CHAPTER 2: ATOMIC STRUCTURE

2.1 **a.** $$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{J s}}{(9.110\times10^{-31}\text{kg})\times(0.1)\times(2.998\times10^{8}\text{m s}^{-1})} = 2.426\times10^{-11}\text{ m}$$

b. $$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{J s}}{0.400\,\text{kg}\times(10\text{ km/hr}\times10^{3}\text{m/km}\times1\text{hr/3600s})} = 6\times10^{-34}\text{m}$$

c. $$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{J s}}{8.0\text{ lb}\times0.4536\text{ kg/lb}\times2.0\text{ m s}^{-1}} = 9.1\times10^{-35}\text{ m}$$

d. $$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{J s}}{13.7\text{ g}\times\text{kg}/10^{3}\text{g}\times30.0\text{ mi hr}^{-1}\times1\text{ hr/3600s}\times1609.3\text{ m/mi}}$$

$$= 3.61\times10^{-33}\text{ m}$$

2.2 $$E = R_H\left(\frac{1}{2^2}-\frac{1}{n_h^2}\right);\; R_H = 1.097\times10^{7}\text{m}^{-1} = 1.097\times10^{5}\text{cm}^{-1};\; \lambda = \frac{hc}{E} = \frac{1}{\bar{\nu}}$$

$n_h = 4$ $$E = R_H\left(\frac{1}{4}-\frac{1}{16}\right) = R_H\left(\frac{12}{64}\right) = 20{,}570\,\text{cm}^{-1} = 4.085\times10^{-19}\,\text{J}$$

$$\lambda = 4.862\times10^{-5}\text{cm} = 486.2\text{ nm}$$

$n_h = 5$ $$E = R_H\left(\frac{1}{4}-\frac{1}{25}\right) = R_H\left(\frac{21}{100}\right) = 23{,}040\,\text{cm}^{-1} = 4.577\times10^{-19}\,\text{J};$$

$$\lambda = 4.341\times10^{-5}\text{cm} = 434.1\text{ nm}$$

$n_h = 6$ $$E = R_H\left(\frac{1}{4}-\frac{1}{36}\right) = R_H\left(\frac{8}{36}\right) = 24{,}380\,\text{cm}^{-1} = 4.841\times10^{-19}\,\text{J};$$

$$\lambda = 4.102\times10^{-5}\text{cm} = 410.2\text{ nm}$$

2.3 $$E = R_H\left(\frac{1}{4}-\frac{1}{49}\right) = R_H\left(\frac{45}{196}\right) = 25{,}190\text{cm}^{-1} = 5.002\times10^{-19}\,\text{J}$$

$$\lambda = \frac{1}{\bar{\nu}} = 3.970\times10^{-5}\text{cm} = 397.0\text{ nm}$$

2.4 383.65 nm $$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\text{J s})(2.998\times10^{8}\text{m/s})}{(383.65\,\text{nm})(\text{m}/10^{9}\text{nm})} = 5.178\times10^{-19}\text{J}$$

379.90 nm $$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\text{J s})(2.998\times10^{8}\text{m/s})}{(379.90\,\text{nm})(\text{m}/10^{9}\text{nm})} = 5.229\times10^{-19}\text{J}$$

$$E = R_H\left(\frac{1}{2^2} - \frac{1}{n_h{}^2}\right); \quad \frac{1}{n_h{}^2} = \frac{1}{4} - \frac{E}{R_H} \text{ and } n_h = \left(\frac{1}{4} - \frac{E}{R_H}\right)^{-\frac{1}{2}}$$

For 383.65 nm: $n_h = \left(\frac{1}{4} - \frac{5.178\times10^{-19} J}{2.1787\times10^{-18} J}\right)^{-\frac{1}{2}} = 9$

For 379.90 nm: $n_h = \left(\frac{1}{4} - \frac{5.229\times10^{-19} J}{2.1787\times10^{-18} J}\right)^{-\frac{1}{2}} = 10$

2.5 The least energy would be for electrons falling from the $n = 4$ to the $n = 3$ level:

$$E = R_H\left(\frac{1}{3^2} - \frac{1}{4^2}\right) = 2.1787\times10^{-18} J\left(\frac{7}{144}\right) = 1.059\times10^{-19} J$$

The energy of the electromagnetic radiation emitted in this transition is too low for humans to see, in the infrared region of the spectrum.

2.6

$$\Delta E = 102823.8530211\text{ cm}^{-1} - 97492.221701\text{ cm}^{-1} = 5331.6313201\text{ cm}^{-1}$$

$$\Delta E = hc\overline{\nu} = (6.626\times10^{-34}\text{ J s})(2.998\times10^{8}\text{ m/s})(100\text{ cm/m})(5331.6313201\text{ cm}^{-1})$$

$$\Delta E = 1.059\times10^{-19}\text{ J}$$

This is the same difference found via the Balmer equation in Problem 2.5 for a transition from $n = 4$ to $n = 3$. The Balmer equation does work well for hydrogen.

2.7 **a.** We begin by symbolically determining the ratio of these Rydberg constants:

$$R_{\text{He}^+} = \frac{2\pi^2\mu_{\text{He}^+}(Z_{\text{He}^+})^2 e^4}{(4\pi\varepsilon_0)^2 h^2} \qquad R_{\text{H}} = \frac{2\pi^2\mu_{\text{H}}(Z_{\text{H}})^2 e^4}{(4\pi\varepsilon_0)^2 h^2}$$

$$\frac{R_{\text{He}^+}}{R_{\text{H}}} = \frac{\mu_{\text{He}^+}(Z_{\text{He}^+})^2}{\mu_{\text{H}}(Z_{\text{H}})^2} = \frac{4\mu_{\text{He}^+}}{\mu_{\text{H}}} \text{ (since } Z = 2 \text{ for He}^+\text{)}$$

The reduced masses are required (in terms of atomic mass units):

$$\frac{1}{\mu_{\text{H}}} = \frac{1}{m_e} + \frac{1}{m_{proton}} = \frac{1}{5.4857990946\times10^{-4} m_u} + \frac{1}{1.007276466812\ m_u}$$

$$\frac{1}{\mu_{\text{H}}} = 1823.88\ m_u^{-1};\ \mu_{\text{H}} = 5.482813\times10^{-4} m_u$$

$$\frac{1}{\mu_{\text{He}^+}} = \frac{1}{m_e} + \frac{1}{m_{He^{2+}}} = \frac{1}{5.4857990946\times10^{-4} m_u} + \frac{1}{4.001506179125\ m_u}$$

$$\frac{1}{\mu_{\text{He}^+}} = 1823.13\ m_u^{-1};\ \mu_{\text{He}^+} = 5.485047\times10^{-4} m_u$$

The ratio of Rydberg constants can now be calculated:

$$\frac{R_{\mathrm{He}^+}}{R_{\mathrm{H}}} = \frac{4\mu_{\mathrm{He}^+}}{\mu_{\mathrm{H}}} = \frac{4(5.485047 \times 10^{-4}\, m_u)}{5.482813 \times 10^{-4}\, m_u} = 4.0016$$

b. $R_{\mathrm{He}^+} = 4.0016 R_{\mathrm{H}} = (4.0016)(2.1787 \times 10^{-18}\,\mathrm{J}) = 8.7184 \times 10^{-18}\,\mathrm{J}$

c. The energy difference is first converted to Joules:

$$\Delta E = hc\overline{v} = (6.626 \times 10^{-34}\,\mathrm{J\,s})(2.998 \times 10^{8}\,\mathrm{m/s})(100\,\mathrm{cm/m})(329179.76197\,\mathrm{cm}^{-1})$$

$$\Delta E = 6.5391 \times 10^{-18}\,\mathrm{J}$$

The Rydberg equation is applied, affording nearly the identical Rydberg constant for He$^+$:

$$E = R_{\mathrm{He}^+}\left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right) = 6.5391 \times 10^{-18}\,\mathrm{J} = R_{\mathrm{He}^+}\left(\frac{1}{1} - \frac{1}{4}\right)$$

$$R_{\mathrm{He}^+} = 8.7188 \times 10^{-18}\,\mathrm{J}$$

2.8 **a.** $$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\Psi}{\partial x^2} = E\,\Psi\,; \quad \Psi = A\sin rx + B\cos sx$$

$$\frac{\partial\Psi}{\partial x} = Ar\cos rx - Bs\sin sx$$

$$\frac{\partial^2\Psi}{\partial x^2} = -Ar^2\sin rx - Bs^2\cos sx$$

$$-\frac{h^2}{8\pi^2 m}\left(-Ar^2\sin rx - Bs^2\cos sx\right) = E\left(A\sin rx + B\cos sx\right)$$

If this is true, then the coefficients of the sine and cosine terms must be independently equal:

$$\frac{h^2 Ar^2}{8\pi^2 m} = EA\,; \quad \frac{h^2 Bs^2}{8\pi^2 m} = EB$$

$$r^2 = s^2 = \frac{8\pi^2 mE}{h^2}\,; \quad r = s = \sqrt{2mE}\,\frac{2\pi}{\mathrm{h}}$$

b. $\Psi = A\sin rx\,;$ when $x = 0$, $\Psi = A\sin 0 = 0$
when $x = a$, $\Psi = A\sin ra = 0$

$$\therefore ra = \pm n\pi;\ r = \pm\frac{n\pi}{a}$$

c. $$E = \frac{r^2 h^2}{8\pi^2 m} = \frac{n^2\pi^2}{a^2}\frac{h^2}{8\pi^2 m} = \frac{n^2 h^2}{8ma^2}$$

d.

$$\int_0^a \Psi^2 dx = \int_0^a A^2\sin^2\left(\frac{n\pi x}{a}\right) dx = A^2\frac{a}{n\pi}\int_0^a \sin^2\left(\frac{n\pi x}{a}\right) d\left(\frac{n\pi x}{a}\right)$$

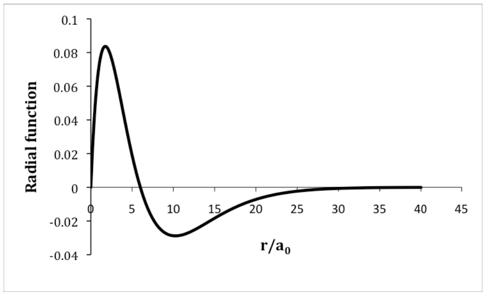
$$= \frac{a}{n\pi}A^2\left[\frac{1}{2}\left(\frac{n\pi x}{a}\right) - \frac{1}{4}\sin\left(\frac{2n\pi x}{a}\right)\right]_0^a = 1$$

$$= \frac{aA^2}{n\pi}\left[\frac{1}{2}\frac{n\pi a}{a} - \frac{1}{4}\sin 2n\pi - 0 + \frac{1}{4}\sin 0\right] = 1$$

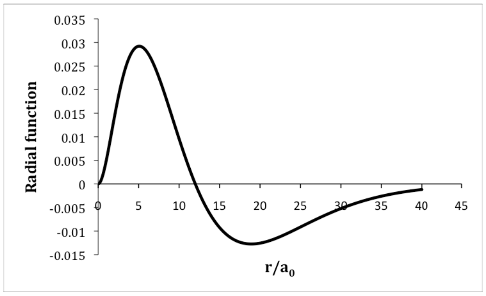
$$A = \sqrt{\frac{2}{a}}$$

2.9 **a.**

$3p_z$

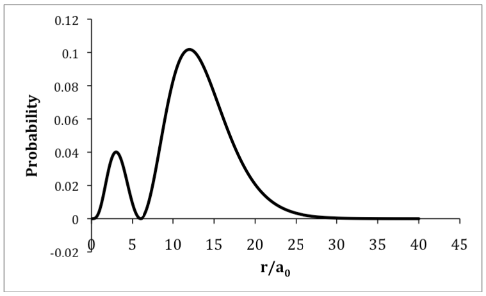


$4d_{xz}$

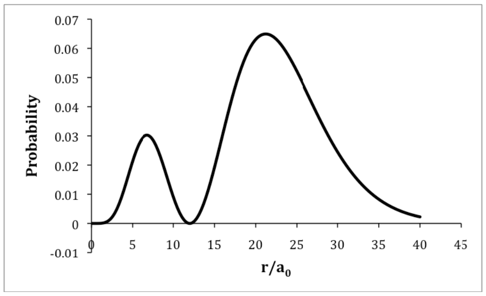


b.

$3p_z$



$4d_{xz}$

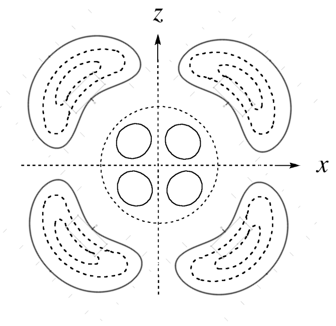


c.

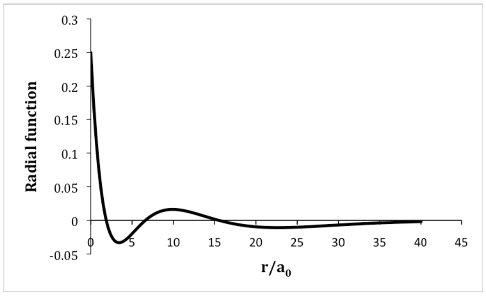
$3p_z$

For contour map, see Figure 2.8.

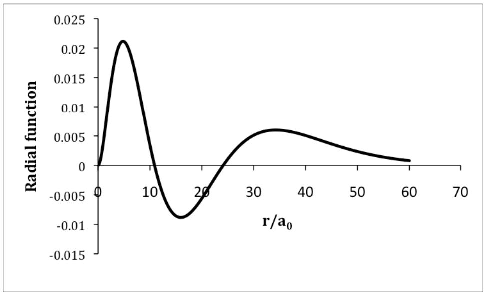
$4d_{xz}$



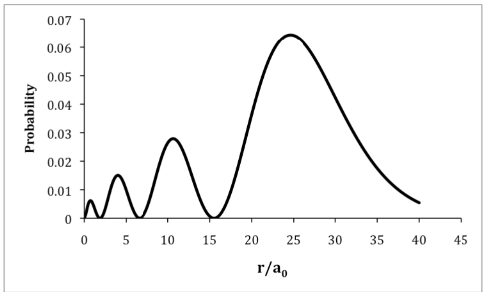
2.10 **a.** 4*s*



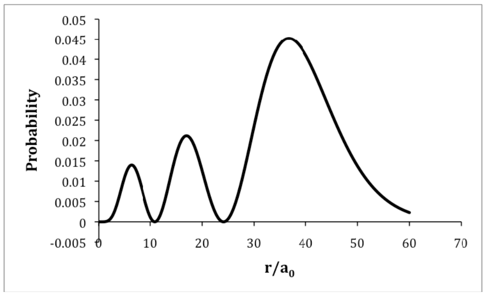
$5d_{x^2-y^2}$



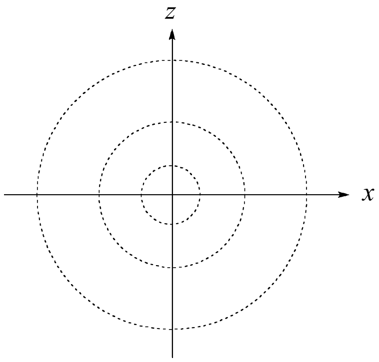
b. 4*s*



$5d_{x^2-y^2}$

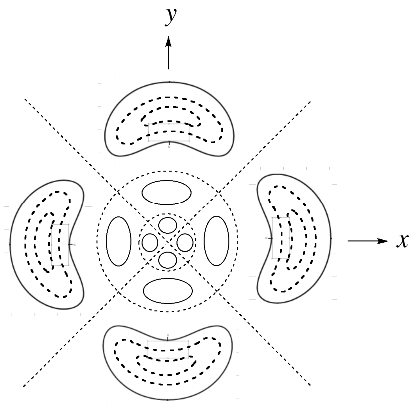


c. 4*s*

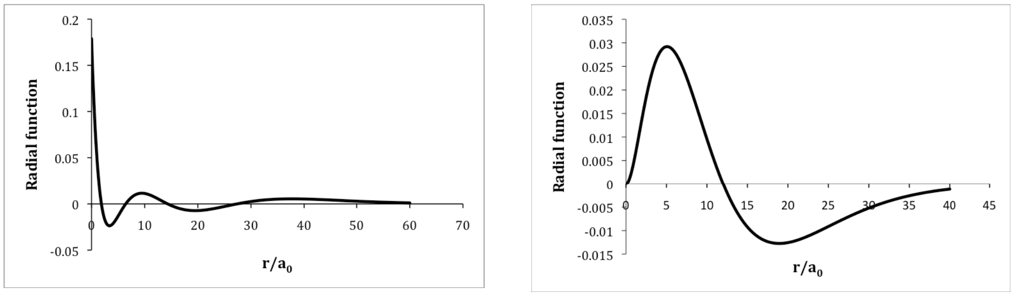


Dashed circles represent radial nodes. Electron density is inside the smallest node, between the nodes, and outside the largest node.

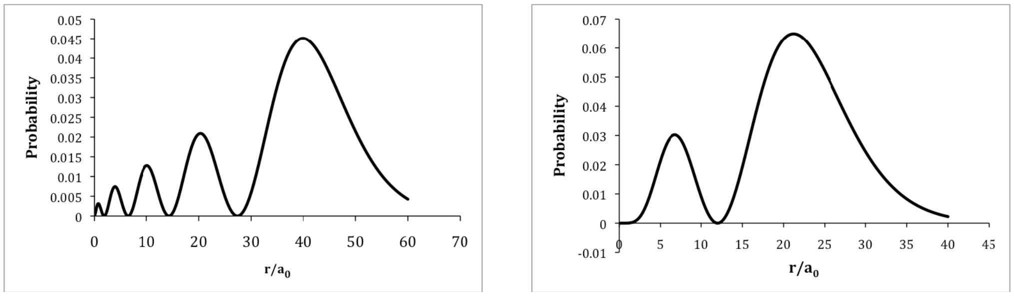
$5d_{x^2-y^2}$



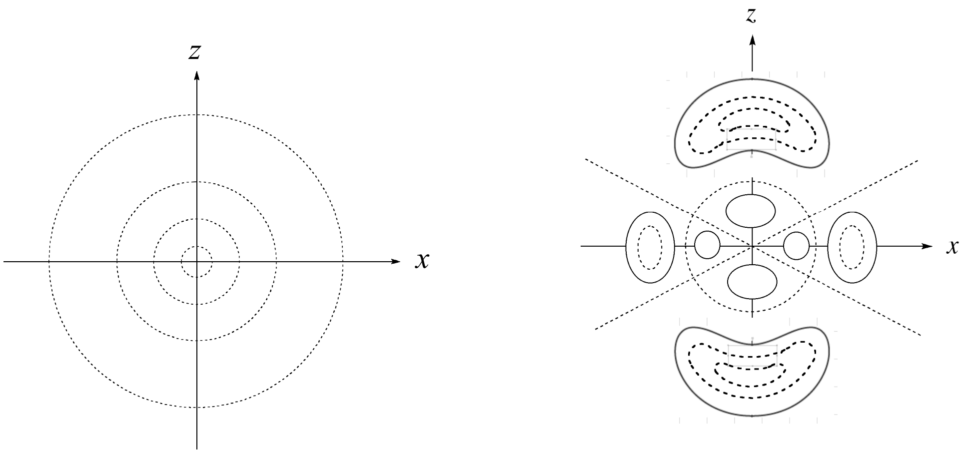
2.11 **a.** 5*s* 4d_{z^2}



b. 5*s* 4d_{z^2}



c. 5*s* 4d_{z^2}



Dashed circles represent radial nodes. Electron density is inside the smallest node, between the nodes, and outside the largest node.

2.12 $4f_{z(x^2-y^2)}$ orbital

a. no radial nodes (The number of radial nodes = $n - l - 1$. Since $n = 4$ and $l = 3$ for f orbitals, $n - l - 1 = 4 - 3 - 1 = 0$ radial nodes.)

b. 3 angular nodes (The number of angular nodes = $l = 3$.)

c. The angular nodes are solutions for $z(x^2 - y^2) = 0$. These solutions are $z = 0$ (xy plane), and the planes where $x = y$ and $x = -y$, both perpendicular to the xy plane.

d. There are 8 lobes, 4 above and 4 below the xy plane. Down the z axis, this orbital looks like a $d_{x^2-y^2}$ orbital, but the node at the xy plane splits each lobe in two. For an image of this orbital, please see http://winter.group.shef.ac.uk/orbitron/ or another atomic orbital site on the Web.

2.13 A $5f_{xyz}$ orbital has the same general shape as the $4f_{z(x^2-y^2)}$, with the addition of a radial node and rotation so the lobes are between the xy, xz, and yz planes.

a. 1 radial node ($= n - l - 1$, as in problem 2.12)

b. 3 angular nodes ($= l$)

c. The angular nodes are solutions for $xyz = 0$. These solutions are the three planes where $x = 0$ (yz plane), $y = 0$ (xz plane), and $z = 0$ (xy plane).

d. The diagram is similar to that in problem 2.12, with a radial node added and rotated by 45° around the z axis. There are 8 lobes, one in each octant of the coordinate system, both inside and outside the radial node, for a total of 16 lobes. For an image of this orbital, please see http://winter.group.shef.ac.uk/orbitron/ or another atomic orbital site on the Web.

2.14 **a.** no radial nodes ($= n - l - 1$, as in problem 2.12)

b. 3 angular nodes ($= l$)

c. The angular nodes are solutions for $z(5z^2 - 3r^2) = 0$
Solutions are $z = 0$ (the xy plane) and $5z^2 - 3r^2 = 0$, or $5z^2 = 3r^2$
Because $r^2 = x^2 + y^2 + z^2$ we can write

$$5z^2 = 3(x^2 + y^2 + z^2)$$
$$2z^2 = 3x^2 + 3y^2$$
$$z^2 = 3/2\,(x^2 + y^2)$$

This is the equation for a (double) cone.

d. For an image of this orbital, please see http://winter.group.shef.ac.uk/orbitron/ or another atomic orbital site on the Web.

2.15 **a.**

	n	l	m_l
$5d$	5	2	–2,–1,0,1,2
$4f$	4	3	–3,–2,–1,0,1,2,3
$7g$	7	4	–4,–3,–2,–1,0,1,2,3,4

b.

	n	l	m_l	m_s
$3d$	3	2	–2	$\pm\frac{1}{2}$
	3	2	–1	$\pm\frac{1}{2}$
	3	2	0	$\pm\frac{1}{2}$
	3	2	1	$\pm\frac{1}{2}$
	3	2	2	$\pm\frac{1}{2}$

10 possible combinations

c. For f orbitals ($l = 3$) possible values of m_l are –3, –2, –1, 0, 1, 2, and 3.

d. 2. (No more than 2 electrons can occupy any orbital!)

2.16 **a.** For a $5d$ electron, $l = 2$ and $n = 5$.

b. At most there can be ten $4d$ electrons, half of which can have $m_s = -\frac{1}{2}$.

c. f electrons have quantum number $l = 3$ and can have m_l = –3, –2, –1, 0, 1, 2, or 3.

d. For $l = 4$ (g electrons), m_l can be –4, –3, –2, –1, 0, 1, 2, 3, or 4.

2.17 **a.** The l quantum number limits the number of electrons. For $l = 3$, m_l can have seven values (–3 to +3) each defining an atomic orbital, and for each value of m_l the value of m_s can be $-\frac{1}{2}$ or $+\frac{1}{2}$; there can be two electrons in each orbital. At most, therefore, there can be 14 electrons with $n = 5$ and $l = 3$.

b. A $5d$ electron has $l = 2$, limiting the possible values of m_l to –2, –1, 0, 1, and 2.

c. p orbitals have $l = 1$ and occur for $n \geq 2$.

d. g orbitals have $l = 4$. There are 9 possible values of m_l and therefore 9 orbitals.

2.18 **a.**

↑__ ↑__ One exchange $E = \Pi_e$	↑↓__ __ One pair in same orbital $E = \Pi_c$	The first configuration is favored. This configuration is stabilized by Π_e (which is negative), and the second is destabilized by Π_c (which is positive).

b.

↑__ ↑__ ↑__ 3 exchanges (1–2, 1–3, 2–3) $E = 3\,\Pi_e$	and ↑↓__ ↑__ __ 1 exchange, 1 pair $E = \Pi_e + \Pi_c$	The first configuration is favored. It is stabilized by $2\Pi_e$ more than the second configuration, and the second configuration is also destabilized by Π_c.

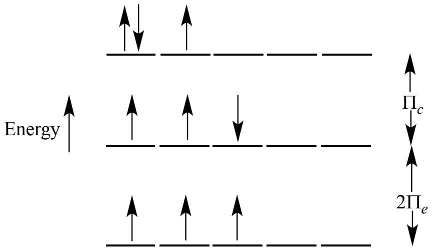
2.19

W: ↑__ ↑__ ↓__ ↓__ 2 exchanges (1–2, 3–4) $E = 2\Pi_e$	**X**: ↑__ ↑__ ↑__ ↓__ 3 exchanges (1–2, 1–3, 2–3) $E = 3\Pi_e$, so this state has lower energy than **W** (because Π_e is negative).

2.20 **Y**: ↑ ↑ ↑ ↓ ↓
4 exchanges (1–2, 1–3, 2–3, 4–5); E = $4\Pi_e$

Z: ↑ ↑ ↑ ↑ ↓
6 exchanges (1–2, 1–3, 1–4, 2–3, 2–4, 3–4)
E = $6\Pi_e$, so this state has lower energy than **Y**. (because Π_e is negative).

2.21 Three states are possible: ↑ ↑ ↑ ___ ___ (three exchanges, $E = 3\Pi_e$); ↑ ↑ ↓ ___ ___ (one exchange, $E = \Pi_e$); ↑↓ ↑ ___ ___ ___ (one exchange and one pair, $E = \Pi_e + \Pi_c$). Energy ranking:



2.22 **a.** Figure 2.12 and the associated text explain this. Electron-electron repulsion is minimized by placing each electron in a separate orbital when the levels are close enough to allow it. At Cr, the second 4*s* electron has an energy higher than the lower five 3*d* electrons, and therefore the configuration is $4s^1\, 3d^5$.

b. Ti is $4s^2\, 3d^2$, since both 4*s* electrons have energies below that of the 3*d* electrons at that *Z*. For ions, the 3*d* levels move down in energy, and are below the 4*s* levels for all transition metal M^{2+} ions, so Cr^{2+} is [Ar] $3d^4$.

2.23 **a.** V $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^3$

b. Br $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^5$

c. Ru^{3+} $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}\, 4s^2\, 4p^6\, 4d^5$

d. Hg^{2+} $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^6\, 5s^2\, 4d^{10}\, 5p^6\, 4f^{14}\, 5d^{10}$

e. Sb $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^6\, 5s^2\, 4d^{10}\, 5p^3$

2.24 **a.** Rb^- [Kr] $5s^2$

b. Pt^{2-} [Xe] $6s^2\, 4f^{14}\, 5d^{10}$

2.25 Electrons fill into atomic orbitals to maximize the nuclear attraction they experience. The more attraction an electron experiences, the more it is stabilized, and the more its energy is reduced (the more negative its energy). The order of orbital filling from $n = 1$ to $n = 2$ to $n = 3$ is rationalized by increasing the most probable distances these orbitals offer their electrons. Note that the most probable distances (the distance *r* where the radial probability is maximized) are roughly the same for all orbitals of the same *n*. As the most probable distance increases, the nuclear charge an electron experiences is attenuated to a greater extent by shielding by other electrons with shorter most probable distances. The 1*s* orbital fills first since its electrons have the most unhindered exposure to the charge of the nucleus; these electrons are subsequently stabilized to the greatest extent. Electrons fill the $n = 2$ orbitals before the $n = 3$ orbitals due to the shorter most probable distance (and greater nuclear charge) offered by the former orbitals.

Within a shell (orbitals with the same n), orbital energies are governed by the varying penetration abilities of orbitals with different l values. Electrons experience an increased nuclear charge (and are stabilized more) when residing in orbitals that penetrate towards the nucleus, affording electrons a reasonable probability of being found much closer to the nucleus than the most probable distance. Examination of the radial probability functions for $n = 3$ (Figure 2.7) reveals that a 3*s* electron has a higher probability of being found closest to the nucleus (inner maximum in graph at say $0.5r$) relative to a 3*p* or 3*d* electron. A 3*d* electron has the lowest probability of being found at this distance from the nucleus; this orbital penetrates poorly and has no inner maximum. The order of filling within this shell reflects these relative penetration abilities; the 3*s* electrons are lower in energy than the 3*p* electrons, while the 3*d* electrons are the highest in energy of the electrons in the third shell.

2.26 **a.** When a fluorine atom gains an electron, it achieves the same electron configuration of the noble gas Ne, with all subshells filled.

b. Zn^{2+} has the configuration [Ar] $3d^{10}$, with a filled 3*d* subshell.

c. This configuration [Kr] $5s^1\ 4d^5$ has each electron outside the Kr core in a separate orbital and has the maximum number of electrons with parallel spins (6). In Mo, this configuration has a lower energy than [Kr] $5s^2\ 4d^4$. The greater stability of the s^1d^5 configuration is also found in the case of Cr (directly above Mo), but W (below Mo) has an s^2d^4 configuration. In Cr and Mo, the n*s* and (n-1)*d* subshells are sufficiently close in energy so that electron pairing is avoided.

2.27 **a.** Ag^+ has the configuration [Kr] $4d^{10}$, with a filled 4*d* subshell.

b. In Cm, the $s^2d^1f^7$ configuration enables the last eight electrons each to occupy a separate orbital with parallel spin. This minimizes Π_c in comparison with the alternative configuration, in which one *f* orbital would be occupied by an electron pair.

c. The ion Sn^{2+} has the configuration [Kr] $5s^2\ 4d^{10}$, with both the 5*s* and 4*d* subshells filled. This is an example of the "inert pair" effect, in which heavier elements of groups 13-16 often form compounds in which the oxidation states of these elements are 2 less than the final digit in the group number (other examples include Tl^+ and Bi^{3+}). The reasons for this phenomenon are much more complex than the ions' electron configurations; see N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, London, 1997, pp. 226-227 for useful comments.

2.28 **a.** Ti^{2+} has the configuration [Ar] $3d^2$; Ni^{2+} has the configuration [Ar] $3d^8$. In each case it should be noted that all the electrons outside the noble gas cores in these transition metal ions are *d* electrons, which occupy orbitals that are lower in energy than the 4*s* orbitals (see Figure 2.12(b) and the associated discussion).

b. The preferred configuration of Mn^{2+} is [Ar] $3d^5$. As in the examples in part a, the 3*d* orbitals of Mn^{2+} are lower in energy than the 4*s*. In addition, the configuration minimizes electron-electron repulsions (because each *d* electron is in a separate orbital) and maximizes the stabilizing effect of electrons with parallel spins (maximum Π_e).

2.29 a.

	$Z \quad (1s^2) \quad (2s^2\,2p^6) \quad (3s^2\,3p^n)$ $1 \quad 0.85 \quad 0.35$	Z^*	r
P	$15 - (2 \times 1 + 8 \times 0.85 + 4 \times 0.35) =$	4.8	106 pm
S	$16 - (2 \times 1 + 8 \times 0.85 + 5 \times 0.35) =$	5.45	102 pm
Cl	$17 - (2 \times 1 + 8 \times 0.85 + 6 \times 0.35) =$	6.1	99 pm
Ar	$18 - (2 \times 1 + 8 \times 0.85 + 7 \times 0.35) =$	6.75	98 pm

The size of the atoms decreases slightly as *Z* increases, even though the number of electrons in the atom increases, because Z^* increases and draws the electrons closer. Ar has the strongest attraction between the nucleus and the 3*p* electron, and the smallest radius.

b.

	$Z \quad (1s^2) \quad (2s^2\,2p^6)$ $0.85 \quad 0.35$	Z^*	r
O^{2-}	$8 - (2 \times 0.85 + 7 \times 0.35) =$	3.85	126 pm
F^-	$9 - (2 \times 0.85 + 7 \times 0.35) =$	4.85	119 pm
Na^+	$11 - (2 \times 0.85 + 7 \times 0.35) =$	5.85	116 pm
Mg^{2+}	$12 - (2 \times 0.85 + 7 \times 0.35) =$	6.85	86 pm

These values increase directly with *Z*, and parallel the decrease in ionic size. Increasing nuclear charge results in decreasing size for these isoelectronic ions, although the change between F^- and Na^+ is smaller than might be expected.

c.

Cu $(1s^2)\,(2s^2\,2p^6)\quad(3s^2\,3p^6)\quad(3d^{10})\,(4s^1)$

4*s* $S = 2 + 8 + (8 \times 0.85) + (10 \times 0.85) = 25.3 \qquad Z^* = 29 - 25.3 = 3.7$

3*d* $S = 2 + 8 + (8 \times 1.00) + (9 \times 0.35) = 21.15 \qquad Z^* = 29 - 21.15 = 7.85$

The 3*d* electron has a much larger effective nuclear charge and is held more tightly; the 4*s* electron is therefore the first removed on ionization.

d.

$(1s^2)\,(2s^2\,2p^6)\,(3s^2\,3p^6)\,(3d^{10})\,(4s^2\,4p^6)\,(4d^{10})\,(4f^n)$

Ce $S = 2 + 8 + 8 + 10 + 8 + 10 = 46$

$[Xe]\,6s^2\,4f^1\,5d^1 \qquad 4f^1 \qquad Z^* = 58 - 46 = 12$

Pr $S = 2 + 8 + 8 + 10 + 8 + 10 + (2 \times 0.35) = 46.7$

$[Xe]\,6s^2\,4f^3 \qquad 4f^3 \qquad Z^* = 59 - 46.7 = 12.3$

Nd $S = 2 + 8 + 8 + 10 + 8 + 10 + (3 \times 0.35) = 47.05$

$[Xe]\,6s^2\,4f^4 \qquad 4f^4 \qquad Z^* = 60 - 47.05 = 12.95$

The outermost electrons experience an increasing Z^*, and are therefore drawn in to slightly closer distances with increasing *Z* and Z^*.

2.30

3*d* electron:

	Sc:	Ti:
Electron configuration	$(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^1)(4s^2)$	$(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^2)(4s^2)$
Contribution of other *d* electrons	None [only one electron in $(3d^1)$]	One other 3*d* electron: Contribution to $S = 1 \times 0.35 = 0.35$
Contribution of electrons to left of $(3d^n)$	18 × 1.00 = 18.00	18 × 1.00 = 18.00
Total *S*	18.00	18.35
Z^*	21 – 18.00 = 3.00	22 – 18.35 = 3.65

4*s* electron:

	Sc:	Ti:
Electron configuration	$(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^1)(4s^2)$	$(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^2)(4s^2)$
Contribution of other $(4s^2)$ electron	Contribution to $S = 0.35$	Contribution to $S = 0.35$
Contribution of $(3s^2, 3p^6)(3d^n)$ electrons	9 × 0.85 = 7.65	10 × 0.85 = 8.50
Contribution of other electrons	10 × 1.00 = 10.00	10 × 1.00 = 10.00
Total *S*	0.35 + 7.65 + 10.00 = 18.00	0.35 + 8.50 + 10.00 = 18.85
Z^*	21 – 18.00 = 3.00	22 – 18.85 = 3.15

In scandium, Slater's rules give the same value for the effective nuclear charge Z^* for the 3*d* and 4*s* electrons, consistent with the very similar energies of these orbitals. In Ti the effective nuclear charge is slightly less for 4*s* than for 3*d*, by 0.50. This difference in the energies of 4*s* and 3*d* increases across the row of transition metals; by nickel, as calculated in the example in Section 2.2.4, the 4*s* orbital has an effective nuclear charge 3.50 less than the 3*d* orbitals.

This is consistent with the experimental observation that transition metal cations have electron configurations in which there are no valence *s* electrons; the 3*d* orbitals are lower in energy than the 4*s* orbital, so *d* orbitals are the ones that are occupied. A similar phenomenon is observed for the second and third row transition metals.

2.31 N $Z^* = 7 - (2 \times 0.85 + 4 \times 0.35) = 3.9$ IE = 1.402 MJ/mol $r = 75$ pm

P $Z^* = 15 - (2 \times 1 + 8 \times 0.85 + 4 \times 0.35) = 4.80$ IE = 1.012 MJ/mol $r = 106$ pm

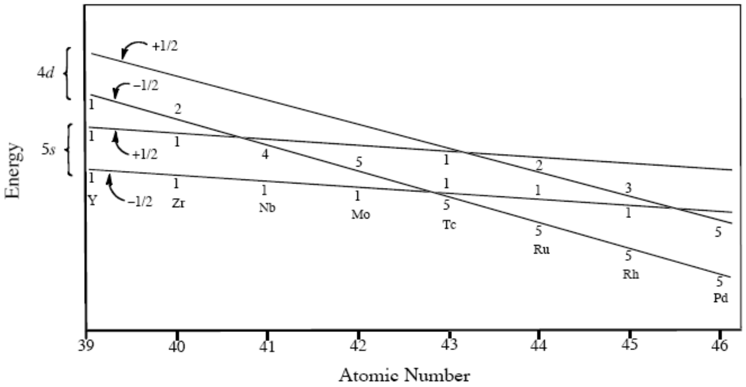
As $Z^* = 33 - (2 \times 1 + 8 \times 1 + 18 \times 0.85 + 4 \times 0.35) = 6.3$ IE = 0.947 MJ/mol $r = 120$ pm

The effect of shielding alone is not sufficient to explain the changes in ionization energy. The other major factor is distance between the electron and the nucleus. Wulfsberg (*Principles of Descriptive Inorganic Chemistry*, Brooks/Cole, 1998) suggests that Z^*/r^2 correlates better, but As is still out of order:

	radius(pm)	Z^*/r^2
N	75	6.93×10^{-4}
P	106	4.27×10^{-4}
As	120	4.375×10^{-4}

2.32 Zr through Pd have the electron configurations shown here:

40	Zr	$5s^2\ 4d^2$
41	Nb	$5s^1\ 4d^4$
42	Mo	$5s^1\ 4d^5$
43	Tc	$5s^2\ 4d^5$
44	Ru	$5s^1\ 4d^7$
45	Rh	$5s^1\ 4d^8$
46	Pd	$4d^{10}$



The lower *d* line crosses the upper *s* line between elements 40 and 41, the upper *d* line crosses the upper *s* line between 43 and 44, and the upper *d* line crosses the lower *s* line between 45 and 46. This graph fits the experimental configurations well.

2.33	Li	>	Na	>	K	>	Rb
IE	5.39		5.14		4.34		4.18
Z^*	1.30		2.20		2.20		2.20
r(pm, covalent)	123		154		203		216
Z^*/r^2	8.59		9.28		5.34		4.72 (all $\times\ 10^{-5}$ pm^{-2})
r(pm, ionic)	90		116		152		166
Z^*/r^2	16.0		16.3		9.52		7.98 (all $\times\ 10^{-5}$ pm^{-2})

The Z^*/r^2 function explains the order, except for lithium, which seems to require more energy for removal of the electron than predicted. Apparently the very small size and small number of electrons on lithium result in the electron being held more tightly than in the other alkali metals. The Z^*/r^2 function also predicts larger differences between the IE values than are observed.

2.34 C^+ $(1s^2)$ $(2s^2\ 2p^1)$

$$Z^* = 6 - (2 \times 0.85 + 2 \times 0.35) = 3.6$$

B $(1s^2)$ $(2s^2\ 2p^1)$

$$Z^* = 5 - (2 \times 0.85 + 2 \times 0.35) = 2.6$$

The energies change by a factor of approximately three, but Z^* changes only by 38%. Based on the data in Table 2.8 and the relative ionic and covalent sizes in problem 2.33, C^+ has a radius of about 58 pm, B a radius of about 83 pm. Z^*/r^2 values are then 10.7×10^{-4} and 3.8×10^{-4}, a ratio of 2.8. The ionization energies have a ratio of 2.99. This function of size and effective charge explains this pair quite well.

2.35 The maxima at 4 electrons correspond to the isoelectronic species Li^-, Be, and B^+ $(1s^2\ 2s^2)$ changing to Li, Be^+, and B^{2+}, respectively $(1s^2\ 2s^1)$**.** The energy requirement to remove electrons from species with completely filled subshells is generally relatively high. The minima at 5 electrons correspond to the isoelectronic species Be^-, B, and C^+ $(1s^2\ 2s^2\ 2p^1)$ changing to Be, B^+, and C^{2+}, respectively $(1s^2\ 2s^2)$. The removal of an electron from a singly occupied subshell requires relatively less energy. These data support the stability of the $1s^2\ 2s^2$ electronic configuration.

2.36 **a.** He and H cannot form +3 cations; the first element under consideration is therefore Li. The third ionization energy of Be^{2+} is expected to be a local maximum on the basis of removing an electron from a $1s^2$ configuration. The third ionization energy of B^{2+} $(1s^2\ 2s^1)$ will be a local minimum on the basis of removing an electron from a singly occupied subshell. The third ionization energy of $\mathrm{C}^{2+}(1s^2\ 2s^2)$ will be a local maximum on the basis of the removal of an electron from a filled subshell. The corresponding energies for N^{2+} $(1s^2\ 2s^2\ 2p^1)$ and Ne^{2+} $(1s^2\ 2s^2\ 2p^4)$ will be local minima on the graph on the basis of removal of an electron from a singly filled subshell, and the formation of a 2*p* subshell with three unpaired electrons (and no coulombic repulsion), respectively. Finally, there will be a maximum at Mg^{2+},which has a filled $n = 2$ subshell and a configuration matching that of neutral Ne.

b. The graph will share the common features of local maxima at 2 and 4 electrons, and local minima at 3, 5, and 8 electrons, as detailed above. The magnitudes of these third ionization energies are all greater than the corresponding second ionization energies for the same electronic configurations.

2.37 Because the second ionization energies involve removing an electron from an ion with a single positive charge, the electron configurations of the cations must be considered:

He^+	$1s^1$	N^+	$1s^2\,2s^2\,2p^2$
Li^+	$1s^2$	O^+	$1s^2\,2s^2\,2p^3$
Be^+	$1s^2\,2s^1$	F^+	$1s^2\,2s^2\,2p^4$
B^+	$1s^2\,2s^2$	Ne^+	$1s^2\,2s^2\,2p^5$
C^+	$1s^2\,2s^2\,2p^1$		

The peaks and valleys now match the peaks and valleys for electron configurations matching those of the atoms in the ionization energy graph in Figure 2.13. For example, because there is a minimum in the ionization energy for Li (electron configuration $1s^2 2s^1$), there should also be a minimum in the graph of second ionization energy for Be^+, which also has the configuration $1s^2 2s^1$. The maximum in the ionization energy for Be (configuration $1s^2 2s^2$) would be matched by a maximum in the second ionization graph for B^+, which has the same configuration as Be. Overall, the maxima and minima in the two graphs are:

Maximum or Minimum	Configuration	1st IE	2nd IE (kJ/mol)	
Maximum	$1s^2$	He	Li^+	(7298)
Minimum	$1s^2 2s^1$	Li	Be^+	(1757)
Maximum	$1s^2 2s^2$	Be	B^+	(2427)
Minimum	$1s^2 2s^2 2p^1$	B	C^+	(2353)
	$1s^2 2s^2 2p^2$	C	N^+	(2856)
Maximum	$1s^2 2s^2 2p^3$	N	O^+	(3388)
Minimum	$1s^2 2s^2 2p^4$	O	F^+	(3374)
	$1s^2 2s^2 2p^5$	F	Ne^+	(3952)

2.38 **a.** Fe (7.87 eV) > Ru (7.37 eV) They have the same Z^* (6.25), but Ru is larger, so Z^*/r^2 is smaller than for Fe.

b. P (10.486 eV) > S (10.36 eV) Z^* is smaller for P (4.8) than for S (5.45), but S has one electron paired in the 3*p* level, which increases its energy and makes it easier to remove.

c. Br (11.814 eV) > K (4.341 eV) Z^* for K is 2.2; for Br it is 7.6, a very large difference. K is also nearly twice as large as Br. Both factors contribute to the difference in IE.

d. N (14.534) > C (11.260) Increasing Z^* (3.9 for N, 3.25 for C) and decreasing size (75 pm for N, 77 pm for C) both work in the same direction.

e. Cd (8.993 > In (5.786) Indium starts a new 5*p* subshell, so the last electron is easily removed in spite of a larger Z^* (2.30 for In, 1.65 for Cd).

f. The smaller F has a higher ionization energy (17.422) than Cl (12.967). An electron is more easily removed from the 3*p* subshell of Cl than from the smaller 2*p* subshell of F.

2.39 **a.** S (2.077 eV) has a smaller EA than Cl (3.617 eV) because Cl has a larger Z^* (6.1 vs. 5.45) and a slightly smaller radius. Both increase the attractive power for an electron.

b. I (3.059) has a smaller EA than Br (3.365) because it is larger, with the same Z^* (7.6).

c. B (8.298) has a smaller IE than Be (9.322) because it is starting a new *p* subshell.

d. S (10.360) has a smaller IE than P (10.486) because S is losing one of a pair of *p* electrons.

2.40 **a.** The maximum at Mg comes at a completed subshell ($3s^2$) and the minimum at Al is at the first electron of a new subshell (3*p*), increasing the energy and making removal of an electron easier. The maximum at P is at a half-filled subshell ($3p^3$) and the minimum at S is at the fourth $3p$ electron, which must pair with one of the others; this also raises the energy of the electron and makes its removal easier.

b. The reasons for the minima and maxima in the electron affinity graph are the same as in the ionization energy graph. The maxima and minima are shifted by one in the two graphs because the reactants in the process defining electron affinity have a negative charge, one more electron than a neutral atom. For example, minima occur for ionization energy at Al ($[\mathrm{Ne}]3s^23p^1 \rightarrow$) and for electron affinity at Mg (($[\mathrm{Ne}]3s^23p^1 \rightarrow$); Al and Mg^- have identical electron configurations.

2.41 The Bohr equation predicts that the energy levels of 1-electron systems should be proportional to Z^2. $Z^2 = 4$ for He^+ and 9 for Li^{2+}, so ratios of the ionization energies to that of H are 4:1 and 9:1.

2.42 In both the transition metals and the lanthanides (problem 2.29.d), the gradual change in Z^* pulls the outer electrons closer. The increase in Z^* is 0.65 for each unit increase in atomic number, so the increase in attraction is relatively small, and the change in radius must also be small.

2.43 **a.** $\mathrm{Se}^{2-} > \mathrm{Br}^- > \mathrm{Rb}^+ > \mathrm{Sr}^{2+}$ These ions are isoelectronic, so the sizes are directly dependent on the nuclear charges. For example, Sr^{2+} has the greatest nuclear charge and is the smallest ion.

b. $\mathrm{Y}^{3+} > \mathrm{Zr}^{4+} > \mathrm{Nb}^{5+}$ These ions are also isoelectronic, so the increasing nuclear charge results in decreasing size.

c. $\mathrm{Co}^{4+} < \mathrm{Co}^{3+} < \mathrm{Co}^{2+} < \mathrm{Co}$ The smaller number of electrons with constant nuclear charge results in a smaller size.

2.44 **a.** F^- has the largest radius. All three choices in this isoelectronic set have 10 electrons, and F^- has the fewest protons (9) to attract these electrons.

b. Te^{2-} has the largest volume. In general, atomic and ionic sizes increase going down a column of main group elements as the number of shells increases, with electrons closer to the nucleus shielding outer electrons from the full effect of the nuclear charge.

c. Mg, with a filled $3s$ subshell, has the highest ionization energy. The situation is similar to that in the second period, where Be has a higher ionization energy than Li and B.

d. Fe^{3+} has the greatest surplus of positive charge (26 protons, 23 neutrons), making it the smallest and the most difficult from which to remove an electron.

e. Of the anions O^-, F^-, and Ne^-, F^- has the configuration of the noble gas Ne, from which it is more difficult to remove an electron than from the other ions; F, therefore, has the highest electron affinity.

2.45 **a.** V is the smallest; the effective nuclear charge on the outer electrons increases across the row of transition metals.

b. These species are isoelectronic; each has 18 electrons. S^{2-}, which has the fewest protons, is therefore the largest.

c. The ionization energy is smallest for the largest alkali metals (weaker attraction between the nucleus and outermost electrons), so Cs has the lowest value.

d. The electron affinity is the greatest for the smallest halogens (stronger attraction between nucleus and outermost electrons), so Cl has the highest value.

e. The Cu^{2+} ion has the greatest surplus of protons and is therefore the smallest and the most difficult from which to remove an electron.

2.46 **a.** 7 orbitals

b. See images.

c. The number of radial nodes increases as n increases: *4f* orbitals have no radial nodes, 5*f* have one radial node, and so forth.

2.47 **a.** 9 orbitals

b. See images.

c. As in problem 2.46.c, with no radial nodes for 5*g*, one for 6*g*, etc.