CHM 3400 – Problem Set 10

Due date: Monday, April 5th (by 11:59pm). Please turn in your homework by sending it to me at my FIU email address joensj@fiu.edu Indicate in your email that you are sending me your Homework 10 solutions.

NOTE: Exam 3 is in class on Friday, April 9th. It will cover material from Chapter 6 (sections F – I); Chapter 7 (all); Chapter 8 (all). Note you are only responsible for material from these chapters that was covered in class.

Do all of the following problems. Show your work.

1) Hydrogen-like ions (ions with a nucleus and a single electron) have energy levels given by a modified form of the Rydberg equation

$$\tilde{E} = -\frac{R_\infty Z^2}{n^2} \qquad Z = \text{charge of nucleus}, \quad n = 1, 2, 3, \ldots \qquad (1.1)$$

In eq 1.1 we have assumed that the mass of the nucleus is sufficiently large that we can use $R_\infty = 109737.\ cm^{-1}$ for the Rydberg constant instead of the value for R found using the reduced mass for the electron+nucleus.

a) Find the energy (in cm^{-1}) and wavelength (in nm) for the $n = 5 \rightarrow n = 4$ light emission for the He^+, Li^{2+}, C^{5+}, and Ne^{9+} ions. For each of your answers indicate the region of the electromagnetic spectrum where the light emission occurs. Those regions are

UV (ultraviolet)	1 – 400 nm
visible	400 – 700 nm
IR (infrared)	700 – 10000 nm

b) Recall that the light emissions for hydrogen atoms are classified by the value for the final state quantum number. So, for example, we have $n_f = 1$ transitions (Lyman), $n_f = 2$ transitions (Balmer), and so forth.

Give the value(s) of n_f that correspond to light emission from a He^+ ion that can appear in the visible region of the spectrum. (HINT: The longest wavelength of light will be from $n_i = n_f + 1$, and the shortest wavelength will be from $n_i = \infty$).

2) An electron configuration gives the number of electrons present in every electron containing orbital of an atom or ion. The most important electron configuration is that for the ground (lowest energy) state of the atom or ion.

a) Give the electron configuration predicted for the following atoms. Give your configurations both as the complete configuration and in the shorthand notation [noble gas] + additional electrons.

i C (carbon)
ii S (sulfur)
iii Co (cobalt)

b) For each of your electron configurations in a, give the total number of unpaired electron spins for the ground state of the atom.

3) If electrons had a spin quantum number s = 0, would you expect a periodic table of the elements to look similar to the one that actually exists? Why or why not?

4) The energies for the first several electronic states of a carbon atom are given below

state	energy (cm^{-1})	state	energy (cm^{-1})
^3P	0.	$^3P'$	60350.
^1D	10190.	^1P	61980.
^1S	21650.	^3D	64100.
^5S	33740.		

a) List all of the allowed transitions that can occur among the electronic states of carbon given above. Label each allowed transition by the lower energy state followed by the higher enegy state (for example, a transition between the first two states above would be labeled (^3P, ^1D). For each allowed transition given the energy (in cm^{-1}) and wavelength (in nm) where the transition would occur.

Recall the selection rules for an allowed atomic transition are:

$\Delta S = 0$
$\Delta L = 0, \pm 1$

Also remember for a transition to be allowed it must satisfy all of the selection rules that apply.

b) Because of interaction between the spin angular momentum and orbital angular momentum, there are small differences in energy due to a new quantum number J (which we have ignored above).

Find all of the possible values of J for the ^1D, ^1S, and ^3D states.

Recall possible values for J are highest $J = | L + S |$
lowest $J = | L – S |$

Any value of J between that falls between the highest and lowest value and differs from them by integer steps is also a possible value for J.

Solutions.

1) a) We want transitions where $n_i = 5$ and $n_f = 4$. Based on eq 2.2 of problem set 9, we can say the energies at which these transitions occur are

$\tilde{E}(Z,n_i = 5,n_f=4) = R_\infty Z^2 [(1/4)^2 – (1/5)^2]$ Since $R\infty = 109737\ cm^{-1}$, substituting gives

$\tilde{E}(Z,n_i = 5,n_f=4) = Z^2 (2469.08\ cm^{-1})$

Ion	Z	$\tilde{E}(Z,n_i = 5,n_f=4)$ (cm^{-1})	λ (nm)
He^+	2	9876.	1012.
Li^{2+}	3	22222.	450.0
C^{5+}	6	88887.	112.5
Ne^{9+}	10	246908.	40.5

b) The visible region is the region from 400 – 700 nm (or $\tilde{E}$ = 14280. – 25000. cm^{-1})

For He^+ (Z = 2), and for a particular value for n_f, the range of energies will be (using the same formula as in part a, and Z = 2).

lowest energy (when $n_i = n_f + 1$) = $(438948\ cm^{-1}) [(1/n_f)^2 – (1/(n_f+1))^2]$

highest energy (when $n_i = \infty$) = $(438948\ cm^{-1}) [(1/n_f)^2]$

We can make the following table

n_f	lowest energy (cm^{-1})	highest energy (cm^{-1})	wavelength region (nm)	
1	329211.	438948.	22.78 – 30.38	UV
2	60965.	109737.	91.13 – 164.0	UV
3	21337.	48772.	205.0 – 468.7	UV + visible
4	9876.	27434.	364.5 – 1013.	UV + visible + IR
5	5365.	17558.	569.5 – 1864.	visible + IR
6	3235.	12173.	820.1 – 3091.	IR

There are transitions with n_f = 3, 4, and 5 that overlap the visible region of the spectrum.

2) C $1s^2 2s^2 2p^2 = [He] 2s^2 2p^2$

↑ ↑ 2p orbitals

So 2 unpaired electron spins.

S $1s^2 2s^2 2p^6 3s^2 3p^4 = [Ne] 3s^2 3p^4$

↑↓ ↑ ↑ 3p orbitals

So 2 unpaired electron spins.

Co $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ = [Ar] $4s^2 3p^7$

↑↓	↑↓	↑	↑	↑	3d orbitals

So 3 unpaired electron spins.

3) Because electrons have s = ½, they are fermions, and so must satisfy the Pauli exclusion principle. That is the reason for the "block structure" of the periodic table – it reflects the filling of particular orbitals by the Aufbau and Pauli principles..

If electrons had s = 0 they would be bosons. The ground state for any atom would be the state with all the electrons in the 1s orbital. So carbon, for example, would be $1s^6$ for its ground state. While it is difficult (for me anyway) to spell out all the implications of this, it would mean that the properties of the elements would vary in a continuous manner (assuming there were still atoms). It would also do away with covalent bonding, as there would be no reason for a bond to be formed by a pair of electrons, as opposed to one, or seven electrons, or any other number of electrons.

One thing that is clear is that there would be no chemistry as we know it – but then, likely no chemists as well.

See, for example: https://www.forbes.com/sites/chadorzel/2015/08/25/how-quantum-pachinko-makes-solid-matter-possible/?sh=d1cc776bf1af

4) a) The transitions that satisfy the selection rules are as follows:

transition	Energy difference (cm^{-1})	Wavelength (nm)
(^3P,$^3P'$)	60350.	165.7
(^3P,^3D)	64100.	156.0
(^1D,^1P)	51790.	193.1
(^1S,^1P)	40330.	248.0
($^3P'$,^3D)	3750.	2667.

It is interesting that none of these transitions occur in the visible region of the spectrum.

b) Using the rule for finding the possible values for J, we get

^1D L = 2, S = 0 so J = 2

^1S L = 0, S = 0 so J = 0

^3D L = 2, S = 1 so J = 3, 2, 1

Note that when there are different values of J, that means there are different states that have similar, but not identical, energy. This is why we normally do not worry about the value for J.