
Structure and shape of polyatomic molecules

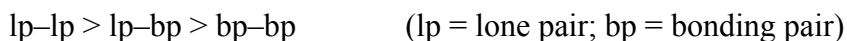
4.1 The Lewis model

- The second period elements, from lithium to neon, generally obey the octet rule and never have more than eight electrons in their valence orbitals.
- Larger atoms can exhibit hypervalency, in which the octet is expanded and there are more than eight electrons in the valence orbitals.
- Possible structures of a molecule can be assessed by calculating formal charges for the atoms. This allows the most likely structure to be predicted.

4.2 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.
- Lone pairs take up more space than bonding pairs, so the strength of repulsions decreases in the order:



- VSEPR theory is a simple but powerful way of predicting the shape of simple 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.
- π 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 TeBr_6^{2-} .

4.3 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.
- If you know the shape of a molecule you can predict whether or not it is polar.
- The polarity of a solvent affects the nature of the compounds that can dissolve in it.

4.4 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 atom in CH_4 and the nitrogen atom in 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 (C_2H_4) and the boron atom in 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 (C_2H_2) and the beryllium atom in gaseous BeH_2 .

4.5 Resonance

- Resonance structures are used to explain the bonding in molecules with bonds that appear to be different in the Lewis structure but are found to be the same experimentally.
- Resonant forms do not have independent existence. The actual structure is an *average* of the different resonance forms.
- In valence bond theory, hypervalency in compounds containing elements of the third period or lower is explained using hybridization schemes involving one or more *d* orbitals.

4.6 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.

4.7 Partial molecular orbital schemes

- Partial molecular orbital energy level diagrams are a useful way of describing the bonding in electron-rich and electron-poor molecules.
- 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.

Learning outcomes

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.
- 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 hypervalent compounds such as XeF_2 , and describe the bonding in terms of a 3-centre 4-electron bond.
- 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.