Electronic Basis for the Properties of the Elements

Objectives

- Electronic basis of Periodic Table
- Interpretation of the physical and chemical properties of the elements based on the atomic orbital description of their electronic structures.

➤ Our discussion of the properties of the atoms will be a qualitative one, but it should be pointed out that many of the properties of atoms can now be accurately predicted by quantum mechanical calculations employing a very extended version of the atomic orbital concept.

Chemical Periodicity

❖ Many elements show strong similarities to one another.

➤ The elements lithium (Li), sodium (Na), and potassium (K) are:

- all soft

- very reactive metals….

➤ The elements helium (He), neon (Ne), and argon (Ar) are:

- all nonreactive gases.

➤ Arranging elements by atomic number reveals a periodic pattern of properties.

Chemical Periodicity

➢ For example, each of the soft, reactive metals—lithium, sodium, and potassium—comes immediately after one of the nonreactive gases—helium, neon, and argon, respectively—as shown in Figure 2.13.
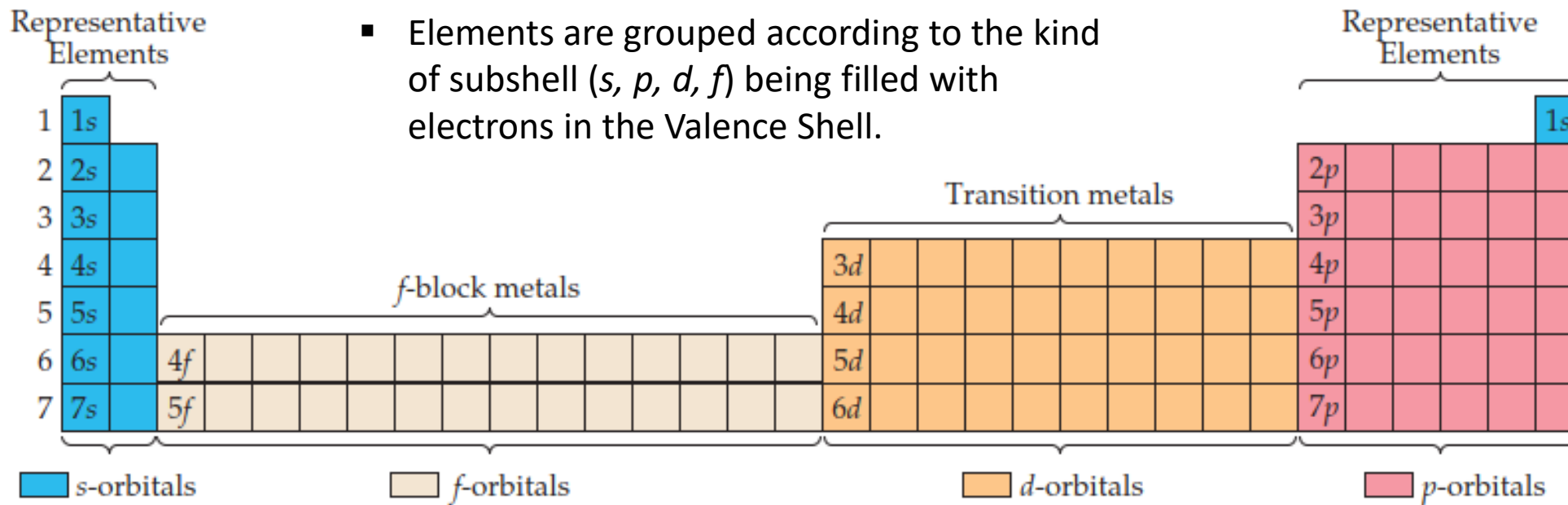

➢ If F *is a reactive nonmetal, which other element or elements shown here are likely to be reactive nonmetals?*

➢ This pattern is the basis of the periodic table.

➢ If the elements are arranged in the order of increasing *atomic number* and *the valence shell electronic configurations*, their chemical and physical properties show a repeating, or periodic, pattern.

❑ **Electron Configurations and the Periodic Table**

➢ As you have learned, the electron configurations of the elements explain the otherwise peculiar shape of the periodic table.

➢ Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these *similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order*.

➢ As a result, the periodic table can be divided into "blocks" corresponding to the type of subshell that is being filled, as illustrated in Figure 6.9.1.

❑Regions of the long periodic table.

Elements are grouped according to the kind of subshell (*s, p, d, f*) being filled with electrons in the Valence Shell.

➤ **p block**: where the valence p orbitals are being filled.
   ❖ The *s* block and the *p* block elements together: ***representative elements***, sometimes called the ***main-group elements***.
➤ ***Transition metals:*** the valence *d* orbitals are being filled and make up the *d*-block.
➤ ***f-block metals:*** 14 columns in which the valence *f* orbitals are being filled and make up the *f*-block.

- ➢ For example, the two columns on the left, known as the s block, consisting of elements in which the *ns* orbitals are being filled.

- ➢ The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p* block.

- ➢ In between are the 10 columns of the *d* block, elements in which the $(n-1)d$ orbitals are filled.

- ➢ At the bottom lie the 14 columns of the *f* block, elements in which the $(n-2)f$ orbitals are filled.

- ➢ *Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell*: 2 for *ns*, 6 for *np*, 10 for $(n-1)d$, and 14 for $(n-2)f$.

- ➢ Within each column, each element has the same valence electron configuration—for example, ns^1 (group 1) or ns^2np^1 (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

Periodic Table of Elements.

Periods — horizontal rows

Groups — vertical columns containing elements with similar properties

Elements arranged in order of increasing atomic number

Steplike line divides metals from nonmetals

The periodic table is the most significant tool that chemists use for organizing and remember-ing chemical facts.

1A 1																	8A 18
1 H	2A 2											3A 13	4A 14	5A 15	6A 16	7A 17	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3B 3	4B 4	5B 5	6B 6	7B 7	8	9	10	1B 11	2B 12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

8B

☐ Metals
☐ Metalloids
☐ Nonmetals

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

➢ The color code of the Periodic Table shows that:

❖ except for hydrogen, all **the elements** on the *left* and in the *middle* of the table are **metallic elements, or metals**.

❖ All the metallic elements share ***characteristic properties***, such as luster and high electrical and heat conductivity, and all of them *except mercury (Hg) are solid at room temperature*.

➢ The metals are separated from the **nonmetallic elements**, or **nonmetals**, by a stepped line that runs from boron (B) to astatine (At).

➢ Nonmetals generally differ from metals in appearance and in other physical properties.

➢ At room temperature and pressure, some of the nonmetals are gaseous, some are solid, and one (Br) is liquid.

➢ Many of the elements that lie along the line that separates metals from nonmetals have properties that fall between those of metals and nonmetals. These elements are often referred to as **metalloids**.

- In the long form of the periodic table, families are labelled by both a number and by the letter A or B.
- filled, there is a IA family and a IB family.
- It will be noted that the elements in a B family all occur in the series of transition elements in which the *d* orbitals are being filled.
- In the A families, however, the *d* orbitals are either absent or are present as closed inner shells.
- For example, consider the electronic configurations of K (IA) and Cu (IB):

$$\text{K} \quad [\text{Ar}]4s^1 \qquad\qquad \text{Cu} \quad [\text{Ar}]3d^{10}4s^1$$

- Note that the most stable configuration for Cu is not [Ar] $3d^9 4s^2$ as expected. By transferring one of the $4s$ electrons to the $3d$ vacancy, the *d* subshell is filled and the electronic energy is lowered.
- The ***electron density distribution of the Cu atom is therefore a spherical one***. Both *K and Cu have one outer electron with a spherical charge distribution*. They should have some properties in common, such as a tendency to lose one electron and form a positive ion.

- For this reason both families are labelled I.
- However, the shell underlying the outer electron in the K atom possesses a rare gas configuration, while in the Cu atom it is a set of filled d orbitals. This difference in electronic structure is sufficient to cause considerable differences in their chemistry, hence the further labels A and B.
- A rare gas configuration is always one of great stability, particularly when it occurs in a positive ion. (Recall that I_2 = 47.3 ev for sodium.) The species K^{+2} is never observed in solution chemistry and could be produced in the gas phase only by an expenditure of energy far in excess of that observed in ordinary chemical reactions.
- The Cu^+ ion, on the other hand, very readily loses a second electron to form the Cu^{+2} ion. Indeed, Cu^{+2} is the more common ionic form of copper. Thus, the d^{10} closed shell structure is more easily broken than a rare gas configuration, giving to Cu a variable valency of one or two.

❑The order in which electrons are added to orbitals is read left to right beginning in the top-left corner.

Outer-shell electron configurations of the elements.

➢ Elements in a **group** often exhibit **similarities** in **physical** and **chemical properties**. ...WHY?

➢They have the same valence shell electronic configurations.....

	1A 1															8A 18
	1 H $1s^1$	2A 2										3A 13	4A 14	5A 15	6A 16	7A 17	2 He $1s^2$
Core [He]	3 Li $2s^1$	4 Be $2s^2$										5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$

8B

[Ne]	11 Na $3s^1$	12 Mg $3s^2$	3B 3	4B 4	5B 5	6B 6	7B 7	8	9	10	1B 11	2B 12	13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
[Ar]	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$	31 Ga $4s^2 3d^{10} 4p^1$	32 Ge $4s^2 3d^{10} 4p^2$	33 As $4s^2 3d^{10} 4p^3$	34 Se $4s^2 3d^{10} 4p^4$	35 Br $4s^2 3d^{10} 4p^5$	36 Kr $4s^2 3d^{10} 4p^6$
[Kr]	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^2 4d^3$	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 $4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$	49 In $5s^2 4d^{10} 5p^1$	50 Sn $5s^2 4d^{10} 5p^2$	51 Sb $5s^2 4d^{10} 5p^3$	52 Te $5s^2 4d^{10} 5p^4$	53 I $5s^2 4d^{10} 5p^5$	54 Xe $5s^2 4d^{10} 5p^6$
[Xe]	55 Cs $6s^1$	56 Ba $6s^2$	71 Lu $6s^2 4f^{14} 5d^1$	72 Hf $6s^2 4f^{14} 5d^2$	73 Ta $6s^2 4f^{14} 5d^3$	74 W $6s^2 4f^{14} 5d^4$	75 Re $6s^2 4f^{14} 5d^5$	76 Os $6s^2 4f^{14} 5d^6$	77 Ir $6s^2 4f^{14} 5d^7$	78 Pt $6s^1 4f^{14} 5d^9$	79 Au $6s^1 4f^{14} 5d^{10}$	80 Hg $6s^2 4f^{14} 5d^{10}$	81 Tl $6s^2 4f^{14} 5d^{10} 6p^1$	82 Pb $6s^2 4f^{14} 5d^{10} 6p^2$	83 Bi $6s^2 4f^{14} 5d^{10} 6p^3$	84 Po $6s^2 4f^{14} 5d^{10} 6p^4$	85 At $6s^2 4f^{14} 5d^{10} 6p^5$	86 Rn $6s^2 4f^{14} 5d^{10} 6p^6$
[Rn]	87 Fr $7s^1$	88 Ra $7s^2$	103 Lr $7s^2 5f^{14} 6d^1$	104 Rf $7s^2 5f^{14} 6d^2$	105 Db $7s^2 5f^{14} 6d^3$	106 Sg $7s^2 5f^{14} 6d^4$	107 Bh $7s^2 5f^{14} 6d^5$	108 Hs $7s^2 5f^{14} 6d^6$	109 Mt $7s^2 5f^{14} 6d^7$	110 Ds $7s^2 5f^{14} 6d^8$	111 Rg $7s^2 5f^{14} 6d^9$	112 Cn $7s^2 5f^{14} 6d^{10}$	113 Nh $7s^2 5f^{14} 6d^{10} 7p^1$	114 Fl $7s^2 5f^{14} 6d^{10} 7p^2$	115 Mc $7s^2 5f^{14} 6d^{10} 7p^3$	116 Lv $7s^2 5f^{14} 6d^{10} 7p^4$	117 Ts $7s^2 5f^{14} 6d^{10} 7p^5$	118 Og $7s^2 5f^{14} 6d^{10} 7p^6$

	Lanthanide series [Xe]	57 La $6s^2 5d^1$	58 Ce $6s^2 4f^1 5d^1$	59 Pr $6s^2 4f^3$	60 Nd $6s^2 4f^4$	61 Pm $6s^2 4f^5$	62 Sm $6s^2 4f^6$	63 Eu $6s^2 4f^7$	64 Gd $6s^2 4f^7 5d^1$	65 Tb $6s^2 4f^9$	66 Dy $6s^2 4f^{10}$	67 Ho $6s^2 4f^{11}$	68 Er $6s^2 4f^{12}$	69 Tm $6s^2 4f^{13}$	70 Yb $6s^2 4f^{14}$
	Actinide series [Rn]	89 Ac $7s^2 6d^1$	90 Th $7s^2 6d^2$	91 Pa $7s^2 5f^2 6d^1$	92 U $7s^2 5f^3 6d^1$	93 Np $7s^2 5f^4 6d^1$	94 Pu $7s^2 5f^6$	95 Am $7s^2 5f^7$	96 Cm $7s^2 5f^7 6d^1$	97 Bk $7s^2 5f^9$	98 Cf $7s^2 5f^{10}$	99 Es $7s^2 5f^{11}$	100 Fm $7s^2 5f^{12}$	101 Md $7s^2 5f^{13}$	102 No $7s^2 5f^{14}$

Metals   Metalloids   Nonmetals

➤ Many other *groups* in the periodic table also have *names*, listed in Table 2.3.

TABLE 2.3   Names of Some Groups in the Periodic Table

Group	Name	Elements
1	Alkali metals	Li, Na, K, Rb, Cs, Fr
2	Alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra
16	Chalcogens (pronounced kal'-ke-jens)	O, S, Se, Te, Po
17	Halogens	F, Cl, Br, I, At
18	Noble gases	He, Ne, Ar, Kr, Xe, Rn

➤ Elements in a group often ***exhibit similarities in physical and chemical properties***.

➤ For example, the "**coinage metals**"—copper (Cu), silver (Ag), and gold (Au)—belong to group 11. These elements are less reactive than most metals, which is why they have been traditionally used throughout the world to make coins.

❑ Penetration & Shielding

➢ We can **predict basic properties of elements** and **their trends** by using **penetration** and **shielding** characteristics. **Penetration** and **shielding are two underlying principles in determining the physical** and **chemical properties of elements**.

➢ The orbital (n) and subshell (l) define how close an electron can approach the nucleus. The ability of an electron to get close to the nucleus is **penetration**.

➢ Electrons are negatively charged and are pulled pretty close to each other by their attraction to the positive charge of a nucleus. Every electron in an atom does not feel the same amount of "pull" from the nucleus.

➢ When considering the **core electrons** (or the electrons closest to the nucleus), the nuclear charge "felt" by the electrons is **close to the actual nuclear charge**.

➢ As **you proceed** from the core electrons to the outer valence electrons, the effective nuclear charge (Z_{eff}) felt by the electrons **falls significantly**.

➢ This is because of **shielding**. The electrons are attracted to the nucleus at the same time as electrons repel each other, *the balance between attractive and repulsive forces* results in *shielding*. Or simply the electrons closest to the nucleus decrease the amount of nuclear charge affecting the outer electrons.

✓ **Shielding is caused by** the **combination** of *partial neutralization of nuclear charge by core electrons* and by ***electron-electron repulsion***.

➢ The amount of charge felt by an electron depends on its distance from the nucleus. ***The closer an electron comes to the nucleus,*** *or* ***the more it penetrates***, the stronger its attraction to the nucleus.

➢ Core electrons *penetrate* more and feel more of the nucleus than the other electrons.

➤ The amount of charge felt by an electron depends on its distance from the nucleus. The closer an electron comes to the nucleus, or the more it *penetrates*, the stronger its attraction to the nucleus.

➤
$$F_{electron-nucleus} = kZe^2/r^2$$

With *Z* is the charge of the nucleus (i.e., number of protons)

e is the charge of an electron or proton

r is the radius, or distance between the proton and the electron.

➤ *Penetration and shielding result in an* **Effective force** (**F_{eff}**) *that holds the outer* electrons to the atom, akin to Equation 2, but with **Z_{eff}** substituted for *Z*:

$$F_{eff} = kZ_{eff}e^2/r^2$$

❑ **Orbital Penetration**

➢ *Penetration describes the proximity to which an electron can approach to the nucleus.*

➢ In a multi-electron system, electron penetration *is defined by an electron's relative electron density (probability density) near the nucleus* of an atom.

➢ Electrons in different orbitals have different wavefunctions and therefore different radial distributions and probabilities (defined by quantum numbers n and l around the nucleus).

➢ In other words, penetration depends on the shell (n) and subshell (l). For example, we see that since a 2s electron has more electron density near the nucleus than a 2p electron, it is penetrating the nucleus of the atom more than the 2p electron.

➢ The penetration power of an electron, in a multi-electron atom, is dependent on the values of both the shell and subshell.

Radial Distribution Graphs

➤ A radial distribution function graph describes the distribution of orbitals with the effects of shielding (Figure 2). The small peak of the 2s orbital shows that the electrons in the 2s orbital are closest to the nucleus. Therefore, it is the electrons in the 2p orbital of Be that are being shielded from the nucleus, by the electrons in the 2s orbital.

➤ The following is the radial distribution of the 1s and 2s orbitals. Notice the 1s orbital is shifted to the right, while the 2s orbital has a node.

Figure 2: **Orbital Penetration**. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.
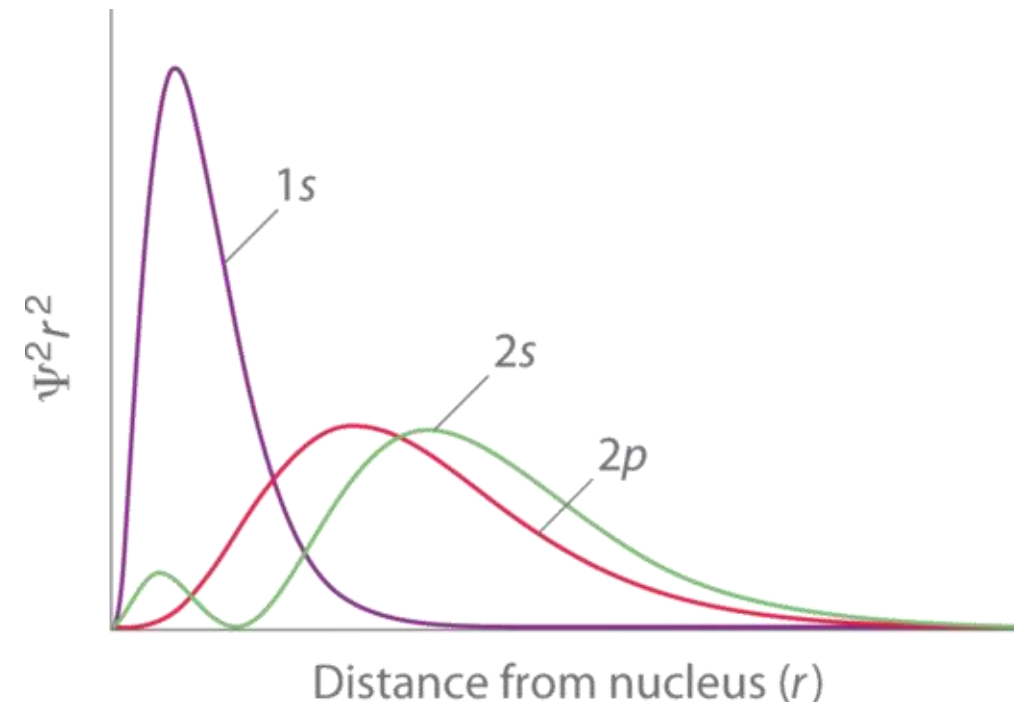
➢ Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (l): $s > p > d > f$

➢ And for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

    ➢ $1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f$....

    and the energy of an electron for each shell and subshell goes as follows...

        $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$....

➢ Electrons which experience *greater penetration experience stronger attraction to the nucleus, less shielding,* and therefore experience a **larger *Effective Nuclear Charge*** (Z_{eff}) *but* **shield other electrons more effectively**.

❑ **Shielding**

➢ An atom (assuming its atomic number is greater than 2) has core electrons that are extremely attracted to the nucleus in the middle of the atom. However, the number of protons in the nucleus are never equal to the number of core electrons (relatively) adjacent to the nucleus. The number of protons increase by one across the periodic table, but the number of core electrons change by periods.

➢ The ***first period has no core electrons, the second has 2, the third has 10,*** and so on. This number is not equal to the number of protons. So that means that the core electrons feel a stronger pull towards the nucleus than any other electron within the system. The valence electrons are farther out from the nucleus, so they experience a smaller force of attraction.

➢ *Shielding refers to the core electrons repelling the outer rings and thus lowering the 1:1 ratio*. Hence, the nucleus has "less grip" on the outer electrons and are shielded from them.

➢ Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity.

➢ For example, Z_{eff} is calculated by subtracting the magnitude of shielding from the total nuclear charge.

➢ The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.
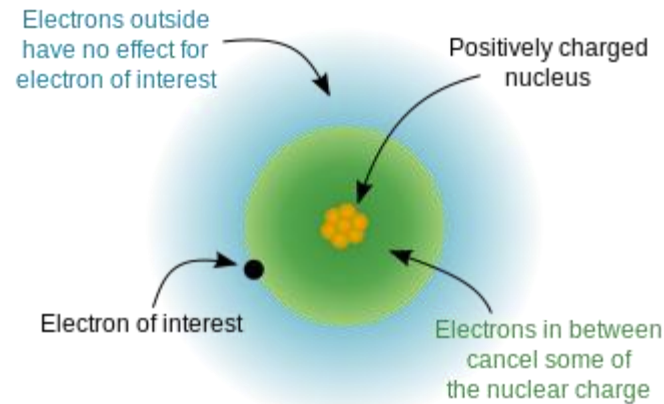
Figure 1: This image shows how inner electrons can shield outer electrons from the nuclear charge. (CC BY-SA 3.0; from Wikipedia).

➢ Because the order of **electron penetration from greatest to least is s, p, d, f;** **the order of the amount of shielding done is also in the order s, p, d, f**.

➢ Since the 2s electron has more density near the nucleus of an atom than a 2p electron, it is said to shield the 2p electron from the full effective charge of the nucleus. Therefore the 2p electron feels a lesser effect of the positively charged nucleus of the atom due to the shielding ability of the electrons closer to the nucleus than itself, (i.e. 2s electron).

➢ These electrons that are shielded from the full charge of the nucleus are said to experience an effective nuclear charge (Z_{eff})of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogen-like ions.

➢ The effective nuclear charge of an atom is given by the equation:

$Z_{eff} = Z–S$ *where Z is the atomic number (number of protons in nucleus) and S is the shielding constant.*

➢ We can see from this equation that the effective nuclear charge of an atom increases as the number of protons in an atom increases.

➢ Therefore **as we go from left to right on the periodic table the effective nuclear charge of an atom increases in strength** and holds the outer electrons closer and tighter to the nucleus.

➢ *This phenomena can explain **the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge**.*

Example 1: Fluorine, Neon, and Sodium

What is *the effective attraction Z_{eff} experienced by the valence electrons* in the three isoelectronic species: the fluorine anion, the neutral neon atom, and sodium cation?

Solution

Each species has 10 electrons, and the number of **nonvalence electrons is 2** (10 total electrons - 8 valence) but the effective nuclear charge varies because each has a different atomic number.

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals.

$Z_{eff}(F^-) = 9-2 = 7+$

$Z_{eff}(Ne) = 10-2 = 8+$

$Z_{eff}(Na+) = 11-2 = 9+$

So the *sodium cation* has the *greatest effective nuclear charge,*
*and thus the **smallest radius**.*

Non-shielding outer shell (7e-)

Helium filled shell (2e-, shielding)

Neon shell

Nucleus (9+)
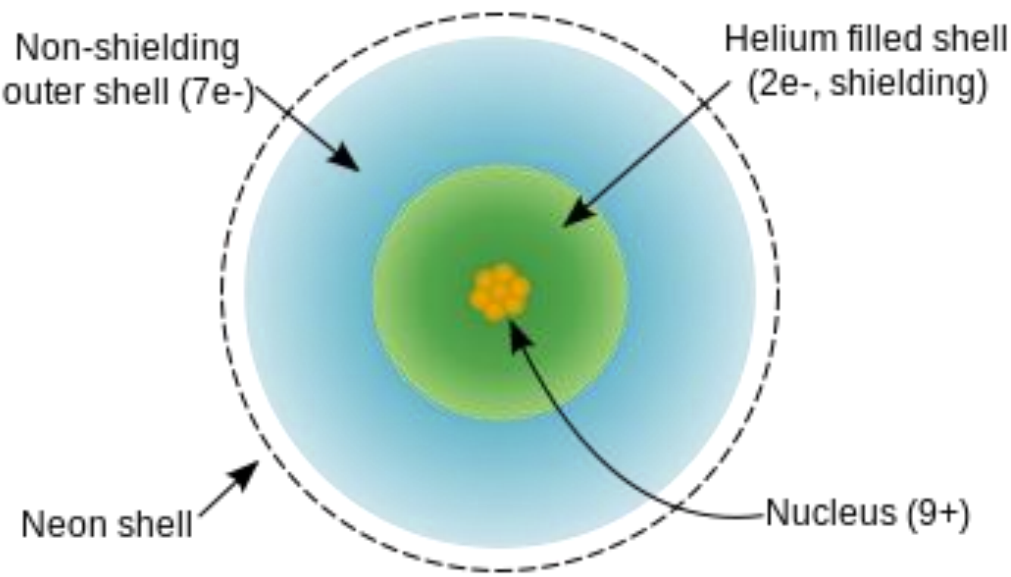
Diagram of a fluorine atom showing the extent of effective nuclear charge. (CC BY-SA- 3.0; Wikipedia).

❑ **Periodic Trends Due to Penetration and Shielding**

➢ **Effective Nuclear Charge (Z_{eff}):** The effective nuclear charge *increases* from left to right and *increases* from top to bottom on the periodic table.

➢ **Atomic Radius:** The atomic radius decreases from left to right and increases from top to bottom.

➢ **Ionization Energies:** The ionization energies increase from left to right and decrease from top to bottom.

➢ **Electronegativity:** The electronegativity of the elements is highest near fluorine. In general, it increases from left to right and decreases from top to bottom.

❖ Horizontal Variations

➢ The experimental values of the atomic radii and the first and second ionization potentials of the elements (labelled as I_1 and I_2 respectively) in the third row of the periodic table are listed in Table 5-1. A study of these values will indicate the basic trends observed as the number of electrons is increased one at a time until all the orbitals with a given value of n are fully occupied.

Table 5-1: The Atomic Radii and Ionization Potentials* of Third Row Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Radius (Å)	1.86	1.60	1.48	1.17	1.0	1.06	0.97	
I_1 (ev)	5.14	7.64	5.98	8.15	11.0	10.4	13.0	15.8
I_2 (ev)	47.3	15.0	18.8	16.3	19.7	23.4	23.8	27.6

*The values for I_1 and I_2 are taken from C. E. Moore, *Atomic Energy Levels*, Vol. 1, N.B.S. Circular 467, Washington, D.C. (1949). I_2 is the energy required to remove an electron from the singly-charged ion, i.e., the energy required to ionize a second electron.

❖ **Atomic radii**

➢ The diameter of an atom is difficult to define precisely as the density distribution tails off at large distances. However, there is a limit as to how close two atoms can be pushed together in a solid material.

➢ We shall *take one half of the distance between the nuclei of two atoms in an **elemental solid** as a rough **measure** of the **atomic radius**.*

➢ Any consistent method of defining the radius leads to the same trend we see in Table 5-1.

➢ The size of the atom in general decreases as the number of electrons in the quantum shell is increased.

➢ This observation, which at first sight might appear surprising, finds a ready explanation through the concept of an ***effective nuclear charge***.

➢ The electric field and hence the attractive force exerted by the nucleus on an electron in the outer quantum shell is reduced because of the screening effect of the other electrons which are present in the atom.

➢ An outer electron does not penetrate to any great extent the tightly bound density distribution of the inner shell electrons.

➢ Consequently each inner electron (an electron with an n value less than the n value of the electron in question) reduces the value of the nuclear charge experienced by the outer electron by almost one unit.

➢ *The remaining **outer electrons** on the other hand are, **on the average, all at the same distance away from the nucleus** as is the electron under consideration.*

➢ Consequently each outer electron screens considerably less than one nuclear charge from the other outer electrons.

➢ Thus *the higher the ratio of outer shell to inner shell electrons, the larger will be the "effective nuclear charge" which is experienced by an electron in the outer shell.*

➢ All of the elements in a given row of the periodic table possess the same number of inner shell electrons. For example, the elements in the third row have the inner shell configuration of $1s^2 2s^2 2p^6$.

➢ As we move across the periodic table from left to right the nuclear charge increases, and each added electron is placed in the outer shell until a total of eight is reached and the quantum shell is full.

➢ *The number of outer shell electrons increases along a given period, but the number of inner shell electrons remains fixed.* Thus the effective nuclear charge increases from a minimum value for sodium, where the ratio of outer shell to inner shell electrons is 1:10, to a maximum value for argon where the same ratio is 8:10.

➢ The *atomic radius undergoes a gradual decrease since the outer electrons become more tightly bound as the effective nuclear charge increases*.
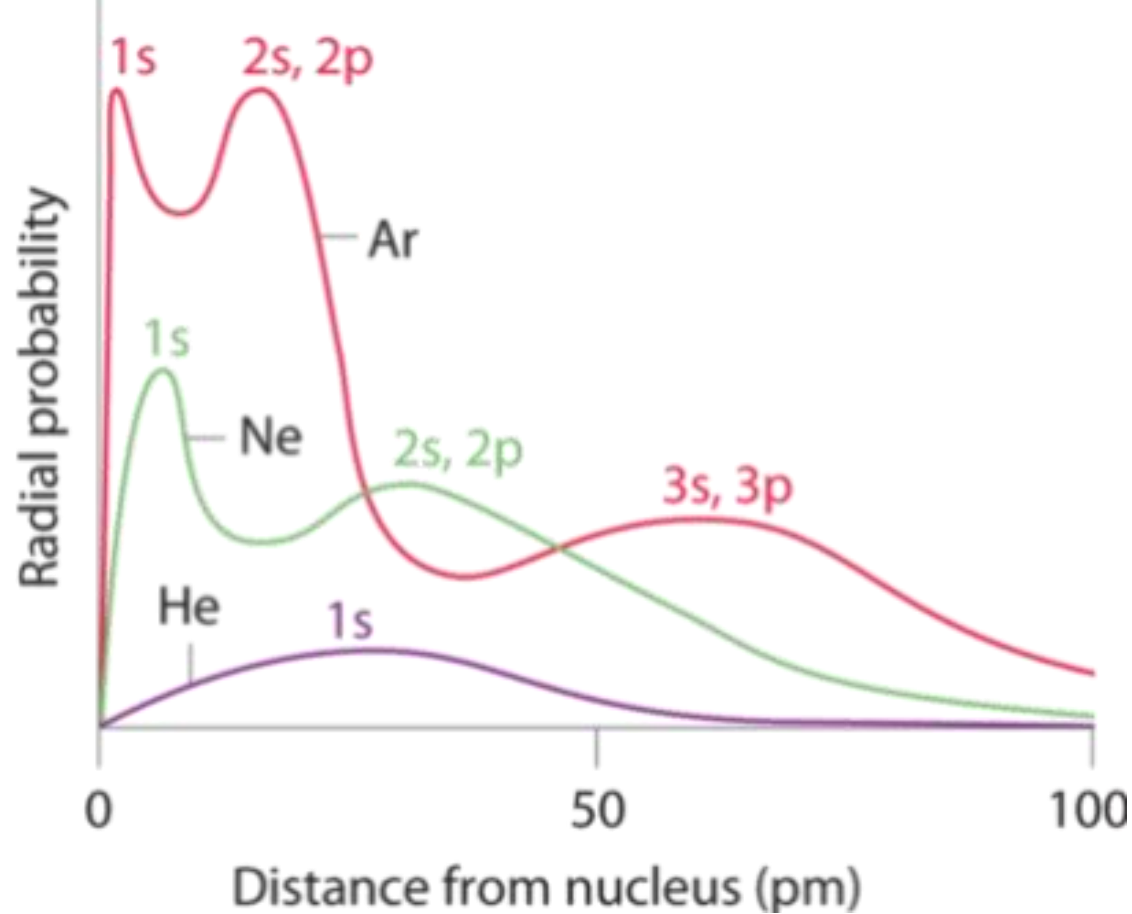
Figure 7.3.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1s electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈8 pm, and the 2s and 2p electrons combine to form another maximum at ≈35 pm (the n = 2 shell). In Ar, the 1s electrons have a maximum at ≈2 pm, the 2s and 2p electrons combine to form a maximum at ≈18 pm, and the 3s and 3p electrons combine to form a maximum at ≈70 pm.

➢ Figure 7.3.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell.

➢ Because helium has only one filled shell (n = 1), it shows only a single peak. In contrast, neon, with filled n = 1 and 2 principal shells, has two peaks.

➢ Argon, with filled n = 1, 2, and 3 principal shells, has three peaks.

➢ The **peak for the filled n = 1 shell occurs at successively shorter distances for neon (Z = 10) and argon (Z = 18) because, with a greater number of protons, their nuclei are more positively charged than that of helium**. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the n = 1 shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus.

➢ The energy of the n = 1 shell also decreases tremendously (the filled 1s orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled n = 2 shell in argon is located closer to the nucleus and has a lower energy than the n = 2 shell in neon.

➢ These features of the atomic density distributions are clearly evident in a graph of the radial distribution function, $Q(r)$. This function, it will be recalled, gives the number of electronic charges within a thin shell of space lying between two concentric spheres, one of radius r and the other with a radius only slightly larger. The **radial distribution functions for atoms may be determined experimentally by X-ray or electron diffraction techniques**.

➢ Plots of $Q(r)$ versus r for sodium and argon (Fig. 5-1), the first and last members of the third row of the periodic table, clearly reveal the persistence of a "shell structure" in the many-electron atoms.
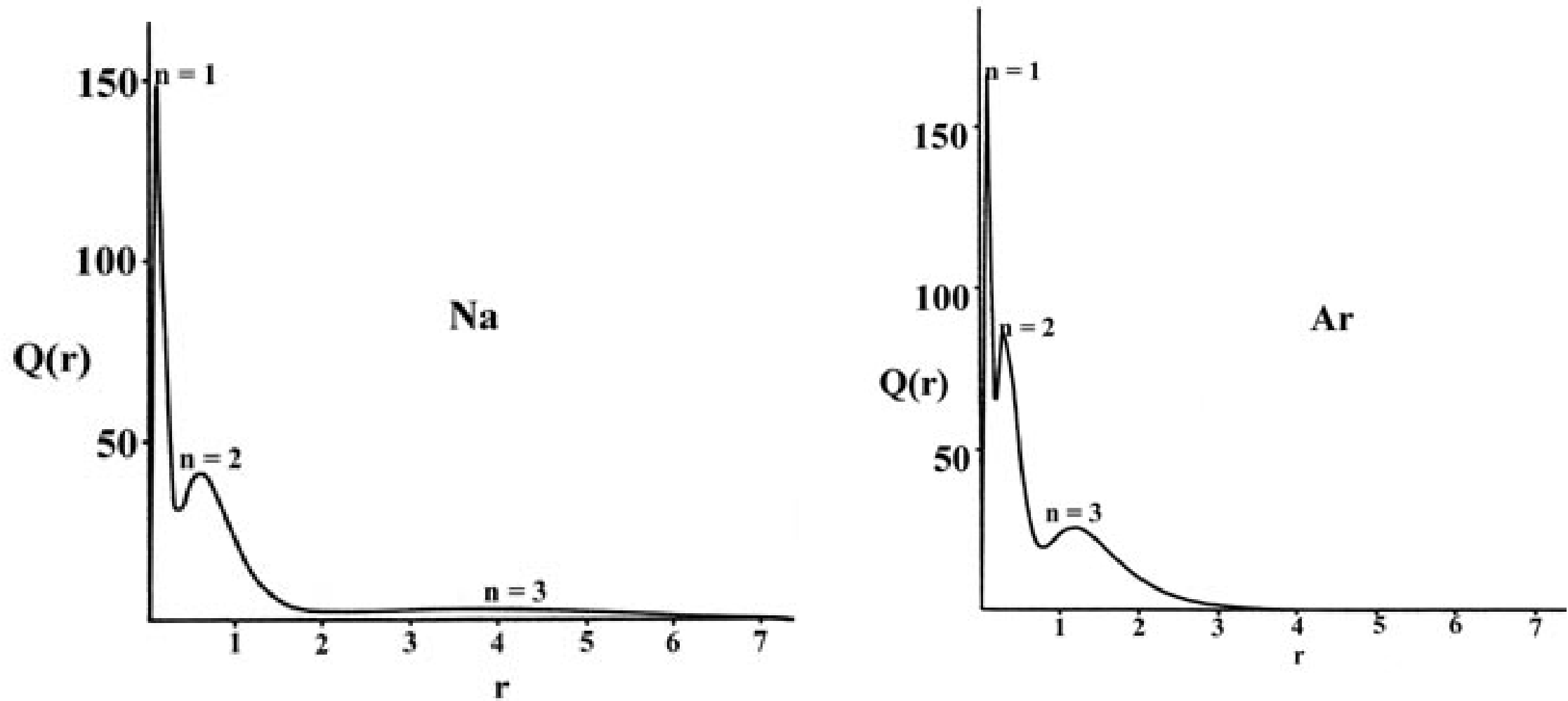
Fig. 5-1. The radial distribution functions $Q(r)$ for the Na and Ar atoms.

➤ There are three peaks in the density distribution corresponding to the presence of three principal quantum shells in the orbital model of the electronic structure of sodium and argon.

➤ The peak closest to the nucleus may be identified with the charge density in the 1s orbital, the middle peak with that in the 2s and 2p orbitals and the outer peak with the charge density in the 3s orbital in sodium and in the 3s and 3p orbitals in argon.

➤ The maxima in $Q(r)$ occur at smaller values of r for argon than for sodium as expected on the basis of a larger effective nuclear charge for argon than for sodium.

➤ Most of the 1s charge density is found within a very thin shell close to the nucleus in both cases as the inner shell density experiences the field of the full nuclear charge, $Z_{Na} = 11$ and $Z_{Ar} = 18$. The charge density in the $n = 2$ orbitals is confined to a shell which is narrower and closer to the nucleus in argon than in sodium. The electrons in this second shell experience a nuclear charge of approximately sixteen in argon but of only nine in sodium.

➢ The ***most dramatic effect of the difference in the effective nuclear charges*** of argon and sodium is evidenced by ***the appearance of the electron density in the valence shell***.

▪ *In sodium, this shell is **broad and diffuse** as there are **ten inner electrons shielding** eleven nuclear charges*.

▪ In argon where there are ten inner electrons to shield eighteen nuclear charges the valence shell is more contracted and it ***peaks at roughly one third of the corresponding distance in sodium***. The valence shell density is clearly more tightly bound in argon than in sodium.
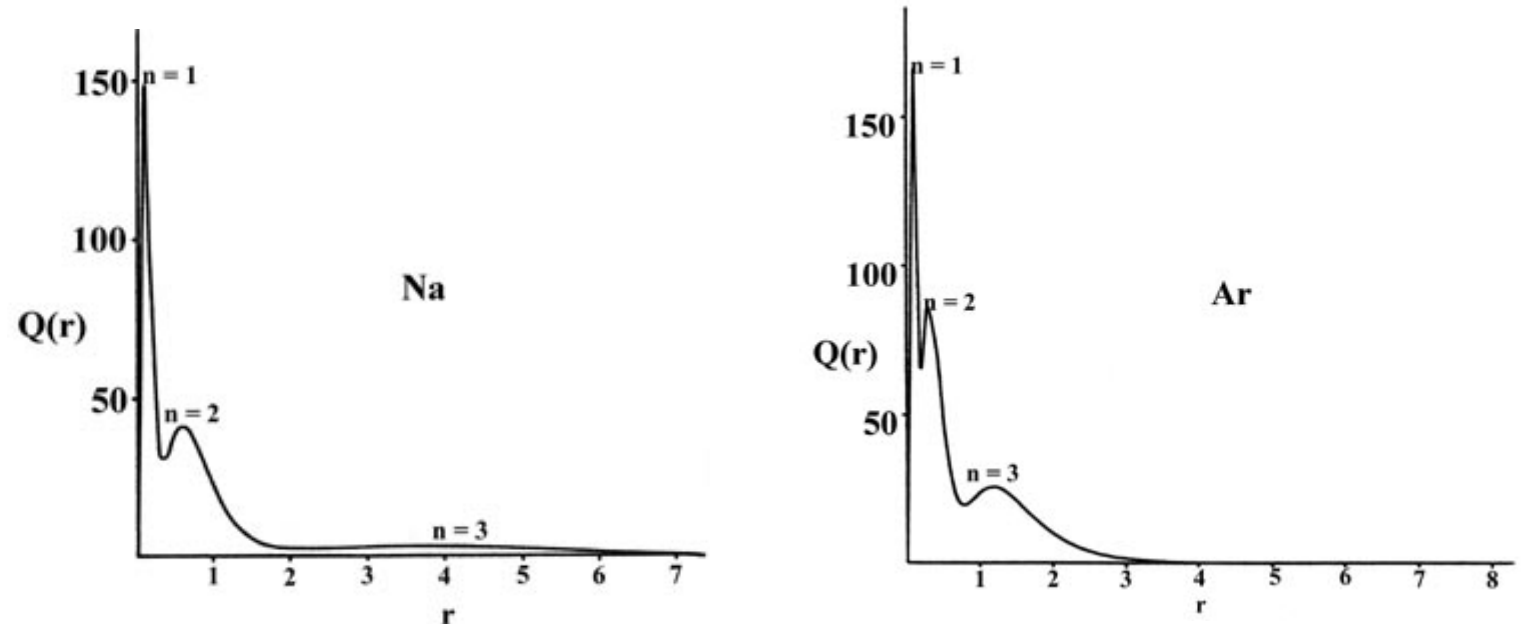
Fig. 5-1. The radial distribution functions $Q(r)$ for the Na and Ar atoms.

➢ Figure 7.3.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms.

➢ For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure 7.3.2a).

➢ Atomic radii are often measured in angstroms (Å), a non-SI unit: 1 Å = 1 × 10^{-10} m = 100 pm.
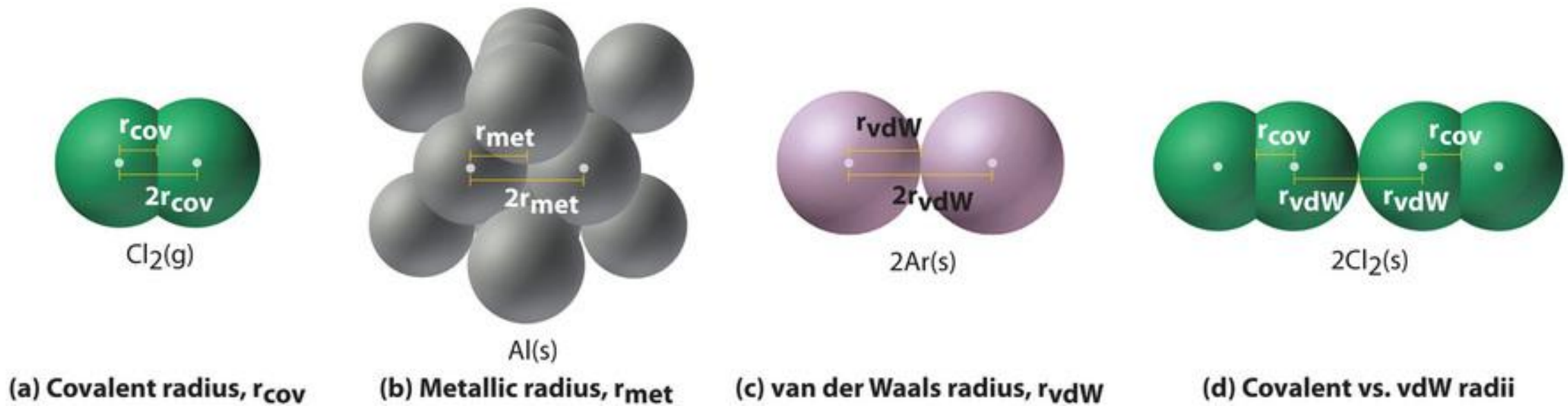
Figure 7.3.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is half the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is half the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

➢ In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds. A similar approach for measuring the size of ions is discussed later in this section.

➢ Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure 7.3.2b).

➢ For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (Figure 7.3.2c). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, Cl_2(s) at low temperatures). These radii are generally not the same (Figure 7.3.2d).

➢ **There is one exception** to the trend of a decrease in diameter across a given row in that **phosphorus has an atomic radius slightly smaller than** that of **sulfur** which follows it in the table.

- ✓ The configuration of the outer electrons in phosphorus is $3s^2 3p^3$. Each of the p orbitals contains a single electron and according to Hund's rule all will have the same spin quantum number.

- ✓ *Electrons **with identical spins have smaller electron-electron repulsion energies** than do electrons with paired spins, for reasons we have previously mentioned.*

- ✓ Therefore, ***the larger the number of parallel spins in an atom, the smaller will be the average energy of repulsion between the electrons***.

- ➢ Three is the maximum number of unpaired spins possible in any of the short periods as this corresponds to a half-filled set of p orbitals. *The stabilizing effect of the decreased energy of repulsion between the electrons is **comparable to the effect obtained by increasing the effective nuclear charge by approximately one***. This can be seen by comparing phosphorus with sulphur.

➢ ***Sulfur has an increased nuclear charge, but the added electron must be paired up with one of the electrons in the p orbitals***. The number of unpaired electrons with parallel spins is thus reduced to two, the average energy of repulsion between the electrons is increased, and the ***sulfur atom is slightly larger than the phosphorus atom***.

➢ The decrease in energy which is obtained by maximizing the number of parallel spins is not sufficient to change the **most stable outer configuration actually found for silicon, $3s^23p^2$**, to that in which all four outer electrons have parallel **spins, $3s^13p^3$**. *This latter configuration could be **obtained only by promoting** an electron from a 3s orbital to a 3p orbital*. The 3s orbital is more stable than a 3p orbital because of the penetration effect, and the energy increase caused by the promotion of an electron from the 3s to a 3p orbital would not be offset by the energy decrease obtained by maximizing the number of parallel spins.

➢ It is interesting to note, however, that the reverse of this is true for some of the elements in the transition series.

➢ In these **transition elements** the $4s$ and $3d$ (or in general the ns and $(n-1)d$) orbitals are the outer orbitals.

➢ **The energy difference between an ns and an $(n-1)d$ orbital is much less** than that between an **ns** and an **np** orbital. *Thus, **the effect of maximizing the number of parallel spins can be overriding in these cases**.*

➢ The outer electronic structure of vanadium is $4s^2 3d^3$. (Recall that there are five d orbitals and hence the configuration d^5 will represent five electrons with parallel spins.)

➢ We would expect the outer electronic configuration of the next element, chromium, to be $4s^2 3d^4$ with four parallel spins. Instead, the configuration is actually $4s^1 3d^5$ resulting in a ***total of six parallel spins and a reduction in the energy of repulsion between the electrons***.

❏ Vertical Relationships

➢ Table 5-2 lists the atomic radii and the ionization potentials of the elements found in the first column of the periodic table, the group I elements.

Table 5-2: Atomic Radii and Ionization Potentials of Group I Elements

Element	Li	Na	K	Rb	Cs
Radius (Å)	1.50	1.86	2.27	2.43	2.62
I_1 (ev)	5.4	5.1	4.3	4.2	3.9

➢ The average value of the distance between the electron and the nucleus increases as the value of the principal quantum number is increased.

➢ The increase in the atomic diameters down a given group in the periodic table is thus understandable. Each of the group I elements represents the beginning of a new quantum shell.

➢ *There will be a very sharp decrease in the effective nuclear charge on passing from the preceding closed shell element to a member of group I, as the number of the inner shell electrons is increased by eight*.

➢ This large sudden reduction in the effective nuclear charge and the fact that the electron, because of the Pauli exclusion principle, must enter a new quantum shell, causes the Group I elements to be larger in size and much more readily ionized than the preceding noble gas elements. *The decrease in the effective nuclear charge and the increase in the principal quantum number down a given family bring about a steady decrease in the observed ionization potentials*. Thus the outer $6s$ electron in cesium is on the average, further from the nucleus than is the outer $2s$ electron in lithium. It is also more readily removed.

➢ So far, we have considered the periodic variations in the energy required to remove an electron from an atom:

$$M \rightarrow M^+ + e^- \qquad I_1 = \text{a positive value}$$

➢ In some favorable cases it is possible to determine the energy released when an electron is added to an atom:

$$M + e^- \rightarrow M^- \qquad \Delta E = \text{a negative value}$$

➢ The magnitude of the energy released when an atom captures an extra electron is a measure of the atom's **electron affinity**.

➢ It might at first seem surprising that a neutral atom may attract an extra electron. Indeed many elements do not have a detectable electron affinity. However, consider the outer electronic configuration of the group VII elements, the halogens:

ns²np⁵

➢ There is a single vacancy in the outer set of orbitals and the effective nuclear charge experienced by the valence electrons in a halogen atom is almost the maximum value possible for any given row.

➢ Because of the incomplete screening of the nuclear charge by the outer electrons, the remaining vacancy in the outer shell will, in effect, exert an attractive force on a free electron large enough to bind it to the atom.

➢ The electron affinities for the rare gas atoms will be effectively zero even though the effective nuclear charge is a maximum for this group of elements there are no vacancies in the outer set of orbitals in a rare gas atom and as a result of the Pauli principle, an extra electron would have to enter an orbital in the next quantum shell.

➢ The electron in this orbital will experience only a very small effective nuclear charge as all of the electrons originally present in the atom will be in inner shells with respect to it.

➢ Elements to the left of the periodic table, the alkali metals for example, do have vacancies in their outer quantum shell but their effective nuclear charges are very small in magnitude. Thus these elements do not exhibit a measurable electron affinity.

➢ The electron affinity increases across a given row of the periodic table and reaches a maximum value with the group VII elements. *This is a direct reflection of the variation in the effective nuclear charge.*

➢ The orbital vacancy in which the extra electron is placed is found at larger distances from the nucleus when the principal quantum number is increased. Thus the electron affinity should decrease down any given family of elements in the periodic table. For example, the electron affinities for the halogens **should** decrease in the order F > Cl > Br > I.

➢ The variation in the ionization potentials across a given row is reflected in the values shown in the **atomic orbital energy level diagram for the elements from hydrogen *through to* neon**.
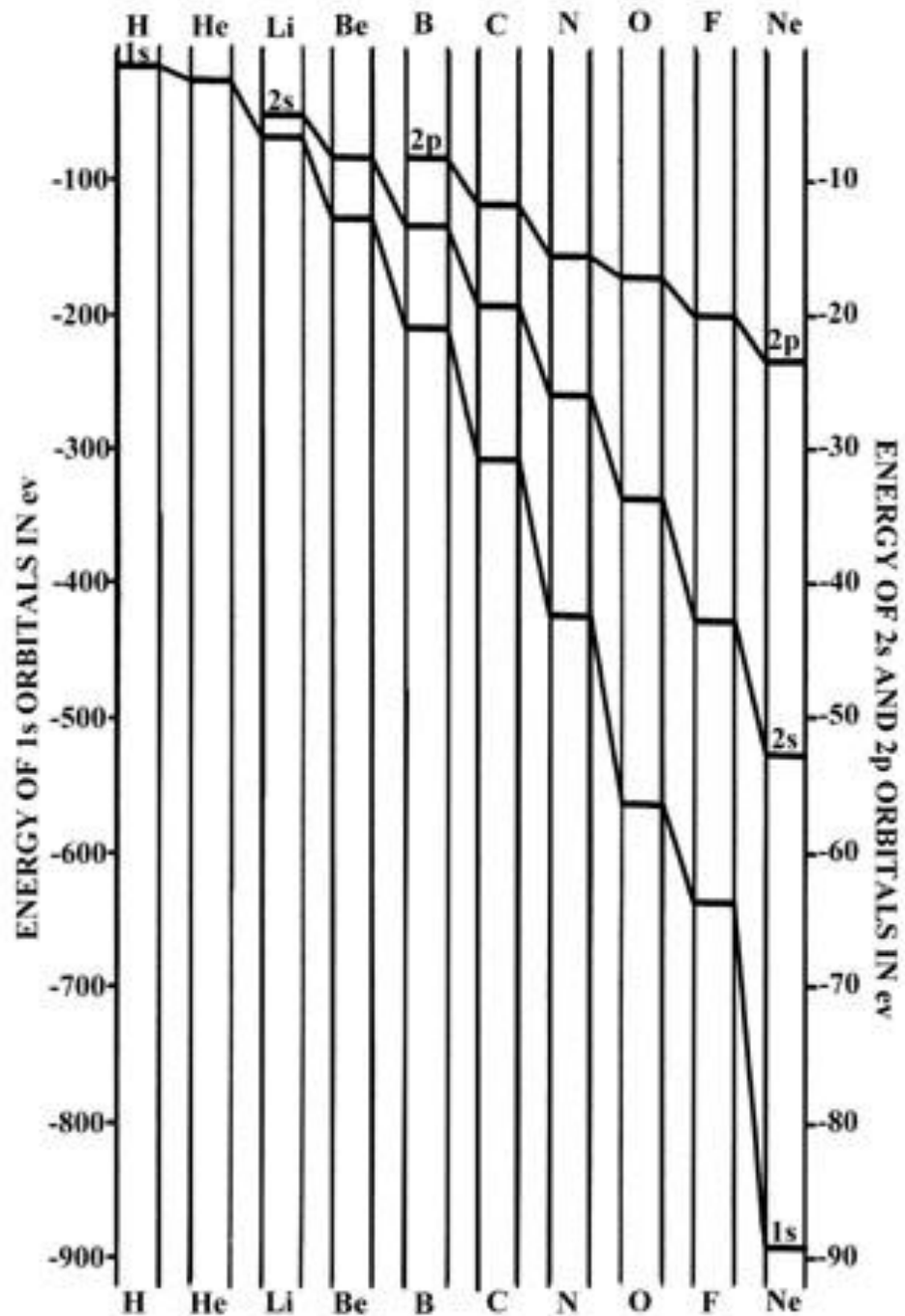
Fig. 5-3. An orbital energy level diagram for the elements H to Ne

➢ (Note that the energy scale used for the 1s orbital differs by a factor of ten from that for the 2s and 1p orbitals.)

➢ The orbital energies show a uniform decrease when the nuclear charge is increased, reflecting an increase in the binding of the electrons.

➢ The *total energy of a many-electron atom* is **not** simply **the sum** of the orbital energies. ***Summing the orbital energies does not take proper account of the repulsions between the electrons***. The orbital energies do, however, provide ***approximate*** estimates of the ionization potentials.

➢ The ionization potential is the energy required to remove one electron from an atom, and an orbital energy is a measure of the binding of a ***single electron*** in a given orbital.

➢ Thus the ionization potential should be ***approximately*** equal to ***minus*** the orbital energy. For example, the ionization potential of lithium is 5.39 eV and the 2s orbital energy is -5.34 eV. Similarly I_1, for neon is 21.56 ev and the 2p orbital energy is -23.14 ev.

- ➢ ***Shell structure is also evident in the ionization potentials and orbital energies of atoms.***
- ➢ By ***exposing the atom to light of very short wavelength (in the X-ray region of the spectrum), it is possible to ionize one of the inner shell electrons***, rather than a valence electron. That is, the energy of an ***X-ray photon*** is comparable to the binding energy of an inner shell electron.
- ➢ The resulting ion is in a very unstable configuration and after a very brief period of time an electron from the outer shell "falls" into the vacancy in the inner shell.
- ➢ In falling from an outer to an inner shell the binding of the electron is greatly increased and a photon is emitted.
- ➢ The energy of this photon should be ***approximately*** equal to the difference in energies of the outer shell and inner shell orbitals.
- ➢ For example, the photon emitted when neon loses an inner shell electron has an energy of 849 ev.

➢ The difference in energy between the 2p and 1s orbitals of neon is 869 eV. Photons with energies in this range occur in the X-ray region of the spectrum.

➢ It is apparent from the variation in the 1s orbital energies shown in Fig. 5-3 that the energies and hence the frequencies of the X-ray photons will increase as the nuclear charge is increased.

➢ It was from a study of the X-ray photons emitted by the elements that Moseley was first able to determine the nuclear charges (the atomic numbers) of the elements.

Variation of the effective nuclear charge (Z_{eff}) for the outermost valence electron with atomic number
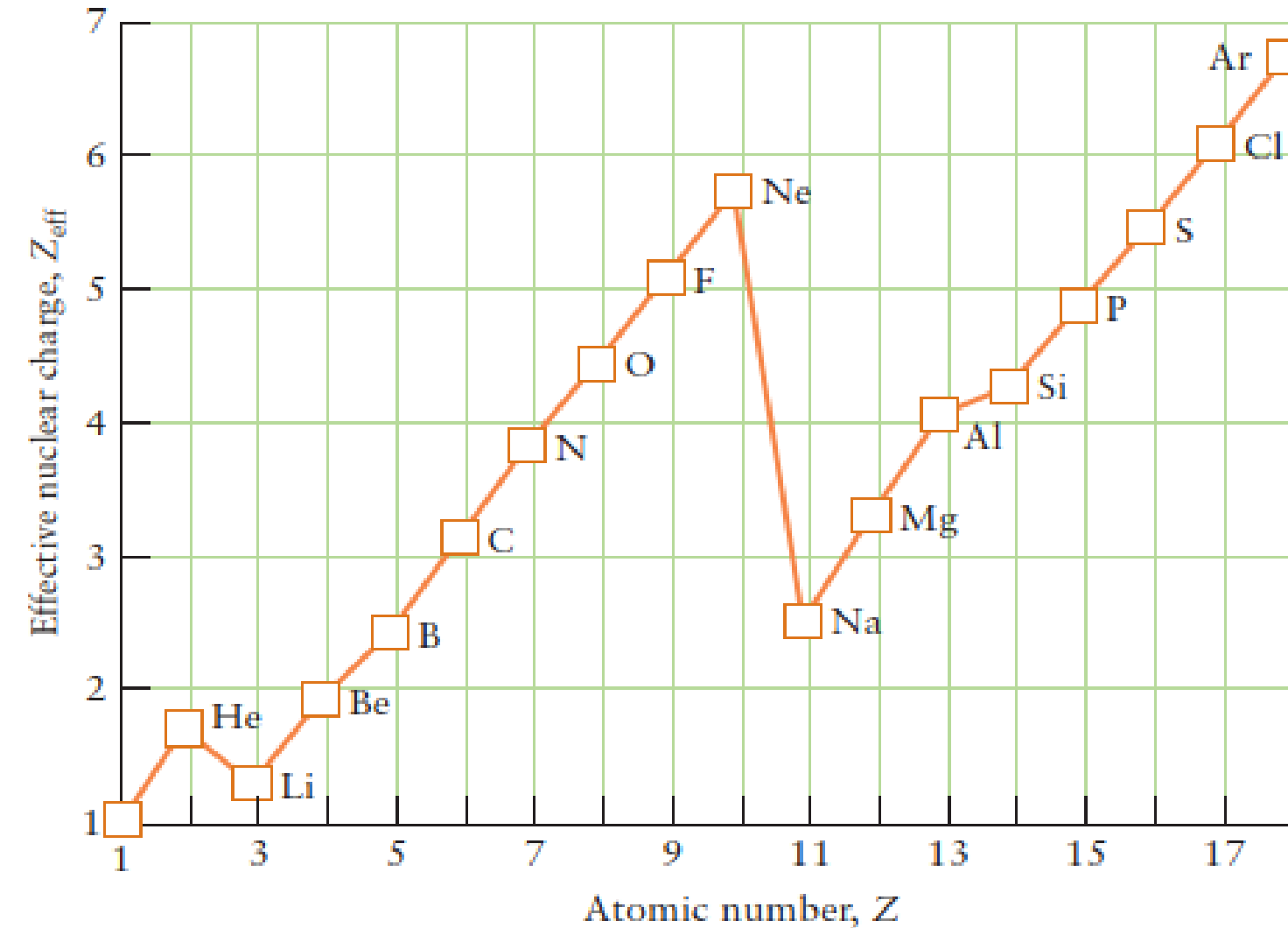
FIGURE 1.45 The variation of the effective nuclear charge for the outermost valence electron with atomic number. Notice that the effective nuclear charge increases from left to right across a period but drops when the outer electrons occupy a new shell. (*The effective nuclear charge is actually $Z_{eff}e$, but Z_{eff} itself is commonly referred to as the charge.*)

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 7.3.3).
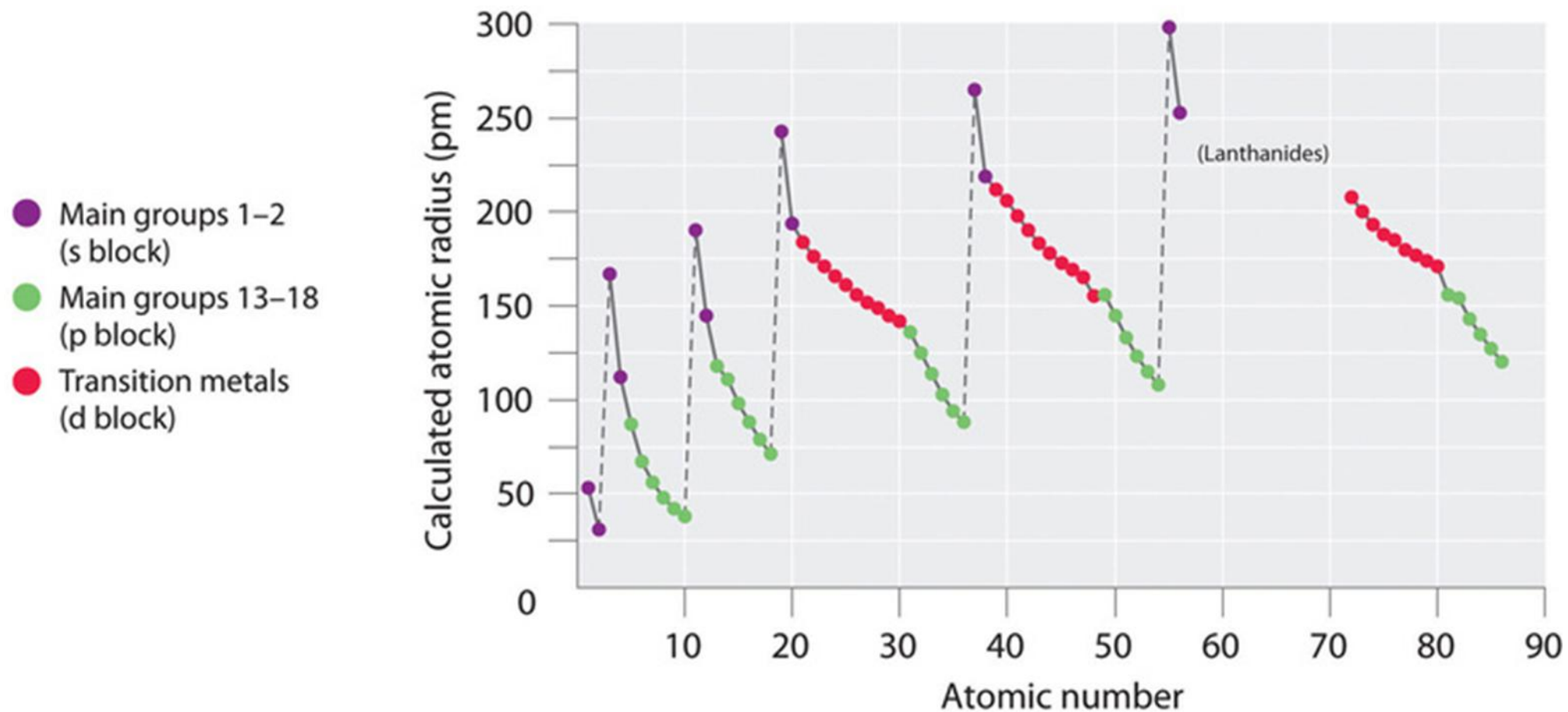
Figure 7.3.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 7.3.4).

Trends in atomic size result from differences in the effective nuclear charges (Z_{eff}) experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always less than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.
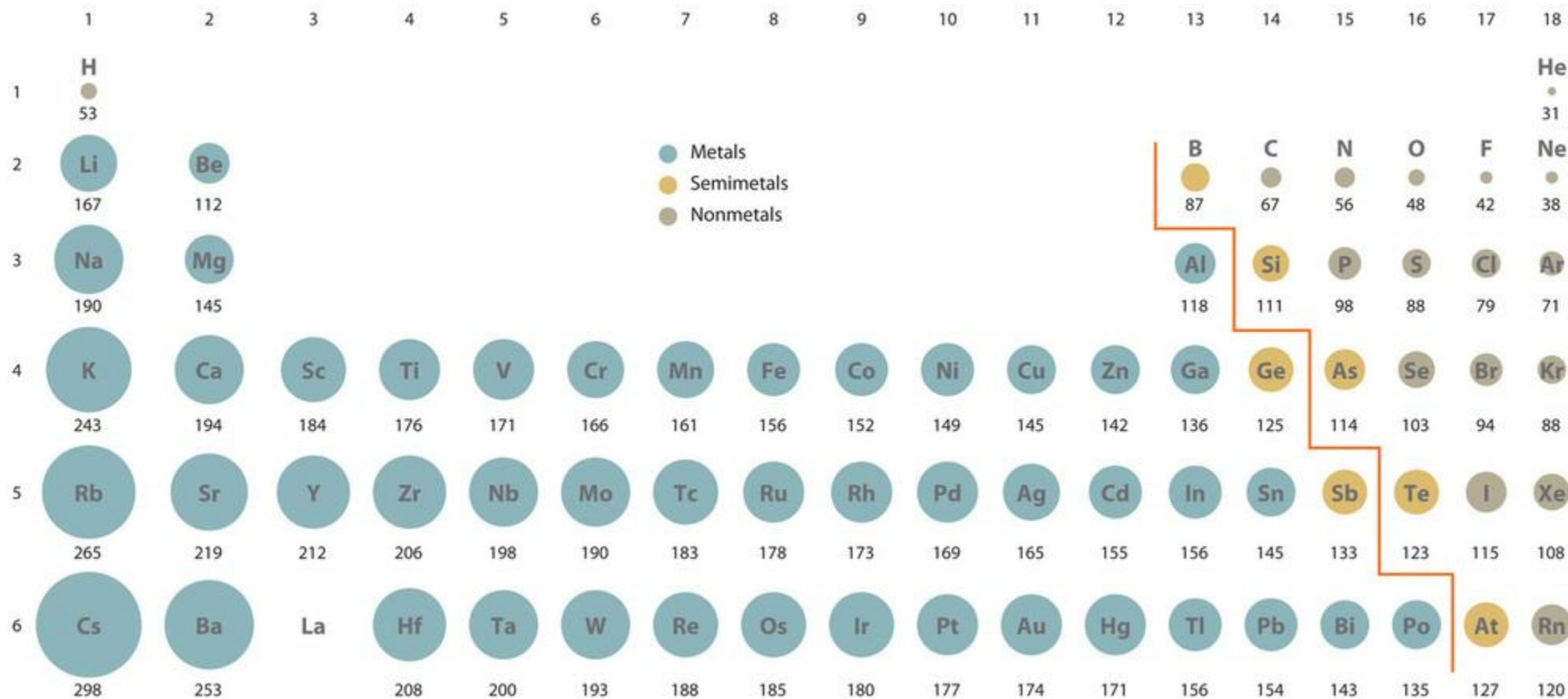
Figure 7.3.4 Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions.

Source: Web elements [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties.

➤ *Variation of atomic radii*
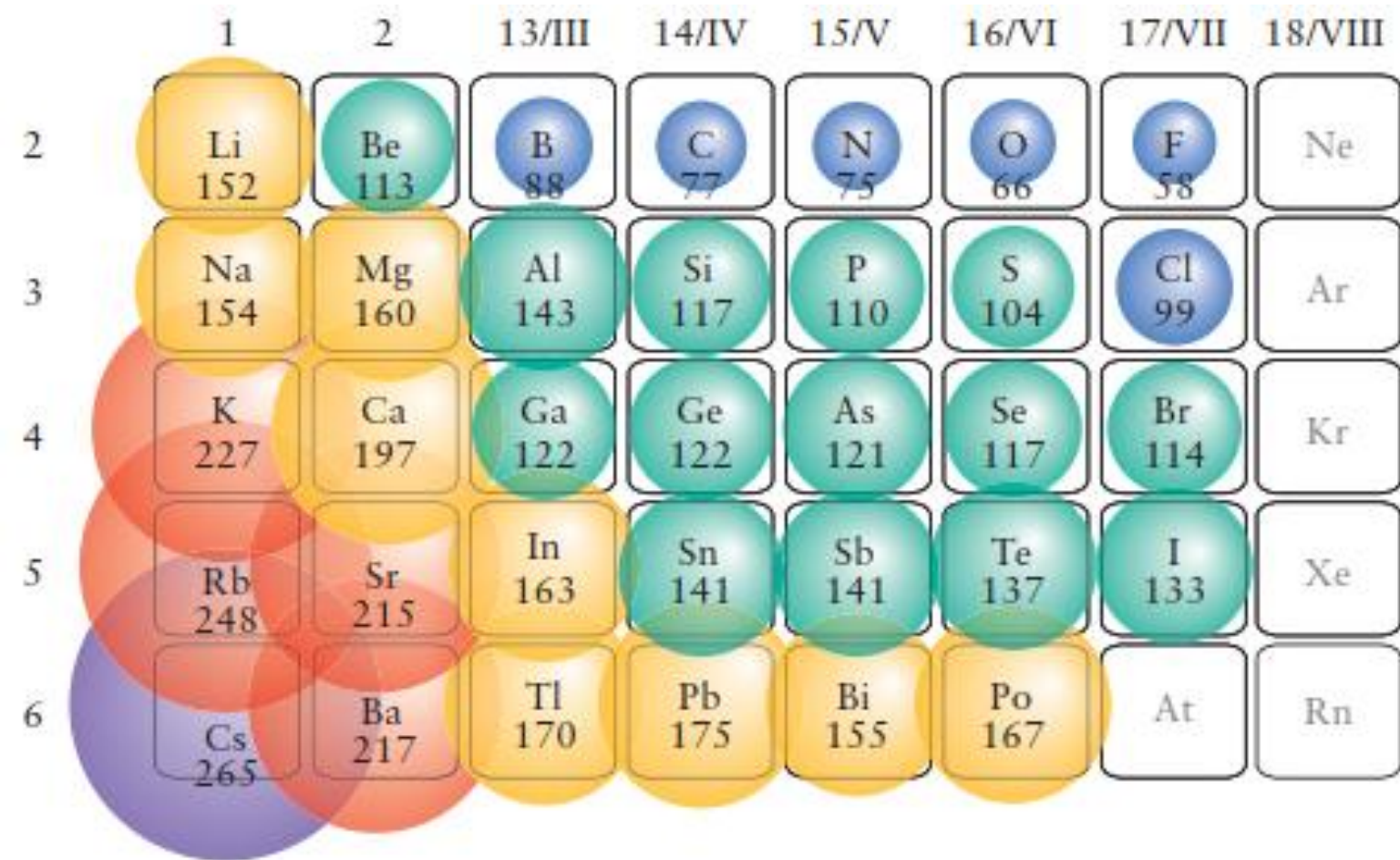
FIGURE 1.46 The **atomic radii** (in picometers) of the main-group elements.
The radii decrease from left to right in a period and increase down a group. The colors used here and in subsequent charts represent the general magnitude of the property.

➤ Atomic radii generally decrease from left to right across a period as the effective atomic charge increases, and they increase down a group as successive shells are occupied.

➢ The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10.

➢ Although electrons are being added to the 2s and 2p orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2s electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.)

➢ In contrast, the two 2s electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2s electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium.

➢ Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2s and 2p orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size.

➢ The ***increase in atomic size going down a column*** is also due to ***electron shielding***, but the situation is more complex because the principal quantum number *n* is not constant. ***The size of the orbitals increases*** *as n increases,* ***provided the nuclear charge remains the same***.

➢ In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to ns orbitals with increasing values of n. However, ***it is important to remember that the radius of an orbital depends dramatically on the nuclear charge.*** *As we go down the column of the group 1 elements, the principal quantum number n increases from 2 to 6, but the nuclear charge increases from +3 to +55!*

➢ As a consequence, the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the inner electrons.

➢ If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration.

➢ The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$ shells, abbreviated as $[Xe]5s^24d^{10}5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus.

➢ The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table.

➢ Irregularities can usually be explained by variations in effective nuclear charge.

❑ **Ionic Radii and Isoelectronic Series**

➢ An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion).
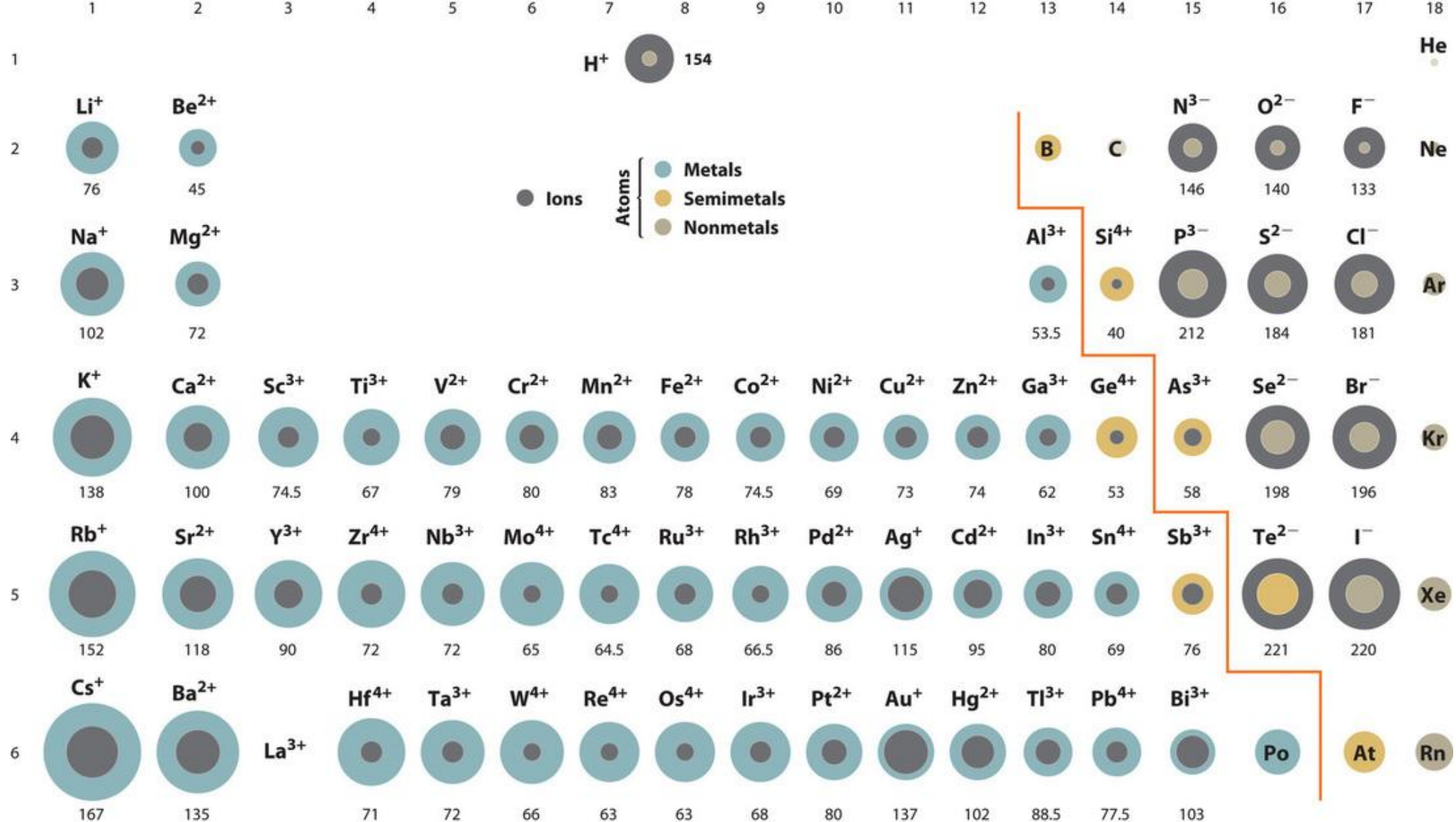
Figure 7.3.7: Ionic Radii (in Picometers) of the Most Common Ionic States of the s-, p-, and d-Block Elements. Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

➤ *Variation of ionic radii*
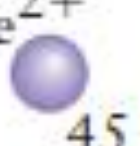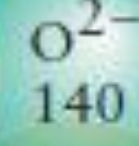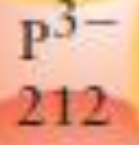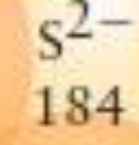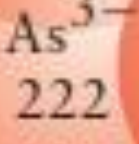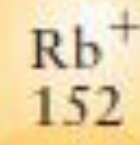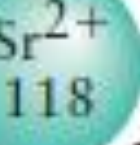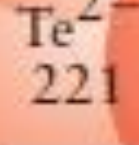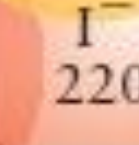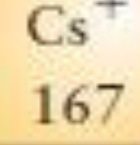
FIGURE 1.48 The **ionic radii** (in picometers) of the ions of the main-group elements. Note that cations are typically smaller than anions—in some cases, very much smaller.

➢ *Variation of ionic radii*

❖ *Cations are smaller than their parent atoms while anions are larger.*

❖ *Ionic radii generally increase down a group and decrease from left to right across a period.*
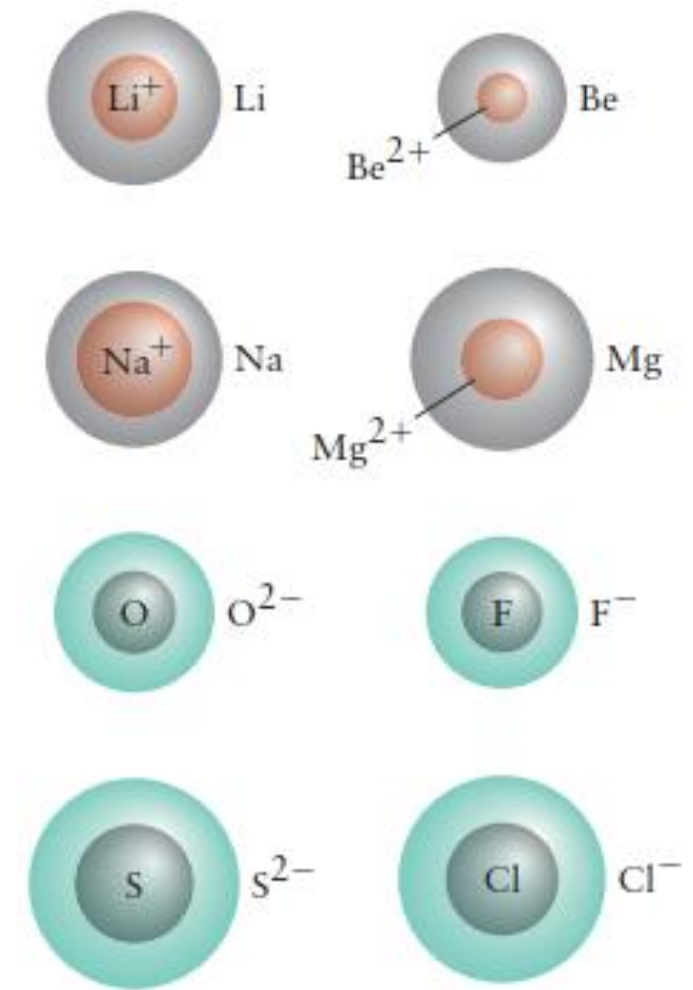
FIGURE 1.49 The relative sizes of some cations and anions compared with their parent atoms. Note that cations (pink) are smaller than their parent atoms (gray), whereas anions (green) are larger.

➤ *All cations are smaller than their parent atoms*, because the atom loses one or more electrons to form the cation and exposes its core, which is generally much smaller than the parent atom.

❖ For example, the *atomic radius of Li, with the configuration $1s^2 2s^1$, is 152 pm*, but the ionic radius of *Li^+, the bare helium-like $1s^2$ core of the parent atom, is only 76 pm*.

➤ The *anions are larger than their parent atoms*. The reason can be traced to the **increased *number of electrons in the valence shell of the anion and the repulsive effects exerted by electrons*** on one another.

➤ The variation in the radii of *anions* shows the same diagonal trend as that for atoms and cations, with *the smallest at the upper right of the periodic table*, close to fluorine.

❏ *Isoelectronic series*

➢ *Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table.*

➢ Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an **isoelectronic series**.

➢ For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^2 2s^2 2p^6$) is shown below.

N^{3-} 146	O^{2-} 140	F^- 133	Na^+ 98	Mg^{2+} 79	Al^{3+} 57
N 71	O 66	F 71	Na 186	Mg 160	Al 143

➢ The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1s, 2s, and 2p orbitals, but the nuclear charge varies from +7 (N) to +13 (Al).

➢ As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table 7.3.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

➢ Atoms and ions with the same number of electrons are called **isoelectronic**.

❖ For example, Na^+, F^-, and Mg^{2+} are isoelectronic. All three ions have the same electron configuration, $[He]2s^2 2p^6$, but *their radii differ because they have different nuclear charges* (see Fig. 1.48). *The Mg^{2+} ion has the largest nuclear charge*; so, it has the strongest attraction for the electrons and therefore the *smallest radius*. The *F^- ion has the lowest nuclear charge* of the three isoelectronic ions and, as a result, it has *the largest radius*.

❑ Ionization Energy

FIGURE 1.50 The **first ionization energies** of the main-group elements, in kilojoules per mole.

❖ *In general*, low values are found at the lower left of the table and high values are found at the upper right.

❑ The Ionization Potentials

➢ Reference to Table 5-1 indicates that in general the amount of energy required to remove one of the outer electrons increases as the effective nuclear charge increases.

➢ The increase in I_1 from approximately 5 eV for sodium to approximately 16 eV for argon dramatically illustrates the increase in the force which the nucleus exerts on the outer electrons as the nuclear charge and the number of **outer** electrons is increased.

➢ The effect of the half-filled set of p orbitals is again evident as I_1 is slightly larger for phosphorus than for sulphur.

➢ There is an apparent discrepancy in the value for I_1 observed for magnesium. The outer electronic configuration of magnesium is $3s^2$ and for aluminum is $3s^2 3p^1$. The value of 7.64 ev observed for magnesium is the energy required to remove a $3s$ electron, while the value quoted for aluminum is the energy required to remove a $3p$ electron.

➢ An s orbital is more stable than a p orbital because of its greater penetration of the inner core of electron density.

➢ Thus the penetration effect overrides the increase in the effective nuclear charge.

➢ We can test the validity of this explanation by comparing the energies required to remove a second electron (I_2) from the magnesium and aluminium atoms.

➤ The outer electronic configurations of the singly-charged magnesium and aluminum ions are $3s^1$ and $3s^2$. Thus a comparison of the second ionization potentials (I_2) will be free of the complication due to the penetration effect because we will be comparing the amount of energy required to remove an *s* electron in each case The values in Table 5-1 indicate that the removal of an *s* electron requires more energy in aluminum than in magnesium, a result which is consistent with the greater effective nuclear charge for aluminium than for magnesium.

❖ What explanation can be given to the second ionization potential of sulfur being almost equal to that for chlorine?

➤ It is worthwhile noting the large value of the second ionization potential observed for sodium. The sodium ion has the electron configuration $1s^2 2s^2 2p^6$, i.e., there are no remaining outer electrons. The second ionization potential for sodium is, therefore, a measure of the amount of energy required to remove one of what were initially inner shell electrons in the neutral atom. The effective nuclear charge experienced by a $2p$ electron in the sodium ion will be very large indeed, because the number of inner shell electrons for an $n = 2$ electron is only two. That is, only the two electrons in the $1s$ orbital exert a large screening effect. Therefore, coupled to the fact that the ion bears a net positive charge, is the fact that the ratio of outer to inner shell electrons is 8:2, which is even more favourable than that

➢ obtained for argon. (Recall that in the neutral sodium atom the ratio is 1:10.) The value of I_2, for sodium again emphasizes the electronic stability of a closed shell, a stability which is a direct reflection of the large value of the effective nuclear charge operative in such cases.

Ionization Energy

➢ ***First ionization energies typically decrease down a group.***

❖ The *decrease down a group* can be explained by the finding that, *in successive periods, the outermost electron occupies a shell that is farther from the nucleus and is therefore less tightly bound*.

❖ Therefore, it takes less energy to remove an electron from a cesium atom, for instance, than from a sodium atom.

➢ ***First ionization energies generally increase across a period.***

❖ This trend can be traced to the increase in *effective nuclear charge across* a period.

❖ The small departures from this trend can be traced to repulsions between electrons, particularly electrons occupying the same orbital.

❖ For example, *the ionization energy of oxygen is slightly lower than that of nitrogen* because *in a nitrogen atom each p-orbital has one electron, but in oxygen the eighth electron is paired with an electron already occupying an orbital*. The repulsion between the two electrons in the same orbital raises their energy and makes one of them easier to remove from the atom than if the two electrons had been in different orbitals.

❑ **Ionization Energies of Transition Metals & Lanthanides**

➢ As we noted, ***the first ionization energies of the transition metals and the lanthanides change very little across*** *each* **row**.

➢ *Differences in their second and third ionization energies are also rather small,* in sharp contrast to the pattern seen with the *s*- and *p*-block elements.

➢ The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n-1)d$ or $(n-2)f$ electrons, respectively. This means that transition metal cations have $(n-1)d^n$ valence electron configurations, and lanthanide cations have $(n-2)f^n$ valence electron configurations.

➢ ***Because the $(n-1)d$ and $(n-2)f$ shells are closer to the nucleus than the ns shell, the $(n-1)d$ and $(n-2)f$ electrons screen the ns electrons quite effectively***, *reducing the effective nuclear charge felt by the ns electrons*.

➢ As Z increases, *the increasing positive charge is largely canceled* by the electrons added to the $(n-1)d$ or $(n-2)f$ orbitals.

➢ *That the ns electrons are removed before the (n − 1)d or (n − 2)f electrons may surprise you because the orbitals were filled in the reverse order.*

➢ In fact, the *ns*, the $(n − 1)d$, and the $(n − 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. ***As the d orbitals are filled, the effective nuclear charge causes the 3d orbitals to be slightly lower in energy than the 4s orbitals.*** The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n − 2)f^n$ valence electron configuration.

➢ Because their first, second, and third ionization energies change so little across a row, ***these elements have important horizontal similarities in chemical properties*** in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Ionization Energy

- *The s- and p-block elements show a larger range of I_1 values than do the transition-metal elements.*

- Generally, the ionization energies of the *transition metals increase **slowly** from left to right in a period.*

- The f-block metals also show *only a small variation* in the values of I_1.

❑ The low ionization energies of elements at the lower left of the periodic table account for their metallic character. *A block of metal consists of a collection of cations of the element surrounded by a sea of valence electrons that the atoms have lost* (Fig. 1.53).

FIGURE 1.53 A block of **metal consists of an array of cations (the spheres) surrounded by a sea of electrons**. The charge of the electron sea cancels the charges of the cations.
The electrons of the sea are mobile and can move past the cations quite easily and hence conduct an electric current.

Metal block

Cation
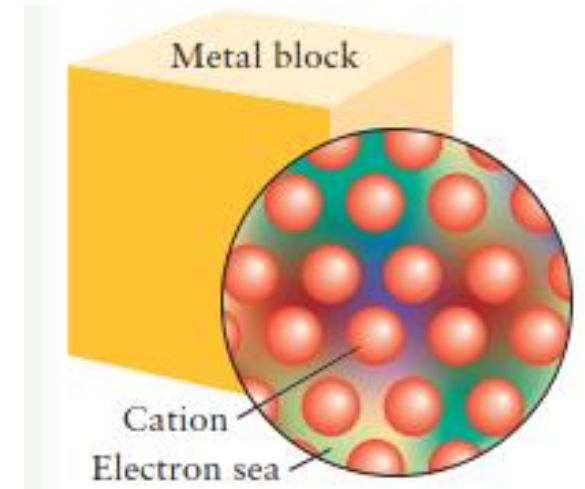
Electron sea

➢ *Only **elements with low ionization energies**—the members of the s-block, the d-block, the f-block, and the lower left of the p-block—can form **metallic solids**, because only **they can lose electrons easily**.*

➢ **Metals are found toward the lower left of the periodic table because these elements have low ionization energies and can readily lose their electrons.**

➢ *The elements at the upper right of the periodic table have high ionization energies*; so, they do not readily lose electrons and are therefore not metals. *—the nonmetals are found toward the upper right of the periodic table*.

➢ **The first ionization energy is highest for elements close to helium and is lowest for elements close to cesium.**

➢ **Second ionization energies are higher than first ionization energies (of the same element) and very much higher if the electron is to be removed from a closed shell**.

❑ Electron Affinity

FIGURE 1.54 The variation in **electron affinity** in kilojoules per mole of the main-group elements.

➢ Where two values: first refers to the formation of a singly charged anion and the second is the additional energy needed to produce a doubly charged anion. The negative signs of the second values indicate that energy is required to add an electron to a singly charged anion.

❑ Electron Affinity

➢ The *variation is less systematic than that for ionization energy*, but high values tend to be found close to fluorine (but not for the noble gases).

➢ Where two values are given, the first refers to the formation of a singly charged anion and the second is the additional energy needed to produce a doubly charged anion.

➢ The negative signs of the second values indicate that energy is required to add an electron to a singly charged anion.

❑ **Electron Affinity**

❖ *A Group 16/VI atom, such as O or S, has two vacancies in its valence-shell p-orbitals and can accommodate two additional electrons. The first electron affinity is positive because energy is released when an electron attaches to O or S.* However, **attachment of the second electron requires energy because of the repulsion by the negative charge already presen**t in O^- or S^-. *Unlike that of a halide ion, however, the valence shell of the O^- anion has only seven electrons and thus can accommodate an additional electron.*

✓ Therefore, we expect that less energy will be needed to make O^{2-} from O^- than to make F^{2-} from F^-, where no such vacancy exists. In fact, 141 kJ·mol^{-1} is released when the first electron adds to the neutral atom to form O^-, but 844 kJ·mol^{-1} must be supplied to add a second electron to form O^{2-}; so, the total energy required **to make O^{2-} from O is -703 kJ·mol^{-1}**.

✓ **This energy can be achieved in chemical reactions/interactions, and O^{2-} ions are common in metal oxides.**

❑ **Predicting trends in electron affinity**

➤ *The electron affinity of carbon is greater than that of nitrogen; indeed, the latter is negative.*

➤ *We expect more energy to be released when an electron enters the N atom, because an* N atom is smaller than a C atom *and its nucleus is more highly charged: the effective nuclear charges for the outermost electrons of the neutral atoms are 3.8 for N and 3.1 for C.* However, the opposite is observed.

➤ *Suggest a reason for this observation.*

✓ We must also consider the ***effective nuclear charges experienced by the valence electrons*** in the anions (Fig. 1.55). When C^- forms from C, the additional electron occupies an empty 2p-orbital. The *incoming electron is well separated from the other p-electrons,* and so *it experiences an effective nuclear charge close to 3.1*.

✓ When N^- forms from N, the additional electron must occupy a 2p-orbital that is already half full. The effective nuclear charge experienced by this electron is therefore much less than 3.8; so, energy is required to form N, and the electron affinity of nitrogen is lower than that of carbon.
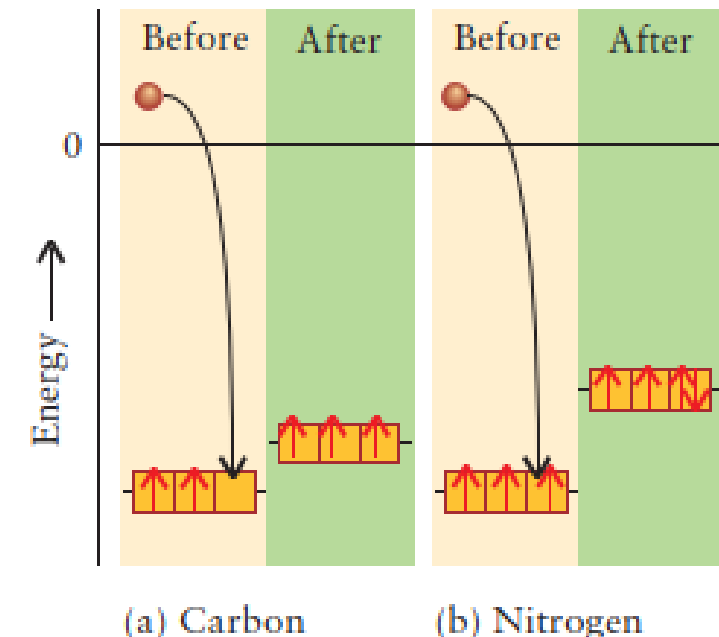
(a) Carbon

(b) Nitrogen

FIGURE 1.55 The energy changes taking place when an electron is added to a carbon atom and a nitrogen atom.
(a) ***A carbon atom can accommodate an additional electron in an empty p-orbital***.
(b) When an electron is added to a nitrogen atom it must pair with an electron in a p-orbital. The incoming electron experiences so much repulsion from those already present in the nitrogen atom that the electron affinity of *nitrogen is less than that of carbon and is in fact negative*.

❑ Polarizability

➢ For an isolated atom, the **average distribution of electronic charge** about the nucleus is **spherical** (Fig. 9-17a). *This is not the case for an atom in the vicinity of another atom, molecule, or ion or in an externally applied electric field*. For example, when an atom is placed in the electric field between two oppositely charged parallel plates (Fig. 9-17b), the position of the much heavier nucleus is left essentially unchanged, but the electron cloud is distorted (shifted toward the positively charged plate). *Such an atom is said to be polarized*. For *a polarized atom, the centers of positive and negative charges are displaced from each other*. The magnitude of this displacement depends on how easily the electron cloud of the atom can be distorted.

Center of positive charge (the nucleus)   Center of electronic charge
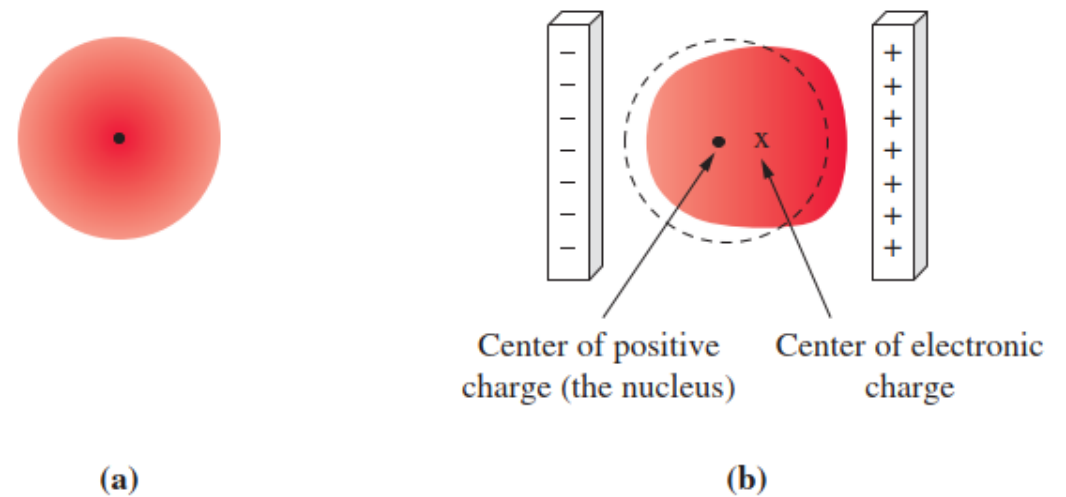
(a)   (b)

FIGURE 9-17 *Polarization of an atom*
(a) For an isolated atom, the distribution of electronic charge about the nucleus is spherical.
(b) *In an electric field*, the distribution of electronic charge is nonspherical, and the centers of positive and negative charge no longer coincide. The atom is said to be *polarized*.

❑ **Polarizability**

➢ **The _polarizability of an atom provides a measure of the extent to which its electron cloud can be distorted_**, for example, by the application of an externally applied electric field or by the approach of another atom, molecule, or ion.

➢ It is often _expressed in units of volume_.

➢ The polarizability of an atom depends on how diffuse or spread out its electron cloud is, and in general.

❑ **Polarizability**

➢ *Polarizability increases with the size of the atom.*

❖ Thus, polarizability **decreases from left to right across a period** and **increases from top to bottom within a group**.

❖ The polarizability of an atom is similar in magnitude to the atomic volume calculated from atomic radii, as suggested by Figure 9-18.
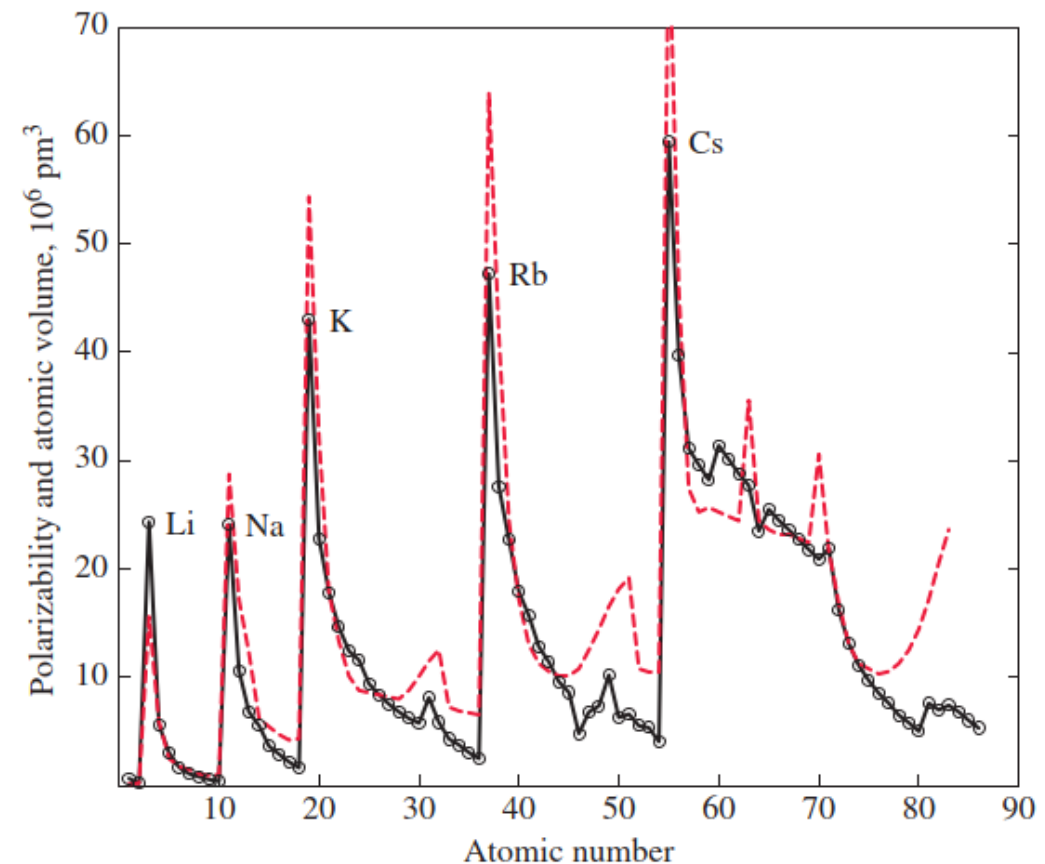
FIGURE 9-18
Polarizabilities and atomic volumes
The variation of polarizability with atomic number (solid black line) closely resembles that of atomic volume (dashed red line). The atomic volume is calculated as , where r is the atomic radius as defined in Figure 9-4. Both polarizability and atomic volume decrease from left to right across a period and increase from top to bottom in a group.

❑ **Polarizability**

❖ **Do all the electrons in an atom contribute equally to the polarizability**?

➢ No.

➢ Quantum mechanical calculations on atoms reveal that the *loosely bound valence electrons contribute more to the polarizability than the tightly bound inner electrons.* This result is not totally unexpected because, as we have already learned, the valence electrons are, on average, farther from the nucleus and experience a smaller effective nuclear charge than do the inner electrons. Thus, *the valence electrons experience a greater shift in position than the inner electrons when an atom is placed in an externally applied electric field or is approached by another atom, molecule, or ion.*

➢ We will see later that *the polarizabilities of atoms, molecules, and ions enter into discussion of, for example, chemical bonding, intermolecular forces, phase changes, solvation, and chemical reactivity.*

❑Ionization Energy and Electron Affinity: Electronegativity and Hardness

➢ One parameter which is widely used in general discussion of the chemical character of an element is its **electronegativity**. This is *defined as the ability of an atom in a molecule to attract an electron to itself*.

➢ There is **no direct** way of **measuring** this ability *though a number of indirect methods* have been suggested.

➢ Robert S. Mulliken proposed that the ***arithmetic mean of the first ionization energy (I_1) and the electron affinity (E)*** should be a measure of the tendency of an atom to attract electrons **(as the electron affinity is a measure of the tendency of the atom to gain an electron, and the ionization potential indicates its tendency to lose an electron)**. As this definition is not dependent on an arbitrary relative scale, it has also been termed ***absolute electronegativity***.

➢ $\chi = |EI_1 + E_{ea}| = |(I_1 + A)/2|$.　　　　(Eq. 1)

➢ This is the most fundamental of a number of proposed definitions of electronegativity.

➢ By definition, the magnitude of a quantity is a positive number. Our definition of electron affinity produces negative values for the electron affinity for most elements, so vertical lines indicating **absolute value** are needed in the above Equation to make sure that we are **adding two positive numbers** in the numerator.

➢ Elements with a *large first ionization energy and a very negative electron affinity* have a large positive value in the numerator of the above Equation 1, *so their electronegativity is high*.

➢ Elements with a small first ionization energy and a small electron affinity have a small positive value for the numerator in the above Equation 1, so they have a low electronegativity.

➢ The classic one is the Pauling electronegativity, based on bond energies. Despite all attempts at improvement, the Pauling values are still the most generally used. A major difficulty is that the attraction for an electron is clearly not expected to be the same for different valences of an element.

➢ Inserting the appropriate data into the above Equation gives a Mulliken electronegativity value for fluorine of 1004.6 kJ/mol. To compare Mulliken's electronegativity values with those obtained by Pauling, Mulliken's values are divided by 252.4 kJ/mol, which gives Pauling's value (3.98).

➢ However, it is more usual to use a linear transformation to transform these absolute values into values that resemble the more familiar Pauling values. For ionization energies and electron affinities in electron-volts (eV):

➢ $\chi_{Mulliken} = 0.187(EI_1 + E_{ea}) + 0.17.$ (Eq. 2)

➢ Zhang has proposed a set of values, based on covalent radii and ionization potentials and geared to Pauling values, which are defined for each of the main oxidation states of the element. These values are one of the more general sets available, though they have some deficiencies for the Main Group elements.

➢ The Mulliken electronegativity can only be calculated for an element for which the electron affinity is known, fifty-seven elements as of 2006.

➢ The **Mulliken electronegativity (χ) of an atom is sometimes said to be the** negative **of the chemical potential (μ)**. By inserting the energetic definitions of the ionization potential and electron affinity into the Mulliken electronegativity, it is possible to show that the **Mulliken chemical potential** is a finite difference approximation of the electronic energy with respect to the number of electrons., i.e., $\mu_{\text{Mulliken}} = -\chi_{Mulliken} = -(EI_1 + E_{ea})/2.$ (Eq. 3)

➢ Another parameter related and complementary to electronegativity is **hardness**. Hardness η can be approximated as half the difference between these two values: $\eta = (EI_1 - E_{ea})/2 = (I - A)/2.$

✓ The hardness of an atom is a parameter which attempts to quantify the ability of electrons to redistribute themselves within the atom and thus is a measure of the **polarizability** of the atom, as described earlier.

➤ Atoms with small ionization energies and small electron affinities, such as the *heavy* (halogens and oxygen) Group elements (i.e. those elements on the bottom right-hand side of the p-block), are termed '*soft*'.

➤ Small atoms, such as sodium, oxygen and fluorine, are termed '*hard*'.

❖ The hardness of the *donor atoms of a ligand bonding to a metal atom is of great consequence in determining the strength of the bonding interaction*.

➤ The general rule is that '*like bonds to like*', i.e. *soft metal centers such as Hg(II) and Ag(I) have a strong preference for binding to soft donor atoms* such as P, S, Se and I. And vice versa. This is known as the **Soft Hard Acid-Base (SHAB) Principle**.

TABLE 2.14a Pauling's values of the electronegativity of elements

$H = 2.1$

Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1														

Lanthanides range from 1.0 to 1.2
Actinides range from 1.3 to 1.4

TABLE 2.14b Electronegativity values after Zhang

H
1 2.25

Element	Values (oxidation state in boldface)
Li	**1** 0.95
Be	**2** 1.45
B	**3** 1.95
C	**4** 2.55
N	3.05
O	3.65
F	4.2
Na	**1** 0.95
Mg	**2** 1.2
Al	**3** 1.5
Si	**4** 1.75 / **3** 1.7
P	**5** 2.1 / **3** 2.0
S	**6** 2.45
Cl	**7** 2.85 / **5** 2.35

Element	Values
K	**1** 0.9
Ca	**2** 1.05
Sc	**3** 1.3
Ti	**4** 1.6 / **3** 1.4 / **2** 1.2
V	**5** 2.0 / **4** 1.85 / **3** 1.6 / **2** 1.35
Cr	**6** 2.3 / **4** 1.9 / **3** 1.65 / **2** 1.4
Mn	**7** 2.5 / **6** 2.4 / **4** 1.95 / **2** 1.45
Fe	**6** 2.4 / **3** 1.7 / **2** 1.45
Co	**3** 1.75 / **2** 1.45
Ni	**2** 1.5
Cu	**2** 1.5 / **1** 1.25
Zn	**2** 1.45
Ga	**3** 1.55 / **1** 1.1
Ge	**4** 1.8 / **2** 1.4
As	**5** 2.05 / **3** 1.6
Se	**6** 2.3 / **4** 1.85
Br	**7** 2.55 / **5** 2.1

Element	Values
Rb	**1** 0.9
Sr	**2** 1.0
Y	**3** 1.2
Zr	**4** 1.5 / **3** 1.35 / **2** 1.2
Nb	**5** 1.75 / **4** 1.65 / **3** 1.5
Mo	**6** 2.0 / **4** 1.8 / **2** 1.4
Te	**7** 2.3 / **4** 1.8 / **2** 1.4
Ru	**4** 1.9 / **3** 1.65 / **2** 1.45
Rh	**4** 1.85 / **3** 1.65 / **2** 1.45
Pd	**4** 1.85 / **2** 1.45
Ag	**1** 1.15
Cd	**2** 1.3
In	**3** 1.45 / **1** 1.1
Sn	**4** 1.6 / **2** 1.25
Sb	**5** 1.75 / **3** 1.45
Te	**6** 1.95 / **4** 1.6
I	**7** 2.15 / **5** 1.8

Element	Values
Cs	**1** 0.9
Ba	**2** 1.0
La	**3** 1.2
Hf	**4** 1.55 / **3** 1.45 / **2** 1.3
Ta	**5** 1.9 / **4** 1.75 / **3** 1.55
W	**6** 2.15 / **5** 2.0 / **4** 1.85
Re	**7** 2.35 / **6** 2.2 / **4** 1.9
Os	**8** 2.6 / **6** 2.3 / **4** 1.95
Ir	**4** 1.9 / **3** 1.7 / **2** 1.5
Pt	**4** 1.9 / **2** 1.5
Au	**3** 1.7 / **1** 1.25
Hg	**2** 1.35 / **1** 1.2
Tl	**3** 1.5 / **1** 1.1
Pb	**4** 1.55 / **2** 1.25
Bi	**5** 1.7 / **3** 1.4
Po	**6** 1.9 / **4** 1.6
At	**7** 2.05 / **5** 1.75

Element	Values
Fr	**1** 0.9
Ra	**2** 0.95
Ac	**3** 1.25

Lanthanides   **4** 1.4 to 1.5
               3 1.2 to 1.35
               2 1.05 to 1.2

Note: Values rounded to 0.05. Oxidation states in boldface.

- Electronegativities are most useful in the guidance they give to the electron distribution in a bond. In a bond A-B between two atoms, the electron density in the bond may lie evenly between the two atoms or be concentrated more towards one atom, say B, than towards the other, when the bond is said to be polarized.
- In the limiting case, when the electron density of the bonding electrons is entirely on B, an electron has been fully transferred from A to B and an ionic compound, A^+B^-; forms.
- The electron density distribution in the bond may be predicted from the electronegativities of A and B.
- **If A and B have the same electronegativities**, it follows from the definition that A and B attract the electrons in the bond equally and **no polarization** results.
- If B is more electronegative than A, its attraction for the bond electrons is the stronger and polarization results, the degree of polarization being proportional to the difference in electronegativity. A large electronegativity difference favors the formation of ions and, as a rough guide, an ionic compound forms between A and B if they differ in electronegativity by more than two units.
- Thus elements with very high or very low electronegativities are more likely to form ionic compounds than those with intermediate values.
- The electronegativity of an element depends on the other atoms attached to the one in question. Thus, carbon in H_3C-X is less electronegative than carbon in F_3C-X, as the highly electronegative fluorine atoms in the trifluoromethyl compound remove more electron density from the carbon in the C-F bonds than do the hydrogen atoms in the C-H bonds of the methyl compounds. As a result, the carbon atom in F_3C-X has more tendency to attract the electrons in the C-X bond than has the carbon atom in H_3C-X.
- It follows that the electronegativity values given in Table 2.14 represent the behaviour of the elements in an 'average' chemical environment and the effective electronegativity of an element in any particular compound depends in detail on its environment.

❑ **Some Chemical Implications**

➢ A detailed study of the chemical implications of the *orbital theory of electronic structure must await our discussion of the chemical bond*. However, we can at this point correlate the gross chemical behavior of the elements with the general results of the orbital theory.

➢ The **effective nuclear charge is a minimum for the group I elements** in any given row of the periodic table. Therefore, it requires less energy to remove an outer electron from one of these elements than from any other element in the periodic table. ***The strong reducing ability of these elements is readily accounted for.***

➢ The variation in the *relative reducing power of the elements across a given period or within a given group will be determined by the variation in the effective nuclear charge*.

➢ The ***ability of the elements in a given row of the periodic table to act as reducing agents should undergo a continuous*** ***decrease*** ***from group I to group VII***, since the ***effective nuclear charge*** ***increases*** across a given row.

➢ Similarly, ***the reducing ability should increase down a given column (group) in the table since the effective nuclear charge decreases as the principal quantum number is increased***. Anticipating the fact that electrons can be transferred from one atom (the ***reducing agent***) to another (the ***oxidizing agent***) during a chemical reaction, we expect the elements to the left of the periodic table to exhibit a strong tendency to form positively charged ions.

➢ The ability of the elements to act as ***oxidizing agents*** should ***parallel directly*** the ***variations in the effective nuclear charge***.

➢ Thus, the ***oxidizing ability should increase across a given row*** (from group I to group VII) and ***decrease down a given family***.

- These trends are, of course, just the opposite of those noted for the reducing ability.

- We can also relate the chemical terms "reducing ability" and "oxidizing ability" to the experimentally determined energy quantities, "ionization potential" and "electron affinity."

- The ***reducing ability should vary inversely with the ionization potential***, and the ***oxidizing ability should vary directly with the electron affinity***.

- The elements in groups VI and VII should exhibit a strong tendency for accepting electrons in chemical reactions to form negatively charged ions.

- ***Francium, which possesses a single outer electron in the 7s orbital, should be the strongest chemical reducing agent*** and ***fluorine, with an orbital vacancy in the 2p subshell, should be the strongest oxidizing agent***.

- ➢ A great deal of chemistry can now be directly related to the electronic structure of the elements.

- ✓ For example, the reaction $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

  is explained chemically by stating that Cl$_2$ is a stronger oxidizing agent than Br$_2$.

- ✓ The **electronic interpretation** is that the orbital vacancy in Cl is in a 3p orbital and closer to the nucleus than the 4p orbital vacancy in Br.

- ✓ Thus, **the effective nuclear charge which attracts the extra electron is larger for the Cl atom** than for the Br atom.

- ➢ We could of course interpret this same reaction by stating that the **Br$^-$ ion is a stronger reducing agent than is the Cl$^-$ ion**.

- ✓ In other words, *the extra electron in the Br$^-$ ion is less tightly held than is the extra electron in the Cl$^-$ ion*.

- ✓ The explanation in terms of the relative effective nuclear charges is the same as that given above.

- The *decrease in the effective nuclear charge down the halogen family of elements leads to some interesting differences in their chemistry*.

- For example, hydrogen chloride may be prepared from sodium chloride and sulphuric acid: $2Cl^- + 2H^+ + SO_4^{2-} \rightarrow 2HCl + SO_4^{2-}$

- However, the **same** method **cannot be employed** in the preparation of **hydrogen bromide** or **hydrogen iodide**. In the preparation of hydrogen bromide from sodium bromide, $2Br^- + 2H^+ + SO_4^{2-} \rightarrow 2HBr + SO_4^{2-}$

- some of the HBr reacts further, $2HBr + 2H^+ + SO_4^{2-} \rightarrow 2H_2O + SO_2 + Br_2$
- and the **HBr is** thus **contaminated**.

- In preparation of hydrogen iodide, a further reaction again occurs:
  - $2HI + 2H^+ + SO_4^{2-} \rightarrow 2H_2S + H_2O + 4I_2$
- The last two reactions are clearly redox reactions in which **the halide ions reduce the sulphur** in the SO_4^{-2} anion **to a lower oxidation state**.

➢ Since Cl has the **highest effective nuclear charge**, the **Cl⁻ ion should be the weakest** reducing agent of the three halide ions.

➢ Indeed, the Cl⁻ ion **is not a strong enough reducing agent** to change the oxidation state of S in SO_4^{2-}.

➢ The *Br⁻ ion possesses an intermediate value for the effective nuclear charge and thus it is a stronger reducing agent* than the Cl⁻ ion. The Br⁻ ion reduces the oxidation number of sulfur from (+6) to (+4).

➢ Since the **I⁻** ion binds the extra electron least of all (the electron is in an $n = 5$ orbital and *the effective nuclear charge of iodine is the smallest* of the three), it should be **the strongest reducing agent** of the three halide ions. The **I⁻ ion** in fact reduces the sulfur from (+6) to (-2).

A word about **oxidation numbers** and electron density distributions is appropriate at this point. An oxidation number does not, in general, represent the formal charge present on a species. Thus S is not S^{+6} in the SO^{-2} ion, nor is it S^{-2} in the H_2S molecule. However, the average electron density in the direct vicinity of the sulfur atom does increase on passing from SO_4^{-2} to H_2S. From their relative positions in the periodic table it is clear that oxygen will have a greater affinity for electrons than sulfur. Thus when sulfur is chemically bonded to oxygen the electron density in the vicinity of the sulfur atom is decreased over what it was in the free atom and increased in the region of each oxygen atom. Again it is clear from the relative positions of H and S in the periodic table that sulfur has a greater affinity for electrons than does hydrogen. Thus in the molecule H_2S, the electron density in the vicinity of the sulfur atom is increased over that found in the free atom. *In changing the immediate chemical environment of the sulfur atom from that of four oxygen atoms to two hydrogen atoms, the electron density (i.e., the average number of electrons) in the vicinity of the sulfur atom has increased.* The assignment of actual oxidation numbers is simply a book-keeping device to keep track of the number of electrons, but *the sign of the oxidation number does indicate the direction of the flow of electron density*. Thus sulfur has a positive oxidation number when combined with oxygen (the sulfur atom has lost electron density) and a negative one when combined with hydrogen (the electron density around sulfur is now greater than in the sulfur atom).

➢ The above are only a few examples of **how a knowledge of the electronic structure of atoms may be used to understand and correlate a large amount of chemical information**. It should be remembered, however, that chemistry is a study of very complex interactions and the few simple concepts advanced here cannot begin to account for the incredible variety of phenomena actually observed. Our discussion has been based solely on energy, and energy alone never determines completely the course of a reaction on a macroscopic level, i.e., when many molecules undergo the reaction. There are statistical factors, determined by the changes in the number of molecules and in the molecular dimensions, which must also be considered. Even so, the energy effect can often be overriding.

❑ Diagonal Relationships

➢ *A diagonal relationship is a similarity in properties between diagonal neighbors in the main groups of the periodic table* (Fig. 1.58).

FIGURE 1.58 The pairs of elements represented by similarly colored boxes show a strong diagonal relationship to each other.

➢ A part of the ***reason for this similarity*** can be seen in Figs. 1.46 and 1.50 by concentrating on the colors that show the ***general trends in atomic radius and ionization energy***. The colored bands of similar values lie in diagonal stripes across the table.

➢ Because *these characteristics affect the chemical properties of an element, it is not surprising to find that the elements within a diagonal band show similar chemical properties*.

❑ **Diagonal Relationships**

➢ Diagonal relationships are helpful for making predictions about the properties of elements and their compounds.

➢ The diagonal band of metalloids dividing the metals from the nonmetals is one example of a diagonal relationship.

➢ So is the chemical similarity of lithium and magnesium and of beryllium and aluminum.

❖ For example, *both lithium* and *magnesium react directly with nitrogen to form nitrides*.

❖ Like *aluminum, beryllium reacts with both acids and bases*.

❑ **The Inert-Pair Effect**

➤ One of the more *unusual periodic trends* is known as the inert-pair effect.

➤ *The inert-pair effect is the tendency to form ions two units lower in charge than expected from the group number;* it is most pronounced for **heavy elements in the p-block**.

Al	Si	P	S		
Zn	Ga	Ge	As	Se	
In$^+$ / In^{3+}	Sn^{2+} / Sn^{4+}	Sb^{3+} / Sb^{5+}			
Tl$^+$ / Tl^{3+}	Pb^{2+} / Pb^{4+}	Bi^{3+} / Bi^{5+}			

FIGURE 1.57 The typical ions formed by the heavy elements in **Groups 13/III through 15/V** show the influence of the **inert pair**—the tendency to form compounds in which the oxidation numbers differ by 2.

❑ The Inert-Pair Effect

➢ The **elements that immediately** *follow the 4d and 5d transition series* are *considerably less reactive* than **their group properties might have predicted**, and they also *prefer oxidation states that are two lower than the usual group valence*.

❖ Consider, for example, the Group 13/IIIA elements. The lighter elements, B, Al, and Ga take only the +3 oxidation state predicted by their group valence.

❖ However, the heavier elements, In and Tl, take both the 3+ and 1+ oxidation states.

➢ The same trend is observed for the Group 14/IVA elements. Again, the lighter elements C, Si, and Ge take the +4 valence predicted by their period. However, Sn and Pb can exist in either the 4+ or the 2+ oxidation state.

➢ The tendency to form ions two units lower in charge than expected from the group number is called the **inert-pair effect**.

❑ The Inert-Pair Effect

❖ *An example of the inert-pair effect is found in Group 14/IVA*:

➢ **Lead** *exhibits the inert-pair effect more strongly than* **tin**.

✓ Tin forms tin(IV) oxide when heated in air, but the heavier lead atom loses only its two p-electrons and forms lead(II) oxide. Tin(II) oxide can be prepared, but it is readily oxidized to tin(IV) oxide.

Explanation:

➢ The **relative stability of the lower oxidation states** for the fifth and sixth series post-transition elements (In, Sn, Sb, Tl, Pb, Bi, and Po) *has been attributed to* the *(i)* **higher-than-expected ionization energies** for these seven elements and *(ii)* **weaker bond enthalpies**.

❑ **The Inert-Pair Effect causes: (i)** *higher-than-expected ionization energies*

➤ *The larger-than-expected ionization energies for the post-transition series Group IIIA elements result from the fact that the valence **s electrons are not shielded** from the nucleus very effectively **by the intervening d electrons.***

➤ As the two *s* electrons are both held tighter by the nucleus in the post-transition series elements, the ionization energies for these two electrons are unusually large.

➤ **Relativistic effects**, which are discussed later, also contribute to the higher-than-expected ionization energies of the valence *s* electrons.

➤ Due to **higher-than-expected ionization energies**, *it costs these elements relatively more energy to achieve a higher oxidation state than their lighter group congeners*.

❑ **The Inert-Pair Effect causes:** **(ii)** weaker bond enthalpies

➤ At the same time, *less energy is gained as a result of bond formation* because they also exhibit lower-than-predicted bond dissociation enthalpies.

➤ *Weaker bond* *enthalpies* are expected for the *heavier elements* as a result of the *diffuse nature of orbital overlap* *with increasing orbital size.*

➤ *The end result* is that these *elements prefer oxidation states that are two lower than their typical group valence*.

❑ The inert-pair effect is most *pronounced among the heaviest members* of a group, *where the difference in energy between s- and p-electrons* is greatest (Fig. 1.57).

❑ Even so, *the pair of s-electrons can be removed from the atom under sufficiently vigorous conditions.* An inert pair would be better called a "lazy pair" of electrons.

Main-Group Elements in the Periodic Table

Summary of trends in r, I_1, and E_{ea}
→ All depend on Z_{eff} and n of outer subshell electrons.
→ Recall that there are many exceptions to the general trends.
Example: For electron affinity, the value for N is actually less than that for O.
→ The diagram on the next page indicates the general behavior of the three properties (r, I_1, and E_{ea}) with respect to both Z_{eff} and n (exceptions ignored, many in the case of electron affinity).
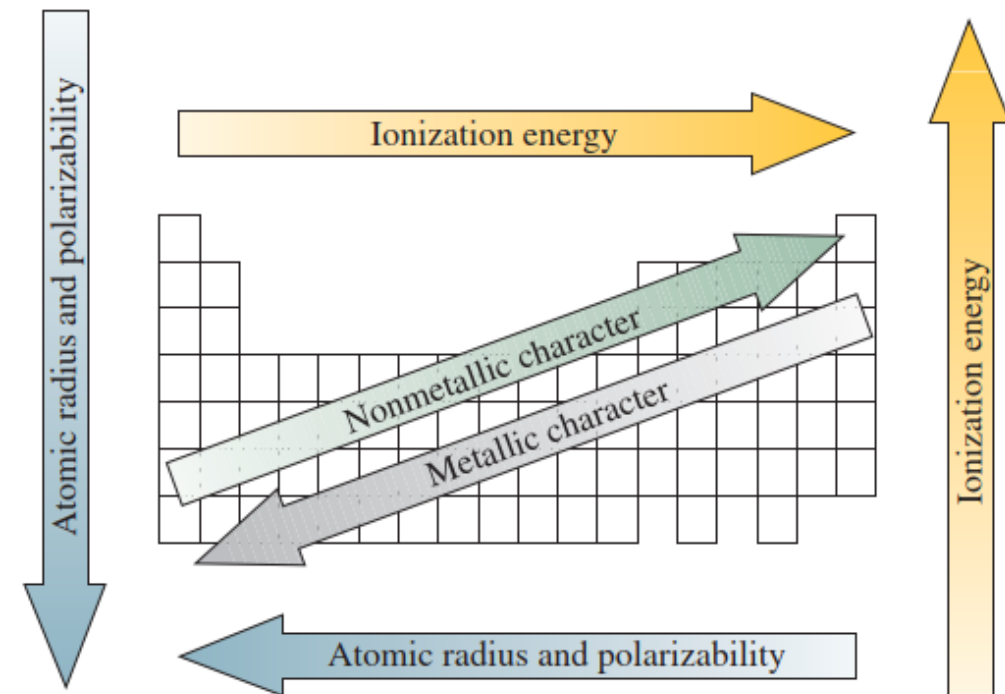
FIGURE 9-19
Atomic properties and the periodic table—a summary
Atomic radius refers to metallic radius for metals and covalent radius for nonmetals. Ionization energies refer to first ionization energy. Metallic character relates, generally, to the ability to lose electrons, and nonmetallic character to the ability to gain electrons.

Later, we will use our knowledge of the variation of ionization energy, electron affinity, and polarizability to explain various aspects of bonding. Figure 9-19 provides a useful summary.

❑ Trends in Melting Point and Hardness

➢ *Some metals are hard, and some are soft.*

➢ *Some metals have high meting point and some low.*

➢ *The hardness and melting point in transition elements increase from left, reaches maximum at the central elements, and then decreases towards the right.*

➢ *A material's **melting point** has everything to do with **the energy associated** with the **bonds between metal atoms**.*

➢ *Metal is full of bonds between the atoms that make it up that determines its m.p.* Most metal atoms readily share valence electrons with other atoms. Both **hardness** and **melting point increase** as **metal–metal bonding increases.**

➢ *Hg is liquid,* basically *it suggests that* mercury atoms form weak bonds and are bad at sharing electrons. …WHY…???

## Electronic Configurations
➤ **Compare Gr. 2 (2A) with Gr. 12 (2B)**

Solids   Solids & Liquids

1A 1												3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1 **H** $1s^1$	2A 2																2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$	3B 3	4B 4	5B 5	6B 6	7B 7	8	9	10	1B 11	2B 12	13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^23d^1$	22 **Ti** $4s^23d^2$	23 **V** $4s^23d^3$	24 **Cr** $4s^13d^5$	25 **Mn** $4s^23d^5$	26 **Fe** $4s^23d^6$	27 **Co** $4s^23d^7$	28 **Ni** $4s^23d^8$	29 **Cu** $4s^13d^{10}$	30 **Zn** $4s^23d^{10}$	31 **Ga** $4s^23d^{10}4p^1$	32 **Ge** $4s^23d^{10}4p^2$	33 **As** $4s^23d^{10}4p^3$	34 **Se** $4s^23d^{10}4p^4$	35 **Br** $4s^23d^{10}4p^5$	36 **Kr** $4s^23d^{10}4p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^24d^3$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^24d^5$	44 **Ru** $5s^14d^7$	45 **Rh** $5s^14d^8$	46 **Pd** $4d^{10}$	47 **Ag** $5s^14d^{10}$	48 **Cd** $5s^24d^{10}$	49 **In** $5s^24d^{10}5p^1$	50 **Sn** $5s^24d^{10}5p^2$	51 **Sb** $5s^24d^{10}5p^3$	52 **Te** $5s^24d^{10}5p^4$	53 **I** $5s^24d^{10}5p^5$	54 **Xe** $5s^24d^{10}5p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	71 **Lu** $6s^24f^{14}5d^1$	72 **Hf** $6s^24f^{14}5d^2$	73 **Ta** $6s^24f^{14}5d^3$	74 **W** $6s^24f^{14}5d^4$	75 **Re** $6s^24f^{14}5d^5$	76 **Os** $6s^24f^{14}5d^6$	77 **Ir** $6s^24f^{14}5d^7$	78 **Pt** $6s^14f^{14}5d^9$	79 **Au** $6s^14f^{14}5d^{10}$	80 **Hg** $6s^24f^{14}5d^{10}$	81 **Tl** $6s^24f^{14}5d^{10}6p^1$	82 **Pb** $6s^24f^{14}5d^{10}6p^2$	83 **Bi** $6s^24f^{14}5d^{10}6p^3$	84 **Po** $6s^24f^{14}5d^{10}6p^4$	85 **At** $6s^24f^{14}5d^{10}6p^5$	86 **Rn** $6s^24f^{14}5d^{10}6p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	103 **Lr** $7s^25f^{14}6d^1$	104 **Rf** $7s^25f^{14}6d^2$	105 **Db** $7s^25f^{14}6d^3$	106 **Sg** $7s^25f^{14}6d^4$	107 **Bh** $7s^25f^{14}6d^5$	108 **Hs** $7s^25f^{14}6d^6$	109 **Mt** $7s^25f^{14}6d^7$	110 **Ds** $7s^25f^{14}6d^8$	111 **Rg** $7s^25f^{14}6d^9$	112 **Cn** $7s^25f^{14}6d^{10}$	113 **Nh** $7s^25f^{14}6d^{10}7p^1$	114 **Fl** $7s^25f^{14}6d^{10}7p^2$	115 **Mc** $7s^25f^{14}6d^{10}7p^3$	116 **Lv** $7s^25f^{14}6d^{10}7p^4$	117 **Ts** $7s^25f^{14}6d^{10}7p^5$	118 **Og** $7s^25f^{14}6d^{10}7p^6$

Core: [He] [Ne] [Ar] [Kr] [Xe] [Rn]

Solids

❑ **Melting Point and Hardness**

➢ The following pictures show the electron populations of the composite s–d bands for three different transition metals (corresponding to 1, 2, & 3).

➢ ***The red color in the bands indicates occupied MO (molecular orbital) band.***

(1)   (2)   (3)

Energy
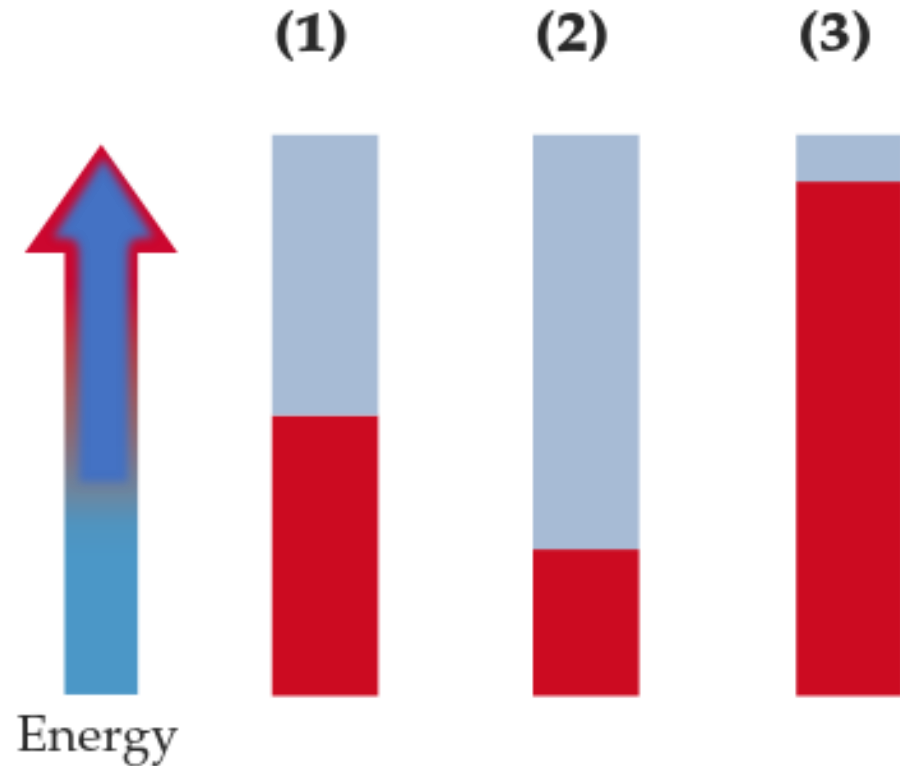
(a) Which metal has the highest melting point?

(b) Which metal has the lowest melting point?

(c) What about their hardness?

➢ Both **hardness** and **melting point increase** as **metal–metal bonding increases.**

➢ They will depend on the **occupancy of the** *bonding* and *antibonding* **MOs.**

➢ The **melting point** and **hardness** of a metal is *expected to increase* as the *difference between the number of bonding and antibonding electrons increases*.

➢ Transition metals have maximal *two ns* and *ten* $(n - 1)d$ valence electrons.

➢ All the valence electrons will occupy **a composite s–d band, which can accommodate 12 electrons per metal atom**.

➢ Picture (1) Metal: Its s–d band is exactly **half-filled**, which corresponds to **six valence electrons** (and **all are in bonding MOs**). Its bonding MOs are completely filled, and its antibonding MOs are completely vacant. Therefore, it has the **highest melting point**.

➤ Picture (2) Metal: Its s–d band is *one-fourth filled*, which corresponds to *three valence electrons (bonding)*.

➤ Picture (3) metal: Its s–d band is *eleven-twelfths filled*, which corresponds to **11 valence electrons**. It has the **lowest melting point** because it has *six bonding* electrons and *five antibonding* electrons per atom, *an excess of only one bonding electron per atom*.

➤ Metal 1 is very hard because it has an excess of six bonding electrons per atom. Metal 3 is very soft because it has an excess of only one bonding electron per atom. Therefore, metals in order of *increasing hardness*: 3<2<1.

❑ **Melting points: 3033, 2446, 1768, 1064, & -39ºC.**

76 Os	77 Ir	78 Pt	79 Au	80 Hg
$6s^2 5d^6$	$6s^2 5d^7$	$6s^1 5d^9$	$6s^1 5d^{10}$	$6s^2 5d^{10}$

➢ Gold is also a **_fairly soft metal_**. Pure gold, which is 24 carats, is seldom used in the manufacture of jewelry because it is so soft that ordinary wear and tear will damage the metal. Instead, an alloy of 18k or 14k gold is generally used. A typical piece of 18k jewelry consists of 75.0% Au, 12.5% Ag, and 12.5% Cu, by mass. The presence of the other metals helps harden the alloy.

❑ **Melting points: 3033, 2446, 1768, 1064, & -39°C.**

Z →

76 Os	77 Ir	78 Pt	79 Au	80 Hg

❑**Why is** mercury liquid at normal temperature and pressure**?**

29 **Cu** $4s^1 3d^{10}$

47 **Ag** $5s^1 4d^{10}$

79 **Au** $6s^1 4f^{14} 5d^{10}$

Metal	Atomic Radius (pm)	Ionization Energy (kJ/mol)	Electron Affinity (kJ/mol)
Cu	135	746	118
Ag	160	741	126
Au	135	890	223

❑*Au is extremely difficult to oxidize.*
❑**Why is gold** the **least reactive** of the coinage metals....?

❑ **Trends in Relativistic Effects and Consequences**

➢ **…..Relativity** behind **Mercury's liquidity** and **Gold's nobility.**

(Reference: F Calvo *et al, Angew. Chem., Int. Ed..* 2013. DOI: 10.1002/anie.201302742**)**

✓ **Trend** in the **contraction** of **6s electron orbitals…**

❑ RELATIVISTIC EFFECTS

➢ According to Einstein's theory of relativity, ***particles that are traveling at velocities (v) approaching the speed of light (c)*** *are **more massive** than they are at rest*, as shown by Equation (5.37), where m_{rel} is the relativistic mass of the electron and m_0 is its rest mass.

$$m_{rel} = \frac{m_0}{\sqrt{1 - (v/c)^2}} \qquad (5.37)$$

➢ As a result of their *relativistic heavier mass*, the accelerated electrons have a **smaller** average **radius**, as indicated by Equation (5.38), which results from the derivation of the Bohr model of the atom:

$$r = \frac{4\pi\varepsilon_0 n^2 \hbar^2}{m_e Z e^2} \qquad (5.38)$$

➢ One basic consequence of the special theory of relativity is that *mass increases towards infinity as a body's velocity approaches c (speed tof light)*, which is expressed mathematically as

$$m = m_0/[1 - (v/c)^2]^{1/2},$$

where m is the corrected (relative) mass, m_0 is non-relativistic (rest) mass, and v is electron's speed.

➢ **For a given atom, *the average radial velocity of the 1s electrons is $V_r = Z$, where Z is the atomic number. The expression v/c can therefore be calculated as Z/137 (where c = 137 atomic units (a.u.)).***

❖ For example, in Hg, $Z = 80$ and v/c for the 1s electrons is $80/137 = 0.58$; that is, the 1s electrons have a radial velocity that is 58% of c.

➢ In fact, ***the larger the nucleus gets,*** *the greater the electrostatic attraction* and ***the faster the electrons have to move*** *to avoid falling into it*.
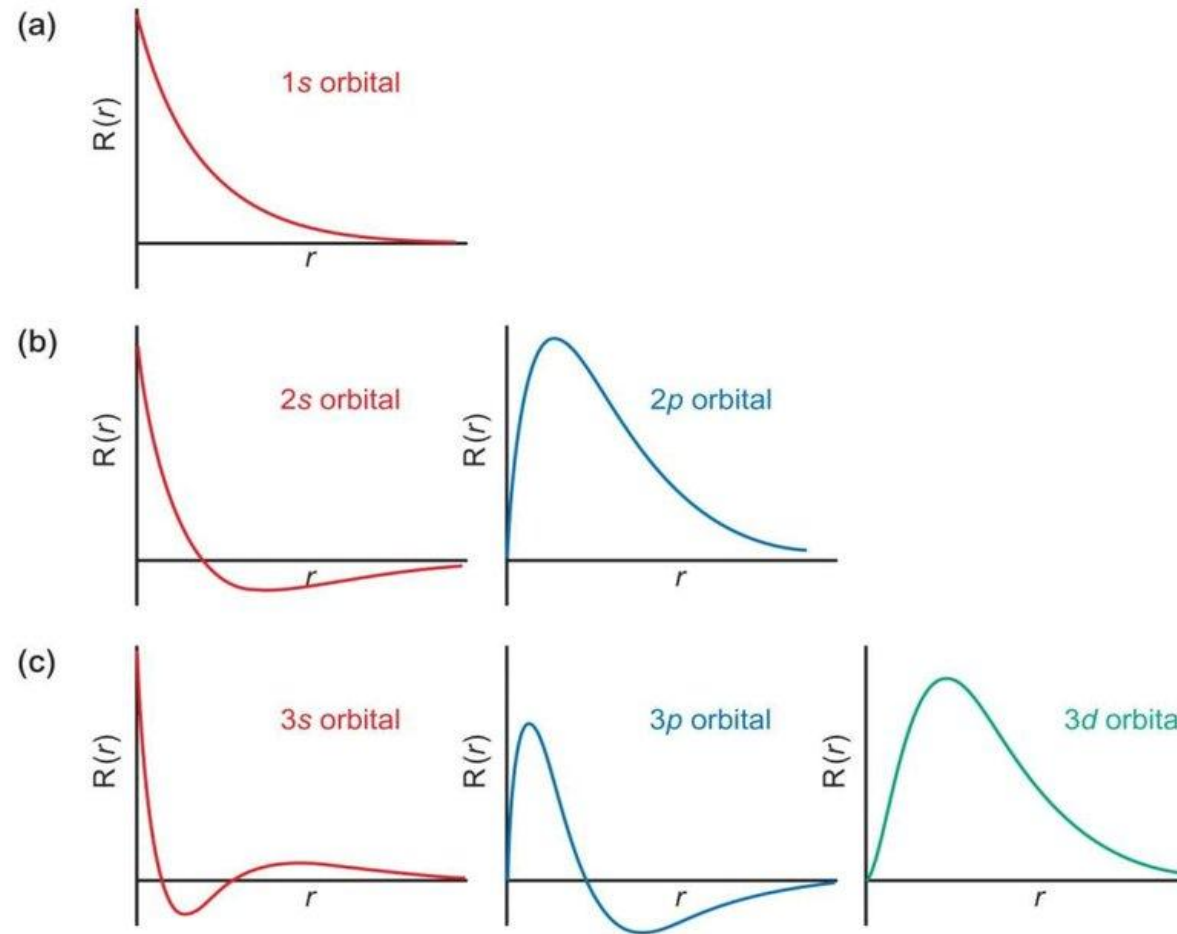
❑ **RELATIVISTIC EFFECTS** (contd.)

➢ For *most applications of chemistry,* the *effect of relativity* on electronic motion can largely be *ignored*. ….WHY…???

➢ For ***the smaller elements (small Z's)***, Schrödinger's **non***relativistic model is perfectly* appropriate, as *the velocities of the electrons in the* **lighter elements rarely approach** *the speed of light.*

✓ However, ***the larger Z's of the heavier elements*** *exerts a stronger electrostatic pull on the inner-most electrons,* sometimes accelerating them to speeds in excess of 10^8 m/s.

➢ It was long **believed** that ***valence electrons,*** *which are important for* **chemical reactions, move rather slowly** *compared to the velocity of light (v ≪ c) and should therefore* **not show significant effects** *coming from special relativity.*

➢ In contrast, the importance of ***relativistic effects*** for inner K- or L-shell electrons of heavy elements was long recognized.

- An international team led by Peter Schwerdtfeger of Massey University Auckland in New Zealand used quantum mechanics to make calculations of *the heat capacity of the metal either including or excluding relativistic effects*.

- They showed that if they ignored relativity when making their calculations, *the predicted melting point of mercury was 82°C*. But if they ***included relativistic effects*** their answer closely matched the ***experimental value of -39°C***.

❑ RELATIVISTIC EFFECTS: *s, p, d, & f electrons*

➤ *s and **p electrons penetrate the nucleus better** than the* d *or* f *electrons do.*

Plot of Radial Wave Function

❑ **RELATIVISTIC EFFECTS:** *s, p, d, & f electrons*

➢ *Because the s and p electrons* **penetrate** *the nucleus* **better** than the *d* or *f* electrons do, *the s and p electrons* **are accelerated** *to a greater extent*.

➢ Thus, *the* **s** *and* **p orbitals** *effectively* **contract** *as relativistic effects become more prominent*.

➢ Furthermore, *as the* **s and p electrons migrate** **closer** *to the* **nucleus**, this **enhances** *their ability to* **shield** *the d* and *f electrons* from **experiencing the full attraction of the nucleus**.

➢ Thus, the **d and f orbitals expand** as a **result of relativity**.

➢ The **combined effect** is to **lower the energies of the s and p electrons**, as shown in Figure 5.12, **while raising the energy of the d and f electrons**.
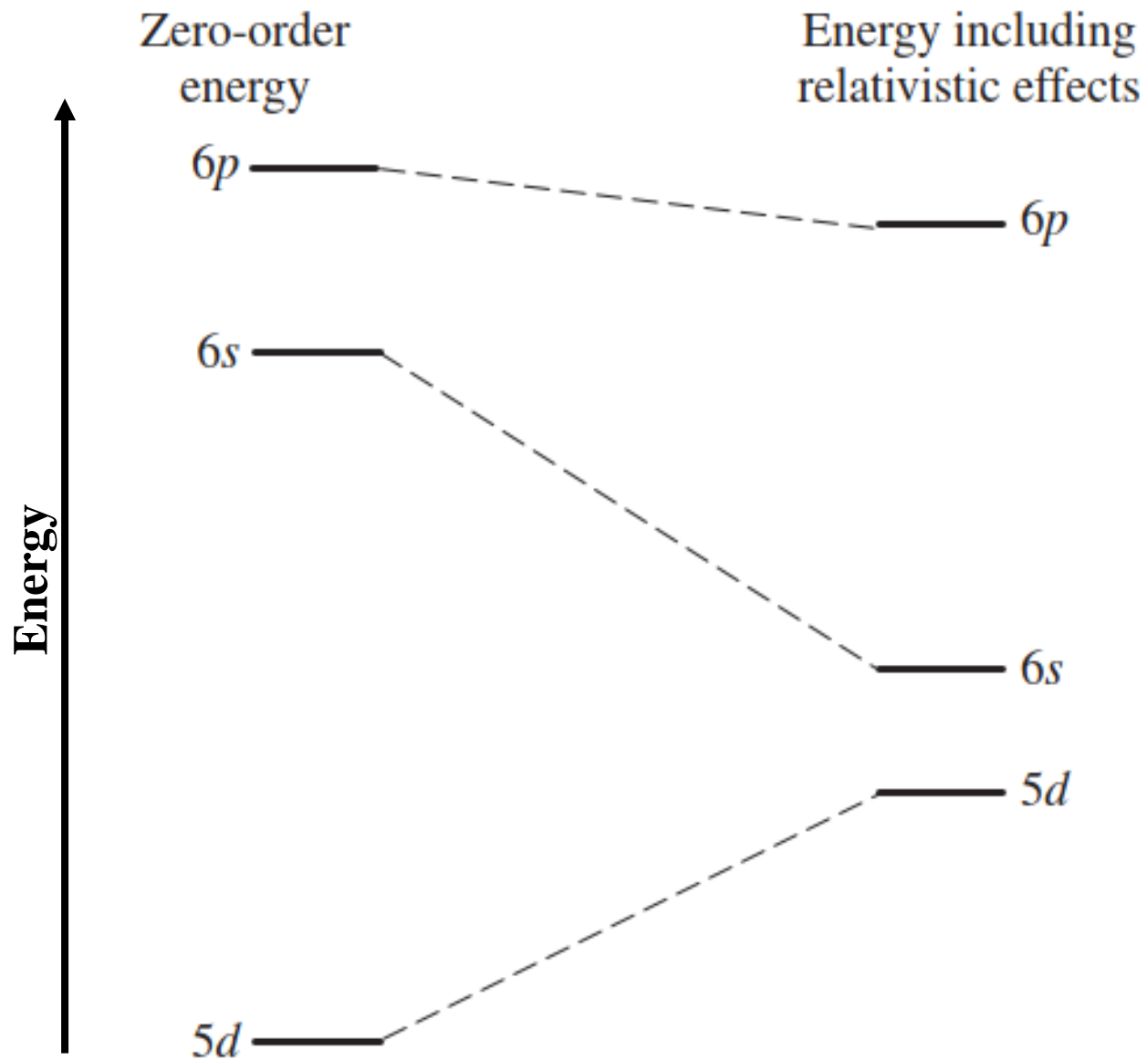
> ➤ **s** and **p** orbitals **effectively** **contract** (stabilized in energy) and
> ➤ **d** and **f** orbitals **expand** (destabilized) as a **result of relativity.**

FIGURE 5.12 **Valence orbital energies** for Au and Hg in the ***absence*** of relativistic effects and ***with relativistic effects*** included.

Table 1
Relativistic effects: **There are three major phenomena that result from relativistic effects**

---

1. Direct   ***Contraction of s and p orbitals***

The contraction is due to the relativistic mass increase as followed by the decrease of the Bohr radius. The contraction of the spherical $p_{1/2}$ subshell is comparable to the contraction of $s_{1/2}$. The $p_{3/2}$ subshell contracts much less.

2. Direct   ***Spin-orbit splitting***

Instead of the orbital angular momentum l and the spin angular momentum s their vector sum $j = l + s$ is used (e.g., splitting of a p orbital to the $p_{1/2}$ (l-s $= 1$ - ½ = ½) and $p_{3/2}$ (l+s $= 1 +$ ½ = 3/2) subshells).

3. Indirect   ***Expansion of d and f orbitals***

The s and p orbitals contracting inside and outside the d and f orbitals screen the nuclear attraction of the latter thus leading to their radial expansion.

❑ **There are three major phenomena that result from relativistic effects**:

➢ The *first* can easily be rationalized by considering the equations above. In non-relativistic calculations, $c = \infty$ and *v/c,* therefore, approaches 0, so no mass correction need be applied to the particles under consideration.

✓ In situations in which *c* is considered to be 137 a.u., the mass of an electron will increase considerably. Because the Bohr radius of an electron orbiting a nucleus is inversely proportional to the mass of the electron, this ***increase in mass corresponds to a decrease in radius***. This relativistic contraction of the 1*s* orbital also applies to all other *s* and *p* orbitals. Thus, the electrons are closer to the nucleus and have greater ionization energies.

✓ *Practically,* this *contraction is only significant for elements in which the 4f and 5d orbitals are filled* (Figure 1).

➢ The ***second*** effect of a relativistic treatment is *spin–orbit coupling*, which accounts for the fine splitting in the atomic spectrum.

➢ The ***third*** manifestation of relativistic effects is *indirect*. Because of the relativistic contraction of all *s* orbitals, the nucleus becomes more screened resulting in a smaller effective nuclear charge, and therefore the higher angular momentum orbitals (the *d* and *f* orbitals) see a weaker nuclear attraction and expand.

- ***The magnitude of the relativistic effect increases*** roughly *as* the ***square of the atomic number***.

- Thus, the ***heavier elements experience considerably larger relativistic effects*** than do the lighter ones.

- *For a number of elements heavier than Pt, the magnitude of the effect is even comparable to the strength of a chemical bond!*

- ***Relativistic effects are crucial to understanding the electronic structure of heavy elements.***

Fig. 1. The relativistic contraction of the 6s orbital and expansion of the 5*d* and the 5*d** orbitals for the elements with Z from 55 to 100 based on *calculations* by Desclaux (Ref. J.-P. Desclaux, At. Data Nucl. Data Tables 12 (1973) 311.)
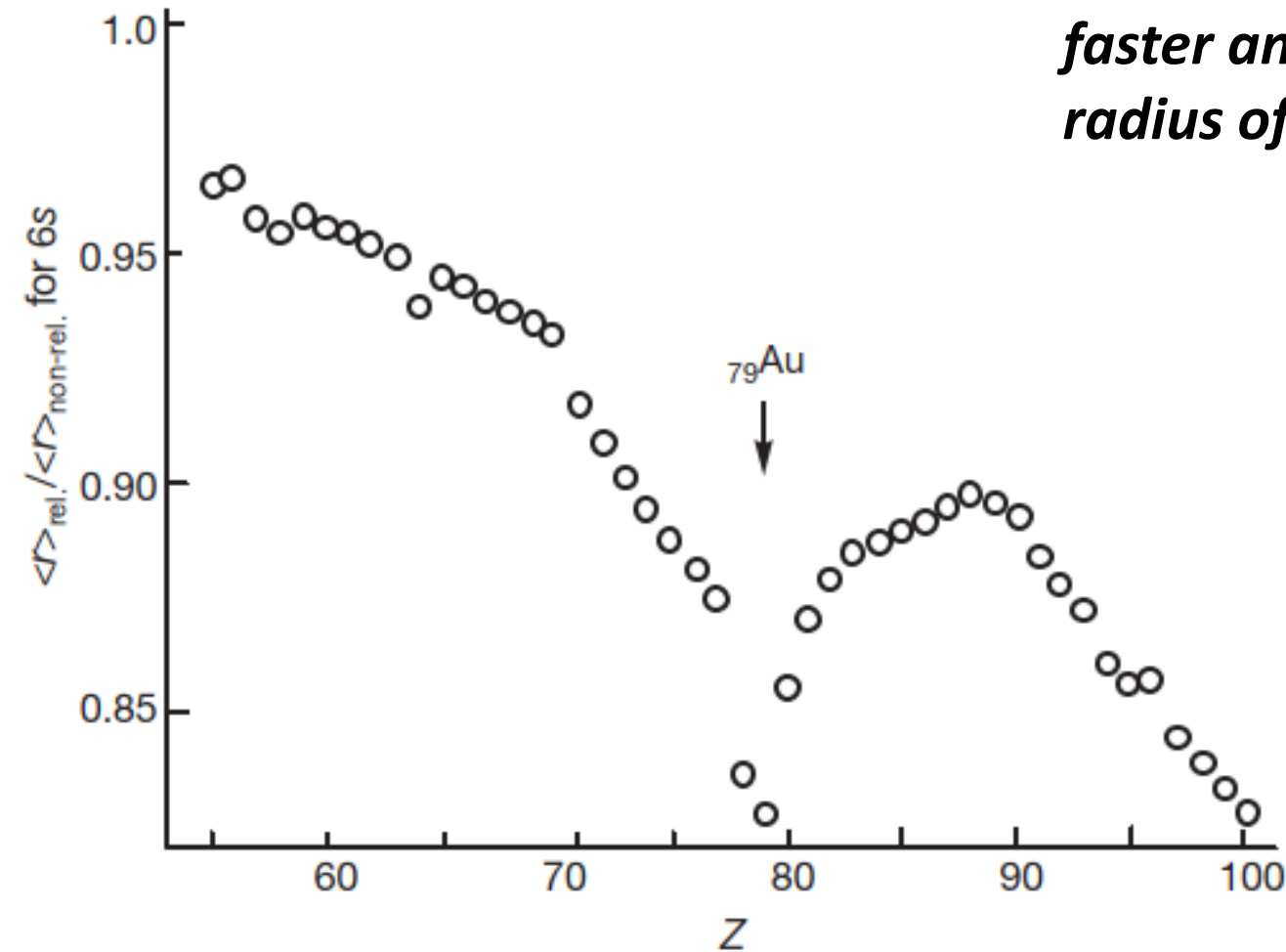
The graph of the 6s orbital contraction over the atomic number.

Here also the 5d shell is included, showing an orbital expansion due to an indirect relativistic effect.
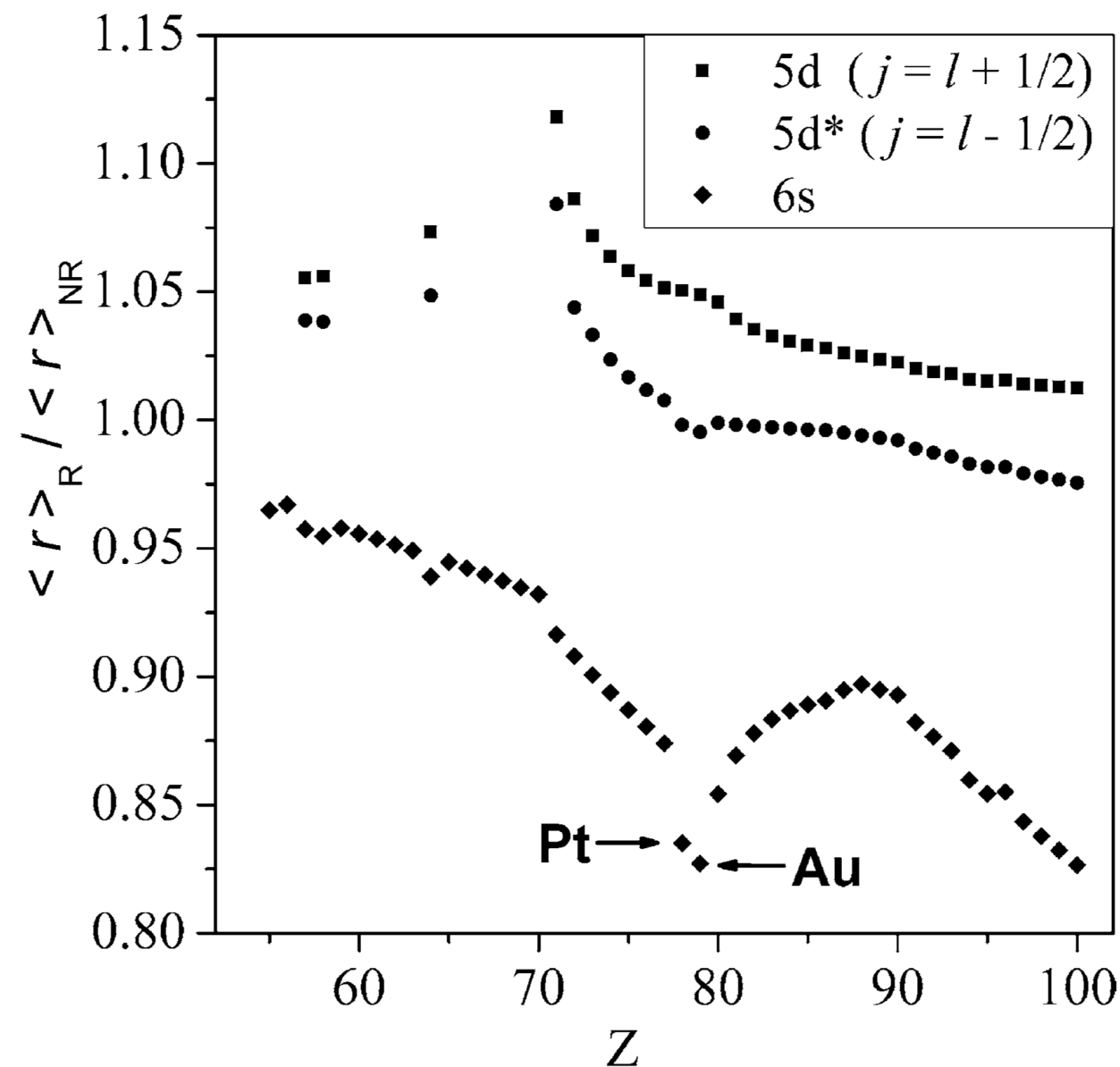
➤ The electron configuration of Au is *[Xe] 4f¹⁴5d¹⁰6s¹*.

Calculated relativistic contraction of the 6s orbital. The relativistic and non-relativistic *6s* orbital radii were determined computationally.
Notably, Pt, Au and Hg are markedly influenced.

➢ As you go down the periodic table the **1s electrons get faster and faster, and therefore heavier, causing the radius of the atom to shrink**.

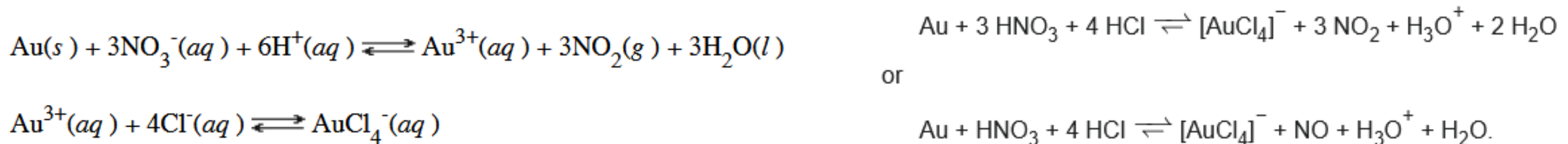✓ In atoms of high nuclear charge (Z), as a consequence of a relativistic effect, the *s* electrons of an atom become more bound and their orbitals smaller than if this effect were absent. Simultaneously, the *d* (and *f*) electrons are less bound because of this effect, which scales roughly as Z^2.

✓ Gold exhibits a large relativistic effect. **This accounts for gold being more resistant to oxidation than silver**. ……**HOW…?** *It also accounts for* **higher oxidation** *states being more accessible* **in gold** *than in silver.*

- ❖ The *relativistic effect enhances the **inert-pair effect*** mentioned in the preceding section.

- ✓ *The smaller radius of the 6s orbital* in Tl, for instance, ***causes the 6s electrons to be held more tightly*** than they would have been in the absence of relativity and ***raises their ionization energies***. Hence, Tl will commonly prefer the lower 1+ oxidation number over its 3+ state.

- ❖ However, unlike the inert-pair effect, any of the heavier elements can experience the relativistic effect.

- ✓ As an example, ***gold is the least reactive of the coinage metals***. This explains why it was one of the first elements to be discovered by ancient Civilizations (about 10,000 years ago).

- ✓ *Gold exists in nature in its elemental form* and is only rarely found in minerals, such as calverite, $AuTe_2$, and sylvanite, $AuAgTe_4$.

➢ As a result of *the relativistic effect in gold, the 6s electron has an unusually*
- *large ionization energy (890kJ/mol),*
- *compared with 746kJ/mol for Cu and*
- *741kJ/mol for Ag*

✓ *and is extremely difficult to oxidize.*

➢ Hence, *gold will not rust in air, nor will it react with the oxidizing acid HNO₃.*

➢ In fact, in order to dissolve gold, a combination of one-part nitric acid with three-parts HCl (aqua regia) must be employed, although neither constituent acid will do so alone. Aqua regia can dissolve gold because each of its two component acids carries out a different function. The nitric acid is a good oxidizing agent, which will dissolve a very small quantity of gold, forming gold(III) ions (Au^{3+}), tetrachloroaurate(III) anions ($[AuCl_4]^-$). Chloride ions from the hydrochloric acid from coordination complexes with the gold ions, removing them from solution. Reducing the concentration of the Au^{3+} ions shifts the equilibrium towards the oxidized form. In addition, gold may be dissolved by the chlorine present in aqua regia. Appropriate equations are:

$$Au(s) + 3NO_3^-(aq) + 6H^+(aq) \rightleftharpoons Au^{3+}(aq) + 3NO_2(g) + 3H_2O(l)$$

$$Au^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons AuCl_4^-(aq)$$

$$Au + 3\,HNO_3 + 4\,HCl \rightleftharpoons [AuCl_4]^- + 3\,NO_2 + H_3O^+ + 2\,H_2O$$

or

$$Au + HNO_3 + 4\,HCl \rightleftharpoons [AuCl_4]^- + NO + H_3O^+ + H_2O.$$

➢ As a result of *relativistic orbital contraction, the atomic radius of Au is less than that expected* on the basis of its periodic trends:

• *Cu (135 pm),*

• *Ag (160 pm), and*

• *Au (135 pm).*

➢ Because of the *small size of its half-filled 6s orbital, the electron affinity (E.A.) of Au (223kJ/mol) is considerably larger*

• *than that for Ag (126kJ/mol) or*

• *Cu (118kJ/mol).*

✓ The *E.A. of Au is so large* that *gold exists as the Au⁻ anion in the compound cesium auride (*CsAu*).*

➢ **Colour of Au:** When the 6s orbital shrinks and is therefore stabilized by the relativistic effect, the 5d orbital expands and is destabilized.

➢ *Thus, the* **energy gap between the 5d and 6s orbitals** *is fairly* **small***, and it means that the* **energy required to excite an electron** *from the* **5d band to the Fermi level (largely 6s** *in character)* **lies in the visible** *rather than UV range of light for most of the metals.*
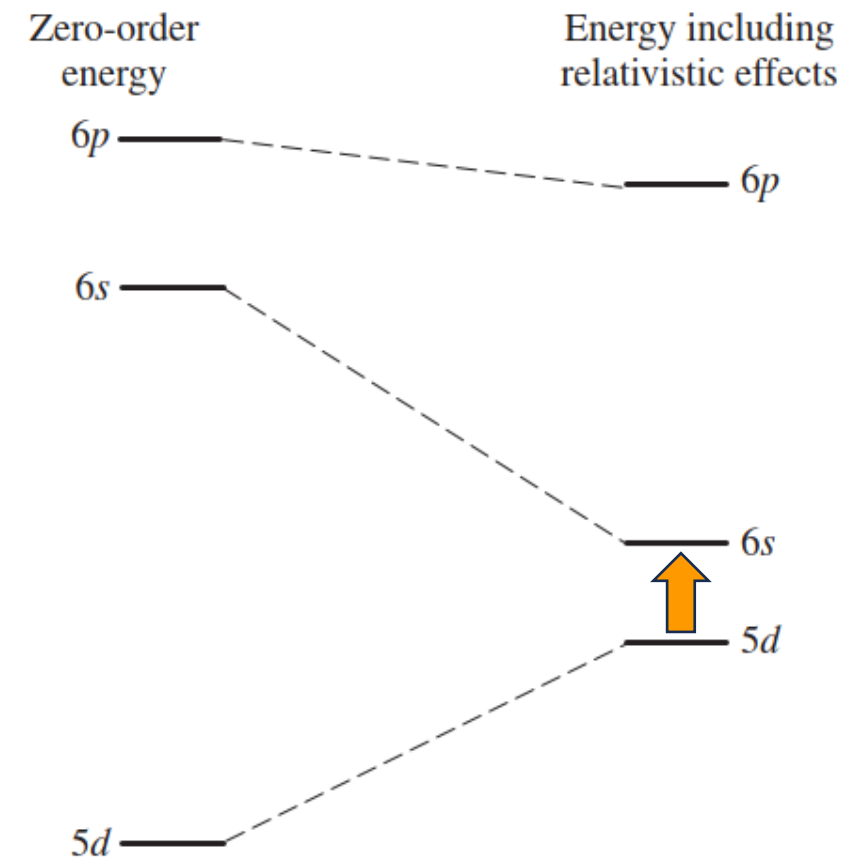

FIGURE 5.12 Valence orbital energies for Au in the absence of relativistic effects and with relativistic effects included.

- ➢ Among the experimental observations conventionally explained by relativistic effects is the **colour of Au**.
- ✓ In the 1960s, Pekka Pyykkö discovered that gold's color was the result of relativistic effects.
- ✓ *He showed that the relativistic effect causes the s electrons (and to a lesser extent, the p electrons) to be in smaller orbitals than if this effect were absent.*
- ✓ *Therefore, in the heavier elements, the s electrons are more strongly bound and shield the nuclear charge from the other electrons (especially d and f) more effectively than if the relativistic effects were absent. The d and f electrons are therefore less bound and occupy larger orbitals when relativistic effects are large.*
- ✓ *The **raising of the Au 5d electron energies** and the **lowering of the valence 6s electron energies** of gold means that the **energy required to excite an electron** from the **5d band to the Fermi level (largely 6s** in character) **lies in the visible** rather than UV range of light. **This accounts for the yellow color of gold.***

- ✓ ***The golden color is due to excitation of the 5d electrons to the Fermi level (6s), which occurs with a bandgap of 2.38 eV****; blue visible light is therefore absorbed, while **reflecting** yellow **and** red **light***, *and it is this that gives the metal its characteristic hue.*

- ✓ ***In silver****, in contrast, the bandgap is much larger, and **no visible light is absorbed***. *The related **absorption** in silver (4d band to the Fermi level of ~5s character) is in the **ultraviolet**, at ~**3.7 eV***.

- ✓ *Further calculations have subsequently shown the influence of relativity on the color and bond lengths of heavy metal compounds, as well as its importance in catalysis.*

- The unusual *differences between Au and Hg*, which are neighbors on the periodic table, *can also be ascribed to the relativistic energies* of the orbitals shown in Figure 5.12.

- Gold has a melting point of 1064°C, whereas Hg is a liquid at room temperature and has a melting point of −39°C.

- In many ways, *Au acts as a pseudo-halogen*, as evidenced by its ability to form the *auride anion*. *The low-lying 6s orbital in Au is singly occupied*. Therefore, like the halogens, gold can exist as the diatomic Au_2.

- In fact, Au_2 has a *gas-phase bond dissociation energy (BDE) of 221kJ/mol, which is even larger than that for I_2 (151kJ/mol)* and only slightly smaller than that of Cl_2 (242kJ/mol).

- **Mercury, on the other hand, has two electrons in the low-lying *6s* orbital** ($4f^{14}5d^{10}6s^2$ electronic configuration) **and it behaves as a pseudo-noble gas.**

✓ Mercury is unique among the transition metals because *it exists in the gas phase almost exclusively as monomeric Hg just like the noble gases do.*

✓ By **analogy with the noble gases, Hg(0) is fairly unreactive. Its unusually low melting point can be ascribed to the fact** that Hg atoms can only aggregate together in the *condensed phases as a result of weak van der Waals forces.*

✓ **Hg(0) cannot form a diatomic like Au(0) because its electrons are all paired.**

✓ However, *oxidation of Hg by one electron* to form Hg(I), *which is isoelectronic with Au(0),* leads to a **stable diatomic cation, Hg_2^{2+}** (as in Hg_2Cl_2).

➢ In comparison with H, whose relativistic mass is 1.00003 times its rest mass and where its *1s* electron has an average velocity of 0.0073c, the relativistic mass of a *1s* electron in Hg is 1.23 times its rest mass and its average velocity is 0.58c, so that its size shrinks by a factor of nearly a quarter.

➢ *Because of the behavior of the valence electrons,* mercury has a low melting point, is a poor electrical and thermal conductor and doesn't form diatomic mercury molecules in the gas phase.

Periodicity in the Main-Group Elements

The physical and chemical properties of the main-group elements clearly display periodic character. We have seen it above for some properties.

The variations of metallic–nonmetallic character can be attributed in part to variations in the ionization energies of the corresponding atoms. *Elements with low ionization energy tend to be metallic, whereas those with high ionization energy tend to be nonmetallic.* As you saw in the previous section, ionization energy is a periodic property, so it is not surprising that the metallic–nonmetallic character of an element is similarly periodic.

The **basic–acidic behavior of the oxides of the elements is a good indicator of the metallic–nonmetallic character** of the elements. Oxides are classified as basic or acidic depending on their reactions with acids and bases. A basic oxide is an oxide that reacts with acids. **Most metal oxides are basic**. An acidic oxide is an oxide that reacts with bases. Most **nonmetal oxides are acidic** oxides. An **amphoteric oxide** is an oxide that has both basic and acidic properties.

In the following brief descriptions of the main-group elements, we will note the metallic–nonmetallic behavior of the elements, as well as the basic–acidic character of the oxides. **Although elements in a given group are expected to be similar, the degree of similarity does vary among the groups.** The alkali metals (Group 1A) show marked similarities, as do the halogens (Group 7A). On the other hand, the Group 4A elements range from a nonmetal (carbon) at the top of the column to a metal (lead) at the bottom. In either case, however, the changes from one element in a column to the next lower one are systematic, and the periodic table helps us to correlate these systematic changes.

Acid-Base Behavior of Oxides Metals are also distinguished from nonmetals by the acid-base behavior of their oxides in water:

❑ Most main-group metals transfer electrons to oxygen, so their oxides are ionic. In water, these oxides act as bases, producing OH^- ions from O^{2-} and reacting with acids.

❑ Nonmetals share electrons with oxygen, so nonmetal oxides are covalent. In water, these oxides act as acids, producing H^+ ions and reacting with bases.

➤ Some metals and many metalloids form oxides that are ***amphoteric***: they can act as acids or bases in water.

In Figure 8.16, the acid-base behavior of some common oxides of elements in Group 5A(15) and Period 3 is shown with a gradient from blue (basic) to red (acidic):

1. *As elements become more metallic down a group (larger size and smaller IE), their oxides become more basic.*

2. *As the elements become less metallic across a period (smaller size and higher IE), their oxides become more acidic.*


Figure 8.16 Acid-base behavior of some element oxides.

Hydrogen ($1s^1$)

Although the electron configuration of hydrogen would seem to place the element in Group 1A, its properties are quite different, and it seems best to consider this element as belonging in a group by itself. The element is a colorless gas composed of H_2 molecules. ***At very high pressures, however, hydrogen is believed to have metallic properties.***

Group 1A Elements, the Alkali Metals (ns^1)

The alkali metals are soft and reactive, with the reactivities increasing as you move down the column of elements. All of the metals react with water to produce hydrogen.

$$2Li \ (s) + 2H_2O \ (l) \rightarrow 2LiOH \ (aq) + H_2 \ (g)$$
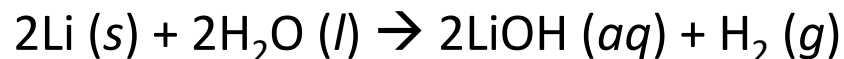
The vigor of the reaction increases from lithium (moderate) to rubidium (violent).

➤ All are reactive metals (except H); they form basic oxides (O^{2-}), peroxides (O_2^{2-}), or superoxides (O_2^{-}).
➤ *All alkali metals react, combine directly with hydrogen to form **hydrides,** MH. In hydrides of the alkali metals (LiH, NaH, and so forth), hydrogen is present as **H⁻**, the hydride ion.*

Group 2A Elements, the Alkaline Earth Metals (ns^2)

The alkaline earth metals are also chemically reactive but much less so than the alkali metals. Reactivities increase going down the group. The alkaline earth metals form basic oxides with the general formula MO.

➤ ***Compounds of s-block elements are ionic, except for beryllium.***

Group 3A Elements (ns²np¹)

Groups 1A and 2A exhibit only slight increases in **metallic character down a column**, but **with Group 3A we see a significant increase**. The first Group 3A element, **boron, is a metalloid**. Other elements in this group—aluminum, gallium, indium, and thallium—are metals. (Gallium is a curious metal; it melts readily in the palm of the hand.)

The oxides in this group have the general formula M_2O_3. Boron oxide, B_2O_3, is an **acidic oxide**; aluminum oxide, Al_2O_3, and gallium oxide, Ga_2O_3, are **amphoteric oxides**. Indium oxide, In_2O_3, and thallium oxide, Tl_2O_3, are **basic**. *The change in the oxides from acidic to amphoteric to basic is indicative of an increase in metallic character* of the elements.

Group 4A Elements (ns²np²)

This group shows the **most distinct change in metallic character**. It begins with the **nonmetal carbon**, C, followed by the **metalloids** silicon, Si, and germanium, Ge, and then the **metals** tin (Sn), and lead (Pb). Both tin and lead were known to the ancients. All the elements in this group form oxides with the general formula RO_2, which progress from acidic to amphoteric. Carbon dioxide, CO_2, an acidic oxide, is a gas. (Carbon also forms the monoxide, CO.) Silicon dioxide, SiO_2, an acidic oxide, exists as quartz and white sand (particles of quartz). Germanium dioxide, GeO_2, is acidic, though less so than silicon dioxide. Tin dioxide, SnO_2, an **amphoteric** oxide, is found as the mineral cassiterite, the principal ore of tin. Lead(IV) oxide, PbO_2, is **amphoteric**. Lead has a more stable monoxide, PbO.

Figure… Oxides of some Group 4A elements Powdered Pb(II)O (yellow), Pb(IV)O_2 (dark brown), SnO_2 (white), and crystalline silicon dioxide (clear quartz).

Group 5A Elements (ns²np³)

The Group 5A elements also show the distinct transition from nonmetal (nitrogen, N, and phosphorus, P) to metalloid (arsenic, As, and antimony, Sb) to metal (bismuth, Bi). Nitrogen occurs as a colorless, odorless, relatively unreactive **gas** with N_2 molecules; white phosphorus is a white, waxy **solid** with P_4 molecules. Gray arsenic is a **brittle solid with metallic luster**; antimony is a brittle solid with a **silvery, metallic luster**. Bismuth is **a hard, lustrous metal** with a pinkish tinge.

The Group 5A elements form oxides with empirical formulas R_2O_3 and R_2O_5. In some cases, the molecular formulas are twice these formulas—that is, R_4O_6 and R_4O_{10}. Nitrogen has the **acidic oxides** N_2O_3 and N_2O_5, although it also has other, better-known oxides, such as NO. Phosphorus has the **acidic oxides** P_4O_6 and P_4O_{10}.
Arsenic has the **acidic oxides** As_2O_3 and As_2O_5; antimony has the **amphoteric oxides** Sb_2O_3 and Sb_2O_5; and bismuth has the **basic oxide** Bi_2O_3.

Group 6A Elements, the Chalcogens (ns²np⁴)

These elements, the chalcogens (pronounced kal'-ke-jens), show the transition from nonmetal (oxygen, O, sulfur, S, and selenium, Se) to metalloid (tellurium, Te) to metal (polonium, Po). Oxygen occurs as a colorless, odorless **gas** with O_2 molecules. It also has an allotrope, ozone, with molecular formula O_3. Sulfur is a brittle, yellow **solid** with molecular formula S_8. Tellurium is a shiny **gray, brittle solid**; polonium is a **silvery metal**.

Sulfur, selenium, and tellurium form oxides with the formulas RO_2 and RO_3. (Sulfur burns in air to form sulfur dioxide). These oxides, except for TeO_2, are **acidic**; TeO_2 is **amphoteric**. Polonium has an oxide PoO_2, which is **amphoteric**, though more basic in character than TeO_2.

Group 7A Elements, the Halogens (ns^2np^5)

The halogens are reactive nonmetals with the general molecular formula X_2, where X symbolizes a halogen. Fluorine, F_2, is a pale yellow **gas**; chlorine, Cl_2, a pale greenish yellow **gas**; bromine, Br_2, a reddish brown **liquid**; and iodine, I_2, a bluish black **solid** that has a violet vapor. All isotopes of astatine have very short half-lives, and observable quantities of the element have not been prepared. Astatine might be expected to be a metalloid.

Each halogen forms several compounds with oxygen; these are generally unstable, acidic oxides.

Group 8A Elements, the Noble Gases (ns^2np^6)

The Group 8A elements exist as gases consisting of uncombined atoms. For a long time these elements were thought to be chemically inert, because no compounds were known. Then, in the early 1960s, several compounds of xenon were prepared. Now compounds are also known for argon, krypton, and radon. These elements are known as the noble gases because of their relative unreactivity.

- **p-block elements**

→ Members are metals, metalloids, and nonmetals.

Metals: Group 13 (Al, Ga, In, Tl); Group 14 (Sn, Pb); Group 15 (Bi). Note: These metals have relatively low I_1, but larger than those of the s block and d block.

Metalloids: Group 13 (B); Group 14 (Si, Ge); Group 15 (As, Sb); Group 16 (Te, Po). Note: *Metalloids have the physical appearance and properties of metals but behave chemically as nonmetals*.

Nonmetals: Group 14 (C); Group 15 (N, P); Group 16 (O, S, Se); Groups 17 & 18 (All). Notes: High Eea in Groups 13–17; these atoms tend to gain electrons to complete their subshells.

• d-block elements (Groups 3–12)

→ All are metals (most are transition metals), with properties intermediate to those of s-block and p-block metals.

→ The Chemistry of Transition Metal Elements depends upon their *d* orbital electrons. When a *transition metal atom ionizes, electrons from the ns orbital are removed first*.

Note: **All Group 12 cations retain the filled d-subshell**. For this reason, these elements (Zn, Cd, Hg) are **not classified as transition metals**. *Recall that in this text d-orbital electrons are considered to be valence electrons for all the d-block elements*.

• Transition metals

→ Form compounds with a variety of oxidation states (oxidation numbers)

→ Form alloys

→ Facilitate subtle changes in organisms

• f -block elements (lanthanides and actinides)

→ Rare on Earth

→ Lanthanides are incorporated in superconducting materials.

→ Lanthanides are used in electronic devices such as plasma TVs, disk drives, and mobile phones.

→ Actinides are all radioactive elements; most do not occur naturally on the Earth.