Chem 131	Name
Exam 1, Ch 8-10.6	September 11, 2019
100 Points	

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

Part 0: Warmup. 4 points each

- 1. How many unpaired electrons are present in an oxygen atom?
 - a. 0 b. 1 c. 2 d. 3
- 2. Which of the following photons has the **highest** energy?
 - a. $v = 7.5 \times 10^{14} \text{ s}^{-1}$ b. $\lambda = 560 \text{ nm}$ c. $\lambda = 242 \text{ nm}$ d. $v = 3.3 \times 10^{14} \text{ s}^{-1}$ Answer _____
- 3. Arrange the following in terms of increasing electron affinity: K, F, P, O
 - a.
 K<F<P<O</td>

 b.
 K<P<O<F</td>

 c.
 F<O<P<K</td>

 d.
 P<K<O<F</td>
- 4. Which of the following orbitals <u>cannot exist</u> according to modern quantum theory: 2s, 3p, 2d, 3f, 5p, 6p? Briefly justify your reasoning.

For an orbital to be valid, ℓ must be between 0 and n-1. If we recall that for $\ell = 0$ for s orbitals, $\ell = 1$ for p orbitals, $\ell = 2$ for d orbitals, and $\ell = 3$ for f orbitals then we can make some decisions. From the list above, the 2d and 3f orbitals have $n = \ell$, which violates our rule for valid quantum numbers, therefore they do not exist.

5. We can write resonance structures for ozone as shown below. What does the "↔" mean? Why do we sometimes need to invoke resonance?

The concept of resonance and the double headed arrow we use is an attempt to account for the fact that we cannot, by following our rules, draw an accurate Lewis structure for ozone (and many other compounds). The double headed arrow reminds us that <u>neither structure is accurate</u> and that the true structure for <u>the compound is an average (or hybrid) of the structures</u> drawn and that the compound <u>does not flip between the structures shown.</u>

Part I: Complete all of problems 6-9

6. Calculate the wavelength, in nanometers, of a photon emitted when an electron in a hydrogen atom undergoes a transition from n = 5 to n = 2. (10 points)

$$\Delta E = R_{\rm H} \left(\frac{1}{n_{\rm f}^2} - \frac{1}{n_{\rm i}^2}\right) \text{ or } \Delta E = 2.179 \text{ x } 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{5^2}\right)$$

$$\Delta E = 2.179 \text{ x } 10^{-18} \text{ J} \left(\frac{1}{4} - \frac{1}{25}\right) = 4.5759 \text{ x } 10^{-19} \text{ J}$$

$$E = \frac{\text{hc}}{\lambda} \text{ so } \lambda = \frac{\text{hc}}{E}$$

$$\lambda = \frac{(6.626 \text{ x } 10^{-34} \text{ J s})(2.998 \text{ x } 10^8 \text{ ms}^{-4})}{4.576 \text{ x } 10^{-19} \text{ J}} = 4.341 \text{ x } 10^{-7} \text{ m x } \frac{10^9 \text{ nm}}{1 \text{ m}} = 434 \text{ nm}$$

Answer	_434 nm	
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7. Write the ground state electron configurations for the following species. You may choose to use noble gas notation if you wish. Are all of the electrons in the valence shell of each atom paired? (12 points total, 4 points each)

	1 .
a.	selenium

 $[Ar]4s^23d^{10}4p^4$ 2 unpaired electrons

b. silicon

[Ne]3s²3p² 2 unpaired electrons

c. nickel (II) ion

[Ar]3d⁸ 2 unpaired electrons (note that the 4s electrons are lost in forming Ni²⁺).

8. Each drawing represents a type of an atomic orbital. Give the letter designation of the orbital, its value of ℓ , and specify the number of angular nodes (nodal surfaces). Also provide the minimum necessary value of n for an orbital of each type to exist. (12 points)

orbital diagram			
ℓ value	2	1	0
letter designation	d	р	S
# of angular nodes	2	1	0
minimum value of n for this orbital type	3	2	1

9. Chromium is one of the transition elements that does not follow the predicted trend for filling orbitals (the aufbau principle). Use spectroscopic notation to show (1) the predicted electron configuration following our "standard" trend and (2) predict the actual electron configuration. In 2-3 sentences, explain why the actual configuration is more stable. (10 points)

Configuration following aufbau principle:	[Ar]4s ² 3d ⁴
Actual electron configuration:	_[Ar]4s ¹ 3d ⁵

This "anomalous" electron configuration arises from stability that is present in half-filled d orbitals, as opposed to d-orbitals with more paired electrons. By adopting the $4s^13d^5$ configuration, both the 4s and 3d orbitals are half-filled and all electrons in the orbitals are unpaired.

Part II. Answer three (3) of problems 10-13. Clearly mark the problem you do not want graded. 12 points each.

10. Answer the following in no more than four sentences each:

a. Explain the trend in atom/ion size: $O^{2-} > F^- > Ne > Na^+ > Mg^{2+}$

For the collection of species that are being compared in this question, we are comparing anions, cations and neutral atoms all with the same number of electrons and same electron configuration $(1s^22s^22p^6)$, but with varying numbers of protons. As the number of protons varies while the number of electrons stays the same, the effective nuclear charge varies as well. So, the species with the smallest number of protons (O^{2-}) has the electrons which experience the smallest effective nuclear charge and therefore can get farther from the nucleus.

b. Consider the plot to the right, that shows the trend in atomic radius moving from potassium (atomic number 19) to bromine (atomic number 35). Why is there a decrease in size as you move from left to right across the plot? Why is the decrease much more shallow across the transition metals?



Moving from left to right indicates an increase in atomic number (# of protons) for the atom. For neutral atoms, this corresponds to an increase in electrons as well. This increase in protons causes an increase in nuclear charge and an enhanced attractive interaction between the electrons and the nucleus, causing a decrease in atom size. However, as we move from the s-block to the d-block and p-block, the electrons in the d and p orbitals are less effective at shielding the nuclear charge than s electrons so the trend becomes less pronounced in the transition metals and p-block nonmetals.

11. Complete the table **for three (3)** of the species below, indicating resonances structures, if necessary. If more than one structure is possible, indicate the structure you expect to be most representative of the actual structure of the species.

Species	Lewis Structure	Species	Lewis Structure
OCl2	;ä1−ä−ä:	NO ₂ ¯	[:ö–n=ö]- ↔[ö=n–ö:]-
HCN	H−C≡N:	CH ₂ O	:О: Н—С—Н

12. The Lewis structure for nitrous oxide could be drawn in several ways, four of which are shown below. Each of these structures utilize all of the valence electrons and all atoms have filled octets. Which one of these structures is most likely to be representative of the real structure of nitrous oxide? Justify your answer.

There are a couple of places where we may start. One of the guidelines for drawing Lewis structures is to put the least electronegative atom as the central atom. Since N is less electronegative than O, we expect nitrogen to be the central atom, which rules out the second and fourth structures.

An evaluation of formal charges gets us to the same point, and takes us the rest of the way. Formal charges have been assigned to each of the atoms in the structures above. Recall that preferred structures are those who have formal charges closest to zero for the atoms, and for whom positive formal charges are on less electronegative atoms and negative formal charges are on more electronegative atoms. After omitting the second and fourth structures, we must choose between structures I and III. An examination of the formal charges shows that structure III places the negative formal charge on the most electronegative atom, which is preferred. Therefore, we expect structure III to be most representative of the true structure of N_2O .

13. Consider the following diagrams of the same orbital. Which orbital do the pictures represent? Provide the values for n, ℓ , and m_{ℓ} for the orbital and *justify your reasoning*.





90% Probability Density Plot (dark = high probablility)

To assign values for n and ℓ , we need to look for nodes in the orbitals. From the probability plot on the right, it appears that there are no angular nodes in this orbital. For this to be true, the value of ℓ must be 0, resulting in an <u>s</u> orbital. From the plots above, we observe 2 radial nodes in the orbital, as evidenced by the two places where the Distribution Function is zero (above right) and the two spheres of white in the Probability Density plot (above left). Therefore n - ℓ - 1 must equal 2. If ℓ = 0, then the value of n must be <u>3</u>. With n = 3, and ℓ = 0, we must have a <u>3s</u> orbital. The third quantum number, m₁ depends on the value of ℓ (m₁ ranges from - ℓ through zero to + ℓ). Since ℓ =0 for this orbital, the only possible value of m₁ is zero. So,

$$n = 3$$
$$\ell = 0$$
$$m_{\ell} = 0$$

$h = 6.626 \text{ x } 10^{-34} \text{ J s}$	$c = 2.998 \text{ x } 10^8 \text{ ms}^{-1}$	$E = hv = \frac{hc}{\lambda}$	$\Delta E \bullet \Delta(mv) > h$
$R_{\rm H} = 2.179 \text{ x } 10^{-18} \text{ J/atom}$	$E = -\frac{R_H}{n^2}$	$\Delta E = R_{\rm H} \left(\frac{1}{n_{\rm f}^2} - \frac{1}{n_{\rm i}^2} \right)$	$H\psi = E\psi$

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