1. For each of the 9 hydrogen orbitals with $n = 3$ draw a set of $x$, $y$, $z$ coordinate axes and then a sketch of the orbital. Show the phase of each orbital by shading.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$m_l$</th>
<th>Orbital Notation</th>
<th>Axis Orientation</th>
<th>Orbital Sketch</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$s$</td>
<td></td>
<td>![s orbital sketch]</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>$p_z$</td>
<td>$z$</td>
<td>![p_z orbital sketch]</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0</td>
<td>$p_y$</td>
<td>$y$</td>
<td>![p_y orbital sketch]</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>$p_z$</td>
<td></td>
<td>![p_z orbital sketch]</td>
</tr>
<tr>
<td>3</td>
<td>-2</td>
<td>0</td>
<td>$d_{x^2-y^2}$</td>
<td>$x$</td>
<td>![d_x2-y2 orbital sketch]</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0</td>
<td>$d_{z^2}$</td>
<td>$z$</td>
<td>![d_z2 orbital sketch]</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$d_{xy}$</td>
<td>$x$</td>
<td>![d_xy orbital sketch]</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0</td>
<td>$d_{yz}$</td>
<td>$y$</td>
<td>![d_yz orbital sketch]</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>0</td>
<td>$d_{xz}$</td>
<td>$x$</td>
<td>![d_xz orbital sketch]</td>
</tr>
</tbody>
</table>
2. Without looking at the tables write down the electronic configurations of the following atoms. You can look at a periodic table to find the element.

a. Ca(20)  
b. Ni(28)  
c. In(49)  
d. Zr(40)  
e. Te(52)  
f. Cs(55)  
g. Au(79) (gold’s configuration is an exception to the rules. What do you think it is?)

a. Ca  \[1s^22s^22p^63s^23p^64s^2\] or \([\text{Ar}]4s^2\)

b. Ni  \[1s^22s^22p^63s^23p^64s^23d^8\] or \([\text{Ar}]4s^23d^8\)

c. In  \[1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^1\] or \([\text{Kr}]5s^24d^{10}5p^1\)

d. Zr  \[1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^2\] or \([\text{Kr}]5s^24d^2\)

e. Te  \[1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^4\] or \([\text{Kr}]5s^24d^{10}5p^4\)

f. Cs  \[1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^1\] or \([\text{Xe}]6s^1\)

g. Au  \[1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^64f^{14}5d^{10}6s^1\] or \([\text{Xe}]4f^{14}5d^{10}6s^1\)

The exception to the rule is because \(5d^{10}6s^1\) is a full and half shell electronic configuration whereas, \(5d^96s^2\) is just a full shell and partially full shell electronic configuration. Obviously, the former has more stability, and so, the exception occurs. \textit{Pairing Energy Concept}

3. Consider the following trend in atomic radii (in pm): Fe (156), Ru (178), Os (185). They are all in the same group but Fe is a first-row, Ru is a second-row and Os is a third-row transition element.

a. Why the radii of Ru and Os are almost identical?

b. Why do they differ from Fe a lot?

a. The reason that the radii of Ru and Os are almost identical is \textit{lanthanide contractions}. Let us start with the electronic configurations of these two elements.

Ru: \([\text{Kr}]5s^24d^6\) \& Os: \([\text{Xe}]6s^24f^{14}3d^6\)

The 4f orbitals are buried deep inside the atom. And hence, these extra electrons do not aid in increasing the size of the atoms. With the increase in the net nuclear charge on going from
left to right the radius decreases considerably in the lanthanide series. This is known as lanthanide contraction. This phenomenon offsets the size increase from 4d to 5d series. Hence, the atoms in 4d and 5d series in the same groups have almost identical atomic radii. {Page 939 of Text Book}

b. Let us start with the electronic configurations of these two elements.

Fe: [Ar]4s²3d⁶ & Ru: [Kr]5s²4d⁶ & Os: [Xe]6s²4f⁴3d⁶

Going from 3d to 4d series we have an increase in size due to an additional shell being added. In other words, the orbital sizes increase because of increase in principal quantum number. So, there is a big leap in size from Fe to Ru (difference is \( r_{Ru} - r_{Fe} = 22 \text{ pm} \)). As \( r_{Ru} \) and \( r_{Os} \) are very similar, this explains why \( r_{Ru} \) and \( r_{Os} \) are different from \( r_{Fe} \). {Page 577 of Text Book}

4. How many radial node and how many planar nodes are in each of the following orbitals?

<table>
<thead>
<tr>
<th>#</th>
<th>Orbital</th>
<th>( n )</th>
<th>( l )</th>
<th>radial nodes = ( n-l-1 )</th>
<th>planar nodes = ( l )</th>
<th>total nodes = ( n-1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td>5f</td>
<td>5</td>
<td>f = 3</td>
<td>5 – 3 – 1 = 1</td>
<td>3</td>
<td>5 – 1 = 4</td>
</tr>
<tr>
<td>b.</td>
<td>3d</td>
<td>3</td>
<td>d = 2</td>
<td>3 – 2 – 1 = 0</td>
<td>2</td>
<td>3 – 1 = 2</td>
</tr>
<tr>
<td>c.</td>
<td>7s</td>
<td>7</td>
<td>s = 0</td>
<td>7 – 0 – 1 = 6</td>
<td>0</td>
<td>7 – 1 = 6</td>
</tr>
<tr>
<td>d.</td>
<td>6p</td>
<td>6</td>
<td>p =1</td>
<td>6 – 1 – 1 = 4</td>
<td>1</td>
<td>6 – 1 = 5</td>
</tr>
</tbody>
</table>

5. Let’s talk about ionization energy now. We have learnt in the last work-shop that it is different from the work-function of an element.

a. Define ionization energy.

b. Explain the following trend in IE (kJ/mol):

\( \text{B (800.6), C (1086.5), N (1402.3), O (1313.9).} \)

a. Ionization Energy It is defined as the minimum energy required to remove an electron from a gaseous atom or ion, where the atom or ion is assumed to be in its ground state. \( \text{X(g) + energy (I.E.)} \rightarrow \text{X}^+(g) + \text{e}^- \) {Page 571 of Text Book}
b. To explain the trend we should, at first, write down the electronic configuration of them.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic Configuration</td>
<td>$1s^22s^22p^1$</td>
<td>$1s^22s^22p^2$</td>
<td>$1s^22s^22p^3$</td>
<td>$1s^22s^22p^4$</td>
</tr>
<tr>
<td>I.E. (kJ/mol)</td>
<td>800.6</td>
<td>1086.5</td>
<td>1402</td>
<td>1313.9</td>
</tr>
</tbody>
</table>

The trend of increasing I.E. from B to N can be simply attributed to the increase of nuclear charge and consequently, the attraction force between the nucleus and the electrons. Also, the fact that the electrons do not shield each other effectively if in the same $n$-value contributes here. The 2p electrons do not shield each other. The I.E. value of oxygen, however, does not increase even though the attraction force is increasing. This is because for N-atom, the 2p subshell is half-filled. This gives an extra stability to the N-atom as opposed to 2p$^4$ subshell of O-atom. Hence, the I.E. values increase from B-atom to N-atom, but decreases for O-atom. Page 573 of Text Book}
6. The halogens show the following periodic trend in electron affinity (kJ/mol):
   F (-328), Cl (-349), Br (-324), I (-295). We can see that Cl, Br, & I follow a trend.
   a. How can you rationalize the trend?
   b. Why does F not follow the trend?

   a. Electron affinity is the minimum amount of energy released when an electron is placed in an
   atom in its ground state in gas phase. \[ X(g) + e^{-} \rightarrow X^{-}(g) + \text{energy (E.A.)} \].

   Let us consider the electronic configuration of the atoms given.

   F: [He]2s²2p⁵
   Cl: [Ne]3s²3p⁵
   Br: [Ar]4s²3d¹⁰4p⁵
   I: [Kr]5s²4d¹⁰4f⁴5p⁵

   When going from Cl to Br to I, we are going down a group (group 17). As we go down a
   group, the distance of the outermost orbital from the nucleus increases. So, it becomes easier to
   add the electron to the atom. \{Page 577 of Text Book\}

   b. But in case of F-atom, the 2p orbital is very small and occupied by 5 electrons. Addition of
   another will lead to severe electron-electron repulsion causing the release of energy to be more
   positive than expected. \{Page 577 of Text Book\}

7. Chromium (Cr) has 24 electrons and copper (Cu) has 29 electrons.
   a. Write the electronic configurations of (i) Cr & (ii) Cu.
   b. Explain the reason behind writing the configuration this way.

   a. (i) Cr : 1s²2s²2p⁶3s²3p⁶4s¹3d⁵ or [Ar]4s¹3d⁵
      (ii) Cu : 1s²2s²2p⁶3s²3p⁶4s¹3d¹⁰ or [Ar]4s¹3d¹⁰

   b. The reason behind writing the configuration this way is because 3d⁵4s¹ is a half and half filled
   shell electronic configuration whereas, 3d⁴4s² is a full shell and partially filled shell electronic
   configuration. Obviously, the former has more stability, and so, the exception occurs. The same
   reason can be extended to 3d¹⁰4s¹ vs 3d⁹4s² configuration in Cu. \{Pairing Energy Concept\}