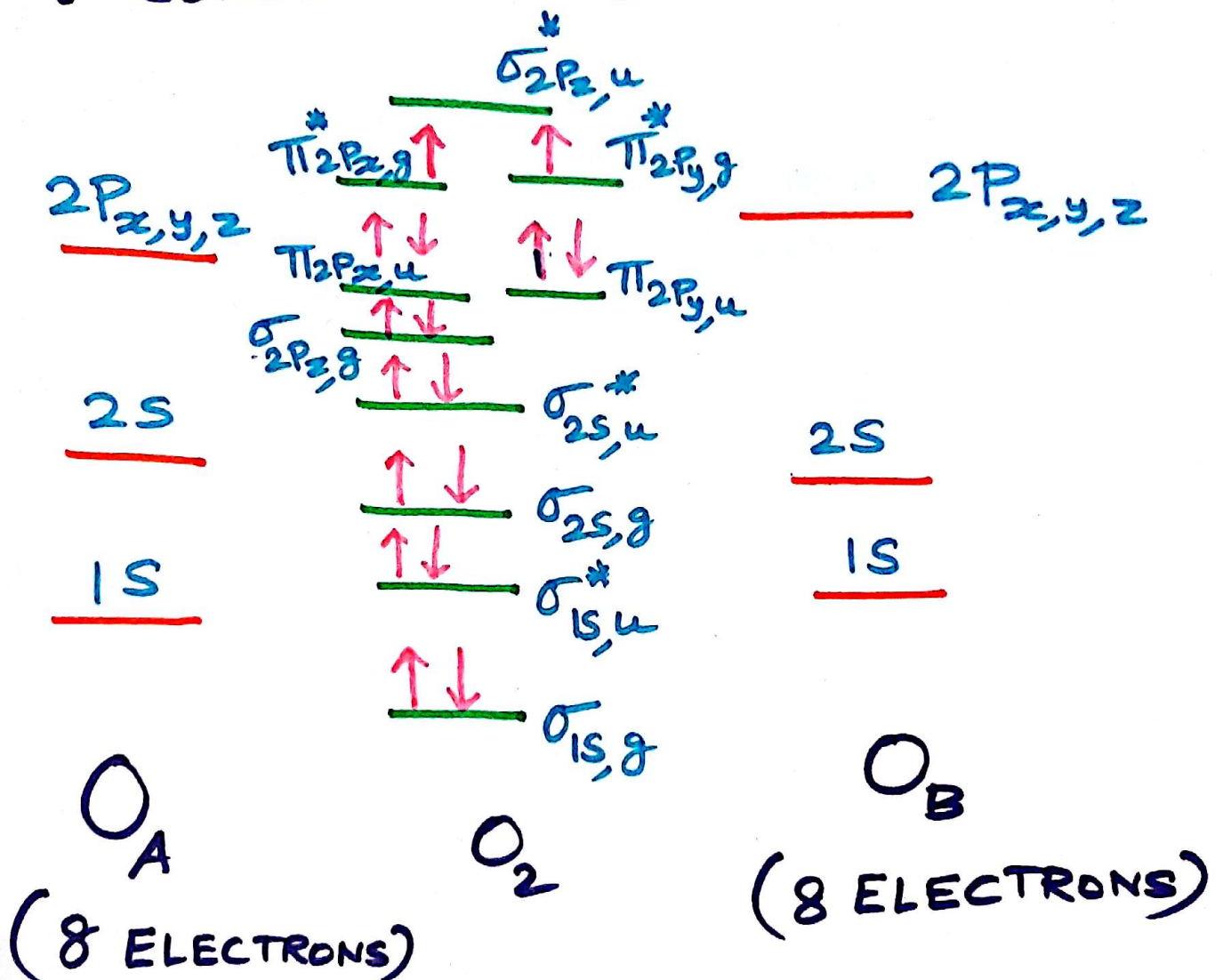


# HOW DO WE DISTRIBUTE ELECTRONS IN MOLECULAR ORBITALS/LEVELS:

- CONSIDER  $O_2$  MOLECULE

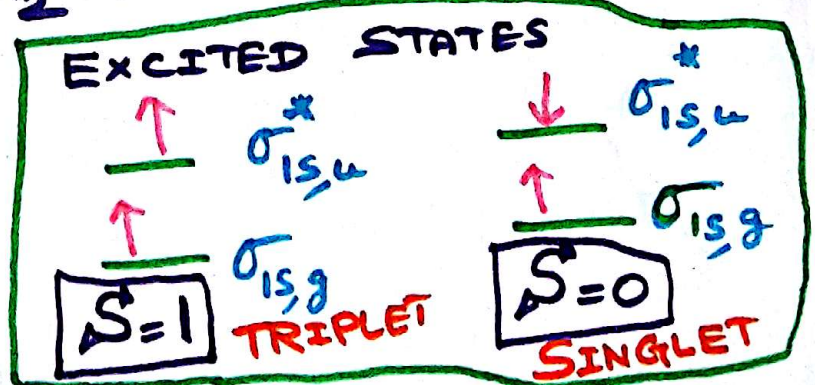
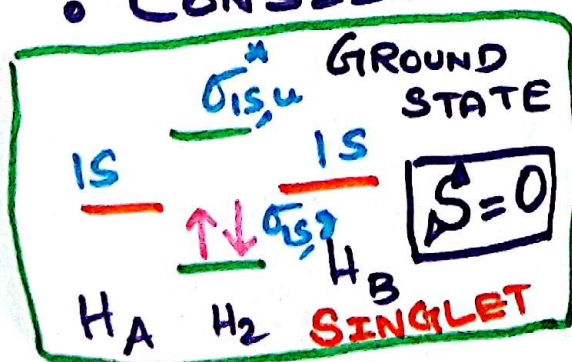


HOMO: HIGHEST OCCUPIED MOLECULAR ORBITAL

LUMO: LOWEST UNOCCUPIED MOLECULAR ORBITAL.

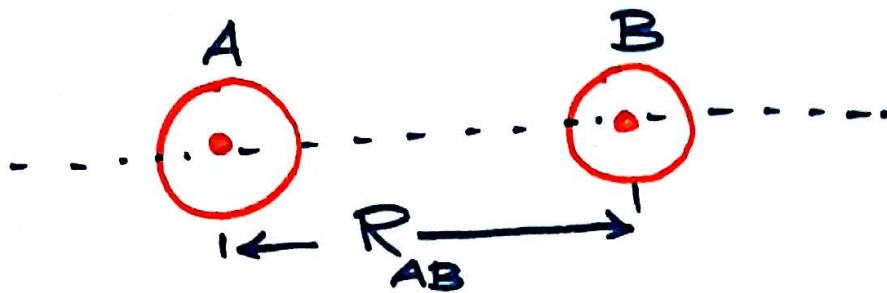
SPIN MULTIPLICITY =  $2S+1$

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

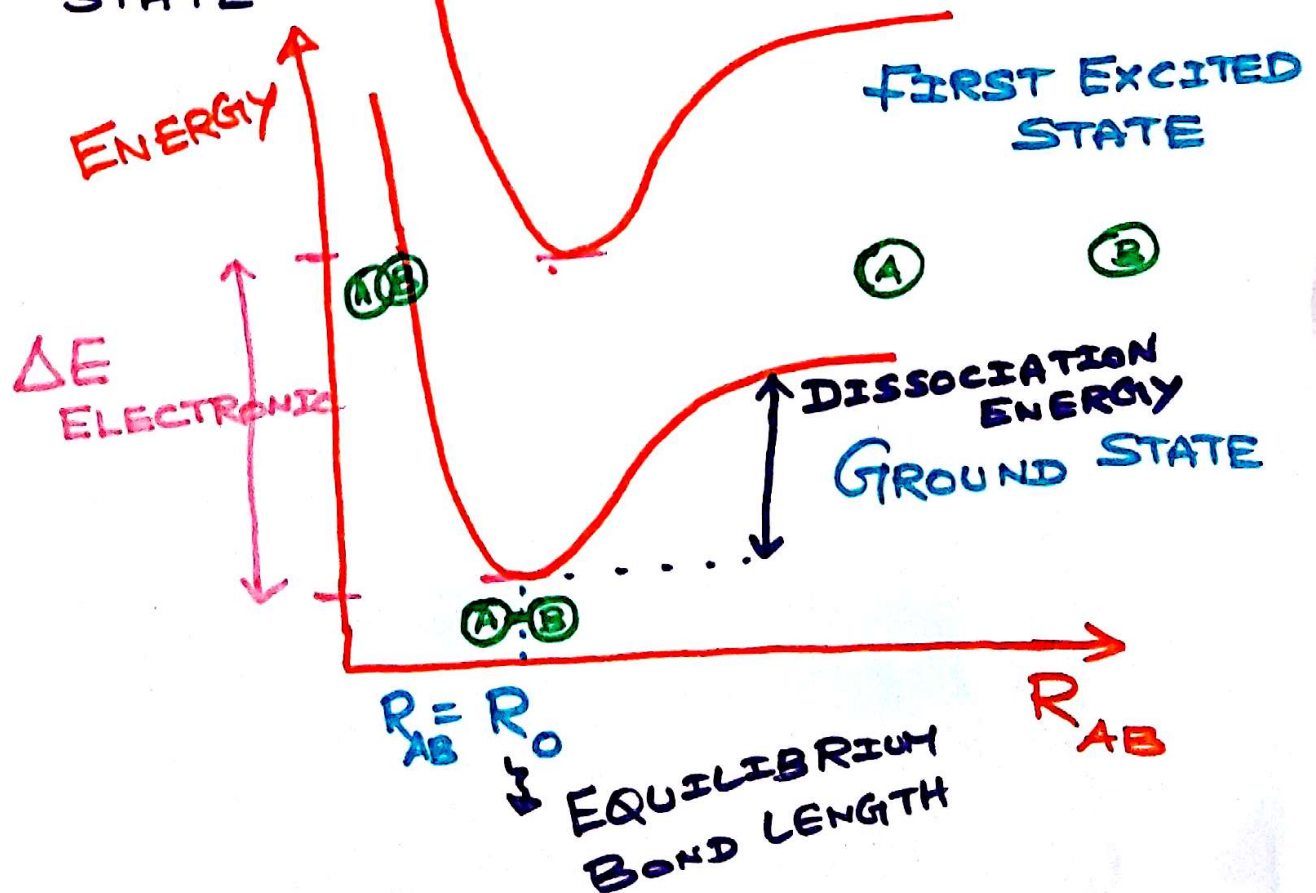


# ELECTRONIC ENERGY SURFACES

- CONSIDER A DIATOMIC MOLECULE

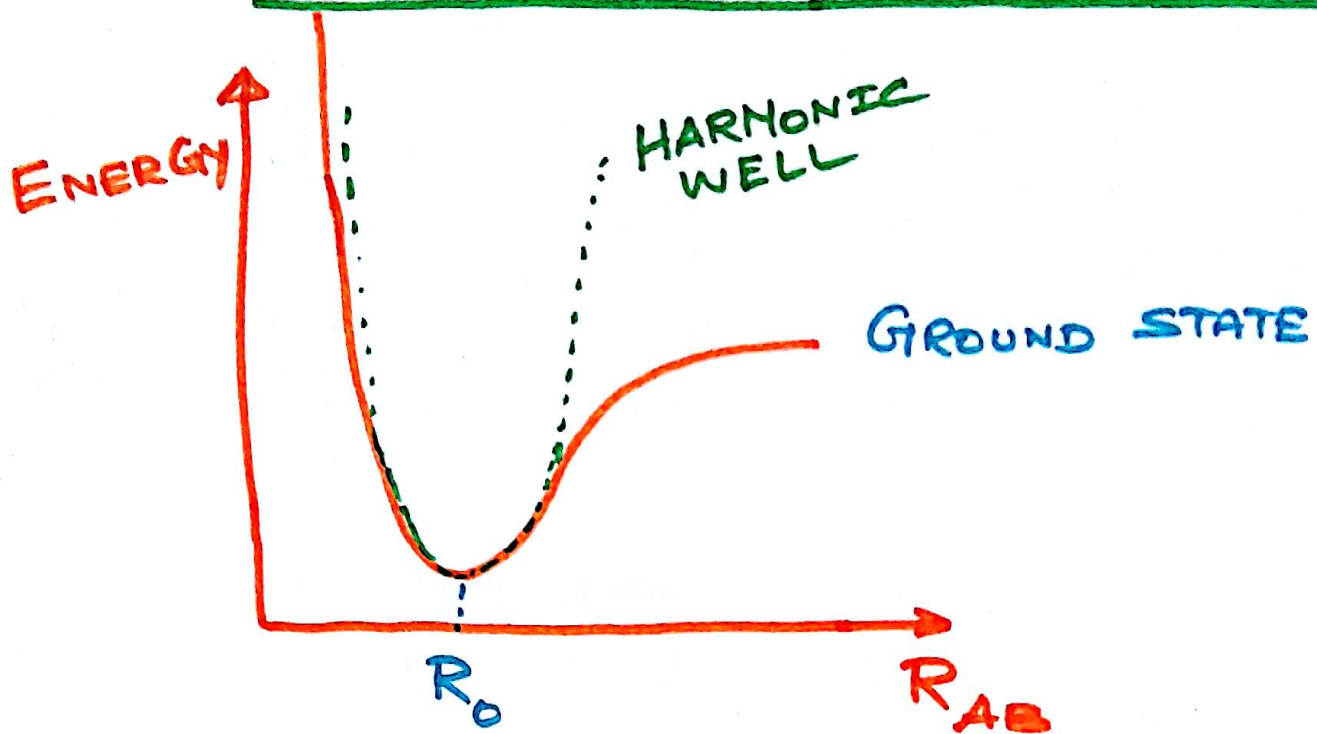


- $R_{AB} \Rightarrow$  INTER NUCLEAR DISTANCE
- VARY  $R_{AB}$ , BUT ENSURE THAT THE SYSTEM IS ALWAYS IN ITS GROUND STATE





# VIBRATIONAL SPECTROSCOPY



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

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

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

A diagram of a mass-spring system. A mass (represented by a circle with a cross) is attached to a spring. A horizontal dashed line extends from the mass to the right, labeled 'x axis'. A vertical arrow points down from the mass, labeled 'x=0'. The potential energy function is given as  $U(x) = \frac{1}{2} k x^2$ .

# VIBRATIONAL SPECTROSCOPY

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

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

DIFFERENT FROM  $U(x_A, y_A, z_A, x_B, y_B, z_B)$

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

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

- SMALL AMPLITUDE OSCILLATION

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

⇒ IGNORE HIGHER-ORDER TERMS

⇒ USE  $\left. \frac{dU}{dR_{AB}} \right|_{R_0} = 0$

⇒ 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

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

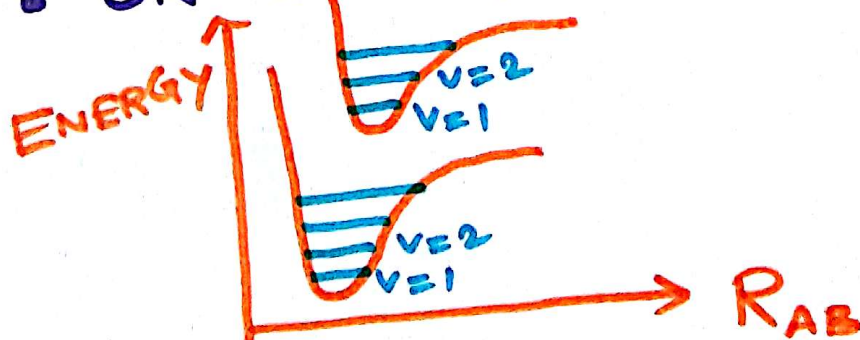
$\hbar\omega \{$

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

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

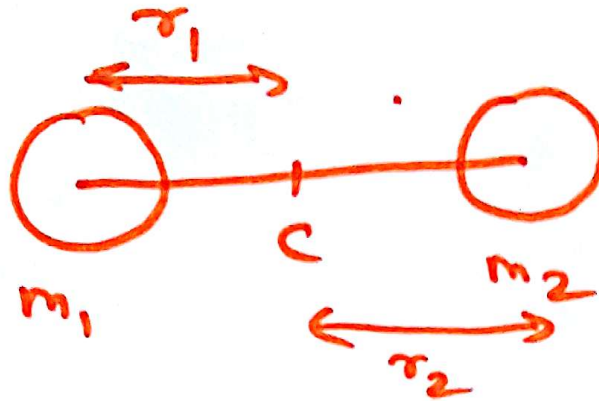
$$\hbar\omega \ll \Delta E_{\text{ELECTRONIC}}$$

- ON ENERGY SURFACE



# ROTATIONAL SPECTROSCOPY

- RIGID DIATOMIC MOLECULE



→ 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