
Diatomic molecules

3.1 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 two atoms in a molecule.
- 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.

3.2 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 O₂ contains unpaired electrons.

3.3 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.

3.4 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.

3.5 Valence bond theory

- Valence bond theory uses resonance to describe covalent and ionic contributions to the molecular wavefunction.
- Double-headed arrows are used to link 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.
- In heteronuclear diatomics, the resonance form with the negative charge on the more electronegative atom is more important than the resonance form with the negative charge on the more electropositive atom. This explains the polarity of the bond.

3.6 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.

3.7 Molecular orbitals in hydrogen (H₂)

- 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.

3.8 Molecular orbital energy level diagrams

- Molecular orbitals in an energy level diagram are filled 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 bond 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.

3.9 Linear combinations of *p* orbitals

- In a diatomic molecule X_2 , the two p_z orbitals point at each other. They interact to form a σ_g bonding orbital and a σ_u^* antibonding orbital.
- The two p_x orbitals point at right angles 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.

3.10 Bonding in fluorine (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 the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).
- Isoelectronic species have the same number of electrons.

3.11 *s-p* mixing

- Molecular orbitals of the same symmetry interact through *s-p* mixing.
- *s-p* mixing is important for B₂, C₂, and N₂. 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 O₂ and F₂. The molecular orbital energy levels are in the expected order.

3.12 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.
- Heteronuclear diatomics can have non-bonding orbitals, in addition to bonding and antibonding orbitals.

Learning outcomes

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.
- Understand the meaning of the valence bond terms resonance and hybridization.
- Draw the resonance forms for homonuclear and 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 N₂ and O₂ 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.