Problem Set #10 CHEM101A: General College Chemistry

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What are the possible values of m_{ℓ} and m_s for a 4f electron?

23.1 Solution

The value of ℓ is 3. This means that the values of m_{ℓ} are $\left[-3,-2,-1,0,1,2,3\right]$. The electron can have either positive or negative spin, so the possible values of m_s are $\left[+\frac{1}{2},-\frac{1}{2}\right]$.

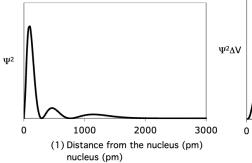
24 Topic E Problem 24

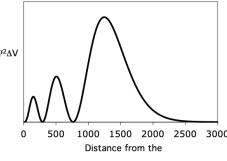
Explain why it is impossible for an orbital to have n=3 and $\ell=3$. (Hint: think about what these numbers are telling you about nodes.)

24.1 Solution

The value of n is 0 and it is 1 more than the number of nodes. ℓ describes the number of angular nodes. If the value of n is 3, there are n-1=2 total nodes. If the value of ℓ is 3, there are 3 angular nodes. The prior two statements contradict each other.

The two graphs below show the electron density and radial probability for an atomic orbital. (Both graphs show the same orbital.) Use the graphs to answer questions a through e below.

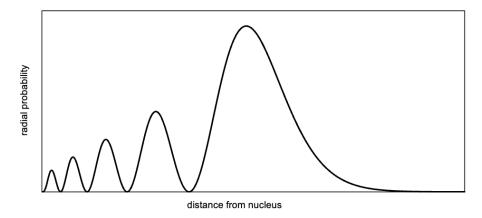




- a) Which graph is the electron density plot?
- b) What is the most probable distance between the electron and the nucleus for this orbital? (You will need to estimate it from one of the graphs.)
- c) How many radial nodes does this orbital have? How can you tell?
- d) Does this orbital have any angular nodes? How can you tell?
- e) If n = 4 for this orbital, what orbital is it?

- a/ The electron density plot is the one on the left (Ψ^2) .
- b/ The most probably distance from the center would be about 1250 pm.
- c/ The electron density plot goes to zero at two points, so there would be two radial nodes.
- d/ Since the graph of the electron density is zero at the origin, this means that there are radial nodes.
- e/ 4p

The radial probability plot below is for a p orbital. What type of p orbital is it (2p, 3p, 4p, etc.)? Explain your reasoning.

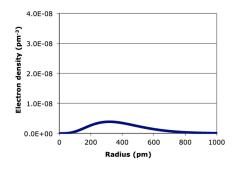


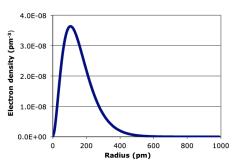
26.1 Solution

It's a p orbital, so $\ell=1$ and there is one angular node. There are four points at which the radial probability goes to zero, meaning four (4) radial nodes. Adding the number of radial and angular nodes together, we get 4+1=5. Add one to the number of total nodes to get the value of n to get n=1+5=6. The answer is 6p.

One of the electron density graphs below is for a 2p orbital and one is for a 3d orbital.

- a) Which one is which? Explain your answer.
- b) Explain why both of these graphs show just one "hump" (i.e. there is no place where the graph goes to zero).
- c) Explain why both of these graphs start at the origin.
- d) Give two examples of orbitals whose electron density plots would not start at the origin, and explain your answer.





- a/ The graph on the left is the 3d orbital graph. The 2p graph would be generally further in due to having a smaller orbital radius.
- b/ Both the 2p and 3d orbitals have their highest possible number of angular orbitals. For the 2p, $\ell=1$ and n=2 allows for only 1 total nodes, meaning no radial orbitals. For the 3d, $\ell=2$ and n=3 allows for only 2 total nodes, meaning no radial orbitals.
- $\ensuremath{\mathrm{c}}/$ Both have angular nodes as previously stated, so both start at zero at the origin.
- d/1s and 5s

A partial energy diagram for lithium (Li) is shown below. Answer questions a through d, using the information on this diagram and your understanding of emission spectra. This is a review problem.

ionized state	 0 kJ/mol
4p	 -83 kJ/mol
3p	 -150 kJ/mol
2p	 -342 kJ/mol
2s	 -520 kJ/mol

- a) Calculate ΔE for the 2p \rightarrow 2s transition in lithium, in kJ/mol.
- b) Calculate the wavelength of light emitted during the 2p \rightarrow 2s transition, in nm.
- c) When the outer electron undergoes a $5p \rightarrow 2s$ transition, the atom emits 256nm light. Calculate the energy of the 5p orbital, in kJ/mol.

28.1 Solution (a)

Calculate the difference.

$$\Delta E = E_f - E_i = -520 \,\text{kJ/mol} - (-342 \,\text{kJ/mol}) = \boxed{-178 \,\text{kJ/mol}}$$
 (1)

28.2 Solution (b)

Take the absolute value and divide by Avogadro's number to get the energy of the emitted photon.

$$E = \frac{|\Delta E|}{N_A} = \frac{178 \,\text{kJ/mol}}{6.022 \times 10^{23} \,\text{mol}^{-1}} = 2.956 \times 10^{-19} \,\text{J}$$
 (2)

Convert this to the wavelength.

$$\lambda = \frac{hc}{E} = \frac{1.9864748 \times 10^{-25} \,\text{J}\,\text{m}}{2.956 \times 10^{-19} \,\text{J}} = \boxed{672 \,\text{nm}}$$
(3)

28.3 Solution (c)

First convert wavelength to energy.

$$\Delta E = \frac{hc}{\lambda} * N_A = \frac{1.9864748 \times 10^{-25} \,\mathrm{J m}}{256 \times 10^{-9} \,\mathrm{m}} * 6.022 \times 10^{23} \,\mathrm{mol}^{-1} \tag{4}$$

$$= 476.3 \,\mathrm{kJ/mol} \tag{5}$$

Add this to the 2s energy to get the 5p energy.

$$E_i = E_f + \Delta E = -520 + 476.3 = \boxed{-53 \,\text{kJ/mol}}$$
 (6)

Write ground-state electron configurations for the following atoms and ions. You may use inert gas abbreviations (for example, [Ne]3s¹ instead of 1s²2s²2p⁶3s¹).

a) Rb

d) S²⁻

g) Co

b) Rb⁺

e) Cd

h) Co²⁺

c) S

f) Cd²⁺

i) Co³⁺

29.1Solution

a/ Rb \rightarrow [Kr] $5s^1$

 $f/ \operatorname{Cd}^{2+} \to [\operatorname{Kr}] \operatorname{4d}^{10}$

 $b/ Rb^+ \rightarrow [Kr]$

g/ Co \rightarrow [Ar] $4s^23d^7$

c/ S \rightarrow [Ne] $3s^23p^4$

 $h/ Co^{2+} \rightarrow [Ar] 3d^7$

 $d/S^{2-} \rightarrow [Ar]$

e/ Cd \rightarrow [Kr] $5s^24d^{10}$

- a) Which has the higher energy in a hydrogen atom, the 3s orbital or the $3\mathrm{p}_x$ orbital?
- b) Which has the higher energy in a phosphorus atom, the 3s orbital or the $3p_x$ orbital?
- c) Which has the higher energy in a hydrogen atom, the 4s or the $3d_{xy}$ orbital?
- d) Which has the higher energy in a Mn atom, the 4s or the $3d_{xy}$ orbital?
- e) Which has the higher energy in a Mn^{2+} ion, the 4s or the $3\mathrm{d}_{xy}$ orbital?

30.1 Solution

a/ Identical energy c/ 4s e/ 4s

b/ $3p_x$ d/ $3d_{xy}$

Which of the following configurations are ground states, which are excited states, and which are impossible configurations for an uncharged lithium atom?

a) $1s^{3}$

- c) $1s^2 2s^1$
- e) $1s^287f^1$

- b) $1s^21p^1$
- d) $1s^22p^1$

- a/ Impossible
- c/ Ground
- e/ Excited

- b/ Impossible
- d/ Excited

One possible electron configuration for an oxygen atom is [He]2s²2p⁴. Which of the following orbital energy diagrams represent the ground state, which represent excited states, and which represent impossible arrangements for the 2p electrons in an uncharged oxygen atom?

- e) _____ ___ ___ f) _______

Solution 32.1

a/ Excited

d/ Impossible

b/ Excited

e/ Ground

c/ Ground

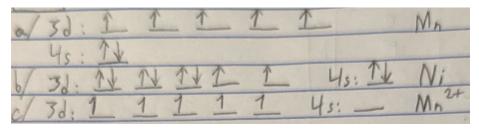
f/ Impossible

Draw orbital energy diagrams for the 3d and 4s orbitals in the ground states of the following atoms. Do not show any other orbitals (but include arrows for the electrons).

a) Mn

b) Ni

c) Mn^{2+}



Which ground-state atoms in period 4 (elements 19 through 36) have...

- a) no unpaired electrons?
- b) two unpaired electrons?

- a/ Ca, Zn, Kr
- b/ Ti, Ni, Ge, Se

Draw an orbital energy diagram for the following configurations.

- 1. An atom that has the configuration $1\mathrm{s}^22\mathrm{s}^22\mathrm{p}^4$ and is diamagnetic.
- 2. An atom that has the configuration $1s^22s^22p^4$ and is paramagnetic.

a/15:11	6/15:11
25: 11	25:14
2p: 11 11 -	2p: 11 1 1

Which of the following configurations must be paramagnetic, which could be paramagnetic, and which cannot possibly be paramagnetic (i.e. they must be diamagnetic)?

a) [Ne]3s

c) $[Ne]3s^23p$

b) [Ne]3s²

d) $[Ne]3s^23p^2$

36.1 Solution

a) Paramagnetic

c) Paramagnetic

b) Diamagnetic

d) Could be paramagnetic

37 Topic E Problem 37

a) How many electrons have n=4 in a ground-state atom of technetium (Tc)?

b) How many electrons have $\ell = 1$ in a ground-state atom of arsenic (As)?

c) How many electrons have $m_{\ell} = 1$ in a ground-state atom of krypton (Kr)?

d) How many electrons have $m_s = -\frac{1}{2}$ in a ground-state atom of radium (Ra)?

e) What is the maximum number of electrons that could have $m_\ell=2$ in a ground-state atom of iron?

f) What is the minimum number of electrons that could have $m_s=\frac{1}{2}$ in a ground-state atom of oxygen?

37.1 Solution

a) 13

c) 8

e) 2

b) 15

d) 44

f) 3

Explain each of the following observations. Explanations such as "Ca is larger than Mg because atoms get larger as you down a column of the periodic table" are not acceptable; you must tell me why this trend occurs.

- a) The atomic radius of Na is larger than the atomic radius of Mg.
- b) The atomic radius of K is larger than the atomic radius of Na.
- c) The ionic radius of S²⁻ is larger than the ionic radius of Cl⁻.
- d) The ionic radius of Zr^{3+} is larger than the ionic radius of Zr^{4+} .

38.1 Solution

I will assume all of these occur in ground state.

- a/ Na has a nuclear charge of 11 + e, less than Mg's nuclear charge of 12 + e. This is a physical chemical property and how the two are distinguashed on an atomic/subatomic level. This difference in charge causes Mg to pull its electrons in closer to the nucleus than the Na.
- b/ Potassium (K) has many more electrons than sodium (Na). This results in more electron orbital shells filling up and pushing away outer/valence electrons. This results n a larger atomic radius.
- c/ S²⁻ has a lower nuclear charge than Cl⁻. This results in less pull on the electrons by the nucleus. This results in a larger radius.
- d/ ${\rm Zr}^{3+}$ has its 4d shell and all lower-energy shells full, as well as a single electron in the 5s shell. ${\rm Zr}^{4+}$ does not have that extra electron. This results in a lower atomic radius due to no electrons filling the most outer orbitals.

Arrange the elements Al, Ga, Ne, and S in order of increasing ionization energy (i.e. from lowest to highest). You should not need to look up the ionization energies to answer this question.

39.1 Solution

Atoms with a larger radius (i.e. closer to the metals) have lower ionization energies. The same applies for atoms with a larger number of core electrons.

$$Ga < Al < S < Ne$$
 (7)

40 Topic E Problem 40

The list below shows the ionization energies for elements 36 through 40, in kJ/mol:

Element 36: 1351 Element 38: 549 Element 40: 640 Element 37: 403 Element 39: 600

- a) Explain why the ionization energies increase as you go from element 37 to element 40.
- b) Explain why the ionization energy drops dramatically as you go from element 36 to element 37.
- c) Would you expect the ionization energy of element 35 to be lower than 1351 kJ/mol, or higher than 1351 kJ/mol?

40.1 Solution

For the hell of it, I'm going to answer this in the voice of Heisenberg, the well-known chemist.

- a) A higher element number without a completed shell means the charge in and attraction from the nucleaus is higher. This results in a higher first ionization energy because the valence electron is pulled on harder by the nucleus of the atom.
- b) Element 36 happens to be a noble gas. Noble gases have full shells. This means that the electrons have maximum pull by the nucleus and the outermost shell has minimum push by core electrons. This results in overall lower energy required for first ionization of the noble gas.
- c) I expect it to have lower first ionization energy due to a lower charge from the nucleus and an equal number of core electrons. This would mean that the nucleus pulls less on the electrons.

An element in period 3 (elements 10 through 18) has the following ionization energies. Identify the element. Note: IE 1 is the energy required to remove the first electron, IE 2 is the energy required to remove the second electron, etc.

41.1 Solution

Note that there is a giant jump between IE 4 and IE 5. We can assume that that would be the point where it starts breaking into a lower shell. There is only one possible column break that would take place in this range, being from Sodium to Neon. Assuming neon's electron configuration to be the appearance after IE 4, we can count the previous shifts.

• IE 4 initial appearence: Na

• IE 3 initial appearance: Mg

• IE 2 initial appearance: Al

• IE 1 initial appearance: Si

This solidifies out final answer to be Si

42 Topic E Problem 42

The ionization energy of chlorine is 1251 kJ/mol. Based on this value, which of the following conclusions is reasonable? Select the correct statement, and fill in the blank with the correct orbital name.

- a) The energy of the ____ orbital(s) in chlorine is 1251 kJ/mol.
- b) The energy of the ____ orbital(s) in chlorine is -1251 kJ/mol.

42.1 Solution

The energy of the 3p orbital(s) in chlorine is -1251 kJ/mol.

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