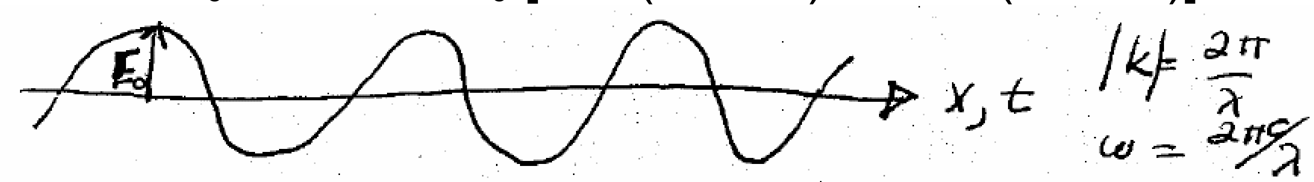
Model Problems – 09 - Ch.14 - Engel/ Particle in box - all texts

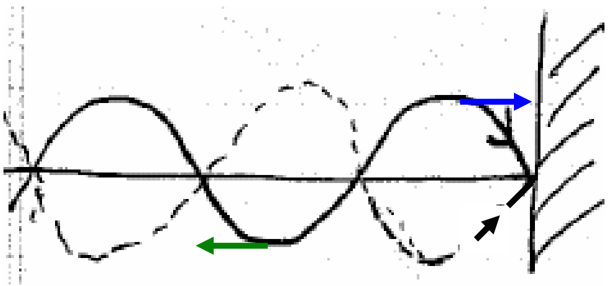
Consider E-M wave 1st

wave: $E_0 e^{i(kx - \omega t)} = E_0 [\cos(kx - \omega t) - i \sin(kx - \omega t)]$

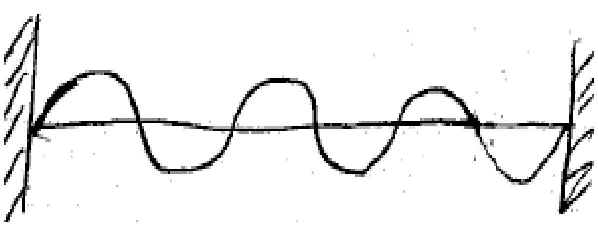


magnitude: $|k| = 2\pi/\lambda$ $\omega = 2\pi c/\lambda = 2\pi\nu$ $\nu = c/\lambda$

moves in space and time – traveling wave



reflect at the node
keeps the wave continuous
(if not create an interference)
- - - - is other cycle, at $\Delta t = \lambda/2c$



if trap wave like violin string
tied down at end
→ standing wave

(principle of laser → light trap in cavity
– specific frequency / phase amplified)

restriction - number wavelengths integral divisor of length
integer representation of frequencies – not continuous

Now think of traveling particle → 1-D no forces ⇒ $V = 0$

$\boldsymbol{H}\psi = E\psi = \boldsymbol{T}\psi$ let $V = 0$, free moving particle

$\boldsymbol{H}\psi = -\hbar^2/2m \, d^2/dx^2 \, \psi(x)$

Solution: need some function that can
take derivatives twice and get function back

choices:

a) $de^{ax}/dx = ae^{ax}$ derivative works $d^2/dx^2\, e^{ax} = a^2e^{ax}$
(but Energy must be positive, so 2[nd] deriv. must be negative, so need $a = i\alpha$, $e^{i\alpha x}$ wavefunction complex)

b) $d^2/dx^2 \sin kx = -k^2 \sin kx$
(Note: $e^{i\alpha x} = \cos \alpha x - i \sin \alpha x$ → general form wave)
No constraint → traveling wave (but for particle)

Solve Schroedinger Equation for free particle:

$-(\hbar^2/2m)\, d^2/dx^2\, \psi = E\psi$

if $\psi = e^{i\alpha x}$ → plug in $-(\hbar^2/2m)(i\alpha)^2 e^{i\alpha x} = E\, e^{i\alpha x}$

from (b): $\alpha = \mathbf{k} = (2mE)^{1/2}/\hbar$ →

$E = \alpha^2\hbar^2/2m$ (all K.E. - positive, not quantized)

no restrictions – free particle, any energy or wavelength

Boundary Conditions

Restrictions must fit postulates → B.C.
– relate to continuous and finite properties of wavefct., etc. → relates to properties of wave/fct on both sides of boundary--must match

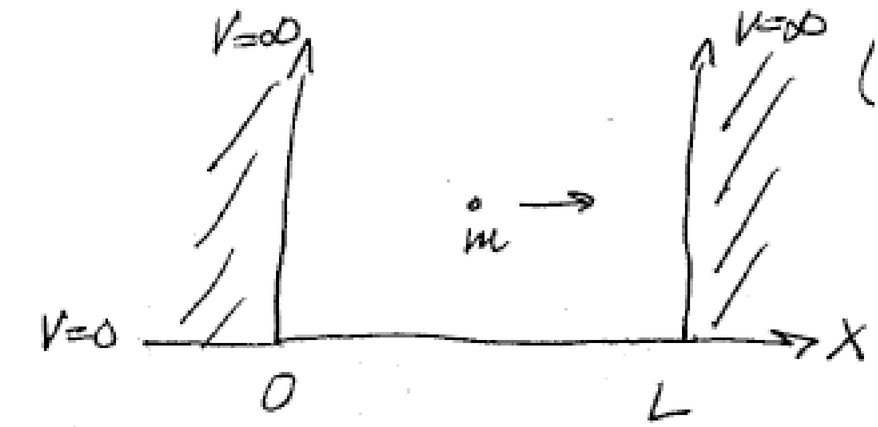
Note effect of momentum: (for $\psi = e^{ikx}$)

$\mathbf{p}\psi = -i\hbar(ik)\,\psi$ → Magnitude: $|p| = \hbar k$

signs → direction $\mathbf{p} = \hbar k$ (motion in +x)

[opposite: $\psi = e^{-ikx}$, (motion -x)]

Particle in a box



in box $V = 0$
outside $V = \infty$

For E to be finite:

– particle must be in box (need definite E-state
also think of as $F = -dV/dx$, force at wall is ∞)

$-\hbar^2/2m\ d^2/dx^2\ \psi = E\psi$ try $\psi = A \sin \alpha x + B \cos \beta x$

B.C. $\psi(0) = 0 \Rightarrow$ restrict: $B = 0$ (since $\cos 0 = 1$)
$\psi(L) = 0 \Rightarrow$ restrict: $\alpha = n\pi/L$ (since $\sin n\pi = 0$)
for $\psi(x) \neq 0$, must have: $A \neq 0$, $n \neq 0$ and $n=1,2,3,\ldots$

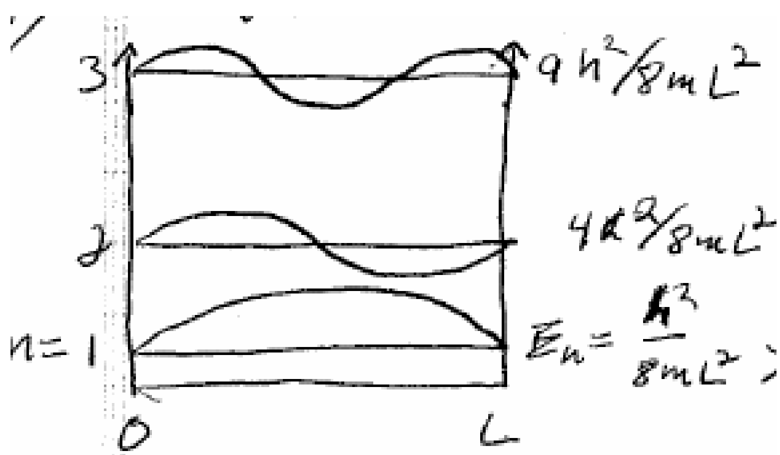
(i.e. must be node both sides – integral number modes
and be non-zero someplace--non-trivial solution)

forms a standing wave -- quantized (recall - laser)

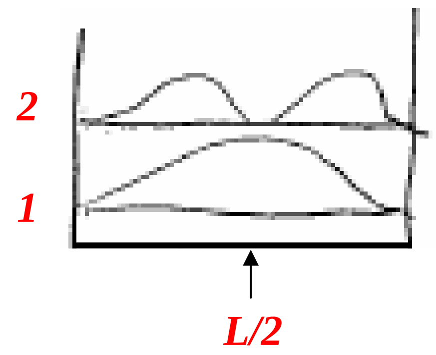
$$-\hbar^2/2m\ d^2/dx^2\ (A \sin n\pi x/L) = E\ (A \sin n\pi x/L)$$

$$(-\hbar^2/2m)(-\ n^2\pi^2/L^2) = E_n = n^2h^2/8mL^2$$

Expanding E-levels ~ n^2
each has increasing
number of nodes
restricted energy levels
lowest energy $\neq 0$
(particle always moving)



Probability distribution: $\psi^*\psi\, dx$



$\int_0^L \psi^*\psi\, dx = 1$ (if normalize)

but plot $\psi^*\psi \rightarrow$ not uniform in x
n = 1 more probable in middle
n = 2 zero probability at x = L/2

as n increases – probability more even → classical

Orthogonal $\int \psi_m^* \psi_n\, dx = 0$ if $n \neq m$

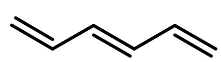
$\int \sin(n\pi x/L)\, \sin(m\pi x/L)\, dx = 0$ – easiest seen graphically

Amplitude? $\int_0^L \psi_n^* \psi_n\, dx = 1$ from normalization

$\int_0^L A^2 \sin^2(n\pi x/L)\, dx = 1 \Rightarrow A^2 (L/2) = 1 \Rightarrow A = (2/L)^{1/2}$

Probability $\int_a^b \psi^*\psi\, dx \Rightarrow$ probability between a + b

Use for pib? Great model / see how potential or B.C. leads to quantization

Application: polyenes  …

π-system delocalize – electrons move through π-bonds

spectra – e^- could be in different levels

$\Delta E = E_{n+1} - E_n = h\nu$
$n \rightarrow n + 1$
$\Delta E = (n+1)^2 h^2/8mL - n^2h^2/8mL$
$= (2n + 1)\, h^2/2mL^2 = h\nu$

Now see properties

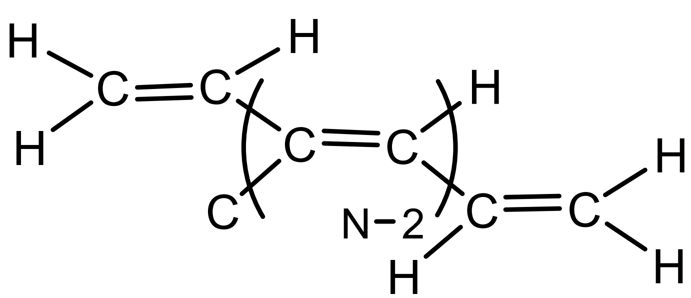
a) bigger n $\rightarrow$ more separation – higher frequency - $h\nu$

b) bigger m $\rightarrow$ less separation (but all same m_e - electron)

c) bigger L $\rightarrow$ less separation (as square), experimental

Sample dye problem:

Polyene



N	λ_{max} (Å) Obs	Calc
1	1600	870
2	2170	2080
3	2600	3360
4	3020	4650
5	3460	5940
6	3690	7200
11	4510	13700
12	4750	15000
15	5040	18900

$\Delta E = (2N + 1)\, h^2/8mL^2$ $\quad$ $L \approx 0.281\, N$ (in nm)

$\lambda = c/\nu = hc/\Delta E$

$= (8mc/h)\,(0.281 \times 10^{-9}\ m)^2\ N^2/2N + 1$ → units! m

Note: trend is as expected $\quad$ N $\rightarrow$ increase, $\lambda \rightarrow$ increase

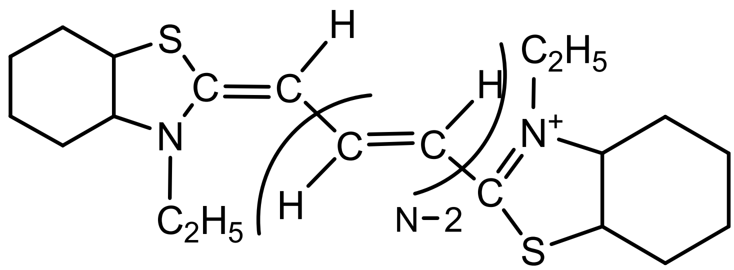
(big boxes lower energy states)

– values off – calc. change much faster than exper.

-- box length approximate

-- and evenness of V (real potential vary over bonds)

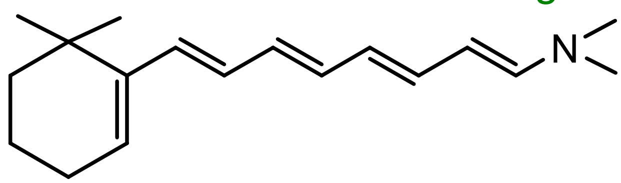
<u>Dye</u>



N	Obs	Calc
2	4250	3280
3	5600	4540
4	6500	5800
5	7600	7060
6	8700	8330
7	9900	9600

Model does better (here use N+1 → N+2) and use different length, but still $\lambda \sim N^2/N$ type term (linear)

Bio-connect -Vision: retinal undergoes cis-trans isomerization



(trans)

Butadiene examples – real spectra shift with length

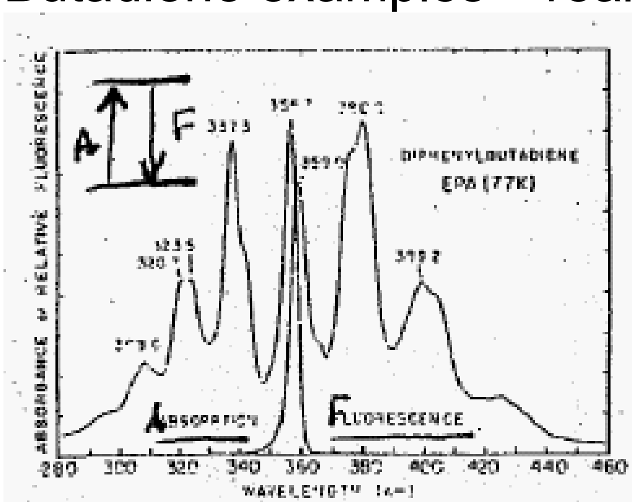


FIG. 2. Absorption and fluorescence spectra of diphenylbutadiene in EPA at 77 K. The excitation wavelength for the emission spectrum was 3?? nm. Sample concentrations were 6.0 × 10⁻ M (absorption) and ?·3 × 10⁻ M (emission). Concentration studies indicate that the 359.0 nm vibronic band in emission is

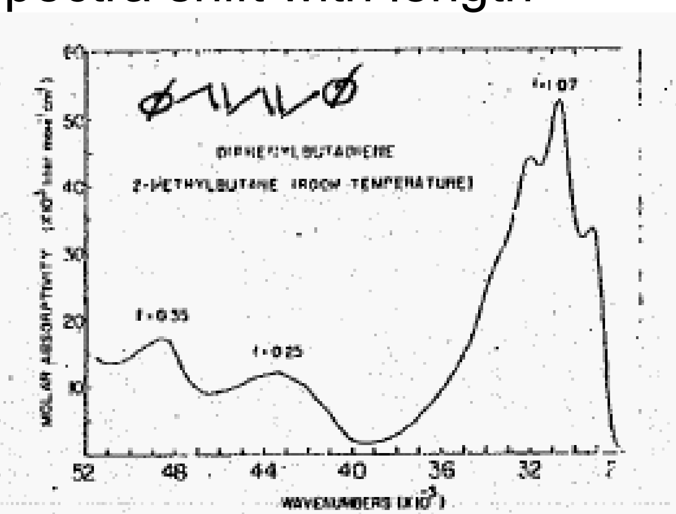


FIG. 3. One-photon absorption spectrum of diphenylbutadiene (DPB) in 2-methylbutane (2MB) solvent at room temperature. The spectrum was taken on a Cary 219 recording spectrophotometer using a sample concentration of 4.03×10^{-4} M. The measured oscillator strengths are indicated above the appropriate

Ionization potential – measures energy of the “orbital” – see decrease ethylene → butadiene (left peak lowest)

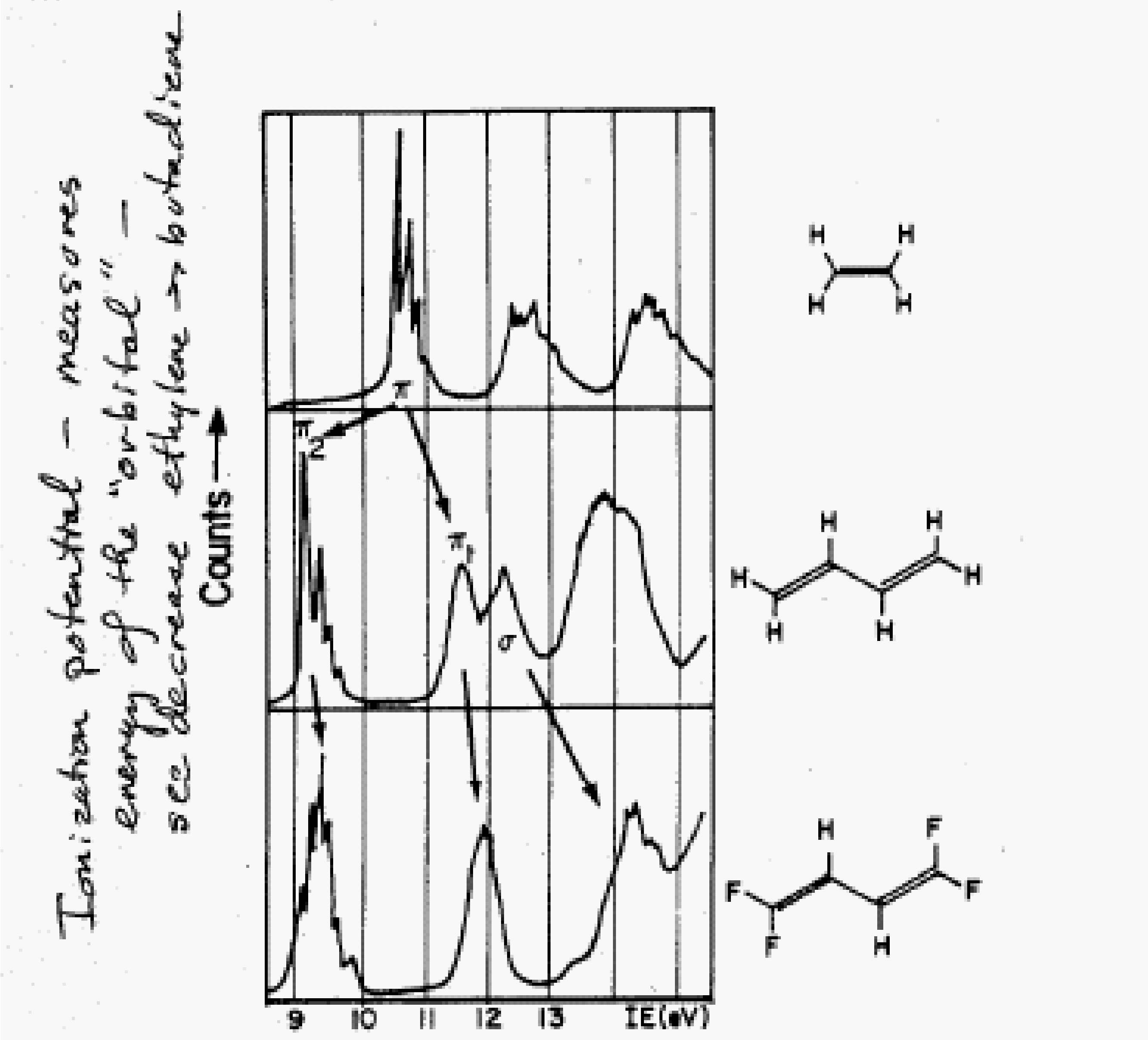
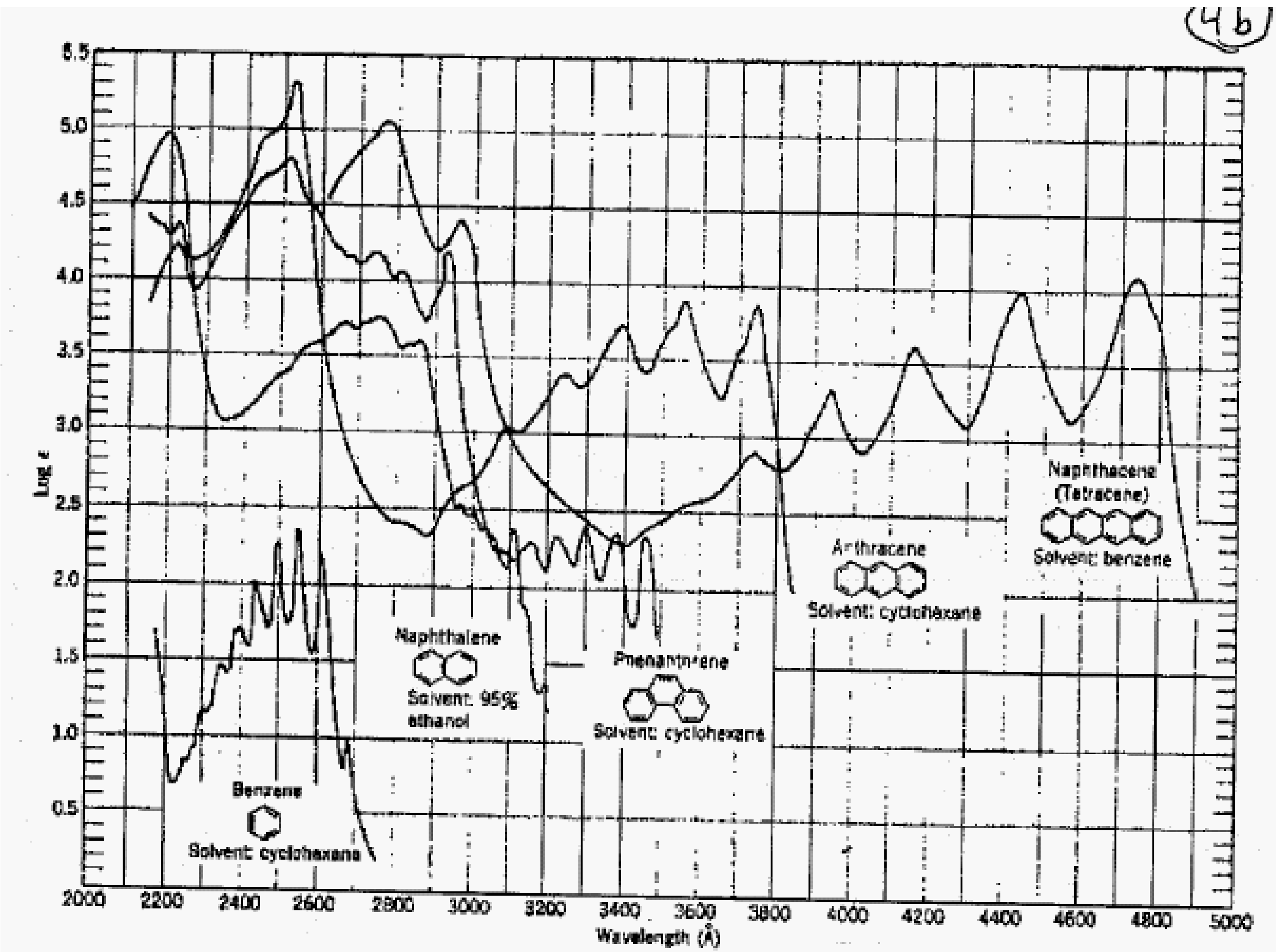


Fig. 4-50. He I (58.4 nm) photoelectron spectra of ethylene, butadiene, and 1,1,4,4-tetrafluorobutadiene, showing that one pi orbital energy of the dienes is greater than that of ethylene and one is less. Additional structure of the bands will be discussed in Chapter Five, Adapted from H. Bock and P.D. Mollère, *J. Chem. Ed.*, *51*, 506 (1974).

2-D box example → π-system expand energy ,
difference gets smaller—big box, small energies

Problems worked out most books (Engel Ch 14.4)

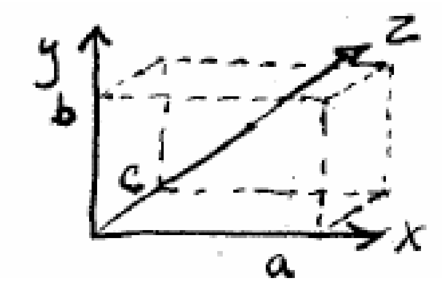
poly arene examples
(in wavelength, so going to right, lower energy):



1 ring 2rings 3 rings 4 rings

3-D Particle in box – Separation of Variables (Engel 14.4)

Method we will need to solve atoms & molecules



V = 0 $\quad 0 < x < a$

$0 < y < b$

$0 < z < c$

V = ∞ $\quad$ outside the box

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

$$\nabla^2\psi = -2mE/\hbar^2\ \psi$$

Note: a) $\partial/\partial x$ → only operate on x-dependent function

b) H is a sum of terms – each depend on 1 variable

IN GENERAL → can find solution -- product function form

$\Psi = X(x)\ Y(y)\ Z(z)$ $\quad$ where $X(x)$ is only fct. of x, etc.

AND → energy also a sum: $E = E_1 + E_2 + E_3$

Substitute:

$$\nabla^2\ XYZ = YZ\frac{\partial^2 X(x)}{\partial x^2} + XZ\frac{\partial^2 Y(y)}{\partial^2 y} + XY\frac{\partial^2 Z(z)}{\partial z^2} = \frac{-2mE}{\hbar^2}XYZ$$

divide by *XYZ*:

$$\frac{-2mE}{\hbar^2} = \frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}$$

⇒ each term must be a constant – since independent

i.e. $1/X\ \ \partial^2 X/\partial x^2 = \alpha$ etc. $\qquad \alpha + \beta + \gamma = -2mE/\hbar^2$

These are pib solutions again:

$$\psi(x,y,z) = \sqrt{\frac{8}{abc}}\ \sin\left(\frac{n_x\pi}{a}x\right)\ \sin\left(\frac{n_y\pi}{b}y\right)\ \sin\left(\frac{n_z\pi}{c}z\right)$$

$$E = \frac{\hbar^2}{8m}\left(\frac{n_x^{\ 2}}{a^2} + \frac{n_y^{\ 2}}{b^2} + \frac{n_z^{\ 2}}{c^2}\right) = E_1 + E_2 + E_3$$

Lowest state $n_x = n_y = n_z = 1$

But 3 ways for next state $\rightarrow$ $n_x = 2$, $n_y = n_z = 1$, etc.

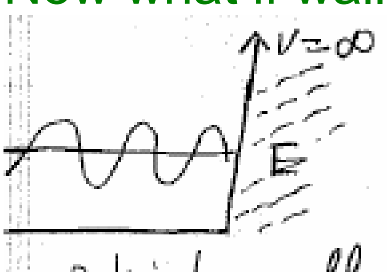
Each of these could have different energies

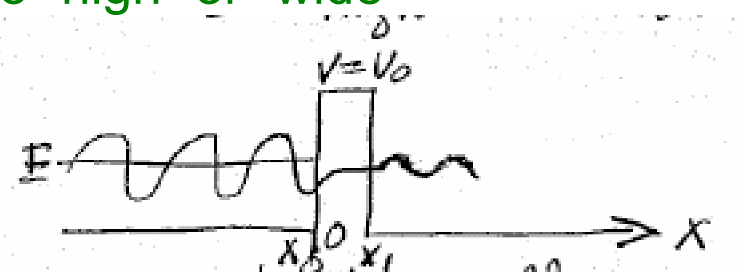
However, if a=b=c, then each has same energy→

degeneracy from symmetry

Barriers (Engel Ch.14.9)

Now what if wall not so "high" or "wide"





∞ high wall wave must have zero amplitude
$\psi^*\psi = 0$ at wall ⇒ reflect

shorter wall wave can be penetrated – also thin wall– go through or "tunneling"

$(-\hbar^2/2m\ d^2/dx^2 + V)\psi = E\psi$

if $\psi = e^{i\alpha x} \Rightarrow [\hbar^2\alpha^2/2m + (V-E)]\psi = 0 \Rightarrow \alpha = \sqrt{2m(E-V)}/\hbar$

now $x < x_0$, $V = 0$ $E - V = (+)$

$\psi = e^{i\alpha x}$ is complex $\rightarrow$ wave but for : $x > x_0$,   V > E   E – V = (–)

so $\alpha = i\frac{\sqrt{2m\,(V-E)}}{\hbar} = iK$ → $\boxed{\psi' = e^{-Kx}}$ → real, decaying function

At wall $\psi(x_0) = \psi'(x_0)$ i.e. must be continuous

If non-zero in wall, then ψ must <u>decay</u> as move → +x

<u>On other side</u>: $\psi'(x_1) = \psi''(x_1)$ (contin. go out: $\psi'' < \psi$)

equation 9.10 Atkins: Tunneling probility, T

$\boxed{T \cong 16\varepsilon\,(1 - \varepsilon)\, e^{-2KL}}$ where : $\varepsilon = E/V$ $L = x_1 - x_0$

$K=[2m(V-E)]^{1/2}/\hbar$

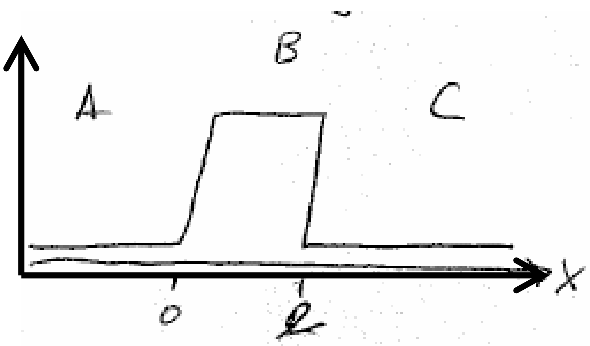
Aside

Solution (*<u>extra-repeat</u>*):

Look at just the barrier:

$H_A = -\hbar^2/2m\; d^2/dx^2 = H_C$

$H_B = -\hbar^2/2m\; d^2/dx^2 + V$



solve each region separately:

$\psi_A = Ae^{ikx} + Be^{-ikx}$ $k = (2mE/\hbar)^{1/2}$

$\psi_B = A'e^{ik'x} + Be^{-ik'x}$ $k' = [2m\,(E - V)/\hbar]$ (in the barrier)

$\psi_C = A''e^{ik''x} + B''e^{-ik''x}$ $k'' = (2mE/\hbar)^{1/2} = k$

Note: if E < V, then k' = imaginary

let $k' = iK$, $K = [2m\,(E - V)/\hbar]^{1/2}$ (= real)

$\psi_B = A'e^{-Kx} + B'e^{+Kx}$

– exponentially decreasing or increasing function

– no oscillation in barrier

– amplitude: $\psi^*\psi \neq 0$ in barrier, thus can tunnel → probability non-zero of in and other side barrier
– damping ~ mass – heavy don't penetrate – classic low energy don't penetrate

"tunnelling" --skip, read

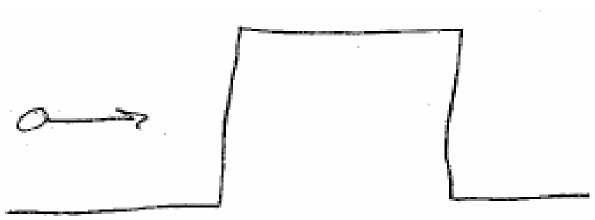
i.e. w/f okay if bound in area of wall – must be thin to solve for A, B 's must set up simultaneous equation based on: boundary constraints

$\psi_A(0) = \psi_B(0)$ $\quad A + B = A' + B'$
$\psi_B(\ell) = \psi_C(\ell)$ $\quad A'e^{-K\ell} + B'e^{+K\ell} = A''e^{ik\ell} + B''e^{-ik\ell}$

and continuous slopes

$\partial\psi_A/\partial x|_0 = \partial\psi_B/\partial x|_0$ $\quad ikA - ikB = -KA' + KB'$
$\partial\psi_B/\partial x|_\ell = \partial\psi_C/\partial x|_\ell$ $\quad -KA'e^{K\ell} + KB'e^{K\ell} = ikA''e^{ik\ell} + ikB''e^{-ik\ell}$

Then consider structure as:



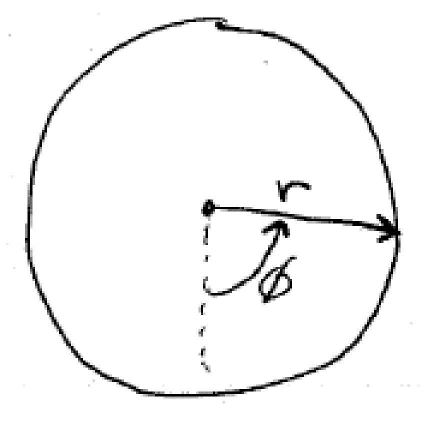
$B = 0$, $A \neq 0$ (come from left)
then $B'' = 0$
and $|A''|^2$ ~ transmission
$|B|^2$ ~ reflection

Probability of tunneling: $|A''|^2 / |A|^2$

$P = 1/(1 + G)$ $\quad G = \dfrac{(e^{K\ell} - e^{-K\ell})^2}{4(E/V)(1-E/V)}$

Note: P – non zero , K > 0
E increased, G decreased, P increased

Particle on a ring:



Circumference = $2\pi r$

B.C. $\psi(\phi) = \psi(\phi + 2\pi)$

continuous but not zero (no wall)

$H\psi = \frac{-\hbar^2}{2mr^2}\frac{\partial^2}{\partial\phi^2}\psi = E\psi$ $\quad \frac{r^2 \to \text{unit length}}{dr^2 \sim r^2 d\phi^2}$

$\psi = Ae^{i\alpha\phi} + Be^{-i\beta\phi}$ $\quad \mathbf{r} = x\mathbf{i} + y\mathbf{j},\ x^2 + y^2 = 1$

$x = |\mathbf{r}|\cos\phi \quad y = |\mathbf{r}|\sin\phi$

B.C. $e^{i\alpha\phi} = e^{i\alpha(\phi + 2\pi)} \Rightarrow e^{i\alpha(2\pi)} = 1 \Rightarrow \alpha = n = 0, \pm 1, \pm 2,$

2nd term (B-dependent) redundant

$E_n = \hbar^2 n^2/2mr^2$

Note: – levels degenerate for $\pm n$

– no zero – point E → $E_0 = 0$, ϕ unknown – on ring

– spacing $\sim n^2$ – same pattern (OK uncert.)

– bigger ring – lower E_n

Angular Momentum

$\mathbf{J} = \mathbf{r} \times \mathbf{p}$ in general $\to$ $J_z = |\mathbf{r}||\mathbf{p}|$ (1-D **z** out of plane)

$I = mr^2$ moment of inertia

$E = p^2/2m = J_z^2/2mr^2 = J_z^2/2I$

from de Broglie $p = h/\lambda$ $\quad \lambda = 2\pi r/n$ (int. # waves ring)

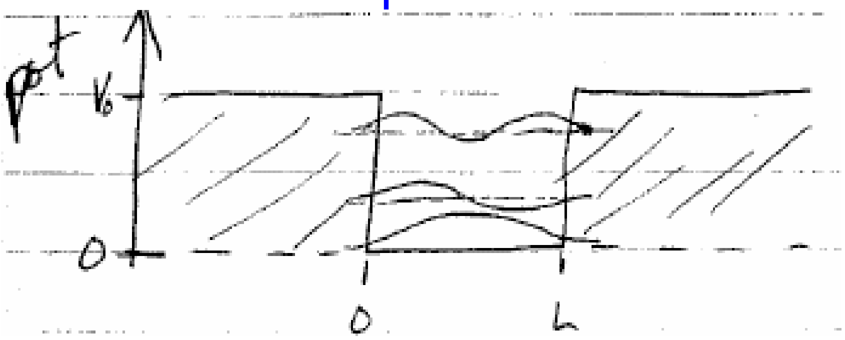
$E_n = p_n^2/2m = (h/2\pi)2\, n^2/2mr^2 = E_n$ from above

$E_n = n^2\hbar^2/2I \Rightarrow$ $E = J_z^2/2I \Rightarrow J_z = n\hbar$

get quantized solution for Energy and angular momentum

This form works for molecular rotation / atom, add dimen.

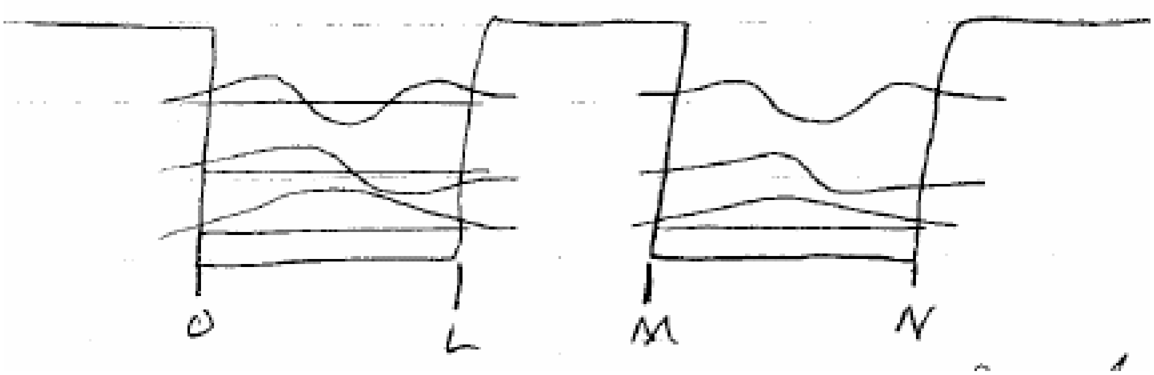
Now consider if particle in box with short side (finite well) (Engel 14.5):



$V = 0 \quad 0 < x < L$
$V = V_0 \quad 0 < x < L$

E_n: Energy no longer ~n^2 (spacing will get closer with n)
ψ: Solution to this more complex but have new property–
$\psi(0)$ & $\psi(L) \neq 0$ -- since $V \neq \infty$
hence w/f non zero inside wall -- from B.C.
(turns out to be exponential $e^{-\beta y}$, i.e. decay function where $y = x - L$, $x > L$;$y = -x$, $x<0$)

Imagine 2 boxes side by side:



as $(L - M) \to 0$ wave functions will overlap, then $\psi^*\psi$ will be non zero in other box and particle will tunnel

Additional property –as $E \to V_0$,
levels must close in together
$E > V_0$ → levels continuous