# PROBLEM SET SOLUTIONS

## CHAPTER 2, Levine, *Quantum Chemistry,* $5^{th}$ Ed.

2.2 (A) $s_1 = s_2 = s$ & $y = e^{sx}$ is a solution of $y'' + p\,y' + q\,y = 0$.
Verify that $y = x\,e^{sx}$ is also a solution.

If $y = x\,e^{sx}$, then $y' = e^{sx} + xs\,e^{sx} = (1 + xs)\,e^{sx}$ &

$y'' = s\,e^{sx} + (1+xs)\,s\,e^{sx} = (2 + xs)\,s\,e^{sx}$

So $y'' + p\,y' + q\,y = (2 + xs)\,s\,e^{sx} + p\,(1 + xs)\,e^{sx} + q\,x\,e^{sx}$

$= (2s + xs^2 + p + psx + qx)\,e^{sx}$

$= [xs^2 + (2 + px)s + (p + qx)]\,e^{sx}$

From the auxiliary eq.: $s^2 + ps + q = 0 \Rightarrow s = -p/2 \pm 0.5\sqrt{(p^2 - 4q)} = s_1, s_2$

If $s_1 = s_2$, then $p^2 - 4q = 0$ & $p = \sqrt{(4q)}$ or $q = p^2/4$. Also $s = -p/2$

So $[xs^2 + (2 + px)s + (p + qx)]\,e^{sx}$

$= [x\,p^2/4 + 2(-p/2) + px\,(-p/2) + (p + x\,p^2/4)]\,e^{-px/2}$

$= [x\,(p^2/4 - p^2/2 + p^2/4) - p + p]\,e^{-px/2}$

$= 0$

2.2 (B) Solve $y'' - 2 y' + y = 0$.

$p = -2, q = 1, y = e^{sx} \Rightarrow s^2 + p s + q = 0$

$\Rightarrow s = 0.5 [-p \pm \sqrt{(p^2 - 4q)}] = 0.5 [ -(-2) \pm \sqrt{(4 - 4)}] = 1$

$y = x e^{sx} = x e^x, y' = e^x + x e^x = (1 + x)e^x$

$y'' = e^x + (1 + x)e^x = (2 + x)e^x$

Verify that $y'' - 2 y' + y = 0$:

$(2 + x)e^x - 2 (1 + x) e^x + x e^x = 2 + x -2 -2x + x = 0$

2.5 Particle with quantum number n in box of length L

(A) Determine the probability of finding the particle in the left quarter of the box.

Region I: $x < 0$, $V = \infty$

Region II: $0 < x < L$, $V = 0$

Region III: $x > L$ , $V = \infty$

In the left quarter of the box: $0 < x < L/4$

Probability of finding the particle in left quarter = $\int_0^{L/4} |\psi_{II}|^2 \, dx$

$= \int_0^{L/4} [\sqrt{(2/L)} \sin (n\pi x/L)]^2 \, dx$

$= (2/L) \int_0^{L/4} [\sin (n\pi x/L)]^2 \, dx$

$= (2/L) [x/2 - (L/4n\pi) \sin (2n\pi x/L)] \Big|_0^{L/4}$ (See (A.2) in Table A.5 in Appendix)

$= (2/L) [L/8 - (L/4n\pi) \sin (2n\pi L/(L4)) - 0 + 0]$

$= 1/4 - (1/(2n\pi)) \sin (n\pi/2)$

Probability depends on the quantum # n.

(B) For what value of n would the probability be a maximum?

| n | Probability |
|---|---|
| 1 | 1/4 - 1/(2π) |
| 2 | 1/4 - 1/(4π) (0) = 1/4 |
| 3 | 1/4 - 1/(6π) (-1) = 1/4 + 1/(6π) MAXIMUM |
| 4 | 1/4 - 1/(8π) (0) = 1/4 |
| 5 | 1/4 - 1/(10π) (1) = 1/4 - 1/(10π) |
| 6 | 1/4 - 1/(12π) (0) = 1/4 |
| 7 | 1/4 - 1/(14π) (-1) = 1/4 + 1/(14π) |
| 8 | 1/4 - 1/(16π) (0) = 1/4 |
| Etc. | Etc. |

(C) As $n \to \infty$, Probability $\to$ 1/4 - (1/∞) (oscillating function) = 1/4

(D) Bohr Correspondence Principal: quantum mechanics approaches classical mechanics in the limit of large quantum number.

2.7 Model the electron in an atom (or molecule) as a particle in a box of diameter of the atom (or molecule).

(A) For an electron in a box of length 1 Angstrom calculate the separation between the lowest two levels.

L = 1 Angstrom, 1 J = 1 kg $m^2/s^2$, 1 Angstrom = $10^{-8}$ cm = $10^{-10}$ m, $10^{-20}$ $m^2$ = 1 $\text{Angstrom}^2$

$\Delta E = E_2 - E_1 = (2^2 - 1^2)\ (h^2/(8mL^2)$

$= 3\ (6.63\text{x}10^{-34}\text{ J s})^2 / [8\ (9.11\text{x}10^{-31}\text{ kg})\ (1.0\text{ Angstrom})^2\ (10^{-8}\text{ cm}/1.0\text{ Angstrom})^2\ (10^{-2}\text{ m}/1\text{ cm})^2]$

$= 1.81\text{x}10^{-17}$ J

(B) Calculate the wavelength of a photon corresponding to a transition between these two levels.

$\Delta E = h\ \nu = h\ c/\lambda \Rightarrow \lambda = h\ c/\ \Delta E = (6.63\text{x}10^{-34}\text{ Js})\ (3.00\text{x}10^{8}\text{ m/s})/ (1.81\text{x}10^{-17}\text{ J})$

$= 10.99\text{x}10^{-9}$m

= 10.99 nm

(C) This wavelength is in the ultraviolet (uv) portion of the electromagnetic spectrum.

2.15 A crude model of pi electrons in a conjugated molecule is as particles in a box of length slightly longer than the conjugated chain. The Pauli Exclusion Principle states that no more than 2 electrons (with opposite spins) can occupy one box level. For butadiene, $CH_2$=CHCH=$CH_2$, take the box length as 7.0 Angstroms & use this model to estimate the wavelength of light absorbed when a pi electron is excited from the highest occupied to the lowest unoccupied box level. (The experimental value is 217 nm.)

There are 2 double bonds, or 4 pi electrons. If only 2 electrons are allowed to occupy one box level, then levels n=1 & n=2 will be occupied (with n=2 being the highest occupied level), & level n=3 will be the lowest unoccupied level. So an electron will be excited from level n=2 to level n=3:

$\Delta E = E_3 - E_2 = (3^2 - 2^2)\ (h^2/(8mL^2)$

$= 5\ (6.63\text{x}10^{-34}\ \text{Js})^2\ /\ [8\ (9.11\text{x}10^{-31}\ \text{kg})\ (7.0\ \text{Angstrom})^2\ 10^{-20}\ \text{m}^2$

$/1\ \text{Angstrom}^2]$

$= 6.15\text{x}10^{-19}\ \text{J}$

$\Delta E = h\ \nu = h\ c\ /\lambda \Rightarrow \lambda = h\ c/\ \Delta E = (6.63\text{x}10^{-34}\ \text{Js})\ (3.00\text{x}10^{8}\ \text{m/s})/$

$(6.15\text{x}10^{-19}\ \text{J})$

$= 3.23\text{x}10^{-7}\ \text{m}\ (10^{9}\text{nm}/1\text{m})$

$= 323\ \text{nm}$