

References

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General References

Additional information on the history of atomic theory can be found in J. R. Partington, *A Short History of Chemistry*, 3rd ed., Macmillan, London, 1957, reprinted by Harper & Row, New York, 1960, and in the *Journal of Chemical Education*. For an introduction to atomic theory and orbitals, see V. M. S. Gil, *Orbitals in Chemistry: A Modern Guide for Students*, Cambridge University Press, Cambridge, 2000, UK, pp. 1–69.

A more thorough treatment of the electronic structure of atoms is in M. Gerloch, *Orbitals, Terms, and States*, John Wiley & Sons, New York, 1986. Many Internet sites provide images of atomic orbitals, their wave equations, nodal behavior, and other characteristics. Two examples are <http://www.orbitals.com> and <http://winter.group.shef.ac.uk/orbitron>.

Problems

- 2.1 Determine the de Broglie wavelength of
 - a. an electron moving at 1/10 the speed of light.
 - b. a 400 g Frisbee moving at 10 km/h.
 - c. an 8.0-pound bowling ball rolling down the lane with a velocity of 2.0 meters per second.
 - d. a 13.7 g hummingbird flying at a speed of 30.0 miles per hour.
- 2.2 Using the equation $E = R_H \left(\frac{1}{2^2} - \frac{1}{n_h^2} \right)$, determine the energies and wavelengths of the visible emission bands in the atomic spectrum of hydrogen arising from $n_h = 4, 5,$ and 6 . (The red line, corresponding to $n_h = 3$, was calculated in Exercise 2.1.)
- 2.3 The transition from the $n = 7$ to the $n = 2$ level of the hydrogen atom is accompanied by the emission of radiation slightly beyond the range of human perception, in the ultraviolet region. Determine the energy and wavelength.
- 2.4 Emissions are observed at wavelengths of 383.65 and 379.90 nm for transitions from excited states of the hydrogen atom to the $n = 2$ state. Determine the quantum numbers n_h for these emissions.
- 2.5 What is the least amount of energy that can be emitted by an excited electron in a hydrogen atom falling from an excited state directly to the $n = 3$ state? What is the quantum number n for the excited state? Humans cannot visually observe the photons emitted in this process. Why not?
- 2.6 Hydrogen atom emission spectra measured from the solar corona indicated that the $4s$ orbital was $102823.8530211 \text{ cm}^{-1}$, and $3s$ orbital $97492.221701 \text{ cm}^{-1}$, respectively, above the $1s$ ground state. (These energies have tiny uncertainties, and can be treated as exact numbers for the sake of this problem.) Calculate the difference in energy (J) between these levels on the basis of these data, and compare this difference to that

obtained by the Balmer equation in Section 2.1.2. How well does the Balmer equation work for hydrogen? (Data from Y. Ralchenko, A. E. Kramida, J. Reader, and NIST ASD Team (2011). *NIST Atomic Spectra Database* (ver. 4.1.0), [Online]. Available: <http://physics.nist.gov/asd> [2012, January 18]. National Institute of Standards and Technology, Gaithersburg, MD.)

- 2.7 The Rydberg constant equation has two terms that vary depending on the species under consideration, the reduced mass of the electron/nucleus combination and the charge of the nucleus (Z).
- Determine the approximate *ratio* between the Rydberg constants for isoelectronic He^+ (consider the most abundant helium-4 isotope) and H. The masses of the electron, proton, and that of the He^+ nucleus (He^{2+} is an α particle) are given on the inside back cover of this text.
 - Use this ratio to calculate an approximate Rydberg constant (J) for He^+ .
 - The difference between the He^+ $2s$ and $1s$ orbitals was reported as $329179.76197(20) \text{ cm}^{-1}$. Calculate the He^+ Rydberg constant from this spectral line for comparison to your value from **b**. (Data from the same reference as Problem 2.6.)
- 2.8 The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:
- Show that if $\Psi = A \sin rx + B \cos sx$ (A, B, r , and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE} \left(\frac{2\pi}{h} \right)$$
 - Show that if $\Psi = A \sin rx$, the boundary conditions ($\Psi = 0$ when $x = 0$ and $x = a$) require that $r = \pm \frac{n\pi}{a}$, where $n =$ any integer other than zero.
 - Show that if $r = \pm \frac{n\pi}{a}$, the energy levels of the particle are given by $E = \frac{n^2 h^2}{8ma^2}$.
 - Show that substituting the value of r given in part **c** into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.
- 2.9 For the $3p_z$ and $4d_{xz}$ hydrogen-like atomic orbitals, sketch the following:
- The radial function R
 - The radial probability function $a_0 r^2 R^2$
 - Contour maps of electron density.
- 2.10 Repeat the exercise in Problem 2.9, for the $4s$ and $5d_{x^2-y^2}$ orbitals.
- 2.11 Repeat the exercise in Problem 2.9, for the $5s$ and $4d_{z^2}$ orbitals.
- 2.12 The $4f_{z(x^2-y^2)}$ orbital has the angular function $Y = (\text{constant}) z(x^2 - y^2)/r^3$.
- How many radial nodes does this orbital have?
 - How many angular nodes does it have?
 - Write equations to define the angular nodal surfaces. What shapes are these surfaces?
 - Sketch the shape of the orbital, and show all radial and angular nodes.
- 2.13 Repeat the exercise in Problem 2.12, for the $5f_{xyz}$ orbital, which has $Y = (\text{constant}) xyz/r^3$.
- 2.14 The label for an f_{z^3} orbital, like that for a d_{z^2} orbital, is an abbreviation. The actual angular function for this orbital is $Y = (\text{constant}) \times z(5z^2 - 3r^2)/r^3$. Repeat the exercise in Problem 2.12, for a $4f_{z^3}$ orbital. (Note: recall that $r^2 = x^2 + y^2 + z^2$).
- 2.15
- Determine the possible values for the l and m_l quantum numbers for a $5d$ electron, a $4f$ electron, and a $7g$ electron.
 - Determine the possible values for all four quantum numbers for a $3d$ electron.
 - What values of m_l are possible for f orbitals?
 - At most, how many electrons can occupy a $4d$ orbital?
- 2.16
- What are the values of quantum numbers l and n for a $5d$ electron?
 - At most, how many $4d$ electrons can an atom have? Of these electrons how many, at most, can have $m_s = -\frac{1}{2}$?
 - A $5f$ electron has what value of quantum number l ? What values of m_l may it have?
 - What values of the quantum number m_l are possible for a subshell having $l = 4$?
- 2.17
- At most, how many electrons in an atom can have both $n = 5$ and $l = 3$?
 - A $5d$ electron has what possible values of the quantum number m_l ?
 - What value of quantum number l do p orbitals have? For what values of n do p orbitals occur?
 - What is the quantum number l for g orbitals? How many orbitals are in a g subshell?
- 2.18 Determine the Coulombic and exchange energies for the following states, and determine which state is favored (has lower energy):
- $\uparrow \quad \uparrow \quad \uparrow \quad \uparrow$ and $\uparrow \downarrow \quad \uparrow \quad \uparrow$
 - $\uparrow \quad \uparrow \quad \uparrow \quad \uparrow$ and $\uparrow \downarrow \quad \uparrow \quad \uparrow$
- 2.19 Two excited states for a d^4 configuration are shown. Which is likely to have lower energy? Explain your choice in terms of Coulombic and exchange energies.
- W: $\uparrow \quad \uparrow \quad \downarrow \quad \downarrow$
- X: $\uparrow \quad \uparrow \quad \uparrow \quad \downarrow$
- 2.20 Two excited states for a d^5 configuration are shown. Which is likely to have lower energy? Why? Explain your choice in terms of Coulombic and exchange energies.
- Y: $\uparrow \quad \uparrow \quad \uparrow \quad \downarrow \quad \downarrow$
- Z: $\uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \downarrow$

- 2.21 What states are possible for a d^3 configuration? Determine the Coulombic and exchange energies for each, and rank the states in terms of relative energy.
- 2.22 Provide explanations of the following phenomena:
- The electron configuration of Cr is $[\text{Ar}] 4s^1 3d^5$ rather than $[\text{Ar}] 4s^2 3d^4$.
 - The electron configuration of Ti is $[\text{Ar}] 4s^2 3d^2$, but that of Cr^{2+} is $[\text{Ar}] 3d^4$.
- 2.23 Give electron configurations for the following:
- V
 - Br
 - Ru^{3+}
 - Hg^{2+}
 - Sb
- 2.24 Predict the electron configurations of the following metal anions:
- Rb^-
 - Pt^{2-} (See: A. Karbov, J. Nuss, U. Weding, M. Jansen, *Angew. Chem. Int. Ed.*, **2003**, *42*, 4818.)
- 2.25 Radial probability plots shed insight on issues of shielding and effective nuclear charge. Interpret the radial probability functions in Figure 2.7 to explain why the general order of orbital filling is $n = 1$, followed by $n = 2$, followed by $n = 3$. Interpret the graphs for $3s$, $3p$, and $3d$ to rationalize the filling order for these orbitals.
- 2.26 Briefly explain the following on the basis of electron configurations:
- Fluorine forms an ion having a charge of $1-$.
 - The most common ion formed by zinc has a $2+$ charge.
 - The electron configuration of the molybdenum atom is $[\text{Kr}] 5s^1 4d^5$ rather than $[\text{Kr}] 5s^2 4d^4$.
- 2.27 Briefly explain the following on the basis of electron configurations:
- The most common ion formed by silver has a $1+$ charge.
 - Cm has the outer electron configuration $s^2 d^1 f^7$ rather than $s^2 f^8$.
 - Sn often forms an ion having a charge of $2+$ (the *stannous* ion).
- 2.28
- Which $2+$ ion has two $3d$ electrons? Which has eight $3d$ electrons?
 - Which is the more likely configuration for Mn^{2+} : $[\text{Ar}] 4s^2 3d^3$ or $[\text{Ar}] 3d^5$?
- 2.29 Using Slater's rules, determine Z^* for
- a $3p$ electron in P, S, Cl, and Ar. Is the calculated value of Z^* consistent with the relative sizes of these atoms?
 - a $2p$ electron in O^{2-} , F^- , Na^+ and Mg^{2+} . Is the calculated value of Z^* consistent with the relative sizes of these ions?
 - a $4s$ and a $3d$ electron of Cu. Which type of electron is more likely to be lost when copper forms a positive ion?
 - a $4f$ electron in Ce, Pr, and Nd. There is a decrease in size, commonly known as the **lanthanide contraction**, with increasing atomic number in the lanthanides. Are your values of Z^* consistent with this trend?
- 2.30 A sample calculation in this chapter showed that, according to Slater's rules, a $3d$ electron of nickel has a higher effective nuclear charge than a $4s$ electron. Is the same true for early first-row transition metals? Using Slater's rules, calculate S and Z^* for $4s$ and $3d$ electrons of Sc and Ti, and comment on the similarities or differences with Ni.
- 2.31 Ionization energies should depend on the effective nuclear charge that holds the electrons in the atom. Calculate Z^* (Slater's rules) for N, P, and As. Do their ionization energies seem to match these effective nuclear charges? If not, what other factors influence the ionization energies?
- 2.32 Prepare a diagram such as the one in Figure 2.12(a) for the fifth period in the periodic table, elements Zr through Pd. The configurations in Table 2.7 can be used to determine the crossover points of the lines. Can a diagram be drawn that is completely consistent with the configurations in the table?
- 2.33 Why are the ionization energies of the alkali metals in the order $\text{Li} > \text{Na} > \text{K} > \text{Rb}$?
- 2.34 The second ionization of carbon ($\text{C}^+ \longrightarrow \text{C}^{2+} + e^-$) and the first ionization of boron ($\text{B} \longrightarrow \text{B}^+ + e^-$) both fit the reaction $1s^2 2s^2 2p^1 \longrightarrow 1s^2 2s^2 + e^-$. Compare the two ionization energies (24.383 eV and 8.298 eV, respectively) and the effective nuclear charge Z^* . Is this an adequate explanation of the difference in ionization energies? If not, suggest other factors.
- 2.35 Explain why all three graphs in Figure 2.14 have maxima at 4 electrons and minima at 5 electrons.
- 2.36
- For a graph of third ionization energy against atomic number, predict the positions of peaks and valleys for elements through atomic number 12. Compare the positions of these peaks and valleys with those for first ionization energies shown in Figure 2.13.
 - How would a graph of third ionization energies against the number of electrons in reactant compare with the other graphs shown in Figure 2.14? Explain briefly.
- 2.37 The second ionization energy involves removing an electron from a positively charged ion in the gas phase (see preceding problem). How would a graph of second ionization energy vs. atomic number for the elements helium through neon compare with the graph of first ionization energy in Figure 2.13? Be specific in comparing the positions of peaks and valleys.
- 2.38 In each of the following pairs, pick the element with the higher ionization energy and explain your choice.
- Fe, Ru
 - P, S
 - K, Br
 - C, N
 - Cd, In
 - Cl, F

- 2.39 On the basis of electron configurations, explain why
- sulfur has a lower electron affinity than chlorine.
 - iodine has a lower electron affinity than bromine.
 - boron has a lower ionization energy than beryllium.
 - sulfur has a lower ionization energy than phosphorus.
- 2.40 a. The graph of ionization energy versus atomic number for the elements Na through Ar (Figure 2.13) shows maxima at Mg and P and minima at Al and S. Explain these maxima and minima.
- b. The graph of electron affinity versus atomic number for the elements Na through Ar (Figure 2.13) also shows maxima and minima, but shifted by one element in comparison with the ionization energy graph. Why are the maxima and minima shifted in this way?
- 2.41 The second ionization energy of He is almost exactly four times the ionization energy of H, and the third ionization energy of Li is almost exactly nine times the ionization energy of H:

	IE (MJ mol ⁻¹)
$\text{H}(g) \longrightarrow \text{H}^+(g) + e^-$	1.3120
$\text{He}^+(g) \longrightarrow \text{He}^{2+}(g) + e^-$	5.2504
$\text{Li}^{2+}(g) \longrightarrow \text{Li}^{3+}(g) + e^-$	11.8149

Explain this trend on the basis of the Bohr equation for energy levels of single-electron systems.

- 2.42 The size of the transition-metal atoms decreases slightly from left to right in the periodic table. What factors must be considered in explaining this decrease? In particular, why does the size decrease at all, and why is the decrease so gradual?
- 2.43 Predict the largest and smallest radius in each series, and account for your choices:

- Se^{2-} Br^- Rb^+ Sr^{2+}
- Y^{3+} Zr^{4+} Nb^{5+}
- Co^{4+} Co^{3+} Co^{2+} Co

- 2.44 Select the best choice, and briefly indicate the reason for each choice:

- Largest radius: Na^+ Ne F^-
- Greatest volume: S^{2-} Se^{2-} Te^{2-}
- Highest ionization energy: Na Mg Al
- Most energy necessary to remove an electron: Fe Fe^{2+} Fe^{3+}
- Highest electron affinity: O F Ne

- 2.45 Select the best choice, and briefly indicate the reason for your choice:

- Smallest radius: Sc Ti V
- Greatest volume: S^{2-} Ar Ca^{2+}
- Lowest ionization energy: K Rb Cs
- Highest electron affinity: Cl Br I
- Most energy necessary to remove an electron: Cu Cu^+ Cu^{2+}

- 2.46 There are a number of Web sites that display atomic orbitals. Use a search engine to find a complete set of the *f* orbitals.

- How many orbitals are there in one set (for example, a set of 4*f* orbitals)?
 - Describe the angular nodes of the orbitals.
 - Observe what happens to the number of radial nodes as the principal quantum number is increased.
 - Include the URL for the site you used for each, along with sketches or printouts of the orbitals. (Two useful Web sites at this writing are orbitals.com and winter.group.shef.ac.uk/orbitron.)
- 2.47 Repeat the exercise in Problem 2.46, this time for a set of *g* orbitals.