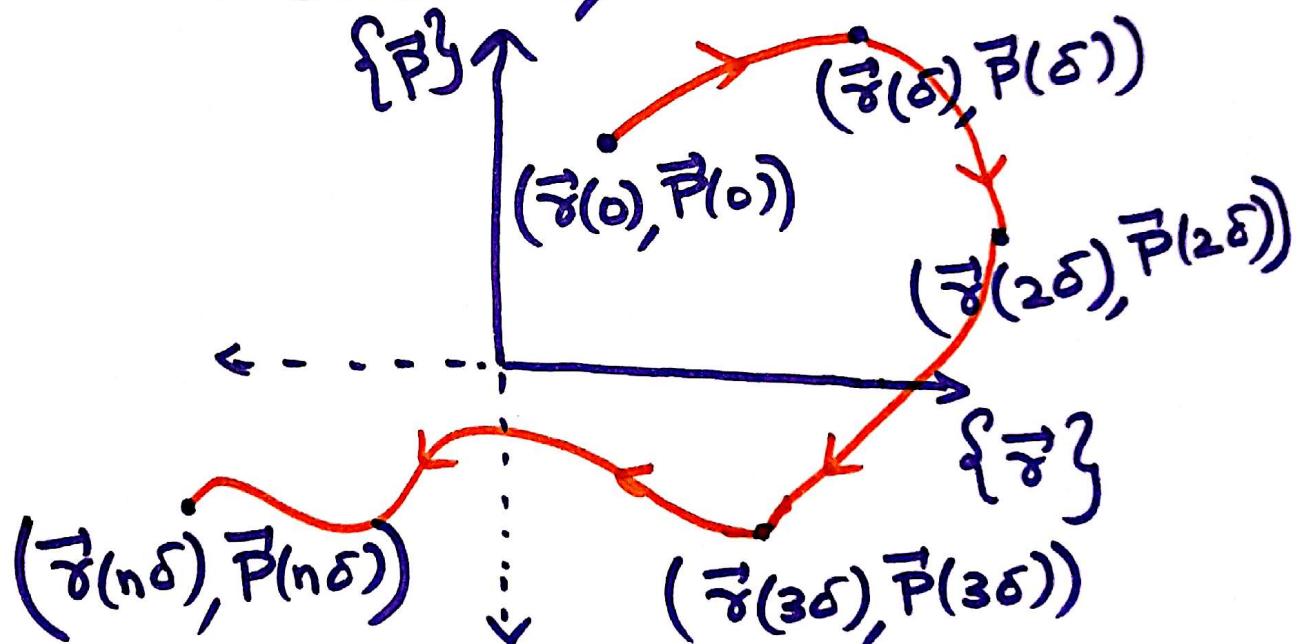
X-RAY DIFFRACTION      NMR      RANDOM

MAXWELL-BOLTZMANN DISTRIBUTION

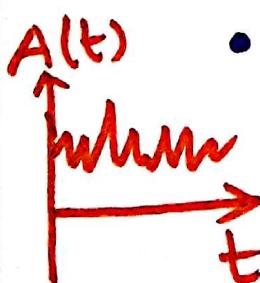
## • TIME EVOLUTION



## • TRAJECTORY ON PHASE SPACE



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



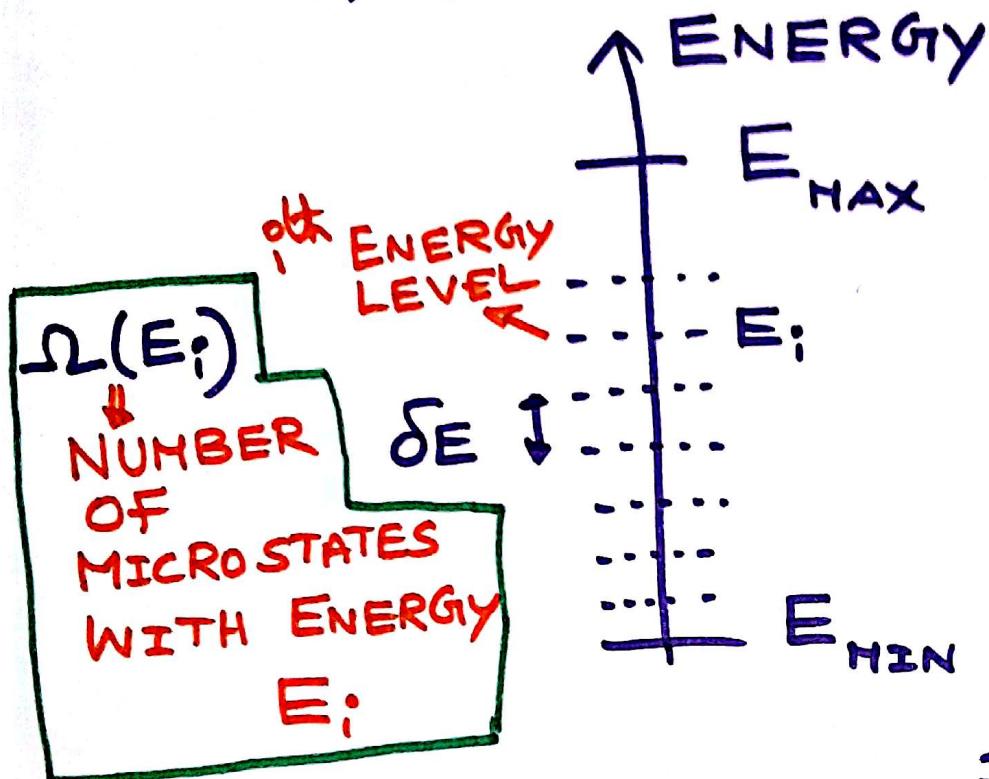
$A(t) = A(\{v(t)\}, \{P(t)\})$

TIME EVOLUTION of "A" CAN BE STUDIED

# ENERGY-LEVEL DIAGRAM

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

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



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

CAN VARY

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

SYSTEM CAN TRANSIT BETWEEN DIFFERENT ENERGY LEVELS

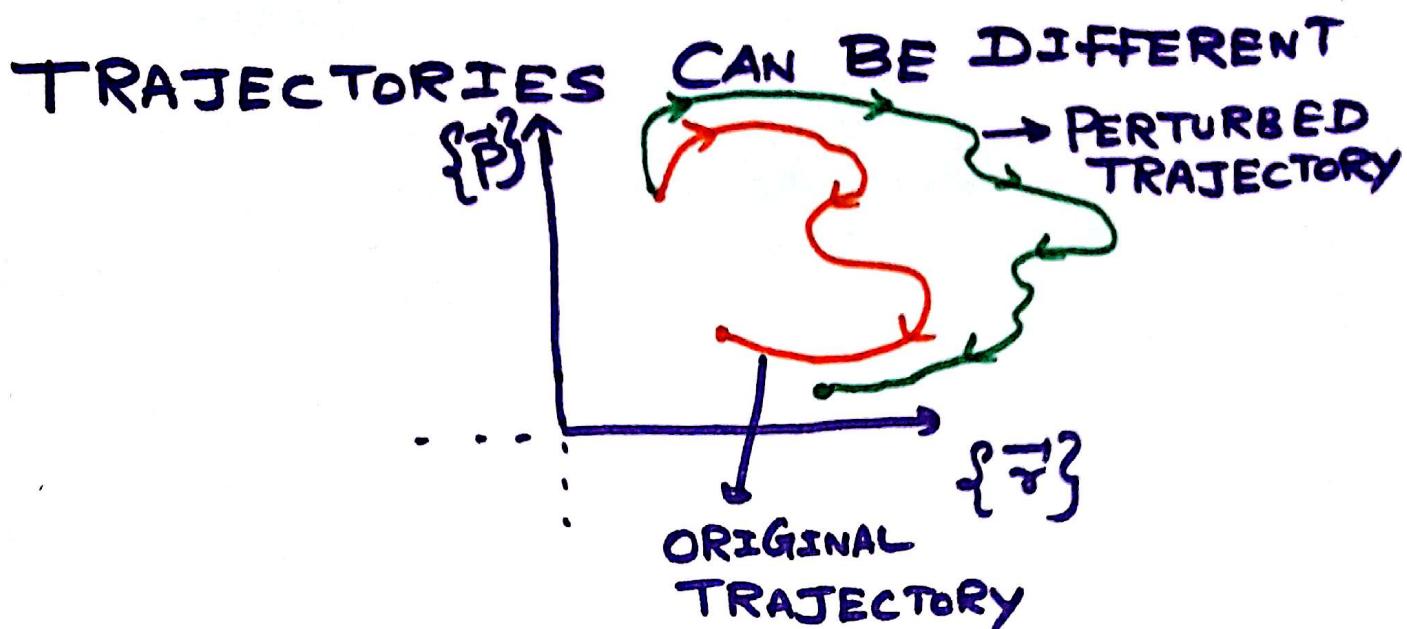
COMPARE ORIGINAL AND PERTURBED SYSTEMS

# COMPARE ORIGINAL AND PERTURBED SYSTEMS

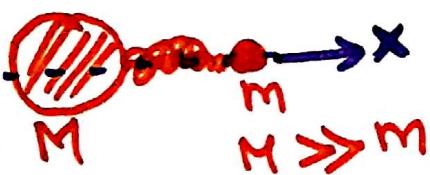
ORIGINAL SYSTEM:

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

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



EXAMPLE: ONE-DIMENSIONAL SIMPLE HARMONIC OSCILLATOR (CLASSICAL)



REDUCED MASS

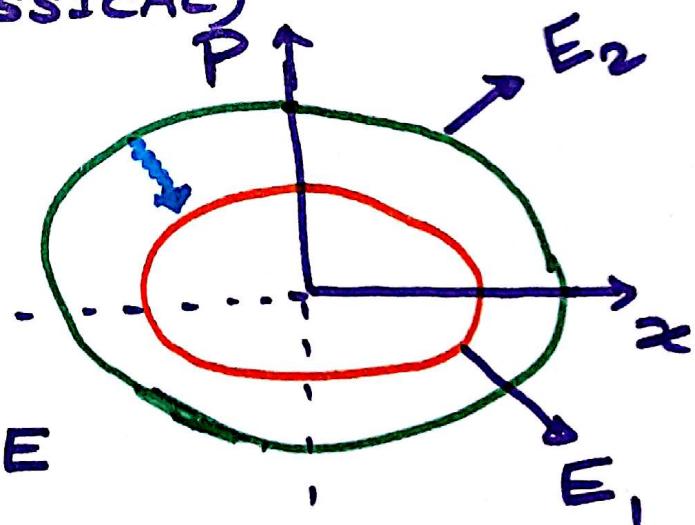
$$\mu = \frac{Mm}{M+m} \approx m$$

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

SET  $H_0 = E$  INITIALLY

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

ELLIPSE



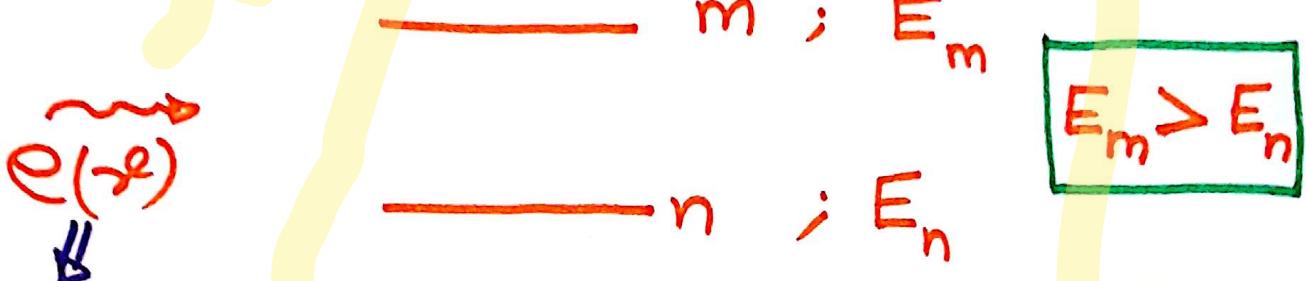
$$E_2 > E_1$$

$$E_2 = E_1 + E_p$$

# QUANTUM THEORY OF RADIATION

- A. EINSTEIN (1917)

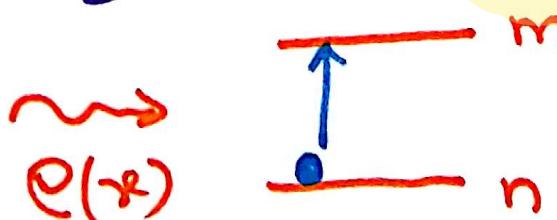
- ABSORPTION
- EMISSION 
- SPONTANEOUS
- STIMULATED
- TWO-LEVEL SYSTEM



$N_n \Rightarrow$  NUMBER OF ATOMS IN THE 'n' STATE  
 $N_m \Rightarrow$  NUMBER OF ATOMS IN THE 'm' STATE  
 $\tau_n, \tau_m \Rightarrow$  LIFETIMES

- ATOMS CAN ABSORB ENERGY FROM THE RADIATION AND UNDERGO THE RADIATION  $n \rightarrow m$  TRANSITION (IN THE PRESENCE OF EXTERNAL RADIATION)

$\Rightarrow$  STIMULATED ABSORPTION



$$E_m - E_n = h\nu$$

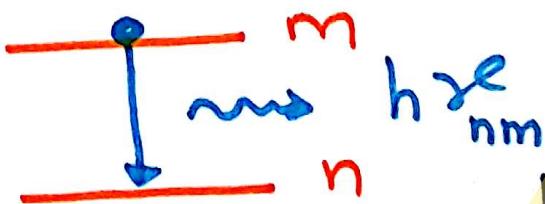
- SIGNATURE OF ABSORPTION  
 $N_n$  SHOULD DECREASE
- RATE OF ABSORPTION

$$-\frac{dN_n}{dt} \propto N_n \epsilon(\gamma_{\text{nm}})$$

$$\frac{dN_n}{dt} = -B N_n \epsilon(\gamma_{\text{nm}})$$

PROPORTIONALITY  
CONSTANT

- SPONTANEOUS EMISSION:  
→ AN EXITED ATOM CAN SPONTANEOUSLY JUMP FROM THE UPPER LEVEL TO THE LOWER LEVEL (IN THE ABSENCE OF EXTERNAL RADIATION)



$h \rightarrow$  PLANCK'S  
CONSTANT

⇒ LIGHT OF ENERGY  $h\epsilon_{\text{nm}}$   
IS EMITTED

- RATE OF SPONTANEOUS EMISSION:

$$\frac{dN_m}{dt} = -A N_m$$

PROPORTIONALITY  
CONSTANT

$A, B$   
EINSTEIN  
COEFFICIENTS

- AT EQUILIBRIUM (at TEMPERATURE  $T$ )

$K_B \rightarrow$  BOLTZMANN CONSTANT

$$N_n \propto e^{-\frac{E_n}{k_B T}}$$

$$N_m \propto e^{-\frac{E_m}{k_B T}}$$

(BOLTZMANN'S IDEA)

$$\frac{N_m}{N_n} = e^{-\frac{(E_m - E_n)}{k_B T}}$$

- USING BOHR'S IDEA

$$\frac{N_m}{N_n} = e^{-\frac{h \gamma_{nm}}{k_B T}}$$

- AT EQUILIBRIUM

$$\frac{dN_n}{dt} = \frac{dN_m}{dt}$$

$$\rho(\gamma_{nm}) = \frac{A N_m}{B N_m}$$

$$\rho(\gamma_{nm}) = \left(\frac{A}{B}\right) e^{-\frac{h \gamma_{nm}}{k_B T}}$$

• WIEN'S DISTRIBUTION LAW

$$\Phi(\frac{h\gamma l}{nm}) = \alpha \gamma l^3 \frac{e^{-\frac{h\gamma l}{nm}}}{k_B T}$$

↓ CONSTANT

ACCURATELY DESCRIBES THE HIGH- $\gamma l$  REGION OF THE SPECTRUM OF THERMAL OR BLACK BODY RADIATION.

$$\Rightarrow \frac{A}{B} = \alpha \gamma l^3$$

• PLANCK'S DISTRIBUTION LAW DESCRIBES THE BLACK BODY RADIATION SPECTRUM WELL.

$$\Phi(\gamma l_{nm}) = \frac{1}{\frac{1}{h\gamma l_{nm}} e^{\frac{h\gamma l_{nm}}{k_B T}} - 1}$$

↓ CONSTANT

• EINSTEIN MODIFIED HIS THEORY. HE INTRODUCED THE PROCESS OF STIMULATED EMISSION. PROPORTIONALITY CONSTANT

$$\frac{dN_m}{dt} = -AN_m - C N_m \Phi(\gamma l_{nm})$$

M → n TRANSITION INDUCED BY EXTERNAL RADIATION

SPONTANEOUS EMISSION

STIMULATED EMISSION

AT EQUILIBRIUM

$$\frac{dN_m}{dt} = \frac{dN_n}{dt}$$

$$(A + C e(\gamma_{nm})) N_m = B N_n e(\gamma_{nm})$$

$$e(\gamma_{nm}) = \frac{(A/B)}{\frac{N_n}{N_m} - \frac{C}{B}}$$

$$e(\gamma_{nm}) = \frac{(A/B)}{e^{\frac{h\gamma_{nm}}{k_B T}} - (C/B)}$$

COMPARE THIS EQUATION WITH  
THE PLANCK'S LAW

$$\frac{A}{B} = T \gamma_{nm}^3$$

$$\frac{C}{B} = 1$$

WHEN  $h\gamma_{nm} \gg k_B T$ ,  $e^{\frac{h\gamma_{nm}}{k_B T}} \gg 1$

$$e(\gamma_{nm}) \sim \left(\frac{A}{B}\right) e^{-\frac{h\gamma_{nm}}{k_B T}}$$

WIEN'S LAW

• WHEN

$$h\nu_{nm} \gg k_B T,$$

$$E_m - E_n \gg k_B T$$

$\Rightarrow$

$$N_m \ll N_n$$

$\Rightarrow$  STIMULATED EMISSION IS NEGLIGIBLE

THE NUMBER OF ATOMS IN THE LOWER LEVEL IS MUCH GREATER THAN THE NUMBER OF ATOMS IN THE UPPER LEVEL



# ELECTROMAGNETIC FIELD

- VECTOR POTENTIAL  $\vec{A}(\vec{r}, t)$
- SCALAR POTENTIAL  $\phi(\vec{r}, t)$
- ELECTRIC AND MAGNETIC FIELDS CAN BE WRITTEN IN TERMS OF  $\vec{A}$  AND  $\phi$

$$\rightarrow \vec{E}(\vec{r}, t) = -\frac{\partial \vec{A}}{\partial t} - \nabla \phi$$

$$\rightarrow \vec{B}(\vec{r}, t) = \nabla \times \vec{A}$$

$$\vec{E}(\vec{r}, t) = E_x(\vec{r}, t) \hat{i} + E_y(\vec{r}, t) \hat{j} + E_z(\vec{r}, t) \hat{k}$$

$$\vec{B}(\vec{r}, t) = B_x(\vec{r}, t) \hat{i} + B_y(\vec{r}, t) \hat{j} + B_z(\vec{r}, t) \hat{k}$$

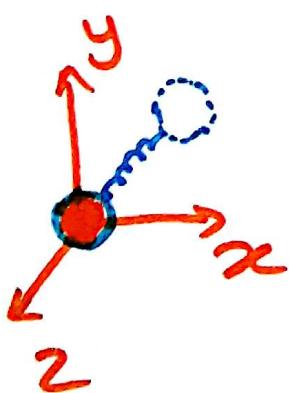
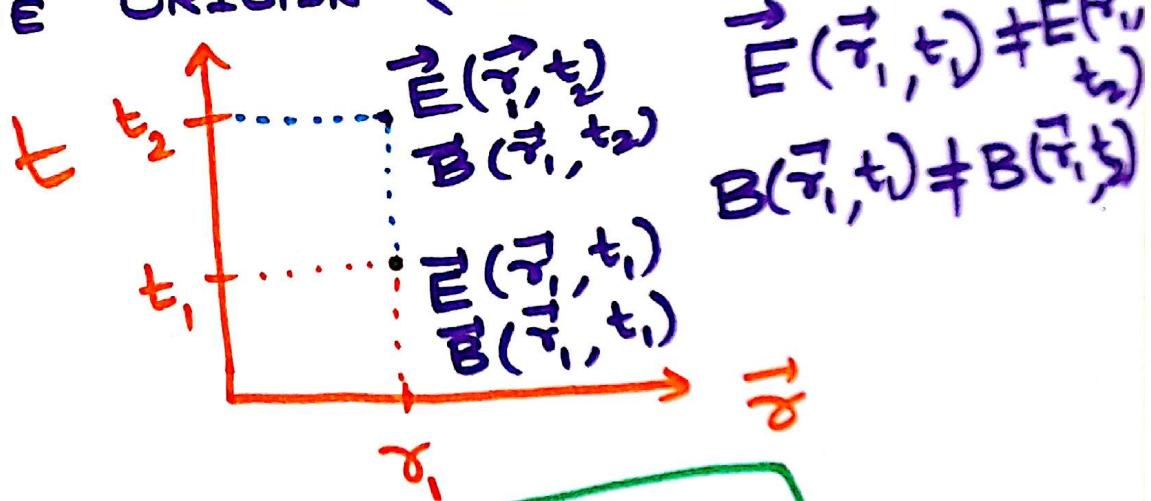
$(E_x, E_y, E_z, B_x, B_y, B_z)$  ARE NEEDED  
SIX VARIABLES ARE NEEDED  
TO DEFINE AN ELECTROMAGNETIC  
WAVE AT A GIVEN  $\vec{r}$  AND  $t$ .

WITH  $\vec{A}$  AND  $\phi$ , ONLY FOUR  
VARIABLES ARE SUFFICIENT  
 $\rightarrow (A_x, A_y, A_z, \phi)$

# A CLASSICAL DESCRIPTION OF SPECTROSCOPY

- SYSTEM COMPOSED OF CHARGED PARTICLES
- CHARGES ARE BOUND TO THE ATOMS/MOLECULES IN THE SYSTEM
- CONSIDER A SINGLE CHARGE  $q$  LOCATED AT THE ORIGIN; MASS  $m$
- 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:  $\vec{E}(\vec{r}, t) = \vec{E}_0(\vec{r}) \cos \omega t$

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

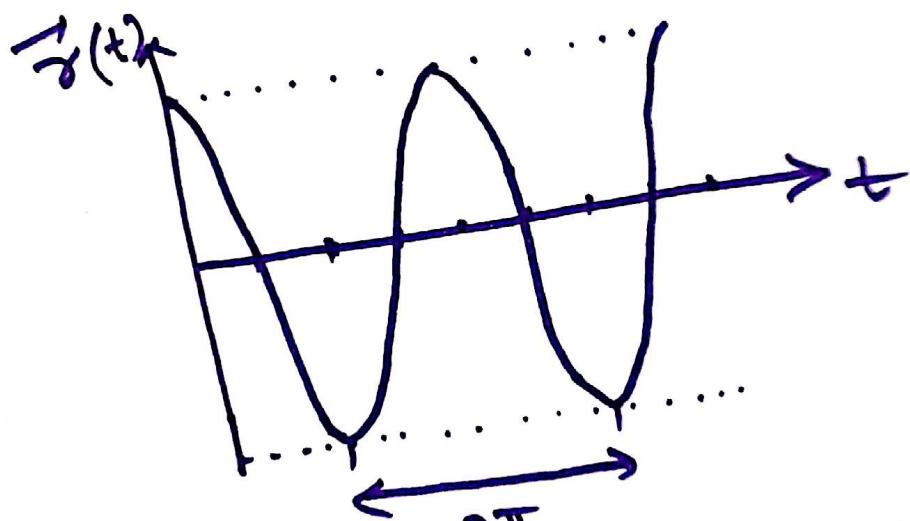
$$\frac{d^2\vec{\gamma}}{dt^2} + 2\gamma \frac{d\vec{\gamma}}{dt} + \omega_0^2 \vec{\gamma} = \frac{F_0}{m} \cos \omega t$$

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 :  $\tau \neq 0$  DAMPING FORCE  
 $f_0 = 0 \Rightarrow$  NO LIGHT

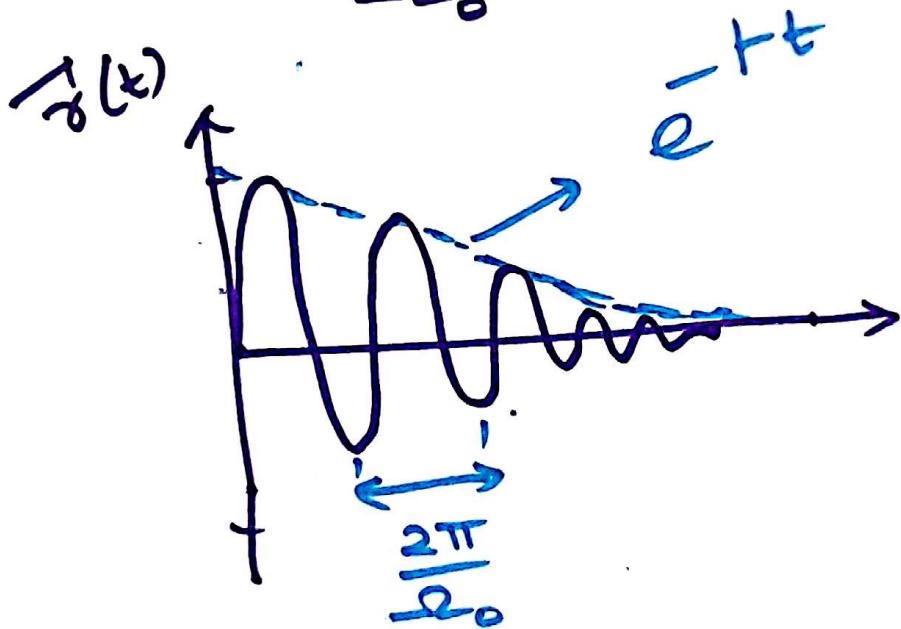
$$\vec{\gamma}(t) = \vec{\gamma}_0 e^{-i\Omega_0 t} e^{-\tau t}$$

REDUCED FREQUENCY  $\Leftarrow$

$$\Omega_0 = \sqrt{\omega_0^2 - \tau^2}$$

WEAK DAMPING :  $\tau \rightarrow 0$

$$\Omega_0 \approx \omega_0$$



- CASE III :  $\tau \neq 0$   
 $f_0 \neq 0$

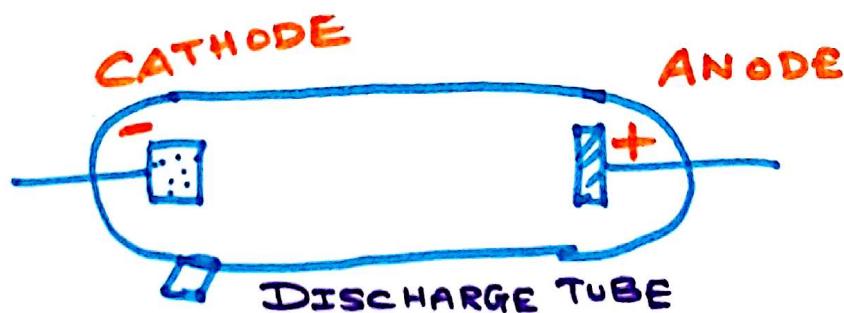
WHEN  $\omega = \omega_0$  ; RESONANCE

# ATOMIC SPECTRA

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

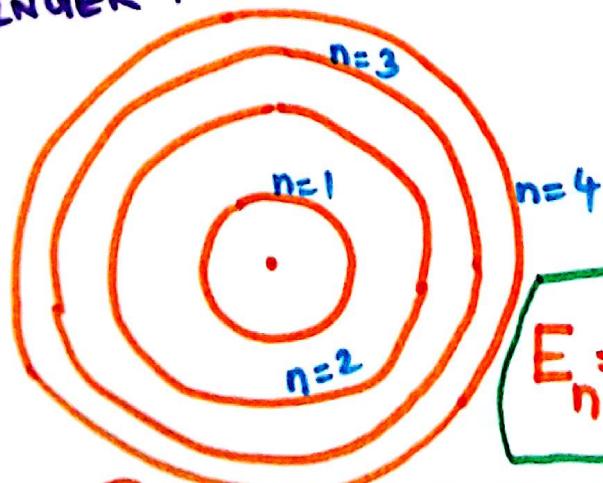
$H_2$  MOLECULE  
 $H_2O$   
 $CH_4, C_2H_6, \dots$

- DISSOCIATION OF  $H_2$  MOLECULE



- BOHR'S MODEL OF THE HYDROGEN ATOM

FINGER PRINT OF HYDROGEN



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

$R \rightarrow$  RYDBERG CONSTANT



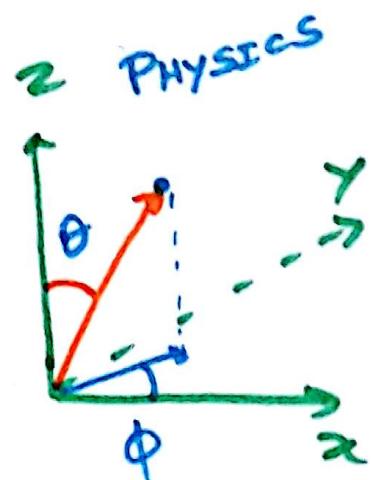
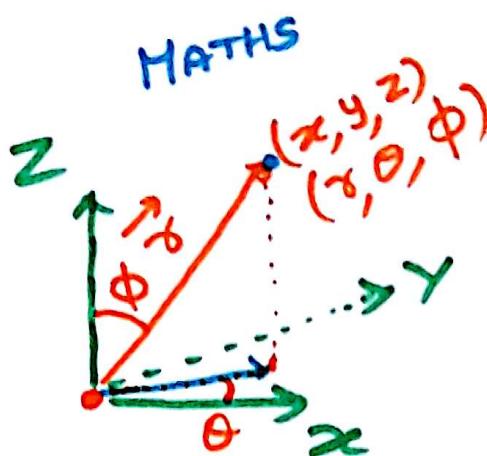
$n=1 \Rightarrow$  LYMAN (ULTRAVIOLET)  $n=4 \Rightarrow$  BRACKETT (FAR IR)  
 $n=2 \Rightarrow$  BALMER (VISIBLE)  $n=5 \Rightarrow$  P-FUND (FAR IR)  
 $n=3 \Rightarrow$  PASCHEN (NEAR INFRARED)  $n=6 \Rightarrow$   $R = 13.6 \text{ eV}$

# QUANTUM MECHANICS OF HYDROGEN ATOM

$$0 \leq \theta \leq 2\pi$$

$$0 \leq \phi \leq \pi$$

$$0 \leq \gamma \leq \infty$$



$$x = \gamma \sin \theta \cos \phi$$

$$y = \gamma \sin \theta \sin \phi$$

$$z = \gamma \cos \theta$$

$$x = \gamma \sin \theta \cos \phi$$

$$y = \gamma \sin \theta \sin \phi$$

$$z = \gamma \cos \theta$$

$$0 \leq \phi \leq 2\pi$$

$$0 \leq \theta \leq \pi$$

→ WAVE FUNCTION  $\psi(x, y, z)$   
 OR  $\psi(\gamma, \theta, \phi)$

→ PROBABILITY DENSITY AT  $\vec{r}$

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

(OR)

$$\psi^*(\gamma, \theta, \phi) \psi(\gamma, \theta, \phi)$$

→ PROBABILITY OF FINDING THE ELECTRON  
 IN AN INFINITESIMAL VOLUME

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

(OR)

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

- 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:

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

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

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

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

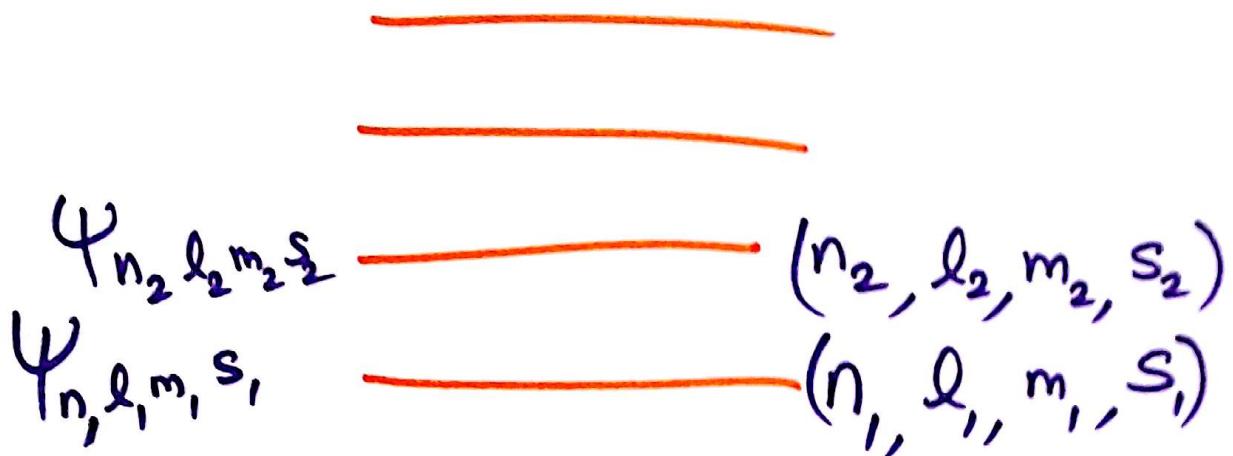
$\Rightarrow n$  GOVERNS THE ENERGY AND SIZE OF THE ORBITAL

$l$  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

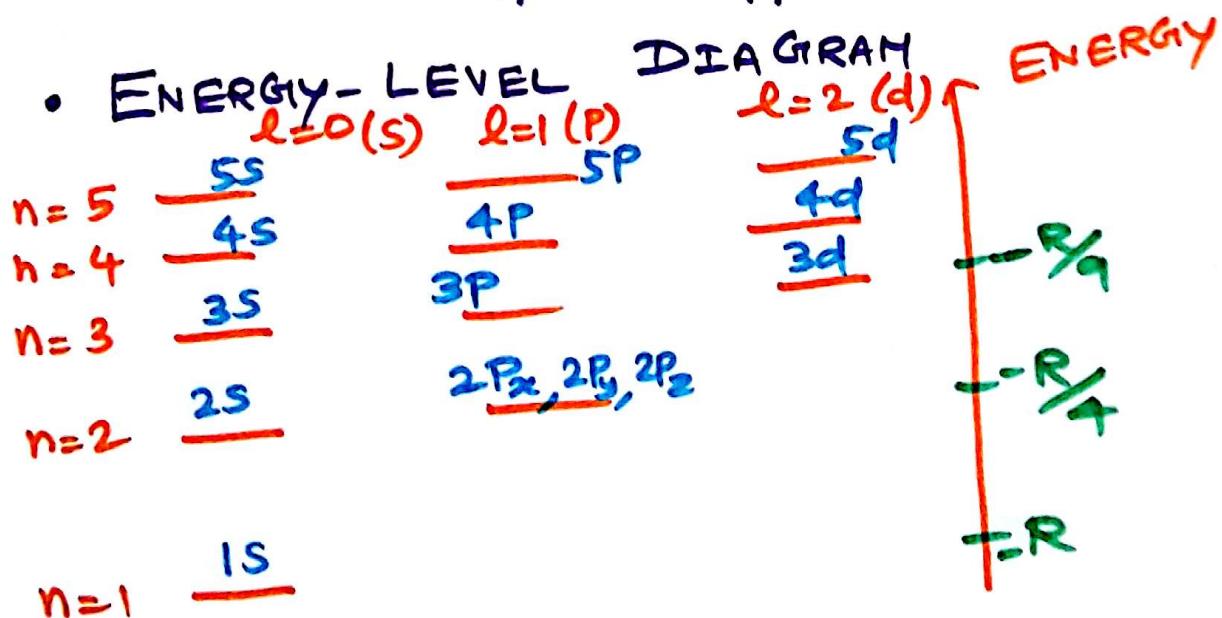


- ENERGIES OF ATOMIC ORBITALS

→ CALCULATE THE ENERGIES OF  $1S, 2S, 2P_x, 2P_y, 2P_z, 3S, 3P_x, 3P_y, 3P_z$ , and  $3d$

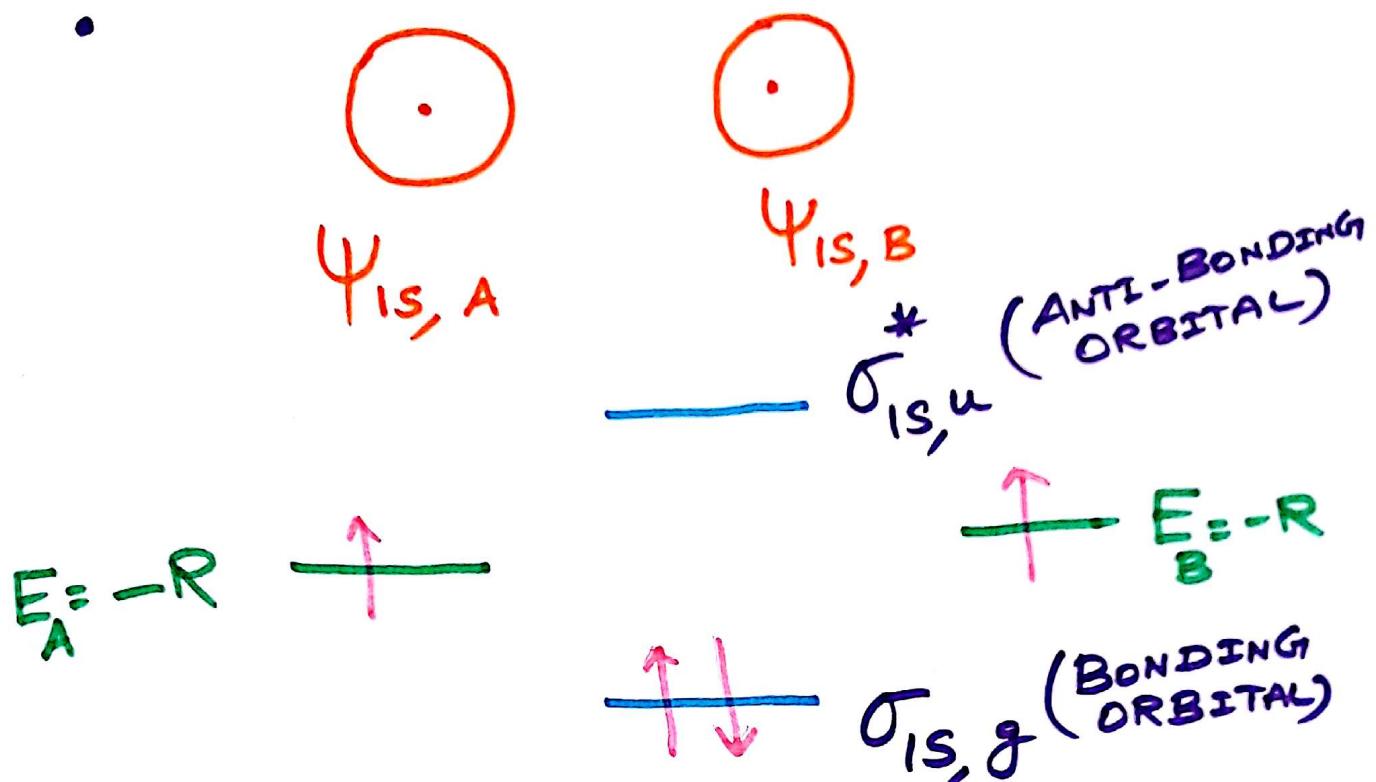
**DEGENERATE** **DEGENERATE**

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

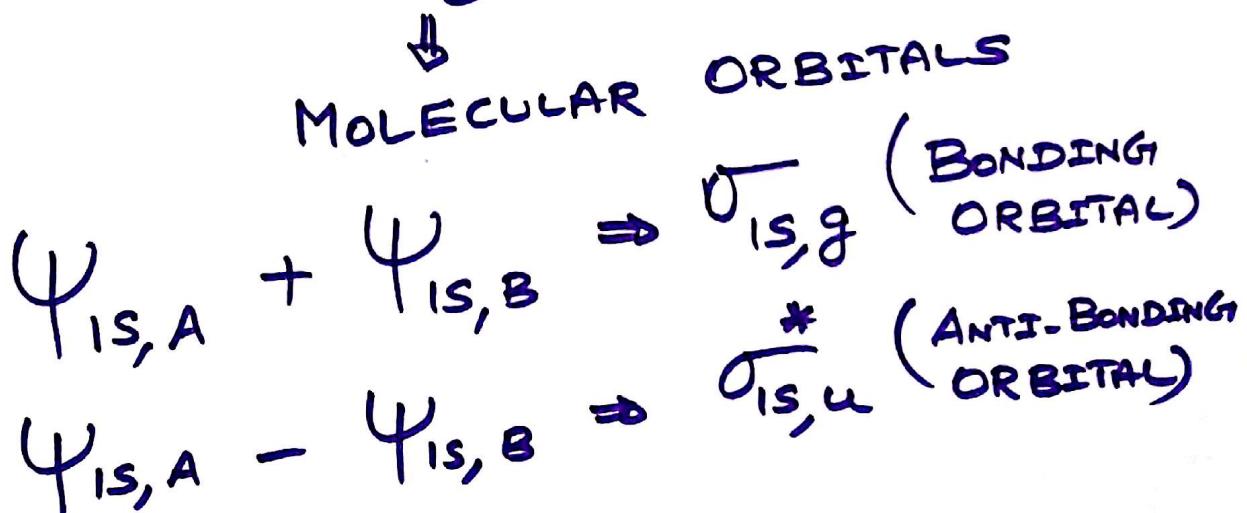


## HYDROGEN MOLECULE

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



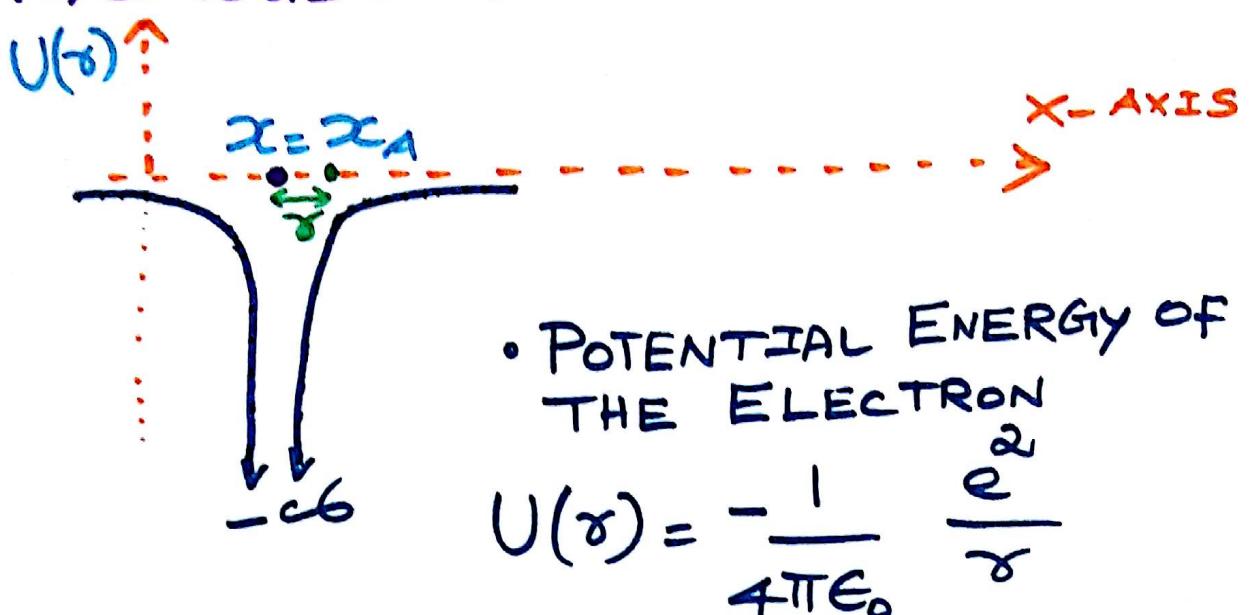
LINEAR COMBINATION OF ATOMIC ORBITALS



CLASS WORK

# ATOM → MOLECULE → SOLID

## • HYDROGEN ATOM

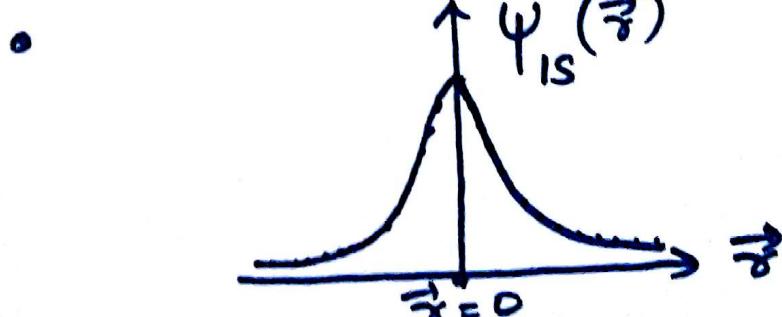


- $U(r)$  IS LESS THAN OR EQUAL TO ZERO ALWAYS (ATTRACTIVE FORCE)
- As  $r \rightarrow 0$ ,  $U(r) \rightarrow -\infty$
- VISUALIZE THIS ENERGY IN 3D SPACE
- GROUND STATE WAVE FUNCTION

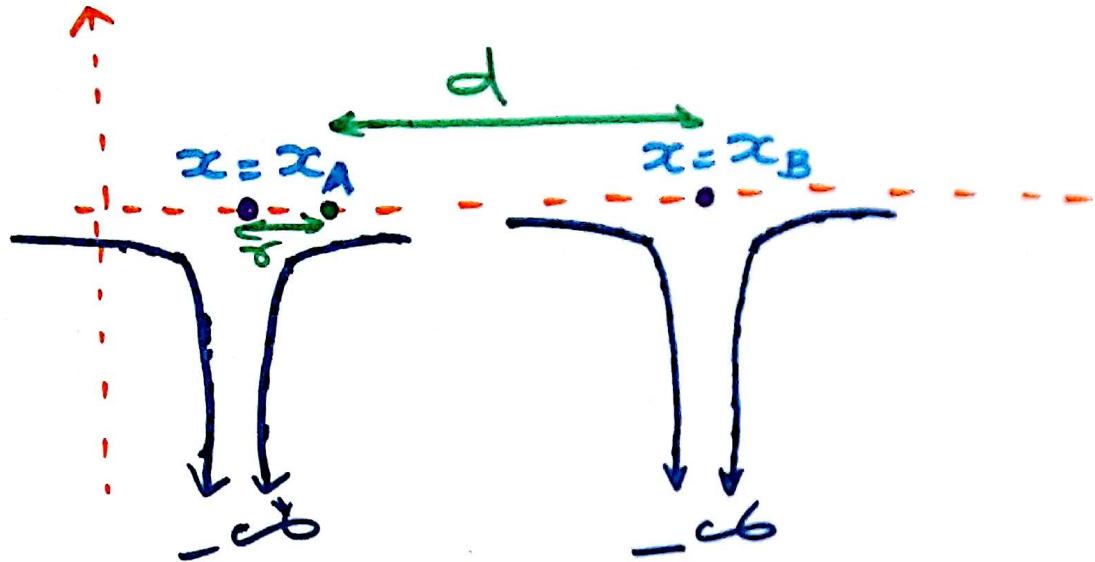
ASSUME  
 $x_A = 0$

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

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



## • AN ELECTRON BETWEEN TWO ATOMS



### • POTENTIAL ENERGY OF THE ELECTRON

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

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

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

(ELECTRON-ELECTRON REPULSION IGNORED)

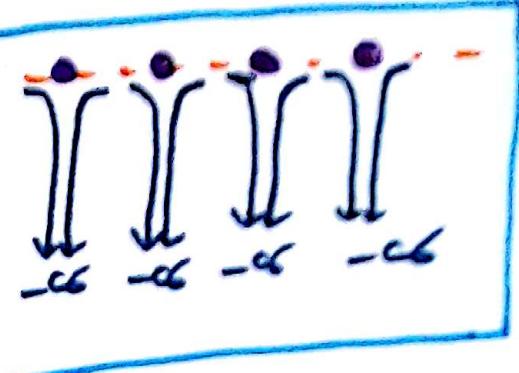
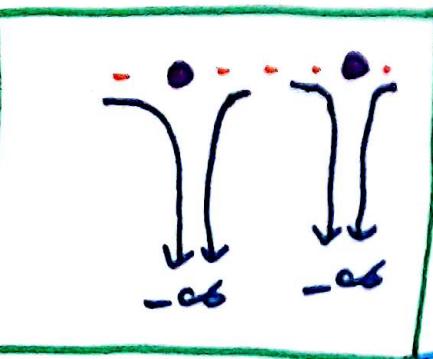
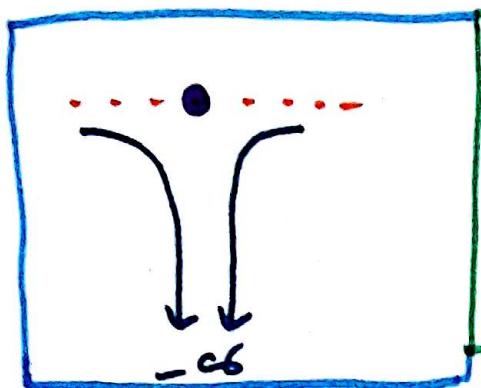
- As you DECREASE  $d$ , THE BARRIER BETWEEN THE ATOMS DECREASES.

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

## ATOM

## MOLECULE

## SOLID



- ATOMIC ORBITALS
- ENERGY LEVELS

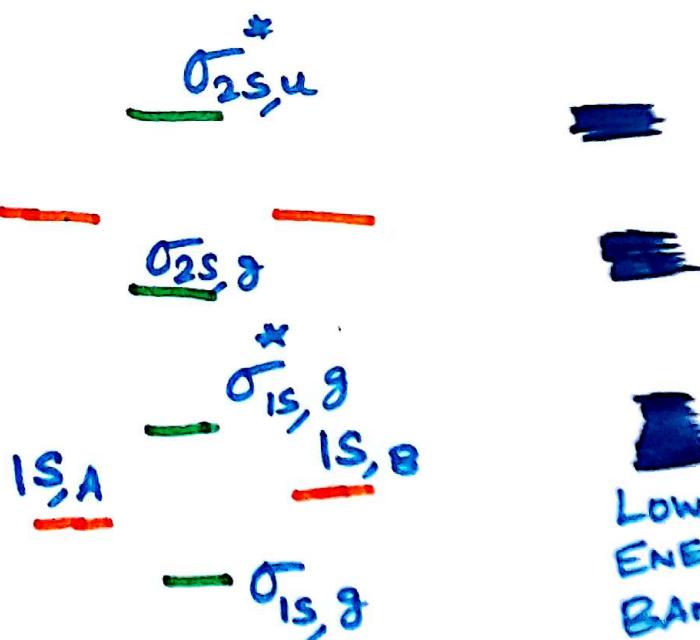
- MOLECULAR ORBITALS
- ENERGY LEVELS

- ENERGY BANDS
- ENERGY LEVELS

3S 3P<sub>x</sub> 3P<sub>y</sub> 3P<sub>z</sub> 3d

2S 2P<sub>x</sub> 2P<sub>y</sub> 2P<sub>z</sub>

1S



LOWEST ENERGY BAND

# 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

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

- HAMILTONIAN

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

$$\hat{H}_{o,A} \Psi_A(\vec{r}) = E_{1s,A} \Psi_A(\vec{r})$$

$$\hat{H}_{o,B} \Psi_B(\vec{r}) = E_{1s,B} \Psi_B(\vec{r})$$

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

↑  
H<sub>o,A</sub>  
↓  
H<sub>o,B</sub>

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

↑  
HAMILTONIAN OF ISOLATED A  
↓  
HAMILTONIAN OF ISOLATED B

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

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

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

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

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

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

|| by  $\times \Psi_B^*(\vec{r})$  AND INTEGRATE

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

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

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

SOLUTION :

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

ANTIBOND

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

BOND

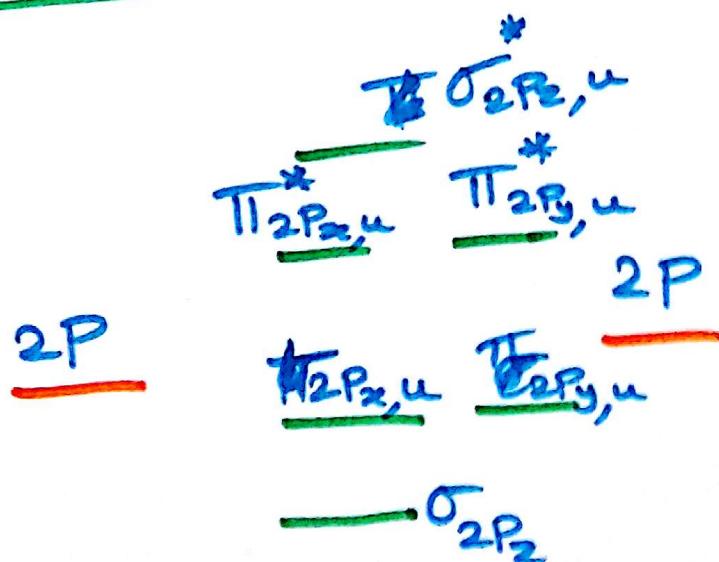
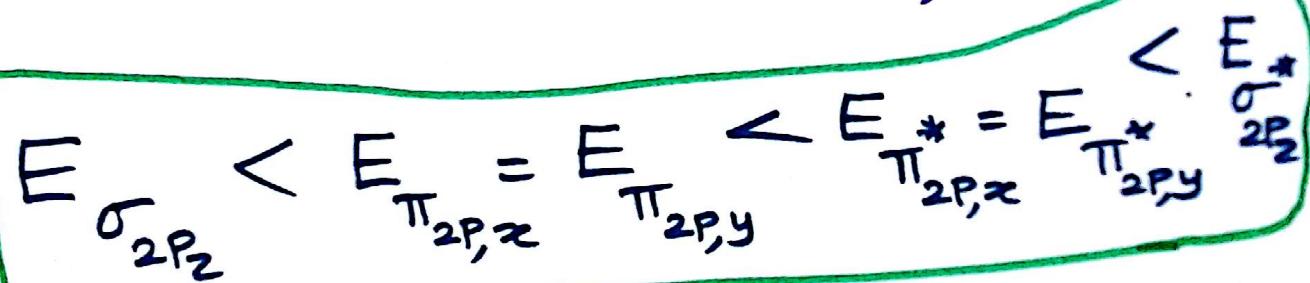
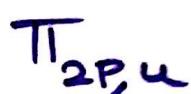
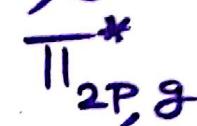
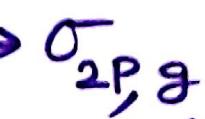
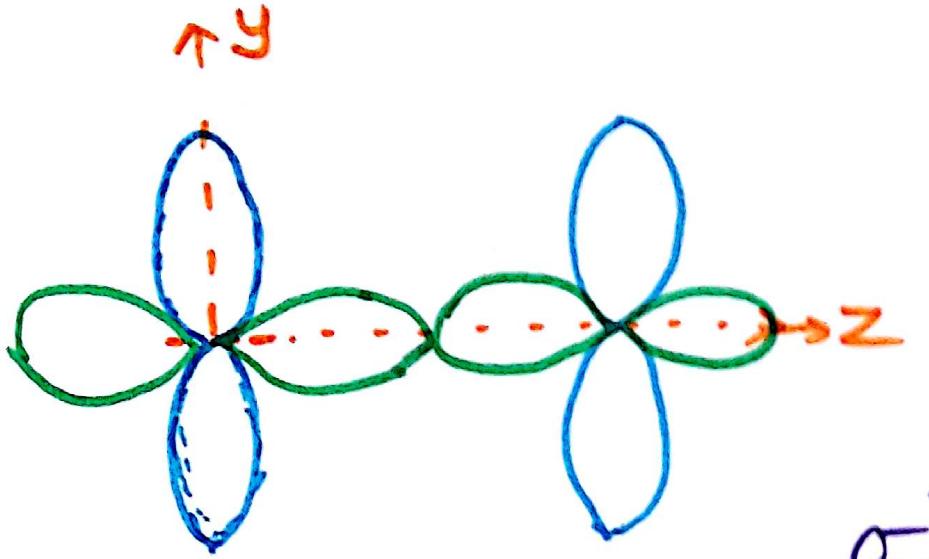
$$\begin{pmatrix} E_{IS,A} - E_H & -V \\ -V & E_{IS,B} - E_H \end{pmatrix} = 0$$

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

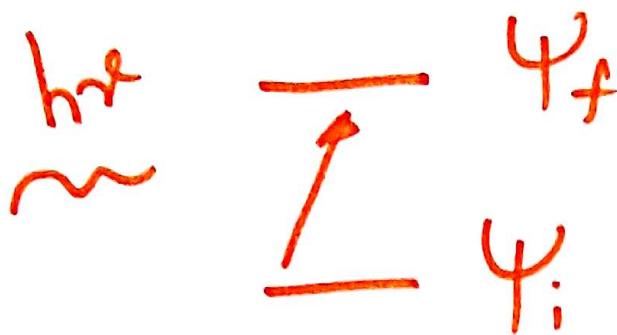
BONDING

$$\begin{aligned} E_H &= E_{IS} + V \\ E_H &= E_{IS} - V \end{aligned}$$

# • OVERLAP OF P ORBITALS



## 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

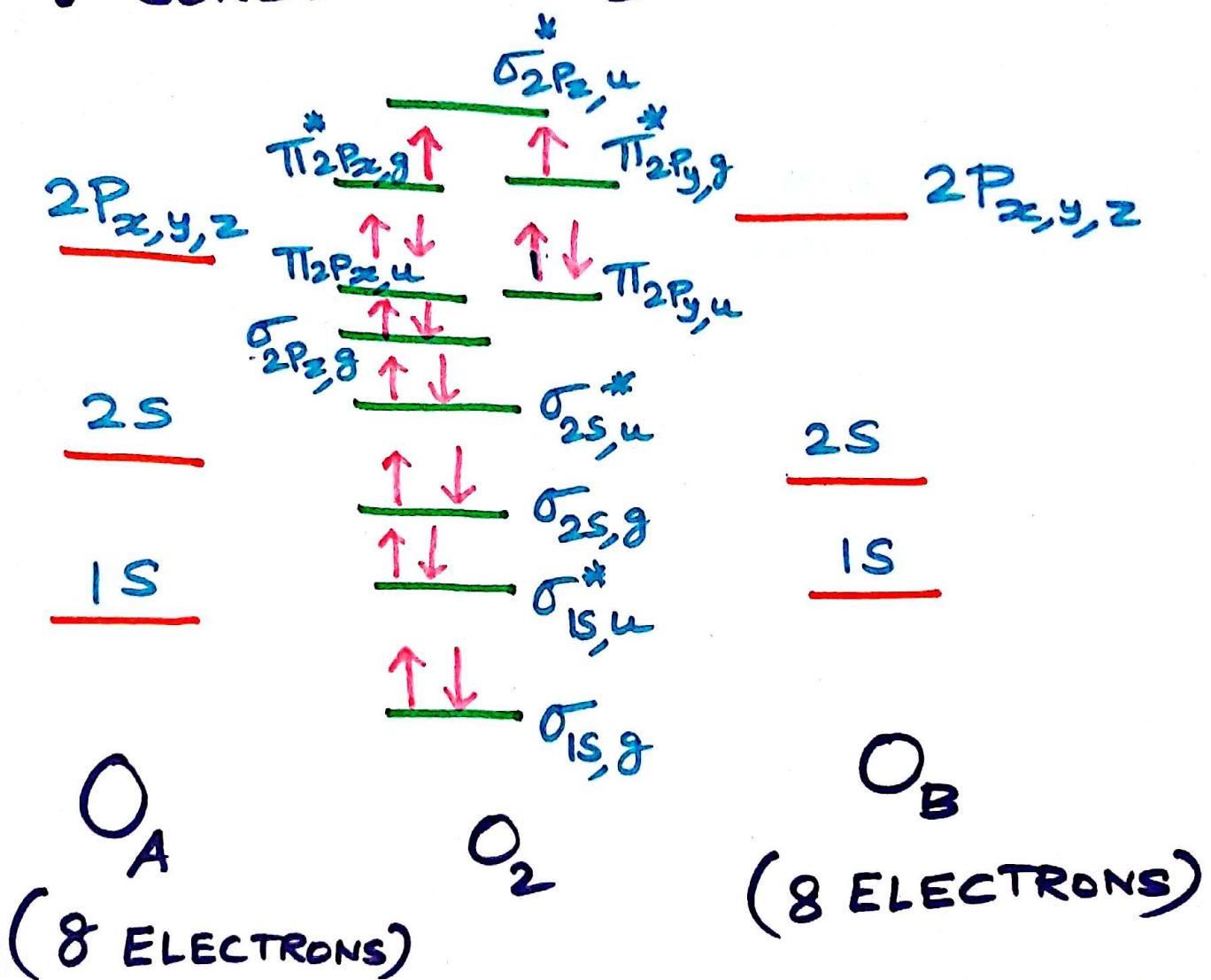
$T_{i \rightarrow f} = 0$  : TRANSITION IS FORBIDDEN

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

SELECTION RULES

# HOW DO WE DISTRIBUTE ELECTRONS IN MOLECULAR ORBITALS/LEVELS :-

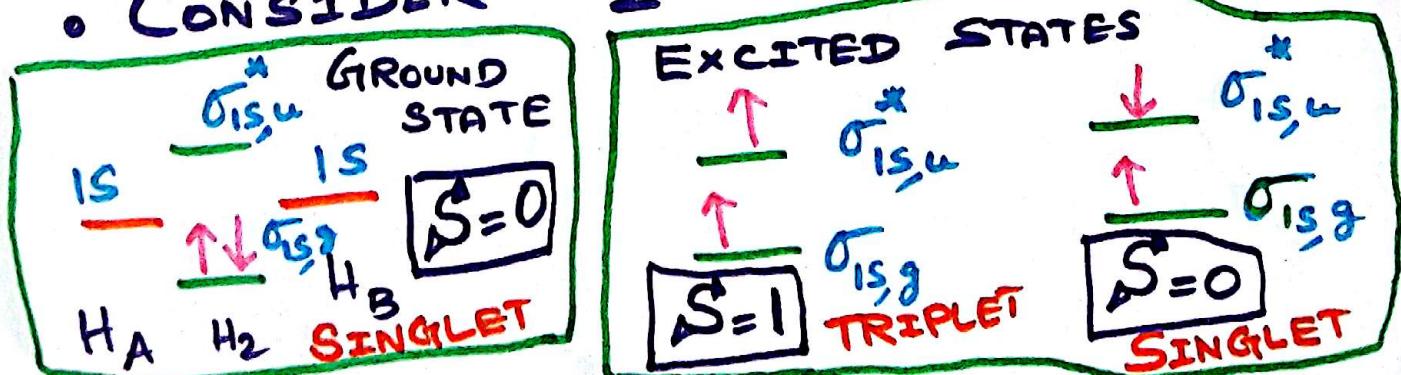
- CONSIDER  $O_2$  MOLECULE



HOMO : HIGHEST OCCUPIED MOLECULAR ORBITAL

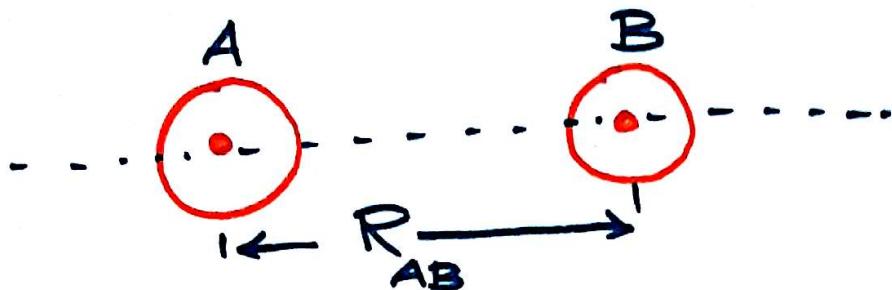
LUMO : LOWEST UNOCCUPIED MOLECULAR ORBITAL.  
 SPIN MULTIPlicity =  $2S+1$       TOTAL SPIN

• CONSIDER  $H_2$  MOLECULE :  $S \rightarrow$  TOTAL SPIN

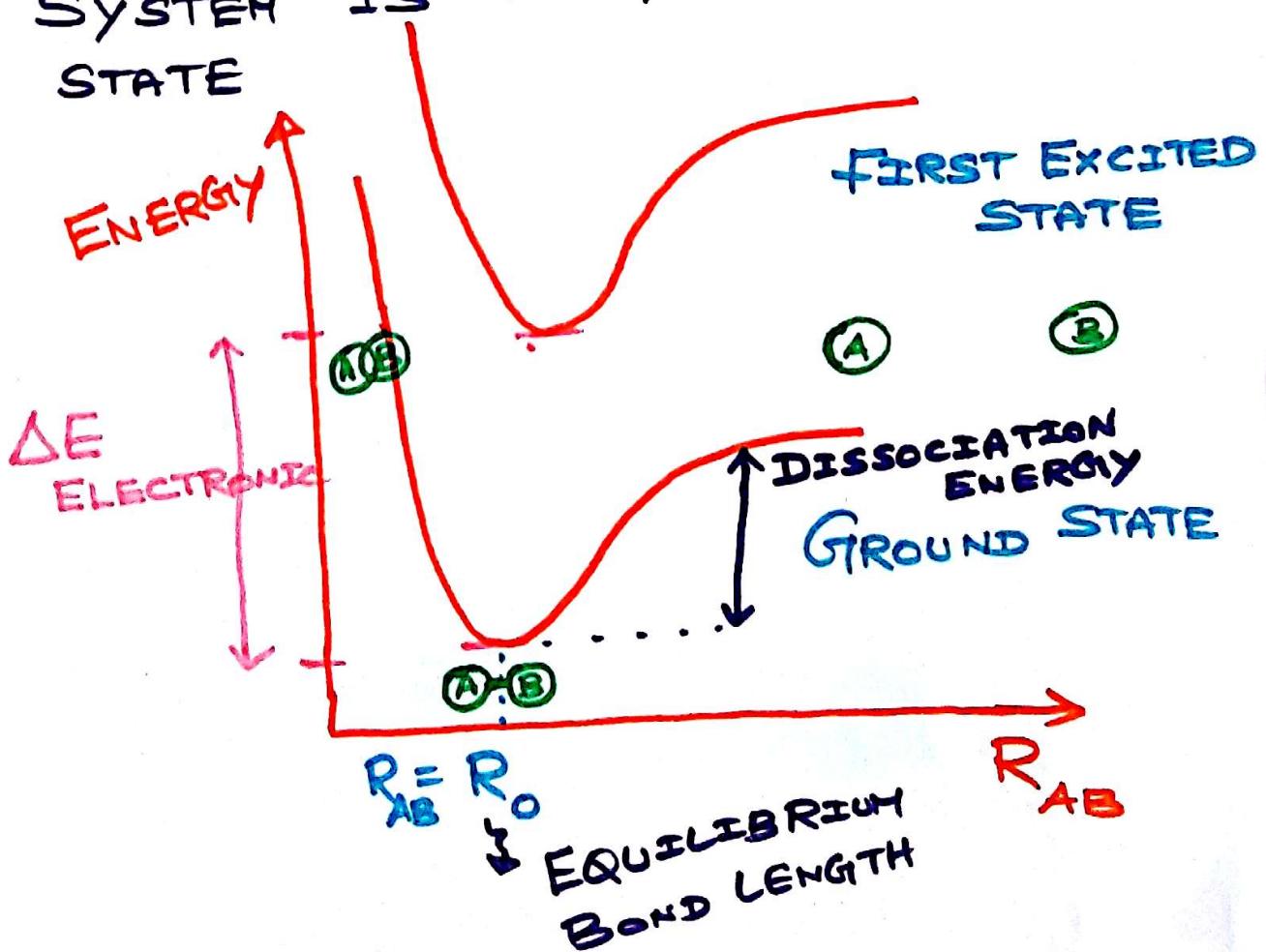


# ELECTRONIC ENERGY SURFACES

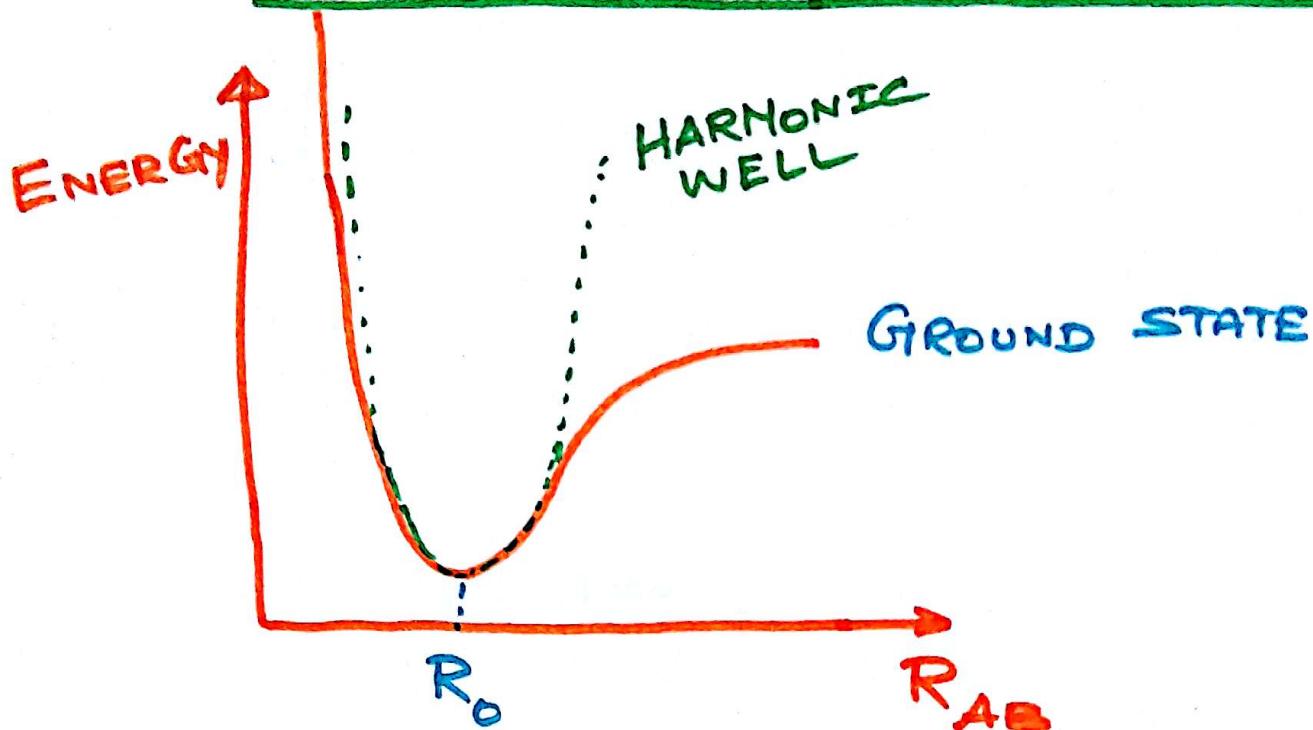
- CONSIDER A DIATOMIC MOLECULE



- $R_{AB} \Rightarrow$  INTERNUCLEAR DISTANCE
- VARY  $R_{AB}$ , BUT ENSURE THAT THE SYSTEM IS ALWAYS IN ITS GROUNDED 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

$$\Delta V \ll \Delta E_{\text{ELECTRONIC}}$$

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

From  $\bullet$   $\dots \rightarrow z\text{ axis}$   
 $\downarrow$  $z=0$

$$U(z) = \frac{1}{2} K z^2$$

# 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

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

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

LIKE SPRING CONSTANT

# 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

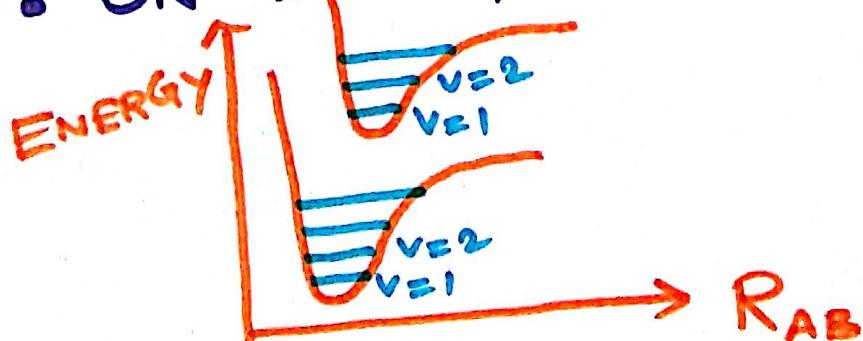
$$E_v = (v + \frac{1}{2}) \hbar \omega ; \omega = \sqrt{\frac{k}{\mu}}$$

Diagram showing energy levels for different vibrational quantum numbers  $v$ :

$v=4$	$\frac{9}{2}\hbar\omega$	$v=0, 1, 2, \dots$ vibrational quantum number
$v=3$	$\frac{7}{2}\hbar\omega$	
$v=2$	$\frac{5}{2}\hbar\omega$	
$v=1$	$\frac{3}{2}\hbar\omega$	
$v=0$	$\hbar\omega$	

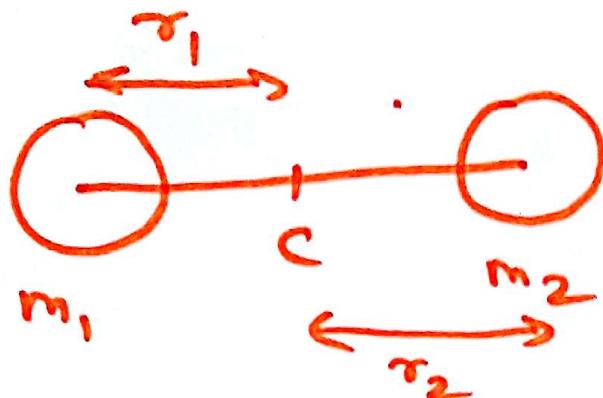
$$\hbar\omega \ll \Delta E_{\text{ELECTRONIC}}$$

- ON ENERGY SURFACE



# ROTATIONAL SPECTROSCOPY

## • RIGID DIATOMIC MOLECULE



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

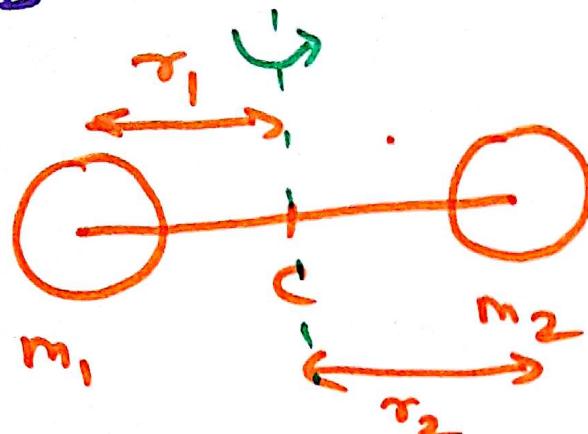
## → ROTATIONAL ENERGY

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

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

# ROTATIONAL SPECTROSCOPY

## RIGID DIATOMIC MOLECULE



$$\gamma_1 + \gamma_2 = \gamma_0$$

→ MOMENT OF INERTIA:  $I = m_1 \gamma_1^2 + m_2 \gamma_2^2$

## 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

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

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

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

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

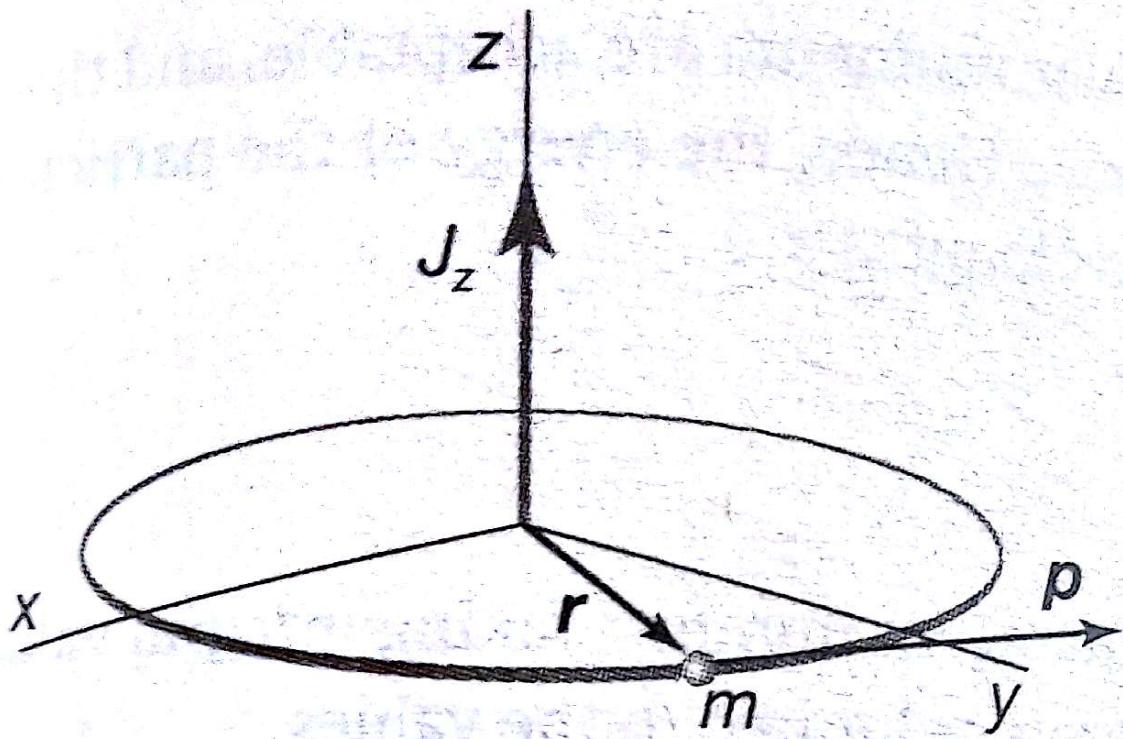
$$\gamma_1 = \frac{m_2 \gamma_0}{m_1 + m_2}$$

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

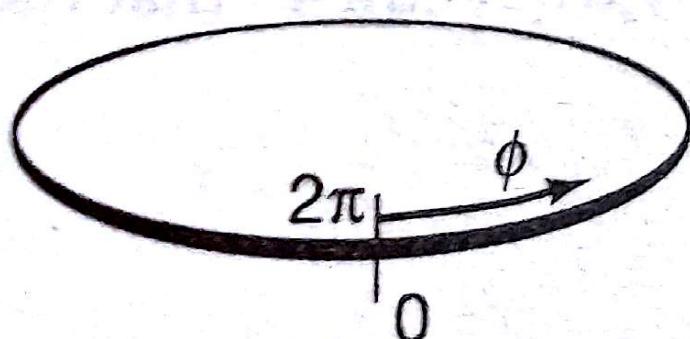


$$I = \left( \frac{m_1 m_2}{m_1 + m_2} \right) \gamma_0^2 = \mu \gamma_0^2$$

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

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \quad (12.51)$$

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

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

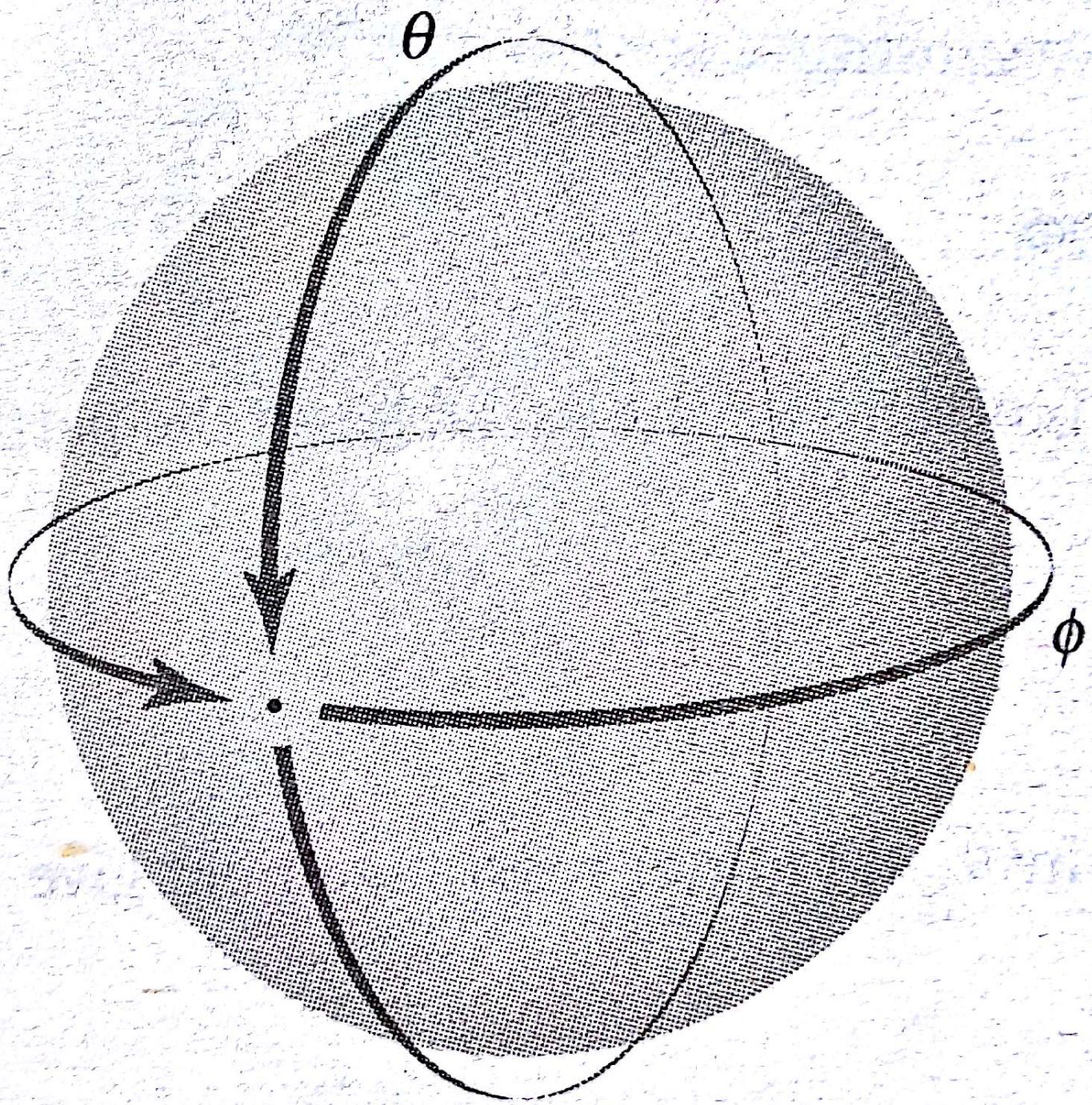
When expressed in terms of the coordinates  $r$  and  $\phi$ , by standard manipulations this equation becomes

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

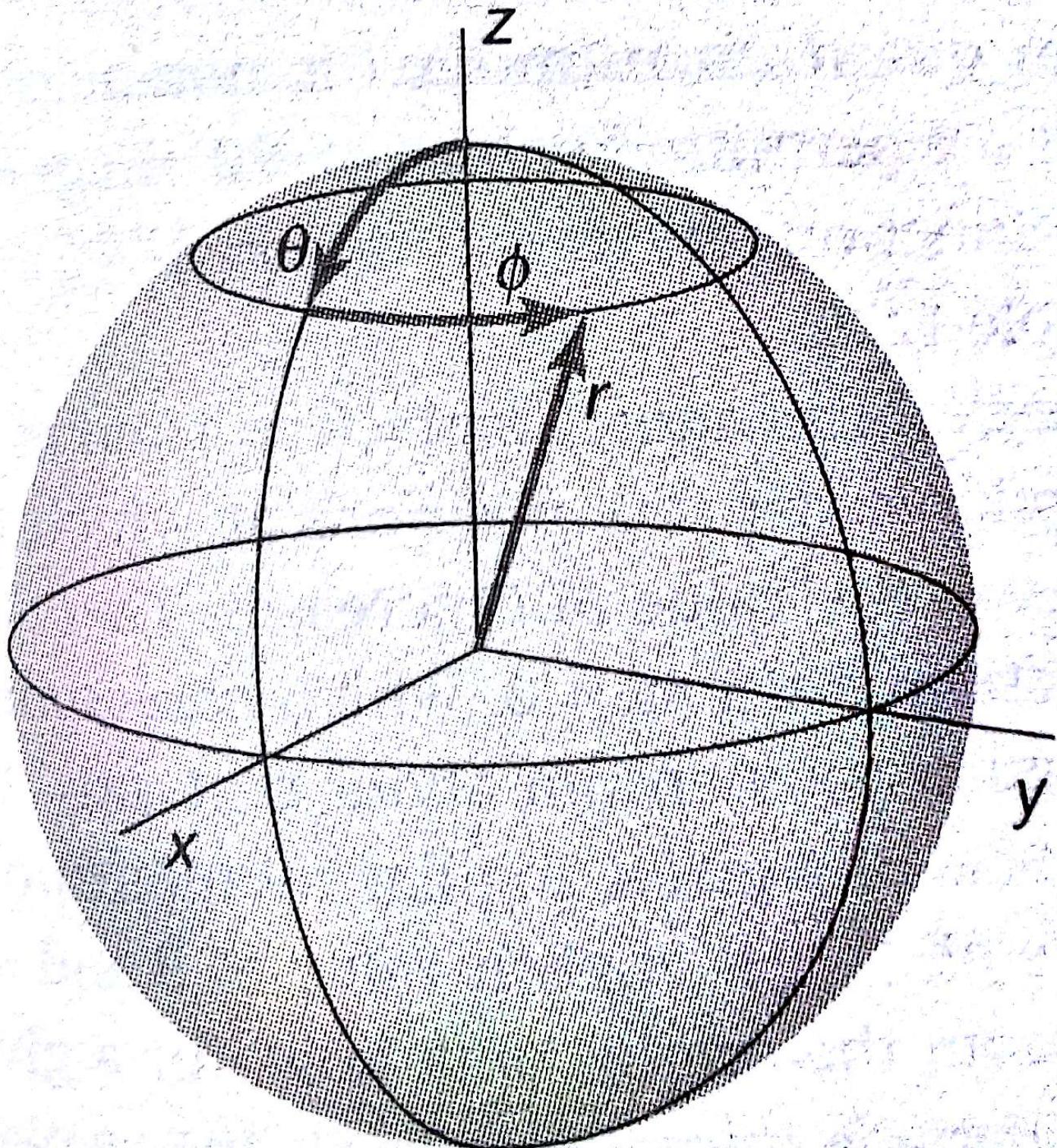
With the angular momentum operator available, we can test the wavefunction in eqn 50. Disregarding the normalization constant, we find

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

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

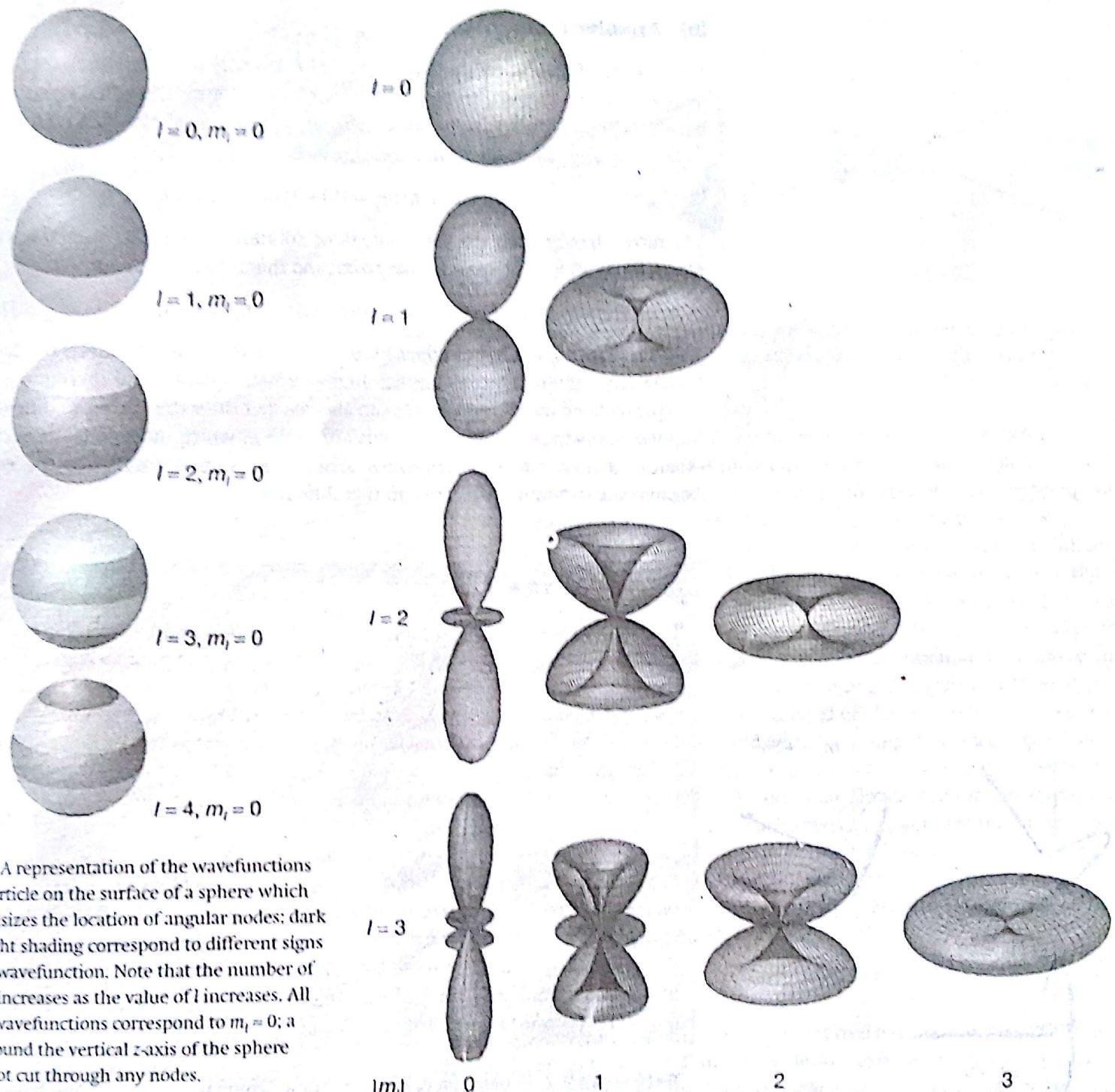
The spherical harmonics are orthogonal and normalized in the following sense:

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

An important 'triple integral' is

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

= 0 unless  $m'' = m' + m_l$  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

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

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

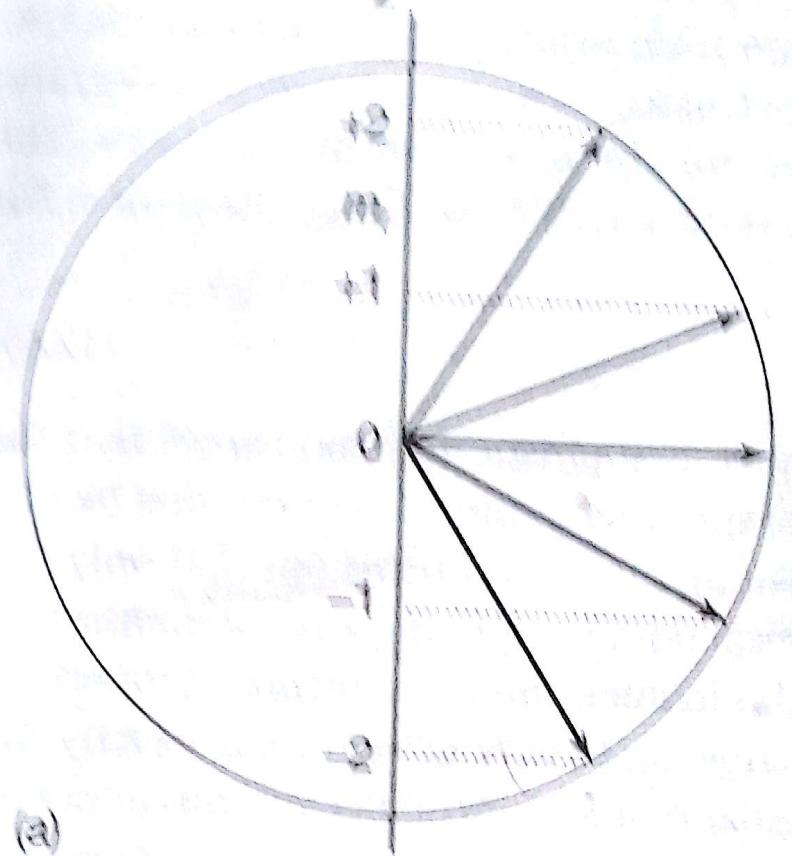
The energy of a rotating particle is related classically to its angular momentum  $J$  by  $E = J^2/2I$  (see *Further information 2*). Therefore, by comparing this equation with eqn 65, we can deduce that, because the energy is quantized, then so to is the magnitude of the angular momentum, and confined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

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

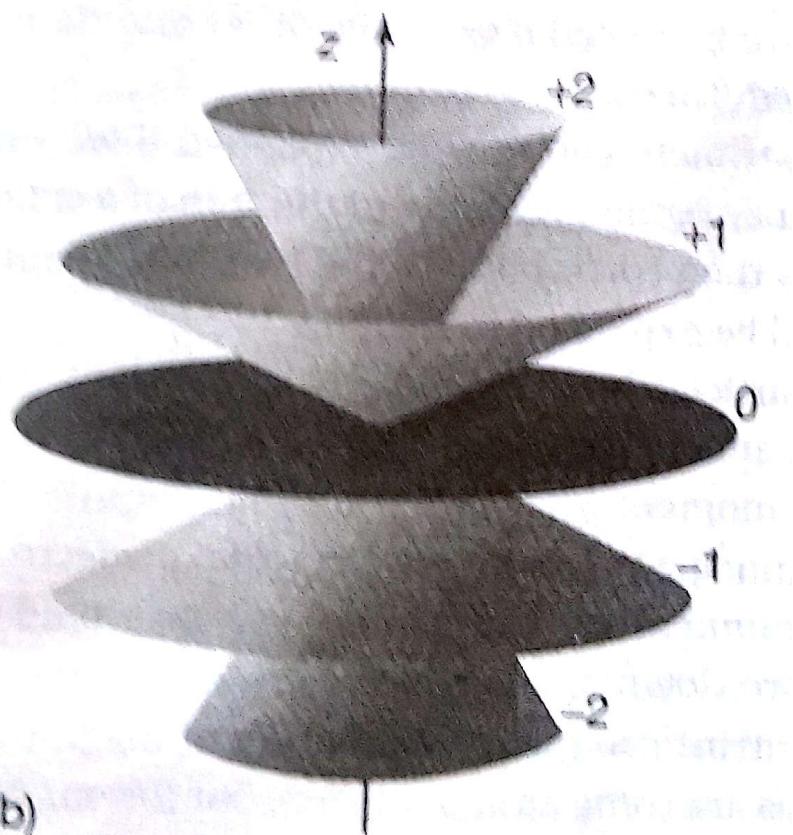
We have already seen (in the context of rotation in a plane) that the angular momentum about the  $z$ -axis is quantized, and that it has the values

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

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.

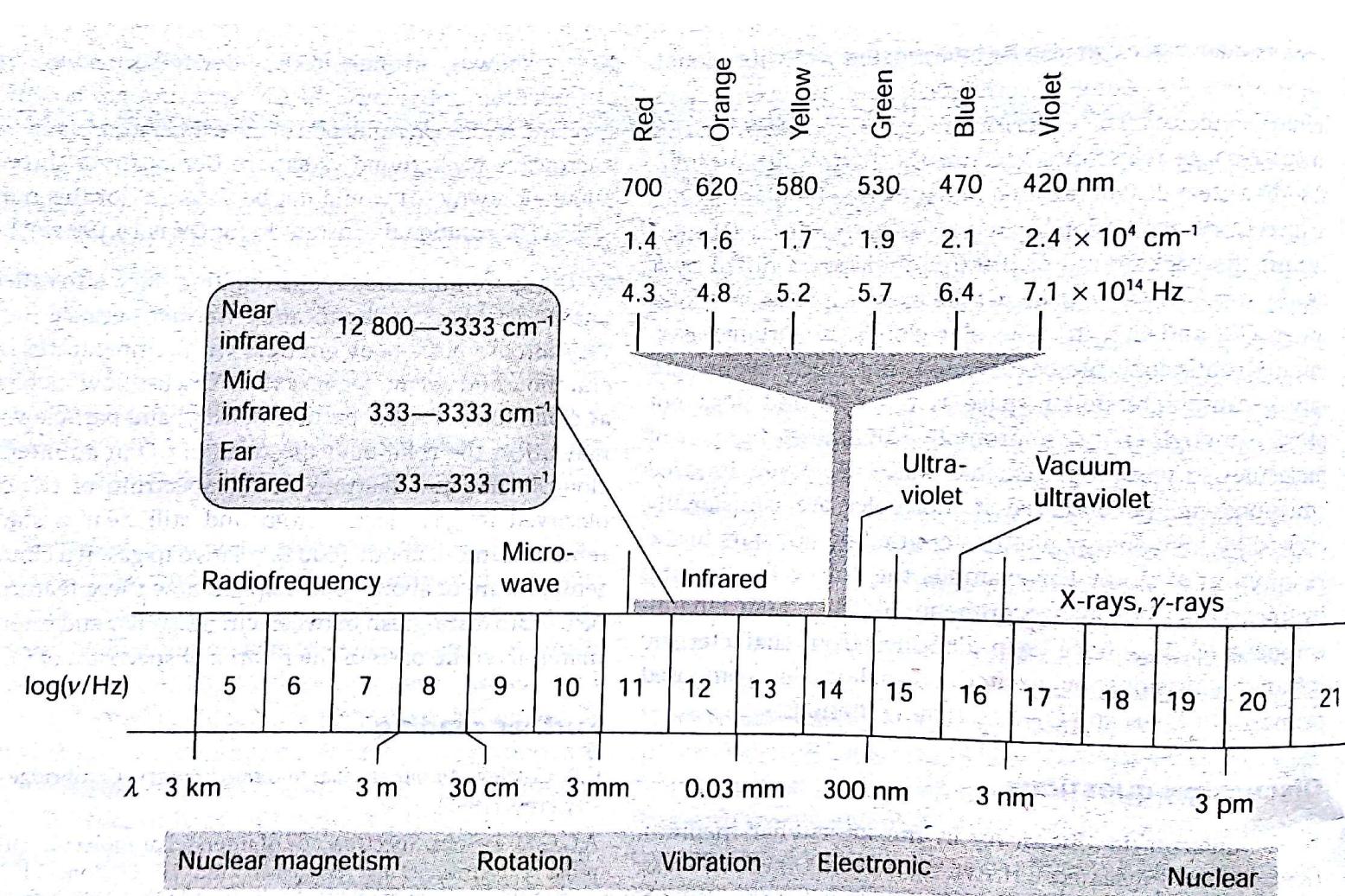


(a)

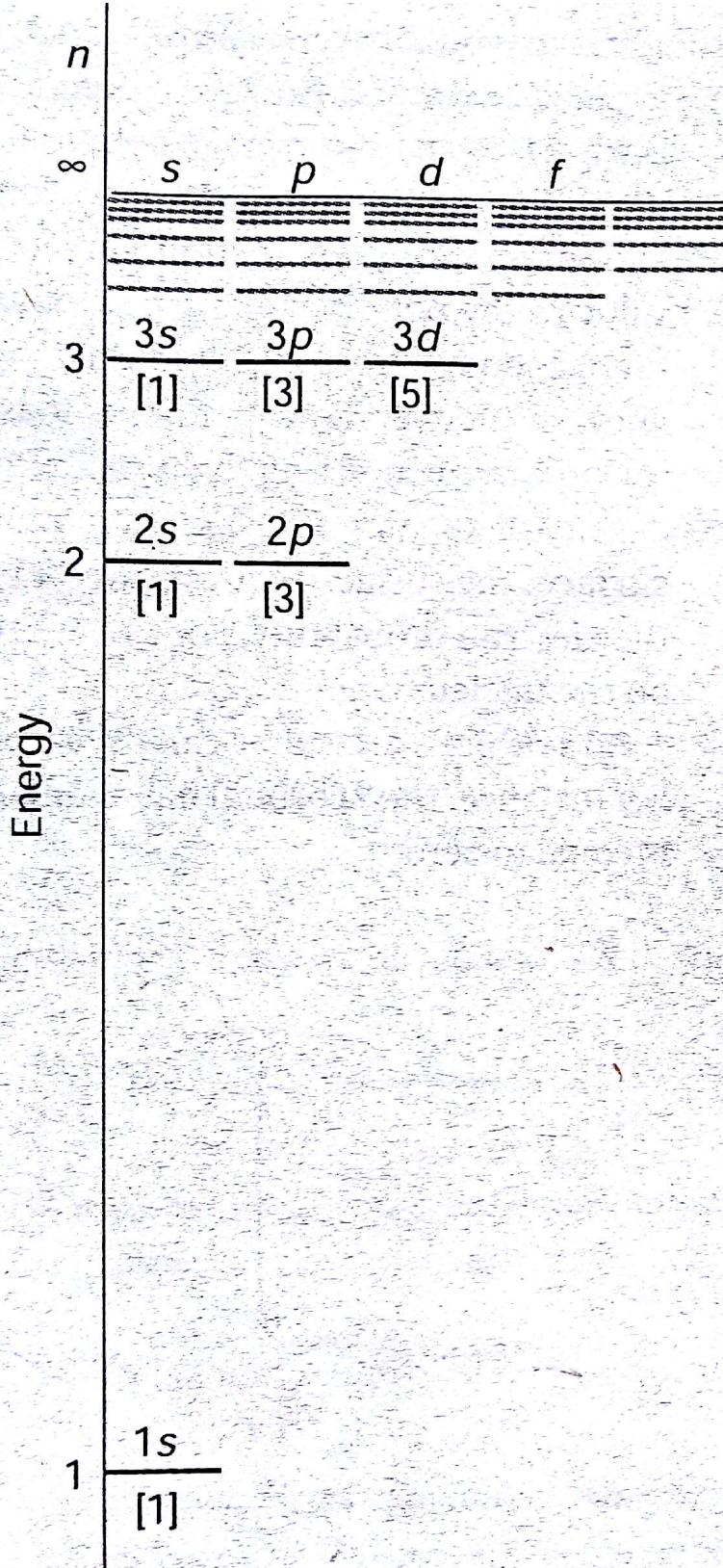


(b)

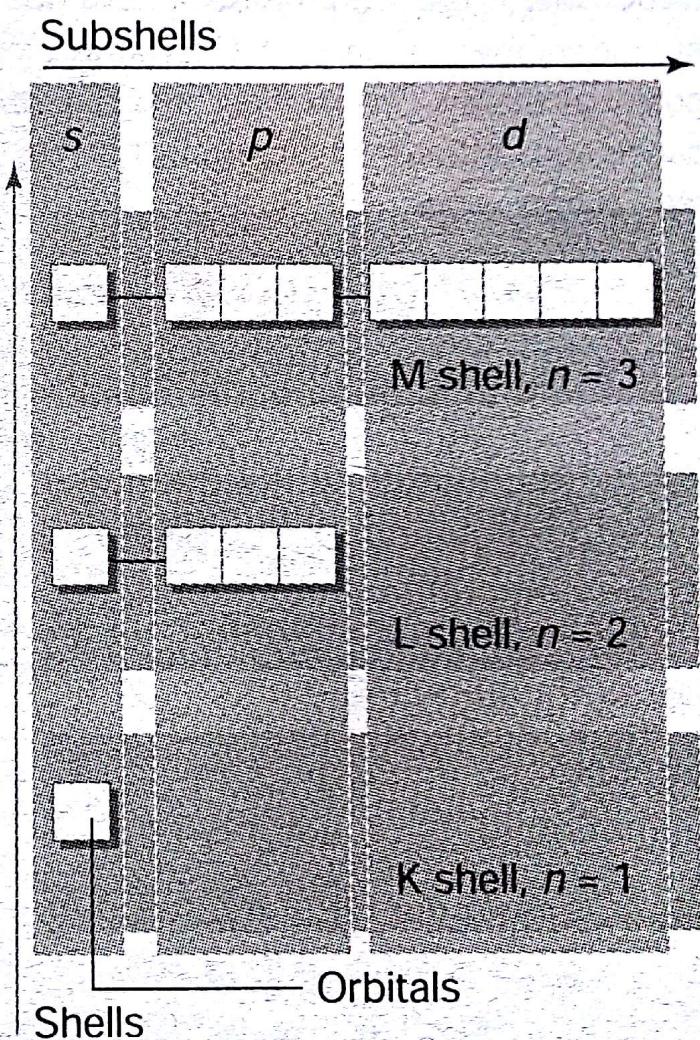
**12.36** (a) A summary of Fig. 12.34. However, because the azimuthal angle of the vector around the  $z$ -axis is indeterminate, a better representation is as in (b), where each vector lies at an unspecified azimuthal angle on its cone.



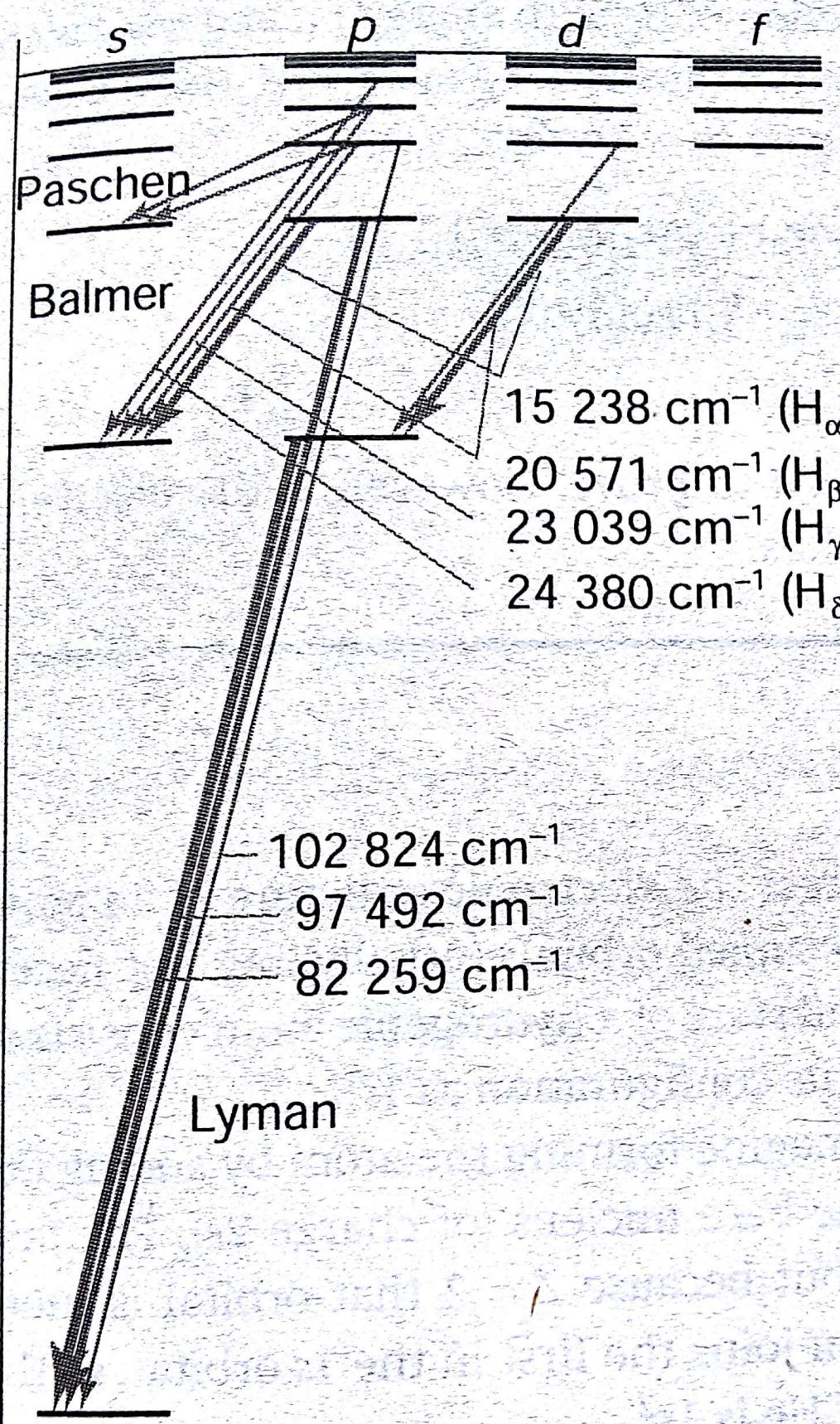
**16.1** The electromagnetic spectrum and the classification of the spectral regions. The band at the bottom of the illustration indicates the types of transitions that absorb or emit in the various regions. ('Nuclear magnetism' refers to the types of transitions discussed in Chapter 18; 'nuclear' refers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

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

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

- IN THE PRESENCE OF LIGHT

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

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

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

$C_i$  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

$$\cdot \hat{H}^{(1)} = -\vec{\mu} \cdot \vec{E} \xrightarrow{\substack{\text{DIPOLE MOMENT} \\ \text{ELECTRIC FIELD}}} \\ = -\mu_x E_x - \mu_y E_y - \mu_z E_z$$

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

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

$$= -\mu_z (2E_z^0 \cos(2\pi\omega t)) \\ = -\mu_z (E_z^0 (e^{-i2\pi\omega t} + e^{i2\pi\omega t}))$$

$$\cdot (\hat{H}_0 + \hat{H}^{(1)}) (C_i \Psi_i^D(\vec{r}, t) + C_f \Psi_f^D(\vec{r}, t)) \\ = -\frac{\hbar}{i} \frac{\partial}{\partial t} (C_i \Psi_i^D(\vec{r}, t) + C_f \Psi_f^D(\vec{r}, t))$$

$$\cdot C_i \hat{H}_0 \Psi_i^D(\vec{r}, t) + C_f \hat{H}_0 \Psi_f^D(\vec{r}, t) \\ + C_i \hat{H}^{(1)} \Psi_i^D(\vec{r}, t) + C_f \hat{H}^{(1)} \Psi_f^D(\vec{r}, t) \\ = -\frac{\hbar}{i} \left[ C_i \frac{\partial \Psi_i^D(\vec{r}, t)}{\partial t} + C_f \frac{\partial \Psi_f^D(\vec{r}, t)}{\partial t} \right. \\ \left. + \Psi_i^D(\vec{r}, t) \frac{\partial C_i}{\partial t} + \Psi_f^D(\vec{r}, t) \frac{\partial C_f}{\partial t} \right]$$

$$\cdot C_i \hat{H}^{(1)} \Psi_i^D(\vec{r}, t) + C_f \hat{H}^{(1)} \Psi_f^D(\vec{r}, t) \\ = -\frac{\hbar}{i} \left[ \Psi_i^D(\vec{r}, t) \frac{\partial C_i}{\partial t} + \Psi_f^D(\vec{r}, t) \frac{\partial C_f}{\partial t} \right]$$

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

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

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

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

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

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

RATE OF CHANGE OF PROBABILITY  
INTEGRATE: TIME EVOLUTION OF  $C_f$

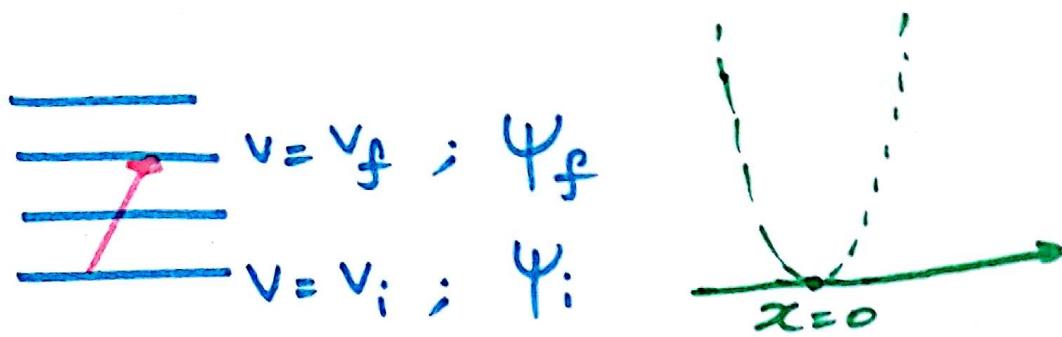
IF  $\frac{\partial C_f}{\partial t} = 0 \Rightarrow$  NO CHANGE IN  $C_f$   
NO TRANSITION

$C_f^2 \Rightarrow$  PROBABILITY

$\hat{H}^{(1)} \Rightarrow$  TRANSITION DIPOLE  
MOMENT INTEGRAL

$\Rightarrow$  SUBSTITUTE

# SELECTION RULES FOR VIBRATIONAL TRANSITIONS



TRANSITION DIPOLE MOMENT INTEGRAL

$$I_{i \rightarrow f} = \int_{\vec{r}} \Psi_f^*(\vec{r}) \hat{\mu} \Psi_i(\vec{r}) d\vec{r}$$

DIPOLE MOMENT OF AN N-PARTICLE SYSTEM

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

CHARGE ↓ POSITION

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

(IGNORE HIGHER-ORDER TERMS)

HERE

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

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

$$\vec{\nabla}_{3N} \equiv \left( \frac{\partial}{\partial \vec{r}_1}, \frac{\partial}{\partial \vec{r}_2}, \dots, \frac{\partial}{\partial \vec{r}_N} \right)$$

$$\vec{\Delta r}_{3N} = (\vec{r}_1 - \vec{r}_{1,0}, \vec{r}_2 - \vec{r}_{2,0}, \dots, \vec{r}_N - \vec{r}_{N,0})$$

FOR A DIATOMIC MOLECULE

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

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

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

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

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

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

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

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

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

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

CONSIDER

$$\int_{-\infty}^{\infty} \Psi_f^*(x) \Psi_i(x) dx$$

RECALL: FOR AN ONE-DIMENSIONAL QUANTUM HARMONIC OSCILLATOR

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

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

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

$H_v(z) \rightarrow$  HERMITE POLYNOMIAL

RECURRENCE OR RECURSION RELATION:

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

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

$$\times N_v e^{-\frac{z^2}{2}} \text{ ON BOTH SIDES}$$

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

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

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

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

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

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

FIRST INTEGRAL

~~if  $\int_x^{\infty} \Psi_{v_f}^*(x) \Psi_{v_i+1}(x) dx \neq 0$~~

ONLY WHEN  $v_f = v_i + 1$

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

SECOND INTEGRAL

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

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:

$$q = \left(\frac{m\omega}{\hbar}\right)^{1/2} x$$

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

$$b^+ \psi_v(x) = c_+ \psi_{v+1}(x)$$

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

$$b^- \psi_v(x) = c_- \psi_{v-1}(x)$$

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

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

$$x \psi_v(x) = \sqrt{\frac{\hbar}{m\omega}} \left( \frac{b^+ \psi_v(x) + b^- \psi_{v-1}(x)}{\sqrt{2}} \right)$$

$$= \sqrt{\frac{\hbar}{m\omega}} \left( \frac{c_{+v} \psi_{v+1}(x) + c_{-v} \psi_{v-1}(x)}{\sqrt{2}} \right)$$

$$\int \psi_{v_f}^*(x) x \psi_v(x) dx$$

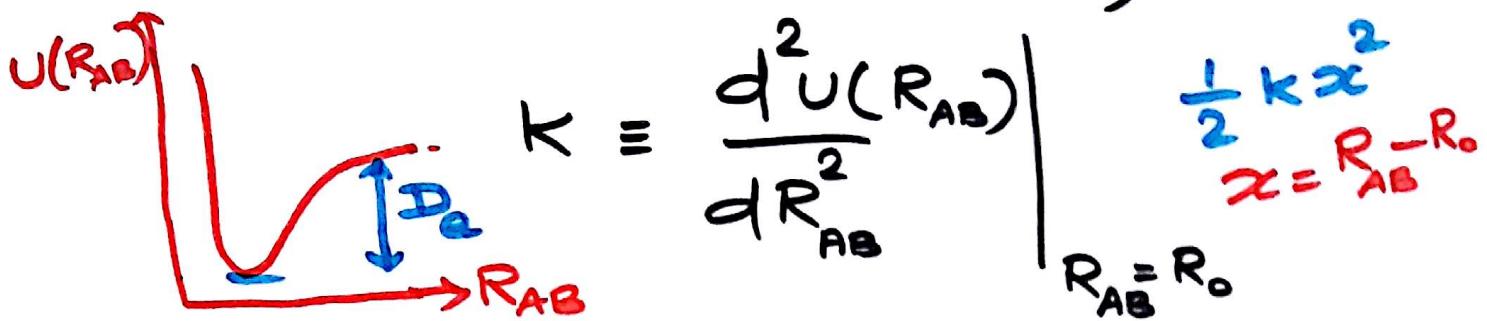
$$= B \int_x \psi_{v_f}^*(x) \psi_{v+1}(x) dx$$

$$+ D \int_x \psi_{v_f}^*(x) \psi_{v-1}(x) dx$$

$$\Rightarrow \boxed{\Delta V = V_f - V_i = \pm 1}$$

## ANHARMONICITY

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



- ANHARMONIC POTENTIAL (OR) MORSE POTENTIAL

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

$x = R_{AB} - R_0$

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

$x \rightarrow 0$ ; IGNORE HIGHER ORDER TERMS

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

$\Downarrow$   
**HARMONIC FORM**

WHAT IF  $x$  IS LARGE!

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

**PERTURBATION TO HARMONIC POTENTIAL** =  $D_e \left( a^2 x^2 + \frac{a^4 x^4}{4} - 2(ax) \left( \frac{a^2 x^2}{2} \right) \right)$

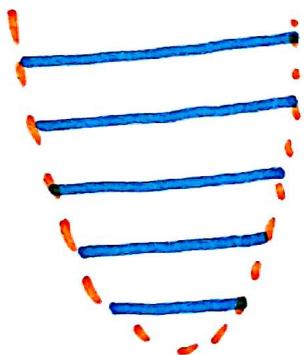
**HARMONIC**  $\frac{1}{2} (2 D_e a^2) x^2$  **ANHARMONIC**  $- a^3 x^3 + \frac{a^4 x^4}{4} - \dots$

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

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

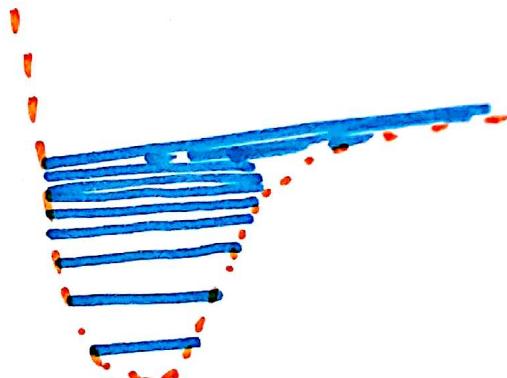
ANHARMONICITY CONSTANT (POSITIVE)

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



### 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

## NORMAL MODES

- CONSIDER A POLYATOMIC SYSTEM
- $(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \Rightarrow$  COORDINATES
- $(\vec{r}_{0,1}, \vec{r}_{0,2}, \dots, \vec{r}_{0,N}) \Rightarrow$  EQUILIBRIUM CONFIGURATION
- $U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \Rightarrow$  POTENTIAL ENERGY OF THE SYSTEM

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = U(\vec{r}_{0,1}, \vec{r}_{0,2}, \dots, \vec{r}_{0,N}) + \vec{\nabla}_{3N} U \cdot \vec{\Delta r}_{3N} + \frac{1}{2} \vec{\nabla}_{3N \times 3N}^2 U \cdot (\vec{\Delta r}_{3N} \cdot \vec{\Delta r}_{3N}) + \dots$$

HERE

$$\vec{\nabla}_{3N} U = \left( \frac{\partial U}{\partial \vec{r}_1}, \frac{\partial U}{\partial \vec{r}_2}, \dots, \frac{\partial U}{\partial \vec{r}_N} \right)$$

$$\vec{\Delta r}_{3N} = \left( \vec{r}_1 - \vec{r}_{0,1}, \vec{r}_2 - \vec{r}_{0,2}, \dots, \vec{r}_N - \vec{r}_{0,N} \right)$$

# RECALL PERTURBATION THEORY

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

$$\hat{H} \psi(x) = -\frac{\hbar^2}{2\mu} \frac{d^2 \psi(x)}{dx^2} + D_e \left[ 1 - e^{-\alpha x} \right]^2 \psi(x) = E \psi(x)$$

$$\begin{aligned} & \approx -\frac{\hbar^2}{2\mu} \frac{d^2 \psi(x)}{dx^2} + \left[ \frac{1}{2} (2D_e \alpha^2) x^2 \right. \\ & \quad \left. - \alpha^3 x^3 + \frac{\alpha^4}{4} x^4 \right] \psi(x) = E \psi(x) \\ & \approx \left[ \hat{H}_0 - \alpha^3 x^3 + \frac{\alpha^4}{4} x^4 \right] \psi(x) = E \psi(x) \end{aligned}$$

$$\Rightarrow \hat{H}^{(1)} = -\alpha^3 x^3 + \frac{\alpha^4}{4} x^4$$

$$E_v^{\text{HAR}} = \int \psi_v^*(x) \hat{H}_0 \psi_v(x) dx = \langle \psi_v | \hat{H}_0 | \psi_v \rangle$$

HARMONIC WAVE FUNCTION

$$E_v^{\text{ANH}} = \int \psi_v^*(x) \hat{H} \psi_v(x) dx = E_v^{\text{HAR}} + \Delta E$$

$$\psi_v(x) = \sum_i c_i \psi_{i,0}(x)$$

SHALL PERTURBATION ;

$$\Delta E \approx \int \psi_{v,0}^*(x) \hat{H}^{(1)} \psi_{v,0}(x) dx$$

$$\Delta E = D \int_{-\infty}^{\infty} H_v(x) x^3 H_v(x) e^{-\alpha x^2} dx$$

~~$\int_{-\infty}^{\infty} H_v(x) x^3 H_v(x) e^{-\alpha x^2} dx = 0$~~

$$+ G \int_{-\infty}^{\infty} H_v(x) x^4 H_v(x) e^{-\alpha x^2} dx \neq 0$$

HERE

$$[H_v(x)]^2 \Rightarrow \text{EVEN} \quad \text{SYMMETRIC}$$

$$e^{-\alpha x^2} \Rightarrow \text{EVEN} \quad \text{SYMMETRIC}$$

$$x^3 \Rightarrow \text{ODD} \quad \text{ANTI SYMMETRIC}$$

$$x^4 \Rightarrow \text{EVEN} \quad \text{SYMMETRIC}$$

$$\boxed{\Delta E \neq 0}$$

$$\hat{H}^{(1)} = -\alpha x^3 + \frac{\alpha^4}{4} x^4$$

CUBIC  
ANHARMONICITY

QUADRATIC  
ANHARMONICITY

IN GENERAL,

$$\hat{H}^{(1)} = \sum_{i=3}^{\infty} \alpha_i x^i$$

$$E_0^{\text{ANH}} = \frac{1}{2} \hbar \omega - \frac{1}{4} \hbar \omega \chi_e$$

$$E_0^{\text{ANH}} = E_0^{\text{HAR}} - \frac{1}{4} \hbar \omega \chi_e$$

$$E_1^{\text{ANH}} = \frac{3}{2} \hbar \omega - \frac{9}{4} \hbar \omega \chi_e$$

$$E_1^{\text{ANH}} = E_1^{\text{HAR}} - \frac{9}{4} \hbar \omega \chi_e$$

$$\begin{aligned} \Delta E_{01}^{\text{ANH}} &= E_1^{\text{ANH}} - E_0^{\text{ANH}} \\ &= (E_1^{\text{HAR}} - E_0^{\text{HAR}}) - \hbar \omega \chi_e^2 \end{aligned}$$

$$\Delta E_{01}^{\text{ANH}} = \Delta E_{01}^{\text{HAR}} - 2 \hbar \omega \chi_e$$

$$\Delta E_{12}^{\text{ANH}} = \Delta E_{12}^{\text{HAR}} - 4 \hbar \omega \chi_e$$

$$\Delta E_{23}^{\text{ANH}} = \Delta E_{23}^{\text{HAR}} - 6 \hbar \omega \chi_e$$

$$\Delta E_{01}^{\text{ANH}} > \Delta E_{12}^{\text{ANH}} > \Delta E_{23}^{\text{ANH}} > \dots$$

$$\text{BUT } \Delta E_{01}^{\text{HAR}} = \Delta E_{12}^{\text{HAR}} = \Delta E_{23}^{\text{HAR}} = \dots$$

- INTENSITY OF EMISSION SPECTRUM DEPENDS ON THE POPULATIONS OF THE EXCITED STATES
- EXCITED STATES ARE LESS POPULATED

$0 \rightarrow 1$  : INTENSE (FUNDAMENTAL)

$|\Delta v| > 1$  : OVERTONES (WEAK)

- FOR A SINGLE DIATOMIC MOLECULE: HARMONIC OSCILLATOR MODEL:
  - USING (NO ROTATION)
  - SINGLE EMISSION FREQUENCY
  - NO OVERTONES
- USING ANHARMONIC OSCILLATOR MODEL:
  - MULTIPLE EMISSION FREQUENCIES
  - OVERTONES

ROUGH ESTIMATION OF POPULATION:

$$N_{v=1} \propto e^{-\beta E_{v=1}} ; \beta = \frac{1}{k_B T}$$

$$N_{v=0} \propto e^{-\beta E_{v=0}}$$

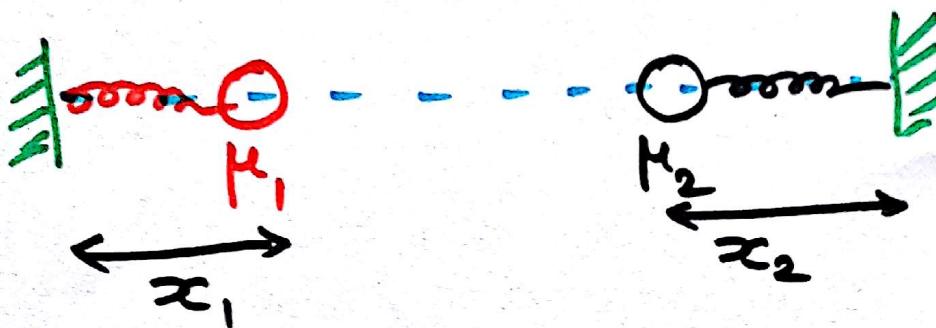
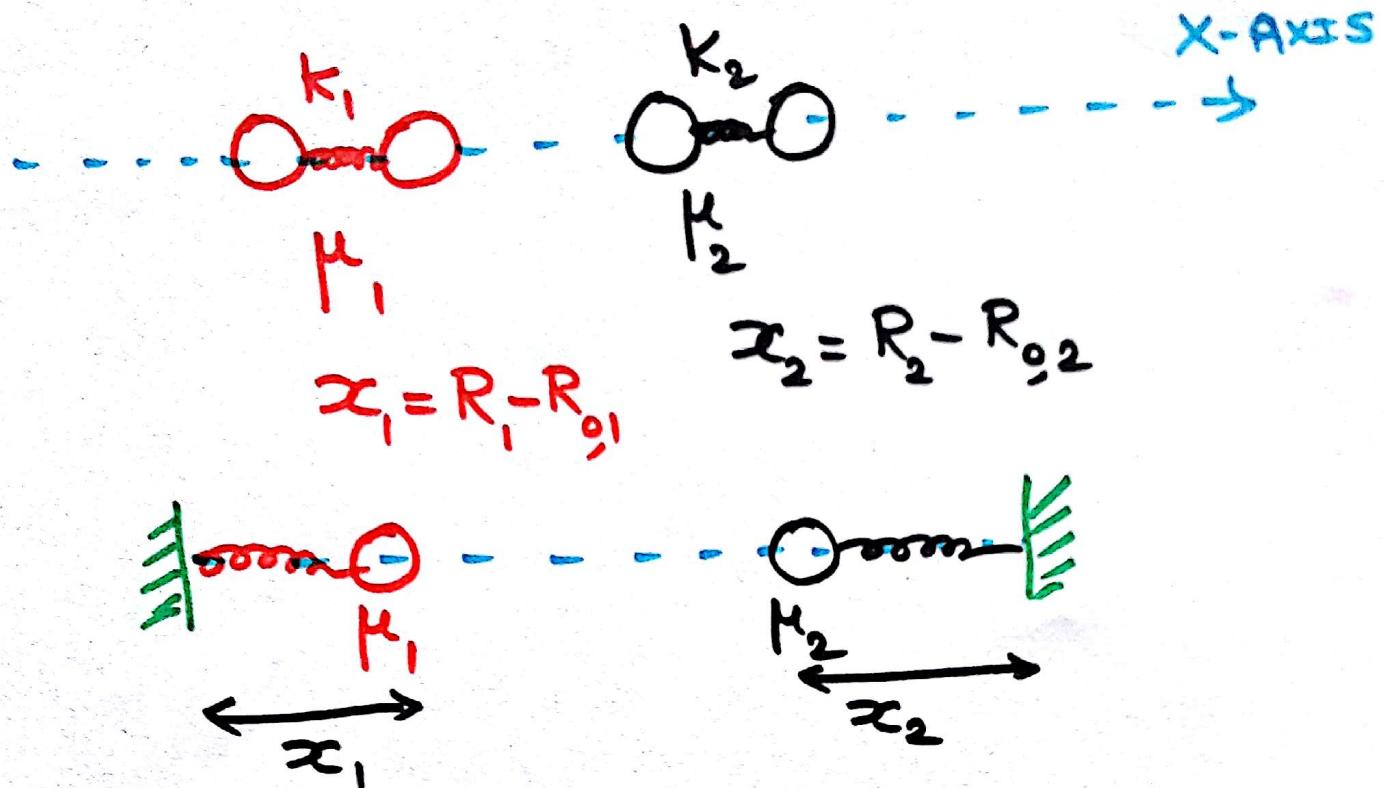
$$\frac{N_{v=1}}{N_{v=0}} = e^{-\beta [E_{v=1} - E_{v=0}]} = e^{-\beta h \nu}$$

$$\text{TAKE } T = 300 \text{ K} ; \nu_{IR} \sim 10^4 - 10^5 \text{ cm}^{-1}$$

$$\nu_{IR} = 1000 \text{ cm}^{-1}$$

# NORMAL MODES

- CONSIDER TWO DIATOMIC MOLECULES



- UNCOUPLED  $\Rightarrow$  TWO INDEPENDENT HARMONIC OSCILLATORS

$$\omega_1 = \sqrt{\frac{k_1}{\mu_1}} \quad ; \quad \omega_2 = \sqrt{\frac{k_2}{\mu_2}}$$

POTENTIAL ENERGY

$$U(x_1, x_2) = U(x_1) + U(x_2)$$

$$= \frac{1}{2} k_1 x_1^2 + \frac{1}{2} k_2 x_2^2$$

~~$$= \frac{1}{2} \mu_1 \omega_1^2 x_1^2 + \frac{1}{2} \mu_2 \omega_2^2 x_2^2$$~~

$$U(x_1, x_2) = (x_1, x_2) \begin{pmatrix} \frac{k_1}{\mu_1} & 0 \\ 0 & \frac{k_2}{\mu_2} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

$$U(x_1, x_2) = (x_1, x_2) \begin{pmatrix} \frac{1}{2} \kappa_1 \omega_1^2 & 0 \\ 0 & \frac{1}{2} \kappa_2 \omega_2^2 \end{pmatrix} (x_1, x_2)$$

SINCE

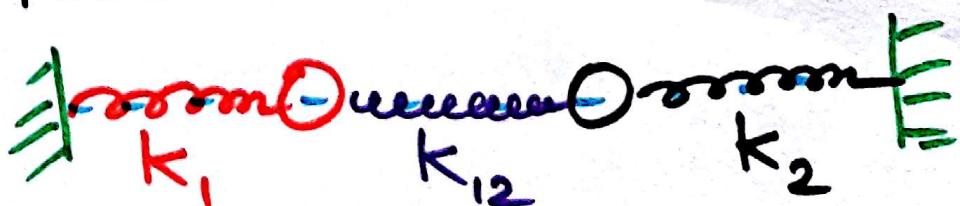
$$\kappa_1 = \frac{\partial^2 U}{\partial x_1^2}; \quad \frac{\partial^2 U}{\partial x_1 \partial x_2} = 0$$

$$\kappa_2 = \frac{\partial^2 U}{\partial x_2^2}; \quad \frac{\partial^2 U}{\partial x_2 \partial x_1} = 0$$

$$U(x_1, x_2) = \frac{1}{2} (x_1, x_2) \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial x_2} \\ \frac{\partial^2 U}{\partial x_2 \partial x_1} & \frac{\partial^2 U}{\partial x_2^2} \end{pmatrix} (x_1, x_2)$$

CURVATURE MATRIX  
OR  
HESSIAN MATRIX

### • COUPLED OSCILLATORS



$$U(x_1, x_2) = \frac{1}{2} \kappa_1 x_1^2 + \frac{1}{2} \kappa_2 x_2^2 + \frac{1}{2} \kappa_{12} (x_1 - x_2)^2$$

SIMPLE FORM

$$= \frac{1}{2} \kappa_1 x_1^2 + \frac{1}{2} \kappa_2 x_2^2 + \frac{1}{2} \kappa_{12} x_1^2 + \frac{1}{2} \kappa_{12} x_2^2 - \frac{1}{2} \kappa_{12} (2x_1 x_2)$$

$\Rightarrow$  NON-DIAGONAL HESSIAN  $\Rightarrow$  EIGENVALUES  $\Rightarrow \omega$   
DIAGONALIZE  $\Rightarrow$  EIGEN VECTORS  $\Rightarrow$  MODES

- HESSIAN FOR AN N-ATOM SYSTEM

$$H = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial y_1 \partial x_1} & \frac{\partial^2 U}{\partial z_1 \partial x_1} & \dots \\ \frac{\partial^2 U}{\partial x_1 \partial y_1} & \frac{\partial^2 U}{\partial y_1^2} & \frac{\partial^2 U}{\partial z_1 \partial y_1} & \dots \\ \frac{\partial^2 U}{\partial x_1 \partial z_1} & \frac{\partial^2 U}{\partial y_1 \partial z_1} & \frac{\partial^2 U}{\partial z_1^2} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

3N x 3N MATRIX

- USE MASS-WEIGHTED COORDINATES

$$(q_{i,x}, q_{i,y}, q_{i,z}) = (\sqrt{m_i} x_i, \sqrt{m_i} y_i, \sqrt{m_i} z_i)$$

- HAMILTON'S EQUATIONS OF MOTION

KINETIC ENERGY  $T = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2$

POTENTIAL ENERGY  $U(q) = \frac{1}{2} \sum_{i=1}^{3N} \left( \frac{\partial^2 U}{\partial q_i \partial q_j} \right) q_i q_j$

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{q}_j} + \frac{\partial U}{\partial q_j} = 0$$

$$\ddot{q}_j + \sum_{i=1}^{3N} H_{ij} q_i = 0$$

• DIAGONALIZATION OF THE HESSIAN

$$\bar{X}^{-1} H X = \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_{3N} \end{pmatrix}$$

$$\Rightarrow H X = X \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_{3N} \end{pmatrix}$$

BLOCK MATRIX

$$X = (x_1, x_2, \dots, x_N)$$

↓  
 3N-  
 COLUMN  
 VECTOR

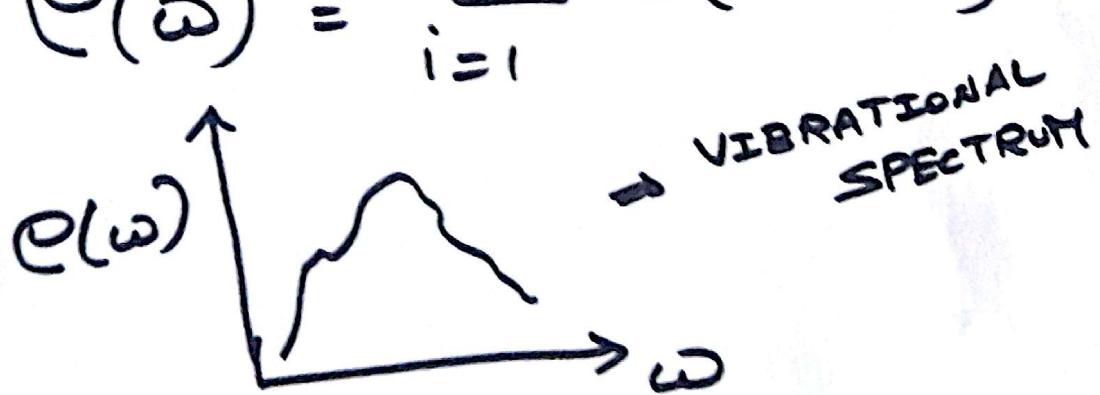
$$H x_i = \lambda_i x_i \quad (i=1, 2, \dots, 3N)$$

↓  
 EIGEN  
 VECTORS

↓  
 EIGEN (ω<sub>i</sub>)  
 VALUES

• VIBRATIONAL DENSITY OF STATES:

$$\rho(\omega) = \sum_{i=1}^{3N-6} \delta(\omega - \omega_i)$$



$3N-6 \Rightarrow$  NON-LINEAR MOLECULES

$3N-5 \Rightarrow$  LINEAR MOLECULES

• DEFINE NORMAL COORDINATES

$$Q_k = \sum_{i=1}^{3N} a_{ik} q_i \quad k = 1, 2, \dots, 3N$$

SUCH THAT

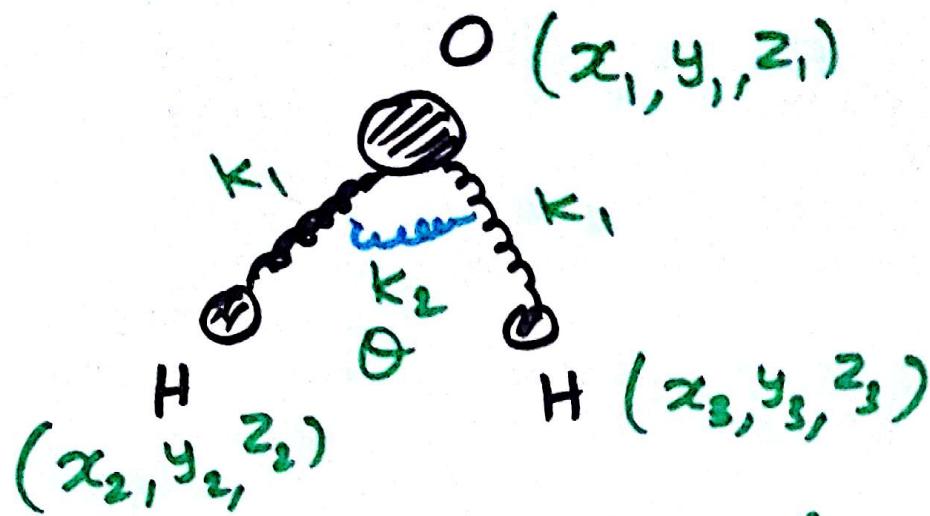
$$T = \frac{1}{2} \sum_{k=1}^{3N} \dot{Q}_k^2$$

$$U = \frac{1}{2} \sum_{k=1}^{3N} \lambda_k Q_k^2$$

$\Rightarrow$  HAMILTONIAN IS SEPARABLE

$$H = \left( \frac{1}{2} \dot{Q}_1^2 + \lambda_1 Q_1^2 \right) + \left( \frac{1}{2} \dot{Q}_2^2 + \lambda_2 Q_2^2 \right) + \dots + \left( \frac{1}{2} \dot{Q}_{3N}^2 + \lambda_{3N} Q_{3N}^2 \right)$$

# WATER MOLECULE



$$U(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{2} k_1 (\vec{r}_1 - \vec{r}_2)^2 + \frac{1}{2} k_2 (\vec{r}_1 - \vec{r}_3)^2 + \frac{1}{2} k_2 (\theta - \theta_0)^2$$

## DIATOMIC MOLECULE

### • NON-ROTATING HARMONIC VIBRATOR :

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

VIBRATIONAL LEVELS ARE  
EQUALLY SPACED

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{SELECTION RULE} \Rightarrow \Delta v = \pm 1 \quad v = 0, 1, 2, \dots$$

### • NON-ROTATING ANHARMONIC VIBRATOR :

$$\text{ENERGY} \Rightarrow E_v^{\text{ANH}} = (v + \frac{1}{2}) \hbar \omega - (v + \frac{1}{2}) \hbar \omega \chi_e^2$$

$$\text{SELECTION RULE} \Rightarrow \Delta v = \pm 1, \pm 2, \pm 3, \dots$$

VIBRATIONAL LEVELS CROWD MORE CLOSELY  
TOGETHER WITH INCREASING  $v$ .

### • RIGID (Non-VIBRATING) ROTATOR :

$$\text{ENERGY} \Rightarrow E_J = \frac{\hbar^2}{2I} J(J+1) \quad I = \mu r^2$$

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

THE ENERGY DIFFERENCE BETWEEN TWO  
SUCCESSIVE/ADJACENT LEVELS INCREASES WITH  $J$ .

$$\text{SELECTION RULE} \Rightarrow \Delta J = \pm 1$$

I INCREASES WITH J

QUICK ROTATION  
INCREASES CENTRIFUGAL  
FORCE

### • NON-RIGID ROTATOR :

$$E_J = BJ(J+1) - D[J(J+1)]^2$$

$$+ H[J(J+1)]^3 + \dots$$

• ALL BONDS ARE ELASTIC  
TO SOME EXTENT  
• BOND LENGTH INCREASES  
WITH  $J$

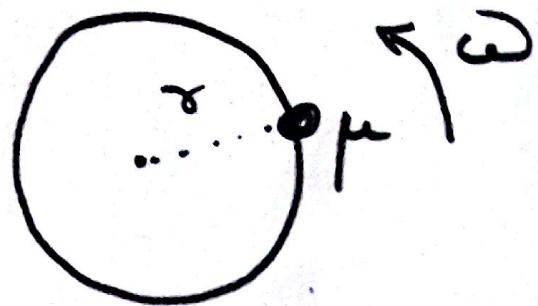
$$\text{STRETCHING; NO VIBRATION} \quad \text{SELECTION RULE} \Rightarrow \Delta J = \pm 1$$

ATOMS MOVE APART

# NON-RIGID ROTATOR

- CENTRIFUGAL FORCE

$$F_D = \mu \omega^2 \gamma$$



- RESTORING FORCE DUE TO CHEMICAL BOND

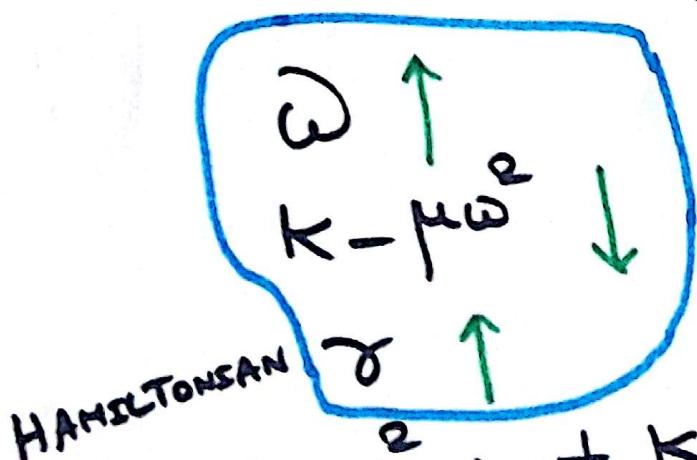
$$F_R = \kappa (\gamma - \gamma_0)$$

$$F_D = F_R$$

$$\kappa (\gamma - \gamma_0) = \mu \omega^2 \gamma$$

$$\gamma - \gamma_0 = \frac{\mu \omega^2}{\kappa} \gamma$$

$$\gamma = \frac{\kappa \gamma_0}{\kappa - \mu \omega^2}$$



$$L \Rightarrow \sqrt{I(\omega^2)} \gamma$$

$$\begin{aligned}
 H &= \frac{1}{2} I \omega^2 + \frac{1}{2} \kappa (\gamma - \gamma_0)^2 \\
 &= \frac{1}{2} I \omega^2 + \frac{1}{2} \kappa \left( \frac{\mu \omega^2 \gamma}{\kappa - \mu \omega^2} \right)^2 \\
 &= \frac{L^2}{2I} + \frac{1}{2} \frac{(I \omega^2)^2}{\kappa \gamma^2} = \frac{L^2}{2I} + \frac{L^4}{2I^2 \kappa \gamma^2}
 \end{aligned}$$

# DIATOMIC VIBRATING-ROTATOR

- ROTATIONAL ENERGY SEPARATIONS

$$1 - 10 \text{ cm}^{-1}$$

- VIBRATIONAL ENERGY SEPARATIONS

$$\sim 3000 \text{ cm}^{-1}$$

- APPROXIMATION:

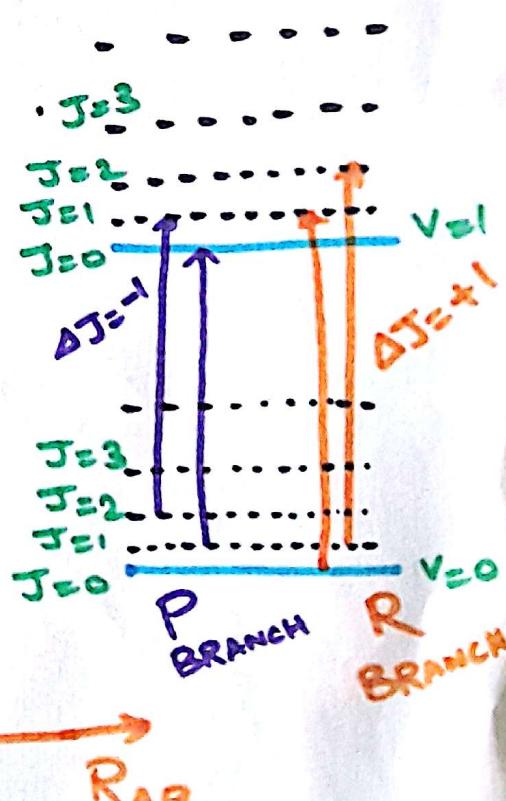
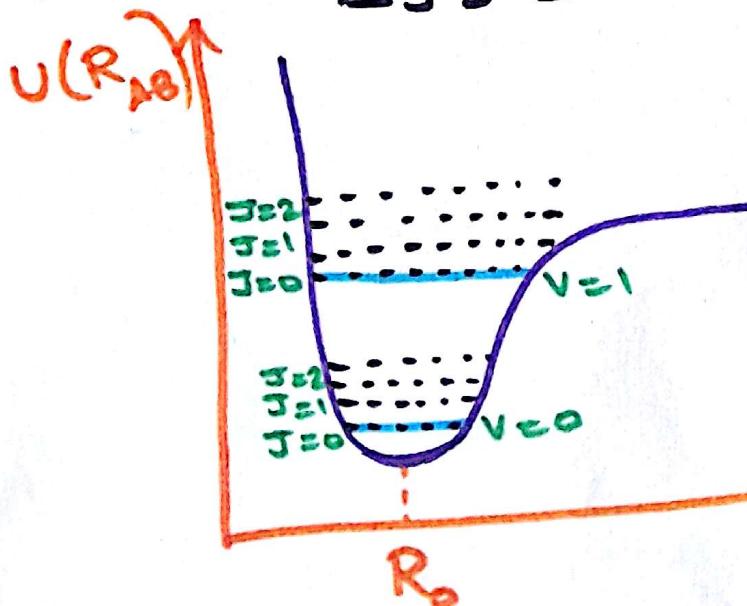
BORN-OPPENHEIMER APPROXIMATION: MOLECULE EXECUTES ROTATIONS AND VIBRATIONS INDEPENDENTLY.

$$\begin{aligned} E_{\text{TOTAL}} &= E_{\text{ROT}} + E_{\text{VIB}} \\ &= B J(J+1) - D J^2 (J+1)^2 \\ &\quad + (v + \frac{1}{2}) \hbar \omega - (v + \frac{1}{2}) \hbar \omega \chi_e \end{aligned}$$

- SELECTION RULES:

$$\Delta v = \pm 1, \pm 2, \dots$$

$$\Delta J = \pm 1$$



# QUIZ - I

12/9/2020

- ① Consider the vibrational mode that corresponds to the uniform expansion of the benzene ring. Assume this vibration as a simple harmonic motion. Do you think this vibrational excitation satisfies the first selection rule for vibrational transitions? Justify your answer.
- ② Consider a pure rotational transition of a diatomic molecule from  $J=2$  to  $J=3$  states. How do you calculate the frequency of this transition? Given this frequency, is it possible to estimate the moment of inertia and the bond length of the molecule? How?
- ③ Consider a system of  $N$  ~~non~~-interacting diatomic molecules at  $T=300K$ .
- Case-I : Assume that molecules ~~can~~ only vibrate harmonically. Let  $N_0$  and  $N_1$  are the numbers of molecules in the ground and the first excited vibrational states of the system. Calculate  $N_1/N_0$ .
- Case-II : Assume that molecules ~~can~~ only rotate. Let  $n_0$  and  $n_1$  are the numbers of molecules in the ground and the first excited rotational states of the system. Calculate  $n_1/n_0$ .
- Compare these ratios.
- ④ How do you determine the normal modes of a polyatomic molecule consisting of  $N$  atoms? You need to define the Hessian matrix and discuss about the road to diagonalize this matrix and about the vibrational density of states. Consider a special vibrational mode in which the coordinates of atoms change from  $(x_0, y_0, z_0)$  to  $(x_i + \Delta x, y_i, z_i)$  ( $i=1, 2, \dots, N$ ) and  $\Delta x$  is same for all atoms. What is the frequency of this mode? Justify your answer.

5 Consider the Potential energy of two one-dimensional harmonic oscillators coupled to each other by a spring of spring constant  $K_{12}$ . (Recall the model discussed in the class), which is given by

$$U(x_1, x_2) = \frac{1}{2} K_1 x_1^2 + \frac{1}{2} K_2 x_2^2 + \frac{1}{2} K_{12} (x_1 - x_2)^2$$

Calculate the Hessian for this model system. Determine the frequencies of the normal modes. Plot ~~schematic~~ schematic graphs showing the variation of these frequencies with  $K_{12}$ .

6 In the class, we discussed about electronic energy surfaces of a diatomic molecule as a function of internuclear separation. How do we determine/calculate the ~~—~~ ground and ~~—~~ first excited electronic energy surfaces?

What do they represent physically? Why do you think the energy gap between these two states is greater than that of vibrational levels?

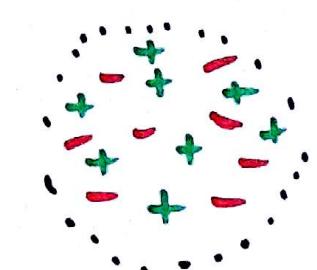
7 By rotating a diatomic molecule about an axis passing through the center of gravity, which is perpendicular to the molecular axis, we can break the molecule.

(dissociate) with this statement?

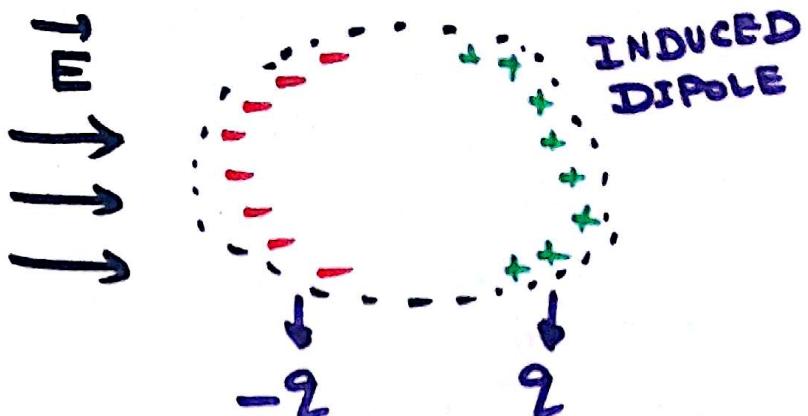
Do you agree  
Justify your answer.

# RAMAN SPECTROSCOPY

## POLARIZATION AND POLARIZABILITY



WITHOUT  
ELECTRIC  
FIELD



WITH ELECTRIC  
FIELD

$$\vec{E} = E_x \hat{i} + E_y \hat{j} + E_z \hat{k}$$

INDUCED DIPOLE MOMENT:

$$\vec{\mu}_I = \beta \vec{E}$$

↳ POLARIZABILITY

$$\mu_{I,x} = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z$$

$$\mu_{I,y} = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z$$

$$\mu_{I,z} = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z$$

$$\begin{pmatrix} \mu_{I,x} \\ \mu_{I,y} \\ \mu_{I,z} \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

IF  $\vec{E}$  IS ALONG X-AXIS,  $E_y = E_z = 0$

$$\rightarrow \mu_{I,x} = \alpha_{xx} E_x ; \mu_{I,y} = \mu_{I,z} = 0$$

→ THINK ABOUT IT:

WHAT HAPPENS WHEN A HYDROGEN ATOM IN THE GROUND STATE IS PLACED IN AN UNIFORM EXTERNAL ELECTRIC FIELD? DOES IT POLARIZE? WHAT IS THE POLARIZABILITY OF THE HYDROGEN ATOM? DO YOU THINK THAT THE ORBITAL OF THE HYDROGEN ATOM WILL BE SPHERICAL IN THE PRESENCE OF THE ELECTRIC FIELD?

- LIGHT  $\Rightarrow$  OSCILLATING ELECTRIC FIELD

X-AXIS

$$E = E_0 \cos(\omega_0 t) \quad \text{FREQUENCY OF THE INCIDENT LIGHT}$$

$$E = E_0 \cos(2\pi \gamma_0 t)$$

$$\mu_I = \alpha E = \alpha E_0 \cos(2\pi \gamma_0 t)$$

- MOLECULES ARE NOT STATIC, BUT THEY ARE DYNAMIC

$$x = x_0 \cos(2\pi \gamma_m t)$$

NORMAL MODE

OR  
DISPLACEMENT FROM EQUILIBRIUM

$$\alpha(x) = \alpha(x_0) + \left. \frac{\partial \alpha}{\partial x} \right|_{x_0} x + \dots$$

$$\alpha(x) = \alpha(x_0) + \left. \frac{\partial \alpha}{\partial x} \right|_{x_0} (x_0 \cos(2\pi \gamma_m t))$$

$$\Rightarrow \mu_I = \left[ \alpha(x_0) + \left. \frac{\partial \alpha}{\partial x} \right|_{x_0} x_0 \cos(2\pi \gamma_m t) \right] E_0 \cos(2\pi \gamma_0 t)$$

$$= \alpha(x_0) E_0 \cos(2\pi \gamma_0 t)$$

$$+ \left( \left. \frac{\partial \alpha}{\partial x} \right|_{x_0} x_0 E_0 \cos(2\pi \gamma_m t) \cos(2\pi \gamma_0 t) \right)$$

$$\cos A \cos B = \frac{1}{2} [\cos(A+B) + \cos(A-B)]$$

$$\mu_I = \alpha(x_0) E_0 \cos(2\pi \gamma_0 t) \xrightarrow{\text{ELASTIC (OR) RAYLEIGH SCATTERING}}$$

$$+ \left( \frac{\partial \alpha}{\partial x} \right)_{x_0} \frac{x_0 E_0}{2} \cos(2\pi(\gamma_0 - \gamma_m) t)$$

INELASTIC SCATTERING (OR) STOKES SCATTERING

$$+ \left( \frac{\partial \alpha}{\partial x} \right)_{x_0} \frac{x_0 E_0}{2} \cos(2\pi(\gamma_0 + \gamma_m) t)$$

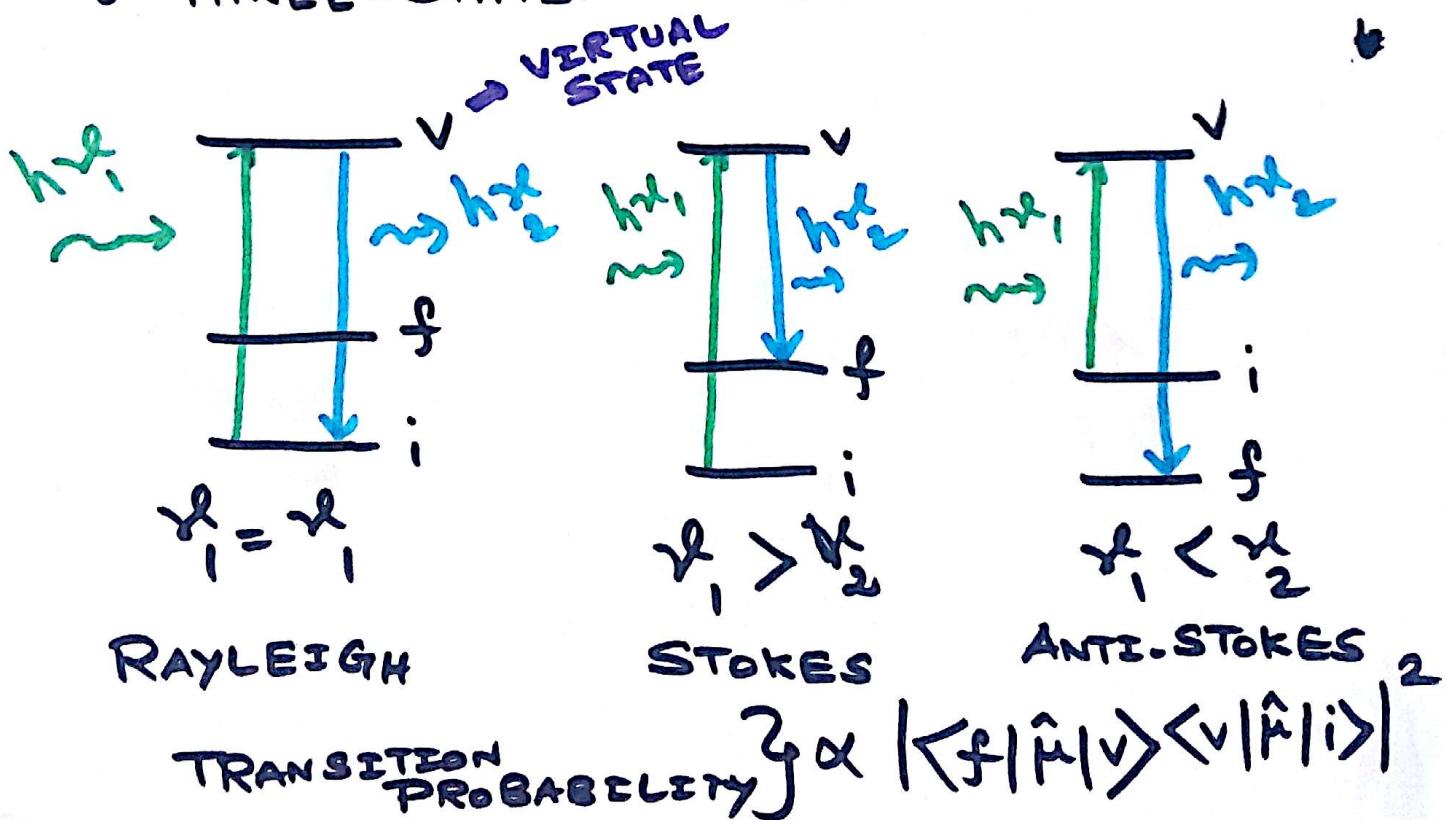
INELASTIC SCATTERING (OR) ANTI-STOKES

### CONDITION FOR RAMAN SCATTERING

$$\left( \frac{\partial \alpha}{\partial x} \right)_{x_0} \neq 0$$

- THE OSCILLATING DIPOLE HAS FREQUENCY COMPONENTS  $\gamma_0 \pm \gamma_m$  AS WELL AS THE EXCITING FREQ.  $\gamma_0$

### THREE-STATE MODEL:



# ROTATIONAL RAMAN SPECTROSCOPY

→ SELECTION RULE  $\Delta J = \pm 2$

- ROTATIONAL ENERGY OF A RIGID DIATOMIC MOLECULE

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1) \quad J=0,1,2,\dots$$

$$E_J = B J(J+1) \quad \begin{matrix} \text{--- } J+2 \\ \text{--- } J \end{matrix}$$

$$\Delta E = E_{J+2} - E_J$$

$$= B(J+2)(J+3) - B J(J+1)$$

$$= B \left[ J^2 + 3J + 2J + 6 - J^2 - J \right]$$

$$\boxed{\Delta E = 2B [2J+3]} \Rightarrow h\gamma_m$$

$$\boxed{\gamma_0 \pm \gamma_m = \gamma_0 \pm \frac{2B}{h} [2J+3]}$$

- SIMILAR RAMAN APPROACH FOR VIBRATIONAL SPECTROSCOPY
- $$\Delta E = E_{V=1} - E_{V=0} = h\gamma_m$$
- WEAK OVERTONES CAN BE IGNORED

# ELECTRONIC SPECTROSCOPY

## → ELECTRONIC TRANSITIONS

↳ ELECTRONIC ABSORPTION  
↳ ELECTRONIC EMISSION

## TRANSITIONS BETWEEN ELECTRONIC STATES

→ DO WE OBSERVE SIGNATURES OF VIBRATIONAL AND ROTATIONAL TRANSITIONS ACCOMPANYING ELECTRONIC TRANSITIONS?

→ ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

• BORN-OPPENHEIMER APPROXIMATION

ELECTRONIC, VIBRATIONAL, AND ROTATIONAL DYNAMICS ARE INDEPENDENT OF EACH OTHER.

⇒ TOTAL ENERGY OF THE MOLECULE :

$$E_{\text{TOTAL}} = E_{\text{ELEC}} + E_{\text{VIB}} + E_{\text{ROT}}$$

↳ ELECTRONIC ENERGY  
↓  
↳ VIBRATIONAL ENERGY

↳ ROTATIONAL ENERGY

⇒ CHANGE IN ENERGY :

$$\Delta E_{\text{TOTAL}} = \Delta E_{\text{ELEC}} + \Delta E_{\text{VIB}} + \Delta E_{\text{ROT}}$$

$$\Delta E_{\text{ELEC}} > \Delta E_{\text{VIB}} > \Delta E_{\text{ROT}}$$

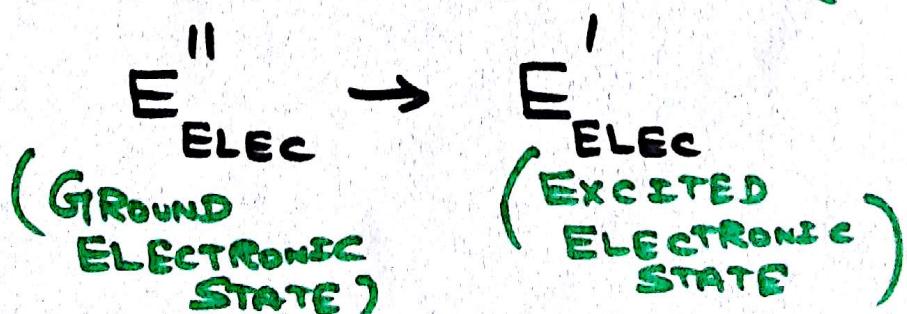
⇒ VIBRATIONAL CHANGES PRODUCE A 'COARSE STRUCTURE' AND ROTATIONAL CHANGES PRODUCE A 'FINE STRUCTURE' ON THE SPECTRA OF ELECTRONIC TRANSITIONS.

- HOMONUCLEAR DIATOMIC MOLECULES ( $H_2$  OR  $N_2$ ) DO NOT SHOW VIBRATION-ROTATION OR ROTATION SPECTRA (NO PERMANENT ELECTRIC DIPOLE MOMENT OR NO CHANGE OF DIPOLE DURING ROTATION OR VIBRATION)

BUT THEY EXHIBIT AN ELECTRONIC SPECTRUM WITH VIBRATIONAL 'COARSE' STRUCTURES AND ROTATIONAL 'FINE' STRUCTURES (USING THESE STRUCTURES, WE CAN ESTIMATE VIBRATIONAL FREQUENCIES AND ROTATIONAL CONSTANTS)

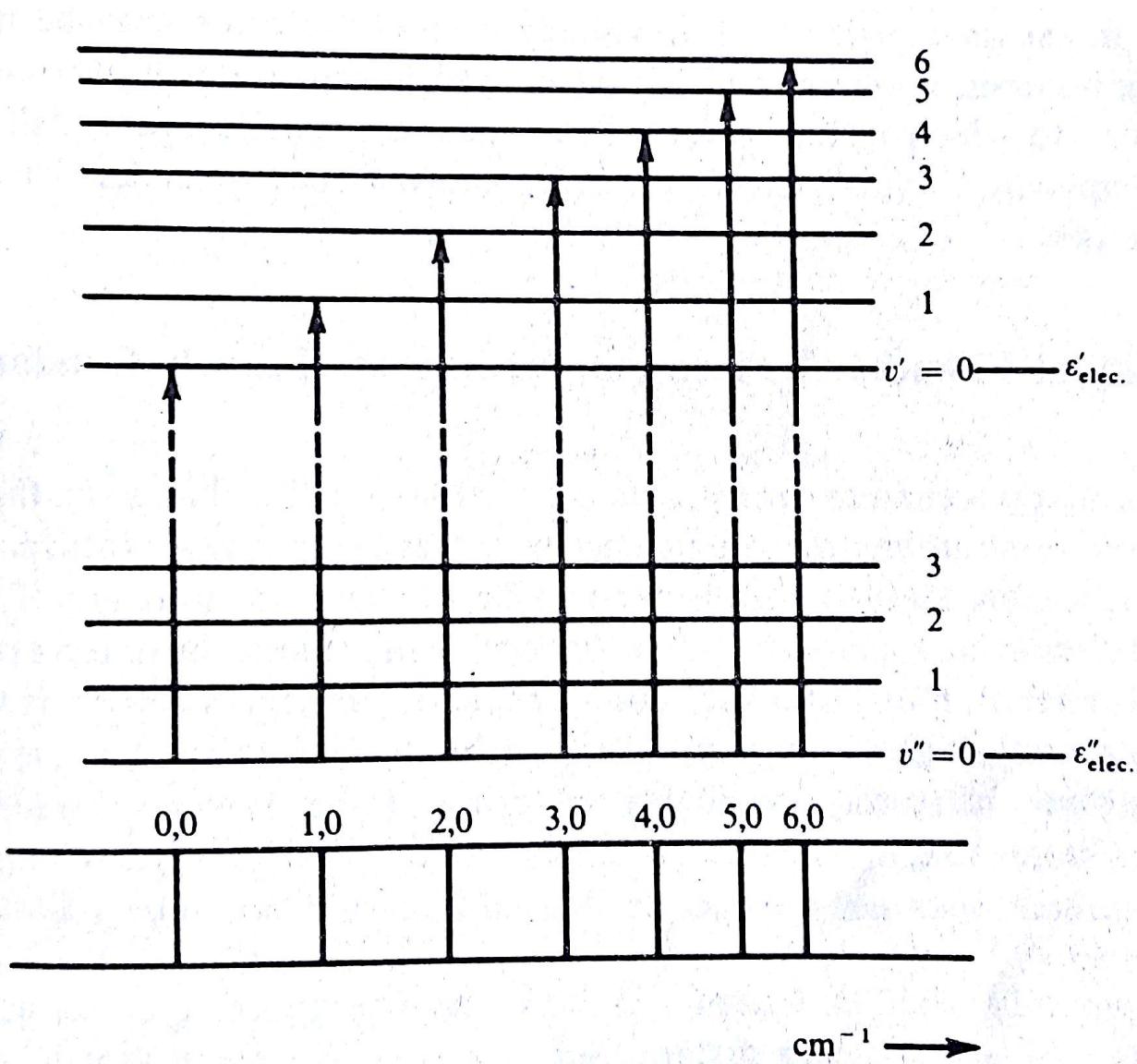
- VIBRATIONAL COARSE STRUCTURE :-  
 → IGNORE ROTATIONAL CHANGES  
 →  $E_{\text{TOTAL}} = E_{\text{ELEC}} + E_{\text{VIB}}$
- $$E_{\text{TOTAL}} = E_{\text{ELEC}} + (v + \frac{1}{2})\hbar\omega - (v + \frac{1}{2})\hbar\omega\chi_e$$
- 2
- ANHARMONIC OSCILLATOR

→ ELECTRONIC TRANSITION (ABSORPTION)



$\chi_e$  AND VIBRATIONAL FREQUENCIES MAY DIFFER BETWEEN ELECTRONIC STATES

$$\Delta E_{\text{TOTAL}} = (E_{\text{ELEC}}' - E_{\text{ELEC}}'') + \left\{ (v' + \frac{1}{2})\hbar\omega - (v'' + \frac{1}{2})\hbar\omega\chi_e \right. \\ \left. - (v'' + \frac{1}{2})\hbar\omega + (v' + \frac{1}{2})\hbar\omega\chi_e \right\}$$



**Figure 6.1** The vibrational 'coarse' structure of the band formed during electronic absorption from the ground ( $v'' = 0$ ) state to a higher state.

→ ALMOST ALL THE MOLECULES EXIST IN THE LOWEST VIBRATIONAL STATE ( $v''=0$ )

TRANSITIONS : ( $v', v''$ )

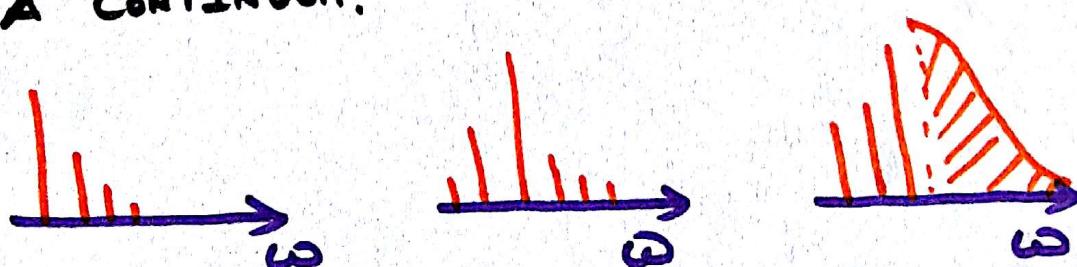
( $v', v''=0$ )  $\Rightarrow$  APPRECIABLE INTENSITY

(0, 0), (1, 0), (2, 0), ...  $\Rightarrow$  BAND  
 $v'$  PROGRESSION

→ THE LINES IN A BAND CROWD TOGETHER MORE CLOSELY AT HIGH FREQUENCIES (DUE TO ANHARMONICITY)

→ THE VIBRATIONAL LINES IN A PROGRESSION DIFFER IN INTENSITY.

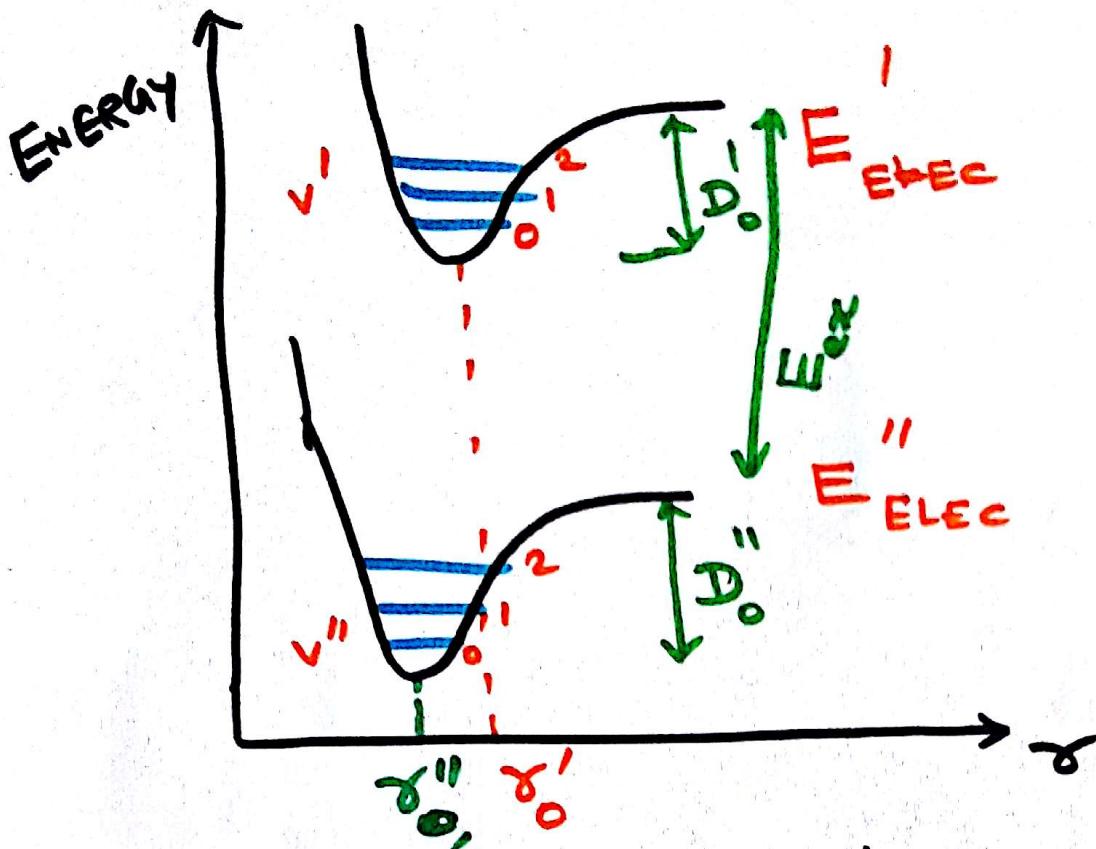
IN SOME SPECTRA, THE (0, 0) TRANSITION IS THE STRONGEST, IN OTHERS THE INTENSITY INCREASES TO A MAXIMUM AT SOME VALUE OF  $v'$ , WHILE IN YET OTHERS ONLY A FEW VIBRATIONAL LINES WITH HIGH  $v'$  ARE SEEN, FOLLOWED BY A CONTINUUM.



→ FRANCK-CONDON PRINCIPLE : AN ELECTRONIC TRANSITION TAKES PLACE SO RAPIDLY THAT A VIBRATING MOLECULE DOES NOT CHANGE ITS INTERNUCLEAR DISTANCE APPRECIABLY DURING THE TRANSITION.

VERTICAL TRANSITION

## • FRANCK-CONDON PRINCIPLE



$$\text{CASE I : } \gamma_0'' = \gamma_0'$$

$(0, 0)$  IS THE STRONGEST SPECTRAL LINE OF THE  $v''=0$  PROGRESSION.

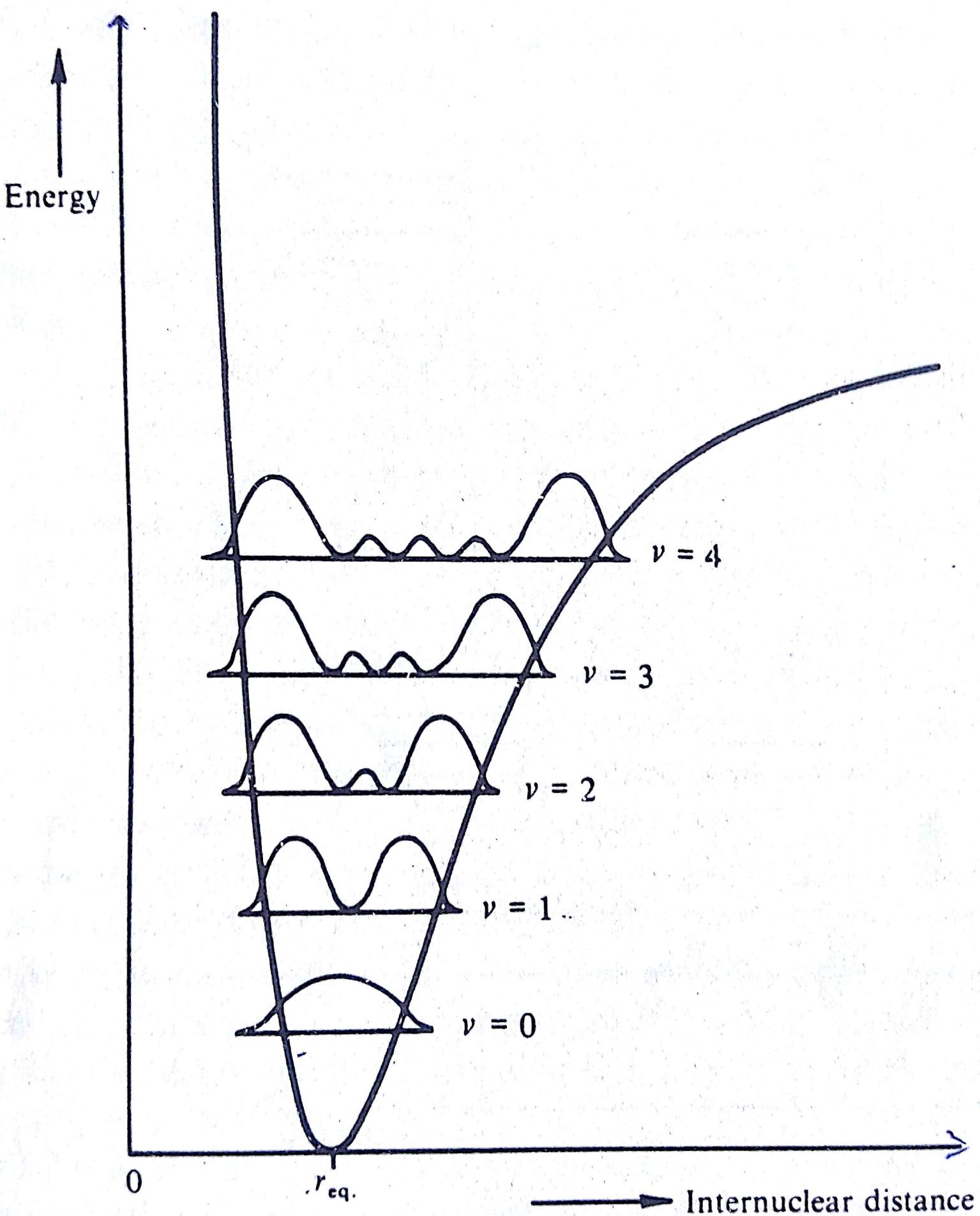
ADDITIONAL TRANSITIONS DUE TO  
DELOCALIZATION OF PROBABILITY IN  
 $v''=0$  STATE

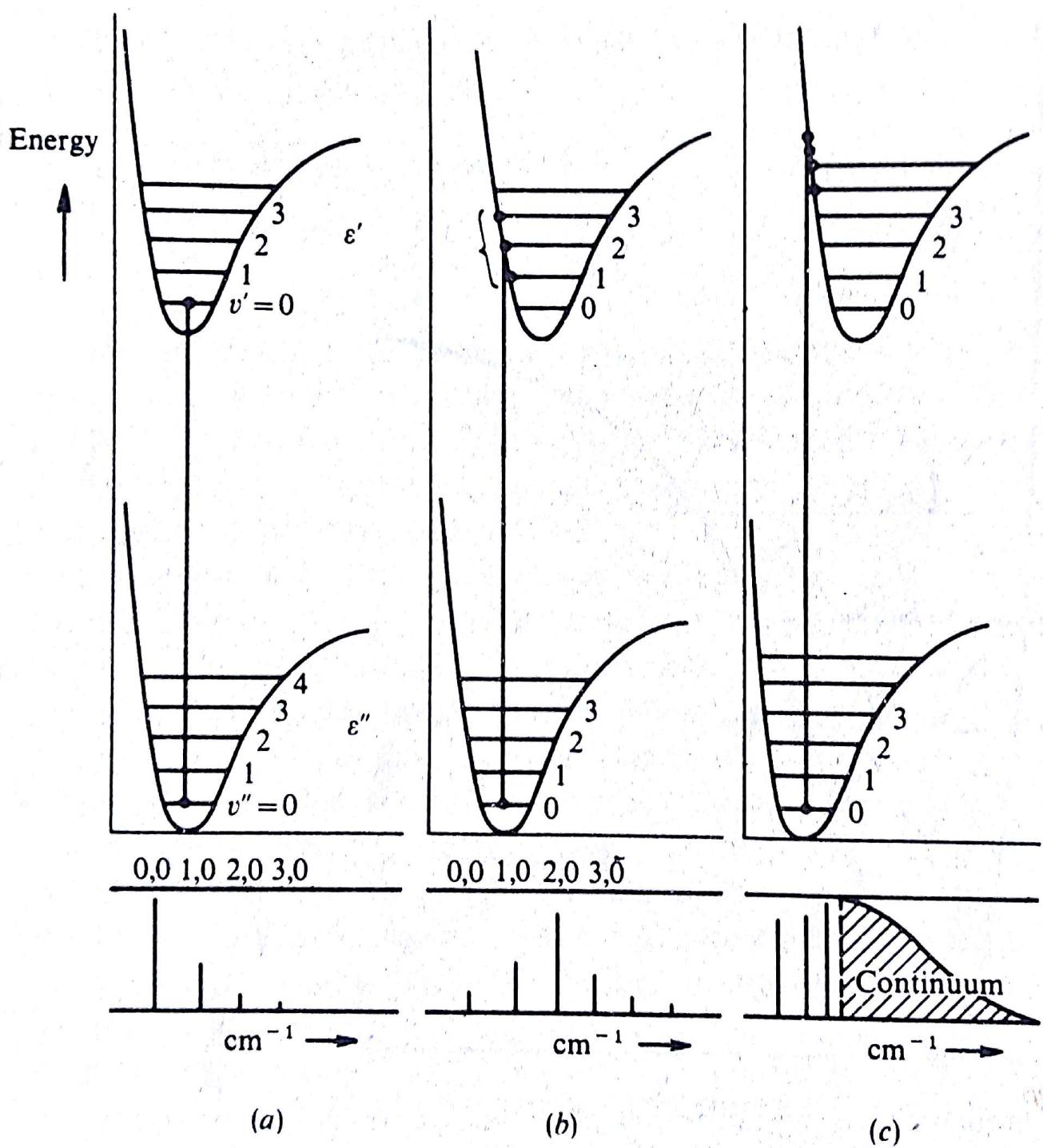
CASE II :  $\gamma_0' > \gamma_0''$   
TRANSITION FROM  $v''=0$  TO  $v' > 0$  STATE

CASE III :  $\gamma_0' \gg \gamma_0''$

DISSOCIATION IS POSSIBLE IN  
THE EXCITED STATE  $\Rightarrow$  DISSOCIATED  
ATOMS CAN TAKE UP ANY VALUE OF KINETIC  
ENERGY

• INCLUDE  $E_{ROT} \Rightarrow$  ROTATIONAL FINE STRUCTURE  
FOR EACH VIB. TRANSITION





**Figure 6.3** The operation of the Franck-Condon principle for (a) internuclear distances equal in upper and lower states, (b) upper-state internuclear distance a little greater than that in the lower state, and (c) upper-state distance considerably greater.

# THE RE-EMISSION OF ENERGY BY AN EXCITED MOLECULE :-

→ DISSOCIATION

→ RE-EMISSION :-

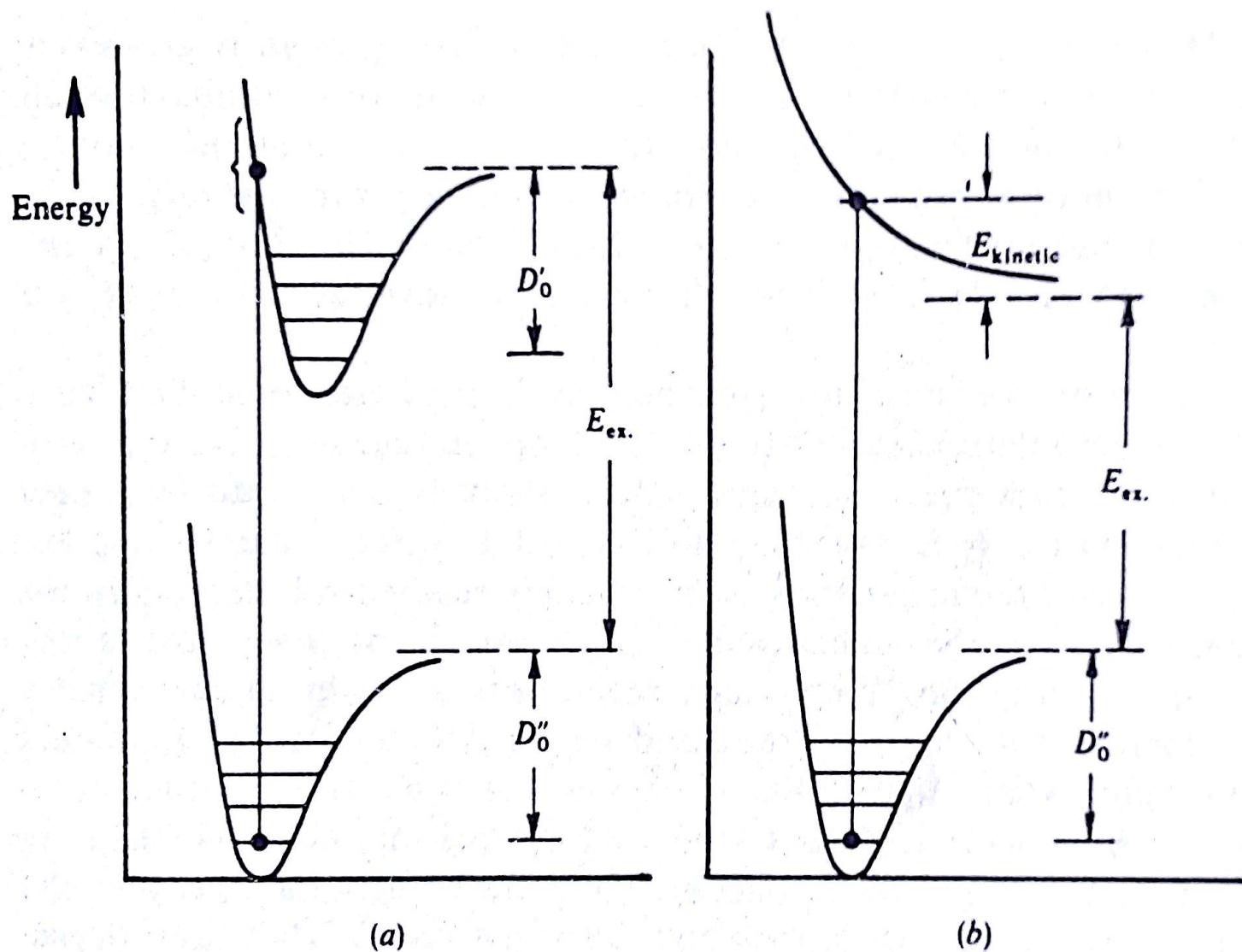
$$\gamma_{\text{ABS}} = \gamma_{\text{EMI}}$$

→ FLUORESCENCE :-

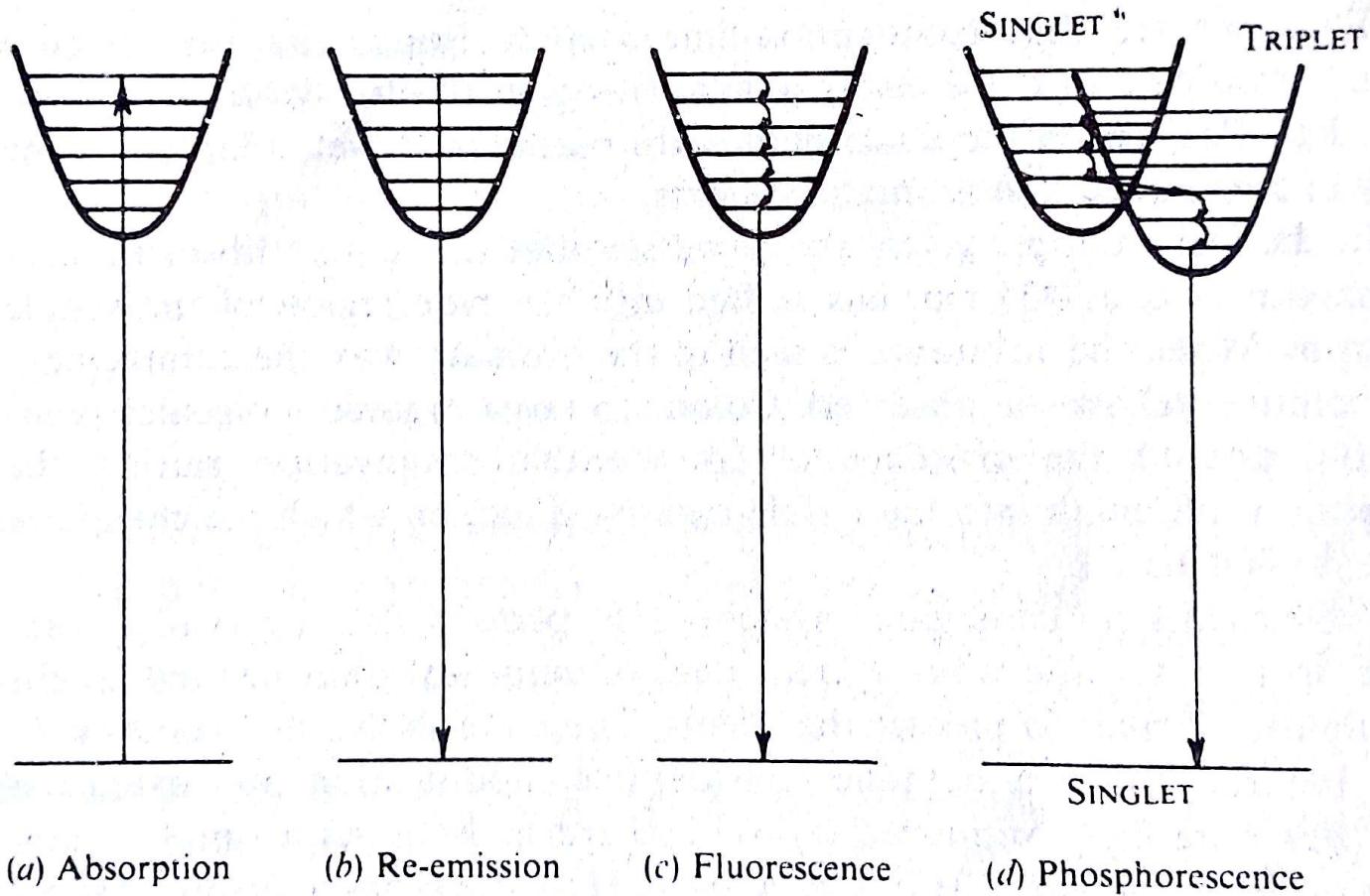
- EXCESS VIBRATIONAL ENERGY IS LOST BY INTERMOLECULAR COLLISIONS
- VIB. ENERGY  $\rightarrow$  KINETIC ENERGY "RADIATIONLESS" ENERGY TRANSFER
- REACHES THE LOWEST VIB. STATE
- REVERT TO THE ELECTRONIC GROUND STATE

→ PHOSPHORESCENCE

- INTER SYSTEM CROSSING BETWEEN TWO EXCITED STATES OF DIFFERENT TOTAL SPIN WITH COMPARABLE ENERGIES.

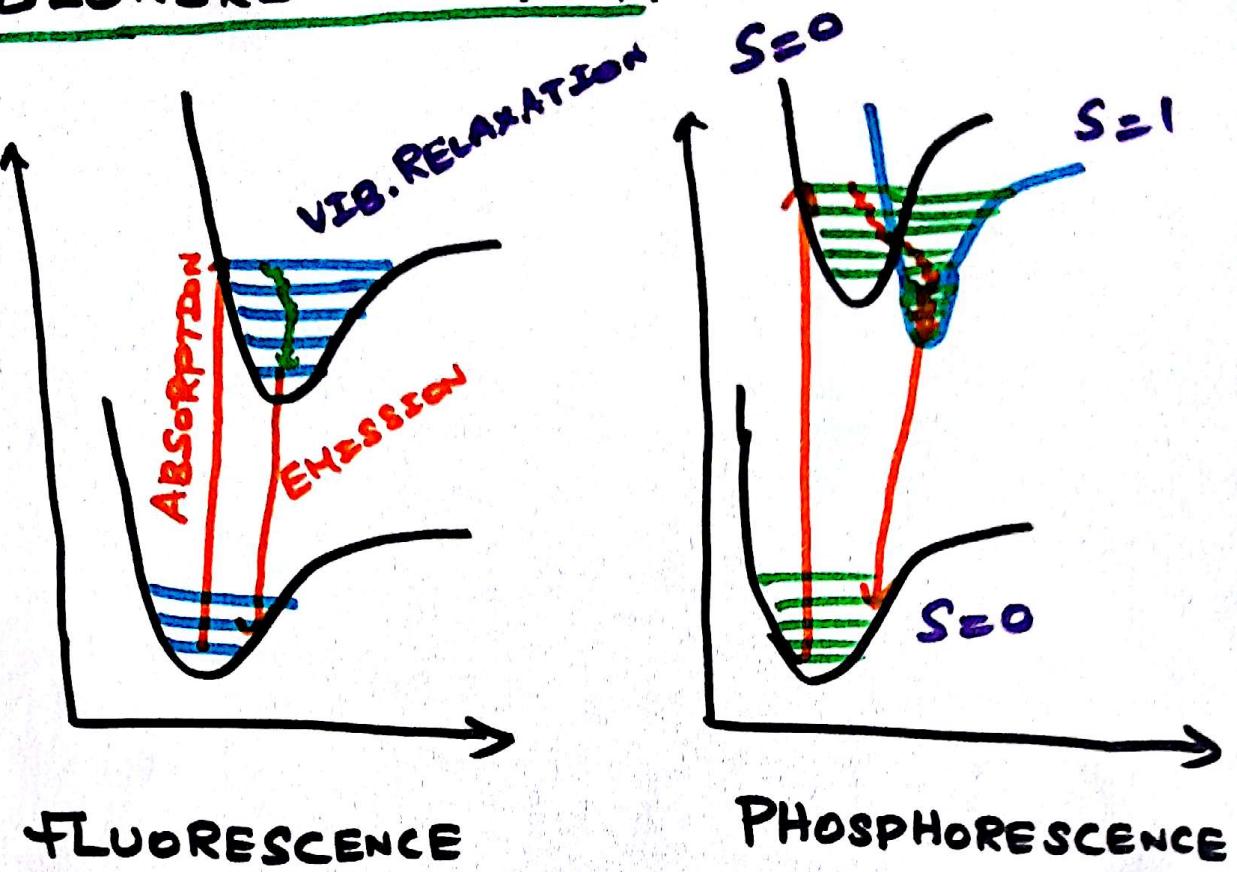


**Figure 6.4** Illustrating dissociation by excitation into (a) a stable upper state, and (b) a continuous upper state.

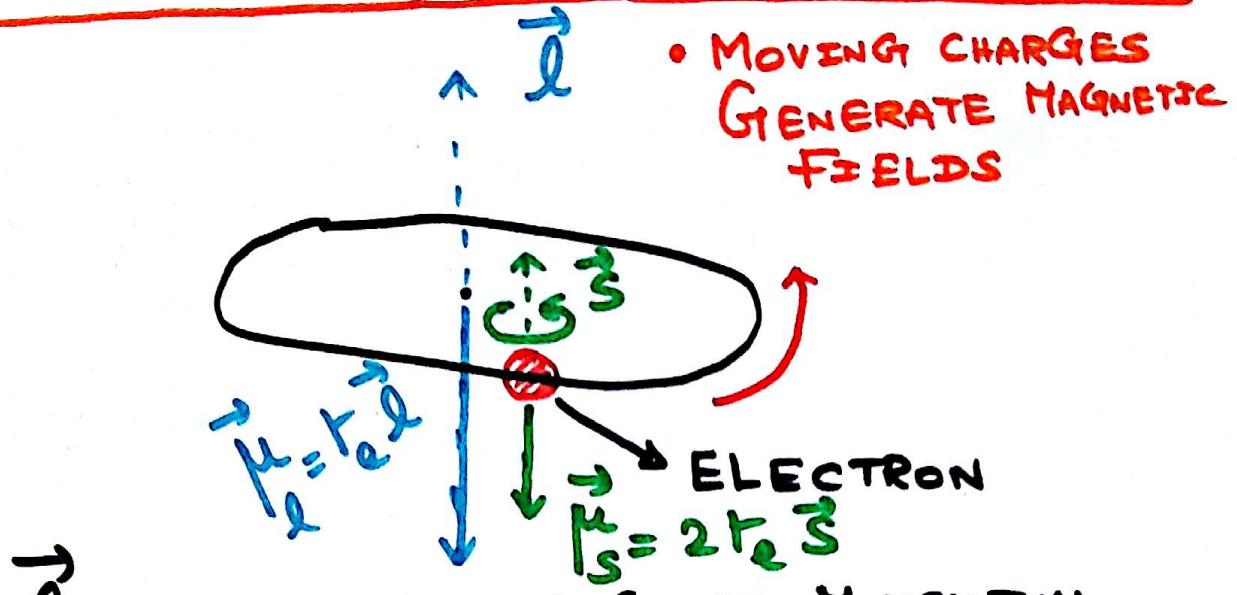


**Figure 6.20** Showing the various ways in which an electronically excited molecule can lose energy.

# JABLONSKI DIAGRAM:



## MAGNETIC MOMENT AND ANGULAR MOMENTUM



$\vec{l}$  = ORBITAL ANGULAR MOMENTUM

$\vec{\mu}_l = \gamma_e \vec{l}$   $\Rightarrow$  MAGNETIC MOMENT DUE TO ORBITAL MOMENTUM

$\vec{s}$  = SPIN ANGULAR MOMENTUM

$\vec{\mu}_s = 2\gamma_e \vec{s}$   $\Rightarrow$  MAGNETIC MOMENT DUE TO ELECTRON SPIN

### SPIN-ORBIT COUPLING:

THE INTERACTION OF THE SPIN MAGNETIC MOMENT WITH THE MAGNETIC FIELD ARISING FROM THE ORBITAL ANGULAR MOMENTUM IS CALLED SPIN-ORBIT COUPLING

$\vec{\mu}_l$  ACTS LIKE A BAR MAGNET

$\vec{\mu}_s$  ACTS LIKE ANOTHER BAR MAGNET

THEY INTERACT WITH EACH OTHER



• TOTAL ANGULAR MOMENTUM

$$\vec{J} = \vec{l} + \vec{s} \quad (\text{VECTOR SUM})$$

## • TOTAL ANGULAR MOMENTUM

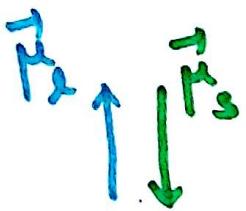
$$\vec{j} = \vec{l} + \vec{s}$$

(VECTOR SUM;  
RELATIVE ORIENTATION OF  $\vec{l}$  AND  
 $\vec{s}$  IS IMPORTANT)



$\vec{l}_e$  AND  $\vec{s}_e$  ARE PARALLEL TO EACH OTHER

$$j = l + s$$



$\vec{l}_e$  AND  $\vec{s}_e$  ARE ANTI-PARALLEL

$$j = l - s$$

## • SPIN-ORBIT COUPLING ENERGY

$$E_{l,s,j} \propto [j(j+1) - l(l+1) - s(s+1)]$$

Quantum  
Mechanics  
 $\left(\frac{1}{2}, \frac{1}{2}\right)$ ,  $\left(\frac{1}{2}, \frac{1}{2}\right)$ ,  $\left(\frac{1}{2}, \frac{1}{2}\right)$ ,  $\left(\frac{1}{2}, \frac{1}{2}\right)$

ENERGY WHEN  $\vec{l}$  AND  $\vec{s}$  ARE COUPLED

ENERGY WHEN  $\vec{l}$  AND  $\vec{s}$  ARE UNCOUPLED

• NOTE:  $\vec{j}$ ,  $\vec{l}$ , and  $\vec{s}$  ARE QUANTIZED.

## • ADDITION OF ANGULAR MOMENTA

$$\vec{j} \cdot \vec{j} = (\vec{l} + \vec{s}) \cdot (\vec{l} + \vec{s})$$

$$j^2 = \vec{l} \cdot \vec{l} + \vec{s} \cdot \vec{s} + 2 \vec{l} \cdot \vec{s}$$

$$j^2 = l^2 + s^2 + 2 \vec{l} \cdot \vec{s}$$

$$\vec{l} \cdot \vec{s} = \frac{1}{2} (j^2 - l^2 - s^2)$$

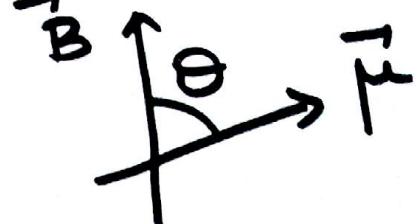
# MAGNETIC MOMENT IN A MAGNETIC FIELD

$\vec{\mu}$   $\Rightarrow$  MAGNETIC MOMENT

$\vec{B}$   $\Rightarrow$  EXTERNAL MAGNETIC FIELD

INTERACTION ENERGY

$$E = -\vec{\mu} \cdot \vec{B}$$



$$E = -\mu B \cos \theta$$

$$\theta = 0 \Rightarrow E = -\mu B \quad (\text{MINIMUM ENERGY})$$

• FOR AN ELECTRON POSSESSING ORBITAL ANGULAR MOMENTUM ( $\vec{l}$ ) AND SPIN ANGULAR MOMENTUM ( $\vec{s}$ ) IN EXTERNAL MAGNETIC FIELD  $\vec{B}$ :

$\Rightarrow$  ORBITAL ANGULAR MOMENTUM PART :

$$E_l = -(\tau_e \vec{l}) \cdot \vec{B}$$

$$E_l = -\tau_e \vec{B} \cdot \vec{l}$$

$$\tau_e = \frac{1e1}{2m_e}$$

MAGNETOGYRIC RATIO  
(OR)

GYROMAGNETIC

RATIO OF  
ELECTRON

MASS  
OF  
ELECTRON

IF UNIFORM MAGNETIC FIELD IS  
APPLIED ALONG Z-AXIS  $\vec{B} = (0, 0, B_0)$

$$\Rightarrow E_l = -\tau_e B_0 \hat{l}_z ; \hat{l}_z \Rightarrow Z\text{-COMPONENT}$$

$$\text{RECALL: } \hat{l}_z \Psi = m_l \hbar \Psi \quad m_l = -l, -l+1, \dots, l-1, l$$

( $2l+1$ ) DEGENERATE STATES ( $B_0=0$ ) —  $m_l=2$   
 SPLIT INTO DIFFERENT LEVELS ( $B_0 \neq 0$ ) —  $m_l=-l+1$   
 $E_l = -\frac{e}{2m_e} \frac{m_l \hbar}{\tau_e} B_0$  —  $m_l=-l$

$$\mu_{l,z} = \frac{e}{2m_e} \frac{m_l \hbar}{\tau_e} = -\frac{e}{2m_e} \frac{m_l \hbar}{\tau_e}$$

$$\mu_{l,z} = -\mu_B \frac{m_l}{\tau_e}$$

HERE  $\mu_B = \frac{e \hbar}{2m_e}$  BOHR MAGNETON

FUNDAMENTAL QUANTUM OF MAGNETIC MOMENT

→ SPIN ANGULAR MOMENTUM PART :

SPIN QUANTUM NUMBER OF AN ELECTRON

$$S = \frac{1}{2}$$

$$\vec{\mu}_s = g_e \tau_e \vec{s}$$

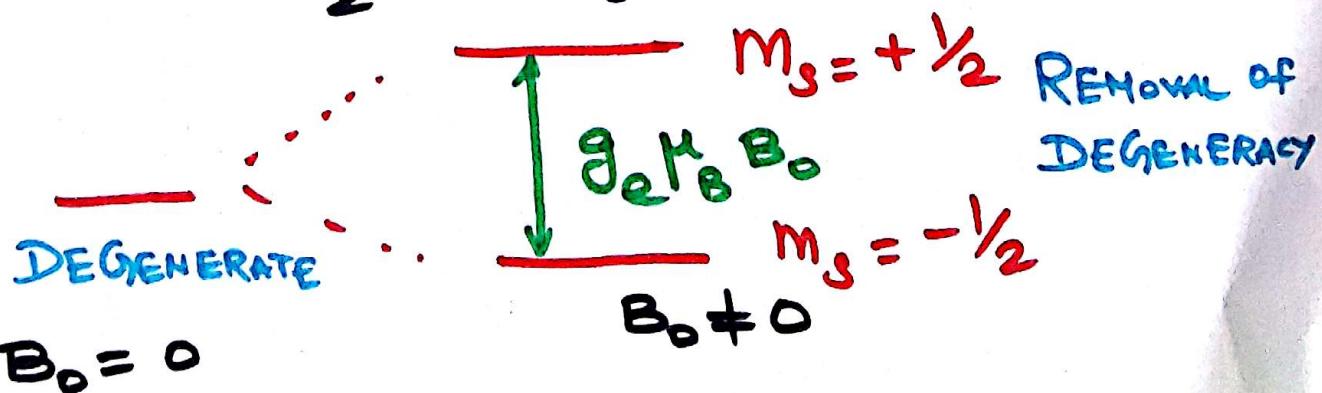
$g_e = 2.002319$   
 g-factor or  
 g-value of the  
 electron

$$E_s = -(\vec{\mu}_s \cdot \vec{B})$$

IF  $\vec{B}$  IS ALONG Z-AXIS  $\vec{B} = (0, 0, B_0)$

$$E_s = -g_e \tau_e \hat{S}_z B_0 ; \hat{S}_z \Rightarrow \text{Z-COMPONENT OF } \vec{S}$$

$$\hat{S}_z \psi = m_s \psi \quad m_s = \pm \frac{1}{2}$$



# NUCLEUS IN MAGNETIC FIELDS

→ SPIN QUANTUM NUMBER OF A NUCLEUS I

$$\rightarrow \hat{I} \psi = \sqrt{I(I+1)} \hbar \psi$$

$$\rightarrow I_z \psi = m_I \hbar \psi ; m_I = -I, -I+1, \dots, I$$

→ I → INTEGER OR HALF-INTEGER, BUT  
POSITIVE

NUMBER OF PROTONS	NUMBER OF NEUTRONS	I
EVEN	EVEN	0
ODD	ODD	INTEGER (1, 2, 3, ...)
EVEN	ODD	HALF-INTEGER ( $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ )
ODD	EVEN	HALF-INTEGER ( $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ )

EXAMPLES :-

INTEGER SPINS :-

$${}^2 \text{H} \Rightarrow I = 1 \quad {}^{10} \text{B} \Rightarrow I = 3$$

$${}^6 \text{Li} \Rightarrow I = 1 \quad {}^{14} \text{N} \Rightarrow I = 1$$

$${}^{50} \text{V} \Rightarrow I = 6$$

HALF-INTEGER SPINS :-

$${}^1 \text{H} \Rightarrow I = \frac{1}{2} \quad {}^{31} \text{P} \Rightarrow I = \frac{1}{2}$$

$${}^{13} \text{C} \Rightarrow I = \frac{1}{2} \quad {}^{11} \text{B} \Rightarrow I = \frac{3}{2}$$

$${}^{15} \text{N} \Rightarrow I = \frac{1}{2} \quad {}^{17} \text{O} \Rightarrow I = \frac{5}{2}$$

$${}^{209} \text{Bi} \Rightarrow I = \frac{9}{2}$$

• FOR A NUCLEUS

$$\vec{\mu} = \gamma \hat{\vec{I}}$$

$$E_I = -\gamma \vec{B} \cdot \hat{\vec{I}}$$

$$T = \frac{g_I}{\hbar} \left( \frac{10th}{2m_p} \right)$$

$$= \frac{g_I}{\hbar} \mu_N$$

↓  
MAGNETO  
GYRIC  
RATIO OF  
THE NUCLEUS

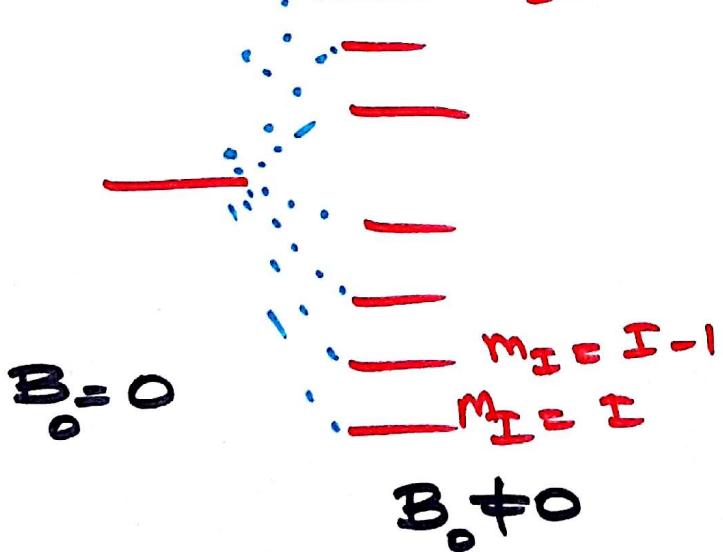
NUCLEAR  
MAGNETON  
↓  
PROTON  
MASS

IF  $\vec{B}$  IS ALONG Z-AXIS  $\vec{B} = (0, 0, B_0)$

$$E_I = -\gamma I_z B_0$$

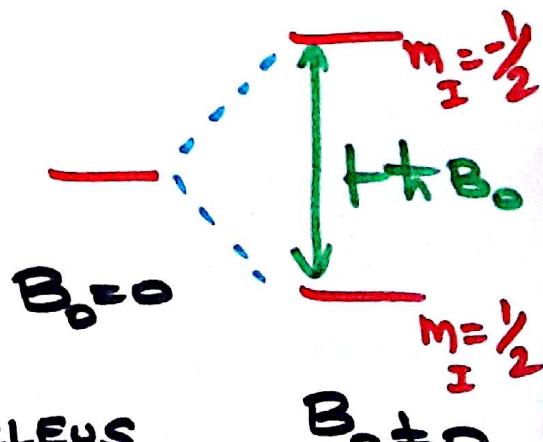
$$E_I = -\gamma m_I \hbar B_0 ; m_I = I, I-1, \dots, -I$$

IF  $B_0 = 0$ ,  $E_I = 0$ ; BUT  $E_I \neq 0$ , WHEN  $B_0 \neq 0$



EXAMPLE :

$$I = 1/2$$



FOR ELECTRON

$$\Delta E = g_e \mu_B B_0$$

$$h\nu_e = g_e \mu_B B_0$$

ELECTRON SPIN  
RESONANCE (ESR)  
(MICROWAVE REGION)

FOR NUCLEUS

$$\Delta E = \gamma \hbar B_0$$

$$h\nu_e = \gamma \hbar B_0$$

NUCLEAR MAGNETIC  
RESONANCE (NMR)  
(RADIOFREQUENCY REGION)

## SHIELDING

- WE DO NOT HAVE AN ISOLATED NUCLEUS IN AN APPLIED MAGNETIC FIELD.
- ALL NUCLEI ARE SURROUNDED BY ELECTRONS AND OTHER NEIGHBORING ATOMS
- WHEN PLACED IN A MAGNETIC FIELD THE SURROUNDING ELECTRON CLOUD TENDS TO CIRCULATE IN SUCH A DIRECTION AS TO PRODUCE SUCH A FIELD OPPOSING THE APPLIED FIELD (DIAMAGNETIC CIRCULATION)  
RECALL  $\vec{F} = q(\vec{J} \times \vec{B})$
- MAGNETIC FIELD EXPERIENCED BY THE NUCLEUS IS

$$B_{\text{EFF}} = B_o - B_{\text{INDUCED}}$$

$\downarrow$   $\downarrow$   
APPLIED FIELD      OPPOSING INDUCED FIELD DUE TO DIAMAGNETIC CIRCULATION

$$B_{\text{INDUCED}} = \sigma B_o$$

$\downarrow$   
SHIELDING CONSTANT

$$B_{\text{EFF}} = B_o (1 - \sigma)$$

- NUCLEI IN DIFFERENT CHEMICAL GROUPS HAVE DIFFERENT  $\sigma$  VALUES.

- THE HYDROGEN NUCLEUS IN O-H BONDS EXPERIENCES GREATER FIELD THAN THE HYDROGEN NUCLEUS IN C-H BONDS

→ OXYGEN IS A BETTER ELECTRON ACCEPTOR THAN CARBON

(OXYGEN HAS THE GREATER ELECTRONEGATIVITY)

→ THE ELECTRON DENSITY ABOUT THE HYDROGEN ATOM IN C-H BONDS IS HIGHER THAN IN O-H BONDS

$$\sigma_{\text{CH}} > \sigma_{\text{OH}}$$

$$B_o(1 - \sigma_{\text{CH}}) < B_o(1 - \sigma_{\text{OH}})$$

$$\Delta E_{\text{CH}} = \text{f} \hbar B_o(1 - \sigma_{\text{CH}})$$

$$\Delta E_{\text{OH}} = \text{f} \hbar B_o(1 - \sigma_{\text{OH}})$$

$$E_{\beta, \text{OH}}$$

$$E_{\alpha, \text{CH}}$$

$$E_{\alpha, \text{OH}}$$

$$\Delta E_{\text{CH}}$$

$$\Delta E_{\text{OH}}$$

$$\gamma_{\text{CH}} = \frac{\Delta E_{\text{CH}}}{\hbar} = \frac{\text{f} B_o(1 - \sigma_{\text{CH}})}{2\pi}$$

$$\gamma_{\text{OH}} = \frac{\Delta E_{\text{OH}}}{\hbar} = \frac{\text{f} B_o(1 - \sigma_{\text{OH}})}{2\pi}$$

## CHEMICAL SHIFT

ALSO  

$$\left( \delta = \frac{\gamma - \gamma_0}{\gamma_0} \right)$$

→  $\delta = \gamma - \gamma_0$

↓  
 RESONANCE  
 FREQUENCY  
 OF THE  
 NUCLEUS

RESONANCE  
 FREQUENCY OF  
 OF A REFERENCE  
 NUCLEUS

(PROTON RESONANCE  
 IN TETRAETHYLSILANE)

TMS  $\text{Si}(\text{CH}_3)_4$

→ LET US CALCULATE  $\rightarrow$  UNIT OF  $B_0$  CAN BE DIFFERENT

$$\gamma_{\text{OH}} - \gamma_{\text{CH}} = \frac{1}{2\pi} B_0 \left( \sigma_{\text{CH}} - \sigma_{\text{OH}} \right)$$

$$\frac{\gamma_{\text{OH}} - \gamma_{\text{CH}}}{\gamma_{\text{CH}}} = \frac{\sigma_{\text{CH}} - \sigma_{\text{OH}}}{(1 - \sigma_{\text{CH}})}$$

UNIT IS NOT A PROBLEM ANYMORE.

→ IN GENERAL :

$$\sigma = \sigma_{\text{LOCAL}} + \sigma_{\text{NEIGHBOUR}} + \sigma_{\text{SOLVENT}}$$

DUE TO  
 ELECTRONS OF  
 THE ATOM THAT  
 CONTAINS THE  
 NUCLEUS

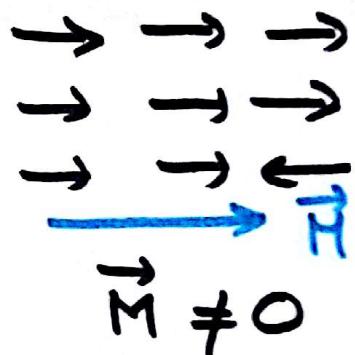
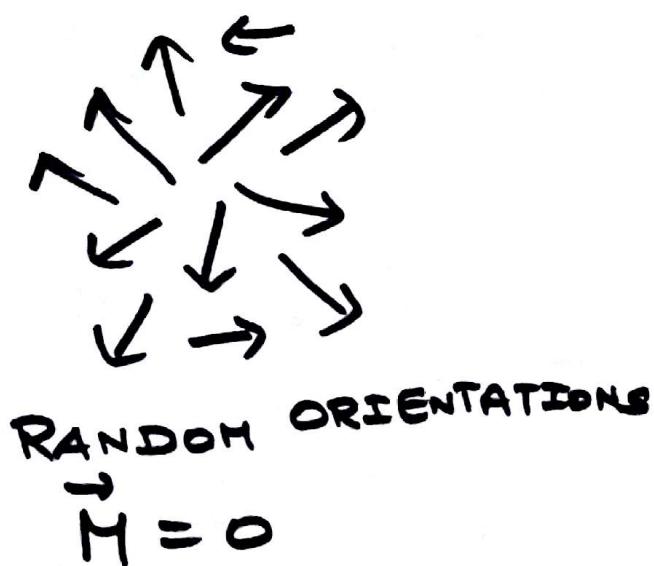
DUE TO  
 NEIGHBOURING  
 ATOMS

↓  
 DUE TO  
 SOLVENT

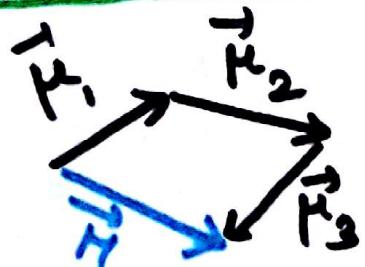
## MAGNETIZATION

- CONSIDER  $N$  NUCLEAR SPINS IN A SAMPLE
- $\vec{\mu}_i$  IS THE NUCLEAR MAGNETIC MOMENT OF  $i^{\text{TH}}$  SPIN
- MAGNETIZATION  $\vec{M}$   
$$\vec{M} = \sum_{i=1}^N \vec{\mu}_i \quad (\text{VECTOR SUM})$$

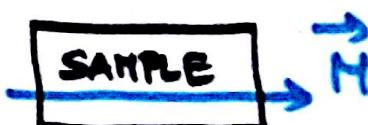
$\vec{M}$  IS THE NET NUCLEAR MAGNETIC MOMENT OF THE SAMPLE



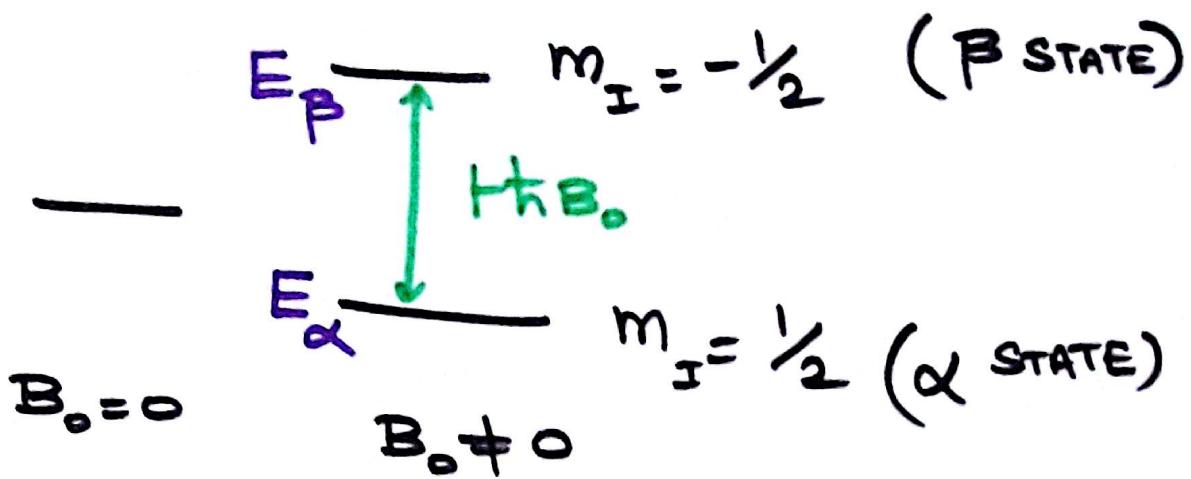
## VECTOR ADDITION



- $\vec{M}$  IS A SYSTEM PROPERTY
- CHANGE IN ANY ONE OR MORE  $\vec{\mu}_i$  WILL BE REFLECTED IN  $\vec{M}$



# NUCLEAR MAGNETIC RESONANCE



$$\Delta E = E_{\beta} - E_{\alpha}$$

POPULATION OF  $\alpha$ -STATE:  $N_{\alpha}$

POPULATION OF  $\beta$ -STATE:  $N_{\beta}$

$$\frac{N_{\beta}}{N_{\alpha}} = e^{-\frac{1}{k_B T} (E_{\beta} - E_{\alpha})} = e^{-\frac{\Delta E}{k_B T}}$$

$$\frac{N_{\beta}}{N_{\alpha}} = e^{-\frac{\Delta E}{k_B T}} \approx 1 - \frac{\Delta E}{k_B T} \quad (\Delta E \ll k_B T)$$

$$1 - \frac{N_{\beta}}{N_{\alpha}} = \frac{\Delta E}{k_B T}$$

$$\frac{N_{\alpha} - N_{\beta}}{N_{\alpha}} \approx \frac{\Delta E}{k_B T} = \frac{T \hbar B_0}{k_B T}$$

$\frac{N_{\alpha} - N_{\beta}}{N_{\alpha}}$        $\propto$        $T \hbar B_0$

- WHEN  $B_0 = 0$

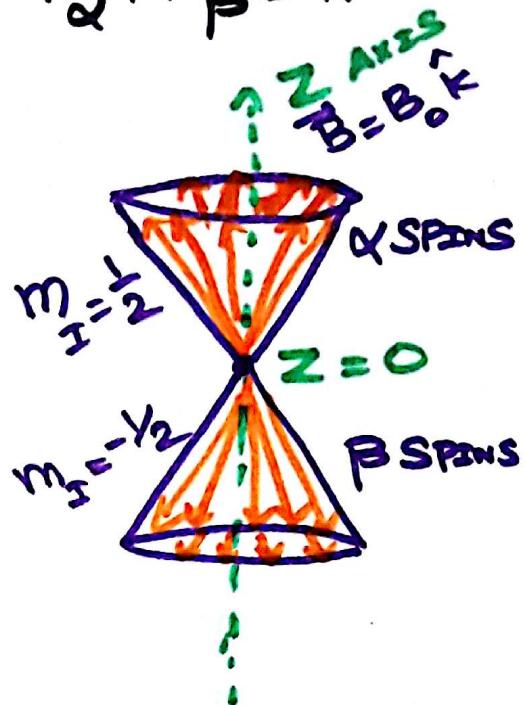
$$N_\alpha - N_\beta = 0$$

$$N_\alpha = N_\beta$$

$$\begin{aligned} \vec{M} &= N_\alpha \left( g_I \frac{\mu_N}{2} \right) \hat{k} \\ &\quad - N_\beta \left( g_I \frac{\mu_N}{2} \right) \hat{k} \end{aligned}$$

$$\vec{M} = 0$$

$$N_\alpha + N_\beta = N$$



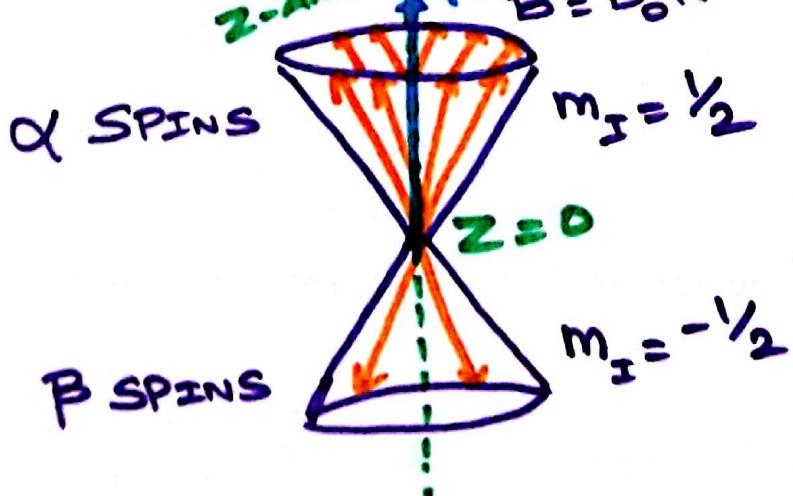
- WHEN  $B_0 \neq 0$

$$N_\alpha > N_\beta$$

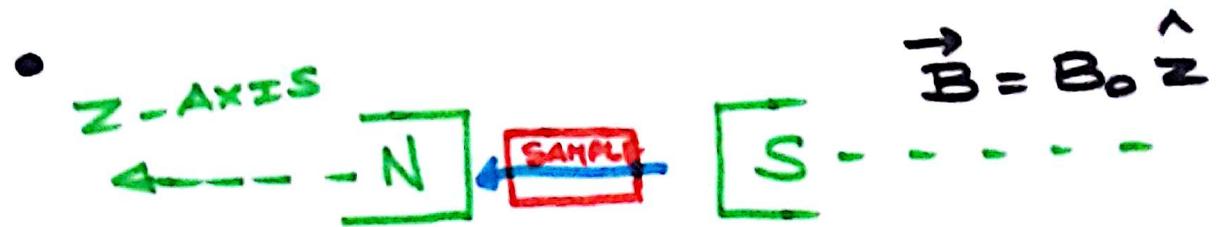
$$\vec{M} = \frac{g_I \mu_N}{2} \hat{k} (N_\alpha - N_\beta)$$

$$\vec{M} \neq 0$$

$\vec{M}$  IS ALONG +Z-AXIS

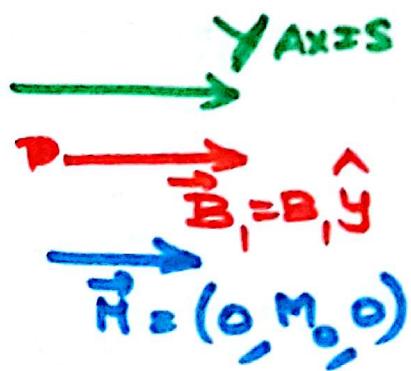
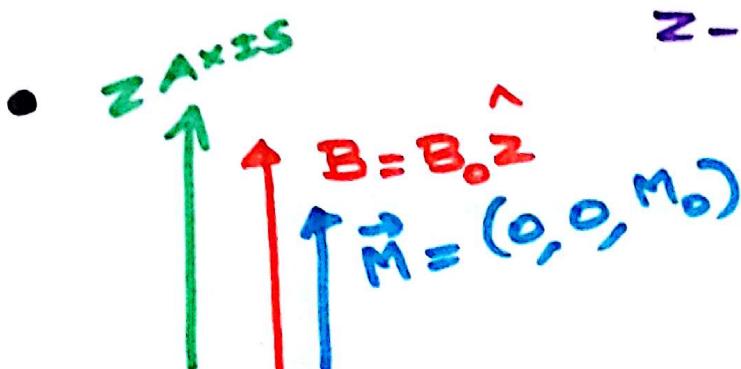


# PULSE TECHNIQUES IN NMR

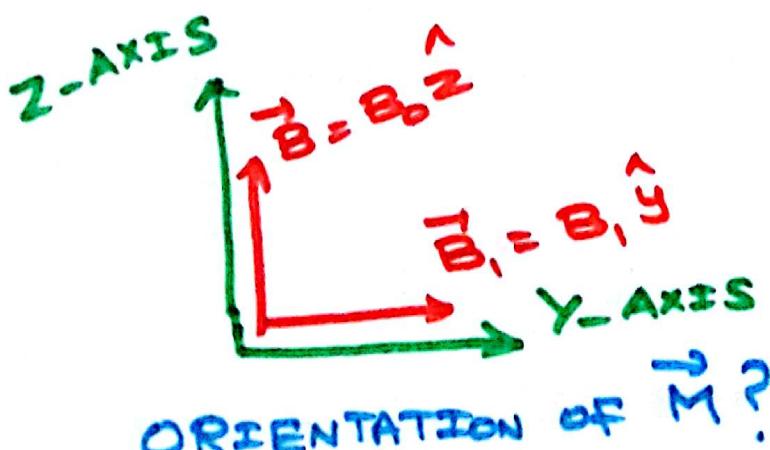


$$\vec{B} = B_0 \hat{z}$$

RF FIELD  
(MAGNETIC FIELD OF THIS RF FIELD IS PERPENDICULAR TO Z-AXIS)



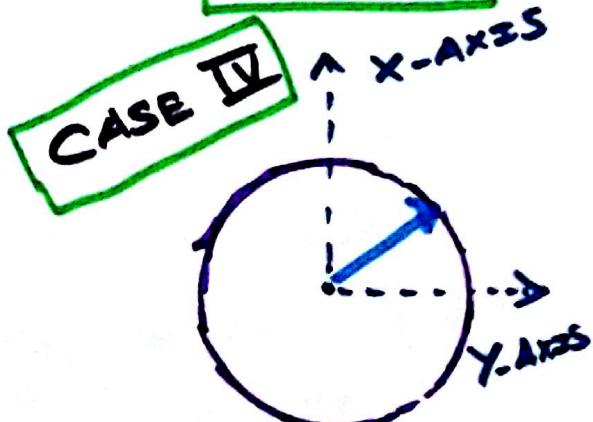
## CASE I



$\vec{M}$  WILL HAVE NON-ZERO Y-COMPONENT!

$B_0 = 0$   
 $B_1 \neq 0$

## CASE - II



## CASE III

CIRCULARLY POLARIZED RF FIELD ( $B$  ROTATES ON  $XY$  PLANE)

- 90° RF PULSE

→ APPLY  $\vec{B}$  AND  $\vec{B}_1$  SUCH THAT  $\vec{M}$  IS ROTATED TO THE XY PLANE

EXCITED STATE  $\vec{M} = (M_x, M_y, 0)$  (FINAL STATE)

IN THE ABSENCE OF  $\vec{B}_1$ ,

EQUILIBRIUM STATE  $\vec{M} = (0, 0, M_z)$  (INITIAL STATE)

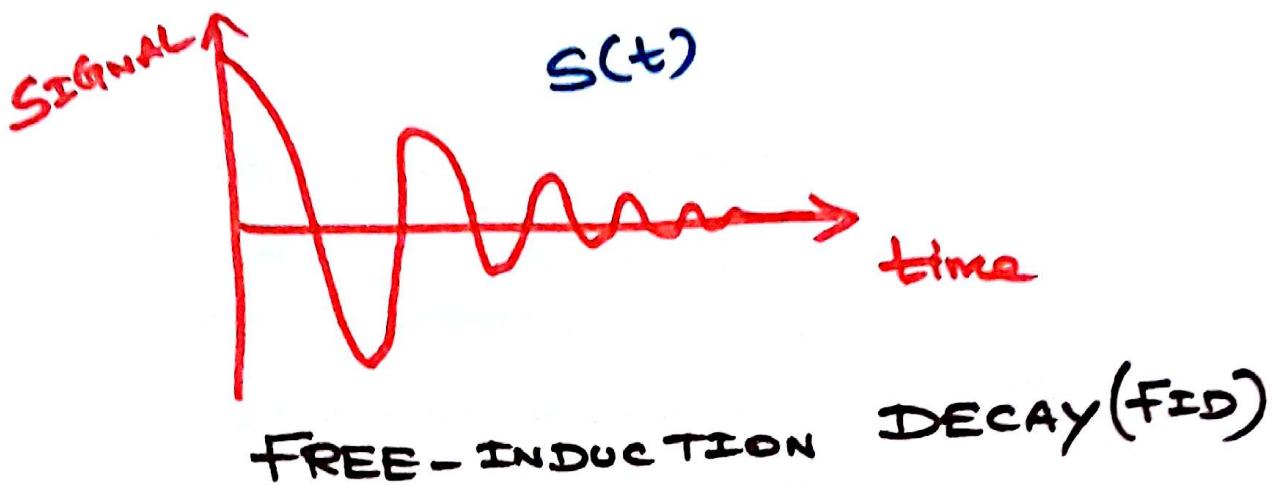
- $\vec{M}$  ROTATES IN XY PLANE; ROTATING  $\vec{M}$  INDUCES CURRENT IN A COIL AROUND IT  
(THIS CURRENT CAN BE MEASURED AND AMPLIFIED)

- TURN ON  $\vec{B}$  AND  $\vec{B}_1$  AND MAKE  $\vec{M}$  TO ROTATE IN XY PLANE FOR SOME TIME. NOW, TURN OFF  $\vec{B}_1$ . WHAT WOULD HAPPEN?

RETURN OF  $\vec{M}$  FROM THE EXCITED STATE TO THE EQUILIBRIUM STATE IS CALLED SPIN RELAXATION

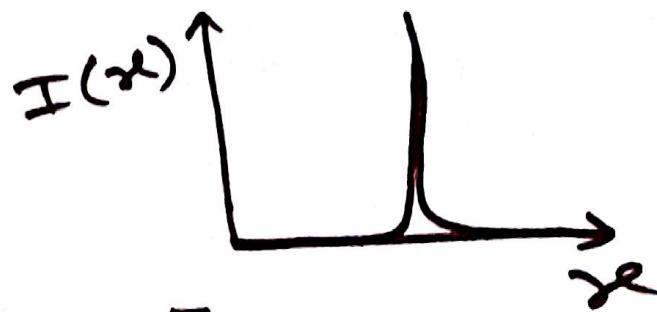
(ENERGY EXCHANGE HAPPENS WITH THE SURROUNDINGS)

- WHEN THE SPIN  $\vec{M}$  VECTOR RELAXES FROM THE EXCITED STATE TO THE GROUND STATE, THE PROJECTION OF  $\vec{M}$  ON XY PLANE DECREASES.  
 $\Rightarrow$  DETECTED CURRENT SIGNAL WOULD DECREASE WITH TIME.



$\Rightarrow$  FOURIER TRANSFORM OF  $S(t)$

$$I(\gamma) = 2 \text{ REAL} \left[ \int_0^{\infty} S(t) e^{-2\pi i \gamma t} dt \right]$$



- $\Rightarrow$  FID FREQUENCY IS DIFFERENT FOR DIFFERENT NUCLEI AND IT DEPENDS ON THE LOCAL ENVIRONMENT OF THE NUCLEI.

- $180^\circ$  PULSE

EQUILIBRIUM STATE  $\vec{M} = (0, 0, M_z)$

EXCITED STATE  $\vec{M} = (0, 0, -M_z)$

POPULATION INVERSION  
(MORE SPINS IN THE  
B STATE THAN IN THE  
A STATE)

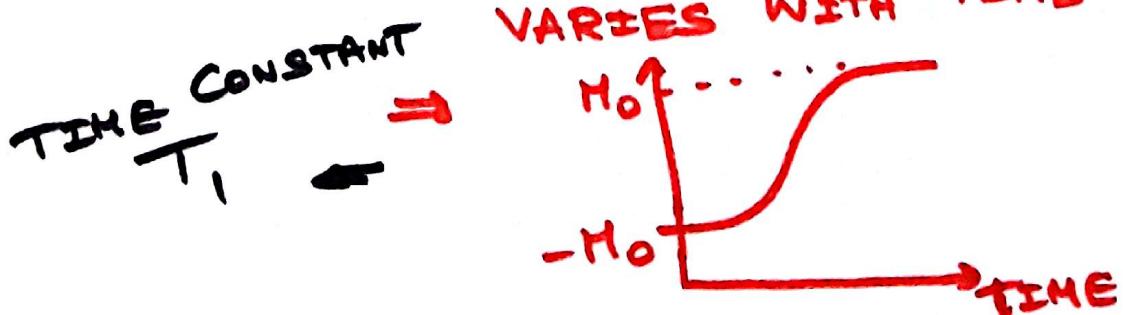
THIS IS POSSIBLE WHEN  $B_z \neq 0$ ;  
(WHEN  $B_z = 0$ , THIS WOULD BE A  
HIGHER ENERGY STATE)

- TWO TYPES OF SPIN RELAXATION

→  $T_1$  RELAXATION OR  
LONGITUDINAL RELAXATION  
OR  
SPIN-LATTICE RELAXATION

→  $T_2$  RELAXATION OR  
TRANSVERSE RELAXATION  
OR  
SPIN-SPIN RELAXATION

- $T_1$  RELAXATION: APPLY  $180^\circ$  PULSE  
→ INVESTIGATE HOW  $M_z$   
VARIES WITH TIME



- $T_2$  RELAXATION

→ APPLY  $90^\circ$  PULSE

→ INVESTIGATE HOW  
 $M_y$  VARIES WITH TIME



$$M_y(t) \propto e^{-t/T_2}$$

# FINAL EXAM (SPECTROSCOPY)

$(1\frac{1}{2} \text{ hours} + \frac{1}{2} \text{ hour})$

(5)

- ① CONSIDER A QUANTUM PARTICLE OF MASS  $M$  CONFINED IN A ONE-DIMENSIONAL INFINITE POTENTIAL WELL OF LENGTH  $L$ . AN EXTERNAL ELECTROMAGNETIC WAVE EXCITES THE PARTICLE FROM AN INITIAL STATE DENOTED BY THE QUANTUM NUMBER  $n_i$  TO A FINAL STATE WITH QUANTUM NUMBER  $n_f$ . DETERMINE THE SELECTION RULE FOR  $n_i \rightarrow n_f$  TRANSITIONS. Do you think that  $n_i = 1 \rightarrow n_f = 2$  is an allowed transition? Justify your answer.

(4)

- ② THE INTERNUCLEAR POTENTIAL ENERGY OF A HYDROGEN MOLECULE IS GIVEN AS  $U(R) = D_e \left[ 1 - e^{-a(R-R_e)} \right]^2$  WHERE  $D_e$  IS THE DEPTH OF THE WELL,  $R_e$  IS THE EQUILIBRIUM INTERNUCLEAR SEPARATION, AND  $a$  IS AN EMPIRICAL CONSTANT. GIVEN THAT  $R_e = 0.749 \text{ \AA}$ ,  $D_e = 456 \text{ kJ/mol}$ , AND  $a = 1.963 \times 10^8 \text{ cm}^{-1}$ , CALCULATE THE FUNDAMENTAL VIBRATIONAL FREQUENCY OF  $\text{H}_2$  AND COMPARE IT TO THE EXPERIMENTAL VALUE OF  $4.40 \times 10^3 \text{ cm}^{-1}$ . YOU CAN USE THE HARMONIC OSCILLATOR APPROXIMATION FOR THIS PROBLEM. HOW WOULD THE FUNDAMENTAL VIBRATIONAL FREQUENCY CHANGE IF WE EMPLOY AN ANHARMONIC OSCILLATOR MODEL FOR THIS PROBLEM.

(1)

- ③ DISCUSS THE BORN-OPPENHEIMER APPROXIMATION. WHY DO WE NEED IT?

④ Using the explicit formulas for the spherical harmonics, show that the rotational transition  $J=0 \rightarrow J=1$  is allowed, but  $J=0 \rightarrow J=2$  is forbidden in microwave spectroscopy. (use the rigid-rotator approximation).

⑤ (a) We know that the electric and magnetic fields of an electromagnetic wave vary in space and time. However, when we discussed the light-matter interaction, we ignored the spatial variation of these fields. How do you justify this assumption? Under what conditions you would need spatial variations of these fields.

(b) For light-matter interaction, we considered only the electric field of the electromagnetic wave. We ignored the interaction of magnetic field with matter. Justify this assumption.

⑥ Using Jablonski diagrams, discuss the fluorescence and phosphorescence processes.

⑦ (a) Discuss about  $90^\circ$  and  $180^\circ$  pulses in NMR experiments.

(b) What are  $T_1$  and  $T_2$  relaxations in NMR experiments?

⑧ Discuss the Franck-Condon principle.

⑨ Discuss the theory of Raman spectroscopy.