

# Structure and shape of polyatomic molecules

## 5.1 The Lewis model

- The second period elements, from lithium to neon, generally obey the octet rule and never have more than eight electrons in their valence orbitals. Molecules with fewer than eight valence electrons are said to be electron poor and are generally very reactive. Examples of electron-poor molecules include  $\text{NO}_2$  and  $\text{BH}_3$ .
- Larger atoms can exhibit hypervalency, in which the octet is expanded and there are more than eight electrons in the valence orbitals. Examples of hypervalent molecules include  $\text{PCl}_5$  and  $\text{XeO}_3$ .
- Possible structures of a molecule can be assessed by calculating formal charges for the atoms. This allows the most likely structure to be predicted.



For practice questions on these topics, see questions 1 and 2 at the end of this chapter (p.253).


## 5.2 Valence shell electron pair repulsion theory

- VSEPR theory is used to predict the shapes of molecules by looking at the repulsions between electron pairs in the valence shell on the central atom in a molecule.
- Pairs of electrons are arranged to minimize the repulsions between them. For 2–7 pairs of electrons around a central atom, the regular geometries are:
  - $n = 2$ , linear;
  - $n = 3$ , trigonal planar;
  - $n = 4$ , tetrahedral;
  - $n = 5$ , trigonal bipyramidal;
  - $n = 6$ , octahedral;
  - $n = 7$ , pentagonal bipyramidal.
- The electron pairs include bonding pairs and lone pairs. The shape of the molecule is described by the positions of the bonding pairs only.
- A molecule with four electron pairs is tetrahedral if there are no lone pairs, trigonal pyramidal if there is one lone pair, and bent if there are two lone pairs.
- A molecule with six electron pairs is octahedral if there are no lone pairs, square pyramidal if there is one lone pair, and square planar if there are two lone pairs (see Figure 5.17, p.230).
- Lone pairs take up more space than bonding pairs, so the strength of repulsions decreases in the order:
  - $\text{lp-lp} > \text{lp-bp} > \text{bp-bp}$  (lp = lone pair; bp = bonding pair)



For a practice question on this topic, see question 3 at the end of this chapter (p.253).

- VSEPR theory is a simple but powerful way to predict the shapes of molecules.
- The electron pairs take up positions as far away from each other as possible to minimize electron–electron repulsions.
- Lone pairs take up more space around an atom than bonding pairs. This means that lone pair–lone pair repulsion is greater than lone pair–bonding pair repulsion, which in turn is greater than bonding pair–bonding pair repulsion.
- $\pi$  electrons do not contribute to the molecular shape, but double and triple bonds take up more space than single bonds. Consequently, the repulsion is greater between the electrons in a double (or triple) bond and the electrons in a single bond, than between the electrons in two single bonds.
- VSEPR theory does not work for transition metal compounds and for a few exceptions such as  $\text{TeBr}_6^{2-}$  for which the assumptions made in the theory are incorrect.

 For practice questions on these topics, see questions 3–6 at the end of this chapter (p.253).


### 5.3 Bond polarity and polar molecules

- Bonds between different atoms are normally polar, and the magnitude of the dipole moment depends on the difference in electronegativity between the atoms involved.
- Whether a polyatomic molecule is polar or not depends on its shape, and whether the polarities of the individual bonds cancel out.
- The polarity of a solvent affects the nature of the compounds that can dissolve in it.

 For practice questions on these topics, see questions 7–9 at the end of this chapter (p.253).


### 5.4 Valence bond theory for polyatomic molecules

- The bonding in molecules with tetrahedral geometry around one or more atoms is explained using  $sp^3$  hybridization. Examples of  $sp^3$  hybridization include the carbon atoms in  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , and the nitrogen atom in  $\text{NH}_3$ .
- The bonding in molecules with trigonal planar geometry around one or more atoms is explained using  $sp^2$  hybridization. Examples of  $sp^2$  hybridization include the carbon atoms in ethene ( $\text{C}_2\text{H}_4$ ) and the boron atom in  $\text{BH}_3$ .
- The bonding in molecules with linear geometry around one or more atoms is explained using  $sp$  hybridization. Examples of  $sp$  hybridization include the carbon atoms in ethyne ( $\text{C}_2\text{H}_2$ ) and the beryllium atom in gaseous  $\text{BeH}_2$ .

 For practice questions on these topics, see questions 10–12 at the end of this chapter (p.253).

### 5.5 Resonance

- Resonance is used to explain the bonding in molecules with bonds that appear to be different in a Lewis structure but are found to be the same experimentally.
- Resonance forms do not exist independently. The actual structure is an *average* of the different resonance forms and has a lower energy than any individual resonance form.
- In valence bond theory, hypervalency in compounds containing elements of the third period (or heavier elements) is explained using hybridization schemes involving one or more  $d$  orbitals or by assuming charge separation in the resonance forms.

 For practice questions on these topics, see questions 13–15 at the end of this chapter (p.253).

## 5.6 A molecular orbital approach to the bonding in polyatomic molecules

- Molecular orbital theory is more difficult to extend to polyatomic molecules than valence bond theory.
- For a molecule  $AX_n$ , the best approach is to treat the  $n$  X atoms together, then interact the combinations of these orbitals with those on the central A atom.
- The linear molecule  $BeH_2$  has two filled bonding orbitals of different energies. These are both delocalized over the molecule so that the two Be–H bonds are equivalent.

## 5.7 Partial molecular orbital schemes

- Partial molecular orbital energy level diagrams are a useful way of describing the bonding in molecules that break the octet rule.
- The bonding in hypervalent compounds such as  $XeF_2$  can be described using 3-centre 4-electron bonds that consist of a filled bonding orbital and a filled non-bonding orbital.
- The bonding in electron-deficient compounds such as  $B_2H_6$  can be described using 3-centre 2-electron bonds that consist of a filled bonding orbital and an empty non-bonding orbital.



For practice questions on these topics, see questions 16 and 17 at the end of this chapter (p.253).



### Concept review

By the end of this chapter, you should be able to do the following.

- Work out the formal charges on the atoms in a molecule or ion and use these to predict which of several possible structures a compound is likely to adopt.
- Predict the shapes of molecules and ions using VSEPR theory.
- Understand the limitations of VSEPR theory.
- Understand the bonding in a compound by predicting the hybridization of the central atom(s), and describe how the hybrid orbitals interact with the orbitals on other atoms.
- Use resonance forms to describe the bonding in compounds that contain bonds that appear to be different in the Lewis structure but are found to be the same experimentally.
- Construct partial MO energy level diagrams to explain the bonding in hypervalent compounds such as  $XeF_2$ , and describe the bonding in terms of a 3-centre 4-electron bond.
- Describe the bonding in a linear triatomic molecule such as  $BeH_2$  using MO theory.
- Construct partial MO energy level diagrams to explain the bonding in electron-deficient compounds such as  $B_2H_6$ , and describe the bonding in terms of a 3-centre 2-electron bond.