Valence Bond Theory

Formation of a Covalent Bond Between Two H Atoms

Valence Bond Theory

- a localized approach to bonding
- the region of space formed by the overlapping orbitals has a maximum capacity of two electrons that must have opposite spins (cf. Pauli Exclusion Principal for atoms)
- the greater the overlap between orbitals, the stronger the bond

Revision: Molecular Geometry

Lewis Structures

how many groups of electrons around an atom

VSEPR (including repulsion of different electron groups)

Molecular Geometry

Covalent Bond Formation in H₂

Covalent bonds result from the spatial overlap of half-filled orbitals of neighbouring atoms

Lewis Representation

Valence Bond

H⁺ + .H ⇒ H₂

[He] 2s² 2p xy 2p y 2p z

NH₃, BeH₂

( N = [He] 2s² 2p³ )

( Be = [He] 2s² )

Mixing atomic orbitals ⇒ VSEPR Geometries

We can obtain new orbitals by “mixing” (i.e., adding or subtracting multiples of) simple atomic orbitals.

Justification: Since the wavefunctions \( \Psi_2s \) (defining the 2s orbital) and \( \Psi_2p_y \) (defining the 2p y orbital) are solutions to the Schrödinger Equation, \( H \Psi_2s = E \Psi_2s \) and \( H \Psi_2p_y = E \Psi_2p_y \), it follows that the hybrid orbitals \( \Psi_{sp}(1) = (\Psi_2s + \Psi_2p_y) \) and \( \Psi_{sp}(2) = (\Psi_2s - \Psi_2p_y) \) are also solutions.
The atomic orbitals that are represented by these new “mixed” solutions are called **hybrid orbitals**, and the process of generating these is called **hybridisation**.

**Orbital Hybridisation**

- Hybrid orbitals are directed in space and so overlap more effectively with orbitals of other atoms to form stronger σ-bonds (than would be the case without hybridisation).
- The number of orbitals being mixed is equal to the number of hybrid orbitals being formed.
- Hybrid orbitals may be occupied either by single unpaired electrons (capable of forming a bond) or by non-bonding ('lone') electron pairs.

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**The sp Hybrid Orbitals in Gaseous BeCl₂**

**The sp² Hybrid Orbitals in BF₃**

**The sp³ Hybrid Orbitals in CH₄**

**The sp³ Hybrid Orbitals in NH₃ and H₂O**

**The sp³d³ Hybrid Orbitals in PCl₅**

**The sp³d² Hybrid Orbitals in SF₆**
### Types of Bonds

- **σ-bonding** = direct end-to-end overlap between neighbouring orbitals, so that the maximum electron density lies along the bond axis.

- **π-bonding** = indirect side-to-side overlap between neighbouring orbitals, so that there are two regions of maximum electron density, one on each side of the bond axis.

### Representing the double bond in ethene

- **cis-1,2-dichloroethene**
- **trans-1,2-dichloroethene**

### Triple Bonds

Consider Ethyne

- **5 important hybridisation schemes:**
  - σ-bonding and π-bonding