SECOND EDITION

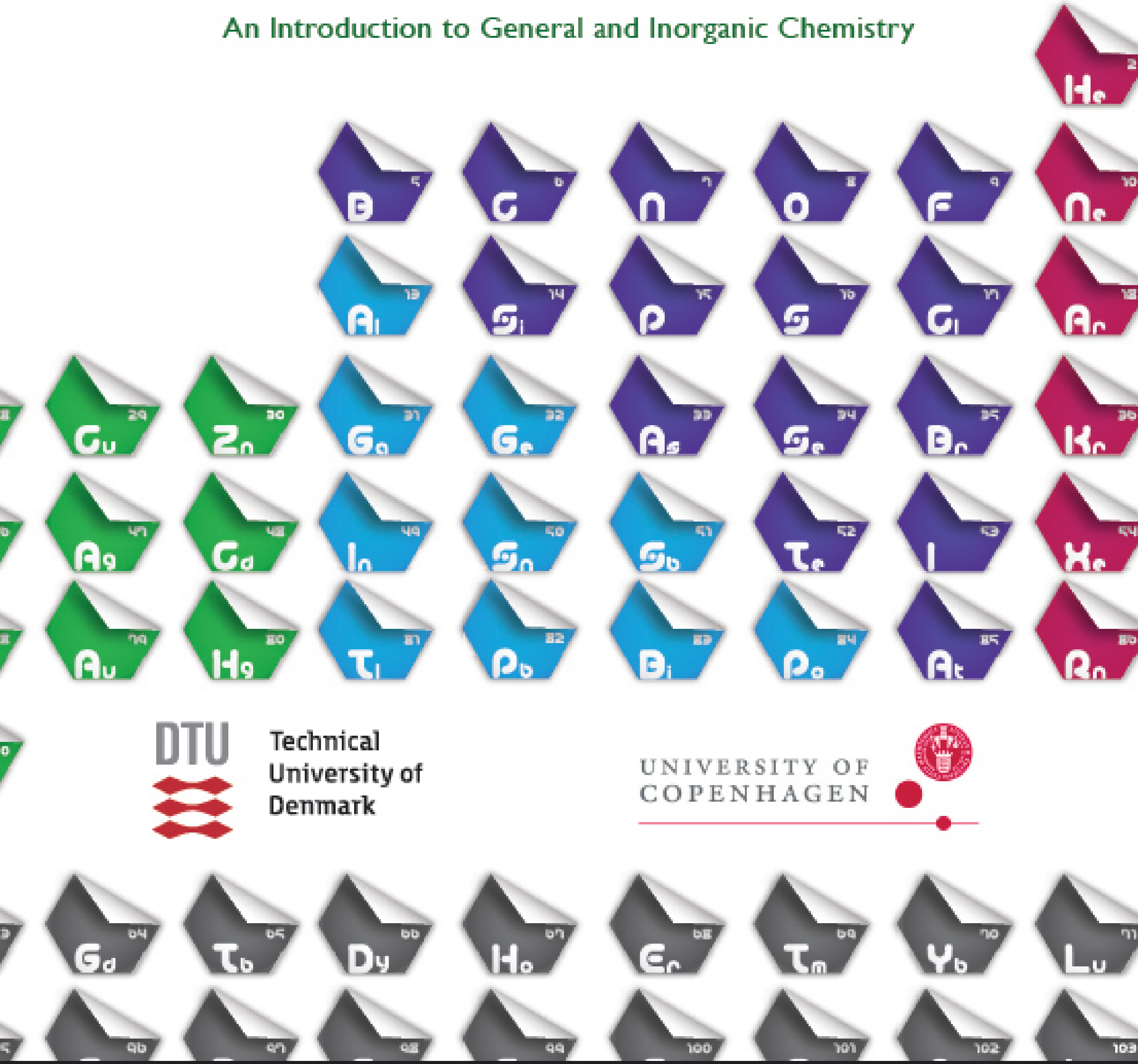
SELECTED CHAPTERS FROM

CHEMISTRY

FOURTH EDITION

Catherine E. Housecroft and Edwin C. Constable

An Introduction to General and Inorganic Chemistry



DTU Technical University of Denmark

UNIVERSITY OF COPENHAGEN

ALWAYS LEARNING

PEARSON

Periodic table

1 ← Atomic number, Z
H ← Element symbol
1.008 ← Relative atomic mass, A_r

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.01	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.54	30 **Zn** 65.41	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.34	**La–Lu**	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226.03	**Ac–Lr**	104 **Rf** [261]	105 **Db** [262]	106 **Sg** [266]	107 **Bh** [264]	108 **Hs** [277]	109 **Mt** [268]	110 **Ds** [271]	111 **Rg** [272]	112 **Uub** [285]	113 **Uut** [284]	114 **Uuq** [289]	115 **Uup** [288]	116 **Uuh** [291]		118 **Uuo** [294]

Lanthanoids	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
Actinoids	89 **Ac** 227.03	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** 239.05	95 **Am** 241.06	96 **Cm** 244.07	97 **Bk** 249.08	98 **Cf** 252.08	99 **Es** 252.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 259	103 **Lr** 262

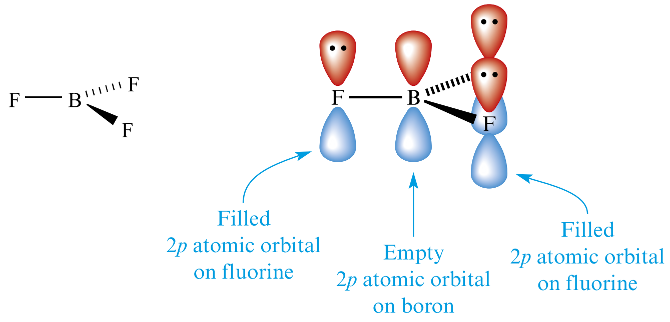


Fig. 7.16 Valence bond theory in BF_3. After the formation of the σ-bonding framework using an sp^2 hybridization scheme, the remaining $2p$ atomic orbital on the B atom is of the correct symmetry to overlap with an occupied $2p$ atomic orbital of an F atom. A π-bond is formed.

However, in the case of an sp^2 hybridized atom, the atom retains one pure p atomic orbital, while an sp hybridized atom has two 'left-over' p atomic orbitals. Similarly, when an atom is sp^3d or sp^3d^2 hybridized, either four or three (respectively) atomic d orbitals on the central atom remain unhybridized.

In this section we consider the roles that 'left-over' p atomic orbitals play in bonding.

A trigonal planar molecule: BF_3

In BF_3, the σ-bonding framework is similar to that in BH_3. Each localized B–F σ-bond is formed by the overlap of a B sp^2 hybrid orbital and an orbital from an F atom; each resultant σ-bonding orbital is occupied by two electrons.

As in BH_3, once the σ-bonding framework has been formed in the BF_3 molecule, an unhybridized, empty $2p$ atomic orbital remains on the B atom. However, *unlike* the situation in BH_3, in BF_3 each F atom possesses three lone pairs, and one may be considered to occupy a $2p$ atomic orbital with the same orientation as the unused $2p$ atomic orbital on the B atom (for example, they may be $2p_z$ atomic orbitals). Figure 7.16 illustrates that it is possible for the B atom to form a π-bond with any one of the F atoms by overlap between the B and F $2p$ atomic orbitals. Look back at the resonance structures for BF_3 in Figure 7.4. One group of three resonance structures includes B=F double bond character.

The valence bonding picture for the BF_3 molecule illustrates a general point: *unhybridized p orbitals can be involved in π-bonding*. Related examples are BCl_3, $[BO_3]^{3-}$, $[CO_3]^{2-}$ and $[NO_3]^{-}$. These species all possess trigonal planar structures in which the central atom may be sp^2 hybridized. In each case, the central atom possesses an unhybridized $2p$ atomic orbital which can overlap with a p atomic orbital on an adjacent atom to form a π-bond.

Exercise Which atomic orbitals are involved in π-bond formation in BCl_3 and $[CO_3]^{2-}$?

A linear molecule: CO_2

The C atom in the linear CO_2 molecule is sp hybridized and retains two $2p$ atomic orbitals (Figure 7.17). The σ-bonding framework in the molecule involves two sp hybrids on C which overlap with orbitals on the two O atoms. Each localized σ-bonding orbital contains two electrons (one from C and one from O).

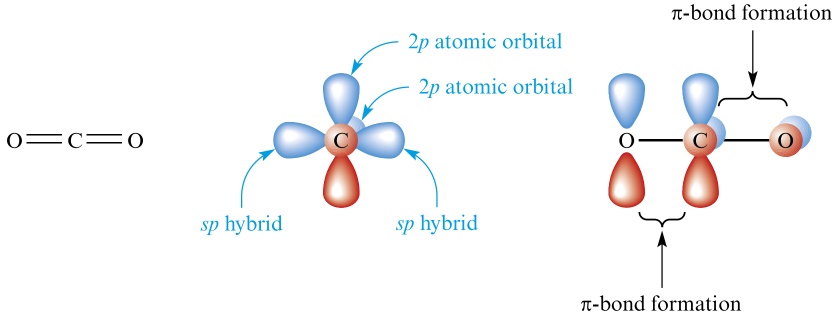


Fig. 7.17 Valence bond theory in CO_2. After forming the σ-bonding framework using an *sp* hybridization scheme, the two remaining 2*p* atomic orbitals on the C atom can be used to form two C–O π-bonds. Each O atom uses a 2*p* atomic orbital for π-bonding.

The two remaining 2*p* atomic orbitals on the C atom lie at right angles to one another and each overlaps with a 2*p* atomic orbital on one of the O atoms. This produces two C–O π-bonds (Figure 7.17) and each π-bonding orbital is occupied by two electrons (formally, one from C and one from O).

The overall result is the formation of two C=O double bonds, each consisting of a σ- and a π-component.

7.8 Molecular orbital theory and polyatomic molecules

Polyatomic molecules create a problem

In this section, we look briefly at the way in which MO theory is used to approach the bonding in polyatomic molecules.[§] A key question is how to represent the problem. If we look back at MO diagrams such as Figure 4.15 (the formation of H_2) and Figure 5.8 (the formation of HF), we notice that each side of each diagram represents one of the two atoms of the diatomic molecule. What happens if we wish to represent an MO diagram for a polyatomic molecule? Any diagram that represents the composition of MOs in terms of contributions from various atomic orbitals will become very complicated, and, probably, unreadable!

An approach that is commonly used is to resolve the MO description of a polyatomic molecule into a *two-component* problem. Instead of looking at the bonding in CH_4 in terms of the interactions of the 2*s* and 2*p* atomic orbitals of the carbon atom with the individual 1*s* atomic orbitals of the hydrogen atoms (this would be a five-component problem), we consider the way in which the atomic orbitals of the carbon atom interact with the *set* of four hydrogen atoms. This is a two-component problem, and is called a *ligand group orbital* approach.

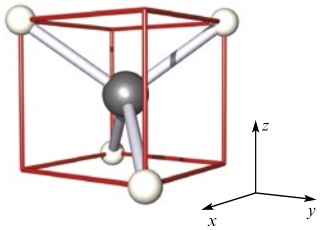


Fig. 7.18 The relationship between the tetrahedral shape of CH_4 and a cubic framework. Each edge of the cube runs parallel to one of the three Cartesian axes.

Ligand group orbitals

Methane is tetrahedral and to make an MO bonding analysis for CH_4 easier, it is useful to recognize that the tetrahedron is related to a cube as shown in Figure 7.18. This conveniently relates the positions of the H atoms to the Cartesian axes, with the C atom at the centre of the cube.

The valence orbitals of C are the 2*s*, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals (Figure 7.19a). Remember that the 2*s* atomic orbital is spherically

---

[§] For a more detailed introduction including the use of group theory, see: C. E. Housecroft and A. G. Sharpe (2008) *Inorganic Chemistry*, 3rd edn, Prentice Hall, Harlow, Chapter 5.

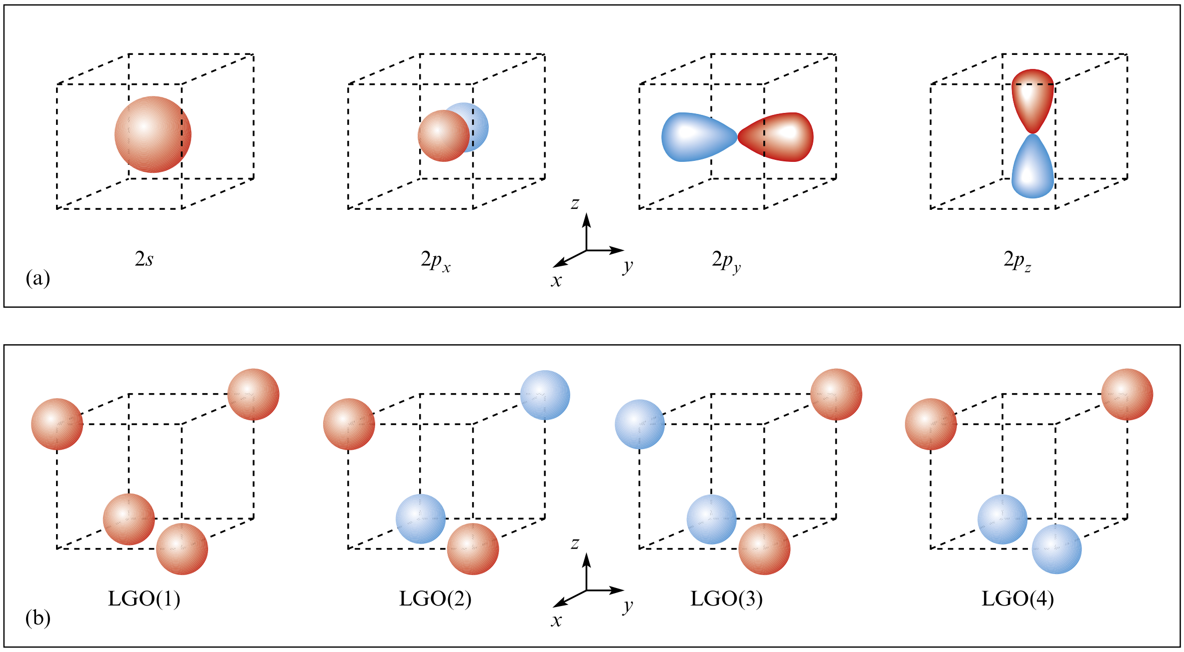


Fig. 7.19 (a) The 2*s*, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals are the valence orbitals of carbon. (b) The four hydrogen 1*s* atomic orbitals combine to generate four ligand group orbitals (LGOs). The rigorous approach to the construction of ligand group orbitals uses group theory.

symmetric. The orientations of the 2*p* atomic orbitals are related to a cubic framework; the same axis set is used in Figures 7.18 and 7.19.

Consider now the four 1*s* atomic orbitals that the 4 H atoms contribute. Each 1*s* orbital has two possible phases and, *when the four orbitals are taken as a group*, various combinations of phases are possible. With four atomic orbitals, we can construct four *ligand group orbitals* (LGOs) as shown in Figure 7.19b. The in-phase combination of the four 1*s* atomic orbitals is labelled as LGO(1). We now make use of the relationship between the arrangement of the H atoms and the cubic framework. Each of the *xy*, *xz* and *yz* planes bisects the cube in a different direction. In Figure 7.18, mentally sketch the *xy* plane through the cube – two H atoms lie above this plane, and two lie below. Similarly, the four H atoms are related in pairs across each of the *yz* and *xz* planes. Now look at Figure 7.19b. In LGO(2), the four 1*s* orbitals are drawn as two pairs, one pair on each side of the *yz* plane. The orbitals in one pair are in phase with one another, but are out of phase with the orbitals in the second pair. Ligand group orbitals LGO(3) and LGO(4) can be constructed similarly.

The number of ligand group orbitals formed = the number of atomic orbitals used.

Combining the atomic orbitals of the central atom with the ligand group orbitals

The next step in the ligand group orbital approach is to 'match up' the valence orbitals of the C atom with LGOs of the four H atoms. The criterion for matching is *symmetry*. Each carbon orbital has to 'find a matching partner' from the set of LGOs.

The carbon 2*s* orbital has the same symmetry as LGO(1). If the 2*s* orbital is placed at the centre of LGO(1), overlap will occur between the 2*s* orbital and

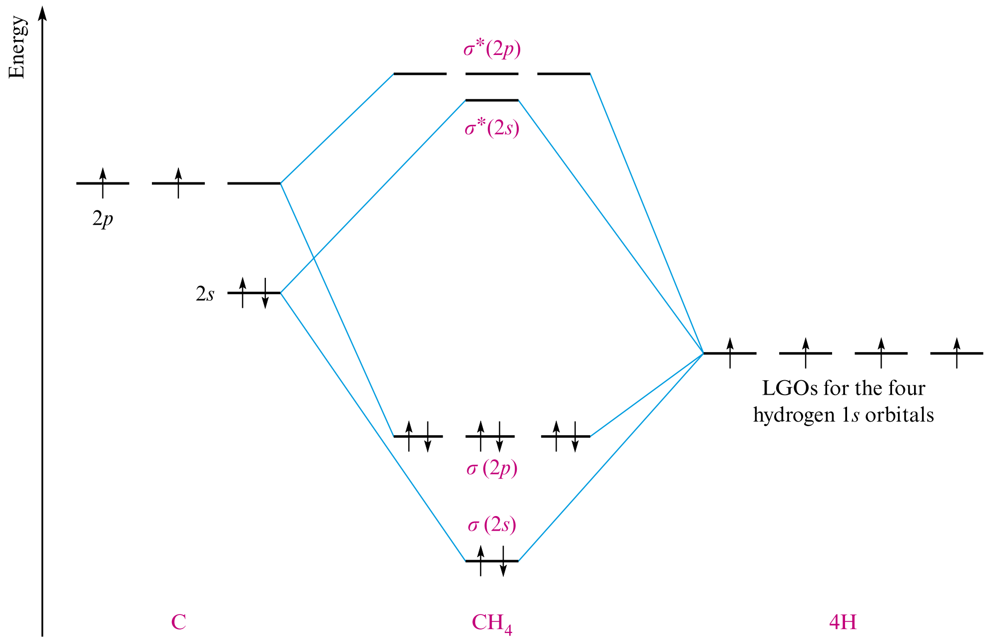


Fig. 7.20 Molecular orbital diagram for the formation of CH_4.

each of the hydrogen 1s orbitals. This interaction leads to one bonding MO in the CH_4 molecule: $\sigma(2s)$. This is the lowest-lying MO in Figure 7.20. It possesses C–H bonding character which is *delocalized over all four of the C–H interactions*.

The carbon $2p_x$ orbital has the same symmetry as LGO(2), and if it is placed at the centre of LGO(2), overlap occurs between the $2p_x$ orbital and *each* of the hydrogen 1s orbitals. This interaction leads to a second bonding MO in the methane molecule: $\sigma(2p_x)$. This MO contains a nodal plane coincident with the yz plane. Similarly, we can match the carbon $2p_y$ orbital with LGO(3), and the $2p_z$ orbital with LGO(4). These combinations generate two more bonding molecular orbitals. The three MOs that are formed from the combinations of the carbon 2p orbitals and LGOs (2) to (4) are equivalent to one another except for their orientations. These MOs are degenerate and are labelled $\sigma(2p)$ in Figure 7.20. Each MO contains C–H bonding character which is *delocalized over all four of the C–H interactions*.

There are therefore four bonding MOs (and hence four antibonding MOs) that describe the bonding in CH_4. In each orbital, the C–H bonding character is *delocalized*.

Putting in the electrons

As usual in MO theory, the last part of the operation is to count the available valence electrons and place them in the molecular orbitals according to the *aufbau* principle.

In CH_4 there are eight valence electrons and these occupy the MOs as shown in Figure 7.20. All the valence electrons in the molecule are paired and CH_4 is predicted to be diamagnetic, in keeping with experimental data.

7.9 How do the VB and MO pictures of the bonding in methane compare?

The valence bond and molecular orbital descriptions of methane

Valence bond theory describes the bonding in the CH_4 molecule in terms of an sp^3 hybridized carbon atom, and four equivalent σ-bonding orbitals (see Figure 7.14). Each orbital is *localized*, meaning that each C−H bond is described by one σ-bonding orbital.

Molecular orbital theory also produces a description of CH_4 which involves four molecular orbitals. However, unlike the valence bond model, the molecular orbital approach gives one unique MO and a set of three degenerate MOs (see Figure 7.20). In each MO, the C−H bonding character is *delocalized over all four of the C−H vectors*.

Are these two pictures really different? If so, is one of them wrong? Indeed, is either of them realistic?

Photoelectron spectroscopy

One of the major differences between the results of the VB and MO treatments of the bonding in the CH_4 molecule is that the former suggests that there are four equivalent MOs (equal energy) while the latter is consistent with there being two molecular orbital energy levels, one associated with a unique MO and one with a set of three degenerate orbitals.

In Box 4.4, we briefly mentioned the experimental technique of photoelectron spectroscopy in the context of probing the energies of molecular orbitals. This method can be used to investigate the question of the MO energy levels in CH_4 and the photoelectron spectroscopic data support the results of MO theory. But, does this mean that the VB model gives the wrong 'answer'?

Valence bond versus molecular orbital theory

Molecular orbital theory describes the bonding in the CH_4 molecule in terms of four MOs. The unique $\sigma(2s)$ MO is spherically symmetric and provides equal bonding character in all of the four C−H interactions. The $\sigma(2p_x)$, $\sigma(2p_y)$ and $\sigma(2p_z)$ MOs are related to one another by rotations through 90°. Because they are degenerate, we must consider them *as a set and not as individual orbitals*. Taken together, they describe the four C−H bonds equally. Thus, the MO picture of CH_4 is of a molecule with four equivalent C−H bonds. This result arises *despite* the fact that the four MOs are not all identical.

The sp^3 hybrid model (VB theory) of CH_4 describes four equivalent C−H bonds in terms of four *localized* σ-bonds. The associated bonding orbitals are of equivalent energy.

Both the VB and MO approaches are bonding *models*. Both models achieve a goal of showing that the CH_4 molecule contains four equivalent bonds. While the MO model appears to give a more realistic representation of the energy levels associated with the bonding electrons, the VB method is simpler to apply. While MO theory can be applied to small and large molecules alike, it very quickly goes beyond the 'back-of-an-envelope' level of calculation.

SUMMARY

In this chapter, we have considered the bonding in polyatomic molecules. We have considered the octet rule, and introduced hybridization schemes that can be applied to different spatial arrangements of bonding and lone pairs of electrons around a central atom. Finally, we have introduced the use of MO theory, applying it to a simple example, methane.

Do you know what the following terms mean?

- the valence shell
- hybrid orbital
- ligand group orbital approach

You should now be able:

- to work out the number of electrons in the valence shell of atom X in a molecule XY_n
- to draw a set of resonance structures for a simple polyatomic molecule or molecular ion
- to discuss what is meant by orbital hybridization
- to relate hybridization schemes to arrangements of bonding and lone pairs of electrons around a central atom
- to relate hybridization schemes to molecular shapes
- to use hybridization schemes to describe the bonding in simple polyatomic molecules containing both single and multiple bonds
- to develop a bonding scheme for CH_4 using MO theory and to understand why a 'ligand group orbital approach' is useful

PROBLEMS

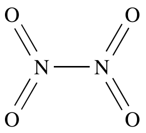
7.1 In which of the following molecular species does the central atom possess an octet of valence electrons? (a) BBr_2F; (b) OF_2; (c) PH_3; (d) CO_2; (e) NF_3; (f) $[PCl_4]^+$; (g) AsF_3; (h) BF_3; (i) $AlCl_3$.

7.2 In which of the molecular species in problem 7.1 does the central atom possess a sextet of valence electrons?

7.3 What is the origin of the 'octet rule'?

7.4 For each of the following, draw Lewis structures that are consistent with the central atom in each molecule obeying the octet rule: (a) H_2O; (b) NH_3; (c) AsF_3; (d) SF_4.

7.5 N_2O_4 is a planar molecule. Explain why **7.5** is not a reasonable resonance structure. Suggest what resonance structures do contribute to the bonding in N_2O_4. Does this approach indicate why N_2O_4 readily decomposes to give NO_2?



(7.5)

7.6 How many single bonds may each of the (a) N^-, (b) B^- and (c) C^- centres form while obeying the octet rule?

7.7 Place charges on the atomic centres in each of the following resonance structures such that each centre obeys the octet rule.

(a) For $[N_3]^-$:

$$N{=}N{=}N$$

(b) For $[NCS]^-$:

$$N{=}C{=}S$$

(c) For $[NO_2]^+$:

$$O{=}N{=}O$$

(d) For $[NO_2]^-$:

$$O{-}N{=}O \longleftrightarrow O{=}N{-}O$$

Comment on the shapes of these species.

7.8 The azide ion, $[N_3]^-$, is linear with equal N–N bond lengths. Give a description of the bonding in $[N_3]^-$ in terms of valence bond theory.

7.9 Outline how the combination of carbon 2*s* and 2*p* atomic orbitals leads to hybrid orbitals that can be used to describe the carbon centres in