2 Bonding and Structure

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   Atomic radii, bond angles, and the valence electrons of the atoms or ions constituting compounds govern the bonding, structure, reactions, and physical properties of the compounds. It is desirable that the chemical properties of known and new compounds can be explained and predicted using universal parameters characteristic of the constituent elements. Inorganic chemistry has developed along with the discovery of new compounds and novel bonding modes. Therefore, it is important to understand the bonding modes, the geometrical and electronic factors governing the bonding, and to learn the basic concepts of molecular orbital theory.

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2.1 Classification of bonding

   The bond in which a pair of electrons bind atoms A and B is called a covalent bond, and it is written as A-B or A:B. Since two pairs of electrons are involved in a double bond and three pairs in a triple bond, they are designated by A=B, $A\equiv B$ or A::B, or A:::B, respectively. The covalent bond is a simple but very useful concept proposed by G. N. Lewis at the beginning of this century and its representation is called the **Lewis structure**. Unshared pair of valence electrons are called lone pairs, and they are expressed by a pair of dots like A:.

   Exercise 2.1 Describe the Lewis structures of the nitrogen molecule N_2 and the oxygen molecule O_2.
   [Answer]   : N:::N: , : O::O :

   Eight electrons are required to fill an *s* and three *p* orbitals, and when the total number of electrons used for the bonds and lone pairs is eight, a stable molecular structure results. This is called the **octet rule** and is useful when qualitatively discussing the molecular structures of main group compounds. Of course, this rule is not applied to a hydrogen molecule, H_2, but is applicable to covalent molecules, such as simple two-atomic molecules O_2 or CO and even to complicated organic compounds. For the

elements after the 3rd period, the number of covalent bonds is sometimes five (*e.g.* PCl_5) or six (*e.g.* SF_6), and the central atom of these molecules shows **hypervalency**. In this case, because *s* and *p* electrons run short to form more than four 2-electron covalent bonds, it was once believed that *d* electrons were partly involved. The present view is, however, that these hypervalent bonds use only *s* and *p* orbitals but that the bond orders are lower than those of single bonds.

The electrostatic bond between cations (positive ion) and anions (negative ion), such as in sodium chloride, NaCl, is called an ionic bond. Since the total electrical charge in a compound should be zero, the electrical charges of cations and anions are equal. There is a partial contribution from covalent bonds even in an ionic compound, and the ions are not necessarily bonded only by the electrostatic interaction.

Pauling's electroneutrality principle states that the net electrical charge of each component of a compound is essentially neutral. As will be mentioned later, the structures of many solid compounds are described as an alternate array of cations and anions, and are classified into several representative crystal types.

Metal atoms are bound together by means of the **conduction electrons** originating from the valence electrons of metal atoms. The bond due to the conduction electrons in a bulk metal is called the **metallic bond**.

Generally, chemical bonds can be assigned to either of the three kinds mentioned above, but new compounds have been synthesized one after another which cannot always be classified by the simple **2-center electron pair covalent bond**. They include **electron-deficient bonds** in boron hydrides, **coordinate bonds** in transition metal complexes, the **metal-metal bonds** in metal cluster compounds, *etc.*, and new concepts have been introduced into bond theory to account for these new kinds of chemical bonds. As has already been described, a weak bonding interaction called the **van der Waals interaction** has been recognized in neutral atomic or molecular compounds. The potential of this interaction is inversely proportional to the 6th power of the distance between atoms. The adjacent but non-bonded distance between atoms is estimated by the sum of the van der Waals radius assigned to each atom.

The weak interaction X-H-Y that a hydrogen atom forms with the atoms X, Y (nitrogen, oxygen, fluoride, *etc.*.) with larger electronegativity than that of hydrogen is called the **hydrogen bond**. Hydrogen bonding plays an important role in ice, the structure of the double helix of DNA (deoxyribonucleic acid), *etc*.

2.2 Geometrical factors governing bonding and structure

Two parameters, radii and the electron attracting power of atoms or ions, determine

the bonding, structure, and reaction of elementary substances and compounds. Much effort has been devoted to finding numerical values for these two factors applicable to all materials. It is hoped that the chemical properties of a known compound, and of a still non-existent new material, can be predicted with a combination of suitable numerical values. Firstly, geometrical factors will be described.

Table 2.1 Atomic radii (pm)

H 32								
Li 123	Be 89							
Na 154	Mg 136							
K 203	Ca 174	Sc 144	Ti 132	V 122	Cr 118	Mn 117	Fe 117	Co 116
Rb 216	Sr 191	Y 162	Zr 145	Nb 134	Mo 130	Tc 127	Ru 125	Rh 125
Cs 235	Ba 198	La 169	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 127

			B 82	C 77	N 75	O 73	F 72	
			Al 118	Si 111	P 106	S 102	Cl 99	
Ni 115	Cu 117	Zn 125	Ga 126	Ge 122	As 120	Se 117	Br 114	
Pd 128	Ag 134	Cd 148	In 144	Sn 140	Sb 140	Te 136	I 133	
Pt 130	Au 134	Hg 149	Tl 148	Pb 147	Bi 146			

(a) Atomic and ionic radii

The electron density in atoms gradually approaches, but never reaches, zero as the distance from the nucleus increases. Therefore, strictly speaking the radius of an atom or ion is indeterminable. However, it is possible to determine the bond distance between atomic nuclei experimentally. Atomic radii determined experimentally are one of the most important atomic parameters describing the structural chemistry of compounds. It is reasonable to define the metal radius of a bulk metal as half of the distance between metal atoms. Half of the distance between atoms is defined also as the **covalent radius** of a

covalent elementary substance (Table 2.1).

Table 2.2 Ionic radii (in pm).*

$Li^+(4)$	$Be^{2+}(4)$	$B^{3+}(4)$	$N^{3+}(6)$	$O^{2-}(6)$	$F^-(6)$
59	27	11	16	140	133
$Na^+(6)$	$Mg^{2+}(6)$	$Al^{3+}(6)$	$P^{3+}(6)$	$S^{2-}(6)$	$Cl^-(6)$
102	72	54	44	184	181
$K^+(6)$	$Ca^{2+}(6)$	$Ga^{3+}(6)$	$As^{3+}(6)$	$Se^{2-}(6)$	$Br^-(6)$
138	100	62	58	198	196
$Rb^+(6)$	$Sr^{2+}(6)$	$In^{3+}(6)$		$Te^{2-}(6)$	$I^-(6)$
152	118	80		221	220
$Cs^+(6)$	$Ba^{2+}(6)$	$Tl^{3+}(6)$			
167	135	89			

*Numbers in parentheses are the coordination number of the ions.

Since the cations and anions of different elements in an ionic compound are bonded by electrostatic interactions, the bond distance is the sum of **ionic radii** assigned to the cation and anion. The standard ionic radius of one species is fixed first and is then subtracted from the distance between ions to decide the radius of the partner ion. As the standard, the radius of O^{2-} ion in a number of oxides is set to 140 pm (1 pm = 10^{-12} m) (R. D. Shannon). Cationic radii in oxides are the difference between the bond distance and 140 pm. After cation radii in oxides are decided, other anion radii can be calculated by subtraction of the cation radii from the distances between the atoms in ionic compounds. By applying such methods to many ionic compounds, ionic radii have been compiled in such a way that experimental and calculated values are generally consistent (Table 2.2).

Even ionic compounds have some covalent contribution and it is not expected that calculated and experimental bond distances will agree exactly. Even if the ionic radius assigned to a standard ion is changed, we can still compile a set of ionic radii that are consistent across many compounds. Other examples of the proposed radii of O^{2-} ion are 132 pm (V. M. Goldschmidt) or 60 pm (J. C. Slater). We must also be mindful that the cation-anion distances of the same ion pair become larger as the **coordination number** of opposite ions increases. Therefore, in any discussion of the structural features of ionic compounds from a viewpoint of ionic radii, a set of the ionic radii calculated using the same standard radius for the compounds with the same coordination number should be used.

Exercise 2.2 Which ionic radius is larger, Cs^+ or F^-?
[Answer] Cs^+(167 pm) > F^-(133 pm). The anion radius is not always larger.

The metal and covalent radii, also called the **atomic radii**, become smaller in the same period of the periodic table as the group of the element goes to the right and then increase again in the next period. The **lanthanide contraction** is responsible for the 5th period ($4d$) elements having almost the same atomic radii as those of the 6th period ($5d$) ones. In the periodic table, the lanthanide elements are inserted before the $5d$ elements. The atomic radii of lanthanide elements decrease noticeably as the effective nuclear charge increases because the screening effects of the $4f$ orbitals of lanthanide elements are weak due to their orbital shapes. Consequently, the atomic radii of the elements following lanthanides are very similar to those of the $4d$ elements.
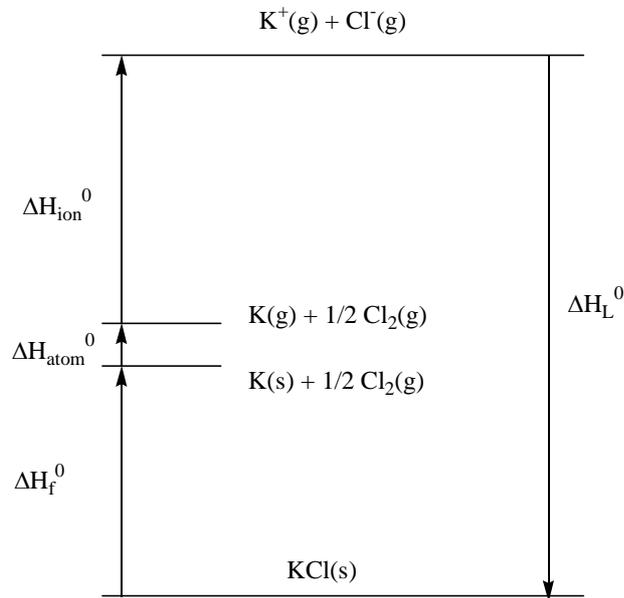
(b) Lattice enthalpy

Although the stability of a crystal at constant temperature and pressure depends on the Gibbs free energy change of the crystal's formation from its constituent ions, the stability of a crystal is determined mostly by the enthalpy change alone since the lattice formation is very exothermic, and the entropy term is negligibly small (refer to Section 3.1). **Lattice enthalpy, ΔH_L,** is defined as the standard enthalpy change of the reaction in which an ionic crystal decomposes into gaseous ions (s is solid, g is gas and L is lattice).

$$MX(s) \rightarrow M^+(g) + X^-(g) \qquad \Delta H_L$$
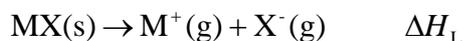
Lattice enthalpy is indirectly calculated from the values of the enthalpy change at each stage using a Born-Haber cycle (Fig. 2.1). Namely, a closed cycle is formed using enthalpy data; standard enthalpy of formation ΔH_f of an ionic crystal from elements, sublimation enthalpy of an elementary solid, or atomization enthalpy ΔH_{atom} corresponding to the dissociation enthalpy of a gaseous elementary molecule, the ionization enthalpy $\Delta H_{ion,}$ which is the sum of the ionization enthalpy of cation formation and electron acquisition enthalpy of anion formation.   Lattice enthalpy is calculated using the relation that enthalpy change in a cycle is zero.

$$\Delta H^0_{atom} + \Delta H^0_{ion} - \Delta H^0_L - \Delta H^0_f = 0$$

K$^+$(g) + Cl$^-$(g)

ΔH$_{ion}^0$

K(g) + 1/2 Cl$_2$(g)

ΔH$_{atom}^0$

K(s) + 1/2 Cl$_2$(g)

ΔH$_L^0$

ΔH$_f^0$

KCl(s)

Fig. 2.1 Born-Haber cycle of KCl.

(c) Madelung constant

The total Coulomb potential energy that exists between the ions in an ionic crystal consisting of ions A and B should be the sum of the individual Coulomb potential energies V_{ab}. Since the locations of the ions in the crystal lattice are decided by the structure type, the total Coulomb potential between all ions is calculated by setting the distance between the ions to d. A is the **Madelung constant** that is characteristic of each crystal type (Table 2.3).

$$V = N_A \frac{e^2}{4\pi\varepsilon_0}\left(\frac{z_A z_B}{d}\right) \times A$$

N_A is Avogadro's constant and z_A and z_B are the electric charges of the cation and anion. The electrostatic interaction between contiguous ions is the strongest, and the Madelung constant generally becomes larger as the coordination number increases. Because the electrical charges have opposite signs, the potential becomes negative, indicating the stabilization that accompanies the formation of a crystal lattice from well dispersed,

gaseous phase ions. Although it is generally true that the lowest electrostatic potential leads to the most stable structure, this is not strictly correct since there are also other interactions to consider.

Table 2.3 Madelung constants

Structural type	A
Rock-salt	1.748
Cesium chloride	1.763
Sphalerite	1.638
Wurtzite	1.641
Fluorite	2.519
Rutile	2.408

The second largest factor that contributes to the lattice enthalpy is the van der Waals force, and **dispersion forces** or the **London interaction** is the main origin of this force. It is an attractive interaction between electric dipoles, which is inversely proportional to the 6th power of the distance d between ions. The van der Waals force is very small.

$$V = -\frac{N_A C}{d^6}$$

The value of the constant C is a function of each compound. Since it is at most 1% of the Coulombic force, it may be safely neglected in the calculation of lattice enthalpy.

(d) Structure of metal crystals

If we imagine metal atoms as being hard balls, when densely packed in two dimensions each ball will be in contact with six other balls (A). When another layer of this 2 dimensional arrangement is placed on top of the first, the packing will be densest and the structure most energetically stable when the metal atoms are placed on top of the hollows (B) of the first layer. When a 3rd layer is placed on top of the 2nd layer, there are two possibilities. Namely, the 3rd layer (A) overlaps with the 1st layer (A) or the 3rd layer (C) overlaps with neither (A) nor (B). The ABAB...-type packing is called **hexagonally close-packed** (hcp) (Fig. 2.2), and the ABCABC...-type is called **cubic close-packed** (ccp) (Fig. 2.3). In both cases, each ball is surrounded by 12 balls, that is, it is 12-coordinated. The coordination polyhedron of hcp is anti-cubooctahedron,
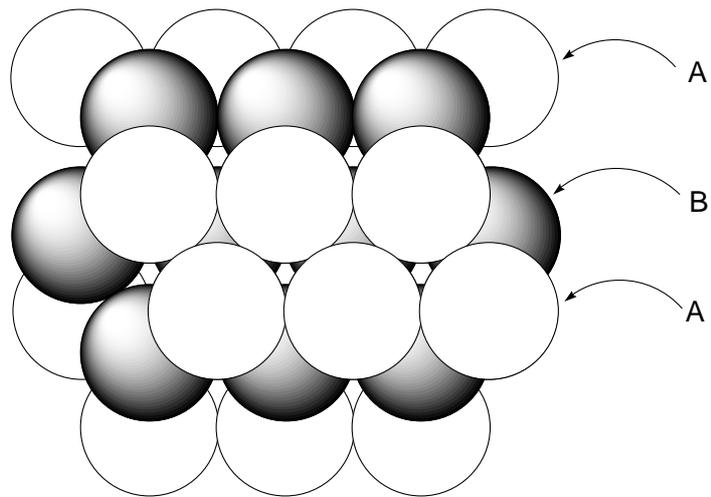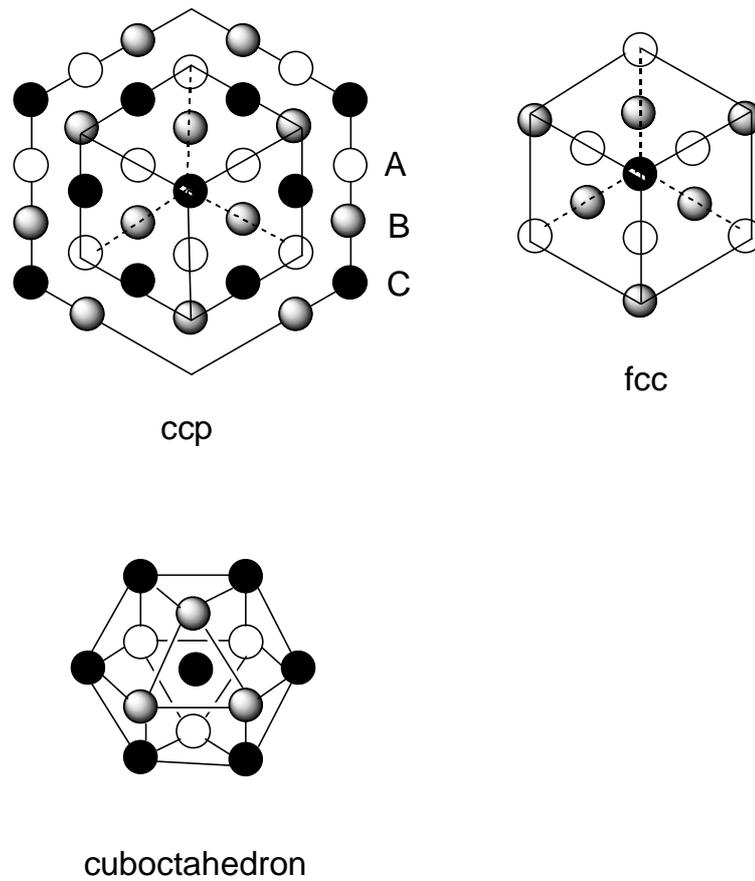
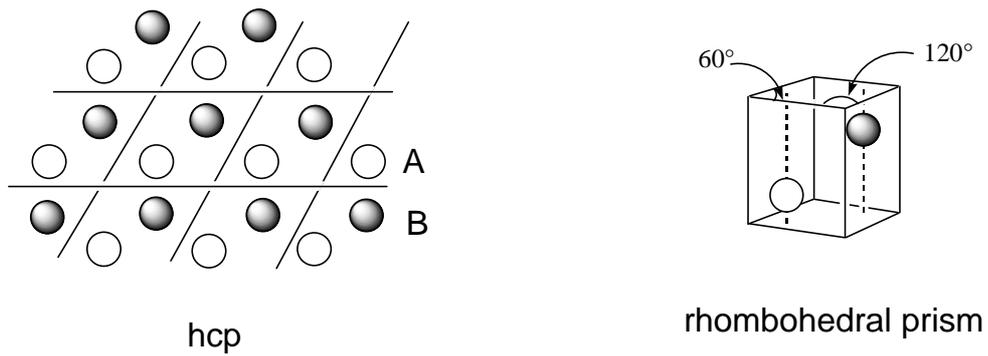**Fig. 2.2** Hexagonally close-packed (hcp) of balls.
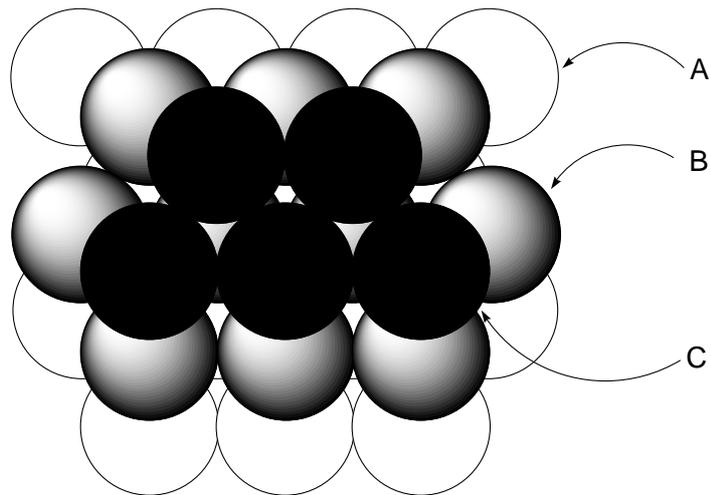
Fig. 2.3 Cubic close-packed (ccp) of balls.

and that of ccp is cubooctahedron. When the lattice is sliced in different planes, the unit lattice of ccp appears to be a **face-centered cubic lattice** (fcc), containing a ball at each cubical apex and on the center of each face (Fig. 2.4). The unit lattice of hcp is a rhombohedral prism in which two balls are located in the positions shown in (Fig. 2.5). There are several different modes of piling up layers other than the normal hcp and ccp,

A
B
C

ccp

fcc

cuboctahedron

Fig. 2.4 Different expressions of cubic close-packed.

A
B

hcp

60°   120°

rhombohedral prism

Fig. 2.5 Different expressions of hexagonally close-packed.

and many examples are known.

The lattice with another ball at the center of a cubic lattice consisting of eight balls is the **body centered cubic lattice** (bcc), and some metals assume this mode of packing.

The ratio of space occupation in a bcc lattice is smaller than that of close-packed ones but the difference is not large. Although the central ball is formally 8-coordinated, it is essentially 14-coordinated since there are a further six balls only 15.5% more distant than the first eight balls. However, because of the smaller ratio of space occupation, bcc appears relatively rarely and pure metals tend to adopt hcp or ccp.

In both hcp and ccp, the cavities among the balls are either the O_h holes enclosed octahedrally by six balls or the T_d holes enclosed tetrahedrally by four balls (Fig. 2.6). (O_h and T_d are the symmetry symbols used in group theory.) In ionic solids, if the anions are in hcp or ccp arrangements, cations enter into either of these cavities.

T_d hole

O_h hole
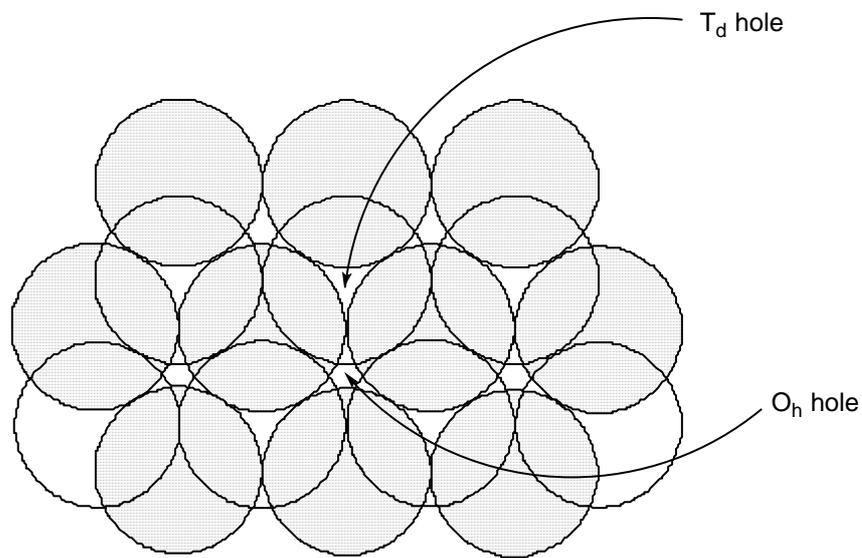
**Fig. 2.6** Octahedral and tetrahedral holes.

(e) Ionic crystal

In ionic crystals, such as metal halides, oxides, and sulfides, metal cations and anions are aligned alternately, and the solid is bound together mainly by electrostatic bonding. Many metal halides dissolve in polar solvents, *e.g.* sodium chloride NaCl dissolves in water; whereas metal oxides and sulfides, in which there is a significant contribution of covalent bonding, are usually insoluble even in the most polar of solvents. The fundamental structure of ionic crystals is that larger ions (usually anions) are close-packed and smaller ions (usually cations) enter into the octahedral or tetrahedral cavities between them. Ionic crystals are classified into several typical structures according to the kinds of cations and anions involved and their ionic radii. Each structure type is called by the name of the typical compound, just as the rock salt structure representing the structures of not only NaCl (rock salt) but also various other compounds.

Representative structure types of solid compounds and examples belonging to each type are shown in Table 2.4.

**Table 2.4** Crystal types of solid-state compounds

Crystal type	Coordination number	Examples of compounds
Rock-salt	(6,6)	LiCl, NaCl, KBr, RbI, AgCl, MgO, NiO, InP
Cesium chloride	(8,8)	CsCl, CsBr, CsI, CuZn
Sphalerite	(4,4)	ZnS, CdS, HgS, CuCl, GaP
Fluorite	(8,4)	CaF_2, SrF_2, CdF_2, ZrO_2, UO_2
Rutile	(6,3)	TiO_2, SnO_2, RuO_2, NiF_2
Cadmium iodide	(6,3)	CdI_2, CoI_2, $Mg(OH)_2$
Rhenium oxide	(6,2)	ReO_3, WO_3, $Sc(OH)_3$
Perovskite	(6,2)	$CaTiO_3$, $BaTiO_3$, $SrTiO_3$

Rock-salt structure   Sodium chloride NaCl is a typical compound in which Cl^- anions are arranged in ccp and Na^+ cations occupy all the octahedral holes (O_h holes) (Fig. 2.7). Each Na^+ cation is surrounded by six Cl^- anions. The same structure results even if the positions of anions and cations are exchanged. In the case of the reversed structure, each Cl^- anion is surrounded by six Na^+ cations. Namely, each ion is 6-coordinated and it is convenient to describe the structure as the (6,6)-structure. The number of ions in a unit lattice is calculated by summing up the ions shown in Fig. 2.7. Since there is one ion inside the lattice, the ions on the faces of the lattice are shared by 2, on the edges by 4, and on the corners by 8 lattices, a net of 4 Cl ions belonging to the unit lattice of NaCl is obtained by multiplying the numbers of ions inside the lattice by 1, on the faces by 1/2, on the edges by 1/4 and on the corners by 1/8. The number of Na ions in the unit lattice is also 4 and the ratio of Cl and Na ions agrees with the formula NaCl.
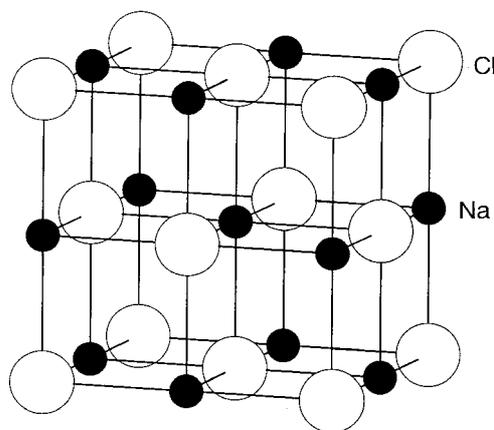

Fig. 2.7 Rock-salt structure.

Cesium chloride structure   Cesium chloride, CsCl, is a typical example of the structure shown in Fig. 2.8. There is a Cs^+ ion at the center and eight Cl^- are located at the eight corners of the cube. Conversely, even if a Cl^- comes to the center and eight Cs^+ come to the corners, the number of each ion in the unit lattice is the same. Thus, this is referred to as the (8, 8)-structure. Since there is one Cs^+ and one Cl^- ion belonging to this unit lattice, it coincides with the formula CsCl.
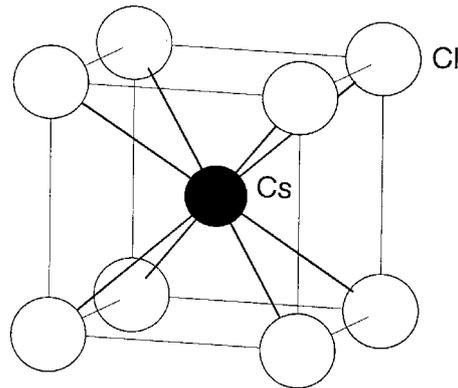

Fig. 2.8 Cesium chloride structure.

Zinc blende structure   Zinc blende has the composition ZnS and its unit lattice is shown in Fig. 2.9. S^{2-} anions are arranged in ccp and Zn^{2+} cations occupy half of the tetrahedral holes (T_d holes).   In this arrangement, each cation is coordinated by four anions, and each anion by four cations. Hence, this is a (4, 4)-structure. There are both four Zn^{2+} and S^{2-} ions belonging to this unit lattice and the atomic ratio coincides with the formula of ZnS.
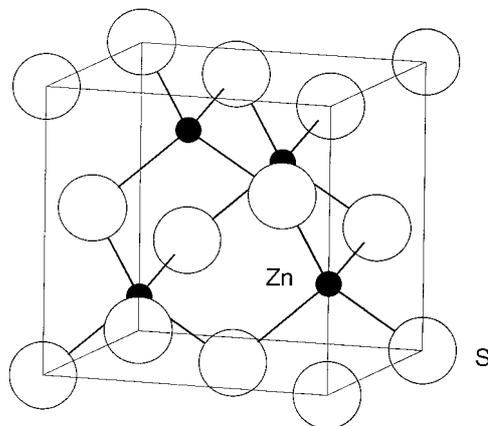
Fig. 2.9 Zinc blende structure.

Fluorite structure The composition of fluorite is CaF_2. Since the number of F^- is twice that of Ca^{2+}, all the tetrahedral holes of Ca^{2+} arranged in ccp are occupied by F^-, as shown in Fig. 2.10. There are four Ca^{2+} and eight F^- ions and the number of ions is 4 times the formula. The anti-fluorite structure exchanges the cations and anions, and is exemplified by potassium oxide K_2O, *etc*.
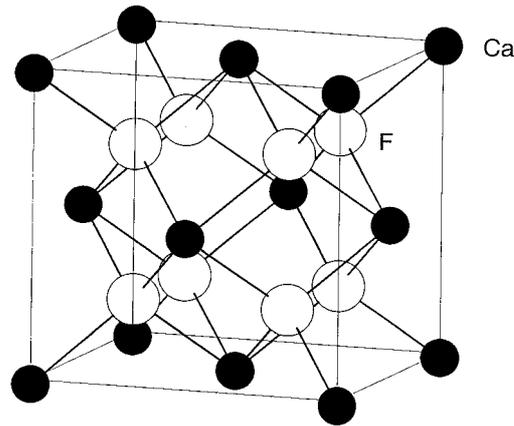
Fig. 2.10 Fluorite structure.

Exercise 2.3 How many cations and anions are there in a unit lattice of zinc blende structure?

[Answer] All four cations are included in a unit lattice . The anions occupy the 8 corners and 6 faces and the number is 8 x 1/8 + 6 x 1/2 = 4.

(f) Radius ratio

Generally, the total Coulombic potential energy E_c of the univalent ionic compound MX is expressed by the following formula.

$$E_c = -\frac{N_A e^2}{4\pi\varepsilon_0 R} A$$

N_A is the Avogadro constant, A the Madelung constant and R the distance between ions. According to this formula, a structure with a larger A / R ratio is more stable. The Madelung constant of an MX compound increases with increasing coordination number. On the other hand, it is advantageous to lower the coordination number and to reduce R in the case of small M, rendering contact between M and X more difficult. In an ionic crystal, the ratio of r_M and r_X with the anions contacting each other and also with the
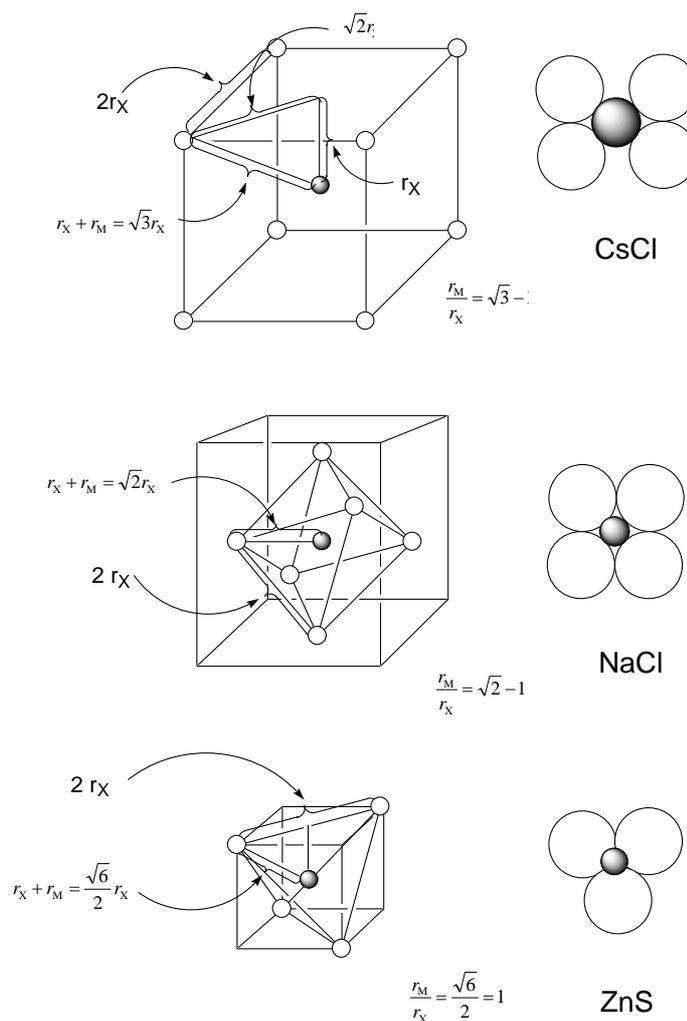
cations depends on the coordination number.

In a partial structure consisting only of anions, the anions form a coordination polyhedron around a cation. The anionic radius r_X is one half of the distance of the edge of the polyhedron and the distance from the cation center to an apex of the polyhedron is the sum of the anion and cation radii $r_X + r_M$. The coordination polyhedron of the CsCl structure is a cube, the NaCl structure an octahedron, and the ZnS structure a tetrahedron. The distance from the center of each polyhedron to an apex is $\sqrt{3}r_X$, $\sqrt{2}r_X$, $\dfrac{\sqrt{6}}{2}r_X$. Therefore, the ratios of the cationic and anionic radii r_M / r_X are $(\sqrt{3}r_X - r_X)/r_X = \sqrt{3}-1 = 0.732$ for CsCl, $(\sqrt{2}r_X - r_X)/r_X = \sqrt{2}-1 = 0.414$ for NaCl,

and $\left(\dfrac{\sqrt{6}}{2}r_X - r_X\right)/r_X = \sqrt{6}/2 - 1 = 0.225$ for ZnS structures (Fig. 2.11).

It has been explained that the coordination number decreases when these radius ratios are smaller than the given values since cations and anions do not come into contact with each other, causing instability. On the other hand, the coordination number increases for larger cations, increasing the radius ratio. However, the relation between a coordination number and a radius ratio is not simple. For example, halides of alkali metals adopt the NaCl structures at normal temperatures except cesium chloride CsCl, cesium bromide CsBr and cesium iodide CsI. It is not possible to assume structure types from the radius ratios even in the case of simple ionic compounds like alkali metal halides. However, the qualitative trend that smaller cations have smaller coordination numbers is generally correct.

$$2r_X$$

$$\sqrt{2}r$$

$$r_X + r_M = \sqrt{3}r_X$$

$$r_X$$

$$\frac{r_M}{r_X} = \sqrt{3} - 1$$

CsCl

$$r_X + r_M = \sqrt{2}r_X$$

$$2\,r_X$$

$$\frac{r_M}{r_X} = \sqrt{2} - 1$$

NaCl

$$2\,r_X$$

$$r_X + r_M = \frac{\sqrt{6}}{2}r_X$$

$$\frac{r_M}{r_X} = \frac{\sqrt{6}}{2} = 1$$

ZnS

Fig. 2.11 The radius ratio r_M / r_X of cations and anions.

(g) Variation of the solid structure expression

Many solid-state inorganic compounds have complicated three-dimensional structures. Different structural illustrations for the same compound help our understanding of its structure. In the case of complicated inorganic compounds, drawing bond lines between atoms, as in most organic compounds, causes confusion. The anions in many metal oxides, sulfides, or halides form tetrahedra or octahedra around the central metal cations. Although there is no bond between anions, the structures are greatly simplified if they are illustrated by the anion polyhedra sharing apexes, edges, or faces. In such illustrations, cationic metal atoms are usually omitted. As has been mentioned, ionic solid structures can be thought of as a close packed arrays of anions.

Figures 2.12 and 2.13 illustrate these three representations for molecular phosphorus pentoxide $P_2O_5 (= P_4O_{10})$ and molybdenum pentachloride $MoCl_5 (= Mo_2Cl_{10})$.

Polyhedral representations are much easier to understand for the structures of large molecules or solid-state compounds formed by an infinite number of atoms. However, the bond line representation is suitable for molecular compounds such as the above examples.
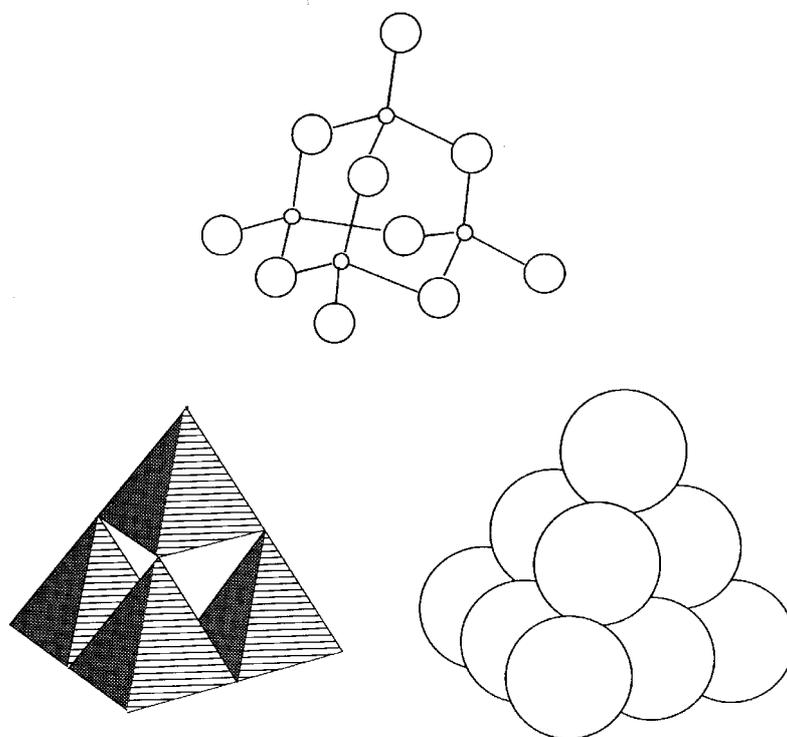
Fig. 2.12 Three expressions for the structure of P_4O_{10}.
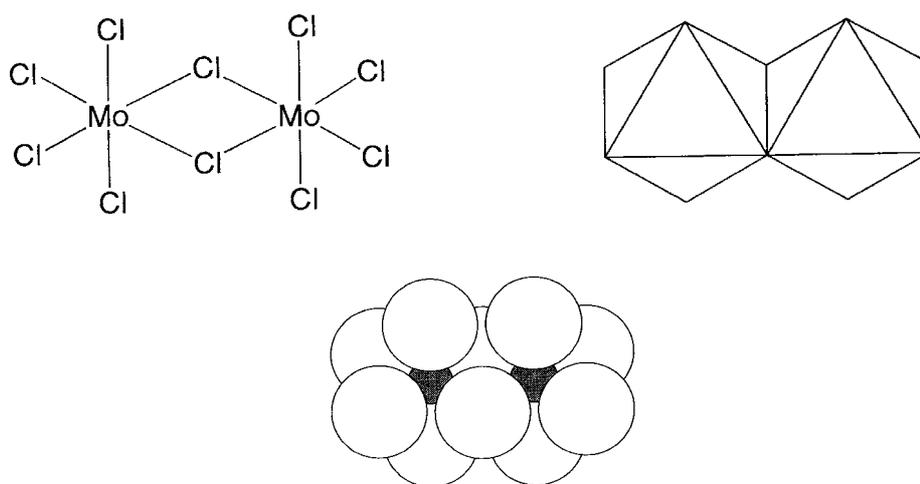
Fig. 2.13 Three expressions for the structure of Mo_2Cl_{10}.

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2.3 Electronic factors which govern bonding and structure

The bonding and structure of a compound are determined by electronic properties such as the power of constituent atoms to attract or repel electrons, the molecular orbitals occupied by valence electrons, *etc*. Geometrical arrangements of atoms are also influenced by the electronic interactions between non-bonding electrons. Here, some fundamental concepts are described.

(a) Effective nuclear charge

Since the positive nuclear charge is generally offset by the negative charge of the internal electrons in the electron shell inside the valence electrons, the nuclear charge that valence electrons feel is smaller than the integer charge, Ze for an atomic number Z. This reduction is expressed by the **shielding constant** σ, and the net nuclear charge is called the **effective nuclear charge**, $Z_{eff}\,e$.

$$Z_{eff} = Z - \sigma$$

The effective nuclear charge varies with different electron orbitals and distances from the nucleus.

(b) Ionization energy

Ionization energy is defined as the minimum energy required to remove an electron from the atom in a gaseous phase (g), as shown in the following equation. Ionization energy is expressed in units of electron volt (eV), where $1\,eV = 96.49\ kJmol^{-1}$.

$$A(g) \rightarrow A^{+}(g) + e^{-}(g)$$

The 1st ionization energy, which removes the outermost electron, is the smallest, and the 2nd and 3rd ionization energies, which further ionize cations, increase rapidly. The ionization enthalpy, which is the standard enthalpy change of the ionization process and is used in thermodynamic calculations, is the ionization energy multiplied by RT (R is the universal gas constant $8.31451\ JK^{-1}mol^{-1}$ and T is temperature, 2.479 kJ (0.026 eV), at room temperature). The difference between these two parameters is small. The 1st ionization energy varies periodically with atomic number across the periodic table, with the lower left (cesium, Cs) being the smallest and the upper right (helium, He) the largest.

It is understandable that alkali metals generally have the lowest ionization energies because they are stabilized by removal of an *s* electron to attain the rare gas configuration. Rare gas elements have stable electronic structures, and their ionization energies are the largest. Although the ionization energy increases almost monotonically from alkali

metals to rare gases in each period, there are reversals at several places, such as nitrogen N and oxygen O, and phosphorus P and sulfur S. The 1st ionization energies are given in Table 2.5.

Table 2.5   Electronic parameters of atoms (eV). I: 1st ionization energy, A_e: electron affinity, χ_M: electronegativity (Mulliken)

atom	I	A	χ	atom	I	A	χ	atom	I	A	χ
H	13.60	0.75	7.18	Cr	6.77	0.67	3.72	Cd	8.99		
He	24.59			Mn	7.44			In	5.79	0.30	3.10
Li	5.39	0.62	3.01	Fe	7.90	0.15	4.03	Sn	7.34	1.11	4.23
Be	9.32			Co	7.88	0.66	4.27	Sb	8.64	1.07	4.86
B	8.30	0.28	4.29	Ni	7.64	1.16	4.40	Te	9.01	1.97	5.49
C	11.26	1.27	6.27	Cu	7.73	1.24	4.48	I	10.45	3.06	6.76
N	14.53			Zn	9.99			Xe	12.13		
O	13.62	1.46	7.54	Ga	6.00	0.30	3.20	Cs	3.89	0.47	2.18
F	17.42	3.40	10.41	Ge	7.90	1.23	4.61	Ba	5.21	0.15	2.68
Ne	21.56			As	9.82	0.81	5.31	La	5.58	0.50	3.09
Na	5.14	0.55	2.85	Se	9.75	2.02	5.89	Hf	6.83	0.00	3.42
Mg	7.65			Br	11.81	3.36	7.59	Ta	7.89	0.32	4.11
Al	5.99	0.44	3.22	Kr	14.00			W	7.98	0.82	4.40
Si	8.15	1.39	4.77	Rb	4.18	0.49	2.34	Re	7.88	0.15	0.40
P	10.49	0.75	5.62	Sr	5.69	0.11	2.90	Os	8.70	1.10	4.90
S	10.36	2.08	6.22	Y	6.22	0.31	3.27	Ir	9.10	1.60	5.40
Cl	12.97	3.61	8.29	Zr	6.63	0.43	3.53	Pt	9.00	2.13	5.61
Ar	15.76			Nb	6.76	0.89	3.83	Au	9.23	2.31	5.77
K	4.34	0.50	2.42	Mo	7.09	0.75	3.92	Hg	10.44		
Ca	6.11	0.02	3.07	Ru	7.36	1.05	4.26	Tl	6.11	0.20	3.16
Sc	6.56	0.19	3.38	Rh	7.46	1.14	4.30	Pb	7.42	0.36	3.89
Ti	6.83	0.08	3.45	Pd	8.34	0.56	4.45	Bi	7.29	0.95	4.12
V	6.75	0.53	3.64	Ag	7.58	1.30	4.44				

(c) Electron affinity

Electron affinity is the negative of the electron-gain enthalpy ΔH_{eg} of an atom in a gas phase, as shown in the following equation and denoted by A_e ($= -\Delta H_{eg}$) (Table 2.5).

$$A(g) + e^-(g) \rightarrow A^-(g)$$
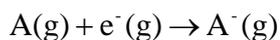
It may be regarded as the ionization enthalpy of an anion. Since halogen atoms achieve rare gas electron configurations if an electron is added to them, their electron affinities are large.

(d) Electronegativity

Electronegativity is one of the most fundamental atomic parameters which expresses numerically the tendency to attract electrons to atoms in a molecule. It is very useful in explaining differences in bonding, structure, and reaction from the standpoint of atomic properties. Various schemes have been proposed to explain the theoretical basis of the power of electron attraction, and studies are still actively seeking new numerical values of electronegativity. The Pauling scale, introduced first in 1932, is still the most frequently used , and subsequent new numerical values have been justified if they are close to those of Pauling.

L. Pauling defined electronegativity as the quantitative ionic character of bonds. Originally, the following equation was proposed as a formula to define the ionic character of the bond between atoms A and B.

$$\Delta = D(\text{AB}) - \frac{1}{2}(D(\text{AA}) + D(\text{BB}))$$

where D is the bond energy of a covalent bond. However, it turned out that Δ is not necessarily positive, and Pauling modified the definition

$$\Delta = D(\text{AB}) - \sqrt{D(\text{AA}) \times D(\text{BB})}$$

and redefined it as the ionic character of the A-B bond. Furthermore, electronegativity χ was defined in such a way that the difference of the electronegativities of atoms A and B is proportional to the square root of the ionic character. Here, the coefficient

$$|\chi_\text{A} - \chi_\text{B}| = 0.208\sqrt{\Delta}$$

0.208 is so determined that the electronegativity of hydrogen H becomes 2.1 when bond energies are expressed in kcal mol^{-1}. Since Pauling electronegativities increase the higher the oxidization states of an atom, these values correspond to the highest oxidization number of each element. The electronegativities calculated using recent values of bond energies are shown in Table 2.6.

Table 2.6 Pauling electronetativities

	1	2	3	4	5	6	7	8	9
1	H 2.2								
2	Li 0.98	Be 1.57							
3	Na 0.93	Mg 1.31							
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28
6	Cs 0.79	Ba 0.89	Lanthanoid	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20
7	Fr 0.7	Ra 0.9	Actinoid						

10	11	12	13	14	15	16	17	18
								He
			B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
			Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
Ni 1.91	Cu 2.0	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.0
Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe 2.6
Pt 2.28	Au 2.54	Hg 2.00	Tl 2.04	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn

A. L. Allred and E. G.. Rochow defined electronegativity as the electric field Z_{eff} / r^2 on the atomic surface. They added a constant in order to make the electronegativity χ_{AR} as near as possible to the Pauling values by using r for the covalent bond radius of atoms.

$$\chi_{AR} = 0.74 + 0.36 \frac{Z_{eff}}{r^2}$$

It turns out that elements with small covalent radii and large effective nuclear charges have large electronegativities (Table 2.6).

R. Mulliken defined electronegativity χ_M as the average of the ionization energy I and electron affinity A_e as follows (Fig. 2.14).

$$\chi_M = \frac{1}{2}(I + A_e)$$

As ionization energy is the energy of electronic excitation from the HOMO and electron affinity the energy of electron addition to the LUMO (refer to Section 2.3 (e)), in this definition electronegativity can also be called the average value of the energy levels of the HOMO and LUMO. Those elements which are hard to ionize and easy to attract electrons have large values. Although the electronegativity is defined for the atoms in a valence state in a molecule and has the dimensions of energy, it is treated as a dimensionless number (Table 2.5).
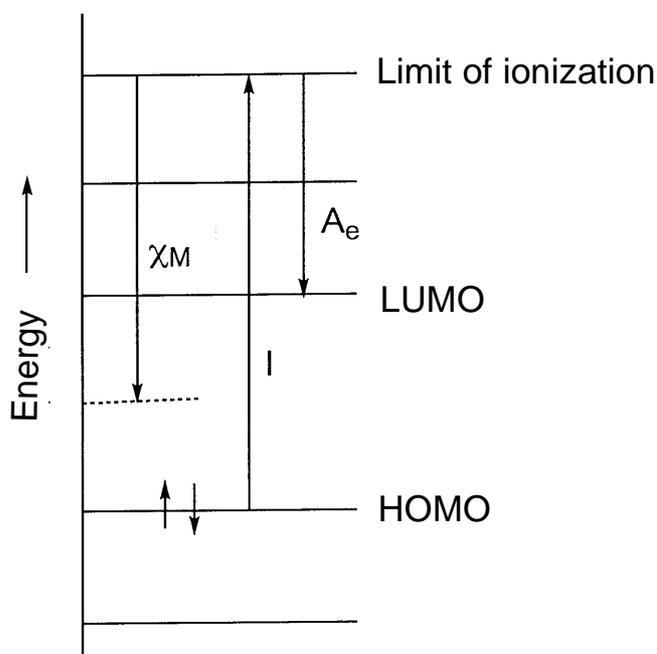
Fig. 2.14 Mulliken electronegativity.

Although the definition of Mulliken is intelligible since it is directly related to atomic orbitals, generally the values of Pauling or Allred-Rochow are used. As these values are not much different, the Pauling electronegativity is appropriate when choosing only one. Electronegativity values change not only by definition, but are also considerably affected by the bonding state of atoms, and they should be used with considerable caution. The electronegativities of the constituent atoms are fundamental to

explaining the differences in bonding, structure, and reactions of compounds. Therefore theoretical chemists continue in their efforts firmly to extend the foundations of this parameter.

Exercise 2.4   Describe the numerical tendency of electronegativities of the elements in the periodic table.

[Answer]   They increase toward the right and decrease down the table. Namely, the electronegativity of alkali metal Cs is the smallest and that of fluorine F is the largest.

(e) Molecular orbitals

The wave functions of electrons in an atom are called **atomic orbitals**. Since the probability of finding electrons in a molecular orbital is proportional to the square of a wave function, the electron map looks like a wave function. A wave function has domains of positive and negative amplitude called lobes. The overlapping positive lobes or negative lobes of the wave functions of atoms in a molecule amplify each other to form a bond, but the positive and negative lobes cancel each other forming no bond. The extent of this interference effect corresponds to the magnitude of the overlap integral in quantum chemistry.

In the formation of a molecule, atomic orbitals overlap to generate a **molecular orbital** which is the wave function of the electrons in the molecule. The number of molecular orbitals is the sum of the atomic orbitals and these molecular orbitals are classified into **bonding, nonbonding, or antibonding molecular orbitals** by the extent of their participation in the bond between atoms. The conditions of the formation of a bonding molecular orbital are as follows.

[Conditions of the formation of bonding molecular orbitals]
   (1) The lobes of the atomic orbitals of the constituent atoms are suitable for an overlap.
   (2) The positive or negative sign of the overlapping lobes is the same.
   (3) The energy levels of atomic orbitals are close.

The simplest case where a molecular orbital is constructed from atomic orbitals A and B is explained here. A bonding molecular orbital is formed between A and B if the above mentioned conditions (1), (2), and (3) are satisfied, but if the sign of one of the atomic orbitals is reversed, condition (2) is not satisfied and an antibonding molecular orbital, in which the signs of the overlapping lobes are different (Fig. 2.15) results. The energy level of a bonding orbital is lower and the level of an antibonding orbital is higher

than those of the constituent atomic orbitals. The larger the energy difference of a bonding and an antibonding orbital, the stronger the bond. When there is no bonding or antibonding interaction between A and B, the resultant molecular orbital is a nonbonding orbital. Electrons occupy the molecular orbitals in order of lowest to highest energy levels. The highest occupied molecular orbital is called the **HOMO** and the lowest unoccupied one the **LUMO**. Ken'ichi Fukui (1981 Nobel prize) named these orbitals **frontier orbitals**.

Two or more molecular orbitals of equal energy are called **degenerate orbitals**. The symbol of a nondegenerate orbital is *a* or *b*, a doubly degenerate orbital *e*, and triply degenerate orbital *t*. The symbol *g* (gerade) is attached as a suffix to the centrosymmetric orbital and *u* (ungerade) to the orbital which changes sign under inversion around an inversion center. The number before the symmetry symbol is used in order of energy to distinguish orbitals of the same degeneracy. Additionally, they are named **sigma(σ) or**
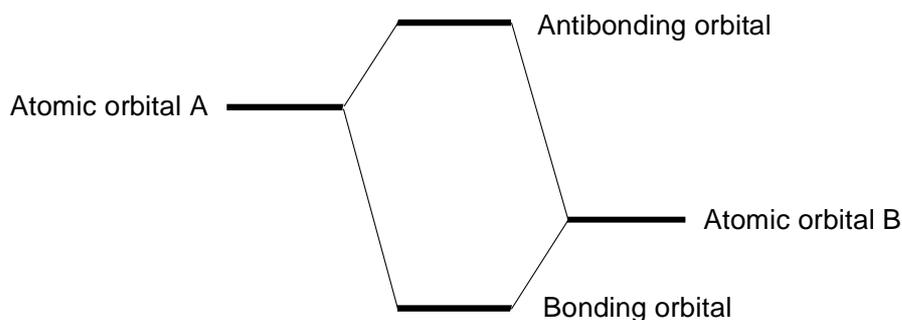

Fig. 2.15 Construction of molecular orbitals.

pi(π) orbitals according to the orbital character. A sigma orbital has rotation symmetry around the bond axis, and a pi orbital has a nodal plane . Therefore, sigma bonds are formed by the overlap of *s-s, p-p, s-d, p-d*, and *d-d* orbitals (Fig. 2.16) and pi bonds the overlap of *p-p, p-d*, and *d-d* orbitals (Fig. 2.17).

Bonding σ orbital   Antibonding σ∗ orbital
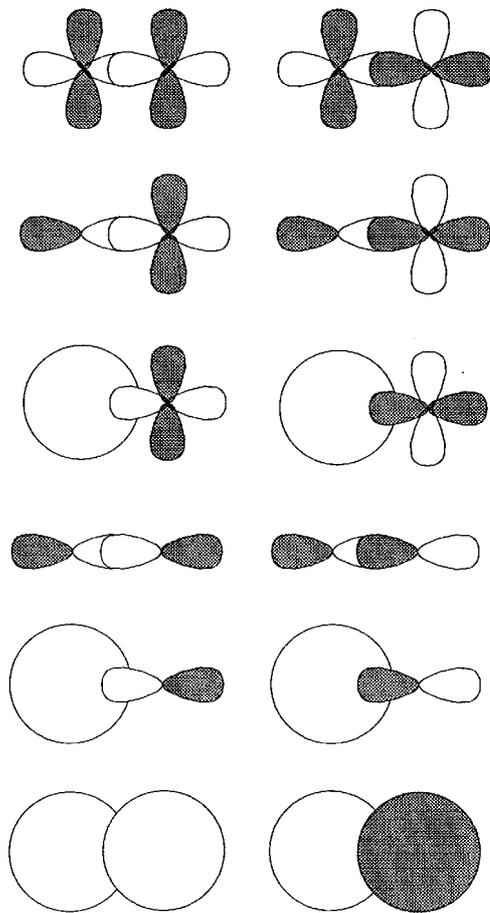
Fig. 2.16 The σ molecular orbitals.

Bonding π orbitals   Antibonding π* orbitals
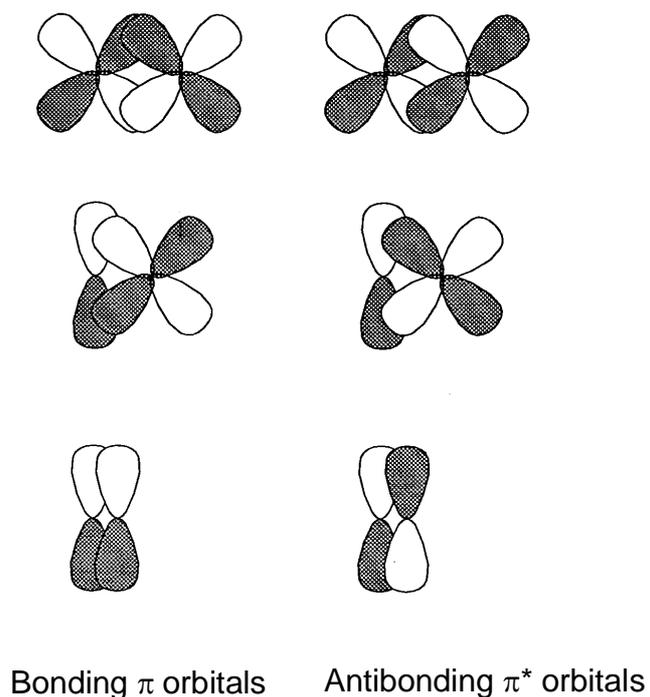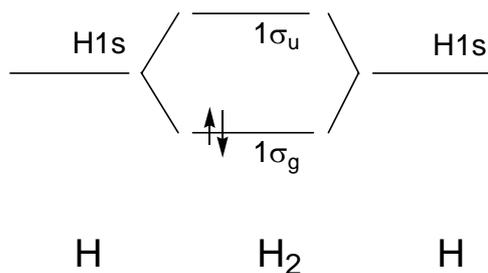
Fig. 2.17 The π molecular orbitals.

When the wave functions of two atoms are set to ϕ_A and ϕ_B, a molecular orbital is a linear combination of the atomic orbitals (LCAO) expressed as

$$\psi = C_A\phi_A + C_B\phi_B$$

Only the atomic orbitals of the valence electron shell are used in the simplest molecular orbital method. Construction of a molecular orbital is illustrated below for the simplest case of the two-atom molecules. All the levels below the HOMO are occupied by electrons and the levels above the LUMO are empty.

In a hydrogen molecule, H_2, the overlap of the $1s$ orbital of each hydrogen atom forms a bonding orbital σ_g if the lobes have equal sign and an antibonding orbital σ_u if they have opposite signs, and two electrons occupy the bonding orbital σ_g (Fig. 2.18).

Fig. 2.18 The molecular orbitals of H_2. The arrows indicate the electron spins.

In the two-atom molecules of the 2nd period, from lithium Li_2 to fluorine F_2, if the z axis is set as a bond axis, $1\sigma_g$ and $1\sigma_u$ are formed by the overlap of $2s$ orbital of each atom and $2\sigma_g$ and $2\sigma_u$ from $2p_z$ orbitals and $1\pi_u$ and $1\pi_g$ from $2p_x$, and $2p_y$. The orbital energy levels for the molecules from Li_2 to N_2 are ordered as $1\sigma_g < 1\sigma_u < 1\pi_u < 2\sigma_g < 1\pi_g < 2\sigma_u$ and electrons occupy the levels sequentially from the bottom. The example of an N_2 molecule with ten valence electrons is shown in Fig. 2.19. Since the ordering of orbitals is somewhat different in O_2 and F_2, in which the $2\sigma_g$ orbital comes under that of $1\pi_u$, the molecular orbital of the oxygen molecule, O_2, is illustrated in Fig. 2.20. The 11th and 12th electrons among the 12 valence electrons occupy the doubly degenerate $1\pi_g$ orbital in the ground state and they have parallel spins under **Hund's rule** and hence an oxygen molecule has two unpaired electrons.
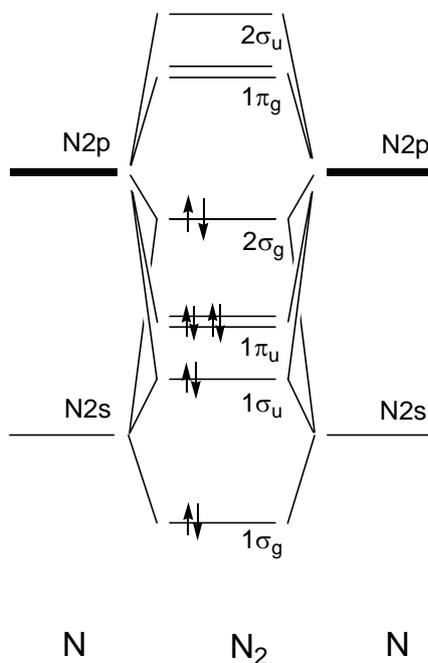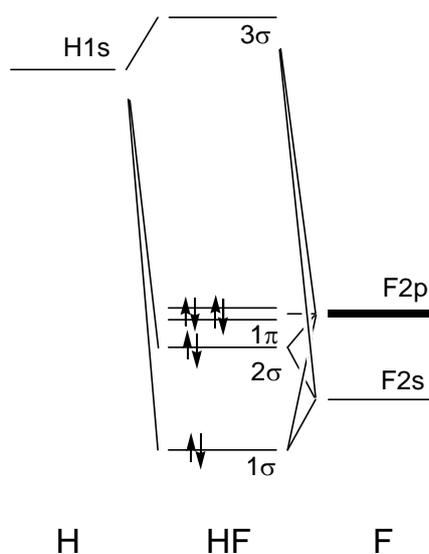

Fig. 2.19 Molecular orbitals of N_2.
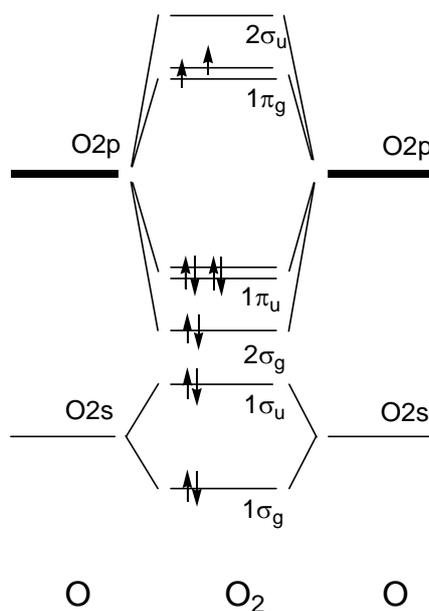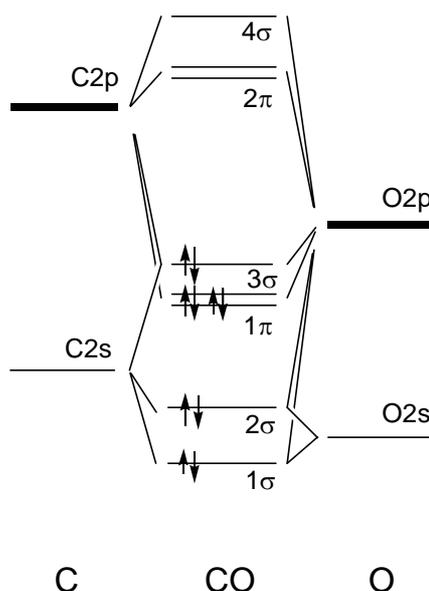
Fig. 2.20 Molecular orbitals of O_2.

The molecular orbitals of two different atoms are formed by the overlap of atomic orbitals with different energy levels. The energy level of the orbital of the atom with larger electronegativity generally is lower, and the molecular orbitals are more characteristic of the atomic orbital with the nearer energy level. Therefore, the bonding orbitals have the character of the atom with the larger electronegativity, and the antibonding orbitals that of the atom with the smaller electronegativity.

For example, five molecular orbitals in hydrogen fluoride, HF, are formed from the $1s$ orbital of hydrogen and the $2s$ and $2p$ orbitals of fluorine, as shown in Fig. 2.21. The bonding 1σ orbital has the $2s$ character of fluorine, and the antibonding 3σ orbital the $1s$ character of hydrogen. Since hydrogen has only one $1s$ orbital, the overlap with the $2p$ orbital of fluorine with π character is not effective, and the fluorine $2p$ orbital becomes a nonbonding orbital. Since HF has eight valence electrons, this nonbonding orbital is the HOMO.

Fig. 2.21 Molecular orbitals of HF.

In carbon monoxide, CO, carbon and oxygen have $2s$ and $2p$ orbitals resulting in both sigma and pi bonds, and a triple bond is formed between the atoms. Although 8 molecular orbitals in this case are qualitatively the same as those of the isoelectronic nitrogen molecule N_2 and 10 electrons occupy the orbital up to 3σ, the energy level of each orbital differs from that of the nitrogen molecule. The bonding 1σ orbital has the $2s$ character of oxygen because of its larger electronegativity, and the bonding 1π orbital also has the $2p$ character of oxygen. The antibonding 2π and 4σ orbitals have the $2p$ character of carbon (Fig. 2.22).

Fig. 2.22 Molecular orbitals of CO.

The bond order between atoms is a half of the number of electrons in the bonding orbitals minus those of the antibonding orbitals. For example, in N_2 or CO, it is equal to $1/2(8-2)$ = 3 and is consistent with the Lewis structure.

Exercise2.5 Why are the atomic orbitals of oxygen atom in the molecular orbital diagram of carbon monoxide, CO, lower than those of carbon?

[Answer] It is because the electronegativity of oxygen is larger than that of carbon.

Problem

2.1 Using the Pauling equation, calculate the electronegativity of chlorine from the bond energies of the hydrogen molecule H_2 (432 kJmol^{-1}), chlorine molecule Cl_2 (239 kJmol^{-1}), and hydrogen chloride HCl molecule (428 kJmol^{-1}) and electronegativity of hydrogen ($\chi = 2.1$).

2.2 Why are the energy levels $\sigma_g < \sigma_u$ in the orbitals of sigma character and $\pi_u < \pi_g$ in those of pi character in the molecular orbital diagram of N_2 or O_2?

Great theory and evaluation

Lewis' valence electron theory proposes that a covalent bond is formed with an electron pair and that there are eight valence electrons around each atom . This is a very important concept with which we understand the bonds between the main group elements. However, the theory was not held in high enough regard for a Nobel prize to be awarded to Lewis. One of the reasons of this disregard seems to be that chemists in the United States, Lewis' homeland, ignored his theory at first, and that a Nobel prize laureate, Langmuir, extended Lewis's theory, which was later known as the Lewis-Langmuir theory. N. Bohr, the eminent physicist who had great influence on the Nobel prize selection, evaluated Langmuir's adsorption theory more highly, which suggests that physicists considered Lewis` theory too simplistic.

There is a similar story about the transition state theory of H. Eyring. Physicists and theoretical chemists, who liked mathematical treatment of chemical phenomena, thought Eyring`s theory too unsophisticated. For this reason, the most important concept in chemical kinetics was not considered for a Nobel prize. It is an episode in the history of chemistry which reminds us of the comment of R. Hoffmann, who pointed out that simple concepts are more important than deceptively complicated mathematical theories.