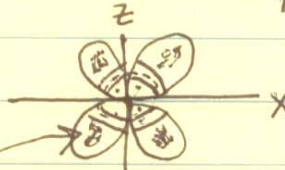
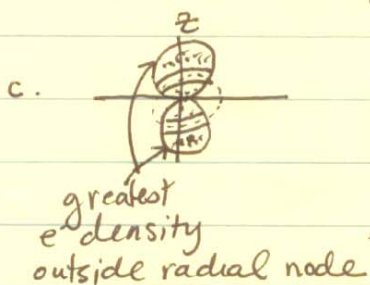
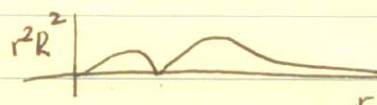
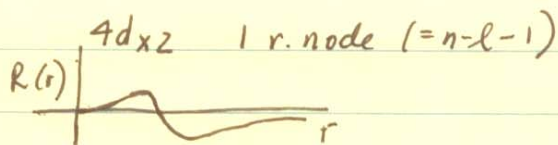
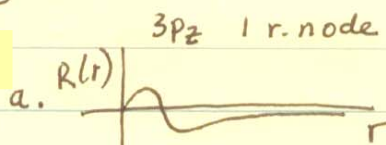


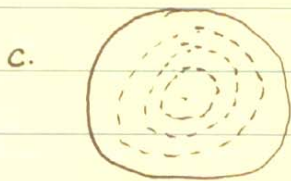
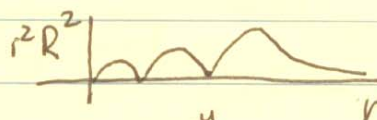
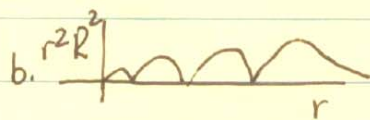
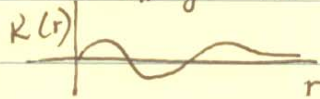
9)



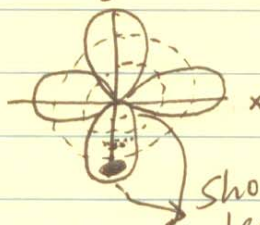
10)

4s n-l-1 = 3 r. nodes

5d_{x²-y²} n-l-1 = 2 r. nodes



3 r. nodes - e density highest outside the last one.



Showing shading ("dot density") for this lobe only - greatest density outside last r. node (all 4 lobes identical)

12)

a. 4f: n-l-1 = 4-3-1 = 0 radial nodes

b. angular nodes = l = 3

c. Angular nodes occur where $Y=0 = (\text{const.}) z(x^2-y^2)/r^3$
 $Y=0$ where $z=0$ (the xy plane) and where $(x^2-y^2)=0$
 $(x^2-y^2)=0$ where $x=y$ and $x=-y$; these define 2 more planes

d. See "Orbitron" online for pictures. There are 8 lobes - 4 above the xy plane and 4 below. Signs alternate.

15)

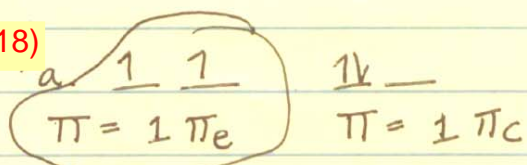
a. Electron	l value	m_l values
5d	2	-2, -1, 0, +1, +2
4f	3	-3, -2, -1, 0, +1, +2, +3
7g	4	-4, -3, -2, -1, 0, +1, +2, +3, +4

b. 3d electron: $n=3$; $l=2$; $m_l = -2, -1, 0, +1, +2$
 $m_s = +\frac{1}{2}, -\frac{1}{2}$

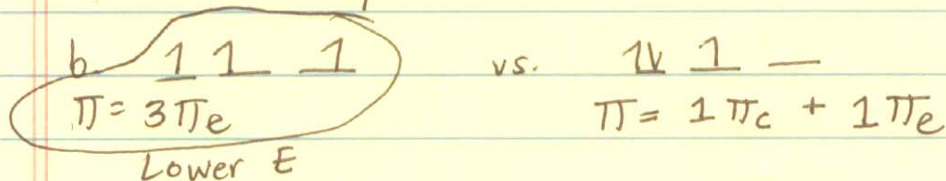
c. f: $l=3$; $m_l = -3, -2, -1, 0, +1, +2, +3$

d. 2 e^- can occupy a 4d orbital (or any single orbital)
 One has $m_s = +\frac{1}{2}$ and the other $m_s = -\frac{1}{2}$.

18)



Lower energy - exchanges reduce the configurational energy;
 Coulombic repulsion increases it.



22)

a. The relative energies of the 4s and 3d orbitals change moving across Period 4. At Cr, it is energetically "cheaper" to put 5 e^- in the 3d subshell (obeying Hund's Rule) than it is to pair a second e^- in the 4s ("paying the cost" of Coulombic repulsion). See Figure 2.12, p. 43.

22) cont.)

b. Both Ti and Cr^{2+} have 22 electrons. The config. for Ti ($[Ar] 4s^2 3d^2$) reflects orbital filling in order of increasing E (i.e., 4s² before 3d² - see Fig. 2.12). In the case of Cr^{2+} , 2 e^- have been removed from the 4s orbital of neutral Cr, because these e^- have the lowest Z_{eff} (least attraction to the nucleus). [The lower portion of Fig. 2.12 shows that the 4s orbital in the Cr ion (Cr^+ here) is higher than the 3d, reflecting this.]

23. a) V: $[\text{Ar}] 4s^2 3d^3$ b) Br: $[\text{Ar}] 4s^2 3d^{10} 4p^5$ c) Ru^{3+} : $[\text{Kr}] 4d^5$ d) Hg^{2+} : $[\text{Xe}] 4f^{14} 5d^{10}$
 e) Sb: $[\text{Kr}] 5s^2 4d^{10} 5p^3$ **For cations (c and d), e- are removed from highest n first. (Z^* is lowest.)

25. **Rationalizing orbital filling: $n = 1 \rightarrow n = 2 \rightarrow n = 3$:**

Comparing the radial probability plots for the 1s, 2s, and 3s orbitals (Fig. 2.7, p. 22), the 1s has by far the highest probability of finding the electron near the nucleus, leading to the strongest attraction and the lowest lying orbital. For 2s and 3s, there is very little probability of finding the electron inside the first radial node (though it is marginally higher in the 2s); however, the most probable radius for the 2s is much shorter than that for the 3s, again leading to stronger electron-nucleus attraction and lower orbital energy.

Rationalizing orbital filling: $3s \rightarrow 3p \rightarrow 3d$ (or $l = 1 \rightarrow l = 2 \rightarrow l = 3$):

Interestingly, the relative energies of these orbitals cannot be explained on the basis of most probable radius; in fact, those values would predict exactly the opposite order of energies, as the 3d has the shortest r_{mp} and the 3s has the longest. The key to understanding orbital filling in this case lies with the probability of finding the electron very close to the nucleus. Both 3s and 3p have small but significant probability inside the first (and in the case of 3s, the second) radial node; in comparison, one has to move a significant distance from the nucleus in order to find meaningful probability in the 3d. The greater probability of finding the electron close to the nucleus increases the attraction and lowers the energy of 3s (the most) and 3p (somewhat) relative to 3d.

29. (b) Comparing Z^* for 2p e- in O^{2-} , F^- , Na^+ and Mg^{2+} , all of which have 10 e- total; only Z varies.

$$\text{Config: } (1s)^2 (2s, 2p)^8 \quad S = (7 \times 0.35) + (2 \times 0.85) = 4.15$$

$$\text{O}^{2-}: Z^* = Z - S = 8 - 4.15 = \mathbf{3.85}$$

$$\text{F}^-: Z^* = 9 - 4.15 = \mathbf{4.85}$$

$$\text{Na}^+: Z^* = 11 - 4.15 = \mathbf{6.85}$$

$$\text{Mg}^{2+}: Z^* = 12 - 4.15 = \mathbf{7.85}$$

Mg^{2+} has the smallest radius and O^{2-} has the largest. The trend in radii **results from** and is explained by these Z^* values: the remaining 2p electrons in Mg^{2+} experience the greatest amount of nuclear charge and are the most strongly attracted, resulting in the smallest ionic radius.

$$\text{(c) Cu: } [\text{Ar}] 4s^1 3d^{10} \rightarrow (1s)^2 (2s, 2p)^8 (3s, 3p)^8 (3d)^{10} (4s)^1$$

$$\mathbf{4s \text{ e-}: } Z^* = 29 - [(0 \times 0.35) + (18 \times 0.85) + (10 \times 1.00)] = \mathbf{3.70}$$

$$\mathbf{3d \text{ e-}: } Z^* = 29 - [(9 \times 0.35) + (18 \times 1.00)] = \mathbf{7.85}$$

The 4s electron is removed first. With a significantly lower Z^* value, it is much less strongly bound to the nucleus.

40. (a) $IE_{\text{Mg}} > IE_{\text{Al}}$: The "dip" at Al can be explained by the fact that Al has the outermost e- in the higher energy 3p subshell, from which it is more easily removed.

$IE_{\text{P}} > IE_{\text{S}}$: Similarly, there is a minimum at S because it is the first element in the period to have an electron paired in the 3p subshell. This coulombic contribution to the pairing energy raises the energy of the configuration, making S easier to ionize.

43)

a. largest: Se^{2-} ; smallest Sr^{2+} All have $36e^-$. Se^{2-} has fewest protons; Sr^{2+} has most protons.

b. largest $\text{Y}^{3+} > \text{Zr}^{4+} > \text{Nb}^{5+}$ smallest The neutral atoms follow this trend (as Z^* increases). Increasing cation charge magnifies the effect (or, at least makes each one significantly smaller).

c. Co largest; Co^{4+} smallest - fewest e^- held tightest (closest to nucleus):

45)

a. smallest r : V - highest Z^* b. largest V: S^{2-} - same $\#e^-$, fewest p^+

(a) and (b)
not assigned

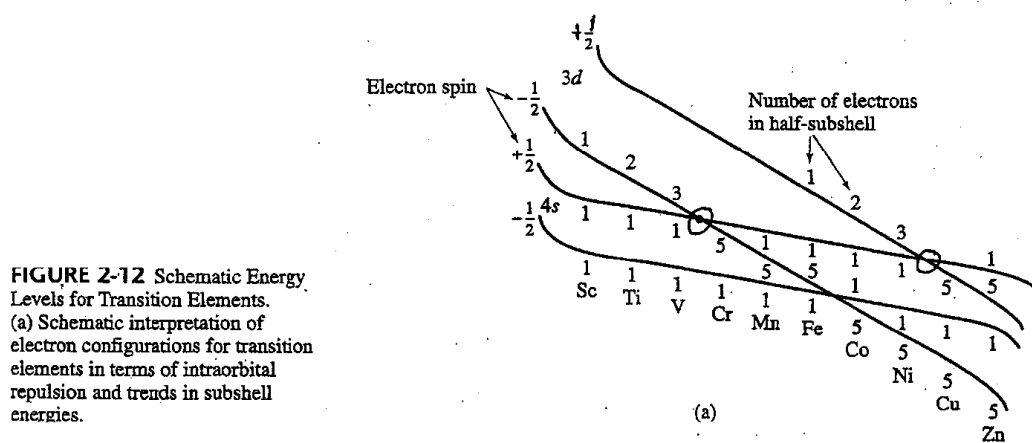
c. lowest IE: Cs - outer e^- farthest from nucleus

d. Highest EA: Cl^- - e^- added closest to nucleus - strong attraction

e. Highest IE Cu^{2+} - With increased charge, remaining e^- held more tight

Additional Problem – Atomic Structure (Chapter 2)

1. The following questions relate to Figure 2.12(a) on page 35 of your text:
 - a. What is the overall goal of this figure? (That is, what is it intended to explain?)
 - b. What do the two pairs of diagonal lines represent? The numbers shown near the lines?
 - c. Why do all of the diagonal lines have negative slopes (decreasing from left to right)? What atomic property or trend explains this?
 - d. One pair of diagonal lines has a steeper slope than the other. Why? (Hint: Think about Slater's rules.)
 - e. How did the author cited in the figure caption determine where the diagonal lines cross? (Hint: What is the first thing you would do in trying to answer Problem 2.32 on p. 43?)



- a. The figure is intended to explain the electron configurations of the first-row transition metals. It shows qualitatively how the energies of the 4s and 3d orbitals change with increasing atomic number, providing a rationalization for the known ground-state configurations.
- b. The diagonal lines represent the energies of the 4s and 3d subshells. Each subshell has two lines, one for the "spin up" electron(s) and one for the "spin down" one(s) ($m_s = +\frac{1}{2}$ and $-\frac{1}{2}$). The numbers are numbers of electrons.
- c. The lines have negative slopes because subshell energies are decreasing from left to right. This can be explained by the increase in effective nuclear charge: as we move left to right across the period, the outer 4s and 3d electrons experience more positive charge from the nucleus and the increased attraction lowers the orbital energies.
- d. The slope is steeper for the 3d subshell, indicating that its energy decreases more significantly with increasing atomic number. This is the case because the 3d subshell is less shielded than the 4s: as Z increases, the 3d electrons experience a greater increase in Z^* , resulting in a more significant lowering of orbital energies.
- e. The diagram and its crossing points were determined from the known (experimentally determined) electron configurations (included in Table 2.7). The author drew the diagram so that the relative energies of the 4s and 3d subshells for each element would be consistent with its known ground-state configuration.