

- (ii) If two electrons do occupy the same orbital their spins must be different. A corollary to this is that there may be a maximum of only two electrons per orbital and these with opposed spins ($m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$). By way of examples an s sub-shell (one orbital) may hold up to two electrons, a p sub-shell (three orbitals) up to six electrons and a d sub-shell (five orbitals) up to ten electrons.

(b) The Aufbau process—Klechkowsky's rule

To determine the electronic configuration of the atom we usually look for that filling of the sub-shells which leads to the lowest energy of the system. This gives rise to the electronic ground state. Such a filling process is often called the *Aufbau* or *building up* process. Other configurations which are possible, but higher in energy, give rise to excited states. For the ground state, electrons fill the sub-shells in the order given by *Klechkowsky's rule*.

In many-electron atoms the sub-shells are filled in the order of increasing $(n + l)$. If two sub-shells have the same value of $n + l$ then the one with the smaller n is filled first. Thus we get the following filling sequence

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p \text{ etc}$$

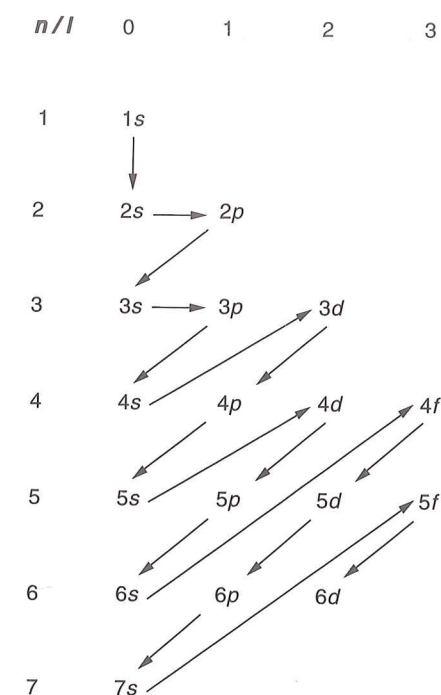
$n + l$	1	2	3	3	4	4	5	5
---------	---	---	---	---	---	---	---	---

For the first five sub-shells this order is the same as that presented earlier. $2p$ ($n + l = 3$) is filled before $3s$ ($n + l = 3$) because the principal quantum number of $2p$ is smaller. For the same reason $3p$ is filled before $4s$. The orbital filling pattern generated by Klechkowsky's rule is usually shown in the form of a chart (2-11) where the arrows indicate the order in which the sub-shells are filled. We can obtain in this way, with some exceptions which we will return to in Section 2.4.1, the electronic configurations of all the atoms. By way of example, the electronic configuration of sodium (Na, $Z = 11$) is: $1s^2 2s^2 2p^6 3s^1$, that of calcium (Ca, $Z = 20$) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, and that of titanium (Ti, $Z = 22$) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$.

2.3.5. Hund's rule

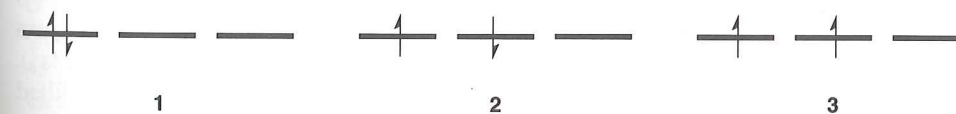
(a) Formulation

When several electrons need to be placed in a degenerate set of orbitals without their number being sufficient to completely fill them (i.e. two electrons in each), there can be several different ways of arranging them. For example in the carbon atom ($1s^2 2s^2 2p^2$) the two electrons in the $2p$ sub-shell may both occupy the same atomic orbital or be located in different ones. Hund's rule tells us which is the most stable arrangement of electrons for the lowest energy configuration. *When several electrons occupy degenerate AOs the most stable configuration is the one containing the largest number of parallel electron spins.*



2-11

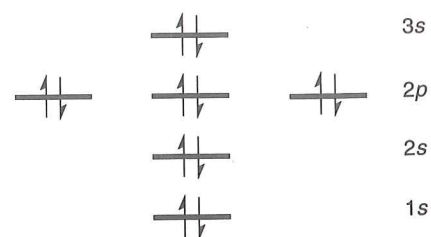
The three $2p$ orbitals of the carbon atom are equivalent, and three ways of arranging the electrons are shown in 2-12. In these diagrams the upward pointing arrow represents an electron with α spin and a downward pointing one an electron with β spin. Using Hund's rule it is the arrangement 3 which is predicted to have the lowest energy. It is relatively easy to understand why arrangement 1 is the least favored. Since the two electrons occupy the same orbital, they can come close to each other in space and experience a strong electrostatic repulsion. This energetically unfavorable interaction is reduced when the two electrons occupy different regions of space as is the case when they occupy different orbitals. Thus arrangements 2 and 3 are more stable than 1. The stabilization of configuration 3 over 2 however does not have a classical explanation at all, but one which only comes from quantum mechanics. A pair of electrons with parallel spins (i.e., the same value of m_s) are lowered in energy relative to the same arrangement with antiparallel spins by a purely quantum mechanical process called the *exchange interaction*.



2-12

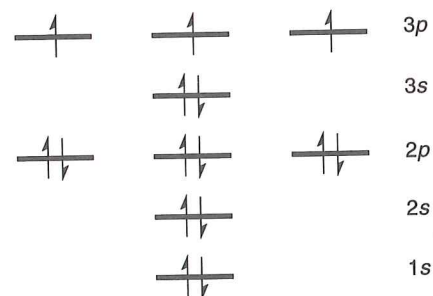
(b) Diamagnetism and paramagnetism

Let us consider the magnesium atom ($Z = 12$) with the ground state configuration $1s^2 2s^2 2p^6 3s^2$. We can represent its atomic structure by the scheme 2-13 in which

**2-13**

the orbitals are arranged in order of increasing energy. In the magnesium atom all of the electrons are paired. In other words each occupied orbital contains one electron with α and one with β spin. The spin magnetic moments of each of the electrons in such a pair cancel each other out so that overall the magnesium atom does not have an intrinsic spin magnetic moment. Systems with such a property are called *diamagnetic*.

The ground state configuration of phosphorus with 15 electrons may be written $1s^2 2s^2 2p^6 3s^2 3p^3$ (2-14). The three $3p$ electrons each occupy a different orbital with

**2-14**

identical spins to satisfy Hund's rule. These electrons are not paired, their spin magnetic moments do not cancel and the total magnetic moment for phosphorus is non-zero. This atom is thus *paramagnetic*.

2.3.6. Core and valence electrons

The electronic configuration of the atom assigns locations to all of its electrons but we will find it convenient to divide the electrons into two groups. The first are the *core electrons* which occupy deep-lying AOs and the second are the *valence electrons* which occupy the higher lying ones. Most often the valence electrons are regarded as all those in orbitals associated with the largest value of the principal quantum number. The remainder make up the core. Thus carbon ($1s^2 2s^2 2p^2$) has two core electrons ($1s^2$) and four valence electrons ($2s^2 2p^2$). Similarly magnesium ($1s^2 2s^2 2p^6 3s^2$) has ten core electrons ($1s^2 2s^2 2p^6$) and two valence electrons ($3s^2$). There is one difficulty with this nomenclature for the elements with a partially filled d sub-shell. (The transition elements are discussed in Section 2.4.1.) In effect since the nd and $(n+1)s$ orbitals are close in energy all of the electrons occupying them are considered to be valence electrons. Thus titanium ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$) contains four valence electrons ($4s^2 3d^2$) not two. This distinction between core and valence electrons is an important one, since it is the valence electrons (those in the outermost shell) which determine the chemical properties of the elements.

As a shorthand notation we often replace the set of core electrons by the chemical symbol of the noble gas which contains this number of electrons when writing down the electronic configuration. So the electronic configuration for phosphorus ($1s^2 2s^2 2p^6 3s^2 3p^3$) may be written more compactly as $\{\text{Ne}\} 3s^2 3p^3$. The part of the electronic configuration actually written out in such an expression is then the *valence configuration* of the atom ($3s^2 3p^3$ for phosphorus).

2.4. The periodic classification of the elements**2.4.1. Organization by rows**

The periodic classification of the elements is shown in Figure 2.3. The labels used to describe the columns (1–18) are those recommended by IUPAC at the end of the 1980s. The way the table is assembled follows directly through the filling of the sub-shells and shells of atomic orbitals using Klechkowsky's scheme described earlier. Each period begins by the filling of an ns sub-shell and is completed by the filling of an np sub-shell, except of course for $n=1$ where there is no p sub-shell. The principal quantum number n increases by one on moving from the end of one period to the beginning of the next.

The first period only contains two elements since it corresponds to the filling of the first shell which only contains a single s orbital ($1s^1$ for H and $1s^2$ for He).

The second period begins with the filling of the $2s$ orbital and continues with the filling of the three $2p$ orbitals. Eight elements result from lithium (Li) with the valence configuration $2s^1$ to neon (Ne) with the configuration $2s^2 2p^6$.

The situation is identical for the third period in that the $3s$ orbital (Na: $3s^1$; Mg: $3s^2$) and then the $3p$ orbitals (from Al: $3s^2 3p^1$ to Ar: $3s^2 3p^6$) are successively filled. An important point to note, and one we will return to, is that the $3d$ orbitals, with the same value of the principal quantum number as the $3s$ and $3p$ orbitals are not filled in this period. Klechkowsky's rule (Section 2.3.4b) prevents their filling until after that of the $4s$ orbital.

The fourth period begins with the filling of the $4s$ sub-shell (K: $4s^1$; Ca: $4s^2$) and ends with the filling of the $4p$ sub-shell (Ga: $4s^2 4p^1$ to Kr: $4s^2 4p^6$). Between these two groups lies a *transitional series*, so named because one set of orbitals, of principal quantum number n , are filled after one of the orbitals of principal quantum number $n+1$ is filled. The collection of elements here are known as the *first transition metal series*, which correspond to the progressive occupation of the $3d$ orbitals. This series contains ten elements since there are a total of five $3d$ orbitals which can hold two electrons each. Therefore the valence electronic configuration of scandium (Sc) is $4s^2 3d^1$ and that of zinc (Zn) $4s^2 3d^{10}$. In total the fourth period contains eighteen elements ($2 + 10 + 6$). We must note, however, two exceptions to Klechkowsky's rule among this transition metal series. The lowest energy configuration for chromium (Cr) is $4s^1 3d^5$, the expected arrangement ($4s^2 3d^4$) being less stable. In the same way the lowest energy configuration of copper (Cu) is $4s^1 3d^{10}$ and not $4s^2 3d^9$. In order to understand these exceptions we must first recognize that the $4s$ and $3d$ orbitals are close in energy for these elements, so that the promotion energy $4s \rightarrow 3d$ is very small. Thus the energies of the configurations, obtained by summing just the orbital

1	2											13	14	15	16	17	18																														
1	H 1s ¹																2	He 1s ²																													
3	Li 1s ² 2s ¹	4	Be 1s ² 2s ²														9	Ne 1s ² 2s ² 2p ⁶																													
5	Na (Ne)3s ¹	6	Mg (Ne)3s ²														16	Ar (Ne)3s ² 3p ⁶																													
7	K (Ar)4s ¹	8	Ca (Ar)4s ²														33	Kr (Ar)3d ¹⁰ 4s ² 4p ⁶																													
9	Rb (Kr)5s ¹	10	Sr (Kr)5s ²														54	Xe (Kr)4d ¹⁰ 5s ² 5p ⁶																													
11	Cs (Xe)6s ¹	12	Ba (Xe)6s ²														86	Rn (Xe)5f ¹⁴ 6s ² 6p ⁶																													
13	Fr (Rn)7s ¹	14	Ra (Rn)7s ²											5	B 1s ² 2s ² 2p ¹	6	C 1s ² 2s ² 2p ²	7	N 1s ² 2s ² 2p ³	8	O 1s ² 2s ² 2p ⁴	9	F 1s ² 2s ² 2p ⁵	10	Ne 1s ² 2s ² 2p ⁶																						
				21	Sc (Ar)3d ¹ 4s ²	22	Ti (Ar)3d ² 4s ²	23	V (Ar)3d ³ 4s ²	24	Cr (Ar)3d ⁵ 4s ¹	25	Mn (Ar)3d ⁵ 4s ²	26	Fe (Ar)3d ⁶ 4s ²	27	Co (Ar)3d ⁷ 4s ²	28	Ni (Ar)3d ⁸ 4s ²	29	Cu (Ar)3d ¹⁰ 4s ¹	30	Zn (Ar)3d ¹⁰ 4s ²	31	Ga (Ar)3d ¹⁰ 4s ² 4p ¹	32	Ge (Ar)3d ¹⁰ 4s ² 4p ²	33	As (Ar)3d ¹⁰ 4s ² 4p ³	34	Se (Ar)3d ¹⁰ 4s ² 4p ⁴	35	Br (Ar)3d ¹⁰ 4s ² 4p ⁵	36	Kr (Ar)3d ¹⁰ 4s ² 4p ⁶												
				37	Rb (Kr)5s ¹	38	Sr (Kr)5s ²	39	Y (Kr)4d ¹ 5s ²	40	Zr (Kr)4d ² 5s ²	41	Nb (Kr)4d ⁴ 5s ¹	42	Mo (Kr)4d ⁵ 5s ¹	43	Tc (Kr)4d ⁵ 5s ²	44	Ru (Kr)4d ⁷ 5s ¹	45	Rh (Kr)4d ⁸ 5s ¹	46	Pd (Kr)4d ¹⁰ 5s ⁰	47	Ag (Kr)4d ¹⁰ 5s ¹	48	Cd (Kr)4d ¹⁰ 5s ²	49	In (Kr)4d ¹⁰ 5s ² 5p ¹	50	Sn (Kr)4d ¹⁰ 5s ² 5p ²	51	Sb (Kr)4d ¹⁰ 5s ² 5p ³	52	Te (Kr)4d ¹⁰ 5s ² 5p ⁴	53	I (Kr)4d ¹⁰ 5s ² 5p ⁵	54	Xe (Kr)4d ¹⁰ 5s ² 5p ⁶								
				55	Cs (Xe)6s ¹	56	Ba (Xe)6s ²	57	La (Xe)5d ¹ 6s ²	58	Ce (Xe)4f ¹ 5d ¹ 6s ²	59	Pr (Xe)4f ³ 6s ²	60	Nd (Xe)4f ⁴ 6s ²	61	Pm (Xe)4f ⁵ 6s ²	62	Sm (Xe)4f ⁶ 6s ²	63	Eu (Xe)4f ⁷ 6s ²	64	Gd (Xe)4f ⁷ 5d ¹ 6s ²	65	Tb (Xe)4f ⁹ 6s ²	66	Dy (Xe)4f ¹⁰ 6s ²	67	Ho (Xe)4f ¹¹ 6s ²	68	Er (Xe)4f ¹² 6s ²	69	Tm (Xe)4f ¹³ 6s ²	70	Yb (Xe)4f ¹⁴ 6s ²	71	Lu (Xe)4f ¹⁴ 5d ¹ 6s ²										
				87	Fr (Rn)7s ¹	88	Ra (Rn)7s ²											81	Tl (Xe)5f ¹⁴ 6s ² 6p ¹	82	Pb (Xe)5f ¹⁴ 6s ² 6p ²	83	Bi (Xe)5f ¹⁴ 6s ² 6p ³	84	Po (Xe)5f ¹⁴ 6s ² 6p ⁴	85	At (Xe)5f ¹⁴ 6s ² 6p ⁵	86	Rn (Xe)5f ¹⁴ 6s ² 6p ⁶																		
								LANTHANIDE SERIES										89	Th (Rn)5f ¹ 6d ² 7s ²	90	Pa (Rn)5f ² 6d ¹ 7s ²	91	U (Rn)5f ³ 6d ¹ 7s ²	92	Np (Rn)5f ⁴ 6d ¹ 7s ²	93	Pu (Rn)5f ⁶ 6d ¹ 7s ²	94	Am (Rn)5f ⁷ 6d ¹ 7s ²	95	Cm (Rn)5f ⁷ 6d ¹ 7s ²	96	Bk (Rn)5f ⁹ 6d ¹ 7s ²	97	Cf (Rn)5f ¹⁰ 6d ¹ 7s ²	98	Es (Rn)5f ¹¹ 6d ¹ 7s ²	99	Fm (Rn)5f ¹¹ 6d ¹ 7s ²	100	Md (Rn)5f ¹² 6d ¹ 7s ²	101	No (Rn)5f ¹² 6d ¹ 7s ²	102	Lr (Rn)5f ¹³ 6d ¹ 7s ²		
								ACTINIDE SERIES										103	La (Xe)5d ¹ 6s ²	104	Ce (Xe)4f ¹ 5d ¹ 6s ²	105	Pr (Xe)4f ³ 6s ²	106	Nd (Xe)4f ⁴ 6s ²	107	Pm (Xe)4f ⁵ 6s ²	108	Sm (Xe)4f ⁶ 6s ²	109	Eu (Xe)4f ⁷ 6s ²	110	Gd (Xe)4f ⁷ 5d ¹ 6s ²	111	Tb (Xe)4f ⁹ 6s ²	112	Dy (Xe)4f ¹⁰ 6s ²	113	Ho (Xe)4f ¹¹ 6s ²	114	Er (Xe)4f ¹² 6s ²	115	Tm (Xe)4f ¹³ 6s ²	116	Yb (Xe)4f ¹⁴ 6s ²	117	Lu (Xe)4f ¹⁴ 5d ¹ 6s ²

Figure 2.3. The Periodic Table. The electronic configuration is given for each element.

energies, $4s^1 3d^5$ and $4s^2 3d^4$ for chromium, and $4s^1 3d^{10}$ and $4s^2 3d^9$ for copper, are very close. The inversion observed for chromium comes about because of the particular stability of the half-filled shell of electrons whose spins are parallel, another manifestation of Hund's rule. The exchange energy which results (see Section 2.3.5a) is sufficient to compensate for the $4s \rightarrow 3d$ promotion energy. A similar effect is responsible for the completion of the filled sub-shell in the case of copper leading to the $4s^1 3d^{10}$ configuration lying lowest in energy.

The structure of the fifth period is identical to that of the fourth. It begins with the filling of the $4s$ sub-shell (Rb, Sr) and ends with that of the $5p$ sub-shell (from In to Xe). Between these two sets of elements lie the ten elements corresponding to the successive filling of the $4d$ sub-shell, giving rise to the *second transition metal series*. The exceptions to Klechkowsky's rule are numerous in this series, namely Nb ($5s^1 4d^4$), Mo ($5s^1 4d^5$), Ru ($5s^1, 4d^7$), Rh ($5s^1 4d^8$), Pd ($5s^0 4d^{10}$) and finally Ag ($5s^1 4d^{10}$). Here the $5s$ and $4d$ levels are very close in energy. Although it is the case that the energetics controlling these observations are indeed a balance between those of the one-electron AO energies and the energies of the electron-electron interactions (the exchange energy for example) it is difficult to give a simple explanation of the origin of all of these inversions.

The sixth period encompasses two transitional series, the *third transition metal series* and the set of elements called the *lanthanides*. The filling of the $6s$ sub-shell (Cs and Ba) is followed by that of the $4f$ sub-shell (leading to the lanthanides) in turn followed by that of the $5d$ sub-shell (leading to the third transition metal series), before the $6p$ sub-shell (from Tl to Rn) is filled to complete the period. The situation is complicated by the fact that the two transitional series overlap in the sense that for lanthanum an electron occupies a $5d$ orbital ($6s^2 5d^1$) but in the following series of fourteen elements, it is the group of seven $4f$ orbitals which are being filled. Following this set of elements the filling of the $5d$ orbitals continues with the nine elements from hafnium (Hf) to mercury (Hg). In this period which contains 32 elements there are four exceptions to Klechkowsky's rule; La ($6s^2 5d^1 4f^0$), Gd ($6s^2 5d^1 4f^7$), Pt ($6s^1 5d^9 4f^{14}$) and Au ($6s^1 5d^{10} 4f^{14}$).

Finally the seventh and last period is not complete since not all of the possible elements are actually known in practice. In this period where the $7s$, $6d$ and $5f$ orbitals (filling of the last giving rise to the actinides) are close in energy, exceptions to Klechkowsky's rule are frequent.

2.4.2. Organization by column: chemical families

The structure of the periodic classification clearly shows how elements with the same valence electron configuration fall neatly into columns. (Some exceptions are found for elements in the transitional series.) Since the valence electrons are responsible for the chemical properties of the elements we can understand why they are often so similar for the elements from the same column. Such a group is often called a *chemical family*. Examples from Figure 2.3 include the alkali metals, the halogens and the noble gases.

- (i) The last column (18) contains the set of elements whose valence configuration is of the form $ns^2 np^6$ (except for helium where it is $1s^2$). This family is called

the inert, rare or noble gases (He, Ne, Ar, Kr, Xe). The fact that the ns and np sub-shells are completely filled confers a special stability on these elements. They are monatomic gases under ambient conditions and are almost completely chemically inert.

- (ii) The penultimate column (17) contains the halogens with valence electron configurations ns^2np^5 (F, Cl, Br, I). The elements are stable as the dimers F_2 , Cl_2 , Br_2 , I_2 . They form simple compounds with hydrogen, the hydrogen halides HF, HCl, HBr, and HI which all have acidic properties in aqueous solution. On the other hand they can readily capture an electron to give the anions F^- , Cl^- , Br^- and I^- , which are isoelectronic with the adjacent noble gas which follows them in the periodic classification. So, for example, Cl^- is isoelectronic with Ar, both having the configuration $3s^23p^6$. Such ions, by analogy with the noble gases have a special electronic stability.
- (iii) The first column (1) of the periodic table contains the alkali metals, Li, Na, K, Rb, and Cs, with the configuration ns^1 . (As we indicated in Chapter 1, hydrogen is not considered an alkali metal since its behavior is often different from that of the other elements of the group.) The alkali metals form water-soluble salts with the halogens, NaCl and KBr for example. The outermost electron of the atom may readily be removed which leads to the generation of a cation, isoelectronic with the adjacent noble gas which precedes it in the periodic classification. Thus K^+ is isoelectronic with Ar, $\{Ne\}3s^23p^6$.

We can put together these last two results to understand the formation of NaCl. For the alkali metals there is a tendency to readily lose an electron, and for the halogens a tendency to accept an electron. Such an ionic salt, written Na^+Cl^- , comes about via electron transfer from alkali to halogen.

2.5. Electronic parameters of many-electron atoms

Starting off from the ground electronic configuration of an atom it is possible to develop several concepts which will be useful in the rest of the book. For this we have to introduce further approximations.

2.5.1. Screening

In many-electron atoms the electrons occupy different AOs which, just as in the one-electron atom, have a radius which increases with the value of the principal quantum number (see Section 2.2.2e). The deepest lying AOs are thus the most contracted or, alternatively, the electron density associated with them lies closest to the nucleus. The higher-lying AOs are contrarily more diffuse. The outer electrons which occupy the higher-energy orbitals not only lie further from the nucleus than the electrons in deep-lying orbitals but see a lower effective nuclear charge since these deep-lying electrons are of the opposite charge to the nucleus. Thus the inner shells of electrons tend to 'screen' the nucleus from the outermost electrons. Effectively the outer electrons 'see' a smaller *effective nuclear charge* Z^* , related to the real charge

Z by the screening constant σ . This parameter σ represents the mean effect exercised by the inner electrons. Thus we may write

$$Z^* = Z - \sigma \quad (40)$$

The constant, σ , depends strongly on the orbital occupied by the electron under consideration. Obviously the $1s$ electron cannot be screened by the electrons in the $2s$ or $2p$ orbitals since it lies closer to the nucleus. On the contrary an electron occupying a $3s$ orbital will be strongly screened by the internal electrons occupying the $1s$, $2s$ and $2p$ orbitals.

2.5.2. The effective charge: Slater's rules

Slater proposed an empirical method for the calculation of the screening constants. It consists first of sorting the AOs into different groups.

$$1s/2s, 2p/3s, 3p/3d/4s, 4p/4d/4f/5s, 5p/etc \dots$$

The value of σ associated with an electron occupying a given AO is determined by the screening contribution by the other electrons occupying orbitals in the same group (weak screening) and by the electrons occupying orbitals in lower groups. The latter are closer to the nucleus and thus exercise a stronger screening. In practice σ is calculated by adding up the different contributions (σ_i) using the following rules.

- (i) For an electron in a $1s$ orbital the screening from another $1s$ electron is equal to 0.30.
- (ii) For an electron occupying an ns or np orbital the screening resulting from an electron in an orbital with principal quantum number n' is

$$\begin{array}{lll} \sigma_i = 1 & \text{if } n' < n - 1 & \text{complete screening} \\ \sigma_i = 0.85 & \text{if } n' = n - 1 & \text{strong screening} \\ \sigma_i = 0.35 & \text{if } n' = n & \text{weak screening} \\ \sigma_i = 0 & \text{if } n' > n & \text{no screening} \end{array}$$

- (iii) For an electron in an nd or nf orbital the screening constant is 0.35 for an electron in the same group and 1 for all the others.

The rules are summarized in Table 2.1. As an example consider the phosphorus atom ($1s^22s^22p^63s^23p^3$). According to the grouping scheme proposed by Slater there are three groups of electrons to consider; two $1s$ electrons, eight electrons in $2s$ and $2p$ and five electrons in $3s$ and $3p$. Each group has a different screening constant.

- (i) A $1s$ electron is screened by one other

$$\sigma_{1s} = 1 \times 0.30 = 0.30$$

Table 2.1: Slater's rules for the calculation of the screening constant.

	$n' < n - 1$	$n' = n - 1$	$n' = n$	$n' > n$
1s	—	—	0.30	0
ns, np	1	0.85	0.35	0
nd, nf	1	1	0.35	0

- (ii) A 2s or 2p electron is screened by two 1s electrons and by seven other 2s or 2p electrons

$$\sigma_{2s,2p} = (2 \times 0.85) + (7 \times 0.35) = 4.15$$

- (iii) A 3s or 3p electron is screened by two 1s electrons, eight 2s or 2p electrons and by four 3s or 3p electrons.

$$\sigma_{3s,3p} = (2 \times 1) + (8 \times 0.85) + (4 \times 0.35) = 10.2$$

Thus the effective charges felt by the different electrons are

$$Z_{1s}^* = 15 - 0.3 = 14.7$$

$$Z_{2s,2p}^* = 15 - 4.15 = 10.85$$

$$Z_{3s,3p}^* = 15 - 10.2 = 4.8$$

These values fall between $Z^* = 15$ (no screening) and $Z^* = 1$ (complete screening). They vary considerably depending upon the orbital under consideration. In particular we note that *the effective charge felt by the valence electrons is much smaller than that felt by the core electrons.*

2.5.3. Orbital radii and atomic size

For the hydrogen-like atoms we noted earlier that the radius of an orbital, defined as the point where a maximum is found in the radial probability density, was given approximately by $n^2 a_0 / Z$. An approximate value (see exercise 2.8) for the radius (ρ) of an AO in a many-electron atom is given by

$$\rho = n^2 a_0 / Z^* \quad (41)$$

Thus the radius depends both on the effective charge Z^* and the principal quantum number associated with the AO. The orbital is most contracted (i.e., ρ is smallest) when Z^* is large and n small. Since as n increases, Z^* decreases, the inner orbitals

are expected to be much more contracted than the outer ones. So for phosphorus

$$\rho_{1s} = 3.6 \text{ pm}, \rho_{2s} = \rho_{2p} = 19.6 \text{ pm}, \rho_{3s} = \rho_{3p} = 99.5 \text{ pm}$$

This example underscores the general result that *in an atom the radii of the valence orbitals are much larger than those of the core orbitals.*

The valence electrons are therefore the electrons which are furthest from the nucleus and those which experience the weakest effective nuclear charge. They are then the electrons which are the most weakly bound to the nucleus since the electrostatic energy between the two is roughly proportional to $(-Z^*/\rho)$. This simple result allows us to readily understand how the valence electrons are the ones which are most sensitive to outside perturbations, such as the approach of another atom, and are therefore primarily responsible for the chemical properties of the elements. We finally note that the radius of the valence orbitals give an estimate of the 'size' of an atom, since it represents the most probable distance from the nucleus of the outermost electrons. This parameter is called the atomic radius. In the case of phosphorus the atomic radius is about 100 pm.

2.6. Evolution of atomic properties

It is useful to study the way certain properties of the atoms depend upon the row and column of the periodic table. In what follows we will consider the elements of the first five rows with the exception of the transition metal series which we will not discuss in this book.

2.6.1. Atomic orbital parameters

(a) Effective charge

Use of Slater's rules (Section 2.5.2) allows the computation of the effective nuclear charge seen by the valence electrons for the elements of the table. These are shown in Table 2.2 and will be considered in order of increasing Z . On moving from the left to the right along a given row of the table the ns and np orbitals are progressively filled. On moving from one element to the next, the actual nuclear charge increases by unity. This is only partially compensated by the increase (of 0.35) in the screening constant. As a result, for a given row of the periodic table the effective charge Z^* seen by a valence electron increases with Z . For example, Z^* increases from 1.30 (Li) to 5.85 (Ne) for the second row and from 2.20 (Na) to 6.75 (Ar) in the third. An important characteristic is the abrupt discontinuity observed on moving from one row to the next, as a result of the increase (by unity) in the value of the principal quantum number, n . So Z^* , equal to 5.85 for neon, drops sharply to only 2.2 for sodium. In this case the change in the screening is much larger than the variation in Z which is always equal to one. All of the other electrons in sodium lie in earlier groups than the single valence electron and thus are highly effective in screening. (σ_i is 1 for the 1s electrons and 0.85 for the 2s and 2p electrons.) In neon the outermost electron is one of a group which screen it much less effectively. The result is a sudden

Table 2.2: Effective charge (Z^*) felt by the valence electrons for the elements of the first five rows.

1	H 1.0						He 1.70	
2	Li 1.30	Be 1.95	B 2.60	C 3.25	N 3.90	O 4.55	F 5.20	Ne 5.85
3	Na 2.20	Mg 2.85	Al 3.50	Si 4.15	P 4.80	S 5.45	Cl 6.10	Ar 6.75
4	K 2.20	Ca 2.85	Ga 5.00	Ge 5.65	As 6.30	Se 6.95	Br 7.60	Kr 8.25
5	Rb 2.20	Sr 2.85	In 5.00	Sn 5.65	Sb 6.30	Te 6.95	I 7.60	Xe 8.25

jump in screening on moving from neon (4.15) to sodium (8.8). Thus the effective charge felt by the valence electrons drops abruptly on moving from one row to the next in the periodic table.

(b) Atomic radius

Recall that the atomic radius is equal to the distance from the nucleus where there is a maximum in the radial probability density associated with the outermost electrons. It is given (equation (41)) in terms of n and Z^* as

$$\rho = n^2 a_0 / Z^* \text{ where } a_0 = 52.9 \text{ pm}$$

There are once again two important characteristics to note when examining the variation in ρ as a function of Z (Table 2.3). On moving from the left to the right of the periodic table along a given row although n is constant Z^* increases (Table 2.2) resulting in a diminution of ρ . These variations can be considerable. Using this measure of size an atom of neon is five times 'smaller' than one of lithium.

On moving from one row to another a sharp discontinuity appears; the atomic radius increases by a factor of six for example between neon ($Z = 10$) and sodium ($Z = 11$). Both the increase in the value of the principal quantum number (from 2 to 3) and the decrease in Z^* (from 5.85 to 2.2) contribute to this effect. Thus the atomic size decreases on moving from left to right across a row of the periodic table (e.g., Li to Ne) and the atomic radius increases abruptly on moving from the end of one row of the periodic table to the beginning of the next.

We finally note that the atomic radius gives information too about the atomic polarizability, a measure of the deformation experienced by the electron cloud when under the influence of an external electric field. When the atomic radius is large, the

Table 2.3: Atomic radii (in pm) calculated using equation (41).

H 53							He 31
Li 163	Be 109	B 82	C 65	N 55	O 47	F 41	Ne 36
Na 217	Mg 168	Al 137	Si 115	P 100	S 88	Cl 78	Ar 71
K 332	Ca 256	Ga 146	Ge 129	As 116	Se 105	Br 96	Kr 88
Rb 386	Sr 300	In 171	Sn 151	Sb 135	Te 122	I 112	Xe 103

peripheral electron density interacts relatively weakly with the nucleus and is easily distorted under these conditions. Atoms with smaller radii, containing more tightly bound electrons are less susceptible to deformation. Simple arguments suggest that the polarizability increases as ρ^3 . From Table 2.3 the most polarizable atom is therefore rubidium (Rb) and the least is helium.

(c) Orbital energies

On moving from one atom to another the energy associated with a given orbital changes. From a purely qualitative point of view we can give two factors which contribute to this effect, namely the variation in the radius of the orbital under consideration and the effective charge seen by the electron in it. The energy of the orbital is lowered when the interaction between the nucleus and electron is strong, that is to say the effective charge is large and the orbital radius small. In Table 2.4 are listed the orbital energies given by Slater* for the occupied valence orbitals of the elements of the first four rows of the periodic table. (Parenthetically we note that although the ns and np orbitals are characterized by the same values of Z^* and therefore have the same orbital radii, their energies are different ($\epsilon_{2s} < \epsilon_{2p}$) and often significantly. This shows that the energy of an orbital doesn't only depend upon the parameters n and Z^* of our simple theory but on the quantum number l too). On moving from left to right across a row of the table, the energy of a given orbital drops considerably. For example the $2s$ orbital drops from -5.4 eV for lithium to -19.4 eV for carbon and then to -48.4 eV for neon. In the same way the $3p$ orbital drops in energy from -6.0 eV for aluminum to -15.8 eV for argon. This stabilization is easy to understand. The effective charge seen by the electron increases (see Table 2.2) and the radius of the orbital correspondingly decreases (see Table 2.3). Both

* J. C. Slater, *Quantum Theory of Atomic Structure*, Vol 1, McGraw-Hill (1960), p. 206.

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2.4

Table 2.4: Valence orbital energies expressed in eV.

	H							He
1s	-13.6							-24.6
	Li	Be	B	C	N	O	F	Ne
2s	-5.4	-9.4	-14.7	-19.4	-25.6	-32.4	-40.1	-48.4
2p	—	—	-5.7	-10.7	-12.9	-15.9	-18.6	-21.6
	Na	Mg	Al	Si	P	S	Cl	Ar
3s	-5.2	-7.6	-11.3	-15.0	-18.4	-20.9	-25.3	-29.2
3p	—	—	-6.0	-7.8	-9.8	-11.7	-13.7	-15.8
	K	Ca	Ga	Ge	As	Se	Br	Kr
4s	-4.4	-6.1	-12.6	-15.6	-17.7	-20.9	-24.5	-27.2
4p	—	—	-6.0	-7.5	-9.2	-10.9	-12.6	-14.0

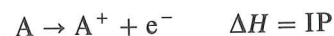
of these related effects contribute to the lowering of the energy of the orbital. Exactly the same relationship in terms of the changes in effective charge and radius lead to the abrupt change in the energies of orbitals of the same type (l quantum number) on moving from one row to the next. So the energy of the 2s orbital in neon lies at -48.4 eV but the 3s orbital of sodium at only -5.2 eV.

The energetic changes associated with the valence orbitals of the elements within a column are more difficult to understand. On descending a column the effective charge increases at first and then remains constant (Table 2.2) but the orbital radius continues to increase from top to bottom (Table 2.3). These two effects tend to work in opposite directions when it comes to determining the orbital energy. In general the increase in radius is the dominant factor, i.e., the valence energy levels drop in energy on moving from the bottom to the top of a column. In general, the energies of the valence s and p orbitals drop on moving from the left to the right along a row of the periodic table and on moving from the bottom to the top of a column.

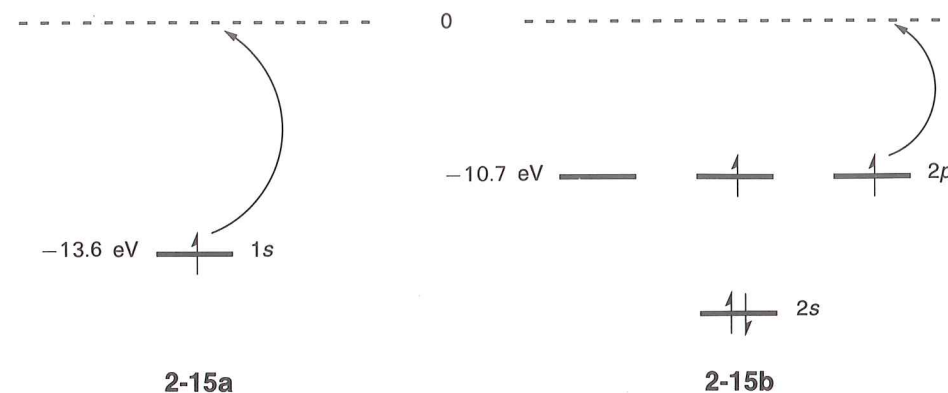
2.6.2. Relationship with measurable properties

(a) Ionization potential

The *ionization potential* (IP) of an atom is the smallest amount of energy needed to remove an electron.



It corresponds therefore to the loss of an electron from the outermost sub-shell. (We will note later the exceptions provided by the transition metals.) It is clear to see that there is a direct correspondence between the IP and the energy of the orbital occupied by the ejected electron. Turning first of all to the simplest case of the



hydrogen atom which has only a single electron (2-15a), its IP is 13.6 eV, i.e., exactly the energy of the 1s orbital with a change of sign. In many-electron atoms the situation is more complex (of course) and the IP depends upon two factors.

- The energy of the orbital which contains the electron to be ejected. If this were the only factor then the IP would be equal to the orbital energy with a change in sign. This result is referred to as *Koopman's theorem*.
- The reorganization energy associated with the cation which is formed. This is a new factor, absent in the hydrogen atom case since the cation is but a proton. The reorganization of the remaining charge density around the nucleus in the cation comes in part from a reduction in the screening constant as the result of the loss of an electron and from a change in the interactions between the electrons.

Invariably the second factor has a relatively small proportional effect on the IP. For example, carbon has an IP of 11.3 eV, not widely different from that expected by consideration of the orbital energy alone (Table 2.4) of 10.7 eV (2-15b). Generally the orbital energy of the outermost electron gives quite a good approximation of the ionization potential.

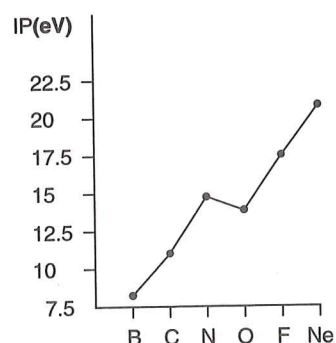
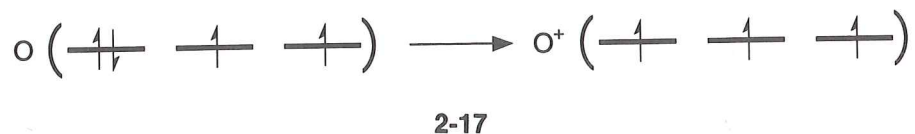
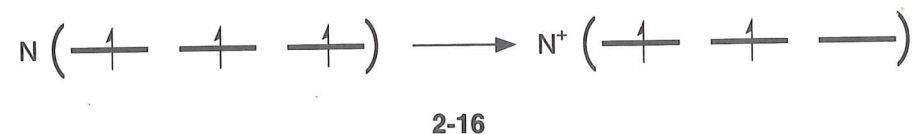
The ionization potentials of the elements of the first five rows of the periodic table are given in Table 2.5. One can compare these experimental values with those for the orbital energies of Table 2.4. The general trends found for the IPs mimic those observed for the orbital energies. The IP increases on moving from the left to the right along a row of the periodic table and on moving from the bottom to the top. The atoms with the smallest IPs are the alkali metal family of the first column. From Table 2.5 the IP is largest for helium (24.6 eV) and smallest for rubidium (4.2 eV).

However, we must note two exceptions to these trends. The first concerns the drop (rather than an increase) in the IP which occurs on moving from column 2 to column 13. This is simple to understand, there is a change in the nature of the orbital holding the outermost electron, from s to p . The IP drops since $\epsilon_{2s}(\text{Be}) < \epsilon_{2p}(\text{B})$. The second exception is an interesting one, since it vividly demonstrates the importance of electron-electron interactions. This is the drop in IP on moving from column 15 to 16. For nitrogen and oxygen this corresponds to a drop from 14.5 eV (for nitrogen) to 13.6 eV (for oxygen). This trend is opposite to that expected on the basis (Table 2.4)

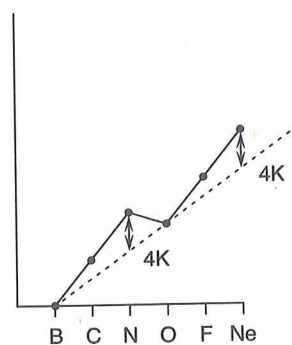
Table 2.5: Ionization potentials expressed in eV.

1							18
H							He
13.6	2	13	14	15	16	17	24.6
Li	Be	B	C	N	O	F	Ne
5.4	9.3	8.3	11.3	14.5	13.6	17.4	21.6
Na	Mg	Al	Si	P	S	Cl	Ar
5.1	7.6	6.0	8.2	10.5	10.4	13.0	15.8
K	Ca	Ga	Ge	As	Se	Br	Kr
4.3	6.1	6.0	7.9	9.8	9.8	11.8	14.0
Rb	Sr	In	Sn	Sb	Te	I	Xe
4.2	5.7	5.8	7.3	8.6	9.0	10.5	12.1

of the orbital energies; -15.9 eV ($\epsilon_{2p}(\text{O})$) and -12.9 eV ($\epsilon_{2p}(\text{N})$). 2-16 and 2-17 show pictorially the ionization processes for the two atoms. 2-18a shows the trends in the ionization potentials for the second-row atoms. The valence orbital energies of Table 2.4 increase smoothly across the series.



2-18a



2-18b

Table 2.6: Exchange energy for the p^1 - p^6 configurations

	Exchange energy		
	neutral (or anion)	cation (or neutral)	Δ
B	0K	0K	0
C (B^-)	2K	0K	2K
N (C^-)	6K	2K	4K
O (N^-)	6K	6K	0
F (O^-)	8K	6K	2K
Ne (F^-)	12K	8K	4K

The obvious difference between the two is that in the case of oxygen the single electron with down spin is ionized but for nitrogen, one of three electrons with the same spin is removed. So for nitrogen, on ionization there is a loss of exchange energy while for oxygen there is no such loss. We may use a very simple model to put this idea on a semiquantitative basis. Table 2.6 shows the exchange energy for each of the neutral atoms with p^n valence configurations and their corresponding cations. These are obtained in the following way. We associate an energy of 2K with each pair of electrons with the same spin relative to the pair of electrons with spins paired. So for the p^1 configuration where there are no pairs of electrons the exchange energy is zero. For p^2 there is just one pair (exchange energy = 2K). For p^3 there are now three pairs of electrons with the same spin (total exchange energy = 6K). For p^4 - p^6 the pattern repeats itself for the electrons of down spin. In the last column of Table 2.6 is the difference (Δ) in exchange energy between neutral atom and cation, obtained by simple subtraction. 2-18b shows then how we might envisage the variation in IP as the $2p$ sub-shell is filled. First there is a sloping background (dashed line) which accommodates the changes in Z^* with electron configuration. Superimposed is the change in exchange energy from Table 2.6 to give the total ionization energy expected (solid line). Notice the resemblance of this plot to the actual saw-tooth behavior of the experimentally determined IPs of 2-18a. The values of the AO energies of Table 2.4 average out these two effects. A similar saw-tooth plot is obtained if we take into account the coulombic repulsion arising from pairs of electrons in the same orbital, rather than the exchange energy. Both effects are of course important, and highlight the influence of electron-electron interactions on the ionization potential variation.

One can equally well eject electrons other than the outermost one. The energy change involved (ionization energy) is directly correlated with how deep lying is the orbital concerned. For example the three different ionization energies for oxygen are

$$1s \text{ electron } E = 543.1 \text{ eV}$$

$$2s \text{ electron } E = 41.6 \text{ eV}$$

$$2p \text{ electron } E = 13.6 \text{ eV (IP)}$$