

9

Electronic Structure and Atomic Properties

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I have been asked sometimes how one can be sure that elsewhere in the universe there may not be further elements, other than those in the periodic system. I have tried to answer by saying that it is like asking how one knows that elsewhere in the universe there may not be another whole number between 4 and 5. Unfortunately, some persons think that is a good question, too.

George Wald, 1964

We now know the wave functions and energy levels for a hydrogen atom. With this information and the *aufbau* (or buildup) process, we can go on to determine the electronic structures for atoms of all the elements. These structures lead directly to the periodic table of Figures 7-3 and 7-4. As we shall see, the structures explain the stability of eight-electron shells in noble gases and the trends in ionization energies and electron affinities of the elements.

9-1 BUILDUP OF MANY-ELECTRON ATOMS

Although we cannot solve the Schrödinger equation exactly for many-electron atoms, we can show that no radical new features are expected as the atomic number increases. There are the same quantum states, the same four quantum numbers (n , l , m , and s), and virtually the same electronic probability functions or electron-density clouds. The energies of the quantum levels are not identical for all elements; rather, they vary in a regular fashion from one element to the next.

In studying the electronic structure of a many-electron atom, we shall assume the existence of a nucleus and the required number of electrons. We shall assume that the possible electronic orbitals are hydrogenlike, if not identical to the hydrogen orbitals. Then we shall build the atom by adding electrons one at a time, placing each new electron in the lowest-energy orbital available. In this way we shall build a model of an atom in its ground state, or the state of lowest electronic energy. Wolfgang Pauli (1900–

1958) first suggested this treatment of many-electron atoms, and called it the *aufbau*, or buildup, process.

The *aufbau* process involves three principles:

1. No two electrons in the same atom can be in the same quantum state. This principle is known as the **Pauli exclusion principle**. It means that no two electrons can have the same n , l , m , and s values. Therefore, one atomic orbital, described by n , l , and m , can hold a maximum of two electrons: one of spin $+\frac{1}{2}$ and one of spin $-\frac{1}{2}$. We can represent an atomic orbital by a circle and an electron by an arrow:



When two electrons occupy one orbital with spins $+\frac{1}{2}$ and $-\frac{1}{2}$, we say that their spins are paired. A **paired spin** is represented as follows:

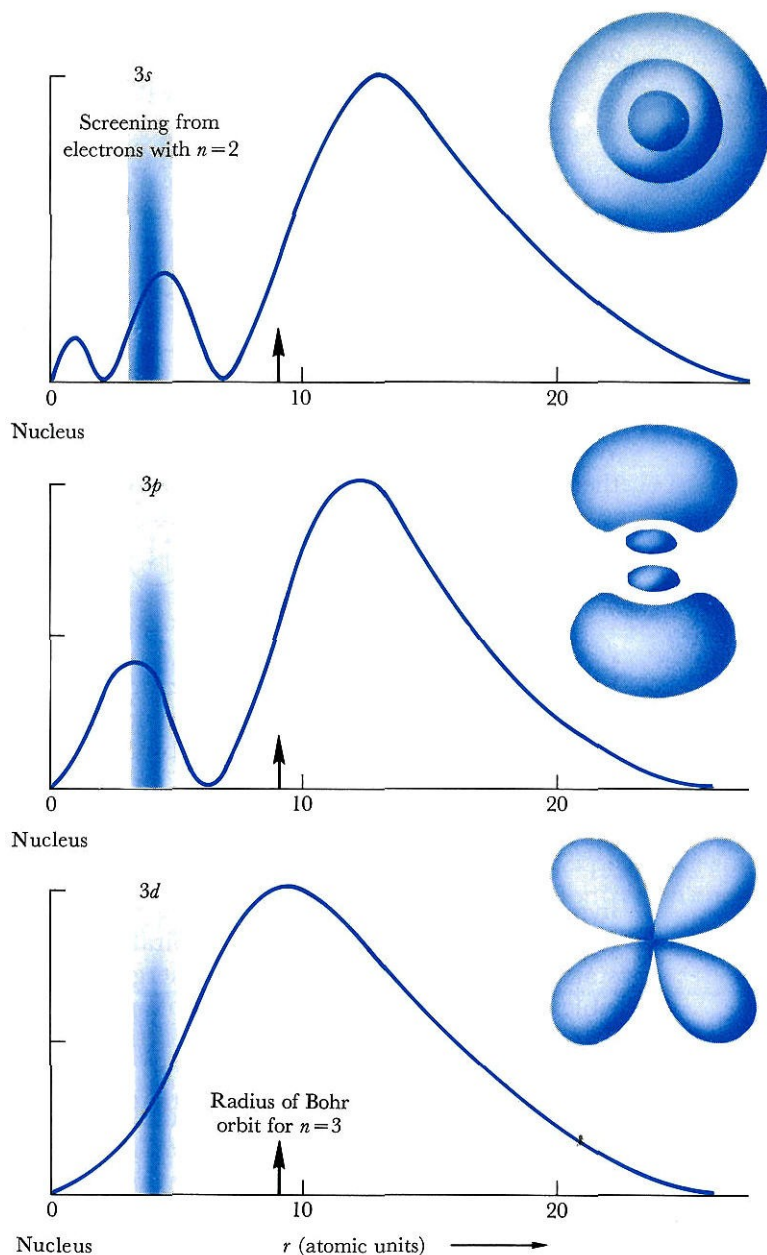


2. Orbitals are filled with electrons in order of increasing energies. The s orbital can hold a maximum of 2 electrons. The three p orbitals can hold a total of 6 electrons, the five d orbitals can hold 10, and the seven f orbitals can hold 14. We must decide on the order of increasing energies of the levels before we can begin the buildup process. For atoms with more than one electron, in the absence of an external electric or magnetic field, energy depends on n and l (the size and shape quantum numbers) and not on m , the orbital-orientation quantum number.

3. When electrons are added to orbitals of the same energy (such as the five $3d$ orbitals), one electron will enter each of the available orbitals before a second electron enters any one orbital. This follows **Hund's rule**, which states that in orbitals of identical energy electrons remain unpaired if possible. This behavior is understandable in terms of electron–electron repulsion. Two electrons, one in a p_x orbital and one in a p_y orbital, remain farther apart than two electrons paired in the same p_x orbital (Figure 8-22). A consequence of Hund's rule is that a **half-filled** set of orbitals (each orbital containing a single electron) is a particularly stable arrangement. The sixth electron in a set of five d orbitals is forced to pair with another electron in a previously occupied orbital. The mutual repulsion of negatively charged electrons means that less energy is required to remove this sixth electron than to remove one of the five in a set of five half-filled d orbitals. Similarly, the fourth electron in a set of three p orbitals is held less tightly than the third.

Relative Energies of Atomic Orbitals

The $3s$, $3p$, and $3d$ orbitals in the hydrogen atom have the same energy but differ in the closeness of approach of the electron to the nucleus (Figure 9-1).



The energy of an electron in an orbital depends on the attraction exerted on it by the positively charged nucleus. Electrons with low principal quantum numbers will lie close to the nucleus and will screen some of this electrostatic attraction from electrons with higher principal quantum numbers. In the Li^+ ion, the **effective nuclear charge** beyond 1 or 2 atomic

Figure 9-1

Radial distribution functions for electrons in the $3s$, $3p$, and $3d$ atomic orbitals of hydrogen. These curves are obtained by spinning the orbital in all directions around the nucleus to smear out all details that depend on direction away from the nucleus, and then by measuring the smeared electron probability as a function of distance from the nucleus. The $3s$ orbital, which is already spherically symmetrical without the smearing operation, has a most probable radius at 13 atomic units and two minor peaks close to the nucleus. The $3p$ orbital has a maximum density near $r = 12$ atomic units, one spherical node at $r = 6$ atomic units and a density peak close to the nucleus. The $3d$ orbital has only one density peak, which occurs very close to the Bohr orbit radius of 9 atomic units. The shapes of the three orbitals before the spherical smearing process are to the right of each curve. An electron in the hydrogen atom with $n = 2$ will be in the neighborhood of $r = 4$ atomic units. The scale of distances changes in many-electron atoms, but relative distances in different orbitals in the atom are the same as in H. An electron in a $3s$ orbital is more stable than one in a $3p$ or $3d$ orbital because it has a greater probability of being inside the orbital of $n = 2$ electrons, in which it experiences a greater attraction from the nucleus. The $3p$ orbital is similarly more stable than the $3d$.

units from the nucleus is not the true nuclear charge of $+3$, but a *net* charge of $+1$ produced by the nucleus plus the two $1s$ electrons. Similarly, the lone $n = 3$ electron in sodium experiences a net nuclear charge of approximately $+1$ rather than the full nuclear charge of $+11$.

If the net charge from the nucleus and the filled inner orbitals were concentrated at a point at the nucleus, then the energies of $3s$, $3p$, and $3d$ orbitals would be the same. But the screening electrons extend over an appreciable volume of space. The net attraction that an electron with a principal quantum number of 3 experiences depends on how close it comes to the nucleus, and whether it penetrates the lower screening electron clouds. As in Sommerfeld's elliptical-orbit model, the s orbital comes closer to the nucleus and is somewhat more stable than the p , and the p is more stable than the d . This is the reason for the variation of the l energy levels in the lithium energy-level diagram in Figure 8-13.

For a given value of the principal quantum number, n , the order of increasing energy is s, p, d, f, g, \dots . It is less easy to decide whether and when the high l -value orbitals of one n overtake the low- l orbitals of the next: for example, whether a $4f$ orbital has a higher energy than a $5s$, or a $3d$ a higher energy than a $4s$. The question was originally settled empirically by choosing the order of overlap that accounted for the observed structure of the periodic table. The energies have since been calculated theoretically, and (fortunately for quantum mechanics) they agree with the observed order of levels. The sequence of energy levels is shown in Figure 9-2.

Orbital Configurations and First Ionization Energies

We shall build up the electronic structures of the atoms in the periodic table by adding electrons to the hydrogenlike orbitals in order of increasing

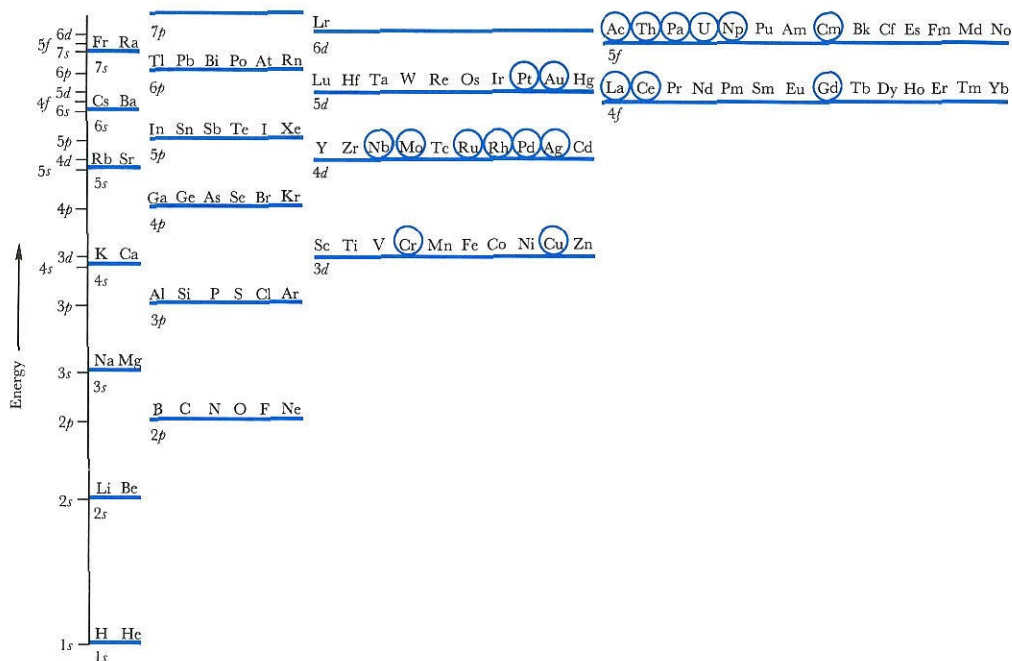
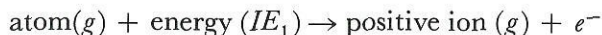


Figure 9-2

Idealized diagram of the energy levels of the hydrogenlike atomic orbitals during the buildup of many-electron atoms. On each level are written the symbols of those elements that are completed with the addition of electrons on that level. Note the nearly equal energies of $4s$ and $3d$ levels, of $5s$ and $4d$, of $6s$, $4f$, and $5d$, and finally of $7s$, $5f$, and $6d$. The near equivalence of energies is reflected in some irregularity in the order of filling levels in the transition metals and inner transition metals. Elements with such irregularities are circled. For example, after the $6s$ and $7s$ orbitals fill, in lanthanum and actinium, the next electron goes into a d rather than an f orbital. See Figure 9-3 for details.

energy, and by increasing the nuclear charge by one at each step. During this process we shall pay particular attention[†] to the relationship between the **orbital electronic configurations** of atoms and their first ionization energies. The **first ionization energy** (IE_1) of an atom is the energy required to remove one electron:

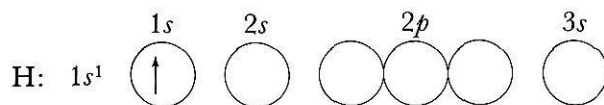


Numerical IE_1 values are given in Table 9-1.* Use the periodic table in Figure 9-3 as an aid as you follow this building process.

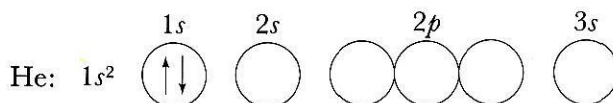
A hydrogen (H) atom has only one electron, which in the ground state must go in the $1s$ orbital. So we write $1s^1$ (the superscript represents the

*It is common to refer to IE_1 simply as IE : This is done in Table 9-1.

number of electrons in the orbital), and illustrate the electronic configuration as follows:



In helium (He), the second electron also can be in the $1s$ orbital if its spin is paired with that of the first electron. In spite of electron–electron repulsion, this electron is more stable in the $1s$ orbital than in the higher-energy $2s$ orbital:



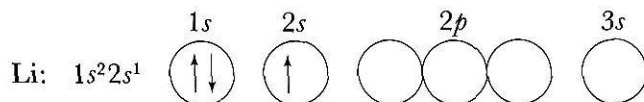
Because of the electron–electron repulsion, the first ionization energy of He is less than we might have expected for an atom with a nuclear charge of $+2$. A simple calculation illustrates this point. If electron–electron repulsion were not important, each electron would feel the full force of the $+2$ nuclear charge, and the first ionization energy could be calculated from the one-electron formula:

$$IE_1 = -E_1 = \frac{Z^2k}{n^2} = \frac{(2)^2(1312 \text{ kJ mole}^{-1})}{(1)^2}$$

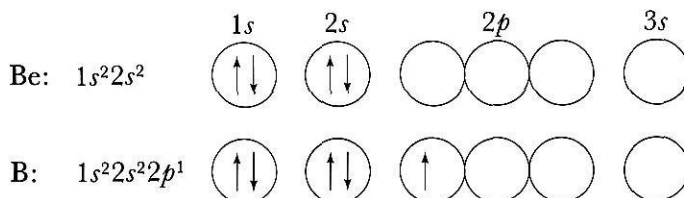
$$= 5248 \text{ kJ mole}^{-1}$$

However, the experimental value of IE_1 for He is much less, $2372 \text{ kJ mole}^{-1}$. Although the strong attraction of a $1s$ electron to the $+2$ He nucleus is partially counterbalanced by the electron–electron repulsion, the IE_1 is still very large, showing how tightly each electron is bound in He.

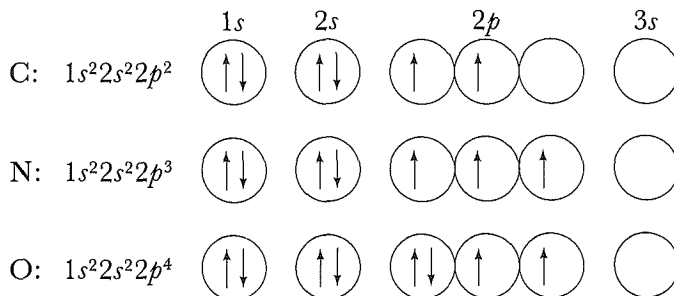
Lithium (Li) begins the next period in the periodic table. Two electrons fill the $1s$ orbital; the third electron in Li must, by the Pauli exclusion principle, occupy the next lowest-energy orbital, namely, the $2s$:



The fourth electron in beryllium (Be) fills the $2s$ orbital, and the fifth electron in boron (B) must occupy one of the higher-energy $2p$ orbitals:

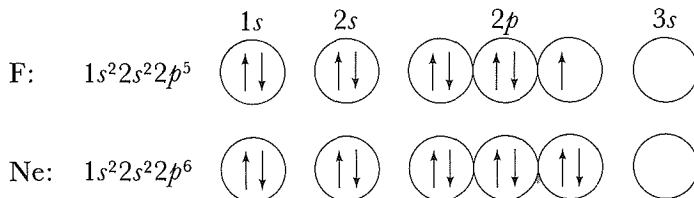


For B, the first ionization energy is less than that of Be because its outermost electron is in a less-stable (higher-energy) orbital. In carbon (C), two of the the three $2p$ orbitals contain an electron. As Hund's rule predicts, in nitrogen (N) the three p electrons are found in all three $2p$ orbitals, instead of two being paired in one:



The fourth $2p$ electron in an oxygen (O) atom is held less tightly than the first three because of the electron–electron repulsion with the other electron in one of the $2p$ orbitals. The first ionization energy of O is accordingly low.

The general trend across this period is for each new electron to be held *more* tightly because of the increased charge on the nucleus. Because the other $2s$ and $2p$ electrons are approximately the same distance from the nucleus, they do not shield the new electron from the steadily increasing charge. This increased charge overcomes the electron repulsion as the fifth $2p$ electron is added in fluorine (F). Therefore, the fifth electron is held very tightly in F, and the first ionization energy increases again. The most stable configuration results when the sixth $2p$ electron is added to complete the $n = 2$ shell with the noble gas neon (Ne):



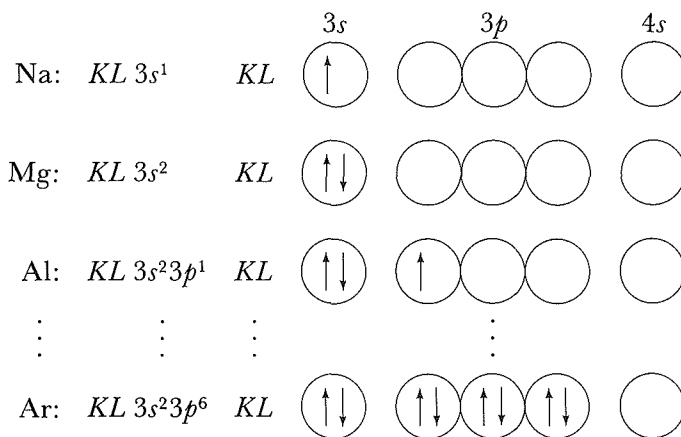
The complete $n = 1$ shell of two electrons is often given the symbol K , and the complete $n = 2$ shell of eight electrons is given the symbol L . A briefer representation of the Ne atom then is

Ne: KL

For all but a few atoms, writing the complete orbital electronic structure is a tedious procedure. It is also unnecessary because only the outer electrons are important in chemical reactions. We call the chemically im-

portant or outer electrons the **valence electrons**. The valence electrons of an atom are the electrons in the s and p orbitals beyond the closed-shell configurations. For example, in Li the two $1s$ electrons are bound tightly to the nucleus of charge $+3$. Like the two electrons in He, they are chemically unreactive. Thus we say that the valence electronic structure of Li is $2s^1$. Similarly, the valence electronic structure of Be is $2s^2$; of B, $2s^2 2p^1$; of C, $2s^2 2p^2$; of N, $2s^2 2p^3$; of O, $2s^2 2p^4$; and of F, $2s^2 2p^5$.

The buildup of the third period of the periodic table proceeds exactly as that of the preceding period did. Each new electron is bound more firmly because of the increasing nuclear charge, except for the fluctuations at aluminum (Al) and sulfur (S) produced by the filling of $3s$ in magnesium (Mg) and the half-filling of $3p$ in phosphorus (P):



The outermost electron for each element in this period is bound *less* firmly than the outermost electron in the corresponding element of the previous period because the $n = 3$ electrons are farther from the nucleus. Therefore, the first ionization energies for the $n = 3$ elements are smaller than for the corresponding $n = 2$ elements. With the completion of the $3s$ and $3p$ orbitals, we have again reached a particularly stable electronic configuration with the noble gas argon (Ar).

Something unusual happens in the fourth period. The $4s$ orbital penetrates closer to the nucleus than does the $3d$ orbital, and at this point in the buildup process the $4s$ has slightly lower energy than the $3d$. Hence, the one and two electrons that are added to form potassium (K) and calcium (Ca) go into the $4s$ orbital before the $3d$ orbital is filled in the elements scandium (Sc) through zinc (Zn). If we assume a constant inner electronic configuration of $KL 3s^2 3p^6$, the valence electronic configurations for the $4s$ and $3d$ elements are

K	$3d^04s^1$	Mn	$3d^54s^2$
Ca	$3d^04s^2$	Fe	$3d^64s^2$
Sc	$3d^14s^2$	Co	$3d^74s^2$
Ti	$3d^24s^2$	Ni	$3d^84s^2$
V	$3d^34s^2$	Cu	$3d^{10}4s^1$
Cr	$3d^54s^1$	Zn	$3d^{10}4s^2$

There are two anomalies in this order of filling. The half-filled (d^5) and filled (d^{10}) levels are particularly stable, therefore the chromium (Cr) and copper (Cu) atoms have only one $4s$ electron each.

Example 1

The valence electronic configuration for the ground state of chromium is $3d^54s^1$. Predict the configuration of the first (i.e., lowest-energy) excited state of chromium.

Solution

The *aufbau* process predicts $3d^44s^2$ for the ground state, but the extra stability of a half-filled level makes the $3d^54s^1$ configuration slightly lower in energy than $3d^44s^2$. The latter configuration thus becomes the first excited state.

For those elements whose ground-state configurations differ from those predicted by the *aufbau* process, the predicted configuration is that of an excited state usually only slightly higher in energy than the ground state.

Although the $4s$ orbital penetrates closer to the nucleus than the $3d$ and therefore has a lower energy, the *majority* of the probability density of the $4s$ orbital is farther from the nucleus than in the $3d$. An electron in a $4s$ orbital is simultaneously farther from the nucleus, on the average, than a $3d$ electron and more stable because of the small but not negligible probability that it will be very close to the nucleus. In chemical bonding, the energies of electrons in such closely spaced levels in atoms are not as significant as distances of the electrons from the nucleus. Therefore, the $4s$ electrons have more of an effect on chemical properties than[†] the relatively buried $3d$ electrons. With the exception of Cr and Cu, all the elements from Ca through Zn have the same outer electronic structure: two $4s$ electrons. The chemical properties of this series of elements will vary less rapidly than those in a series in which s or p electrons are being added. This is the reason for the relatively unchanging properties of the transition metals.

After the $3d$ orbitals are filled, the $4p$ orbitals fill, in a straightforward manner, to form the representative elements from gallium (Ga), $3d^{10}4s^24p^1$, to the noble gas krypton (Kr), $3d^{10}4s^24p^6$. The first ionization energy, which had risen with increasing nuclear charge in the transition metals, plummets at Ga when the next electron is placed in the less stable $4p$ orbital.

The fifth period repeats the same pattern: first the filling of the $5s$ orbitals, then an interruption while the buried $4d$ orbitals are filled in another series of transition metals, and finally the filling of the $5p$ orbitals, ending with the noble gas xenon (Xe), $4d^{10}5s^25p^6$. The common feature of all noble gases is the outermost electronic arrangement s^2p^6 . This is the origin of the stable eight-electron shells that we mentioned in Chapter 7. The late filling of the d orbitals (and f orbitals) produces the observed lengths of the periods of the periodic table: first 2, then 8, then only 8 instead of 18 for $n = 3$, then only 18 instead of 32 for $n = 4$.

According to the energy diagram in Figure 9-2, the $6s$ orbital is more stable than the $5d$, which is not surprising since we have seen the same behavior in the two previous periods. However, the $4f$ orbitals also are generally more stable than the $5d$, although the difference is small and there are exceptions. The *idealized* filling pattern is for the $6s$ orbital to fill in cesium (Cs) and barium (Ba), followed by the deeply buried $4f$ orbitals in the 14 inner transition elements lanthanum (La) through ytterbium (Yb). There are minor deviations from this pattern, as shown in Figure 9-3. The most important of these deviations is that the first electron after Ba goes into the $5d$ orbital in La and not into the $4f$. Lanthanum is more properly a transition metal than an inner transition metal. It is more relevant to understand the idealized filling pattern, however, than to worry about the individual exceptions to it.

The chemical properties of the inner transition metals cesium (Ce) to lutetium (Lu) vary even less than the properties of the transition metals, because successive electrons are in the deeply buried $4f$ orbitals. After the $4f$ orbitals are filled, the balance of the third transition-metal series, hafnium (Hf) to mercury (Hg), occurs with the filling of the $5d$ orbitals. The representative elements thallium (Tl) through radon (Rn) are formed as the $6p$ orbitals fill.

The seventh and last period begins in the same way. First the $7s$ orbital fills, then the inner transition metals from actinium (Ac) to nobelium (No)—with the irregularities shown in Figure 9-3—and finally the beginning of a fourth transition-metal series with lawrencium (Lr). There are more deviations from this simple f -first, d -next filling pattern in the actinides than in the lanthanides (Figure 9-3), and consequently the first few actinide elements show a greater diversity of chemical properties than do the lanthanides.

In summary, the idealized sequence of filling of orbitals across a period is as follows:

1. For period n , the ns orbital is filled first with two electrons. These elements are the alkali metals (Group IA) and the alkaline earths (Group IIA) and are classed with the **representative elements**.
2. The very deeply buried $(n - 2)f$ orbitals are filled next. They exist only for $(n - 2)$ greater than 3, or for Periods 6 and 7. These elements,

which have virtually identical outer electronic structure and therefore virtually identical chemical properties, are the **inner transition metals**.

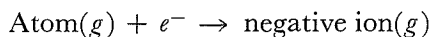
3. The less deeply buried $(n - 1)d$ orbitals are then filled if they exist. They exist only for $(n - 1)$ greater than 2, or for Period 4 and greater. These elements are similar to one another, but not as similar as the inner transition metals. They are called the **transition metals** (B groups).

4. Finally, the three np orbitals are filled to form the remaining **representative elements** (Groups IIIA–VIIA) and to conclude in each period with the outermost s^2p^6 configuration of the **noble gases**.

We can now explain many of the facts that we presented in Chapter 7. The structure of the periodic table, with its groups and periods, can be seen to be a consequence of the order of energy levels (Figure 9-2). Elements in the same group have similar chemical properties because they have the same outer electronic structure in the s and p orbitals. The outer valence electrons that are so important in chemistry are these s and p electrons. The closed, inert shell of the noble gases is the completely filled s^2p^6 configuration. We can understand the mechanism of formation of the transition metals and the inner transition metals in terms of the filling of inner d and f orbitals. We can see the reasons for general trends across a period or down a group, and for local fluctuations within a period.

Electron Affinities

Another atomic property that depends strongly on the orbital electronic configuration is the **electron affinity** (EA), which is the energy change that accompanies the addition of an electron to a gaseous atom to form a negative ion:



If energy is released when an atom adds an electron to form a negative ion, the EA has a positive value. If energy is required, the EA is negative. (Values for the known atomic electron affinities are given in Table 9-1.)

Within a period, the halogens have the highest electron affinities because, after the effect of screening electrons in lower quantum levels has been accounted for, the net nuclear charge is greater for a halogen than for any other element in the period. The noble gases have negative electron affinities because the new electron must be added to the next higher principal quantum level in each atom. Not only would the added electron be farther from the nucleus than the other electrons, it also would receive the full screening effect from all the others.

Lithium and sodium have moderate electron affinities; beryllium has a negative electron affinity, and magnesium has a near zero electron affinity. In Be and Mg the valence s orbital is full and the added electron must go into a higher-energy p orbital. Nitrogen and phosphorus have low electron

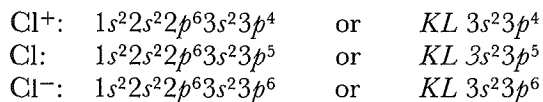
affinities because an added electron must pair with an electron in one of the half-filled p orbitals.

Example 2

Write the ground-state orbital electronic configurations of Cl^+ , Cl , and Cl^- . What are the valence electronic configurations of these species?

Solution

The atomic number of Cl is 17. Therefore the positive ion Cl^+ has 16 electrons, Cl has 17, and Cl^- has 18. The ground-state orbital electronic configurations are as follows:



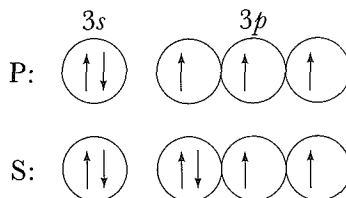
The valence electronic configurations are $3s^2 3p^4$ for Cl^+ , $3s^2 3p^5$ for Cl, and $3s^2 3p^6$ for Cl^- .

Example 3

The first ionization energy of P, 1063 kJ mole^{-1} , is greater than that of S, 1000 kJ mole^{-1} . Explain this difference in terms of the valence orbital electronic configurations of P and S atoms.

Solution

The valence orbital electronic configuration of P is $3s^2 3p^3$; of S, $3s^2 3p^4$. The $3p$ shell is exactly half-filled in a P atom, whereas there is one extra electron in S that is forced to pair with another $3p$ electron:



As a result of the added electron–electron repulsion of the paired $3p$ electrons in atomic S, the normal trend of increasing first ionization energies with increasing atomic number in a given period is reversed, with the IE_1 of P being greater than the IE_1 of S. This effect illustrates the special stability associated with a half-filled p shell. After the half-filled p shell is disrupted (p^3 to p^4), the electron–electron repulsions associated with the addition of the fifth and sixth p electrons in Cl and Ar are not large enough to override the attractive effect of the increasing positive nuclear charge. Thus the ionization energies of S, Cl, and Ar increase in the usual order ($S < \text{Cl} < \text{Ar}$).

Example 4

In each of the following orbital electronic configurations, does the configuration represent a ground state, an excited state, or a forbidden state (that is, a configuration that cannot exist): (a) $1s^2 2s^2 2p^2 4s^1$; (b) $1s^1 2s^2 2p^1$; (c) $1s^2 2s^2 2p^6$; (d) $1s^2 2s^2 2p^5 3s^3$?

Solution

(a) The ground-state configuration for an atom or ion with 7 electrons is $1s^2 2s^2 2p^3$. If it is an atom, then it must be N (atomic number 7). The configuration $1s^2 2s^2 2p^2 4s^1$ represents a state in which a $2p$ electron has been excited to a $4s$ orbital. Therefore the configuration represents an excited state. (b) The configuration $1s^1 2s^2 2p^1$ represents an excited state (for a 4-electron atom or ion, $1s^2 2s^2$ is the ground state; if it is an atom, it is Be). (c) The configuration $1s^2 2s^2 2p^6$ represents a ground state (F^- , Ne, Na^+ , Mg^{2+}). (d) The ground-state configuration for an atom or ion with 12 electrons is $1s^2 2s^2 2p^6 3s^2$ (magnesium atom). In the configuration $1s^2 2s^2 2p^5 3s^3$, 3 electrons are placed in the $3s$ orbital, which can take only 2 (one with $s = +\frac{1}{2}$ and one with $s = -\frac{1}{2}$). The configuration with three $3s$ electrons violates the Pauli principle and cannot exist. It represents a forbidden state.

Example 5

The electron affinity of Si, 138 kJ mole^{-1} , is much larger than that of P, 75 kJ mole^{-1} . Explain why this is so in terms of valence-orbital electronic configurations.

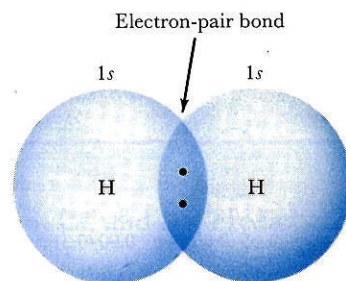
Solution

The valence-orbital configuration of Si is $3s^2 3p^2$; of P, $3s^2 3p^3$. Adding one electron to Si to give Si^- gives a half-filled $3p$ shell (Si^- is $3s^2 3p^3$); addition of one electron to P disrupts a half-filled $3p$ shell (P^- is $3s^2 3p^4$). The special stability of the half-filled shell of Si^- , taken with the extra electron–electron repulsion in the $3s^2 3p^4$ configuration of P^- , accounts for the fact that the EA of Si is larger than the EA of P.

9-2 TYPES OF BONDING

A **covalent bond** forms between combining atoms that have electrons of similar, or equal, valence-orbital energies. For example, two atoms of hydrogen are joined by a covalent bond in the H_2 molecule. The energy required to separate two bonded atoms is known as the **bond energy**. For H_2 , the bond energy (corresponding to the process $H_2 \rightarrow H + H$) is 432 kJ mole^{-1} .

The two electrons in H_2 are shared equally by the two hydrogen $1s$ orbitals. This, in effect, gives each hydrogen atom a stable, closed-shell

**Figure 9-4**

The two hydrogen 1s orbitals overlap to form an electron-pair covalent bond in H_2 .

(helium-type) configuration. An orbital representation of the covalent electron-pair bond in H_2 is shown in Figure 9-4.

An **ionic bond** is formed between atoms with very different ionization energies and electron affinities. This situation allows one atom in a two-atom pair to transfer one or more valence electrons to its partner. An atom of Na is so different from an atom of Cl, for example, that it is not possible for atoms in NaCl to share their electrons equally. The Na atom has a relatively low IE_1 of 498 kJ mole⁻¹ and a small EA of 117 kJ mole⁻¹. Therefore, it will readily form Na^+ in the presence of an atom with a high EA . The chlorine atom has an EA of 356 kJ mole⁻¹ and an IE_1 of 1255 kJ mole⁻¹. Rather than lose an electron, a Cl atom has a strong tendency to gain one. The result is that in diatomic NaCl an ionic bond is formed, Na^+Cl^- , in which the 3s valence electron in Na is transferred to the one vacancy in the 3p orbitals of Cl.

Atomic Radii

The separation of the nuclei of two atoms that are bonded together (such as H_2 or Na^+Cl^-) is called the **bond distance**. In the hydrogen molecule, H_2 , the bond distance is 0.74 Å. Each hydrogen atom in H_2 may be assigned an **atomic radius** of 0.37 Å. The average radii of atoms of some representative elements shown in the periodic-table arrangement of Figure 9-5 were determined from experimentally observed bond distances in many molecules. The atomic radius in most cases is compared with the size of the appropriate closed-shell positive or negative ion.

You will notice (Figure 9-5) that the atomic radii become smaller across a given row (or period) of the periodic table. This shrinkage occurs because in any given period *s* and *p* orbitals acquire additional electrons, which are not able to shield each other effectively from the increasing positive nuclear charge. Thus an increase in the positive charge of the nucleus results in an increase in the effective nuclear charge, thereby decreasing the effective atomic radius. This is why a Be atom, for example, is smaller than a Li atom.

From H to Li there is a large increase in effective atomic radius; the third electron in a Li atom is in an orbital that has a much larger effective

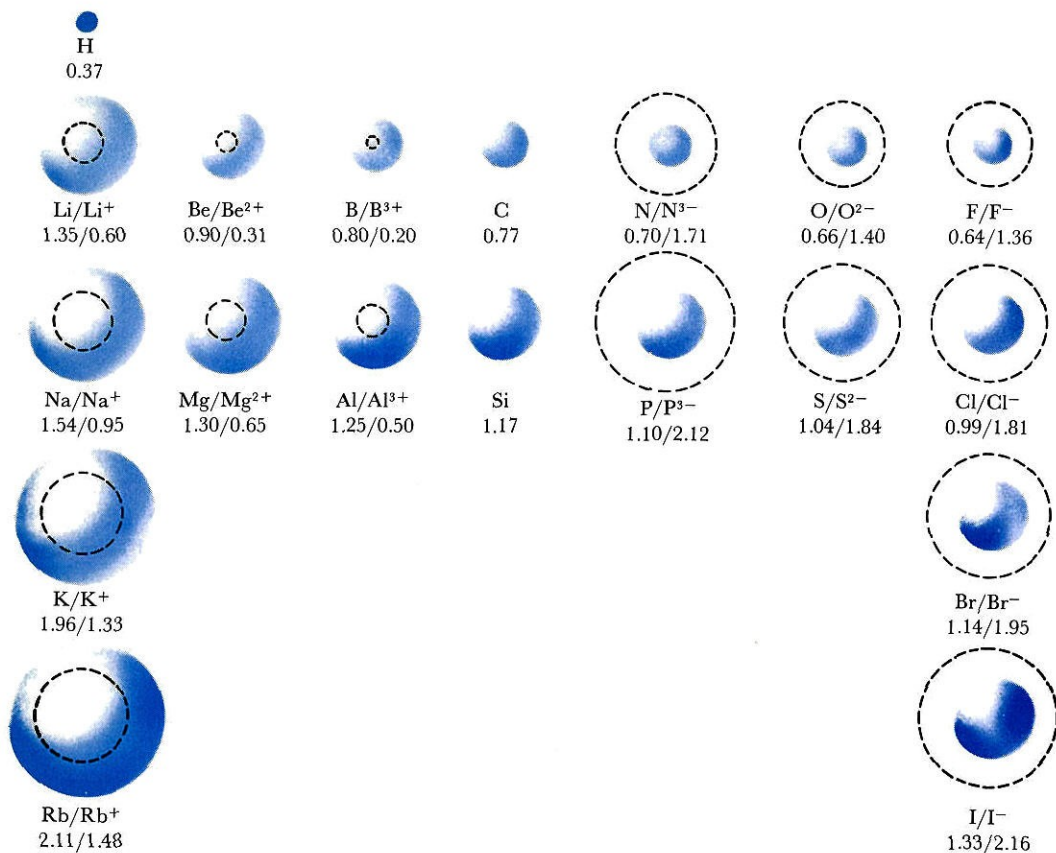


Figure 9-5

Relative atomic radii of some elements compared with the radii of the appropriate closed-shell ions. Radii are in angstroms. Solid spheres represent atoms and dashed circles represent ions. Notice that positive ions are smaller than their neutral atoms and negative ions are larger. Why is this so?

radius than the H 1s orbital has. According to the Pauli principle, the third electron in Li must be in an orbital with a larger principal quantum number, namely the 2s orbital. Seven more electrons can be added to the 2s and 2p orbitals, which have approximately the same radii. However, these electrons do not effectively shield each other from the positive nuclear charge as it increases, and the result is an increase in the effective nuclear charge and a corresponding decrease in radii in the series Li ($Z = 3$) through Ne ($Z = 10$). After Ne, additional electrons cannot be accommodated by the $n = 2$ level. Thus an eleventh electron must go into the $n = 3$ level, specifically, into the 3s orbital. Since the effective radii increase from the $n = 1$ to

$n = 2$ to $n = 3$ valence orbitals, the effective size of an atom also increases with increasing atomic number within each group in the periodic table.

Example 6

Predict the order of decreasing atomic radii for S, Cl, and Ar. Predict the order for Ca^{2+} , Cl^- , Ar, K^+ , and S^{2-} .

Solution

The order $\text{S} > \text{Cl} > \text{Ar}$ is correct for the radii of these atoms, because the nuclear charge increases by one unit from S to Cl and by one unit from Cl to Ar. The valence electrons are attracted more strongly to the nuclei with higher positive charges in any given period, so the atomic radii decrease correspondingly. For isoelectronic atomic and ionic species (those having the same number of electrons), radii decrease as the nuclear charge (atomic number) increases, again because of increasing electron–nucleus attraction. Thus the correct order for the isoelectronic species is $\text{S}^{2-} > \text{Cl}^- > \text{Ar} > \text{K}^+ > \text{Ca}^{2+}$.

9-3 ELECTRONEGATIVITY

Most bonds in molecules fall somewhere between the extremes of the covalent and ionic types. The bond in the HF molecule, for example, is neither purely covalent nor purely ionic. Just how unequal is the sharing of electrons in HF? And which atom in HF is able to attract the greater share of the bonding electrons, H or F? To answer the second question, and to provide a qualitative guide to the first, Linus Pauling (b. 1901) defined a quantity called **electronegativity**, χ (the Greek letter chi), in 1932; two years later R. S. Mulliken (b. 1896) showed that electronegativity could be related to the average of the electron affinity and the ionization energy of an atom.

Pauling obtained electronegativity values by comparing the energy of a bond between unlike atoms, AB, with the *average* energies of the A_2 and B_2 bonds. If HF formed a covalent bond as in H_2 and F_2 , then we would expect the bond energy in HF to be close to the average (say, the arithmetic mean or the geometric mean) of the bond energies in H_2 and F_2 . However, in molecules such as HF, the bonds are stronger than predicted from such averages. The bond energy of HF is 565 kJ mole^{-1} , whereas the bond energies of H_2 and F_2 are 432 and 139 kJ mole^{-1} , respectively. The geometric mean of the last two values is $(139 \times 432)^{1/2} = 245 \text{ kJ mole}^{-1}$, which is much less than the observed bond energy of HF. This “extra” bond energy (designated Δ) in an AB molecule is assumed to be a consequence of the **partial ionic character** of the bond due to the electronegativity difference between atoms A and B. The electronegativity difference between atoms A and B may be defined as

$$\chi_A - \chi_B = 0.102\Delta^{1/2} \quad (9-1)$$

in which χ_A and χ_B are the electronegativities of atoms A and B, and Δ is the extra bond energy in kilojoules per mole. The extra bond energy is calculated from the equation

$$\Delta = DE_{AB} - [(DE_{A_2})(DE_{B_2})]^{1/2}$$

in which DE is the particular bond dissociation energy.

In equation 9-1 the square root of Δ is used because it gives a more consistent set of atomic electronegativity values. Since only differences are obtained from equation 9-1, one atom must be assigned a specific electronegativity value, and then the values for the other atoms can be calculated easily. In a widely adopted electronegativity scale, the most electronegative atom, F, is assigned a value of 3.98. (Electronegativity values based on this assignment are given in Table 9-1.)

Electronegativity is a measure of the attraction that an atom has for electrons in a bond it has formed with another atom. From the data in Table 9-1, we can predict that bonding will be ionic in CsF and covalent in CH_4 . The bonding in HF is intermediate between the CsF and CH_4 extremes. The bonding electrons in the HF molecule are “pulled” toward the F atom because of its higher electronegativity. The bond in HF has partial ionic character, $\text{H}^{\delta+}\text{F}^{\delta-}$ (where $\delta+$ and $\delta-$ represent charges of less than one unit). In general, bonds between atoms have varying degrees of **partial ionic character**, depending on the difference in electronegativity of the atoms involved.*

Example 7

Using electronegativity values, predict whether the bonds in (a) CaO, (b) HI, (c) SiH, (d) Br_2 , and (e) ICl are covalent, ionic, or covalent with some degree of ionic character (partially ionic). For the ionic and partially ionic bonds, show the charges expected.

Solution

(a) The difference in the electronegativities of Ca (1.00) and O (3.44) is large ($\chi_O - \chi_{\text{Ca}} = 2.44$), and the bond is ionic,[†] $\text{Ca}^{2+}\text{O}^{2-}$. (b) For HI, $\chi_I - \chi_H = 0.46$; the bond is covalent with a small degree of ionic character, $\text{H}^{\delta+}\text{I}^{\delta-}$. (c) For SiH, $\chi_H - \chi_{\text{Si}} = 0.30$; the bond is covalent with a very small degree of ionic character, $\text{Si}^{\delta+}\text{H}^{\delta-}$. The ionic character in this case is so small that it is common to regard SiH bonds as covalent. (d) For Br_2 , $\Delta\chi$ is zero. The bond is covalent. (e) For ICl, $\chi_{\text{Cl}} - \chi_{\text{I}} = 0.50$; the ICl bond is covalent with a small degree of ionic character, $\text{I}^{\delta+}\text{Cl}^{\delta-}$.

*A difference of more than 2.0 results in a bond that may be considered ionic; a difference in the range 0.4–2.0 results in a covalent bond with ionic character; a difference of less than 0.4 results in a bond that may be considered covalent.

Example 8

Calculate the electronegativity of bromine (Br) on the Pauling scale, assuming that χ_{H} is equal to 2.20 and taking the following bond energies from Tables 12-2 and 12-4; H_2 , 432 kJ mole⁻¹; Br_2 , 190 kJ mole⁻¹; and HBr , 362 kJ mole⁻¹.

Solution

We may use equation 9-1,

$$\chi_{\text{A}} - \chi_{\text{B}} = 0.102\Delta^{1/2}$$

and the expression for Δ :

$$\Delta = DE_{\text{AB}} - [(DE_{\text{A}_2})(DE_{\text{B}_2})]^{1/2}$$

Evaluating Δ for HBr , we have

$$\begin{aligned}\Delta &= DE_{\text{HBr}} - [(DE_{\text{H}_2})(DE_{\text{Br}_2})]^{1/2} \\ &= 362 - [(432)(190)]^{1/2} \\ &= 362 - 286 = 76 \text{ kJ mole}^{-1}\end{aligned}$$

Therefore, $\chi_{\text{Br}} - \chi_{\text{H}} = 0.102(76)^{1/2} = 0.102(8.7) = 0.89$. So,

$$\begin{aligned}\chi_{\text{Br}} - \chi_{\text{H}} &= 0.89 \\ \chi_{\text{Br}} &= \chi_{\text{H}} + 0.89 = 2.20 + 0.89 = 3.09\end{aligned}$$

Our value for χ_{Br} , 3.09, differs slightly from the accepted $\chi_{\text{Br}} = 2.96$ given in Table 9-1. The slight difference occurs because the value in the table is an average of the results from many calculations of this type.

Summary

By adding electrons one by one to atomic orbitals (in the order $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, and so on), following the **Pauli exclusion principle** (no two electrons can have exactly the same set of four quantum numbers) and **Hund's rule** (in orbitals of the same energy, electrons remain unpaired if possible), we can describe the orbital electronic structures of the ground states of all atoms (the *aufbau* process). The stable shell of eight electrons that was proposed on chemical grounds is the set of eight electrons in the outermost s , p_x , p_y , and p_z orbitals. The detailed structure of the periodic table is a result of the order of energies of the levels, and of the delayed filling of d and f orbitals. The **representative elements** are those formed by filling the ns and three np valence orbitals in any n period. These make up Groups IA (alkali metals; s^1), IIA (alkaline earths; s^2), IIIA (boron family; s^2p^1), IVA (carbon family; s^2p^2), VA (nitrogen family; s^2p^3), VIA (oxygen family; s^2p^4), and VIIA (halogens; s^2p^5). Elements whose atoms have the closed-shell s^2p^6 configuration are called **noble gases**.

The outermost s and p electrons are responsible for most chemical properties; they are the **valence electrons** of the representative elements.

The d and f orbitals are buried more deeply, and the occupancy of these levels in the transition metals and inner transition metals (lanthanides, actinides) has less effect on chemical behavior. Nevertheless, the d electrons do influence the chemical properties of transition metals, and the outermost d , s , and p orbitals are considered to be valence orbitals in atoms of such elements.

In general, ionization energies of atoms increase as one goes from left to right in the periodic table. Electron affinities are highest in the oxygen and halogen families of elements. Atoms with stable orbital configurations (s^2 , s^2p^3 , s^2p^6) have very low (often negative) electron affinities. The separation between two nuclei of bonded atoms is called the bond distance. The atomic radius of H is one-half the bond distance of H_2 . In general, atomic radii decrease from left to right across the periodic table. Electronegativity is a measure of the attraction an atom has for the electrons in a bond it has formed with another atom. Atoms that differ greatly in electronegativity transfer electrons and form ionic bonds; atoms of approximately equal electronegativity combine by sharing electrons in covalent bonds. Atoms such as H and F that differ somewhat in electronegativity form bonds with partial ionic character.

Self-Study Questions

1. What is the Pauli exclusion principle, and how does it permit us to construct models for the electronic configurations of atoms that have more electrons than hydrogen has?
2. What would the periodic table look like if the Pauli exclusion principle did not hold?
3. What is Hund's rule, and what role does it play in the buildup of electronic configurations of atoms? What is the physical justification for Hund's rule?
4. Why do the $4s$, $4p$, $4d$, and $4f$ orbitals have the same energy in the hydrogen atom, but different energies in a many-electron atom?
5. What is "screening" by electrons in an atom?
6. Why is the first ionization energy of S less than that of P?
7. Why is the first ionization energy of Th less than that of Hg?
8. What evidence do we have that the relative order of energy levels in Figure 9-2 is correct?
9. Why are the chemical properties of the transition metals less varied than those of the representative elements?
10. What are the elements in the inner transition metal series, and how are they explained in terms of electronic configurations?
11. Why does the electron affinity, which increases steadily from N to O to F, drop so abruptly at Ne?
12. What are isoelectronic ions? Why do the radii of the isoelectronic ions As^{3-} , Se^{2-} , Br^- , Rb^+ , Sr^{2+} , and Y^{3+} decrease?

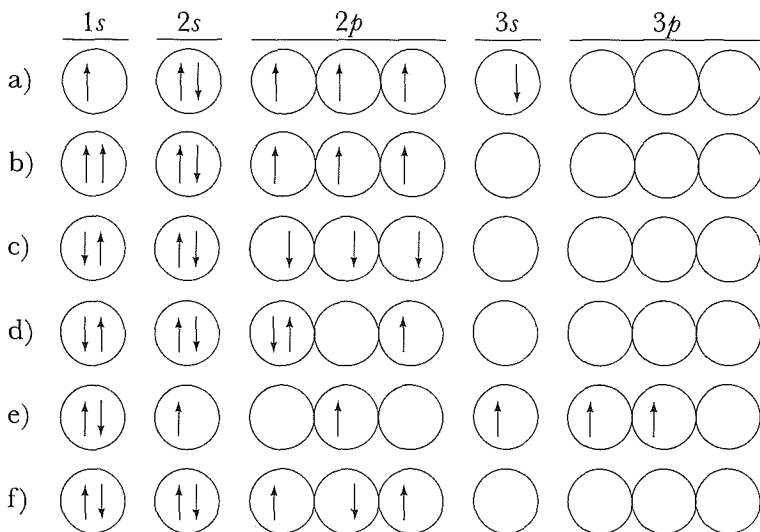
13. Why do the radii of the neutral atoms decrease from K to Ca to Sc to Ti?
14. How is electronegativity related to first ionization energy and electron affinity? How is it related to the bond energies of molecules?
15. In what part of the periodic table are elements with the highest electronegativity found? What three elements have the highest electronegativities? Which element has the lowest?
16. Would you expect the bonding in rubidium chloride to be ionic or covalent? Why? What about in osmium chloride or iridium chloride? On what would you base your predictions?
17. Consider an excited H atom in which the electron is in the $3s$ orbital. The energy required per mole to remove such an electron is 146 kJ. However, to remove the $3s$ electron of Na requires 498 kJ mole⁻¹. Explain this difference.
18. Explain the fact that the second ionization energy of Mg is larger than the first, but not as large as the second ionization energy of Na.
19. Which atom has the lowest first ionization energy: Li, F, Cs, or Xe? Why?
20. Which atom has the greatest electron affinity: Cl, I, O, or Na? Why?
21. Which hydrogen compound is most ionic: LiH, CsH, FH, or IH? In which compound will H have the largest positive charge? The largest negative charge?
22. Explain why the electron affinities of both Si and S are larger than that of P.
23. Predict the relative effective radii of the species H⁻, He, and Li⁺. Explain your choice.
24. Which has the higher electronegativity, Br or Cl? Will the bonding in CBr₄ be more ionic or more covalent than that in CCl₄?
25. What is the order of increasing first ionization energies of C, N, O, and F? What is the order of increasing electron affinities? What is the order of increasing electronegativities? What is the order of decreasing atomic radii? Explain these trends.

Problems

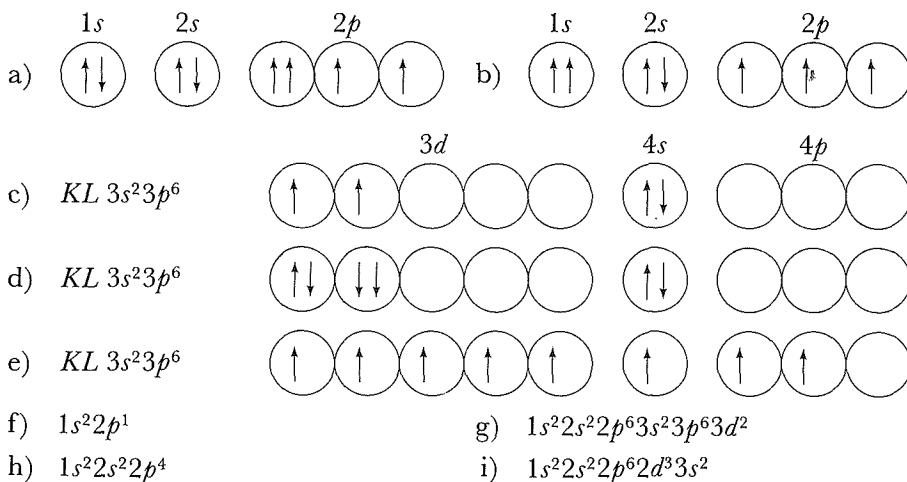
Orbital configurations

1. Write the orbital electronic structure of the ground states of (a) the calcium atom ($Z = 20$) and (b) the Mg²⁺ ion ($Z = 12$). show that you know Hund's rule: P ($Z = 15$); Na ($Z = 11$); As ($Z = 33$); C⁻ ($Z = 6$); O⁺ ($Z = 8$).
2. Write the orbital electronic structures for the ground states of the following atoms and ions and, where appropriate,
3. Determine the number of unpaired electrons in the ground states of the following atoms: C ($Z = 6$); F ($Z = 9$); Ne ($Z = 10$).

4. Write the ground-state electronic configurations of the following atoms or ions: (a) As; (b) Co^{2+} ; (c) Cu; (d) S^{2-} ; (e) Kr; (f) C; (g) W; (h) H^+ ; (i) H^- ; (j) Cl^- .
5. Write the ground-state electronic configurations of the two atoms ^{18}O and ^{16}O .
6. Several electronic configurations that may be correct for the nitrogen atom ($Z = 7$) are listed. For each configuration write one of the following words: *excited*, if the configuration represents a possible excited state of the nitrogen atom; *ground*, if the configuration represents the ground state of the nitrogen atom; *forbidden*, if the configuration in question cannot exist.



7. Which of the following configurations of electrons represent ground states, which represent excited states, and which are impossible? *Why* are the last unacceptable? What neutral atoms can have each permissible configuration?



8. Ten atoms and electronic configurations are listed. For each, decide whether a neutral atom, a positive ion (cation), or a negative ion (anion) is represented. In addition, specify whether the electronic state represented is a ground state, an excited state, or impossible.

- a) ${}_3\text{Li}$ $1s^2 2p^1$
- b) ${}_1\text{H}$ $1s^2$
- c) ${}_{16}\text{S}$ $1s^2 2s^2 2p^6 3s^2 3p^4$
- d) ${}_6\text{C}$ $1s^2 2s^2 2p^1 2d^1$
- e) ${}_{10}\text{Ne}$ $1s^2 2s^1 2p^7$
- f) ${}_7\text{N}$ $1s^2 2s^1 2p^3$
- g) ${}_9\text{F}$ $1s^2 2s^2 2p^5 3s^1$
- h) ${}_2\text{He}$ $1p^1$
- i) ${}_{21}\text{Sc}$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
- j) ${}_8\text{O}$ $1s^2 2s^2 2p^3$

9. Write ground-state electronic configurations for Li, Lu, La, and Lr and also for Li^+ , Lu^{3+} , La^{3+} , and Lr^{3+} .

Atomic numbers

10. If the order of orbital energy levels were in strict numerical order ($1s$, $2s$, $2p$, $3s$, $3p$, $3d$, $4s$, $4p$, $4d$, $4f$, $5s$, $5p$, and so on) and if the stable elements that we call noble gases occurred when the last electron of a given n value was added, what atomic numbers would the noble gases have? Compare them with the true atomic numbers.

11. Suppose you discovered some material from another universe whose atomic "electrons" obeyed the following restrictions on quantum numbers:

$$\begin{aligned} n &> 0 \\ l &= 0, 1, \dots, n-1 \\ m &= +1 \text{ or } -1 \\ s &= +\frac{1}{2} \end{aligned}$$

Assume that usual buildup rules still apply. What atomic numbers would the first two noble gases in that universe have?

Atomic properties

12. The ionization energies of polonium (Po) and astatine (At) are not given in Table 9-1 because these elements are not available in large quantities and no accurate IE measurements have been made. Using the information available in Table 9-1, estimate the values of IE for Po and At.

13. Write the electronic configuration ($1s^2 2s^2 \dots$) for the following: F^- , Na^+ , Ne , O^{2-} , and N^{3-} . What would you predict about the relative sizes of these species?

14. Which atom in each of the following pairs would you expect to have the larger electron affinity (EA): (a) Cu or Zn; (b) K or Ca; (c) S or Cl; (d) H or Li; (e) As or Ge?

15. The atoms of the yet-to-be-discovered "hypotransition" elements, starting at $Z = 121$, will have electrons in the $5g$ orbitals.

- a) How many elements will there be in the hypotransition metal series?
- b) Which electronic configurations in the series will have seven unpaired electrons?
- c) What is the maximum number of unpaired electrons an atom can have in the series? Will this be a new record for atoms in the periodic table?
- d) What is the IE of an electron in a $5g$ orbital of atomic hydrogen? Is this likely to be larger or smaller than the IE of a $5g$ electron in one of the hypotransition elements? Briefly explain your answer.
- e) In atomic hydrogen the $5s$, $5p$, $5d$, $5f$, and $5g$ orbitals all have the same energy. Will this be true for the hypotransition elements? If not, what will the energy order be? Explain briefly.

Electronegativity

16. Compute the electronegativity of a Cl atom. Assume $\chi_{\text{H}} = 2.20$ and take bond energies from Tables 12-2 and 12-4.
17. In Mulliken's first simple definition, the electronegativity of an element was proportional to the sum of its first ionization energy and its electron affinity. This relationship is not strictly true for the numerical values given in Table 9-1 because the ionization energies, electron affinities, and electronegativities in this table have been calculated by different people using different methods. Nevertheless, the proportionality is approximately valid. From the data in Table 9-1, plot a graph of the sum of ionization energy and electron affinity, against electronegativity, for the elements in the second and third periods of the table. (a) Draw the best straight line that you can through these data points and the origin. (b) Use this plot to estimate the electronegativity of Ne. If Ne—F bonds existed, would you expect them to be ionic or covalent? (c) Work backward from your plot to calculate the electron affinities of the fifth-period elements rubidium (Rb) through indium (In). Plot these values as a function of atomic number. In terms of electronic configurations of the atoms, explain the general trend of electron affinities across the transition metals in this period, and the striking behavior at Ag—Cd—In.
18. Calculate the electronegativity of H assuming the value 3.98 for χ_{F} . Bond energies are given in Tables 12-2 and 12-4. (The value you obtain will not agree exactly with that given in Table 9-1 because many χ differences [equation 9-1] were averaged to give the best values reported in the table.)

Suggested Reading

- H. B. Gray, *Chemical Bonds*, W. A. Benjamin, Menlo Park, Calif., 1973.
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R. T. Sanderson, *Chemical Periodicity*, Van Nostrand Reinhold, New York, 1960.
H. H. Sisler, *Electronic Structure, Properties and the Periodic Law*, Van Nostrand Reinhold, New York, 1963.