Chapter 5
Bonding in polyatomic molecules

Polyatomic species: contains three or more atoms

Three approaches to bonding in diatomic molecules
1. Lewis structures
2. Valence bond theory
3. Molecular orbital theory

A comparison of the shape of the H₂O molecule (the framework of which is taken as lying in the yz plane) with the spatial properties of the 2s, 2pₓ, and 2pᵧ atomic orbitals of oxygen.

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Orbital hybridization - sp

Hybrid orbitals – generated by mixing the characters of atomic orbitals

The formation of two sp hybrid orbitals from one 2s atomic orbital and one 2p atomic orbital.

Scheme to show the formation of the sp hybridized valence state of a beryllium atom from its ground state. This is a formalism and is not a ‘real’ observation, e.g. the valence state cannot be observed by spectroscopic techniques. The choice of using the 2p_z orbital for hybridization is arbitrary.
Orbital hybridization – \( sp^2 \)

\[
\psi_{sp^2\_hybrid} = \frac{1}{\sqrt{3}} \psi_{2s} + \sqrt{\frac{2}{3}} \psi_{2p_x}
\]

\[
\psi_{sp^2\_hybrid} = \frac{1}{\sqrt{3}} \psi_{2s} - \frac{1}{\sqrt{6}} \psi_{2p_x} + \frac{1}{\sqrt{2}} \psi_{2p_z}
\]

The formation of three \( sp^2 \) hybrid orbitals from one 2s atomic orbital and two 2p atomic orbitals. The choice of \( p_x \) and \( p_y \) is arbitrary. (If we started with 2\( p_x \) and 2\( p_y \) atomic orbitals, the hybrids would lie in the \( xy \) plane; using the 2\( p_x \) and 2\( p_z \) atomic orbitals gives hybrid orbitals in the \( yz \) plane.) The directionalities of the hybrid orbitals follow from the relative contributions of the atomic orbitals (see equations 4.3–4.5).

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The bonding in trigonal planar \( BH_3 \) can be conveniently described in terms of the interactions between a set of \( sp^2 \) hybrid orbitals centred on the B atom and three H 1s atomic orbitals. Three pairs of electrons are available (three electrons from B and one from each H) to give three 2e–2e σ-bonds.
**sp³ hybrid orbitals** – one s and three p atomic orbitals mix to form a set of four orbitals with different directional properties

\[
\psi_{sp^3\text{ hybrid}} = \frac{1}{2} (\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z})
\]

\[
\psi_{sp^3\text{ hybrid}} = \frac{1}{2} (\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z})
\]

\[
\psi_{sp^3\text{ hybrid}} = \frac{1}{2} (\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z})
\]

\[
\psi_{sp^3\text{ hybrid}} = \frac{1}{2} (\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z})
\]

(a) The directions of the orbitals that make up a set of four sp³ hybrid orbitals correspond to a tetrahedral array.
(b) The relationship between a tetrahedron and a cube: in CH₄, the four H atoms occupy alternate corners of a cube, and the cube is easily related to a Cartesian axis set.

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**sp³d hybrid orbitals** – one s, three p, and one d atomic orbitals mix to form a set of five orbitals with different directional properties

A schematic representation of sp³d hybridization. (a) A combination of s, pₓ, pᵧ, pₜ and dₓ2–y² atomic orbitals gives a set of five sp³d hybrid orbitals corresponding to a trigonal bipyramidal arrangement: the axial sp³d hybrid orbitals are directed along the z axis. (b) A combination of s, pₓ, pᵧ, pₜ, and dₓ2–y² atomic orbitals gives a set of five sp³d hybrid orbitals corresponding to a square-based pyramidal arrangement; the axial sp³d hybrid orbital is directed along the z axis.
**Valence bond theory** – multiple bonding in polyatomic molecules

(a) Ethene is a planar molecule with H–C–H and C–C–H bond angles close to 120°. (b) An sp² hybridization scheme is appropriate to describe the σ-bonding framework. (c) This leaves a 2p atomic orbital on each C atom; overlap between them gives a C–C π-interaction.

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**Valence bond theory** – multiple bonding in polyatomic molecules

(a) The linear structure of HCN; colour code: C, grey; N, blue. (b) An sp hybridization scheme for C and N can be used to describe the σ-bonding in HCN. (c) The π-character in the C–N bond arises from 2p–2p overlap.
Valence bond theory – multiple bonding in polyatomic molecules

(a) BF₃ possesses a trigonal planar structure. (b) 2p–2p overlap between B and F leads to the formation of a π-interaction.

(c) Boron–fluorine double bond character is also deduced by considering the resonance structures for BF₃; only those forms that contribute significantly are shown.
Molecular orbital theory:

*ligand group orbital* approach in triatomic molecules

Application of the ligand group orbital (LGO) approach to construct a qualitative MO diagram for the formation of a linear XH₂ molecule from the interactions of the valence orbitals of X (2s and 2p atomic orbitals) and an H···H fragment. For clarity, the lines marking the 2p orbital energies are drawn apart, although these atomic orbitals are actually degenerate.

The lower diagrams are schematic representations of the MOs in linear XH₂. The wavefunction labels correspond to those in Figure 4.11. The upper diagrams are more realistic representations of the MOs and have been generated computationally using Spartan ‘04, ©Wavefunction Inc. 2003.

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(a) A linear \( \text{XH}_2 \) molecule belongs to the \( D_{\text{sh}} \) point group. Some of the symmetry operations are shown: the X atom lies on a centre of symmetry (inversion centre). (b) A qualitative MO diagram for the formation of linear \( \text{XH}_2 \) from atom X and two H atoms.

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The \( \text{H}_2\text{O} \) molecule possesses a \( C_2 \) axis and two \( \sigma_z \) planes and belongs to the \( C_2v \) point group.

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A qualitative MO diagram for the formation of H₂O using the ligand group orbital approach. The two H atoms in the H₂ fragment are out of bonding range with each other, their positions being analogous to those in H₂O. For clarity, the lines marking the oxygen 2p orbital energies are drawn apart, despite their being degenerate. Representations of the occupied MOs are shown at the right-hand side of the figure. For the a₁ and b₁ MOs, the H₂O molecule is in the plane of the paper; for the b₁ MO, the plane containing the molecule is perpendicular to the plane of the paper.

The BH₃ molecule has D₃h symmetry.

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<th>3C₂</th>
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A qualitative MO diagram for the formation of BH₃ using the ligand group orbital approach. The three H atoms in the H₂ fragment are out of bonding range with each other, their positions being analogous to those in the BH₃ molecule. Orbitals LGO(2) and LGO(3) form a degenerate pair (e' symmetry), although for clarity, the lines marking their orbital energies are drawn apart; similarly for the three 2p atomic orbitals of boron.

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The NH₃ molecule has C₃ᵥ symmetry.

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A qualitative MO diagram for the formation of NH$_3$ using the ligand group orbital approach. For clarity, the lines marking degenerate orbital energies are drawn apart. The diagrams on the right-hand side show representations of three of the occupied MOs; the orientation of the NH$_3$ molecule in each diagram is the same as in the structure at the bottom of the figure.

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1. **5.20** The ligand group orbital approach to the bonding in CH$_4$. (a) The $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of carbon. (b) The four hydrogen 1s atomic orbitals combine to generate four ligand group orbitals (LGOs).
A qualitative MO diagram for the formation of CH₄ from the orbital basis set shown in Figure 5.20. The diagrams on the right-hand side illustrate the four bonding MOs. The orbitals are drawn in a ‘mesh’ representation so that the molecular framework is visible. Each of the t₂₂ MOs contains a nodal plane.

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Molecular orbital theory: BF₃

Fig. 5.22 Schematic representations of the ligand group orbitals (LGOs) for a D₃h F₃ fragment, the geometry of which is analogous to that in BF₃ (the position of the B atom is marked by the dot in the top left-hand diagram); the F₃ triangle lies in the xy plane. Orbitals LGO(5), LGO(8) and LGO(9) contain contributions from the 2pₓ atomic orbitals, directed perpendicular to the F₃ triangle. The relative sizes of the lobes in each diagram approximately represent the relative contributions made by the fluorine atomic orbitals to each ligand group orbital.
Consider the $S_3$ operation ($= C_3 \cdot \sigma_h$) on the $p_z$ orbitals in the $F_3$ fragment.

The resulting wavefunction contributions from the $S_3$ and $S_{3}^{2}$ operations are $-\psi_3$ and $-\psi_2$, respectively.

A qualitative MO diagram for the formation of $BF_3$; the ligand group orbitals (LGOs) are shown in Figure 5.22. The light grey rectangle in the stack of MOs in $BF_3$ represents a group of eight non-bonding MOs. The diagram is an oversimplification of the bonding in $BF_3$, but is sufficiently detailed to account for the $B-F$ bonds possessing partial $\pi$-character. The characters of three of the occupied $B-F$ bonding MOs are shown at the right-hand side of the figure; the orientation of the $BF_3$ molecule in each diagram is same as in the structure at the bottom of the figure.
BF₃ Resonance Structures

The presence of the resonance contributions account for the partial double bond character in BF₃.

5.25

Representation of one of the πₛ⁻ MOs in CO₂

Representation of one of the πₓ MOs in CO₂

5.24 A partial MO diagram that illustrates the formation of delocalized C–O π-bonds using the ligand group orbital approach. The CO₂ molecule is defined as lying on the z axis. The characters of the πₛ⁻ and πₓ MOs are shown in the diagrams at the top of the figure.
**Fig. 5.25** A qualitative, partial MO diagram to illustrate the formation of a delocalized π-system in $\text{[NO}_3^-\text{]}^+$; a ligand group orbital approach is used. The characters of the $a_2^\pi$ and $a_2^\pi^*$ MOs are shown in the diagrams at the right-hand side of the figure.

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(a) An octahedron can be inscribed in a cube; each vertex of the octahedron lies in the middle of a face of the cube. (b) The diagram shows one of each type of rotation axis of an octahedron. An inversion centre lies at the centre of the octahedron.
Find number of unchanged radial 2p orbitals that are unchanged under each $O_h$ symmetry operation.

$C_2$ Note the $C_2$ axis bisect the planes containing 4 p orbitals. The $C_2$ axis contains no 2p orbitals.

Use the reduction formula to find the resulting symmetries: $a_{1g}, t_{1u}, e_g$

Could derive the equations for the LGOs for the $F_6$ fragment.
Three-center two-electron interactions

Qualitative, partial MO diagram for the formation of SF₆ using the ligand group orbital approach with a basis set for sulfur that is composed of the 3s and 3p atomic orbitals.


A qualitative MO diagram for the formation of [HF₃]⁻ using a ligand group orbital approach. The characters of the σₓ and σₜ† MOs are shown at the top of the figure.

A qualitative MO diagram for the formation of XeF₂ using a ligand group orbital approach and illustrating the 3c–2e bonding interaction.

The structure of B₂H₆ determined by electron diffraction.
(a) The structure of B₂H₆ can be broken down into H₂B – BH₃ and H – H fragments. (b) The ligand group orbitals (LGOs) for the H–H fragment. (c) The six lowest energy LGOs for the B₂H₆ unit; the nodal plane in the β₂g orbital is shown.

A qualitative, partial MO diagram showing the formation of the B–H–B bridging interactions. The B–H and D–H bonding character of the α₂ MO, and the D–H bonding character of the β₂g MO are shown in the diagrams on the right-hand side; the orientation of the molecule is the same as in the structure at the bottom of the figure.
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