

Descriptive Inorganic Chemistry

Sixth Edition

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Geoff Rayner-Canham
Tina Overton

5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar

25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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■ >10-25%

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DESCRIPTIVE INORGANIC CHEMISTRY

SIXTH EDITION

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What Is Descriptive Inorganic Chemistry?

Descriptive inorganic chemistry was traditionally concerned with the properties of the elements and their compounds. Now, in the renaissance of the subject, the properties are being linked with explanations for the formulas and structures of compounds together with an understanding of the chemical reactions they undergo. In addition, we are no longer looking at inorganic chemistry as an isolated subject but as a part of essential scientific knowledge with applications throughout science and our lives. And it is because of a need for greater contextualization that we have added more relevance by means of the new chapter openers: **CONTEXT**.

In many colleges and universities, descriptive inorganic chemistry is offered as a sophomore or junior course. In this way, students come to know something of the fundamental properties of important and interesting elements and their compounds. Such knowledge is important for careers not only in pure or applied chemistry but also in pharmacy, medicine, geology, environmental science, and other scientific fields. This course can then be followed by a junior or senior course that focuses on the theoretical principles and the use of spectroscopy to a greater depth than is covered in a descriptive text. In fact, the theoretical course builds nicely on the descriptive background. Without the descriptive grounding, however, the theory becomes sterile, uninteresting, and irrelevant.

This book was written to pass on to another generation our fascination with descriptive inorganic chemistry. Thus, the comments of the readers, both students and instructors, will be sincerely appreciated. Our current e-mail addresses are: gcanham@grenfell.mun.ca and T.L.Overton@hull.ac.uk.

PREFACE

Descriptive Inorganic chemistry goes beyond academic interest; it is an important part of our lives.

The role of inorganic chemistry in our lives is increasing. Thus, the sixth edition of *Descriptive Inorganic Chemistry* now has the following improvements:

Context: Each chapter opens with a *Context*, an aspect of inorganic chemistry which impinges on us in one way or another. Each of these contexts is intended to be thought-provoking and also ties in with an aspect of the chapter content.

Worked Examples: Sprinkled throughout the chapters, we have added *Worked Examples*, so that students can see how content relates to principles.

New Discoveries: In addition to some reorganization of content and an increased use of subheadings, we have added new discoveries to show that descriptive inorganic chemistry is alive and well as the twenty-first century progresses.

Predominance Diagrams: To provide a visual display of which species of an element or ion are present under specific conditions, comparative predominance diagrams have been added, where appropriate.

Chapter 1: The Electronic Structure of the Atom: A Review

Addition of discussion of f-orbitals.

Chapter 2: The Structure of the Periodic Table

Inclusion of relativistic effects.

Improved discussion of electron affinity patterns.

Chapter 3: Covalent Bonding and Molecular Spectroscopy

VSEPR theory now precedes molecular orbital theory.

Improvement of spectroscopy discussion.

Chapter 4: Metallic Bonding and Alloys

Expansion of discussion on alloys.

Addition of subsection on quasicrystals.

Chapter 5: Ionic Bonding and Solid-State Structures

Consolidation of solid-state structures into this one chapter.

Addition of a section on crystal defects and nonstoichiometric compounds.

Chapter 6: Why Compounds Exist—Inorganic Thermodynamics

Discussion on nonexistent compounds.

New section on lattice energies and comparative ion sizes and charges.

Chapter 7: Solvent Systems and Acid-Bases Behavior

Revised section on acid-base reactions of oxides.

Chapter 8: Oxidation and Reduction

Improved discussion of Frost diagrams.
Improved discussion of Pourbaix diagrams.

Chapter 9: Periodic Patterns

Revised section on the “knight’s move” relationship.
Revised section on the lanthanoid relationships.

Chapter 10: Hydrogen

New section on the trihydrogen ion.

Chapter 11: The Group 1 Elements: The Alkali Metals

Restructuring of chapter.

Chapter 12: The Group 2 Elements: The Alkaline Earth Metals

Restructuring of chapter.

Chapter 13: The Group 13 Elements

Minor changes.

Chapter 14: The Group 14 Elements

Revised comparison of carbon and silicon.
Additional subsection in carbides on MAX phases.

Chapter 15: The Group 15 Elements: The Pnictogens

Revised comparison of nitrogen and phosphorus.
Additional discussion of nitrogen species such as pentazole.

Chapter 16: The Group 16 Elements: The Chalcogens

Additional subsections on octaoxygen and dihydrogen dioxide.
New section on oxygen and the atmosphere.

Chapter 17: The Group 17 Elements: The Halogens

Restructuring of chapter.

Chapter 18: The Group 18 Elements: The Noble Gases

New section on compounds of helium, argon, and krypton.
New section on other xenon compounds.

Chapter 19: Transition Metal Complexes

More detailed discussion on crystal field theory.
New section on reaction mechanisms.

Chapter 20: The 3d Transition Metals

New section on the V-Cr-Mn triad.
New section on the Fe-Co-Ni triad.

Chapter 21: The 4d and 5d Transition Metals

Restructuring of chapter.

Chapter 22: The Group 12 Elements

Updating of chapter.

Chapter 23: Organometallic Chemistry

Updating of chapter.

Chapter 24: The Rare Earth, Actinoid, and Postactinoid Elements—web

Updating of chapter.

ANCILLARY SUPPORT

Student Support Resources

Book Companion Site

The *Descriptive Inorganic Chemistry* Book Companion Site, www.whfreeman.com/descriptive6e, contains the following student friendly materials:

- **Chapter 24** Although the lanthanoids, actinoids, and postactinoid elements are of interest and of increasing importance, as few instructors cover these elements, the chapter is only available on-line.
- **Appendices 9 and 10** To save space and paper, these lengthy appendices are also available on the Book Companion Site.
- **Video Demos** Chemistry is a visual subject, thus over 60 video demos are on-line to match reactions described in the text. The text has a margin symbol to identify where there is a corresponding video demo.
- **Laboratory Experiments** A series of experimental exercises are available to enable students to see a selection of the chemical reactions described in the text.

Student Solutions Manual

The *Student Solutions Manual*, ISBN: 1-4641-2560-0, contains the answers to the odd-numbered end-of-chapter questions.

The CourseSmart e-Textbook

The CourseSmart e-Textbook provides the full digital text, along with tools to take notes, search, and highlight passages. A free app allows access to CourseSmart e-Textbooks and Android and Apple devices, such as the iPad. They can also be downloaded to your computer and accessed without an Internet connection, removing any limitations for students when it comes to reading digital text. The CourseSmart e-Textbook can be purchased at www.coursesmart.com.

Instructor Resources

Book Companion Site

The password-protected instructor side of the Book Companion Site contains the *Instructor's Solutions Manual*, with answers to the even-numbered end-of-chapter questions, as well as all the illustrations and tables in the book, in .jpg and PowerPoint format.

Correlation of Descriptive Inorganic Chemistry, 6th Edition, with American Chemical Society Guidelines Committee on Professional Training, Inorganic Chemistry Supplement 2012

Each topic from the ACS guidelines listed below is followed by the corresponding chapter(s) in *Descriptive Inorganic Chemistry*, 6th edition, [DIC6] in brackets.

- Atomic Structure. Spectra and orbitals, ionization energy, electron affinity, shielding and effective nuclear charge. [DIC6, Chapter 1]
- Covalent Molecular Substances. Geometries (symmetry point groups), valence bond theory (hybridization, σ , π , δ bonds), molecular orbital theory (homonuclear and heteronuclear diatomics, multicentered MO, electron-deficient molecules, π -donor and acceptor ligands). [DIC6, Chapter 3 (and parts of 13 and 21)]
- Main Group Elements. Synthesis, structure, physical properties, variations in bonding motifs, acid-base character, and reactivities of the elements and their compounds. [DIC6, Chapters 2, 6 through 18, 22]
- Transition Elements and Coordination Chemistry. Ligands, coordination number, stereochemistry, bonding motifs, nomenclature; ligand field and molecular orbital theories, Jahn-Teller effects, magnetic properties, electronic spectroscopy (term symbols and spectrochemical series), thermodynamic aspects (formation constants, hydration enthalpies, chelate effect), kinetic aspects (ligand substitution, electron transfer, fluxional behavior), lanthanides, and actinides. [DIC6, Chapters 19, 20, 21, 24]
- Organometallic Chemistry. Metal carbonyls, hydrocarbon and carbocyclic ligands, 18-electron rule (saturation and unsaturation), synthesis and properties, patterns of reactivity (substitution, oxidative-addition and reductive-elimination, insertion and deinsertion, nucleophilic attack on ligands, isomerization, stereochemical nonrigidity). [DIC6, Chapter 23]
- Solid-State Materials. Close packing in metals and metal compounds, metallic bonding, band theory, magnetic properties, conductivity, semiconductors, insulators, and defects. [DIC6, Chapters 4 and 5]
- Special Topics. Catalysis and important industrial processes, bioinorganic chemistry, condensed materials containing chain, ring, sheet, cage, and network structures, supramolecular structures, nanoscale structures and effects, surface chemistry, environmental and atmospheric chemistry. [DIC6, Topics incorporated throughout]

THE ELECTRONIC STRUCTURE OF THE ATOM: A Review

To understand the behavior of inorganic compounds, we need to study the nature of chemical bonding. Bonding, in turn, relates to the behavior of electrons in the constituent atoms. Our coverage of inorganic chemistry, therefore, starts with a survey of the quantum (probability) model's applications to the electron configurations of atoms and ions. We will show how these configurations can be used to explain patterns and trends in common physical properties of atoms.

- 1.1 A Review of the Quantum Model
- 1.2 Shapes of the Atomic Orbitals
- 1.3 The Polyelectronic Atom
- 1.4 Ion Electron Configurations
- 1.5 Magnetic Properties of Atoms

Context: The Importance of the Lanthanoids

The cover design of this sixth edition of *Descriptive Inorganic Chemistry* highlights the lack of recycling of most of the metallic elements. In particular, very little of the elements from lanthanum to lutetium—the lanthanoids—is reclaimed. Yet we are depending more and more on the unique properties of each of these metals to serve vital niche roles in our electronic-based civilization. For example, hybrid and all-electric vehicles rely on what are called *nickel-metal hydride* batteries for the energy storage. The metal is, in fact, lanthanum, and a hybrid vehicle battery typically contains between 10 and 15 kilograms of lanthanum. The hybrid electric motor and generator itself contains neodymium,

The lanthanoid elements (and yttrium) used in a typical hybrid vehicle.

praseodymium, dysprosium, and terbium; each metal performing a vital function. The figure above shows the wide-ranging use of the lanthanoids (and yttrium) in a typical hybrid vehicle.

All modern high-performance magnets depend upon alloys containing neodymium, whether they are tiny magnets in the ear-pieces for audio devices or giant magnets in the turbines of commercial wind turbines. The brilliance of color displays for computers and televisions is commonly the result of emission from europium ions (for red), terbium ions (for green), and cerium ions (for blue). There are also many medical applications for these elements. For example, gadolinium gives a strong image in a magnetic resonance imaging (MRI) scan. Thus, to see a finer structure of blood vessels (and of tumors), an intravenous injection of a gadolinium(III) compound is administered to a patient prior to performing an MRI scan.

The common feature of these elements is that, progressing from lanthanum to lutetium, the 4f orbitals are being filled. Thus, in this chapter, we will not only review the s, p, and d orbitals which you have encountered in lower level courses, but also introduce you to the f orbitals.

1.1 A Review of the Quantum Model

The quantum model of atomic structure was derived from the work of Louis de Broglie. De Broglie showed that, just as electromagnetic waves could be treated as streams of particles (photons), moving particles could exhibit wavelike properties. Thus, it was equally valid to picture electrons either as particles or as waves. Using this wave-particle duality, Erwin Schrödinger developed a partial differential equation to represent the behavior of an electron around an atomic nucleus.

The derivation of the equation and the method of solving it are in the realm of physics and physical chemistry, but the solution itself is of great importance to inorganic chemists. We should always keep in mind, however, that the wave equation is simply a mathematical formula. We attach meanings to the solution simply because most people need concrete images to think about subatomic phenomena. The conceptual models that we create in our macroscopic world cannot hope to reproduce the subatomic reality.

Quantum Numbers

There are a number of solutions to a wave equation. Each solution describes a different orbital and, hence, a different probability distribution for an electron in that orbital. Each of these orbitals is uniquely defined by a set of three integers: n , l , and m_l .

In addition to the three quantum numbers derived from the original theory, a fourth quantum number had to be defined to explain the results of an experiment in 1922. In this experiment, Otto Stern and Walther Gerlach found that passing a beam of silver atoms through a magnetic field caused about half the atoms to be deflected in one direction and the other half in the opposite direction. Other investigators proposed that the observation was the result of two different electronic spin orientations. The atoms possessing an electron with

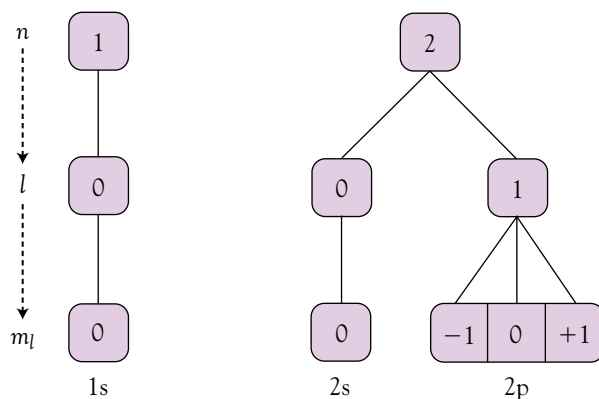


FIGURE 1.1 The possible sets of quantum numbers for $n = 1$ and $n = 2$.

one spin were deflected one way, and the atoms whose electron had the opposite spin were deflected in the opposite direction. This spin quantum number was assigned the symbol m_s .

The possible values of the quantum numbers are defined as follows:

n , the *principal quantum number*, can have all positive integer values from 1 to ∞ .

l , the *angular momentum quantum number*, can have all integer values from $(n - 1)$ to 0.

m_l , the *magnetic quantum number*, can have all integer values from $+l$ through 0 to $-l$.

m_s , the *spin quantum number*, can have values of $+\frac{1}{2}$ and $-\frac{1}{2}$.

Values of Quantum Numbers

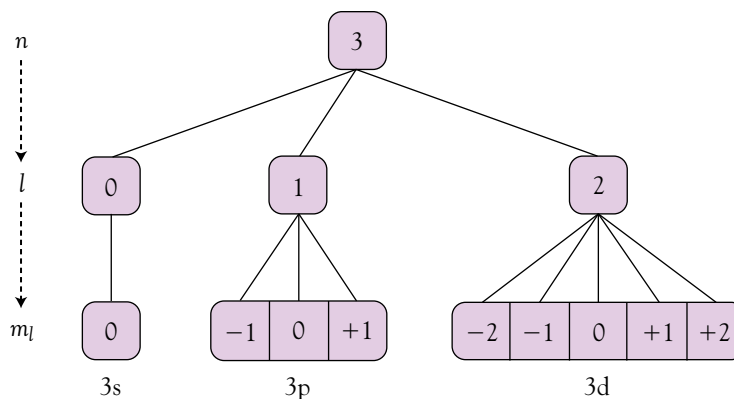
When the value of the principal quantum number is 1, there is only one possible set of quantum numbers n , l , and m_l (1, 0, 0), whereas for a principal quantum number of 2, there are four sets of quantum numbers (2, 0, 0; 2, 1, -1; 2, 1, 0; 2, 1, +1). This situation is shown diagrammatically in Figure 1.1. To identify the electron orbital that corresponds to each set of quantum numbers, we use the value of the principal quantum number n , followed by a letter for the angular momentum quantum number l . Thus, when $n = 1$, there is only the 1s orbital.

When $n = 2$, there is one 2s orbital and three 2p orbitals (corresponding to the m_l values of $+1$, 0, and -1). The letters s, p, d, and f are derived from categories of the spectral lines: sharp, principal, diffuse, and fundamental. The correspondences are shown in Table 1.1.

TABLE 1.1 Correspondence between angular momentum number l and orbital designation

l Value	Orbital designation
0	s
1	p
2	d
3	f

FIGURE 1.2 The possible sets of quantum numbers for $n = 3$.



When the principal quantum number is $n = 3$, there are nine sets of quantum numbers (Figure 1.2). These sets correspond to one 3s, three 3p, and five 3d orbitals. A similar diagram for the principal quantum number $n = 4$ would show 16 sets of quantum numbers, corresponding to one 4s, three 4p, five 4d, and seven 4f orbitals (Table 1.2).

TABLE 1.2 Correspondence between angular momentum number l and number of orbitals

l Value	Number of orbitals
0	1
1	3
2	5
3	7

Theoretically, we can go on and on, but as we will see, the f orbitals represent the limit of orbital types among the elements of the periodic table for atoms in their electronic ground states.

WORKED EXAMPLE 1.1

Give the set of quantum numbers that describe the 4d orbitals.

Answer

The 4d orbital must have a principal quantum number $n = 4$. For d orbitals, $l = 2$ and therefore $m_l = -2, -1, 0, +1, +2$. ■

1.2 Shapes of the Atomic Orbitals

Representing the solutions to a wave equation on paper is not an easy task. In fact, we would need four-dimensional graph paper (if it existed) to display the complete solution for each orbital. As a realistic alternative, we break the wave equation into two parts: a radial part and an angular part.

Each of the three quantum numbers derived from the wave equation represents a different aspect of the orbital:

The principal quantum number n indicates the size of the orbital.

The angular momentum quantum number l represents the shape of the orbital.

The magnetic quantum number m_l represents the spatial direction of the orbital.

The spin quantum number m_s has little physical meaning; it merely allows two electrons to occupy the same orbital.

It is the value of the principal quantum number and, to a lesser extent the angular momentum quantum number, which determines the energy of the electron. Although the electron may not literally be spinning, it behaves as if it were, and it has the magnetic properties expected for a spinning particle.

The s Orbitals

The s orbitals are spherically symmetrical about the atomic nucleus. As the principal quantum number increases, the electron tends to be found farther from the nucleus. To express this idea in a different way, we say that, as the principal quantum number increases, the orbital becomes more diffuse. A unique feature of electron behavior in an s orbital is that there is a finite probability of finding the electron close to, and even within, the nucleus. This penetration by s orbital electrons plays a role in atomic radii (see Chapter 2) and as a means of studying nuclear structure.

An orbital diagram is used to indicate the probability of finding an electron at any point in space. We define a location where an electron is most probably found as an area of high *electron density*. Conversely, locations with a low probability are called areas of low electron density. Orbital diagrams of the angular functions of the 1s and 2s orbitals of an atom are compared in Figure 1.3. In both cases, the tiny nucleus is located at the center of the spheres. These spheres represent the region in which there is a 99 percent probability of finding an electron. The total probability cannot be represented, for the probability of finding an electron drops to zero only at an infinite distance from the nucleus.

The probability of finding the electron within an orbital will always be positive (since the probability is derived from the square of the wave function and squaring a negative makes a positive). However, when we discuss the bonding of atoms, we find that the sign related to the original wave function has importance. For this reason, it is conventional to superimpose the sign of the wave function on the representation of each atomic orbital. For an s orbital, the sign is positive.

In addition to the considerable difference in size between the 1s and the 2s orbitals, the 2s orbital has, at a certain distance from the nucleus, a spherical surface on which the electron density is zero. A surface on which the probability of finding an electron is zero is called a *nodal surface*. When the principal

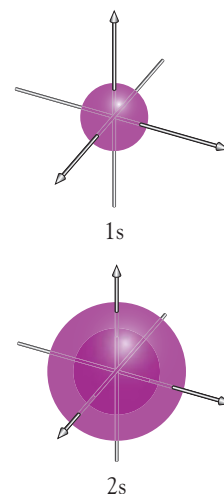
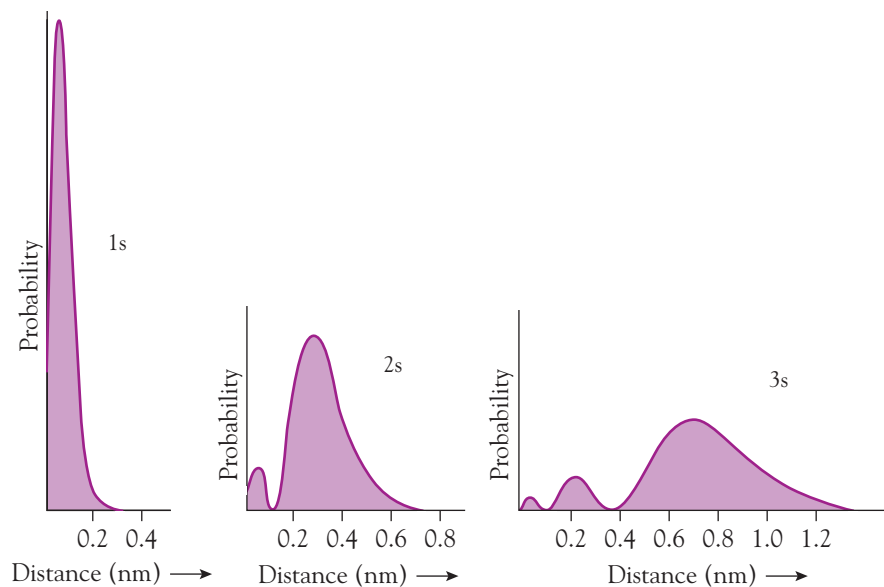


FIGURE 1.3 Representations of the shapes and comparative sizes of the 1s and 2s orbitals (computer-generated representations by Andrzej Okuniewski).

FIGURE 1.4 The variation of the radial density distribution function with distance from the nucleus for electrons in the 1s, 2s, and 3s orbitals of a hydrogen atom.



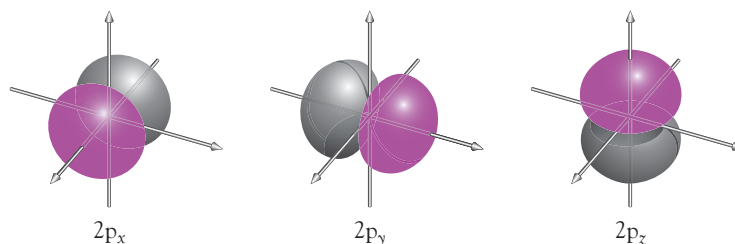
quantum number increases by 1, the number of nodal surfaces also increases by 1. We can visualize nodal surfaces more clearly by plotting a graph of the radial density distribution function as a function of distance from the nucleus for any direction. Figure 1.4 shows plots for the 1s, 2s, and 3s orbitals. These plots show that the electron tends to be farther from the nucleus as the principal quantum number increases. The areas under all three curves are the same.

The p Orbitals

Unlike the s orbitals, the p orbitals consist of two separate volumes of space (lobes), with the nucleus located between the two lobes. Because there are three p orbitals, we assign each orbital a direction according to Cartesian coordinates: p_x , p_y , and p_z . Figure 1.5 shows representations of the three 2p orbitals. At right angles to the axis of higher probability, there is a nodal plane through the nucleus. For example, the $2p_z$ orbital has a nodal plane in the xy plane. In terms of wave function sign, one lobe is positive and the other negative.

If we compare graphs of electron density as a function of atomic radius for the 2s orbital and a 2p orbital (the latter plotted along the axis of higher

FIGURE 1.5 Representations of the shapes of the $2p_x$, $2p_y$, and $2p_z$ orbitals (computer-generated representations by Andrzej Okuniewski).



probability), we find that the 2s orbital has a much greater electron density close to the nucleus than does the 2p orbital (Figure 1.6). Conversely, the second maximum of the 2s orbital is farther out than the single maximum of the 2p orbital. However, the mean distance of maximum probability is the same for both orbitals.

Like the s orbitals, the p orbitals develop additional nodal surfaces within the orbital structure as the principal quantum number increases. Thus, a 3p orbital does not look exactly like a 2p orbital since it has an additional nodal surface. However, the detailed differences in orbital shapes for a particular angular momentum quantum number are of little relevance in the context of introductory inorganic chemistry.

The d Orbitals

The five d orbitals have more complex shapes. Three of them are located between the Cartesian axes, and the other two are oriented along the axes. In all cases, the nucleus is located at the intersection of the axes. Three orbitals each have four lobes that are located between pairs of axes (Figure 1.7). These orbitals are identified as d_{xy} , d_{xz} , and d_{yz} . The other two d orbitals, d_{z^2} and $d_{x^2-y^2}$, are shown in Figure 1.8. The d_{z^2} orbital looks somewhat similar to a p_z orbital (see Figure 1.5), except that it has an additional doughnut-shaped ring of high electron density in the xy plane. The $d_{x^2-y^2}$ orbital is identical to the d_{xy} orbital but has been rotated through 45° .

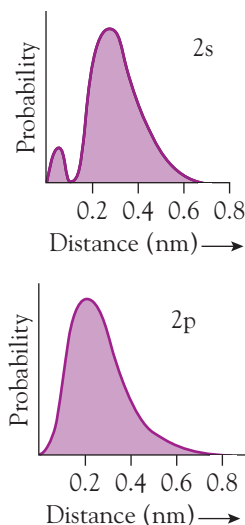


FIGURE 1.6 The variation of the radial density distribution function with distance from the nucleus for electrons in the 2s and 2p orbitals of a hydrogen atom.

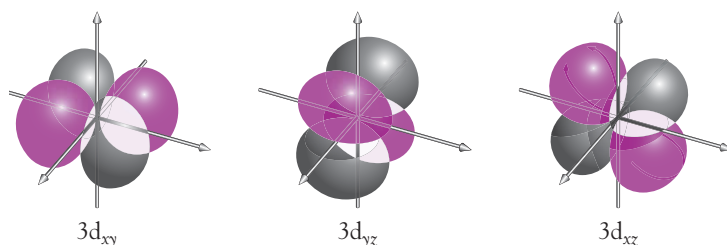


FIGURE 1.7 Representations of the shapes of the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals (computer-generated representations by Andrzej Okuniewski).

The f Orbitals

In the opening section of the chapter, we saw that the elements corresponding to the filling of the 4f orbitals are of great importance in our lives. The f orbitals are

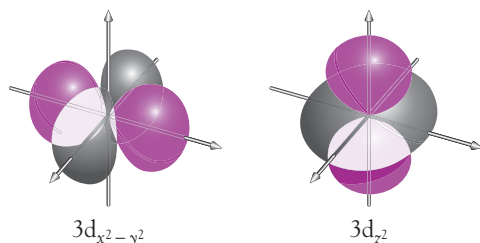
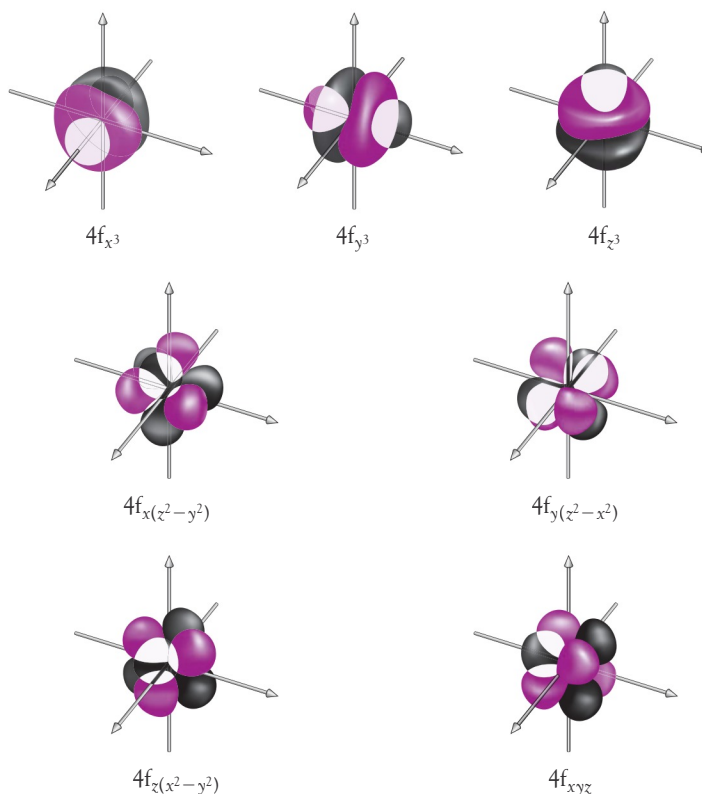


FIGURE 1.8 Representations of the shapes of the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals (computer-generated representations by Andrzej Okuniewski).

FIGURE 1.9 Representations of the shapes of the cubic set of the seven f orbitals (computer-generated representations by Andrzej Okuniewski).



even more complex than the d orbitals. There are seven f orbitals, as there are seven possible m_l values corresponding to $l = 3$. Orbitals are mathematical constructs derived from the wave equation, and particularly for the f orbitals, there are different sets of solutions each set giving rise to a different-shaped set of f orbitals. In Figure 1.9, the cubic set of f orbitals is shown as it logically relates to the d orbitals. First, there is a set of three orbitals, f_x^3 , f_y^3 , and f_z^3 , which resemble the d_{z^2} orbital with lobes along one axis, but with two “doughnut rings” for the f orbitals. Then the other four orbitals of the cubic set have eight lobes each, the first three being identical, but with the lobes rotated 45° from each other: $f_x(z^2-y^2)$, $f_y(z^2-x^2)$, and $f_z(x^2-y^2)$. The fourth of the eight-lobed f electrons is the f_{xyz} which has all eight lobes between all of the axes.

1.3 The Polyelectronic Atom

In our model of the polyelectronic atom, the electrons are distributed among the orbitals of the atom according to the *Aufbau* (German: building-up) *principle*. This simple idea proposes that, when the electrons of an atom are all in the ground state, they occupy the orbitals of lowest energy, thereby minimizing the atom’s total electronic energy. Thus, the configuration of an atom can be described simply by adding electrons one by one until the total number required for the element has been reached.

Before starting to construct electron configurations, we need to take into account a second rule: the *Pauli's exclusion principle*. According to this rule, no two electrons in an atom may possess identical sets of the four quantum numbers. Thus, there can be only one orbital of each three-quantum-number set per atom, and each orbital can hold only two electrons—one with $m_s = +\frac{1}{2}$ and the other with $m_s = -\frac{1}{2}$.

Filling the s Orbitals

The simplest configuration is that of the hydrogen atom. According to the Aufbau principle, the single electron will be located in the 1s orbital. This configuration is the ground state of the hydrogen atom. Adding energy would raise the electron to one of the many higher energy states. These configurations are referred to as excited states. In the diagram of the ground state of the hydrogen atom (Figure 1.10), a half-headed arrow is used to indicate the direction of electron spin. The electron configuration is written as $1s^1$, with the superscript “1” indicating the number of electrons in that orbital.

With a two-electron atom (helium), there is a choice: the second electron could go in the 1s orbital (Figure 1.11a) or the next higher energy orbital, the 2s orbital (Figure 1.11b). Although it might seem obvious that the second electron would enter the 1s orbital, it is not so simple. If the second electron entered the 1s orbital, it would be occupying the same volume of space as the electron already in that orbital. The very strong electrostatic repulsions, the *pairing energy*, would discourage the occupancy of the same orbital. However, by occupying an orbital with a high probability closer to the nucleus, the second electron will experience a much greater nuclear attraction. As the nuclear attraction is greater than the inter-electron repulsion, the actual configuration will be $1s^2$.

In the lithium atom the 1s orbital is filled by two electrons, and the third electron must be in the next higher energy orbital, the 2s orbital. Thus, lithium has the configuration of $1s^2 2s^1$. For beryllium, a fourth electron needs to be added to the electron configuration. As for the helium case above, the energy separation of an s and its corresponding p orbitals is greater than the pairing energy. Thus, the electron configuration of beryllium will be $1s^2 2s^2$ rather than $1s^2 2s^1 2p^1$.

Filling the p Orbitals

Boron marks the beginning of the filling of the 2p orbitals. A boron atom has an electron configuration of $1s^2 2s^2 2p^1$. Because the p orbitals are degenerate (that is, they all have the same energy), it is impossible to decide which one of the three orbitals contains the electron.

Carbon is the second ground-state atom with electrons in the p orbitals. Its electron configuration provides another challenge. There are three possible arrangements of the two 2p electrons (Figure 1.12): (a) both electrons in one orbital, (b) two electrons with parallel spins in different orbitals, and (c) two electrons with opposed spins in different orbitals. On the basis of electron repulsions, the first possibility (a) can be rejected immediately. The

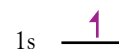


FIGURE 1.10 Electron configuration of a hydrogen atom.

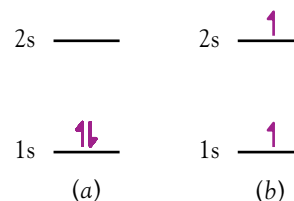


FIGURE 1.11 Two possible electron configurations for helium.

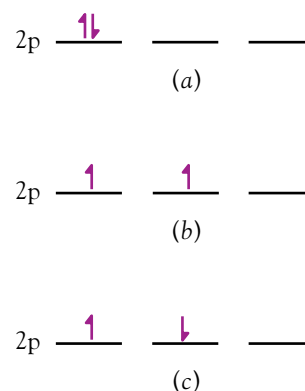


FIGURE 1.12 Possible 2p electron configurations for carbon.

decision between the other two possibilities is less obvious and requires a deeper knowledge of quantum theory. In fact, if the two electrons have parallel spins, there is a zero probability of their occupying the same space. However, if the spins are opposed, there is a finite possibility that the two electrons will occupy the same region in space, thereby resulting in some repulsion and a higher energy state. Hence, the parallel spin situation (*b*) will have the lowest energy. This preference for unpaired electrons with parallel spins has been formalized in *Hund's rule*: When filling a set of degenerate orbitals, the number of unpaired electrons will be maximized, and these electrons will have parallel spins.

After the completion of the 2p electron set at neon ($1s^2 2s^2 2p^6$), the 3s and 3p orbitals start to fill. Rather than write the full electron configurations, a shortened form can be used. In this notation, the inner electrons are represented by the noble gas symbol having that configuration. Thus, magnesium, whose full electron configuration would be written as $1s^2 2s^2 2p^6 3s^2$, can be represented as having a neon noble gas core, and its configuration is written as $[\text{Ne}]3s^2$. An advantage of the noble gas core representation is that it emphasizes the outermost (valence) electrons, and it is these electrons that are involved in chemical bonding. Then filling the 3p orbitals brings us to argon.

Filling the d Orbitals

It is at this point that the 3d and 4s orbitals start to fill. The simple orbital energy level concept breaks down because the energy levels of the 4s and 3d orbitals are very close. What becomes most important is not the minimum energy for a single electron but the configuration that results in the least number of inter-electron repulsions for all the electrons. For potassium, this is $[\text{Ar}]4s^1$; for calcium, $[\text{Ar}]4s^2$.

In general, the lowest overall energy for each transition metal is obtained by filling the s orbitals first; the remaining electrons then occupy the d orbitals. Although there are minor fluctuations in configurations throughout the d-block and f-block elements, the following order can be used as a guide:



Figure 1.13 shows the elements organized by order of orbital filling.

This order is shown as an energy-level diagram in Figure 1.14. The orbitals fill in this order because the energy differences between the s, p, d, and f orbitals of the same principal quantum number become so great beyond $n = 2$ that they overlap with the orbitals of the following principal quantum numbers. It is important to note that Figure 1.14 shows the filling order, not the order for any particular element. For example, for elements beyond zinc, electrons in the 3d orbitals are far lower in energy than those in the 4s orbitals. Thus, at this point, the 3d orbitals have become “inner” orbitals and have no role in chemical bonding. Hence, their precise ordering is unimportant.

Although these are the generalized rules, to illustrate how this delicate balance changes with increasing numbers of protons and electrons, the outer

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb											<i>s</i> -Block																																																													
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	B	C	N	O	F	Ne	Al	Si	P	S	Cl	Ar	Li	Be	Na	Mg	K	Ca	Rb	Sr	Cs	Ba	Fr	Ra	Uut	Fl	Uup	Lv	Uus	Uuo	*	**
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FIGURE 1.13 In this version of the periodic table, the chemical elements are organized in order of orbital filling.