CHEM 481. Chapter 1. Atomic structure and periodic table. Answers

The material on Lewis structures and VSEPR is covered in greater detail in all General Chemistry text books. You are strongly encouraged to consult such a book. Also, consider viewing the Kotz and Treichel CD-ROM (Saunders Interactive Chemistry disc.) The relevant sections in the Kotz and Treichel textbook, 3rd edition, are 9.3 to 9.7 (p. 402 - 450). This book is on reserve for Chem2810 in the library. It is essential that you practice Lewis and VSEPR structures with many different examples. You must be able to do these problems quickly and reliably, or else the whole procedure is not very much use. This comes only by much practice.

1. Using a copy of the blank periodic table distributed with the lecture notes, and without consulting references, identify the s, p, d and f groups. Enter as many element names and symbols as you remember easily.

2. Define the following terms: (a) rare earth elements; (b) van der Waals radius; (c) effective nuclear charge; (d) second ionization energy; (e) enthalpy of electron attachment (electron affinity).

(a) The rare earth elements are another name for the lanthanides; “earth” is an Alchemical name for “oxide”, so these are the elements of the rare oxides, and indeed the natural abundance of these elements is uniformly low.

(b) A van der Waals’ radius refers to the size that atom appears to have to a neighbouring atom when they come in contact without being able to form a chemical bond. Johannes van der Waals obtained the first estimate of this parameter by solving his equation for real gases, of the form:

\[
P + \left(\frac{n}{V}\right)^2 \left[V - bn\right] = nRT\]

where the \(b\) parameter reflects the volume per unit atom or molecule of a real gas atom or molecule.

(c) The effective nuclear charge experienced by any electron in an element reflects the net of the actual nuclear charge (given by the number of protons) and the screening effect of the other electrons in that element’s electron configuration. It is often called \(Z^*\), and is given by Slater’s equation: \(Z^* = Z - S\), where \(S\) is the screening term.

(d) The second ionization energy is defined as the enthalpy required to remove a single electron from the gas-phase monocation of any element to yield the gas-phase dication of that same element, algebraically as:

\[
M^+(g) \rightarrow M^{2+}(g) + e^- (g) \quad \Delta H^o = 2^{nd} I.E.
\]

(e) The (first) enthalpy of electron attachment is defined as the enthalpy required to add an electron to a gas-phase atom of any element to give the gas-phase monoanion of that element, algebraically as:

\[
M (g) + e^- (g) \rightarrow M^- (g) \quad \Delta H^o = 1^{st} E.A.
\]
3. **Give one advantage and one disadvantage of the “long form” of the periodic table.**

The long form of the table is:

```
Li  Be
Na  Mg
K  Ca
Rb Sr
Cs Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac Th Pa U Np Pu Am Cm Bk Cf Es Fr Md No Lr Db Jf Ef Gh Hs Mt Ds Rg Cn Hr Np
```

Advantages: (i) gives the elements in the correct sequence of atomic numbers; (ii) gives the Aufbau sequence of element electron configuration directly; (iii) shows the location of the s, f, d and p blocks in their correct location

Disadvantages: (i) awkward shape does not fit normal paper size very well; (ii) overemphasizes the periodic nature of the f-elements, which behave much more uniformly than any main-group or transition-metal period, actually more closely resembling a typical chemical group than a typical chemical period; (iii) implies that La,Ac belong to the f-elements, and Lu,Lr to the d-elements; in fact the identity of these element pairs is much more ambiguous, so that their location with the f-block elements as in the Chemistry 2810 Standard Periodic Table is a superior method.

4. **What is the ratio of the energy of a ground state He⁺ to that of a ground state Be³⁺ ion?**

The ground-state energy of any one electron system is given by 
\[ E_n = \frac{-Z^2 m e^4}{8\varepsilon_n^2 h^2}, \]

i.e. from the Bohr equation written for just a single state, and with \( n = 1 \). If we are simply comparing He⁺ with Be³⁺, all the constants fall away and we get the ratio 
\[ \frac{E(\text{He}^+)}{E(\text{Be}^{3+})} = \frac{2^2}{4^2} = 0.25 \]

5. **The ionization energy of hydrogen is 13.6 eV. What is the difference in energy between the \( n = 1 \) and \( n = 6 \) levels?**

Here again we use the Bohr equation: 
\[ |E_n - E_m| = h\nu = \frac{Z^2 m e^4}{8\varepsilon_n^2 h^2} \left( \frac{1}{n_m^2} - \frac{1}{n_n^2} \right) \]

first calculating \( n=1 \) to \( n=\infty \) which gives us an experimental ("Rydberg-like") constant \( E_1 = -13.6 \) eV. Then we can use this to calculate 
\[ |E_1 - E_6| = -13.6 \left( \frac{1}{1^2} - \frac{1}{6^2} \right) = -13.2 \text{ eV} \]

6. **What is the relationship between the possible angular momentum quantum numbers to the principal quantum number?**

The rule stemming from the solution to the SE for the H atom is: \( l = 0, 1, 2, \ldots (n - 1) \). In words, the values of the angular momentum quantum number are a family of positive integers ranging from zero to one less than the value of the principal quantum number.

7. **How many orbitals are there in a shell of principal quantum number \( n \)?** (Hint: begin with \( n = 1, 2 \) and 3 and see if you can recognize a pattern.

The number of orbitals in any given shell is simply given by \( n^2 \).

8. **Using sketches of 2s and 2p orbitals, distinguish between (a) the radial wavefunction, (b) the radial density distribution function, and (c) the angular wavefunction.**
9. Give the ground state electron configuration of (a) C, (b) F, (c) Ca, (d) Ga\(^{3+}\), (e) Bi, (f) Pb\(^{2+}\), (g) Sc, (h) V\(^{3+}\), (i) Mn\(^{2+}\), (j) Cr\(^{2+}\), (k) Cu, (l) Gd\(^{3+}\), (m) W, (n) Eu\(^{3+}\), (o) Eu\(^{2+}\), (p) Mo\(^{4+}\).

C: \([\text{He}]^2\text{s}^2\text{p}^2\); F: \([\text{He}]^2\text{s}^2\text{p}^5\); Ca: \([\text{Ar}]^4\text{s}^2\); Ga\(^{3+}\): \([\text{Ar}]^3\text{d}^{10}\); Bi: \([\text{Xe}]^4\text{f}^{14}\text{d}^{10}\text{s}^2\text{p}^3\); Pb\(^{2+}\): \([\text{Xe}]^4\text{f}^{14}\text{d}^{10}\text{s}^2\); Sc: \([\text{Ar}]^3\text{d}^{14}\text{s}^2\); V\(^{3+}\): \([\text{Ar}]^3\text{d}^2\); Cr\(^{2+}\): \([\text{Ar}]^3\text{d}^4\); Cu: \([\text{Ar}]^3\text{d}^{10}\text{s}^1\); Gd\(^{3+}\): \([\text{Xe}]^4\text{f}^7\); W: \([\text{Xe}]^4\text{f}^{14}\text{d}^{46}\text{s}^2\); Eu\(^{3+}\): \([\text{Xe}]^4\text{f}^6\); Eu\(^{2+}\): \([\text{Xe}]^4\text{f}^7\); Mo\(^{4+}\): \([\text{Kr}]^4\text{d}^2\).

10. Which atom should have the larger covalent radius, (a) potassium or calcium; (b) fluorine or chlorine? Give your reasoning.

(a) Potassium should be larger than calcium. They are both in the same period of the PT, and radii decrease from left to right. To prove this, we can calculate \(Z^*\). K: \(Z^* = 19 - [10 + (8 \times 0.85)] = 2.2\) Ca: \(Z^* = 20 - [10 + (8 \times 0.85) + (0.35)] = 2.85\). Thus we expect the forces operating on the valence shell in calcium to be greater than those in potassium, leading to a smaller radius in calcium.

(b) Chlorine should be larger than fluorine. We would expect \(Z^*\) to be very similar, since the two atoms are in the same group of the periodic table. However, the valence electrons in chlorine are \(3\)\text{p}\ electrons, as opposed to the \(2\)\text{p}\ in fluorine. Thus the electrons occupy a shell with a larger Bohr radius, and being further from the nucleus they will be less attracted to the nucleus and the atom will be larger.

11. Rationalize the first four ionization energies of Al (5.98, 18.82, 28.44, 119.96 eV) on the basis of ground-state electronic configurations.

Al (5.98) \([\text{Ne}]^3\text{s}^2\text{p}^1\); Al\(^+\) (18.82) \([\text{Ne}]^3\text{s}^2\); Al\(^{2+}\) (28.44) \([\text{Ne}]^3\text{s}^1\); Al\(^{3+}\) (153.77) \([\text{He}]^2\text{s}^2\text{p}^5\). It is progressively harder to remove an electron from the more positively charged ions. However, there is a huge jump in removing the fourth electron, since this electron comes from a core orbital that experiences a much greater \(Z^*\).

12. Consider the data below for the radii of some atoms and their most common ions.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.91</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1.02</td>
</tr>
<tr>
<td>S</td>
<td>1.27</td>
</tr>
<tr>
<td>S(^2-)</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Use the concept of nuclear shielding to compare these numbers. For example, compare the size of Na with Na\(^+\), S with S\(^2-\), Na with S and Na\(^+\) with S\(^2-\). Make explicit use of the electron configurations of these atoms and ions in your arguments.

Sodium, \([\text{Ne}]^3\text{s}^1\) is much larger than Na\(^+\), \([\text{Ne}]\), since the latter has lost the voluminous \(3\)\text{s}\ valence shell, where the loosely-bound electron is free to move over a large volume. Also, Na is larger than S, \([\text{Ne}]^3\text{s}^3\text{p}^1\), since the \(Z^*\) experienced for S is greater than for Na due to the only partial shielding the electrons in the same shell provide for each other, but the number of protons has increased steadily. S is smaller than S\(^2-\) because the additional 2 electrons added to the neutral atom cause the whole \(3\text{s}^2\text{p}^6\) electron cloud to experience a lower \(Z^*\), and the whole valence cloud expands outward. Similarly, S\(^2-\) is bigger than Na\(^+\), because the former has a deficiency of electrons over protons, while the latter has an excess of electrons over protons.

13. Compare the reactivity with water both among the alkali elements (Li, Na, K, etc.), and with that of the coinage elements (Cu, Ag, Au). Rationalize this chemical behaviour using the concept of nuclear shielding. Look at a plot of the first ionization energy of these elements to aid you in your reasoning.

If you look at the IP's, Cu, Ag and Au are much higher than Li, Na and K. This is due to the much greater \(Z^*\) experienced by the coinage metals, because they come after the filling of the 3\text{d}\ subshell. Thus while Li, Na and K react explosively with water to release hydrogen gas, none of the coinage metals are oxidized by water. Indeed, copper is used to sheathe roofs and the hulls of ships - it had better not react!

14. Compare the first ionization energies of calcium to that of zinc. Explain the difference in terms using concepts of shielding. Use Slatter’s rules explicitly.

1\(^{st}\) IP of Ca = 6.11 eV for \([\text{Ar}]^4\text{s}^2\); 1\(^{st}\) IP of Zn is 9.39 for \([\text{Ar}]^3\text{d}^{10}\text{s}^2\). Between Ca and Zn, 10 additional protons are added, and 10 electrons are added to the 3\text{d}\ level. If we remember that \(d\) orbital electrons are poor at shielding other electrons, we expect that Zn will experience a higher \(Z^*\) than Ca. This is consistent with the larger ionization energy of Zn (i.e. it is harder to remove an electron from Zn than from Ca.) To “prove” this we calculate the \(Z^*\) by Slater’s rules:

Ca: \(Z^* = 20 - [10 + (8 \times 0.85) + (0.35)] = 2.85\)

Zn: \(Z^* = 30 - [10 + (18 \times 0.85) + (0.35)] = 4.35\) Indeed \(Z^*\) is considerably larger for the Zn valence electron.
15. *Suggest a reason why the covalent radius of germanium (1.22 Å) is almost the same as that of silicon (1.17 Å), even though germanium has 18 more electrons than silicon.*

Between Si and Ge lies the 3d\textsuperscript{10} configuration due to the first transition series. This leads to much greater Z* because the d electrons are so poor at shielding. Hence, Ge is smaller than expected for an element in a higher shell than Si. This effect has been called the *Scandide contraction.*

16. *Suggest a reason why the covalent radius of hafnium (1.44 Å) is less than that of zirconium (1.45 Å), even though Nb and Ta lies the 4f\textsuperscript{4} configuration due to the Lanthanides. This leads to much greater Z* because the f electrons are so poor at shielding. Hence, Ta is smaller than expected for an element in a higher shell than Nb. This effect has been called the *Lanthanide contraction.*

17. *Using Slater’s rules, calculate the effective nuclear charge on an electron in each of the orbitals in an atom of potassium.*

Potassium has the configuration: 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{6}3s\textsuperscript{2}3p\textsuperscript{6}4s\textsuperscript{1}. The problem actually simplifies to treating each principal quantum number (shell), since Slater’s rules do not distinguish among s and p electrons:

| K:  n = 1 | Z* = 19 – [0.30] = 18.7 (remember that within the 1s level, each electron shields the other by only 0.30) |
| K:  n = 2 | Z* = 19 – [(2 × 0.85) + (7 × 0.35)] = 14.85 |
| K:  n = 3 | Z* = 19 – [2 + (8 × 0.85) + (7 × 0.35)] = 7.75 |
| K:  n = 4 | Z* = 19 – [10 + (8 × 0.85)] = 2.2 |

18. *Using Slater’s rules, calculate the relative effective nuclear charge on one of the 3d electrons compared to that on one of the 4s electrons for an atom of manganese.*

Manganese has the configuration: (1s\textsuperscript{2})(2s\textsuperscript{2}2p\textsuperscript{6})(3s\textsuperscript{2}3p\textsuperscript{6})(3d\textsuperscript{5})(4s\textsuperscript{2}). We thus contrast the two electrons as follows:

| Mn:  3s | Z* = 25 – [18 + (4 × 0.35)] = 5.6 |
| Mn:  4s | Z* = 25 – [10 + (13 × 0.85) + 0.35] = 3.6 |

19. *The second ionization energies of some Period 4 elements are given in the table below. Identify the orbital from which ionization occurs and account for the trend in values.*

In fact, these values are *not* easy to account for *a priori.* We need to make some assumptions. Slater’s rules give a very nice rationalization so long as we use the electron configuration suggested by removal of the electrons from the normal Aufbau sequence, remembering to remove 4s electrons before 3d electrons, i.e. the electron configurations for the 1+ ions are:

<table>
<thead>
<tr>
<th>Ca\textsuperscript{+}</th>
<th>Sc\textsuperscript{+}</th>
<th>Ti\textsuperscript{+}</th>
<th>V\textsuperscript{+}</th>
<th>Cr\textsuperscript{+}</th>
<th>Mn\textsuperscript{+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.87</td>
<td>12.80</td>
<td>13.58</td>
<td>14.15</td>
<td>16.5</td>
<td>15.64</td>
</tr>
<tr>
<td>(1s\textsuperscript{2})(2s\textsuperscript{2}2p\textsuperscript{6})(3s\textsuperscript{2}3p\textsuperscript{6})(3d\textsuperscript{5})(4s\textsuperscript{1})</td>
<td>(1s\textsuperscript{2})(2s\textsuperscript{2}2p\textsuperscript{6})(3s\textsuperscript{2}3p\textsuperscript{6})(3d\textsuperscript{5})(4s\textsuperscript{1})</td>
<td>(1s\textsuperscript{2})(2s\textsuperscript{2}2p\textsuperscript{6})(3s\textsuperscript{2}3p\textsuperscript{6})(3d\textsuperscript{5})(4s\textsuperscript{1})</td>
<td>(1s\textsuperscript{2})(2s\textsuperscript{2}2p\textsuperscript{6})(3s\textsuperscript{2}3p\textsuperscript{6})(3d\textsuperscript{5})(4s\textsuperscript{1})</td>
<td>(1s\textsuperscript{2})(2s\textsuperscript{2}2p\textsuperscript{6})(3s\textsuperscript{2}3p\textsuperscript{6})(3d\textsuperscript{5})(4s\textsuperscript{1})</td>
<td>(1s\textsuperscript{2})(2s\textsuperscript{2}2p\textsuperscript{6})(3s\textsuperscript{2}3p\textsuperscript{6})(3d\textsuperscript{5})(4s\textsuperscript{1})</td>
</tr>
<tr>
<td>Ionize 4s\textsuperscript{1}</td>
<td>Ionize 4s\textsuperscript{1}</td>
<td>Ionize 4s\textsuperscript{1}</td>
<td>Ionize 4s\textsuperscript{1}</td>
<td>Ionize 3d\textsuperscript{1}</td>
<td>Ionize 4s\textsuperscript{1}</td>
</tr>
<tr>
<td>20 – [10 + 8 × 0.85]</td>
<td>21 – [10 + 9 × 0.85]</td>
<td>22 – [10 + 10 × 0.85]</td>
<td>23 – [10 + 11 × 0.85]</td>
<td>24 – [18 + 4 × 0.35]</td>
<td>25 – [10 + 13 × 0.85]</td>
</tr>
<tr>
<td>3.2</td>
<td>3.35</td>
<td>3.5</td>
<td>3.65</td>
<td>4.6</td>
<td>3.95</td>
</tr>
</tbody>
</table>

This gives a very nice trend – not exactly a linear fit, but nonetheless a good correlation between the measured data and the (very crude) estimation provided by Slater’s rules. Thus the anomalous value for chromium is due to the fact that the electron must come out of a 3d\textsuperscript{1} rather than a 4s electron.

20. *Compare the first ionization energies of strontium, barium and radium. Relate the irregularity to the lanthanide contraction.* Data: IP of Sr = 5.695; IP of Ba = 5.211; IP of Ra = 5.278.

IP of Sr = 5.695 for [Kr]5s\textsuperscript{2}; IP of Ba = 5.211 for [Xe]6s\textsuperscript{2}; IP of Ra = 5.278 for [Rn] 7s\textsuperscript{2}. We are comparing ionizations from exactly the same valence electron configurations in each case. However, the 4f level is filled between Ba and Ra, which are very poor at shielding higher-lying electrons from the additional 14 protons added at the same time as the f electrons. Thus Ra experiences a higher effective nuclear charge than Ba. Thus, despite the fact that its valence electron lies in a higher
shell, which we would expect to be further from the nucleus, it experiences so much additional nuclear charge that it is actually slightly harder to remove a Ra electron than a Ba electron.

21. **Account for the trends, element by element, across period 3 in (a) ionization energy, (b) enthalpy of electron attachment, and (c) electronegativity.**

<table>
<thead>
<tr>
<th>element</th>
<th>electron configuration</th>
<th>1st IP (eV)</th>
<th>Electron-Gain enthalpy</th>
<th>Electronegativity (χ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>[Ne]3s(^1)</td>
<td>5.14</td>
<td>-0.548</td>
<td>0.93</td>
</tr>
<tr>
<td>Mg</td>
<td>[Ne]3s(^2)</td>
<td>7.64</td>
<td>+0.4</td>
<td>1.31</td>
</tr>
<tr>
<td>Al</td>
<td>[Ne]3s(^2)3p(^1)</td>
<td>5.98</td>
<td>-0.441</td>
<td>1.61</td>
</tr>
<tr>
<td>Si</td>
<td>[Ne]3s(^2)3p(^2)</td>
<td>8.15</td>
<td>-1.385</td>
<td>1.90</td>
</tr>
<tr>
<td>P</td>
<td>[Ne]3s(^2)3p(^3)</td>
<td>11.0</td>
<td>-0.747</td>
<td>2.19</td>
</tr>
<tr>
<td>S</td>
<td>[Ne]3s(^2)3p(^4)</td>
<td>10.36</td>
<td>-2.077</td>
<td>2.58</td>
</tr>
<tr>
<td>Cl</td>
<td>[Ne]3s(^2)3p(^5)</td>
<td>13.10</td>
<td>-3.617</td>
<td>3.16</td>
</tr>
<tr>
<td>Ar</td>
<td>[Ne]3s(^2)3p(^6)</td>
<td>15.76</td>
<td>+1.0</td>
<td>n/a</td>
</tr>
</tbody>
</table>

All the magnitudes increase from left to right across the period, since each trend reflects the increasing Z* as electrons are being added to orbitals of the same shell. For IP, this reflects the difficulty of removing an electron. For EG enthalpy, this reflects energy released when an additional electron is attached to the neutral atom, which is more likely when Z* is larger. Electronegativity also grows (remember it is defined as the average of the previous two categories in Mulliken's definition!) There are some reversals: the IP of Al is smaller than that of Mg. This is because the electron removed from the former comes from a new subshell, 2\(p\), which will be easier to do than removing a filled s subshell for Mg. Also, S is easier than P, because phosphorus has a half-filled \(p\) subshell, which also has additional stability. The E-G enthalpies of Mg and Ar are anomalous. Mg is full (3\(s\)), so that the additional electron would have to go into the 3\(p\) level. There is no driving force for this procedure, and it is in fact endothermic. Similarily, Ar needs to attract an additional electron into the next shell, and this is also not favourable. The electronegativity grows much more gently and regularly than the IP, as expected for a property which is the average of IP and E-G.

22. Unlike the electronegativities of the other main groups, those of Groups 13 and 14 pass through a minimum on descending the group. To what can you attribute this trend?

\(\chi\) for groups 13 and 14 is lowest for Al and Si. This can be attributed to the Scandide contraction, i.e. to the filling of the first \(d\) level between Al-Si and Ga-Ge. Thus Ga and Ge have anomalously high electronegativities.

23. **What are the names, symbols, and roles of the four quantum numbers associated with the hydrogen atom?**

- \(n\) = principal quantum number - controls the energy of the electrons in a hydrogen atom
- \(l\) = orbital angular momentum q.n. - dictates the shape of the orbital
- \(m_l\) = orbital magnetic q.n. - determines the orientation of the orbital in 3-D space
- \(m_s\) = electron spin q.n. - determines the spin of the electron, which may be up or down

24. **Sketch the orbitals of atomic hydrogen for the first three quantum shells. In which of these orbitals are the signs associated with the wave functions arranged symmetrically?**

For sketches of the orbitals, see the lecture notes on p.23. Note that the \(s\) and \(d\) orbitals are symmetric.

25. **What orbitals do the following quantum number combinations describe? Are they even permissible solutions of the Schrödinger equation? (i) \(n = 2\) \(l = 1\) \(m_l = -1\) (ii) \(n = 1\) \(l = 0\) \(m_s = -4\)**

(i) \(n = 2\) \(l = 1\) \(m_l = -1\) a 2\(p\) orbital (allowed)
(ii) \(n = 1\) \(l = 0\) \(m_s = -4\) a 1\(s\) orbital, not permissible with a value of \(m_s = -4\)

26. **Which of the following orbitals are allowed for the hydrogen atom by quantum mechanics? 5\(p\); 5\(h\); 6\(d\)**

5\(p\) is permissible, since for \(n = 5\), \(l\) can be up to 4, which includes \(l = 1\)
5\(h\) is not permissible, since this requires \(l = 6\)
6\(d\) is permissible, since for \(n = 6\), \(l\) can be up to 5, which includes \(l = 2\)

27. **Consider the following radial probability density-distribution plot and respond to the associated questions.**
a) How many radial nodes are there?
b) If the total number of nodes is 3, what type of orbital is involved? 
c) Which orbital would it be if there were one more node?

![Graph](image)

a) 1 at 0.1 nm  
b) 2 angular nodes, one radial, \( \therefore 4d \)  
c) 3 angular nodes, one radial, \( \therefore 5f \)

28. On the left-side graph below is a crude sketch of the radial component of a wavefunction for a hydrogen atom. The principle quantum number is given.

![Graph](image)

a) Identify the orbital \((n, l, m_l)\).  
b) Sketch roughly the radial probability density function corresponding to this wavefunction.

a) \((4, 0, 0)\)

b) Sketch filled in below:

![Graph](image)

a) 4s orbital, since all three nodes are radial

29. On the right-side graph below is a crude sketch of the radial probability density function for a hydrogen atom. The principle quantum number is given.

![Graph](image)

a) At the left, sketch the radial component of the wavefunction that corresponds to this probability function. 

b) Identify the orbital by its common name 

b) If instead of \(n = 2\), the sketch at right belonged to an orbital with \(n = 3\), what orbital would that be? (Of course, then the sketch you have drawn at the left would no longer be valid!)

a) Done on sketch below.
b) Done on sketch below.
c) This would make it 3p.

![Wavefunction Graphs]

30. Consider the following plot of ionization energies across the periodic table. Use shielding arguments to rationalize the observed variation in values.

(ignore for now)

31. On the left-side graph below is a crude sketch of the radial component of one wave function of a hydrogen atom.

![Radial Component Sketch]

a) At the right, sketch the corresponding radial probability density distribution function for this wave function.
b) If the total number of nodes is 2, identify the orbital both by its common name and the quantum numbers which uniquely describe it.
c) If instead the total number of nodes is 4, would the sketch on the right still be a valid plot? If so, identify the orbital both by its common name and the quantum numbers which uniquely describe it.

a) Done on sketch below.
b) Done on sketch below.
c) Yes it would still be valid. Now the number of angular nodes is 3, so it must describe a 5f orbital \((n = 5, l = 3)\).

32. For the following molecules and ions, provide the Lewis structure and the VSEPR geometry (the central atom(s) are underlined). Include any resonance, and show all non-zero formal charges. Indicate approximate bond angles around the central atoms. And clearly indicate the isomers you choose if isomerism is possible.

**Molecules and Ions:**
- \(SF_5Cl\), \(CH_3F\), \(HSSH\), \(NHF_2\), \(XeF_6\), \(ICl_3\), \(BeH_2\), \(NO_2F\), \(GeH_4\), \(XeO_3\), \(TeF_6\), \(SeCl_4\), \(OCS\), \(IF_4^-\), \([NH_4]^+\), \([BrBr_3]^+\), \(BrNO\), \(KrF_2\), \(SO_4^{2-}\), \([TeCl_6]^{2-}\), \(NNO\), \(IF_3\), \(OSO\), \(SCN^-\)
- Octahedral: All angles $\approx 90^\circ$
- Tetrahedral: Angles are $\approx 109^\circ$
- Stepped tetrahedral: Angles are $\approx 109^\circ$
- T-shaped: Angles are $\approx 90^\circ$

- Trigonal planar: Angles are $\approx 120^\circ$

- Linear: $180^\circ$
- Bent: $\approx 90^\circ$
- Distorted octahedral: Angles are $\approx 109.5^\circ$

- Spherical: $180^\circ$
- Square planar: $90^\circ$
- Bent: $\approx 120^\circ$
- Tetrahedral: $109.5^\circ$

- Trigonal pyramidal: $\approx 109.5^\circ$
- Square pyramidal: $90^\circ$
- Bent: $\approx 120^\circ$

- Linear: $180^\circ$
- Bent: $\approx 90^\circ$
- Linear: $180^\circ$
- Bent: $\approx 120^\circ$
- Linear: $180^\circ$
- Bent: $\approx 90^\circ$
- Linear: $180^\circ$
- Bent: $\approx 120^\circ$
- Linear: $180^\circ$

- Linear: $180^\circ$
- Bent: $\approx 90^\circ$
- Linear: $180^\circ$
- Bent: $\approx 120^\circ$
- Linear: $180^\circ$
- Bent: $\approx 90^\circ$
- Linear: $180^\circ$
- Bent: $\approx 120^\circ$
33. **Draw Lewis structures for the following molecules for which there are more than one resonance isomer. Show formal charges, and indicate if any resonance hybrids are more important contributors than others to the true electronic structure. The connectivity of the atoms in each of these molecules is shown by a sketch.**

\[
\begin{align*}
\text{[HCO}_2^\text{-}] & \quad \text{S}_2\text{O}_2 & \quad \text{S}_2\text{N}_2 & \quad \text{S} \equiv \text{N} \\
\text{O} & \quad \text{O} & \quad \text{N} & \quad \text{S} \\
\text{O} & \quad \text{O} & \quad \text{N} & \quad \text{S} \\
\end{align*}
\]

34. **Construct Lewis structures of typical resonance contributions of (a) ONC}^-\text{ and (b) NCO}^-\text{ and assign formal charges to each atom. Which resonance contribution is likely to be the dominant one in each case?**

\[
\begin{align*}
\text{N} & \quad \text{C} & \quad \text{O} \\
\text{N} & \quad \text{C} & \quad \text{O} \\
\text{N} & \quad \text{C} & \quad \text{O} \\
\text{N} & \quad \text{C} & \quad \text{O} \\
\end{align*}
\]

Note: Neither ONC}^-\text{ structure is particularly good with a charge on carbon.}
35. What shapes would you expect for (a) $\text{SO}_3$, (b) $\text{SO}_3^-$, (c) $\text{IF}_3$?

\[\text{SO}_3\]
\[\text{SO}_3^-\]
\[\text{IF}_3\]

36. It is possible to synthesize the ion $\text{C(CN)}_3^-$. Draw an electron-dot structure and deduce its most likely geometry. In fact, the ion is planar. Draw one of the resonance structures that would be compatible with this finding.

\[\text{C(CN)}_3^-\]

(a) \text{Normal Carbanion}

\[\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{N}^-\]

leads to pyramidal geometry.

(b) Resonance isomers that are planar

Note this certainly fits the fact that $\chi(N) > \chi(C)$!