$\boxed{\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}$

$$\left[\left[-\frac{\hbar^2}{2m_e}\sum_{i=1}^{2}\nabla^2\right] - \sum_{i=1}^{2}\frac{2e^2}{4\pi\epsilon_0 r_i} + \sum_{i=1}^{2}\sum_{\substack{j>i\\ j=1}}^{2}\frac{e^2}{4\pi\epsilon_0 r_{ij}}\right]\psi = E\psi$$

$Z=2$ for He

iv) **2 points. Write down the Schöedinger equation for two electrons together, in the He atom.** ***Hint:*** **the equation should contain all the components kinetic and potential energy terms for every electron, without double counting.**

with r_1 distance from e_1^- to the nucleus, r_2 distance from e_2^- to the nucleus and r_{12} the distance between the electrons

$$-\frac{\hbar^2}{2m_e}\left(\sum_{i=1}^{2}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)\right)\psi + \left(\frac{-Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi = E\psi$$

v) **2 points. Write down the Hamiltonian for the electron residing in the Li^{2+} cation.**

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{-Ze^2}{4\pi\varepsilon_0 r}$$

$Z=3$ for Li

The kinetic term of iii), iv), and v) could also be in spherical coordinates:

$$-\frac{\hbar^2}{2m_e}\frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

(other forms are possible depending on how you define θ, ϕ, r; the above is from the book's' definition of θ, ϕ, r and ψ)

$\boxed{\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}$

Li^{2+}: $-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{3e^2}{4\pi\epsilon_0 r}$

Write down the Schöedinger equation for two electrons

a) 3→2 ; 9−4=5
b) 4→3 16−9=7

$v = f\lambda$

$E = \frac{n^2h^2}{8mL^2} = \frac{5h^2}{8mL^2}$; $\frac{E}{h} = f$; $f = \frac{5h}{8mL^2}$

$\lambda = \frac{c}{f} = \frac{8cmL^2}{5h}$

$E = \frac{n^2h^2}{8mL^2} = \frac{(16-9)h^2}{8mL^2} = \frac{7h^2}{8mL^2}$; $\frac{E}{h} = f$, $f = \frac{7h}{8mL^2}$

$\lambda = \frac{c}{f} = \frac{8cmL^2}{7h}$

iv) 2 points. Determine the energy, frequency, and wave-length of light that these molecules would absorb upon excitation of an electron from the highest occupied state to the lowest unoccupied.

vary depending on L

1,3 butadiene

$E_n = \frac{n^2h^2}{8mL^2}$

$\nu = \frac{5h}{8mL^2}$ or simplified answer

$\lambda = \frac{8cmL^2}{5h}$

$\Delta E = \frac{5h^2}{8mL^2}$

n=3
n=2
n=1

$\Delta E = \frac{h^2}{8mL^2}[3^2 - 2^2]$

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

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

1,3,5 hexatriene

$\Delta E = \frac{h^2}{8mL^2}[4^2 - 3^2]$

$\Delta E = h\nu = \frac{hc}{\lambda} \Rightarrow \nu = \frac{\Delta E}{h}, \lambda = \frac{hc}{\Delta E}$

$\nu =$

$\nu = \frac{7h}{8mL^2}$

$\lambda = \frac{8cmL^2}{7h}$

$\Delta E = 7h^2/8mL^2$

v) 2 points. If the π-conjugated molecule would be longer than 1,3,5,-hexatriene, would it absorb light of smaller or larger wavelength than does 1,3,5,-hexatriene? Why?

$E_n = \frac{n^2h^2}{8mL^2}$ ⓐ $\Rightarrow \boxed{\Delta E = \frac{h^2}{8mL^2}((n+1)^2 - n^2) = \frac{h^2}{8mL^2}(2n+1)}$ ⓑ where n = # of levels occupied

for 1,3,5 hexatriene L = 3DB + 2SB then if 4DB + 3SB is the new length then 8 pi electrons are in the molecule and n=4 the two equations

$\Delta E_a > \Delta E_b$

$\lambda_a < \lambda_b$

$\nu_a > \nu_b$

this is because the box grows and the # of electrons grow but 2n+1 grows slower than L^2 so therefore the energy needed to excite an electron decreases as the energy levels increase

$\Delta E_a = \frac{7h^2}{8m(3DB+2SB)^2}$ n=3 L=3DB+2SB

$\Delta E_b = \frac{h^2 9}{8m(4DB+2SB)^2}$ n=4 L=4DB+3SB

now let DB = 1.33Å SB = 1.54Å

$\Delta E_a > \Delta E_b$

$\Delta E_a = \frac{7h^2}{8m(7.07\times10^{-10}m)^2}$ $\Delta E_b = \frac{h^2 9}{8m(9.94\times10^{-10}m)^2}$

2) Hamiltonian and Schöedinger equation.

i) 2 points. Write down the Schöedinger equation for a single electron traveling in one dimension and in the absence of any potential.

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial x^2} = E\psi \quad \text{as} \quad V(x) = 0$$

$\frac{\hbar^2}{2me}\frac{\partial^2\psi}{\partial x^2} = E\psi$

ii) 2 points. Write down the Schöedinger equation for a single electron traveling in one dimension and in the presence of the potential V(x) = ½kx².

$\left[-\frac{\hbar^2}{2me}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]\psi = E\psi$

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial x^2} + \frac{1}{2}kx^2\psi = E\psi \quad \text{as} \quad V(x) = \frac{1}{2}kx^2$$

iii) 2 points. Write down the Schöedinger equation for a single electron traveling in three dimensions and in the presence of the potential V(x,y,z).

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

$\boxed{\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}$

$\left[\frac{-\hbar^2}{2me}\nabla^2 + V(x,y,z)\right]\psi = E\psi$

Homework assignment 6 CHEM 20A your name: KEY

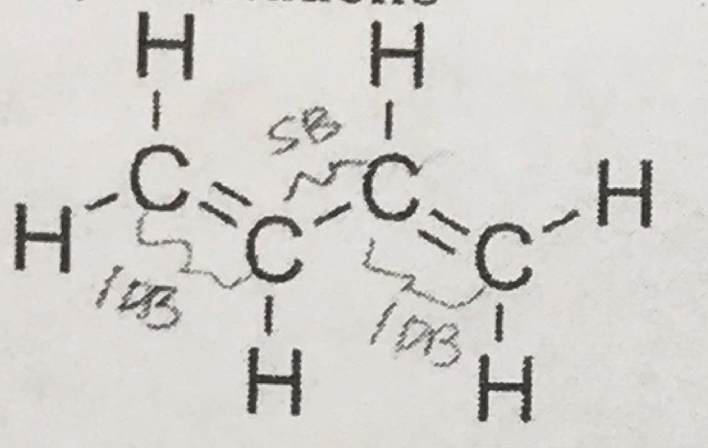
Instructor Prof. Anastassia Alexandrova **UCLA ID:**

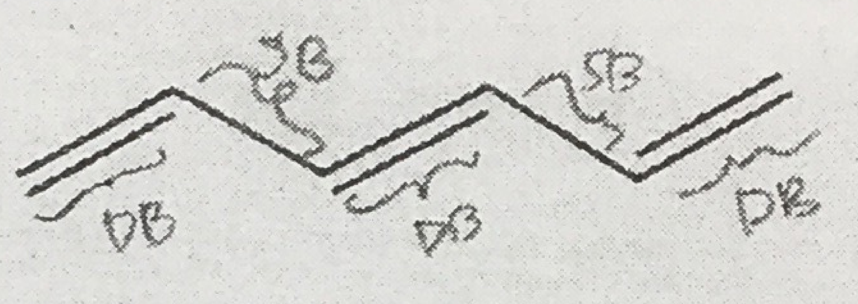
Fall 2016

Due: October 31 by 1 pm (print and bring to the TAs)

1) <u>Particle in 1D box model – I.</u> Consider two π-conjugated hydrocarbons:

1,3-butadene and 1,3,5,-hexatriene





i) 2 points. For each case, estimate the length L of the 1-D box that could be used to describe the behavior of delocalized π-electrons in these systems.

1,3 butadene: 2 × double bond length + 1 × single bond length = $L_{1,3 \text{ butadene}}$

1,3,5 - hexatrene = 3 double bond length + 2 × single bond length = $L_{1,3,5 \text{ hexatrene}}$

ii) 2 points. How many π-electrons are in each molecule? What is the quantum number n of the highest occupied state?

1,3- butadene

4 pi electrons = 2 from each doubl bond

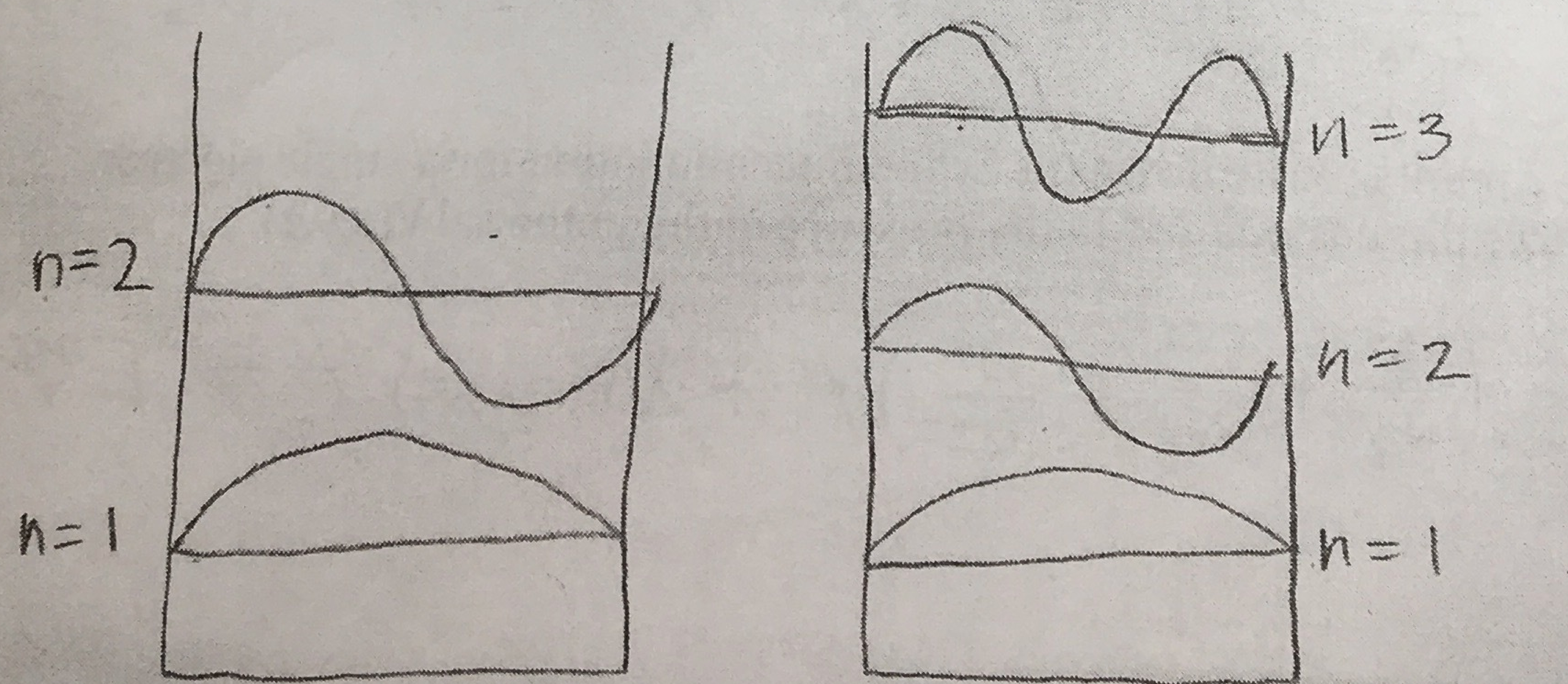
$n = \frac{4}{2} = 2$

1,3,5 hexatriene

6 pi electrons = 2 from each DB

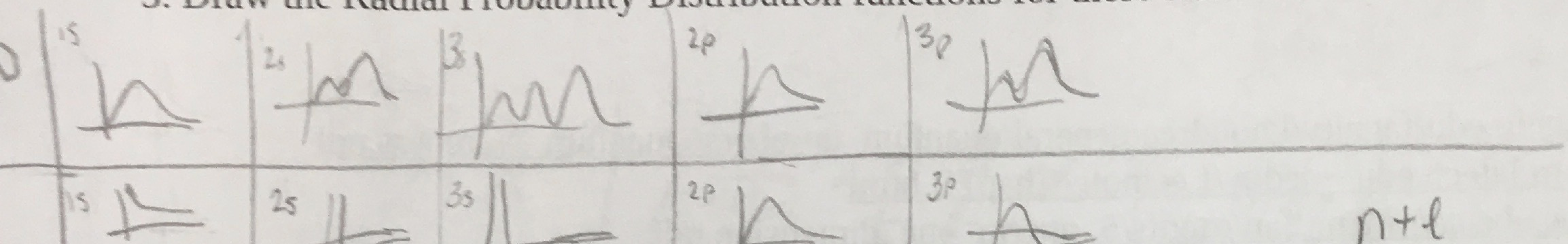
$n = \frac{6}{2} = 3$ highest occupied

iii) 2 points. For each case, draw the box, and sketch the wavefunctions for each energy level in this box, up to the highest occupied state.



n-l-1
2-1

5. Draw the Radial Probability Distribution functions for these states and the Radial Wavefunction



n+l

6. For each of the following pairs of orbitals, indicate which orbital is higher in energy:

a) 1s, 2s b) 2p, 3p c) 3d xy , 3d yz d) 4s, 3d e) 5s, 4f

equal 4, 6 5, 12

degeneate!

$e^- - 2$

7.What group does the element belong to whose X 2+ ion has 1 unpaired electron in its ground state? IIIA, IVA or IB? IIIA X^{2+}

s, d p

8.Indicate which of the elements are s-block, p-block, alkali metals, etc. as well as metal or nonmetal.

a) Sc b) P c) Pu d) Fr e) Ni +2 f) As

d metal p non metal f, metal S alkali d metal P semi

9. Give full and abbreviated electron configurations for: a) Br b) Ag c) Fe d) S 2- e) Ni 2+

Br = [Ar] $4s^2 3d^{10} 3p^5$ | Ag = [Kr] $4d^{10} 5s^1$ | Fe = [Ar] $4s^2 3d^6$ | S^{2-} = [Ar] = [Ne] $3s^2 3p^6$ | Ni^{2+} = [Fe] = [Ar] $4s^2 3d^4$

10. Particle in a Box Model problems:

Photon Energy From a Transition in an Infinite Square Well Potential

Problem 5.9, page 224

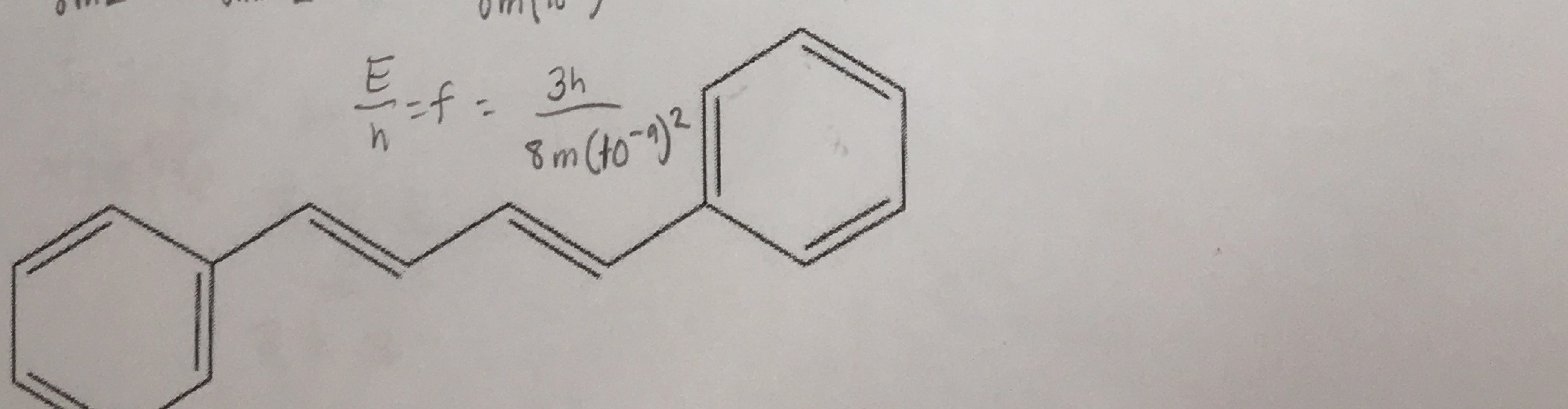
A proton is confined in an infinite square well of width 10 fm. (The nuclear potential that binds protons and neutrons in the nucleus of an atom is often approximated by an infinite square well potential.)

- Calculate the energy and wavelength of the photon emitted when the proton undergoes a transition from the first excited state ($n = 2$) to the ground state ($n = 1$).
- In what region of the electromagnetic spectrum does this wavelength belong?

$hf = E = \frac{n^2h^2}{8mL^2} = \frac{h^2}{8mL^2}[4-1] = \frac{3h^2}{8m(10^{-9})^2}$

Do the same for the electron in *1,4-diphenyl-1,3-butadiene* but for n=10 as the first excited state and then n=9 the ground state :

$\frac{E}{h} = f = \frac{3h}{8m(10^{-9})^2}$



$E = \frac{n^2h^2}{8mL^2} = \frac{h^2}{8mL^2}[100-81] = \frac{19h^2}{8mL^2}$

Roey Paz-Priel

$\Psi(x_i, y_i, z_i, r_i, r_{ij}, \phi)$

Practice Questions :

1. Write a Hamiltonian for the Atoms B, N, H, and Li

$\nabla^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$

B: $\left[\frac{-\hbar^2}{2m_e}\sum_{i=1}^{5}\nabla^2\right] + \sum_{i=1}^{5}\frac{5e^2}{4\pi\epsilon_0 r_i} - \sum_{i=1}^{5}\sum_{j=1, j>i}^{5}\frac{e^2}{4\pi\epsilon_0 r_{ij}}$

H: $\left[\frac{-\hbar^2}{2m_e}\sum_{i=1}^{1}\nabla^2\right] + \sum_{i=1}^{1}\frac{e^2}{4\pi\epsilon_0 r_i} - \sum_{i=1}^{1}\sum_{j=1, j>i}^{1}\frac{e^2}{4\pi\epsilon_0 r_{ij}}$

N: $\left[\frac{-\hbar^2}{2m_e}\sum_{i=1}^{7}\nabla^2\right] + \sum_{i=1}^{7}\frac{7e^2}{4\pi\epsilon_0 r_i} - \sum_{i=1}^{7}\sum_{j=1, j>i}^{7}\frac{e^2}{4\pi\epsilon_0 r_{ij}}$

Li: $\left[\frac{-\hbar^2}{2m_e}\sum_{i=1}^{3}\nabla^2\right] + \sum_{i=1}^{3}\frac{3e^2}{4\pi\epsilon_0 r_i} - \sum_{i=1}^{3}\sum_{j=1, j>i}^{3}\frac{e^2}{4\pi\epsilon_0 r_{ij}}$

2. Write the Hamiltonian for Atoms B, H, N and Li with them in the hydrogen like state

B^{4+}, H, N^{6+}, Li^{2+}

$\nabla^2 = \frac{\partial^2}{\partial x^2} + \ldots$

B: $\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{5e^2}{4\pi\epsilon_0 r}\right]$

N: $\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{7e^2}{4\pi\epsilon_0 r}\right]$

H: $\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right]$

Li: $\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{3e^2}{4\pi\epsilon_0 r}\right]$

3. Draw orbital diagrams for the valence electrons for each of the following. Which would exhibit paramagnetism?

a) C b) O c) N 3- d) Mn 2+ e) Sc 3+

$1s^2 2s^2 2p^2$ $1s^2 2s^2 2p^4$ $1s^2 2s^2 2p^6$ dia

para para dia para

$[Ar]4s^2 3d^5$ ↿ ↿ ↿ ↿ ↿

C: 2p ↿ ↿ –
2s ⥮
1s ⥮

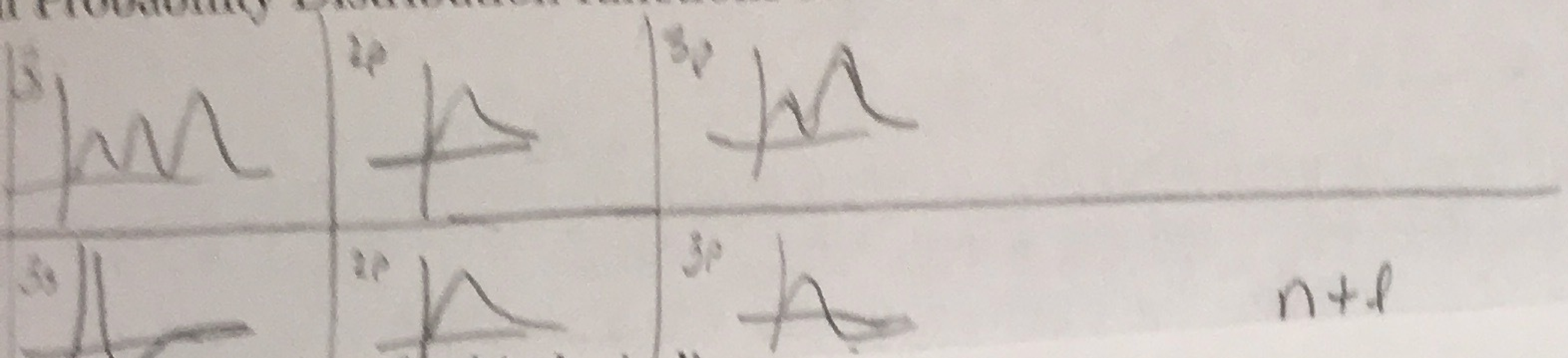
Mn^{2+} ↿ ⥮ ⥮ ⥮
⥮
23
⥮ ⥮ ⥮
$3d^3$
⥮
⥮

O: ⥮ ↿ ↿
⥮
⥮

N^{3-}: ⥮ ⥮ ⥮
⥮

Sc 3^+: Ar = ...$3p^6$
Ar [4s] $3d^1$ ⥮ ⥮ ⥮

l Probability Distribution functions for these states and the Radial Wavefunction



$n+l$

following pairs of orbitals ...

Rocy Paz-Pinel

$\Psi(x_i, y_i, z_i, r_i, r_{ij}, \phi)$

Practice Questions :

$$\boxed{\nabla^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}}$$

1. Write a Hamiltonian for the Atoms B, N, H, and Li

$$B: \left[\left[\frac{-\hbar^2}{2m_e}\sum_{i=1}^{5}\nabla^2\right] + \sum_{i=1}^{5}\frac{5e^2}{4\pi\varepsilon_0 r_i} - \sum_{i=1}^{5}\sum_{\substack{j=1\\ j>i}}^{5}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}\right] \qquad H: \left[\left[\frac{-\hbar^2}{2m_e}\sum_{i=1}\nabla^2\right] + \sum_{i=1}\frac{e^2}{4\pi\varepsilon_0 r_i} - \sum_{i=1}\sum_{\substack{j=1\\ j>1}}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}\right]$$

$$N: \left[\left[\frac{-\hbar^2}{2m_e}\sum_{i=1}^{7}\nabla^2\right] + \sum_{i=1}^{7}\frac{7e^2}{4\pi\varepsilon_0 r_i} - \sum_{i=1}^{7}\sum_{\substack{j=1\\ j>i}}^{7}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}\right] \qquad Li: \left[\left[\frac{-\hbar^2}{2m_e}\sum_{i=1}^{3}\nabla^2\right] + \sum_{i=1}^{3}\frac{3e^2}{4\pi\varepsilon_0 r_i} - \sum_{i=1}^{3}\sum_{\substack{j=1\\ j>1}}^{3}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}\right]$$

2. Write the Hamiltonian for Atoms B, H, N and Li with them in the hydrogen like state $\boxed{\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}$

$B^{4+}, H, N^{6+}, Li^{2+}$

$$B: \left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{5e^2}{4\pi\varepsilon_0 r}\right] \qquad N: \left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{7e^2}{4\pi\varepsilon_0 r}\right]$$

$$H: \left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right] \qquad Li: \left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{3e^2}{4\pi\varepsilon_0 r}\right]$$

3.Draw orbital diagrams for the valence electrons for each of the following. Which would exhibit paramagnetism?

a) C b) O c) N 3- d) Mn 2+ e) Sc 3+

$1s^2 2s^2 2p^2$ $\quad 1s^2 2s^2 2p^4$ $\quad 1s^2 2s^2 2p^6$ $\quad$ para $\quad$ dia

para para dia

$[Ar]4s^2 3d^5$ ↿ ↿ ↿ ↿ ↿

C: 2p ↿ ↿ –
2s ⇅
1s ⇅

Mn^{2+} ⇅ ⇅ ⇅
⇅
3d
⇅ ⇅ ⇅
⇅
⇅

O: ⇅ ↿ ↿
⇅
⇅

Sc^{3+}: Ar = ...$3p^6$

Ar [4s] $3d^1$ ⇅ ⇅ ⇅
⇅
⇅ ⇅ ⇅
⇅

N^{3-}: ⇅ ⇅ ⇅
⇅
⇅