4

Diatomic molecules

4.1 Features of diatomic molecules

- Diatomic molecules contain only two atoms.
- The bond length in a diatomic molecule is defined as the mean distance between the centres of the two atoms.
- The bond dissociation enthalpy is a measure of the bond strength, and is defined as the standard enthalpy change of the reaction, at a specified temperature, in which the bond is broken.

4.2 The Lewis model

- The Lewis model was the first theory to explain bonding through the sharing of electrons.
- The bond order is the number of bonds between a pair of atoms.
- There are many stable molecules in which the atoms do not have filled octets, or have expanded octets.
- The Lewis model cannot explain the paramagnetism of oxygen, which indicates that O_2 contains unpaired electrons.

For a practice question on these topics, see question 1 at the end of this chapter (p.213).

4.3 Electronegativity

- Electronegativity is the power of an atom in a molecule to attract electrons to itself.
- The most commonly used scale for electronegativity is known as Pauling electronegativity, χ^P.
- Electronegativity generally increases across a period and decreases down a group.

For practice questions on these topics, see questions 2–4 at the end of this chapter (p.213).

4.4 Valence bond theory and molecular orbital theory

- Valence bond theory and molecular orbital theory are theories of bonding involving the interactions between atomic orbitals.
- Valence bond theory is good for providing qualitative pictures of bonding, and is especially useful in organic chemistry.
- Molecular orbital theory provides a more quantitative picture, and is very useful for small molecules.

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4.5 Valence bond theory

- Valence bond theory uses resonance to describe covalent and ionic contributions to a molecular wavefunction.
- Double-headed arrows are used to show the different resonance forms that contribute to the wavefunction. The bonding is a weighted average of the resonance forms.
- Hybridization is the mixing of atomic orbitals on an atom as it interacts with another atom.
- For a heteronuclear diatomic, the resonance form with the negative charge on the more electronegative atom makes a greater contribution to the molecular wavefunction than the resonance form with the negative charge on the more electropositive atom. This accounts for the polarity of the bond.

? **For practice questions on the topics in Sections 4.4 and 4.5, see questions 5 and 6 at the end of this chapter (p.213).**

4.6 Molecular orbital theory

- There are two important approximations used in molecular orbital theory: these are the orbital approximation and the formation of molecular orbitals through the linear combination of atomic orbitals (LCAO).
- Using LCAO, molecular orbitals are formed from the addition or subtraction of atomic orbitals.

4.7 Molecular orbitals in hydrogen (H_2)

- The linear combination of two hydrogen 1s orbitals gives a bonding molecular orbital and an antibonding molecular orbital.
- The bonding orbital is labelled $1\sigma_g$ and the antibonding orbital is labelled $1\sigma_u{}^*$.
- In the $1\sigma_g$ orbital, electron density is enhanced between the nuclei, and in the $1\sigma_u{}^*$ orbital, electron density is reduced between the nuclei.

4.8 Molecular orbital energy level diagrams

- Electrons are placed into the molecular orbitals in an energy level diagram using the aufbau principle, in accordance with the Pauli exclusion principle.
- The bond order in a diatomic molecule is equal to the number of filled bonding orbitals minus the number of filled antibonding orbitals, with a single electron in an orbital contributing $\frac{1}{2}$.
- A molecule can exist if the bond order is greater than zero.
- When the degree of overlap between atomic orbitals is large, the interaction between them is large.
- Molecular orbital energy level diagrams can be used to predict whether molecules or ions exist.

? **For practice questions on the topic in Sections 4.6–4.8, see questions 7–10 at the end of this chapter (pp.213–214).**

4.9 Linear combinations of *p* orbitals

- In a diatomic molecule X_2, the two p_z orbitals point towards each other. They interact to form a σ_g bonding orbital and a σ_u^* antibonding orbital.
- The two p_x orbitals point at 90° to the direction of the other atom. The p_x orbitals interact to form a π_u bonding orbital and a π_g^* antibonding orbital. The p_y orbitals interact in an identical manner to the p_x orbitals, so the two π_u orbitals are degenerate, as are the two π_g^* orbitals.
- π-overlap is weaker than σ-overlap and more sensitive to distance.
- Atomic orbitals only interact to give molecular orbitals if they have the correct symmetry.

4.10 Bonding in flourine (F_2) and oxygen (O_2)

- Molecular orbital energy level diagrams can be used to explain trends in bond lengths and bond dissociation enthalpies.
- Unlike the Lewis model, molecular orbital theory is able to explain why O_2 is paramagnetic.
- In a molecule, the two most important orbitals are usually the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).
- Isoelectronic species have the same number of electrons.

? **For practice questions on the topic in Sections 4.9 and 4.10, see questions 11–13 at the end of this chapter (p.214).**

4.11 *s-p* mixing

- Molecular orbitals of the same symmetry interact through *s*–*p* mixing.
- *s*–*p* mixing is important for B_2, C_2, and N_2. The molecular orbital energy level order is different from that expected if you assume independent overlap of the *s* orbitals and *p* orbitals.
- *s*–*p* mixing is less important for O_2 and F_2. The molecular orbital energy levels are in the expected order.

? **For practice questions on these topics, see questions 14–16 at the end of this chapter (p.214).**

4.12 Heteronuclear diatomics

- Atomic orbitals combine together if:
  - (a) they have the correct symmetry, *and*
  - (b) there is efficient overlap, *and*
  - (c) if the orbitals are relatively close together in energy.
- The relative energies of the atomic orbitals of the contributing atoms in a heteronuclear diatomic can be predicted using electronegativities.
- In a linear combination expression, the different atomic orbitals contribute unequally and the bonding orbital lies closer in energy to the atomic orbital that contributes more to it.
- Heteronuclear diatomics can have non-bonding orbitals, in addition to bonding and antibonding orbitals.

? **For practice questions on these topics, see questions 17–19 at the end of this chapter (p.214).**

Concept review

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

- Describe the basis of the Lewis, valence bond, and molecular orbital theories of bonding and understand the similarities and differences between them.
- Draw Lewis structures for molecules and determine their bond orders.
- Understand the meaning of the valence bond terms resonance and hybridization.
- Draw the resonance forms for homonuclear and heteronuclear diatomic molecules.
- Understand the concept of electronegativity, and use the definition of χ^P to predict bond dissociation enthalpies for heteronuclear diatomic molecules.
- Draw boundary surfaces to show how molecular orbitals are formed from the linear combination of atomic orbitals (LCAO).
- Assign symmetry labels to orbitals using σ, π, g, and u.
- Recognize that π-overlap is both less efficient and more distance-sensitive than σ-overlap.
- Construct molecular orbital energy level diagrams for homonuclear diatomics and understand why there is a crossover in the order of the energy levels between N_2 and O_2 in the second period.
- Construct molecular orbital energy level diagrams for heteronuclear diatomics and understand why the degree of interaction between atomic orbitals depends on the energy gap between them.
- Interpret molecular orbital energy level diagrams and extract from them chemical information such as bond order and magnetic properties.
- Understand the basis of photoelectron spectroscopy and how it can be used to measure molecular orbital energy levels.

Key equations

The in-phase linear combinations of atomic orbitals	$\psi_{\text{in phase}} = \phi_{1s}(H_A) + \phi_{1s}(H_B)$	(4.8)
The out-of-phase linear combinations of atomic orbitals	$\psi_{\text{out of phase}} = \phi_{1s}(H_A) - \phi_{1s}(H_B)$	(4.9)
Definition of bond order	$\text{bond order} = \begin{matrix}\text{number of filled}\\ \text{bonding orbitals}\end{matrix} - \begin{matrix}\text{number of filled}\\ \text{antibonding orbitals}\end{matrix}$	(4.16)

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