CHEM 260 "CHEMICAL PRINCIPLES"

?

BETTER: AN INTRODUCTION TO THE PHYSICAL / THEORETICAL BASIS FOR MODERN CHEMISTRY

"INTRODUCTION TO THE QUANTAL NATURE OF MATTER, BASIC CHEMICAL THERMODYNAMICS, AND CHEMICAL KINETICS. DESCRIPTION OF THE FUNDAMENTAL PHYSICAL PRINCIPLES THAT UNDERLIE SPECTROSCOPIC AND ELECTROCHEMICAL ANALYSIS."

CHEM 260 CHEM 261

CHEMICAL PRINCIPLES

"AN INTRODUCTION TO PHYSICAL CHEMISTRY"

1. HOW ARE MOLECULES PUT TOGETHER. CHEMICAL BONDING

2. HOW DO MOLECULES AND/OR ATOMS INTERACT TO PRODUCE MACROSCOPIC PROPERTIES.

   T, V, P, HARDNESS, VISCOSITY...

3. CAN WE UNDERSTAND WHY THINGS ARE AS THEY ARE.

   WELL ENOUGH TO PREDICT!

CHEMISTRY IS A QUANTITATIVE SCIENCE.

1. CONSERVATION OF MASS/ENERGY:

$$H_2O + CO_2 \rightarrow O_2 + H_2CO$$

$$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$$

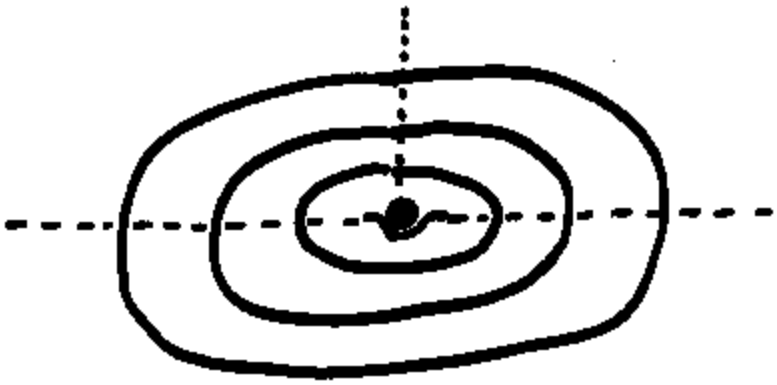
2. THEORETICAL FORMULATION OF PHYSICAL LAWS

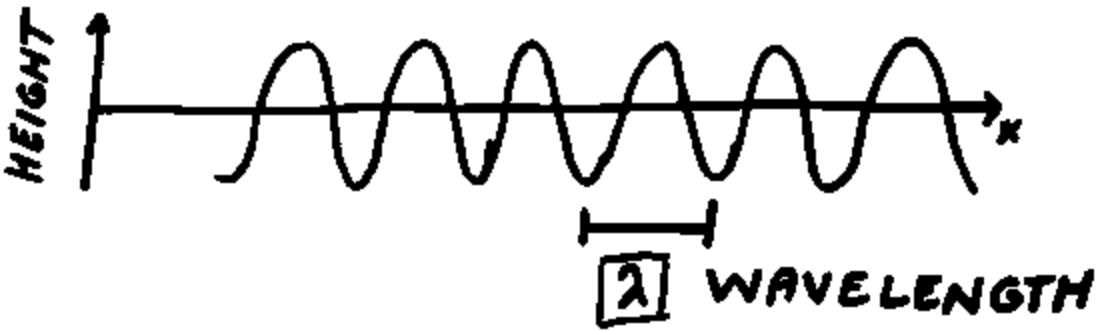
$E = mc^2$ EINSTEIN-RELATIVITY

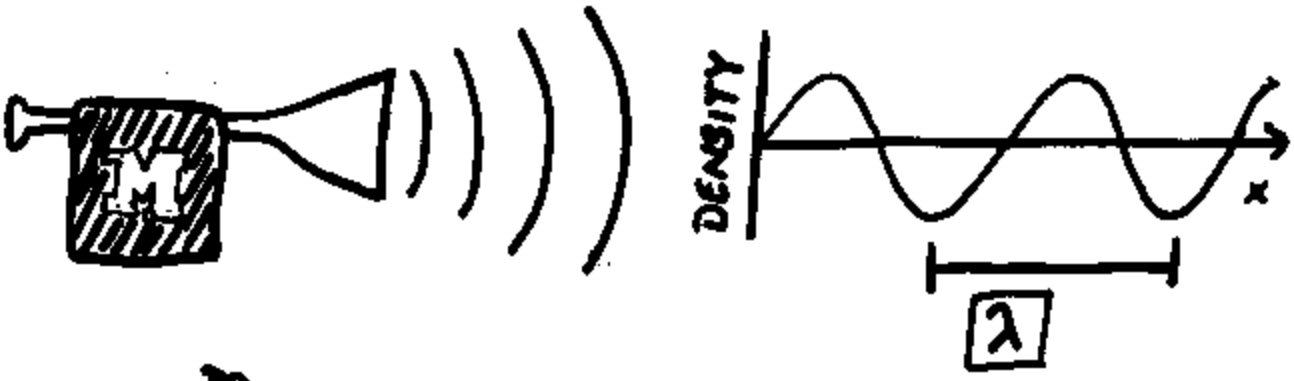
$m_1 v_1 = m_2 v_2$ CONSERVATION OF MOMENTUM

$V(r) = \frac{q_A q_B}{\varepsilon r}$ COULOMB POTENTIAL ENERGY

MATTER WAVES:





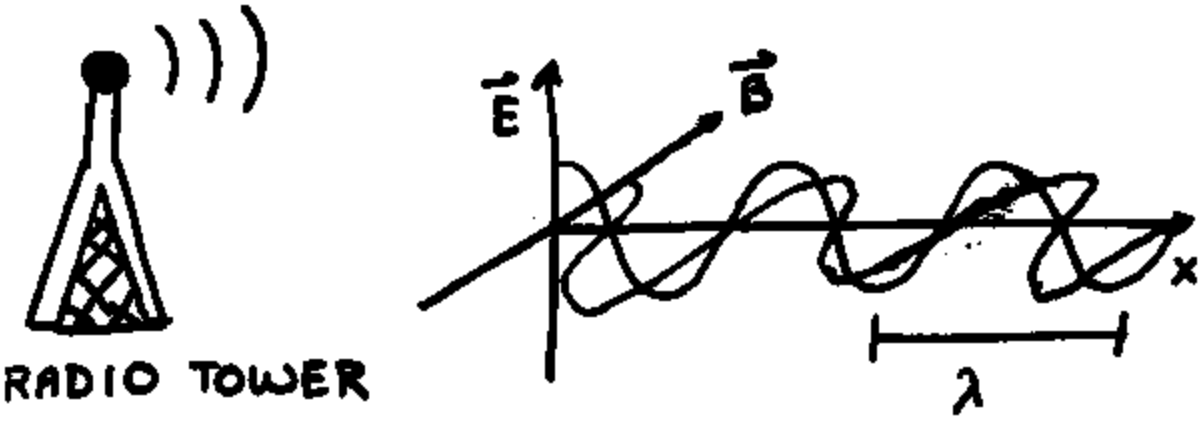


FUNDAMENTAL

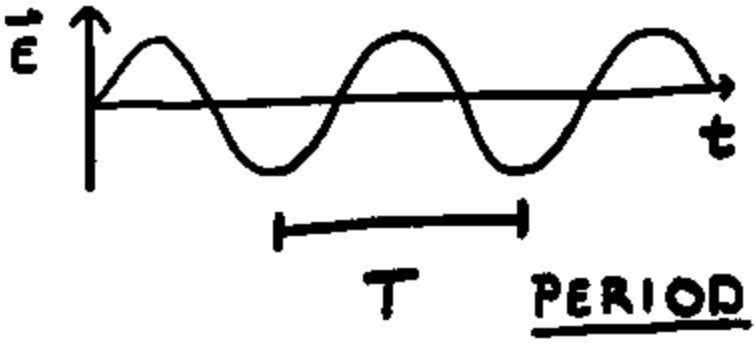
OVERTONE
1 NODE *

2nd OVERTONE
2 NODES

ELECTROMAGNETIC RADIATION:



ELECTROMAGNETIC RADIATION: PERPENDICULAR OSCILLATING MAGNETIC AND ELECTRIC FIELDS.



$\nu = \frac{1}{T}$ FREQUENCY = (PERIOD)$^{-1}$

$\frac{\text{"PEAKS"}}{\text{SECOND}} = s^{-1} = Hz$

$$\boxed{c = \lambda\nu = \text{CONSTANT IN FREE SPACE "VACUUM"}}$$

FUNDAMENTAL CONCEPTS:

ν = FREQUENCY CYCLES/SECOND
s^{-1} OR Hz (HERTZ)

λ = WAVELENGTH, cm, nm, Å, μm

T = PERIOD, s

$\bar{\nu} = 1/\lambda$ = WAVENUMBER cm^{-1}
#WAVES/cm

c = WAVE VELOCITY cm/s
SPEED OF LIGHT

$$* \quad \boxed{\lambda = \frac{c}{\nu} = \frac{1}{\bar{\nu}}} \quad *$$

FUNDAMENTAL
RELATIONSHIP

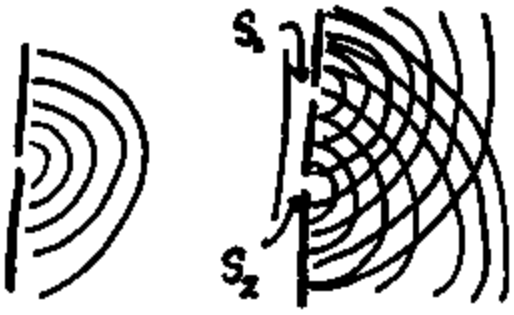
WAVELENGTHS OF EM RADIATION

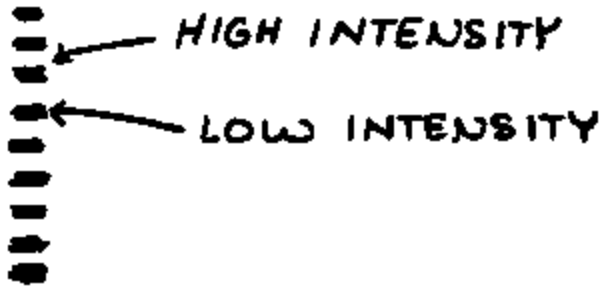
WAVELENGTH

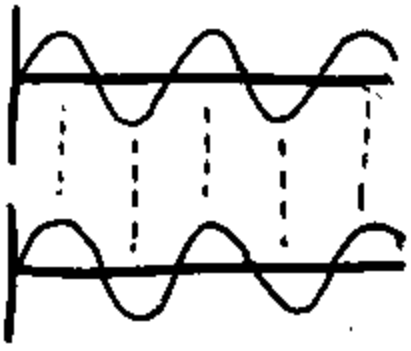
FREQUENCY

λ / ν	
$10^{-1} - 10^{+4}$ m $3\times10^{4} \rightarrow 3\times10^{9}$ Hz	RADIO WAVES AM $(54-170)\,10^{4}$ Hz 760 ⇒ 760 kHz
$10^{-3} \rightarrow 10^{-1}$ m $3\times10^{9} \rightarrow 3\times10^{11}$ Hz	MICROWAVES mm → cm
$10^{-6} \rightarrow 10^{-3}$ m $3\times10^{11} \rightarrow 3\times10^{14}$ Hz	INFRARED μm
$4\times10^{-7} \rightarrow 8\times10^{-7}$ m $3.75\times10^{14} \rightarrow 7.5\times10^{14}$ Hz	VISIBLE 400 - 800 nm
$4\times10^{-7} \rightarrow 10^{-8}$ m $8\times10^{14} \rightarrow 3\times10^{16}$ Hz	ULTRAVIOLET 400 nm → 10 nm
$10^{-8} \rightarrow 10^{-12}$ m $3\times10^{16} \rightarrow 3\times10^{20}$ Hz	X - RAYS 10 — 0.01 nm 100 Å → 0.1 Å
$10^{20} - 10^{24}$ Hz	γ - RAYS COSMIC RAYS

DIFFRACTION / INTERFERENCE

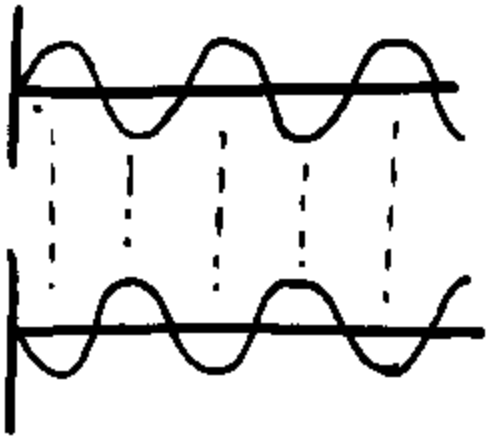






WAVES IN PHASE

⇒ CONSTRUCTIVE INTERFERENCE

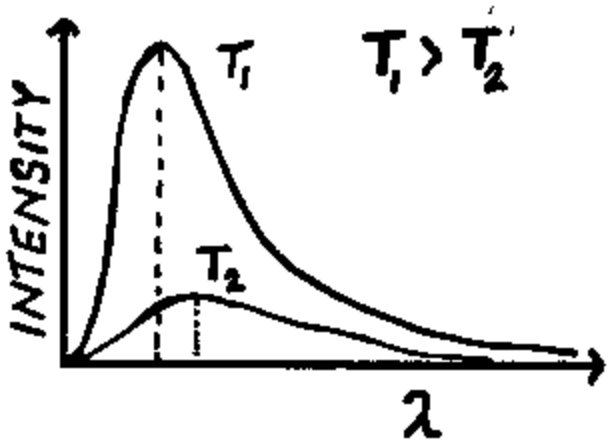


WAVES OUT OF PHASE

⇒ DESTRUCTIVE INTERFERENCE

THREE KEY OBSERVATIONS:

1. BLACKBODY RADIATION:



$T_1 > T_2$

"WHITE HOT"

VS

"RED HOT"

~1900

MAX PLANCK: 1918 NOBEL PRIZE

CLASSICALLY: INTERNAL ENERGY CAN TAKE ANY VALUE "CONTINUOUS"

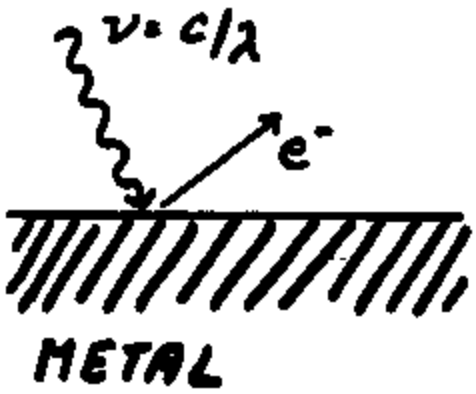
QUANTIZATION HYPOTHESIS: INTERNAL ENERGY MUST BE A INTEGER MULTIPLE OF $h\nu$

ν FREQUENCY OF INTERNAL OSCILLATOR

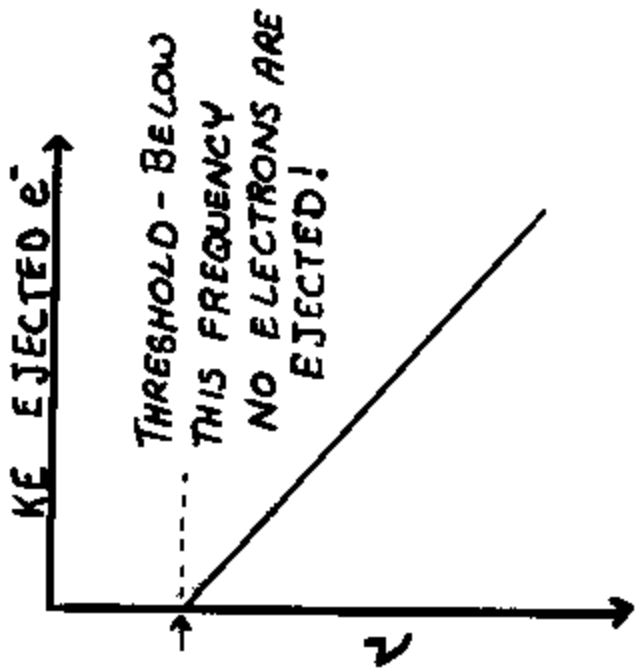
$$\frac{dp}{d\lambda} = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{h\nu/kT}-1}\right)$$

h = PLANCK'S CONSTANT 6.626×10^{-34} Js

2. PHOTOELECTRIC EFFECT:



$$E(EM) = \sum_{e^-} KE - \Phi$$



CLASSICALLY: A WAVE DELIVERS ENERGY IN PROPORTION TO ITS AMPLITUDE.

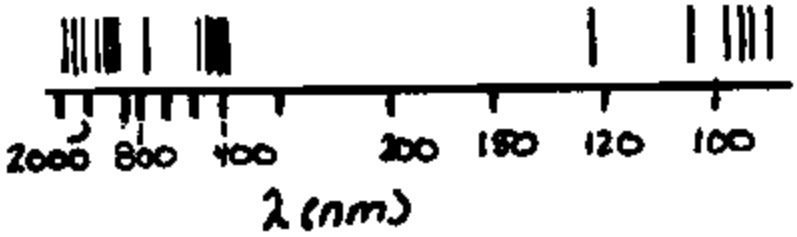
QUANTIZATION HYPOTHESIS: LIGHT EXISTS IN DISCRETE UNITS WITH QUANTIZED ENERGY - $E = h\nu$

1 <u>PHOTON</u> EJECTS 1 ELECTRON

$$\frac{1}{2}mv^2 = h\nu - \Phi$$

ALBERT EINSTEIN - NOBEL PRIZE 1921
~1905

3. LINE SPECTRA OF THE ELEMENTS:



HYDROGEN ATOM EMISSION

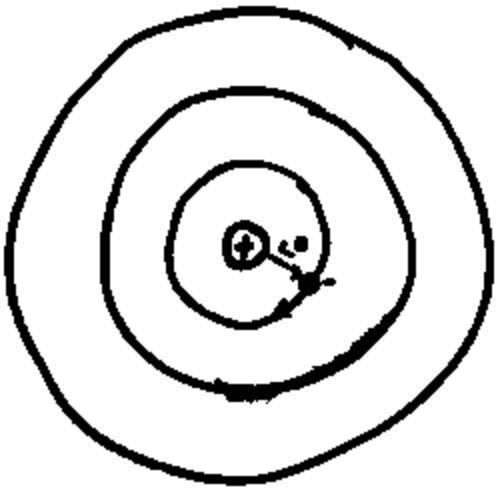
$$\tilde{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$V(r) = \frac{-e^2}{r}$$

CONTINUOUS EMISSION

1913
NIELS BOHR: NOBEL PRIZE 1922

QUANTIZATION HYPOTHESIS:

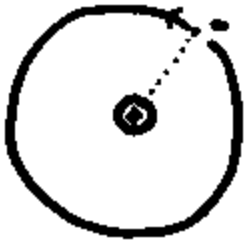


1. DISCRETE ALLOWED ELECTRONIC ORBITS

$$mvr = \frac{nh}{2\pi} = n\hbar$$

ANGULAR MOMENTUM IS QUANTIZED

CONSEQUENCES:



$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

CENTRIPETAL FORCE — COULOMB ATTRACTIVE FORCE

1. $v(mvr) = Ze^2$

$v(n\hbar) = Ze^2$

$v = \frac{Ze^2}{n\hbar}$ — ONLY SPECIFIC VELOCITIES ARE ALLOWED!

2. $\frac{(mvr)^2}{mr^3} = \frac{Ze^2}{r^2} \Rightarrow \frac{(n\hbar)^2}{mr^3} = \frac{Ze^2}{r^2}$

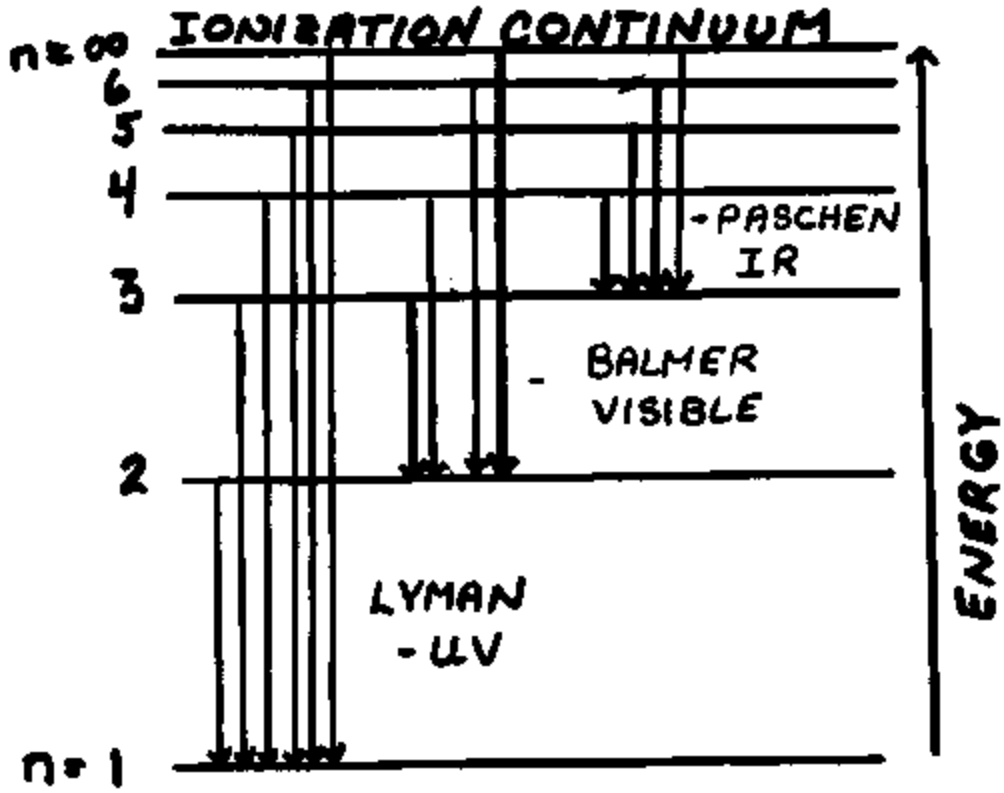
$n^2\hbar^2 = Zme^2 r$

$r = \frac{n^2\hbar^2}{mZe^2}$ — ONLY SPECIFIC ORBITS ARE ALLOWED

3. $E = \frac{1}{2}mv^2 - \frac{Ze^2}{r}$ (T.E. = K.E + P.E.)

$= \frac{1}{2}m\left(\frac{Ze^2}{n\hbar}\right)^2 - Ze^2\left(\frac{mZe^2}{n^2\hbar^2}\right)$

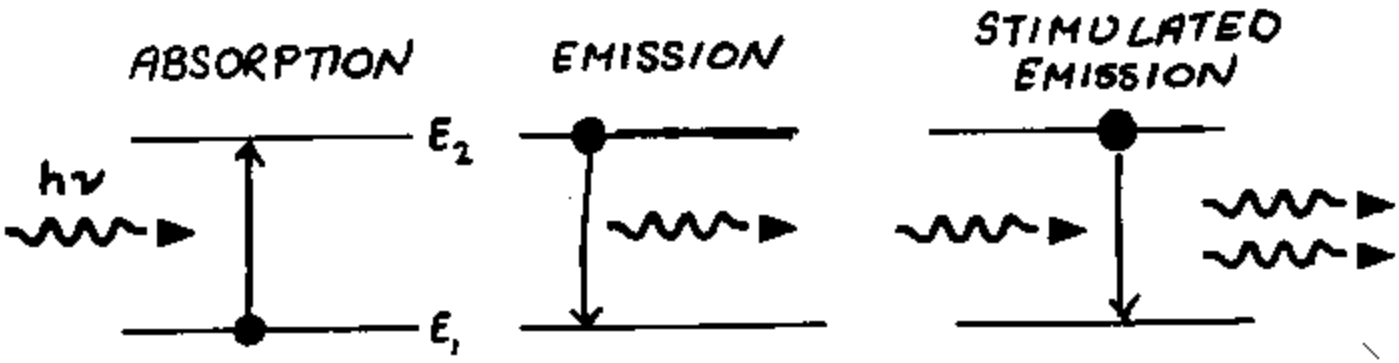
$= -\frac{1}{2}\frac{mZ^2e^4}{n^2\hbar^2} = -\frac{R_H}{n^2}$ — ENERGY LEVELS ARE QUANTIZED



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

$$\nu = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

ENERGY LEVEL DIAGRAMS



$\Delta E = h\nu$

1. LIGHT IS WAVE-LIKE.

2. LIGHT IS PARTICLE-LIKE.

3. MATTER IS PARTICLE-LIKE.

1923 LOUIS De BROGLIE

EINSTEIN

$E = mc^2$ $\quad$ $E = h\nu$

PHOTONS HAVE RELATIVISTIC MASS AND CARRY MOMENTUM

$$E = h\nu = \frac{hc}{\lambda} = \frac{h}{\lambda}c = mc^2 = (mc)c$$

MOMENTUM $= h/\lambda$

de BROGLIE WAVELENGTH

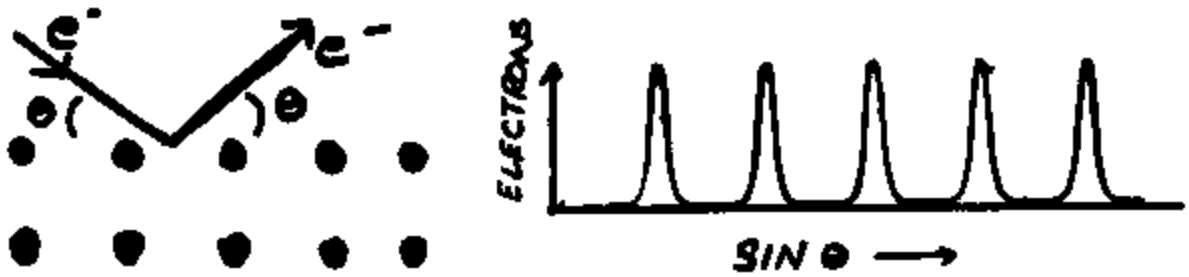
$$\boxed{\lambda = \frac{h}{mv}}$$

MATTER IS WAVE-LIKE

NOBEL PRIZE 1929 (AFTER EXPERIMENTAL VERIFICATION!)

IF ELECTRONS OR NEUTRONS ARE SCATTERED OFF OF CRYSTALS

- THEY DIFFRACT JUST LIKE X-RAYS



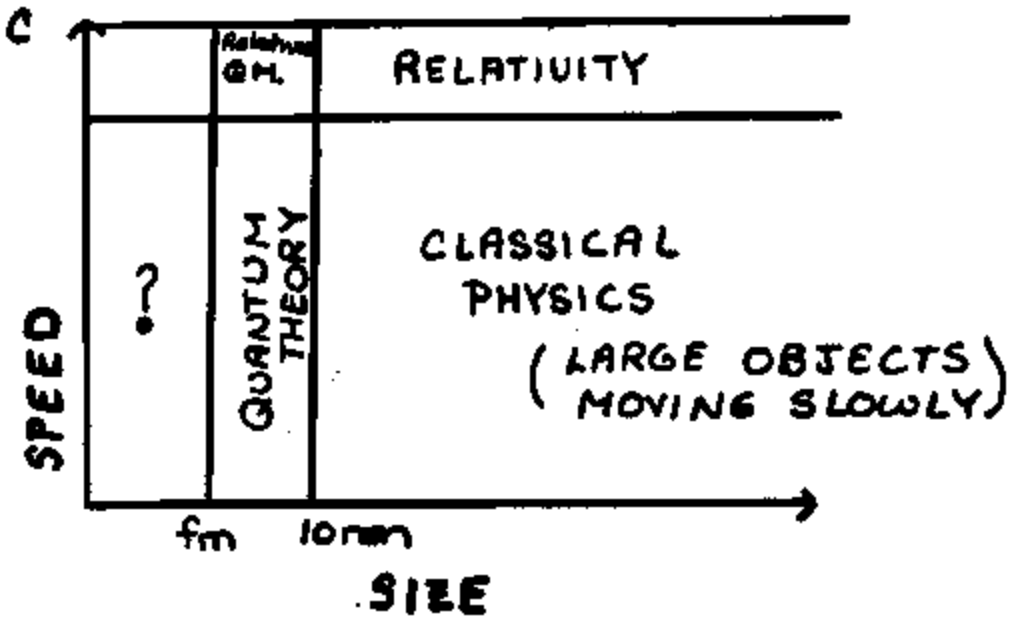
PATTERN DEPENDS ON λ ∴ ON MOMENTUM!

CONSIDER AN ELECTRON WITH A VELOCITY

$$v = 0.01c = 2.9979 \times 10^{6}\ m/s$$

$$\lambda = \frac{6.62608 \times 10^{-34}\ Js}{(9.1096 \times 10^{-31}\ kg)(2.9979 \times 10^{6}\ m/s)}$$

$$\lambda = 2.43 \times 10^{-10}\ m = 2.43\ \mathring{A} = 243\ pm$$



IF $\lambda \ll$ SIZE OF OBJECT $\left(\lambda = \frac{h}{mv}\right)$

OBJECT BEHAVES CLASSICALLY

QM REDUCES TO CLASSICAL BEHAVIOR
"CORRESPONDENCE PRINCIPLE"

BASEBALL AT 60 mph (27 m/s) 0.145 kg

$$\lambda = \frac{6.626 \times 10^{-34}\ \mathrm{Js}}{0.145\ \mathrm{kg}\ (27\ \mathrm{m\,s^{-1}})} = 1.7 \times 10^{-34}\ \mathrm{m}$$

SINCE $\lambda \ll$ SIZE NO WAVE-LIKE PROPERTIES ARE APPARENT

IF $v \ll c$ OBJECT BEHAVES CLASSICALLY

$$p = \gamma m_0 v \qquad \gamma = \frac{1}{\sqrt{1-(v/c)^2}}$$

p: momentum; m_0: rest mass

QUANTIZATION AND WAVE-PARTICLE DUALITY:

1. PLANCK: QUANTIZED ENERGY LEVELS FOR MATERIAL OSCILLATORS.

$$\mathcal{E} = n h \nu$$

ν ← OSCILLATOR FREQUENCY

n: INTEGER 1, 2, 3, ...

h: PLANCK'S CONSTANT $h = 6.626 \times 10^{-34}$ J s

2. EINSTEIN: LIGHT ENERGY IS QUANTIZED AS PHOTONS.

$$E = h\nu = \frac{hc}{\lambda}$$

} ENERGY PER PHOTON DEPENDS ON THE WAVELENGTH.

3. Bohr: ELECTRON ANGULAR MOMENTUM IS QUANTIZED.

$$mvr = n\hbar = \frac{nh}{2\pi}$$

} LEADS TO QUANTIZED ENERGY LEVELS AND ORBITS.

4. de BROGLIE: PARTICLES BEHAVE IN A WAVE-LIKE MANNER

$$\lambda = \frac{h}{mv}$$

WAVELENGTH DEPENDS ON MOMENTUM

HEISENBERG NOBEL PRIZE 1932

SCHRÖDINGER NOBEL PRIZE 1933

THE <u>POSTULATES</u> OF QUANTUM MECHANICS

1. THE PHYSICAL STATE OF A PARTICLE OR SYSTEM OF PARTICLES AT A TIME t IS DESCRIBED BY A COMPLEX WAVEFUNCTION:

$$\Psi(\vec{r},t) = \Psi(\underbrace{x_1, y_1, z_1, x_2, y_2, z_2, \ldots}_{\text{SPATIAL VARIABLES FOR EACH PARTICLE.}}, t)$$

2. THE WAVEFUNCTION IS A SOLUTION TO THE TIME-DEPENDENT SCHRÖDINGER EQUATION:

$$\underbrace{\hat{H}(\vec{r},t)}_{\substack{\text{TOTAL ENERGY OPERATOR} \\ \text{"HAMILTONIAN"}}} \Psi(r,t) = i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t}$$

3. THE AVERAGE VALUE (EXPECTATION VALUE) OF ANY PHYSICAL PROPERTY IS GIVEN BY:

$$\langle F \rangle = \int_{-\infty}^{\infty} \Psi^*(\vec{r},t)\, \hat{F}\, \Psi(\vec{r},t)\, d\vec{r}$$

WHERE F IS A QUANTUM MECHANICAL OPERATOR CORRESPONDING TO A PHYSICAL QUANTITY, (i.e. position, momentum...).

$$\underbrace{\langle x \rangle}_{\text{AVERAGE POSITION}} = \int_{-\infty}^{\infty} \Psi^*(x,t)\, \underbrace{\hat{x}}_{\text{POSITION OPERATOR } x.}\, \Psi(x,t)\, dx$$

$$\underbrace{\langle E \rangle}_{\text{AVERAGE ENERGY}} = \int_{-\infty}^{\infty} \Psi^*(\vec{r},t)\, \underbrace{\hat{H}(\vec{r},t)}_{\text{TOTAL ENERGY OPERATOR}}\, \Psi(\vec{r},t)\, d\vec{r}$$

⋮ + OTHER POSTULATES AND MATHEMATICAL DETAILS

SCHRODINGER'S WAVE EQUATION:

$$\hat{H}(\vec{r},t)\,\Psi(\vec{r},t) = i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t}$$

1. $\hat{H}(r,t)$ IS THE QUANTUM MECHANICAL HAMILTONIAN OR TOTAL ENERGY OPERATOR.

$$\hat{H} = \hat{T} + \hat{V} = K.E. + P.E.$$

IN ONE DIMENSION:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{\text{KINETIC ENERGY OF A PARTICLE OF MASS } m} + \overbrace{V(x)}^{\text{POTENTIAL ENERGY OF THE PARTICLE}}$$

2. WE DON'T USUALLY WORRY ABOUT TIME-DEPENDENCE.

TIME-INDEPENDENT SCHRODINGER EQUATION

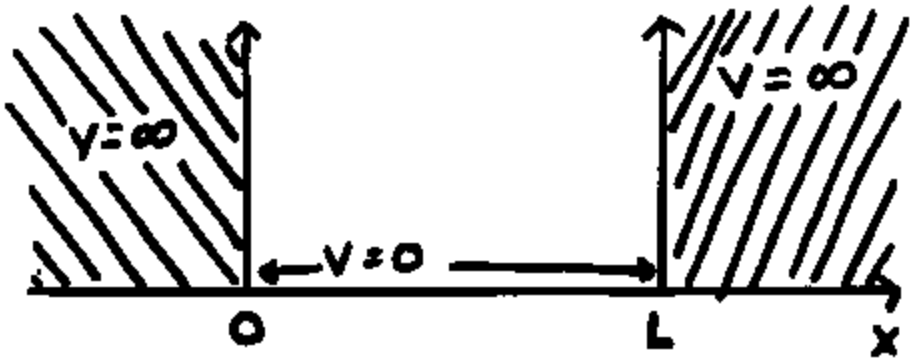
(Eq. 12.9)

$$\hat{H}(\vec{r})\,\psi(\vec{r}) = E\,\psi(\vec{r})$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x) = E\,\psi(x)$$

AN EXAMPLE:

A PARTICLE IN A ONE-DIMENSIONAL BOX



$$H\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \quad 0 \le x \le L}$$

WE WANT TO SOLVE FOR $\psi(x)$ (THE <u>WAVE FUNCTION</u>) AND E (<u>THE ENERGY EIGENVALUE</u>).

* ψ WILL DESCRIBE THE POSITION OF THE PARTICLE

* E WILL BE THE ENERGY OF THE SYSTEM IN THE STATE DESCRIBED BY $\psi(x)$.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

$\boxed{\text{TRIAL SOLUTION:}}$ $\underline{\psi(x) = A\sin ax}$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}A\sin ax = E(A\sin ax)$$

$$-\frac{\hbar^2 A}{2m}\frac{d}{dx}(a\cos ax) = E(A\sin ax)$$

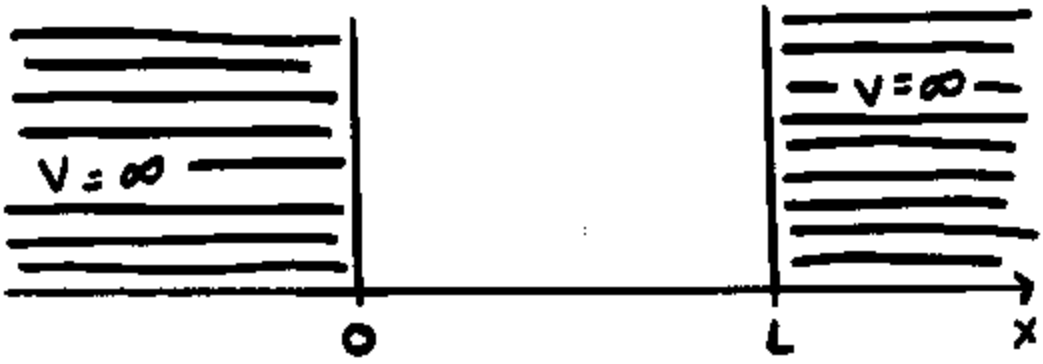
$$-\frac{\hbar^2 A}{2m}(-a^2\sin ax) = E(A\sin ax)$$

$$\frac{\hbar^2 a^2}{2m}\underbrace{(A\sin ax)}_{\psi(x)} = E\underbrace{(A\sin ax)}_{\psi(x)}$$

$$E = \frac{\hbar^2 a^2}{2m} \Rightarrow a = \frac{\sqrt{2mE}}{\hbar}$$

$$\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x$$

BUT WE ALSO HAVE BOUNDARY CONDITIONS:



$\psi(x) = 0 \quad x \leq 0 \qquad \psi(0) = 0$

$\psi(x) = 0 \quad x \geq L \qquad \psi(L) = 0$

$\boxed{\psi \text{ IS CONTINUOUS}}$ POSTULATE – NECESSARY FOR QM TO REPRESENT REALITY

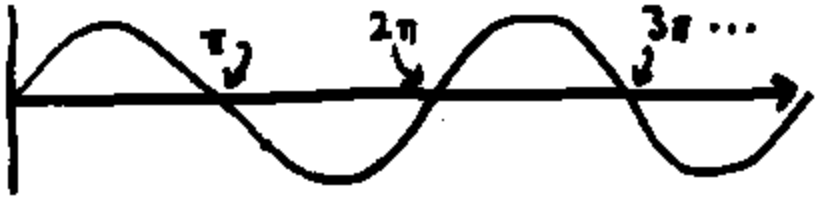
$$\psi(0) = A \sin \frac{\sqrt{2mE}}{\hbar} 0 = 0 \checkmark$$

THIS IS WHY WE DID NO TRY A COSINE TRIAL FNCTN

$$\psi(L) = A \sin \frac{\sqrt{2mE}}{\hbar} L = 0$$

$A = 0$ (TRIVIAL AND NOT HELPFUL)

$$\sin \frac{\sqrt{2mE}}{\hbar} L = 0$$



$$\frac{\sqrt{2mE}}{\hbar} L = n\pi$$

SOLUTION: $\psi_n(x) = A \sin \frac{n\pi x}{L}$ WAVE FUNCTIONS

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$$ POSSIBE ENERGIES

FINAL CONDITION: <u>NORMALIZATION</u>

$$\int_{-\infty}^{\infty} \psi_n^*(x)\, \psi_n(x)\, dx = 1$$

THIS CONDITION ALLOWS $|\psi_n(x)|^2$ TO REPRESENT THE PROBABILITY DISTRIBUTION FOR THE POSITION OF THE PARTICLE.

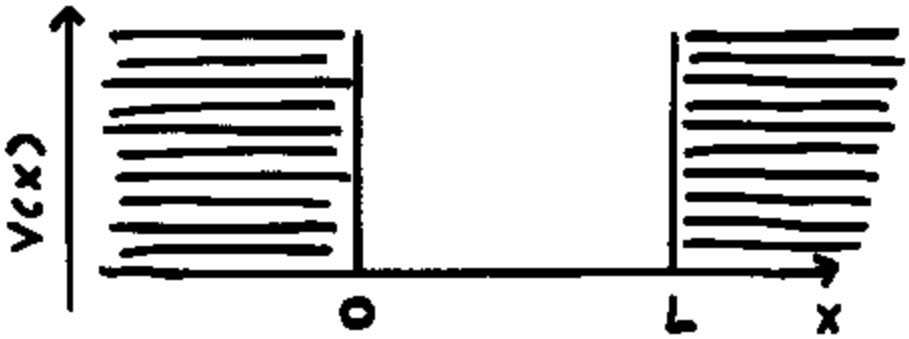
$$\boxed{\text{TOTAL PROBABILITY} = 1}$$

$$\int_0^L A \sin \frac{n\pi x}{L}\, A \sin \frac{n\pi x}{L}\, dx = 1$$

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L}\, dx = 1$$

$$A^2 \left[\frac{x}{2} - \sin \frac{2n\pi x}{L} \left(\frac{L}{4n\pi} \right) \right]_0^L = 0$$

$$A^2 \left[\frac{L}{2} - \frac{0}{2} \right] = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$



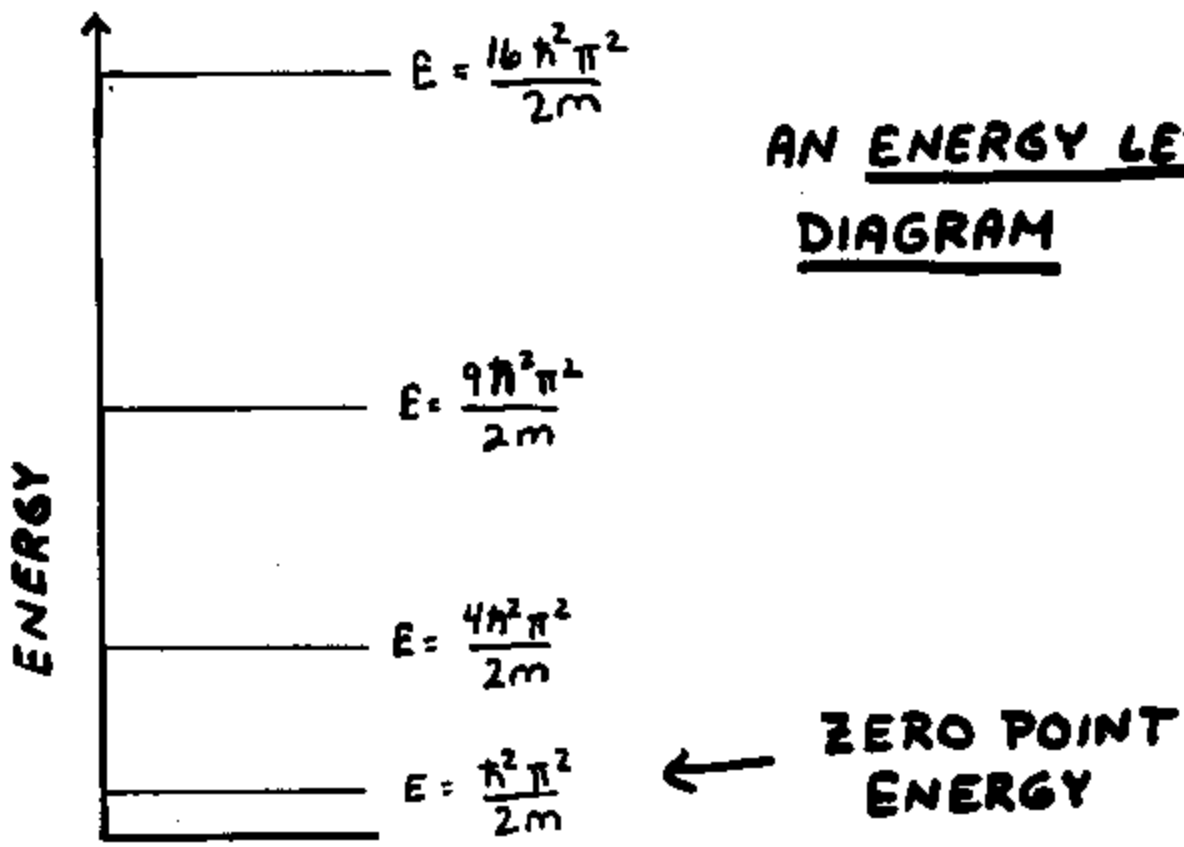
$$H\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\frac{n\pi x}{L} \qquad 0 \le x \le L$$

$$\psi_n(x) \equiv 0 \qquad x \le 0,\ x \ge L$$

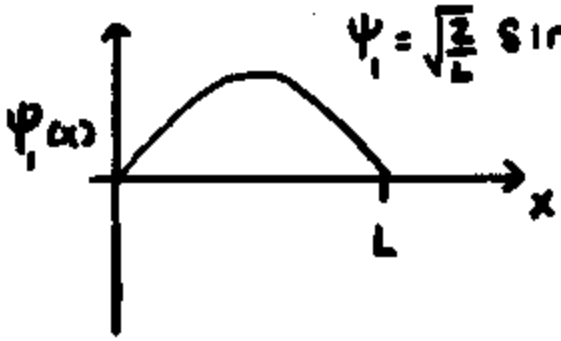
$$E_n = \frac{\hbar^2 n^2 \pi^2}{2m}$$

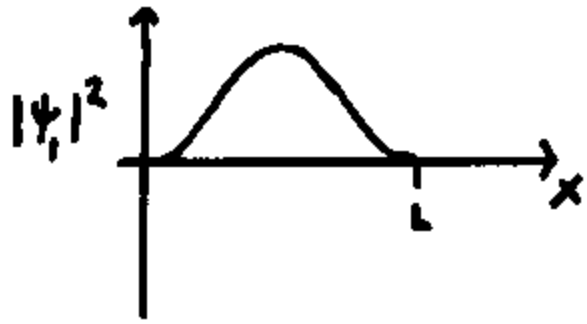


AN <u>ENERGY LEVEL DIAGRAM</u>

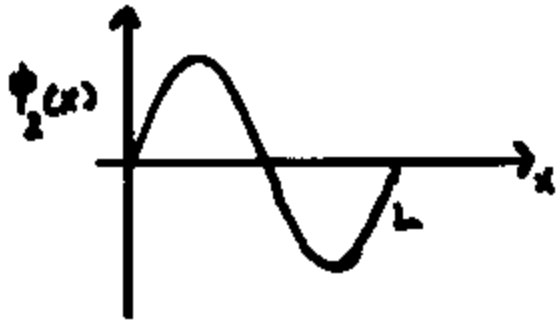
$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

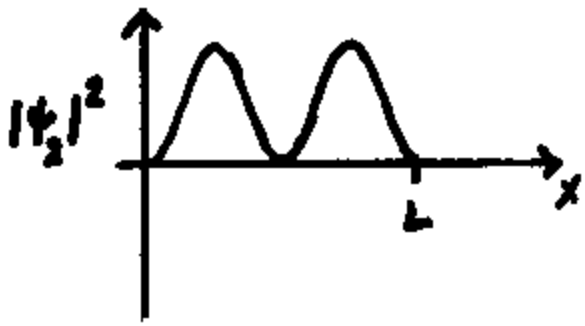
$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$$



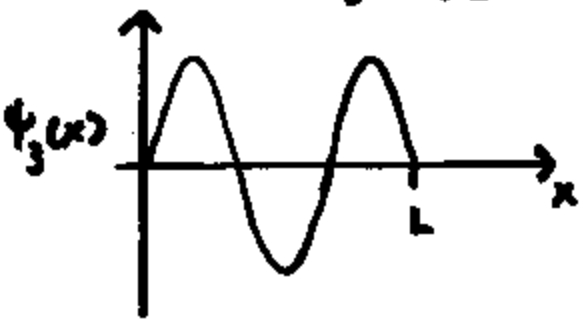


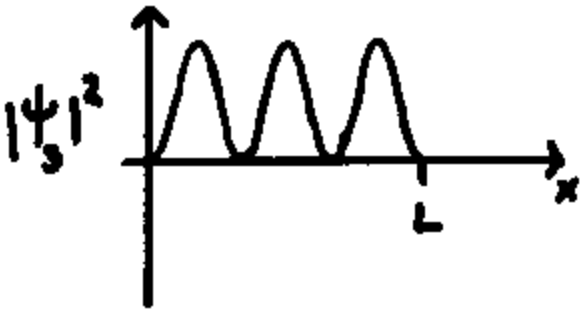
$$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L}$$



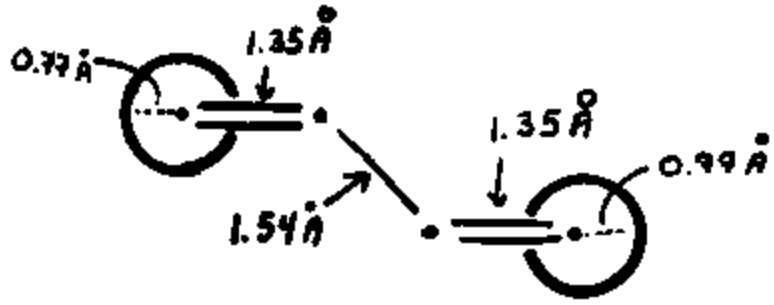


$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

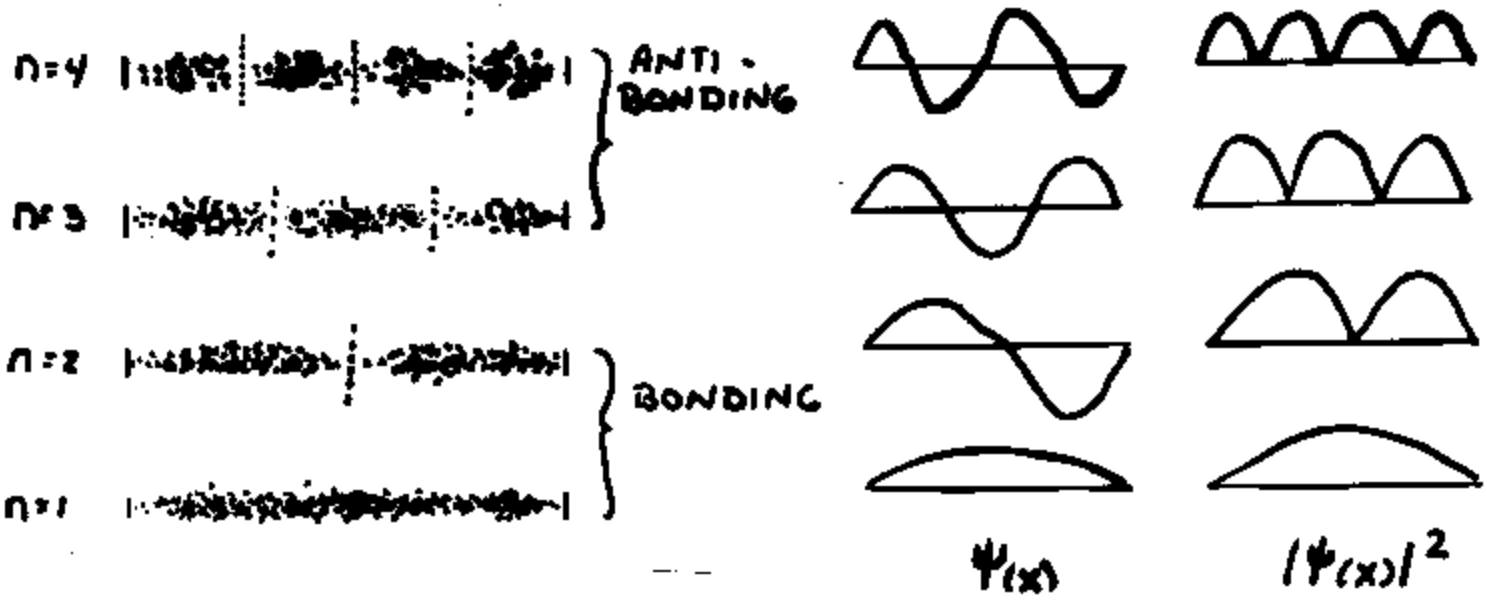




CONSIDER BUTADIENE



$L = 5.78$ Å

"PERFECT CONJUGATION"

$U(x) = 0$