2.14 Non-bonding electron effects

Two types of non-bonding electrons 電子 more diffuse,在 M-X 軸向貢獻低(軌域與軸向重疊度低):
d electrons in the transition metal compounds and the s^2 pair of electrons in the heavy p-block element compounds in low oxidation states.

a) d-electron effects

In transition metal compounds, the majority of the d electrons do not take part in bond formation but do influence the coordination and are responsible for properties such as magnetism.

i) Crystal field splitting of energy levels

In an octahedral environment, the five d orbitals are not degenerate but split into two groups: t_{2g} of lower energy and e_g of higher energy (Fig. 2.8a).
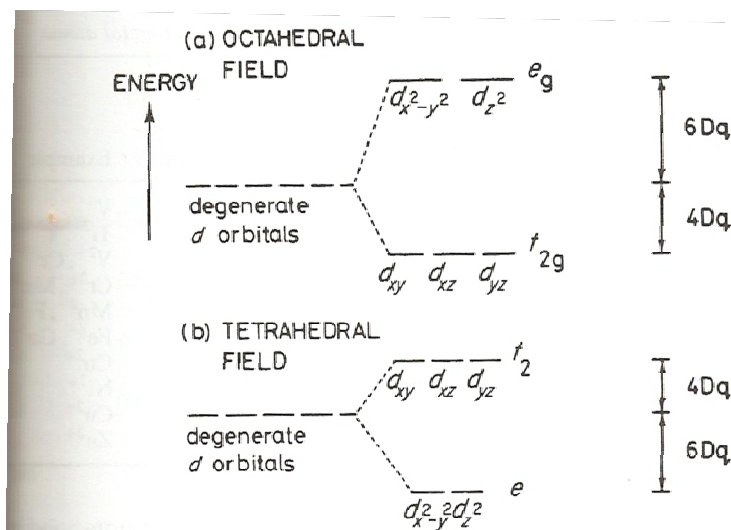

Fig. 2.8   Splitting of d energy levels in (a) an octahedral and (b) a tetrahedral field

According to Hund's rule of maximum multiplicity, electrons occupy orbitals singly if possible. Low spin (LS) and high spin (HS) states for d^4 to d^7 atoms or ions (Fig. 2.9 for a d^7 ion). The energy required to place an

electron in e_g, Δ, for multiplicity has to be balanced against the repulsive energy (pairing energy), P, for two electrons in the t_{2g}.

Fig. 2.9 Low and high spin states for a d^7 transition metal ion in an octahedral environment
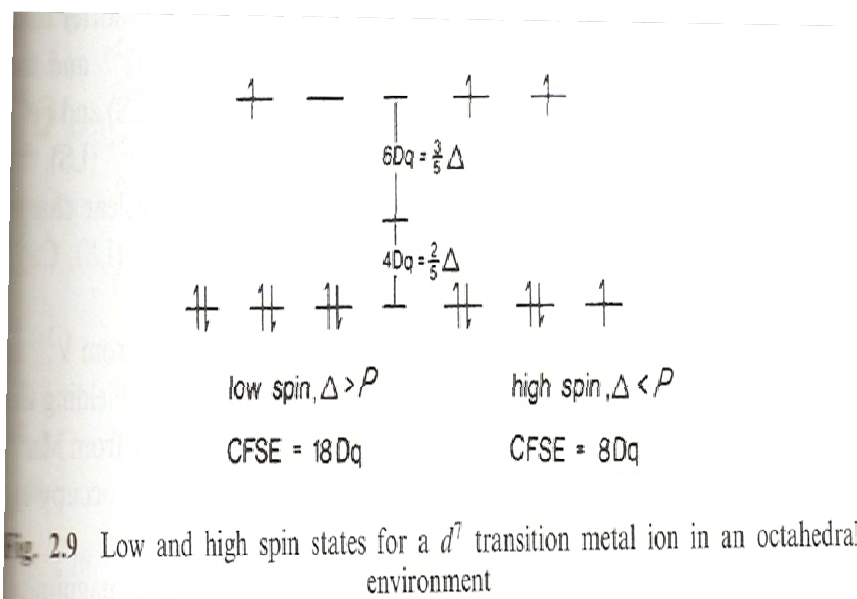
The magnitude of Δ depends on the bonding anions. For weak field anions, Δ is small and HS occurs, and vice versa for strong fields. Also, generally $\Delta(5d) > \Delta(4d) > \Delta(3d)$. HS is rarely observed in the 4d and 5d series. Table 2.13 gives possible spin configurations.

Table 2.13 d-electron configurations in octahedrally coordinated metal atoms

Number of electrons	Low spin, $\Delta > P$ t_{2g}	e_g	High spin, $\Delta < P$ t_{2g}	e_g	Gain in orbital energy for low spin	Example
1	↑		↑			V^{4+}
2	↑ ↑		↑ ↑			Ti^{2+}, V^{3+}
3	↑ ↑ ↑		↑ ↑ ↑			V^{2+}, Cr^{3+}
4	↑↓ ↑ ↑		↑ ↑ ↑	↑	Δ	Cr^{2+}, Mn^{3+}
5	↑↓ ↑↓ ↑		↑ ↑ ↑	↑ ↑	2Δ	Mn^{2+}, Fe^{3+}
6	↑↓ ↑↓ ↑↓		↑↓ ↑ ↑	↑ ↑	2Δ	Fe^{2+}, Co^{3+}
7	↑↓ ↑↓ ↑↓	↑	↑↓ ↑↓ ↑	↑ ↑	Δ	Co^{2+}
8	↑↓ ↑↓ ↑↓	↑ ↑	↑↓ ↑↓ ↑↓	↑ ↑		Ni^{2+}
9	↑↓ ↑↓ ↑↓	↑↓ ↑	↑↓ ↑↓ ↑↓	↑↓ ↑		Cu^{2+}
10	↑↓ ↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓		Zn^{2+}

Fig. 2.10a shows the radii of octahedrally coordinated divalent transition metal ions.

*First trend, Ca^{2+}, Mn^{2+}(HS) and Zn^{2+} by dashed line: a decrease in radius as the d shell is filled. The distribution of d electron is spherically symmetrical because the d orbitals are either empty(Ca), singly occupied (Mn) or doubly occupied (Zn). [For Mn^{2+},3(4Dq)=2(6Dq), no split] Poor shielding of the nuclear charge by d electrons results in a contraction with increasing atomic number (a greater nuclear charge is experienced by the bonding electrons).

*For d^1 to d^4 and d^6 to d^9 by solid line (LS): The d electron distribution is not spherical. The shielding effect is reduced even further and the radii are smaller than expected. (Ex.: Ti^{2+} has the configuration $(t_{2g})^2$ with two t_{2g} orbitals singly occupied.) These non-bonding electrons occupy regions of space that are directed away from the (Ti^{2+}–anion) axes. Ti^{2+}, V^{2+}, Cr^{2+}(LS), Mn^{2+}(LS) and Fe^{2+}(LS) show decreasing trend and all contain only t_{2g} electrons. Beyond Fe^{2+} (LS), the electrons begin to occupy e_g and these do shield the nuclear charge more effectively, so an increasing trend can be seen (Fe^{2+} (LS), Co^{2+} (LS), Ni^{2+}, Cu^{2+} and Zn^{2+}).

*For high spin ions: A different trend is observed. Increasing the atomic number with an increase in e_g electrons results in shielding (V^{2+} to Mn^{2+}). Increasing the atomic number with an increase in t_{2g} electrons results in radius decrease (Mn^{2+} to Ni^{2+}).

Fig. 2.10b: Trivalent transition metal ions show a similar trend.

Fig. 2.8b: A tetrahedral field splits the d orbitals into two groups, but in the opposite manner to an octahedral field; three higher energy orbitals and two lower energy orbitals.
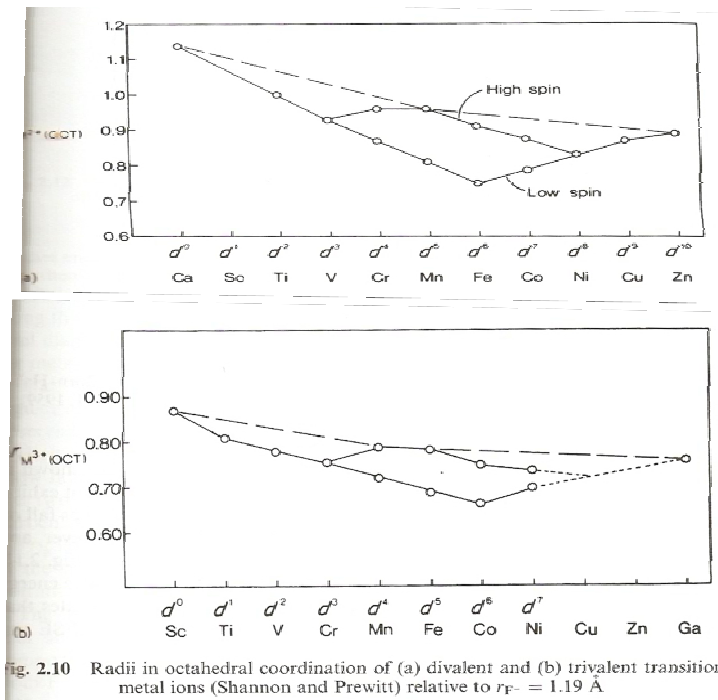
Fig. 2.10   Radii in octahedral coordination of (a) divalent and (b) trivalent transition metal ions (Shannon and Prewitt) relative to $r_{F^-} = 1.19$ Å

Crystal field splitting of d orbitals in transition metal ions may result in crystal field stabilization energies (CFSE) and increased lattice energies of ionic compounds. Ex. CoF_2 has the rutile structure with octahedral Co^{2+} (d^7 HS). Fig. 2.9 : $\Delta = 10$ Dq, the t_{2g} orbitals are stabilized by 4 Dq whereas the e_g orbitals are destabilized by 6 Dq.

LS CFSE = 6×4Dq − 1×6Dq = 18 Dq

HS CFSE = 5×4Dq − 2×6Dq = 8 Dq

Fig. 2.11: Lattice energies of first row transition element difluorides. d^0 (Ca), d^5 (HS Mn), and d^{10} (Zn) do not exhibit CFSE and their lattice energy fall on the lower, dashed curve. Other ions show some degree of CFSE and their lattice energies fall on the upper, solid curve.
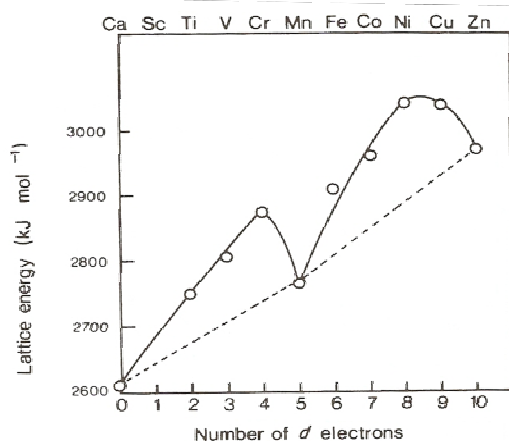
Fig. 2.11 Lattice energies of transition metal difluorides determined from Born–Haber cycle calculations. (Waddington, *Adv. Inorg. Chem. Radiochem.*, 1, 157–221, 1959)

ii) Jahn-Teller distortion

Many transition metal coordination is distorted octahedral and two axial bonds are either shorter or longer than the other four bonds. Jahn-Teller effect is responsible for this in d^9, d^7 (LS) and d^4 (HS), which have odd number of e_g electrons.

Consider the d^9 ion Cu^{2+} in $(t_{2g})^6(e_g)^3$. Since the two e_g levels, d_{z2} and d_{x2-y2}, are occupied unequally, they are no longer degenerate. The e_g orbitals are high energy orbitals since they point directly towards the surrounding ligands. Electrons in the doubly occupied orbitals experience stronger repulsions. This has the effect of lengthening the metal-ligand bonds in the directions of the doubly occupied orbitals.

Fig. 2.12a. If the d_{z2} orbital is doubly occupied, the two metal-ligand bonds along the z axis are longer than the other four bonds. Lengthening leads to a lowering of energy of the d_{z2} orbital by $\frac{1}{2}\delta_2$ relative to the regular e_g. The distorted structure becomes the observed ground state.
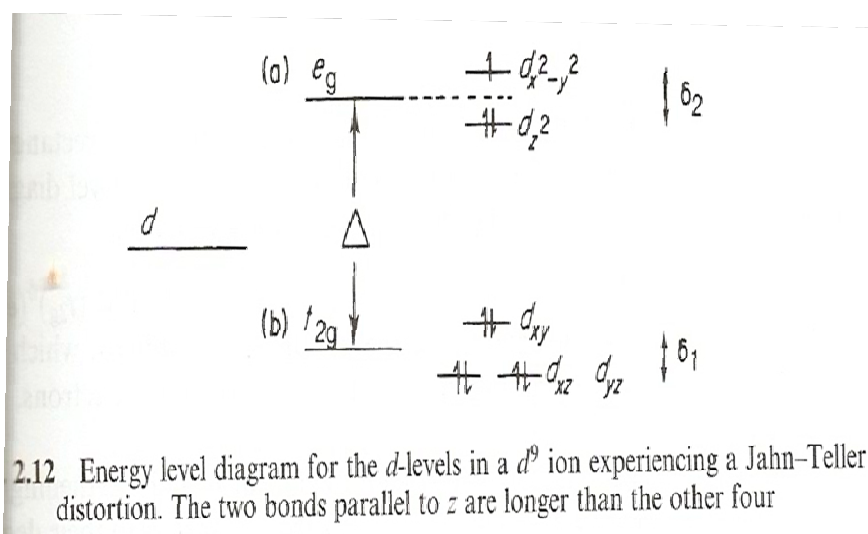
2.12 Energy level diagram for the d-levels in a d^9 ion experiencing a Jahn–Teller distortion. The two bonds parallel to z are longer than the other four

Fig. 2.12b. The degeneracy of the t_{2g} levels may also be removed by the Jahn-Teller effect, but the magnitude of the splitting, δ_1, is small. The effect is unimportant.

The Jahn-Teller distortions in Cu^{2+} and Cr^{2+} are obvious. For the first-row divalent transition metal ions, their oxides, MO, are all in regular rock salt except CuO and CrO. The fluoride series MF_2, all have the regular rutile structure apart from CrF_2 and CuF_2.

iii) Square planar coordination

The d^8 ions, Ni^{2+}, Pd^{2+}, Pt^{2+}, commomly have this type of coordination. Consider such ions in two types of fields:

(a) octahedral field

A d^8 ion in an octahedral field is $(t_{2g})^6(e_g)^2$. The two e_g electrons singly occupy the d_{z2} and d_{x2-y2} orbitals, which are degenerate, and the resulting compounds, with unpaired electrons, are paramagnetic.

(b) distorted octahedral field

Consider lengthening the two bonds along the z axis; i.e. the two electrons doubly occupies the d_{z2} orbital, which becomes stabilized by an amount of $\frac{1}{2}\delta_2$. For small elongations, (pairing energy)$P > \delta_{2(2\,e^-)}$, no gain instability leads no distortion. With increasing elongation, $P < \delta_2$ and the d_{z2} becomes stabilized. This is the preferred ground state for a d^8 ion. The distortion is sufficiently large that the coordination becomes square planar, such as PdO.

Because the 4d and 5d orbital are more diffuse and extend to greater radial distances from the nucleus, square planar coordination is more common with 4d and 5d. The magnitude of the crystal (or ligand) field splitting (Δ,δ) caused by a ligand, e.g. O^{2-}, increases in the series 3d < 4d < 5d. NiO has the rock salt structure whereas PdO and PtO both have square planar coordination (no octahedral Pt^{2+} or Au^{3+} compounds are known)

iv) Tetrahedral coordination

The magnitude of the splitting, Δ, is generally less in a tetrahedral field since none of the d orbitals pointing directly towards the four ligands. The d_{xy}, d_{xz} and d_{yz} orbitals are somewhat closer to the ligands than are the other two (Fig. 2.13). Details of Jahn-Teller distortions have not been well studied.

v) Tetrahedral vs. octahedral coordination

Most transition metal ions prefer octahedral or distorted octahedral coordination because of their large CFSE in octahedral sites.
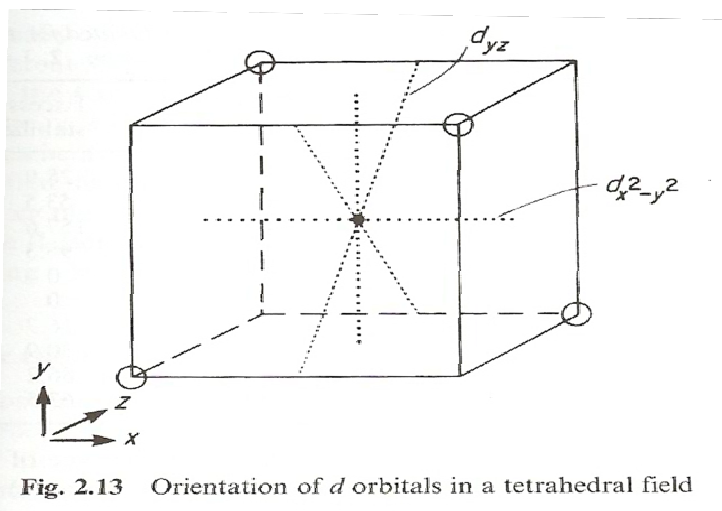
Fig. 2.13 Orientation of d orbitals in a tetrahedral field

Example:

Cr^{3+}, d^3 $(t_{2g})^3$ CFSE = $1.2\Delta^{oct}$ octahedral; CFSE = $0.8\Delta^{tet}$ tetrahedral

Cu^{2+}, d^9 $(t_{2g})^6(e_g)^3$ CFSE = $0.6\Delta^{oct}$ octahedral; CFSE = $0.4\Delta^{tet}$ tetrahedral

In addition, $\Delta^{tet} \cong 0.4\Delta^{oct}$

Table 2.14 shows the CFSE for oxides

HS d^5, d^0 and d^{10} have no preference. Cr^{3+}, Ni^{2+} and Mn^{3+} show strong preference for octahedral coordination.

Table 2.14 *Crystal field stabilization energies* $(kJ\ mol^{-1})$ *estimated for transition metal oxides.* (Data from Dunitz and Orgel, *Adv. Inorg Radiochem.*, **2**, 1–60, 1960)

Ion		Octahedral stabilization	Tetrahedral stabilization	Excess octahedral stabilization
Ti^{3+}	d^1	87.4	58.5	28.9
V^{3+}	d^2	160.1	106.6	53.5
Cr^{3+}	d^3	224.5	66.9	157.6
Mn^{3+}	d^4	135.4	40.1	95.3
Fe^{3+}	d^5	0	0	0
Mn^{2+}	d^5	0	0	0
Fe^{2+}	d^6	49.7	33.0	16.7
Co^{2+}	d^7	92.8	61.9	30.9
Ni^{2+}	d^8	122.1	35.9	86.2
Cu^{2+}	d^9	90.3	26.8	63.5

Coordination preference affects the structure of <mark>spinel</mark> (AB_2O_4)

(a) A (tet), B(oct) – normal, $\gamma=0$;

(b) A(oct), B(tet,oct) – inverse, $\gamma=1$;

(c) Intermediate between normal and inverse.

$MgAl_2O_4$ (type2,3) tends to be normal; $TiMg_2O_4$ (type4,2) to be inverse. CFSE may change these preference.
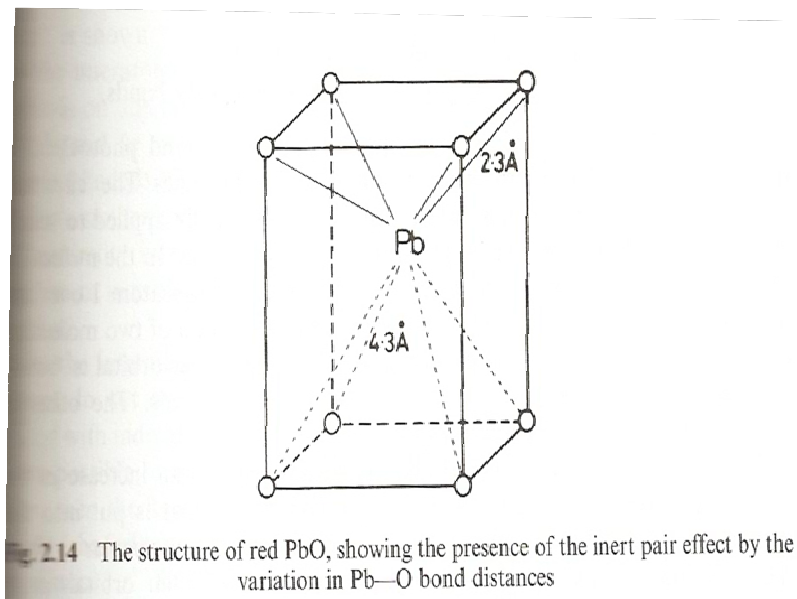

Examples:

(a). All chromate spinels are normal with octahedral Cr^{3+}. In $NiCr_2O_4$, Ni^{2+} are forced into tetrahedral

(b). Co_3O_4 ($\equiv CoO\cdot Co_2O_3$) is normal because LS Co^{3+} gains more octahedral CFSE than Co^{2+} loses in tetrahedral (Tables 2.13, 14). Mn_3O_4 is also normal (Table 2.14). Magnetite (磁鐵礦), Fe_3O_4, is inverse because Fe^{3+} has no preference and Fe^{2+} prefers octahedral (Tables 2.13, 14).

(c). Cubic spinel sometimes shows tetragonal distortions. $CuFe_2O_4$ (tetragonal with c/a = 1.06) is an inverse with octahedral Cu^{2+} and Jahn-Teller effect distorts CuO_6 so that two Cu−O bonds along z are longer. $CuCr_2O_4$ (c/a = 0.9) is normal and CuO_4 tetrahedra are flattened along z due to Jahn-Teller, thereby causing a shortened c axis.

b) Inert pair effect

The heavy, post-transition elements, especially Tl, Sn, Pb, Sb and Bi, commonly exhibit a valence that is two less than the group valence; e.g. Sn^{2+} and Pb^{2+} in the Group IV. This is the inert pair effect leading to a structural distortion. Pb^{2+} has the configuration: (Xe core) $4f^{14}5d^{10}6s^2$, and the $6s^2$ pair is 'stereochemically active' and sticks out to one side of the Pb^{2+} (i.e. not spherical).

Sometimes, the lone pair comes between the metal ion and its anionic neighbors. PbO has a structure that is a tetragonal distortion of the CsCl (Fig. 2.14;Fig. 1.31 for CsCl). Four oxygens are 2.3Å from the Pb^{2+} (reasonable length), but the other four are at 4.3Å.

Fig. 2.14   The structure of red PbO, showing the presence of the inert pair effect by the variation in Pb—O bond distances

SnS has a distorted rock salt structure. The SnS_6 octahedra are distorted along a [111] direction such that 2.64Å for three sulphurs on one side and 3.31Å for the other three because of the repellence of the lone pair.

TlI has five-coordinated structure, in which the lone pair takes the place of one corner anion of "TlI_6", which is missing.

2.15.   Metallic bonding and band theory

Metallic structures and bonding are characterized by <mark>delocalized valence electrons</mark> and these are responsible for the high electrical conductivity of metals. The band theory of solids is used to account for electron delocalization.

In a metal such as Al, the inner core electrons (1s, 2s and 2p) are localized in discrete orbitals on the individual Al atoms. However, the 3s and 3p electrons that form the valence shell occupy levels that are delocalized <mark>over the entire metal crystal</mark>. There must be an enormous number of such levels which are separated from each other by very small energy differences. Thus in a crystal of Al that contains N atoms, the result is a delocalized 3s valence band of N closely spaced energy levels and a delocalized 3p valence band.

The differences between metals, semiconductors and insulators depend on:
(a) the band structure
(b) the valence bands are full or partly full
(c) the energy gap between full and empty bands

Two theoretical approaches for the band theory.
"Chemical approach"—In diatomic molecules, an atomic orbital from atom 1overlaps with that on atom 2, resulting in the formation of two molecular orbitals that are delocalized over both atoms: 'bonding' orbital with lower energy than that of the atomic orbitals; 'antibonding' with higher energy, Fig. 2.15.
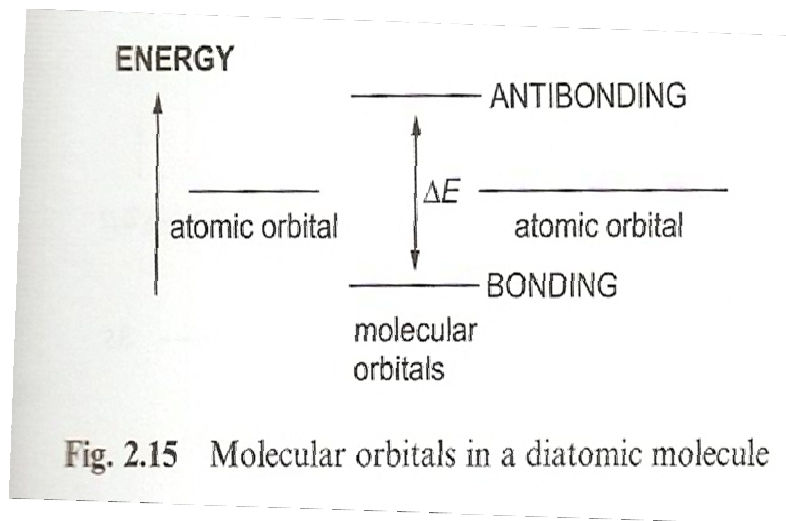
Fig. 2.15 Molecular orbitals in a diatomic molecule

Extension of this approach to larger molecules leads to an increase in the number of molecular orbitals (Fig. 2.16). As the number of molecular orbitals increases, the average energy gap between adjacent molecular orbitals must decrease until essentially, a continuum of energy levels occurs. In a crystal, the delocalized orbitals are referred to as energy levels or energy states.
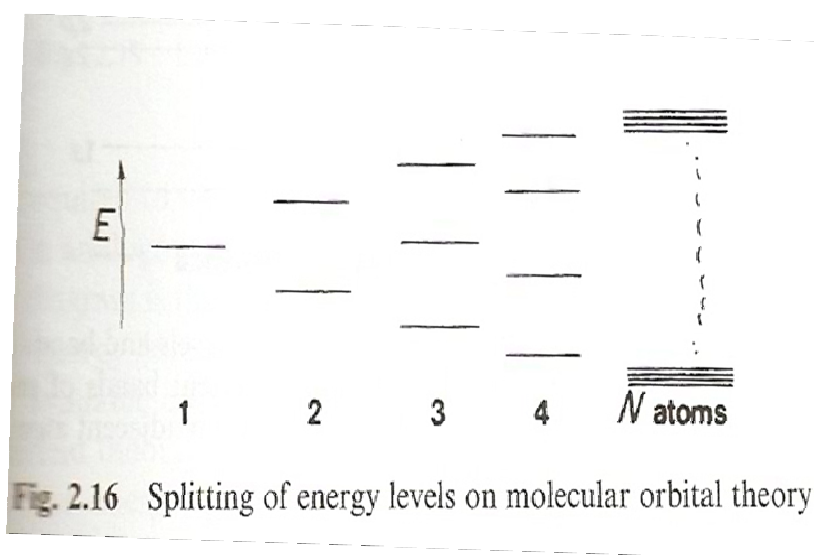

Fig. 2.16 Splitting of energy levels on molecular orbital theory

Fig. 2.17 shows the band structure of Na. The width of a particular band is related to the interatomic separation. At the observed interatomic separation, r_0, the 3s and 3p orbitals on adjacent atoms overlap to form broad 3s and 3p bands (shaded). The upper levels of 3s (B-C) have similar energies to the lower levels of the 3p band. There is no discontinuity in enery between 3s and 3p bands. Such overlap of bands is important for the metallic properties of the alkaline earth elements.
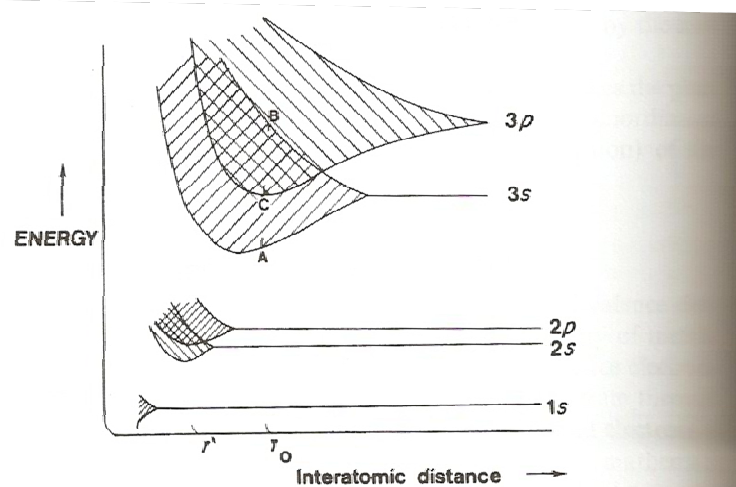

Fig. 2.17   Effect of interatomic spacing on atomic energy levels and bands for sodium calculated using tight binding theory. Shaded areas represent bands of energy levels formed by significant overlap of atomic orbitals on adjacent atoms

At r_0, the 1s, 2s and 2p orbitals do not overlap and remain as discrete atomic orbitals. If the crystal is compressed from r_0 to r' (if possible), the the 2s and 2p orbitals would also overlap to form bands. The 1s would still be present as discrete levels at r'. It has been calculated that hydrogen would become metallic at a pressure $> 10^6$ atm.

Na ($1s^2 2s^2 2p^6 3s^1$) has one valence electron per atom. Since the 3s and 3p bands overlap, the valence electrons are distributed over the lower levels of both the 3s and 3p bands.

'Physical approach'—band theory to consider the energy and wave-length of electrons in a solid. The early *free electron theory* of Sommerfeld regarded metal as a potential well, inside which the more loosely held valence electrons are free to move. The energy levels are quantized and the levels are filled from the bottom of the well with two electrons per level. The highest filled level at T = 0 K is known as the Fermi level, with the corresponding Fermi energy, E_F (Fig. 2.18). The work function, ϕ, is the energy required to remove the uppermost valence electrons from the potential well. It is analogous to the ionization potential of an isolated atom.
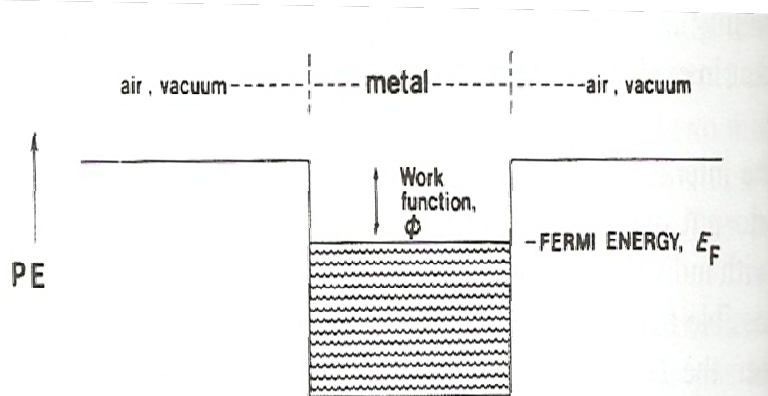

Fig. 2.18 Free electron theory of a metal; electrons in a potential well

Fig. 2.19 shows the density of states diagram: the no. of energy levels (N(E)) vs. energy (E). N(E) increases steadily with E in the Sommerfeld theory. The energy difference between adjacent levels (quantized) is so small that a continuum occurs. At real temperatures some states above E_F are occupied due to thermal promotion and others below E_F are vacant.
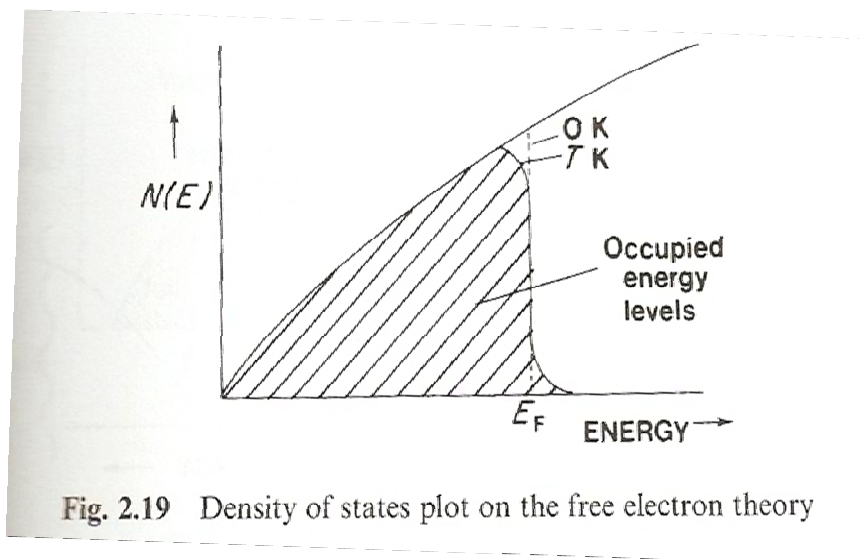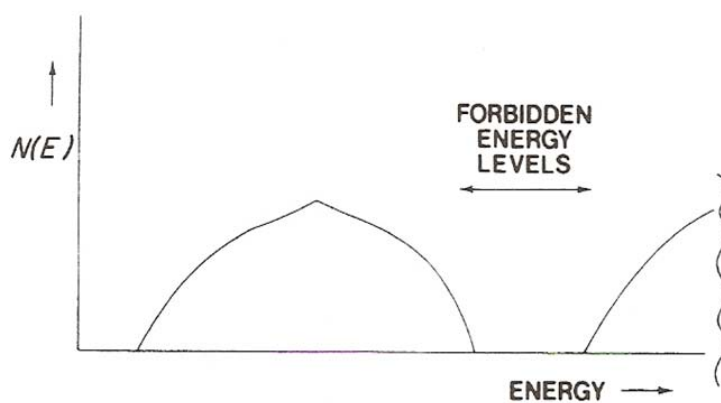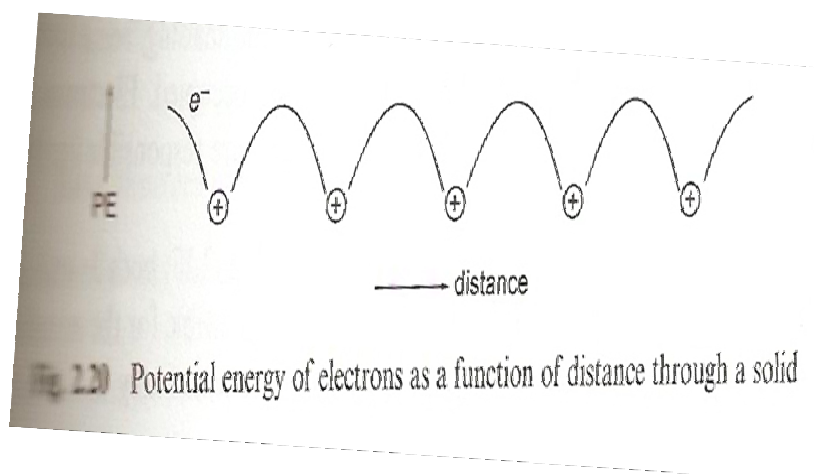
Fig. 2.19 Density of states plot on the free electron theory

The high electrical conductivity of metals is due to the drift of those electrons in half-occupied (singly occupied) states close to E_F. The promotion of an electron from a full level below E_F to an empty one above E_F gives rise to two mobile electrons.

The free electron theory is an oversimplication but is a useful starting model. The potential inside the crystal or well should be regarded as periodic (Fig. 2.20). The potential energy of the electrons passes through minimum at the positions of the nuclei (regularly repeated) and passes through a maximum midway between adjacent nuclei. Solution of Schrödinger equation shows that an uninterrupted continuum of energy level does not occur but, instead, only certain bands of energies are permitted for the electrons (there are forbidden energies), as show in Fig. 2.21.

Fig. 2.20 Potential energy of electrons as a function of distance through a solid

Fig. 2.21 Density of states on band theory

Both the chemical and physical approaches obtain a model with bands of levels for valence electrons. In some materials, overlap of different bands occurs. In others, a forbidden gap exists between energy bands.

Electronic transition between different levels may be observed by experiments using X-ray emission and absorption (visible and UV

spectroscopy also useful). X-ray emission spectra of solids contain peaks or bands of various widths. Transitions between inner levels appear as sharp peaks, indicating discrete atomic orbitals of these levels. Transitions involving valence shell electrons may give broad spectral peaks, indicating a broad distribution of energies for valence electrons (i.e. located in bands).

a) Band structure of metals

In metals, the highest occupied band, the valence band, is only partly full (Fig. 2.22). Electrons in singly occupied states close to E_F are able to move and are responsible for the high conductivity of metals.
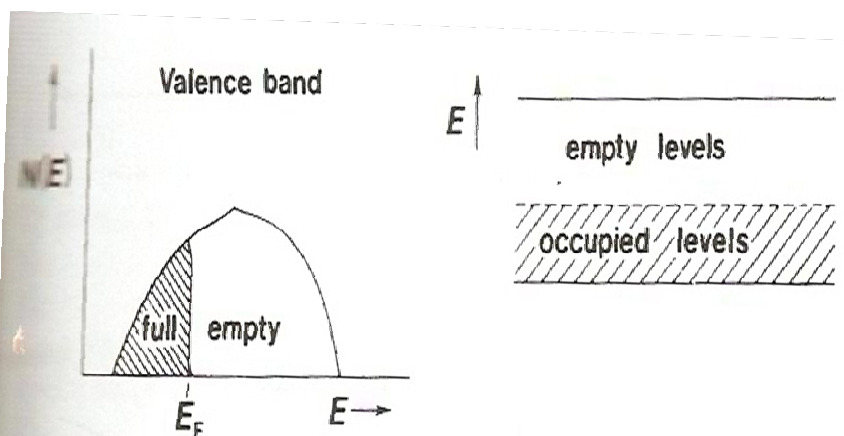

Fig. 2.22 Band structure of a metal

Overlap of bands is responsible for the metallic properties of the alkaline earth metals as shown for Be in Fig. 2.23. It has overlapping 2s, 2p bands, both of which are only partly full. If 2s and 2p bands did not overlap, then the 2s band would be full and Be would not be metallic.
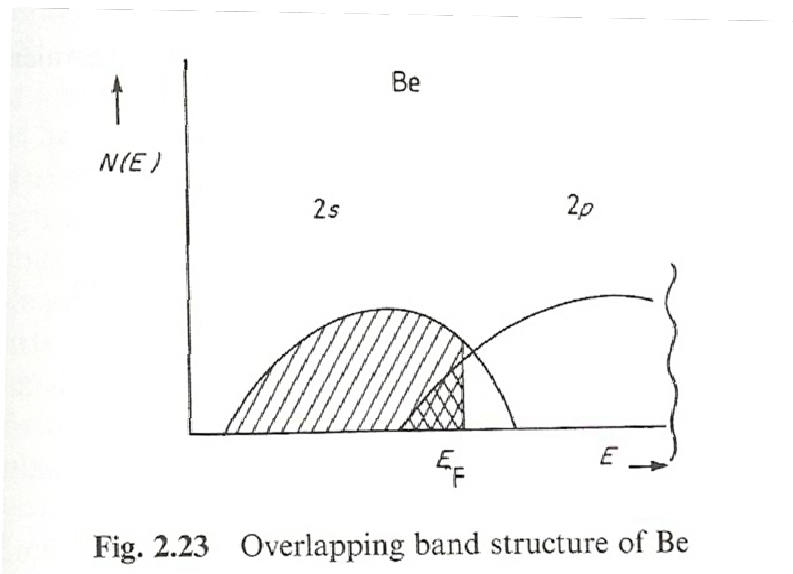
Fig. 2.23   Overlapping band structure of Be

b) Band structure of insulators

The valence band in insulators is full. It is separated by a large, forbidden gap from the next energy band, which is empty (Fig. 2.24). Diamond is an excellent insulator with a band gap of ~6 eV. Few electrons from the valence band have sufficient thermal energy to be promoted into the empty band above. Hence the conductivity is negligibly small.
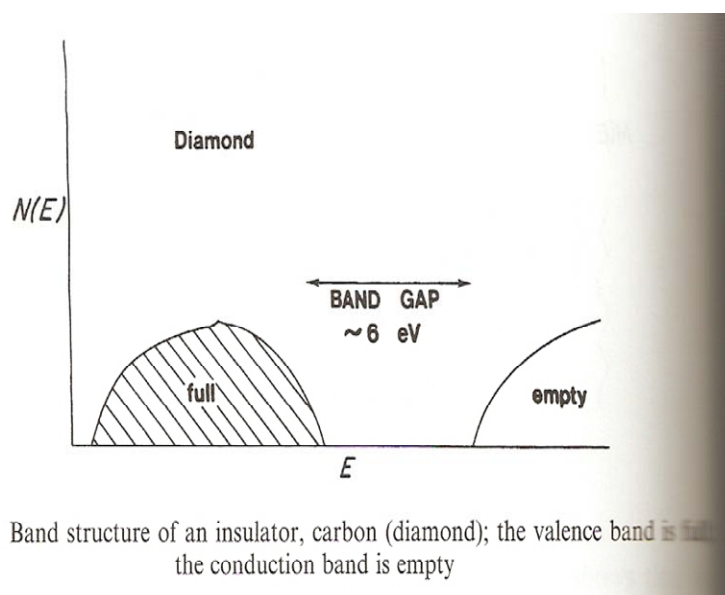

Fig. 2.24   Band structure of an insulator, carbon (diamond); the valence band is full the conduction band is empty

c) Band structure of semiconductors: silicon

Semiconductors have a similar band structure to insulators but the band gap is not very large, usually 0.5 to 3.0 eV. Two types of conduction mechanism may be distinguished in semiconductors, Fig. 2.25. Any electrons that are promoted into an upper, empty band (conduction band), are regarded as negative charge carrier. The valence electron levels that are left behind in the valence band may be regarded as positive holes. Effectively, positive holes move in the opposite direction to electrons under an applied potential.
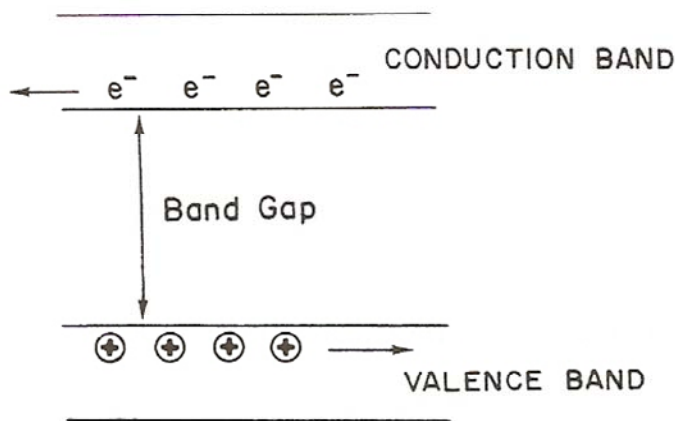

Fig. 2.25 Positive and negative charge carriers

Intrinsic semiconductors are pure materials whose band structure is as shown in Fig. 2.25. The number of electrons in conduction band is governed by the band gap energy and the temperature. Pure Si is an intrinsic semiconductor. Table 2.16 shows the band gap of Group IV elements.

Table 2.16   *Band gaps of Group IV elements*

Element	Band gap (eV)	Type of material
Diamond, C	6.0	Insulator
Si	1.1	Semiconductor
Ge	0.7	Semiconductor
Grey Sn ($>13°C$)	0.1	Semiconductor
White Sn ($<13°C$)	0	Metal
Pb	0	Metal

The band structure of Si is quite different to those of Na and Mg (3s, 3p overlap to give broad bands). Si contains two bands separated by a forbidden gap. The lower band contains four electrons per Si and is full. The separated 3s and 3p cannot be the explanation (3s contains only two electrons).

The structure Na is bcc with a CN of 8 whereas Si is fcc with a CN of 4. Each Si forms four equal bonds arranged tetrahedrally; these bonds can be regarded as sp^3 hybridized. Each hybrid orbital overlaps a similar one on an adjacent Si to form a pair of molecular orbitals: σ (bonding) and σ* (antibonding). Each can contain two electrons, one from each Si. The σ orbitals overlap to form a σ band (the valence band), and the σ* to form the conduction band. The σ band is full since it contains four electrons per Si. The σ* band is empty.

d) Band structure of inorganic solids

Many inorganic solids can also be treated profitably using band theory, whether or not they are regarded as electrical conductors. Band theory compliments the structural information obtained with ionic/covalent models. Most inorganic materials are more complex structurally than metals and semiconducting elements.

i) III−V, II−VI and I−VII compounds

III−V compounds (such as GaP) are closely related with Group IV (such as Si). The valence shells are isoelectric with Group IV elements.

Let us consider more extreme cases with I−VII NaCl or II−VI MgO. The bonding is predominantly ionic. They are white, insulating solids. Addition of dopants tends to produce ionic rather than electronic conductivity. For NaCl

$$Na^+: \quad 1s^2 2s^2 2p^6$$

$$Cl^-: \quad 1s^2 2s^2 2p^6 3s^2 3p^6$$
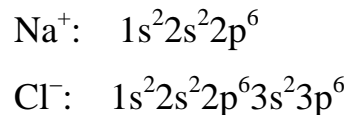
The 3s, 3p valence shell of Cl^- is full and that of Na^+ is empty. The 3p orbitals on Cl^- ions may overlap to form a narrow 3p valence band which is full. The 3s, 3p orbitals on Na^+ ions may also overlap to form a conduction band, which is empty under normal conditions since the band gap is ~ 7 eV (like Fig. 2.24, but the valence band is composed of anion orbitals and the conduction band is the cation orbitals). Any promotion of electrons from the valence band to conduction band may be regarded as back transfer of charge from Cl^- to Na^+.

The band gap and the difference in electronegativity are correlated. A large electronegativity difference favors ionic bonding and back transfer

of charge from anion to cation is difficult, $\therefore$ ionic compounds have large band gaps. Table 2.17 shows the band gaps of some inorganic compounds.

Table 2.17 *Band gaps (eV) of some inorganic solids*

I–VII compounds		II–VI compounds		III–V compounds	
LiF	11	ZnO	3.4	AlP	3.0
LiCl	9.5	ZnS	3.8	AlAs	2.3
NaF	11.5	ZnSe	2.8	AlSb	1.5
NaCl	8.5	ZnTe	2.4	GaP	2.3
NaBr	7.5	CdO	2.3	GaAs	1.4
KF	11	CdS	2.45	GaSb	0.7
KCl	8.5	CdSe	1.8	InP	1.3
KBr	7.5	CdTe	1.45	InAs	0.3
KI	5.8	PbS	0.37	InSb	0.2
		PbSe	0.27	β-SiC	2.2
		PbTe	0.33	α-SiC	3.1

Some of these values, especially for the alkali halides, are only approximate.

For isoelectronic series ZnSe, GaAs, Ge as the examples, a quantitative relation between band gap and ionicity (Philiips and van Vechten):

$$E_g{}^2 = E_h{}^2 + C^2$$

where E_g is a band gap, E_h the homopolar band gap as in pure Ge, C a charge transfer or ionic energy between A and B atoms. The band gap is made of two components:

a) the gap observed in the absence of any difference in electronegativity between constituent elements

b) the energy associated with the degree of ionic character in the bonds
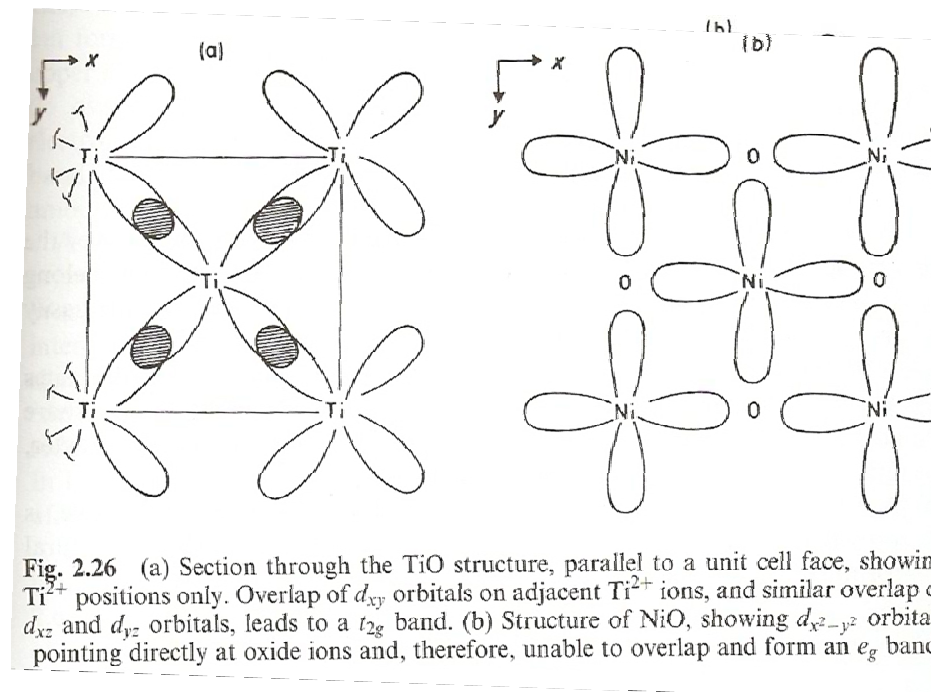
$$\text{Ionicity, } f_i = C^2/E_g{}^2$$

Values of f_i range from zero (C = 0 in a homopolar covalent bond) to unity (C = E_g in a pure ionic bond).

ii) Transition metal compounds

The presence of partly filled metal d orbitals is an influential factor.

a) overlap to give a d band and the material having high conductivity

b) d orbital overlap limited and localized on individual atoms.

For (a), TiO and VO (rock salt) have d orbitals of the type d_{xy}, d_{xz}, d_{yz} overlap strongly (Fig. 2.26a) to form a broad t_{2g} band, which is partly filled. Consequently, TiO and VO have almost metallic conductivity, 10^3 $\Omega^{-1}cm^{-1}$ at 25 °C.

Fig. 2.26   (a) Section through the TiO structure, parallel to a unit cell face, showing Ti^{2+} positions only. Overlap of d_{xy} orbitals on adjacent Ti^{2+} ions, and similar overlap of d_{xz} and d_{yz} orbitals, leads to a t_{2g} band. (b) Structure of NiO, showing $d_{x^2-y^2}$ orbitals pointing directly at oxide ions and, therefore, unable to overlap and form an e_g band

For (b), NiO (rock salt) has pale green color due to internal d–d transitions within individual Ni^{2+} ions. It has a very low conductivity, ~ 10^{-14} $\Omega^{-1}cm^{-1}$ at 25°C. There is no significant overlap of the d orbitals to form a partly filled d band. The t_{2g} band in NiO is full. The two extra electrons in Ni^{2+} are in e_g levels (d_{z2}, d_{x2-y2}), which point directly at the oxide ions (Fig. 2.26b). Becaue of the intervening oxide ions, the e_g orbitals on adjacent Ni^{2+} ions cannot overlap to form a band.

Some guidelines for d band formation being likely to occur if:

a) The formal charge on the cations is small.

b) The cation occurs early in the transition series.

c) The cation is in the second or third transition series.

d) The anion is reasonable electropositive.

Effects a) to c) keep the d orbitals spread out as far as possible and reduce the amount of positive charge felt from the metal ion nucleus. Effect d) is associated with reduced ionicity and band gap.

Examples:

For a), TiO is metallic whereas TiO_2 is an insulator. Cu_2O and MoO_2 are semiconductors whereas CuO and MoO_3 are insulators.

For b), TiO and VO are metallic whereas NiO and CuO are poor semiconductors (後者 t_{2g} full).

For c), Cr_2O_3 is a poor conductor whereas lower oxides of Mo, W are good conductors.

For d), NiO is a poor conductor whereas NiS , $NiSe$, $NiTe$ are good conductors.

Some interesting examples are provided by complex oxides with the spinel structure:

(a) Fe$_3$O$_4$ is almost metallic

$[Fe^{3+}]^{tet}[Fe^{2+}, Fe^{3+}]^{oct}O_4$ inverse spinel

Fe^{2+} and Fe^{3+} are contained in octahedra, which share by their edges.

Consequently, positive holes can migrate easily from Fe^{2+} to Fe^{3+} and hence Fe_3O_4 is a good conductor.

   Mn$_3$O$_4$ is an insulator

$[Mn^{2+}]^{tet}[Mn^{3+}, Mn^{3+}]^{oct}O_4$ normal spinel

The tetrahedral sites, containing Mn^{2+}, share corners with the octahedral

sites containing Mn^{3+}. The distance between Mn^{2+} and Mn^{3+} is greater and electron exchange cannot take place easily.

(b) $LiMn_2O_4$ and LiV_2O_4

$[Li^+]^{tet}[Mn^{3+}, Mn^{4+}]^{oct}O_4$ $\qquad$ $[Li^+]^{tet}[V^{3+}, V^{4+}]^{oct}O_4$

According to guideline b), d orbital overlap is greater for V than for Mn, so $LiMn_2O_4$ is a hopping semiconductor where LiV_2O_4 is metallic.

iii) Fullerenes and graphites

Carbon polymorphs (or allotropes 同素體) and carbon compounds provide very good examples of how bond type can change from covalent, through semiconducting to metallic, depending on the degree of overlap of pπ orbitals on C and the extent of filling of the resulting molecular orbitals or bands.

Early model for C_6H_6 with alternating single and double C−C bonds (Fig. 2. 27a) was followed by delocalization of the π electrons over all 6 C (2.27b). Overlap of p orbitals is greatly assisted by the planarity of C_6H_6, in which the p_z orbital is oriented perpendicular to the plane.

Graphite can be regarded as infinite layers of C_6H_6 (2.27c) in which the π electrons, one for each C, are delocalized over the complete layer. The overlapping p_z orbitals give rise to two band levels, π and π*, with bonding and antibonding characters. This is an extension of the π, π* molecular orbitals in ethene (ethylene) molecule, $CH_2=CH_2$ (2.27d,e), in which the π, π* levels are discrete. In graphite, the π, π* levels form bands (2.27f).

(a)   (b)

(c)   (d)

(e)   (f)
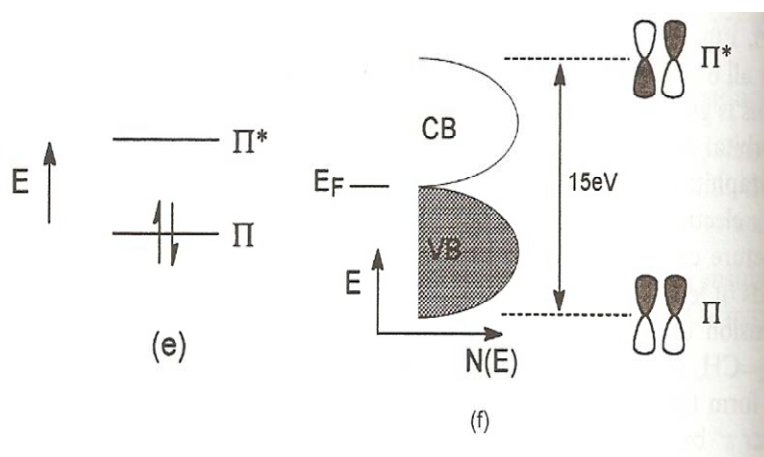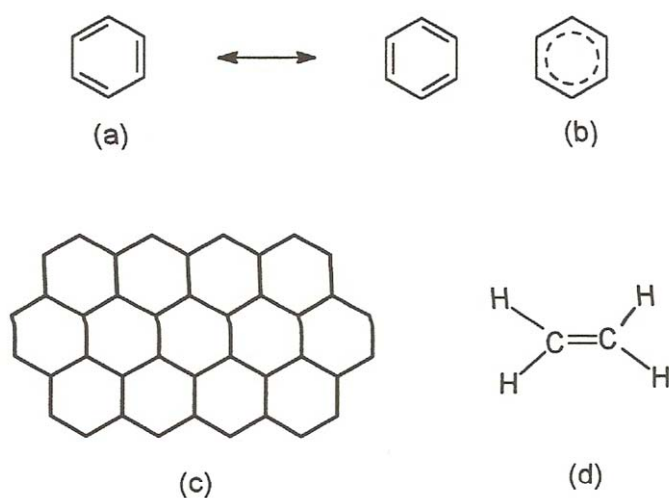
The lower π band (valence) is full and the upper π* band (conduction) is essentially empty. The two bands do not overlap by about 0.04 eV in 3D graphite structure. Consequently, graphite exhibits electronic conductivity (semimetal) and is black, lustrous solid.

The layered crystal structure of graphite, with a large amount of empty space in the van der Waals gap between adjacent layers, makes the

formation of graphite compounds by <mark>intercalation</mark>. In C_8Na and C_8Br (2.27g), electrons are either added to $(C_8^-Na^+)$ or withdrawn from $(C_8^+Br^-)$ the graphite <mark>conduction/valence</mark> bands. Hence Na, as a reducing agent, denotes electrons (2.27h) and may be regarded as a <mark>donor dopant</mark>. Br is an <mark>acceptor dopant</mark> and creates empty electron levels at the top of the valence band.
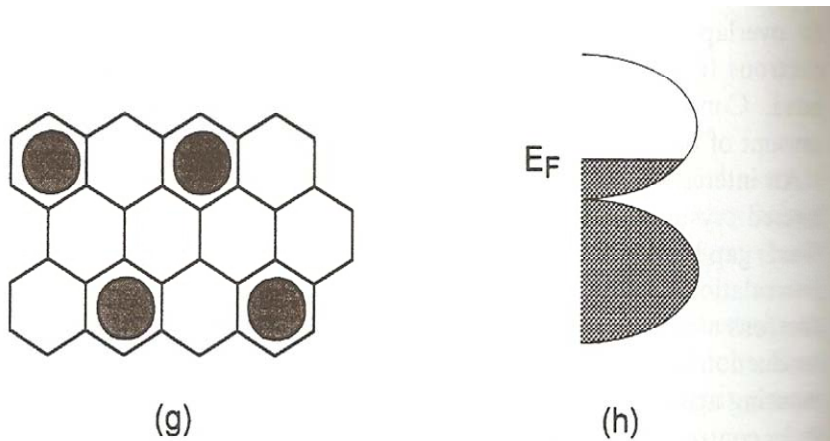

Fig. 2.27 (a) Resonating bond model to explain the structure and properties of benzene, (b) delocalized π electron model for benzene, (c) a layer of graphite, (d) the ethene molecule, (e) molecular orbitals in ethene, (f) band structure of graphite, (g) ordered arrangement of M (e.g. K, Br) between adjacent graphite layers in C_8M, and (h) band structure in C_8Na

Fullerene (C_{60})

The valence and conduction bands are narrower and are separated by a band gap of 2.6 eV (Fig. 2.28), because the delocalized π electron system of C_{60} (curved, not flat) is different. In graphite, 3-coordinated C is sp^2 hybridized, with 120° bond angle and p_z perpendicular to the plane of C rings. In C_{60}, there is some $s-p_z$ mixing in the π orbital. Thus, the C atoms are above the plane of their three C neighbors and the bond angles are 120, 120 and 108°.
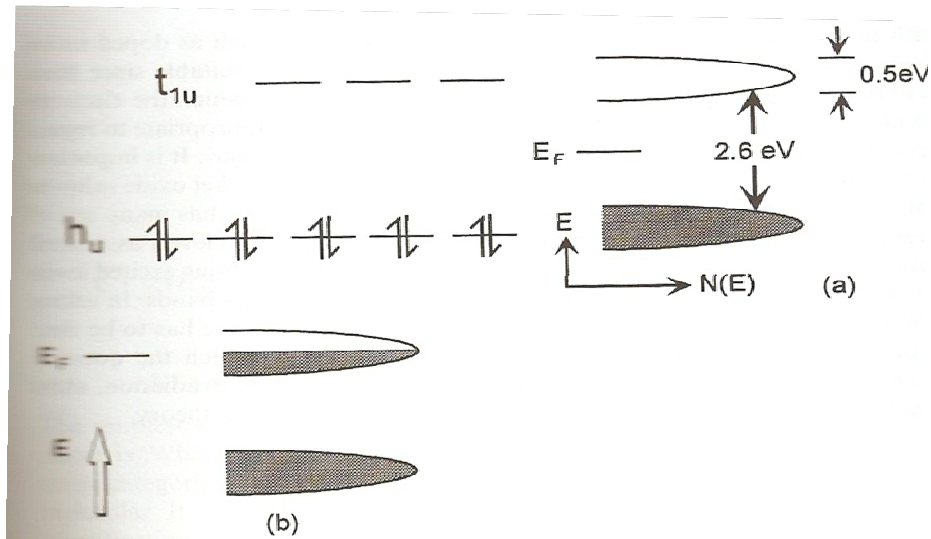
Fig. 2.28 (a) Electronic structure of C_{60} and (b) band filling in A_3C_{60}

The valence band or the highest occupied molecular orbitals (HOMOs, h_u) contain 10e in C_{60}. The conduction band or the lowest unoccupied molecular orbitals (LUMOs, t_{1u}) can contain up to 6e. C_{60} can act as an electron acceptor in its compounds. Thus, in K_3C_{60} (section 1.15f) the conduction band is half full (2.28b), and K_3C_{60} is metallic, in contrast to the insulating C_{60} parent.

2.16. Bands or bonds: a final comment

The three extreme types of bonding in solids:

Ionic—spherical electron distribution; anion-oribtal valence band (full) and cation-orbital conduction band (empty)

Covalent—sharing valence electrons, deviation from spherical distribution, bonding/antibonding

Metallic—band theory, partly filled valence band

Because most materials not exclusively belonging to a particular category, an appropriate way of describing the bonding is important.

The band model is clearly appropriate where there are freely mobile electrons, as in metals and some semiconductors. Experimental measurements of mobility show that these electrons are highly mobile and are not associated with individual atoms.

In certain other semiconductors, such as doped NiO, the band is not suitable since these materials are best regarded as hopping semiconductors in which electrons do not have high mobility. It appears to be more appropriate to regard the d electrons as occupying discrete orbitals on nickel ions. However, the conduction in NiO refers to only one or two sets of energy levels. The lower lying levels are full and are discrete levels associated with the individual anions and cations. At higher energy various excited levels are usually completely empty but may overlap to form energy bands.

A bond or band model? One has to be clear about the property or energy levels to which the question refers. Many ionically bonded solids may, under UV irradiation, show electronic conductivity that is best described in terms of band theory.