**Supplement 2: Chemistry 6854**

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**The 2-D particle in-a-box applied to a real molecule**

A good example of the use of the particle-in-the-box analysis we have just gone through is explored in problem 3.27, page 99 of your text. Paraphrased, the problem statement is as below:

*Assume that the simple porphryin is a 2D square with side length L and 18 electrons1 in the conjugated system around the edge. Compute:*

*A)the allowed energy levels*

*B)enumerate degeneracies for several choices of nx and ny*

*C) compute the expected lowest absorption energy in cm-1 predicted given that L=1000 pm*

L

To intuitively grasp the physical character of the



problem, it is important to see that the outside

L

ring of conjugated electrons obeys the famous

4n+2 Huckel rule for aromaticity. In this case,

n=4.1 Moreover, the porphyrin ring is rigid so that

all three conditions for aromaticity are present

Thus, the electrons in the outside ring circulate freely

around the path sketched in Figure 1 just as they do

 in benzene’s pi system, acting as if the potential

in the ring, V=0.

**Figure 1: porphyrin ring**

Next, to simplify the problem we model the ring

as if it were a box of length L on a side, as sketched

in Figure 2, where L is the length of one side of the ring.

 By additionally assuming the box sits on a Cartesian x-y

plane we can assign coordinates to the box corners (0,L) (L,L)

as shown.

Crucial to understanding how to approach the problem now y

is to grasp that the pi electrons are not moving in the classical

fashion around the `basepaths’ of the square. Instead, as with

1 D particle on a wire, the wave function ψ for the any electron x **must obey the boundary conditions set on both the x and**

**y coordinates, assuming the electron’s wave function** (0,0) (L,0)

**Figure 2: 2D Cartesian Box Model for porphyrin**

**now has an independent x and y component to ψ, e.g,**

 **1 ψ(x,y) = X(x)Y(y)**

with the following

**2D boundary conditions:**

**ψ(0,y) = ψ (L,y) =0 for all y= 0🡪L**

**ψ (x,0) = ψ (x,L) = 0 for all x= 0🡪L**

1It is argued below the lone pairs and double bonds to N also form part of resonance so that a total of 26, not 18 electrons participate =>n=6, contrary to the implications of the problem, but consistent with the answer provided for in the text.

The basic Hamiltonian operator version of the Schrodinger equation for an electron in this system has the form :

-ħ2 ∂2  + ∂2 ψ(x,y) + V(x,y) ψ(x,y) = Eϕ(x,y)

**2**

2m ∂x2  ∂y2

As with the 1D box, V(x,y) will be assumed = 0 along the box edge and infinite everywhere else so **2** simplifies to **3**

ħ2 ∂2  + ∂2  ψ(x,y) + Eϕ(x,y) =0

**3**

 2m ∂x2  ∂y2

Then, by substituting 1 for ψ(x,y) we obtain 4 :

ħ2 ∂2  + ∂2  X(x)Y(y) + EX(x)Y(y) =0

**4**

 2m ∂x2  ∂y2

Since X(x) is independent of y and Y(y) is independent of x, **4** can be re-written as below

 ħ2Y(y) d2X(x) + ħ2 X(x) d2Y(y) + EX(x)Y(y) =0

 2m dx2 2m dy2

Dividing through by X(x)Y(y) we get:

ħ2 d2X(x) + ħ2  d2Y(y) + E =0

 2mX(x) dx2 2mY(y) dy2

But since x and y are independent, it requires that:

ħ2 d2X(x) =- Ex

**5a**

 2mX(x) dx2

ħ2  d2Y(y) = -Ey

**5b**

2mY(y) dy2

Where **Ex+Ey = E.**

We have already solved **5a** and **5b** since they are the 1D particle-on-a wire Schrodinger equations. Thus we can write:

**7a**  **Ex** = **(nx π ħ)2  nx =1,2,3…**

 **2mL2**

**7b Ey = (nyπ ħ)2  ny =1,2,3…**

 **2mL2**

**6a X(x) = C1sin(nxπx/L)**

**6b Y(y) = C2sin(nyπy/L)**

**8** **E = Ex + Ey =** (**π ħ/L)2 { nx2 +ny2}**

 **2m**

Equation 8 above answers question A of problem 3.27

To answer question B, we feed in values for (nx, ny) starting at (1,1) and note degeneracies. We do this up to and beyond the state wherein all 26 electrons have an (nx,ny) address.

Answer to Part B

**(nx,ny**) **E (in ( π ħ)2 /2mL2 unitstotal electroncount1**

**(1,1) 2 2**

**(1,2) (2,1) 5 6**

**Occupied states**

**( 2,2) 8 8**

**(3,1) (1,3) 10 12**

**(2,3) (3,2) 13  16**

**(1,4) (4,1) 17 183**

 **(3,3) 18 22**

 **(4,2) (2,4) 20 HOMO2  26**

Lowest absorption energy, ΔE= E(LUMO)-E(HOMO)

 **26 electron limit (Huckel n=6)**

**( 3,4) (4,3) 25 LUMO2**

**(1,5) (5,1) 26 unoccupied states**

 **(2,5) (5,2) 29**

**(4,4) 32**

**(3,5) (5,3) 35**

1We assume spin pairs in each level…e.g. a third quantum number, s= ± ½ is assigned to each (nx, ny) so that each `orbital (nx,ny) can contain a pair of electrons like they do in molecular orbits

2HOMO = highest occupied molecular orbital; LUMO = lowest, unoccupied molecular orbital

3an electron each can be in (1,4) and (4,1) to satisfy `Hund’s rule’.

To answer C, we compute E(LUMO) = E(nx=3,ny=4) and E(HOMO) = E(nx=4 ny=2)

with L= 1000 pm = 10-9m . Electron mass m=9.1\*10-31 kg, **ħ= 1.054\*10-34J\*s and**

 **h= 6.626\*10-34 J\*s, c= 3\*108 m/s.**

**ΔE = E(3,4) – E(4,2) = [25-20]\* ( π ħ)2 /2mL2 =5( π ħ)2 /2mL2**

**ΔE =5\*(π\*1.054\*10-34J)2/2[**9.1\*10-31\*(10-9)2] in J =3.019\*10-19 J

3.019\*10-19 J/hc = 1/λ(m) = 1.515\*106 m-1 =1.515\*104cm-1

 The text says the transition is between (4,2) and (4,3)=>5( π ħ)2 /2mL2 units and quotes15,200 as the computed energy vs. 17,000 cm-1 observed

This neccessarily requires that we include both the lone pairs and the extra two pi systems to yield a total of 18+ 8=26 electrons => 4n+2 has n= 6, which is sensible since the resonance below occurs involving all 26 electrons. (The text seems to imply only 18 electrons are involved, which leads to an incorrect transition energy from (1,4)🡪(3,3) which occurs near 3030 cm-1)



