CHEM110 – Chapter 5
Chemical Bonding and Molecular Structure

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5.4 VSEPR Theory

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- **V**alence **S**hell **E**lectron **P**air **R**epulsion theory
- molecular shape is determined by repulsions between pairs of electrons
- To minimise these repulsions, electron pairs around an inner atom within a molecule will be situated as far apart as possible

5.4 VSEPR Theory

VSEPR procedure :

- Draw the Lewis structure of the molecule
- Count the number of sets of bonding pairs (BP) and lone pairs (LP) of electrons

5.4 VSEPR Theory

- Use the following table:

Number of sets of electron pairs	Geometry of sets of electron pairs
2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

- Modify the geometry if necessary, considering repulsions are in the order

  LP-LP > BP-LP > BP-BP

5.4 VSEPR Theory

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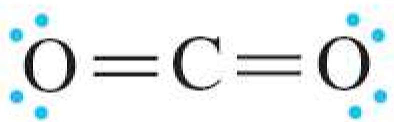
Two sets of electron pairs → linear

The two sets of electron pairs need to be situated as far apart as possible

→ Linear arrangement / linear shape

Example: CO_2



two sets of electron
pairs around the C atom

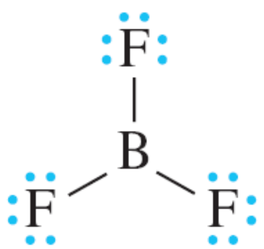
linear shape
bond angle = 180°

5.4 VSEPR Theory

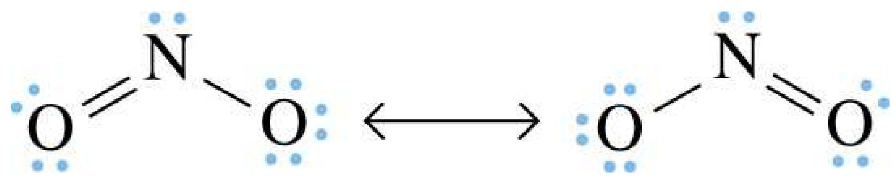
Three sets of electron pairs → trigonal planar

Three sets of electron pairs around an inner atom need to be situated as far apart as possible

→ In trigonal planar, the sets are oriented at 120° to each other and are coplanar



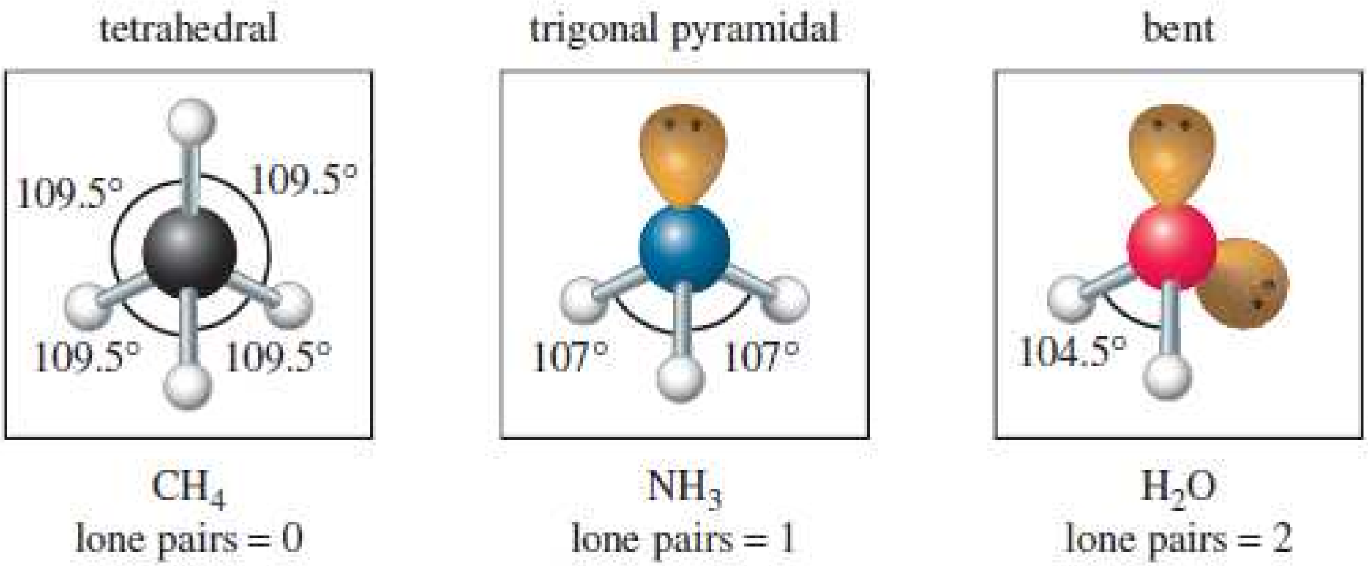
3 BP



2BP+1LP

5.4 VSEPR Theory

Four sets of electron pairs → tetrahedral

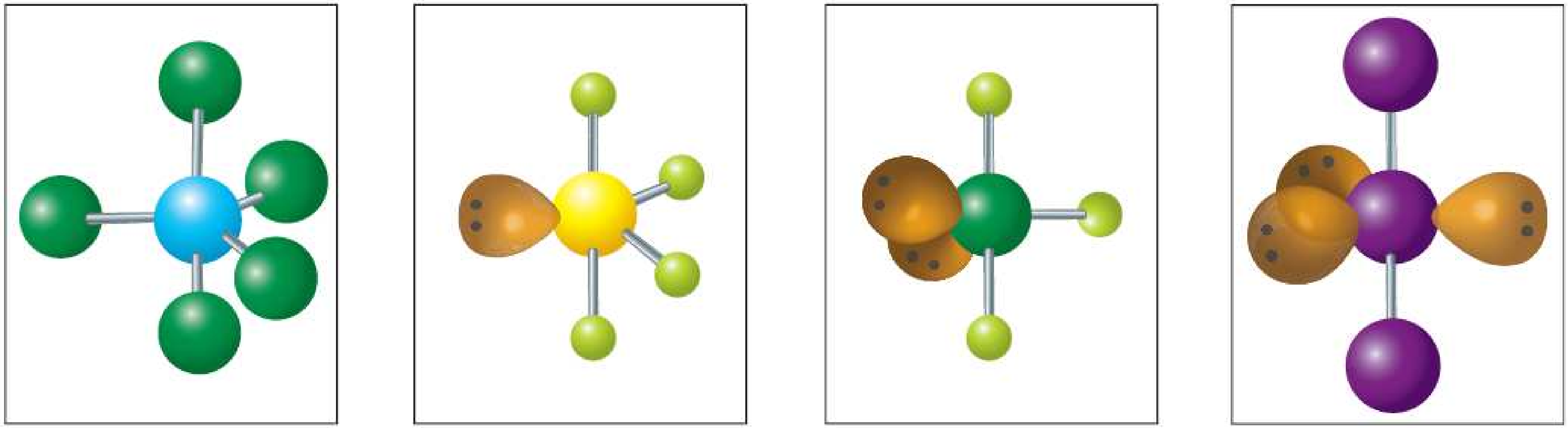


4 BP | 3BP+1LP | 2BP+2LP

5.4 VSEPR Theory

Five sets of electron pairs → trigonal bipyramidal

trigonal bipyramidal | seesaw | T-shaped | linear



PCl_5
lone pairs = 0

SF_4
lone pairs = 1

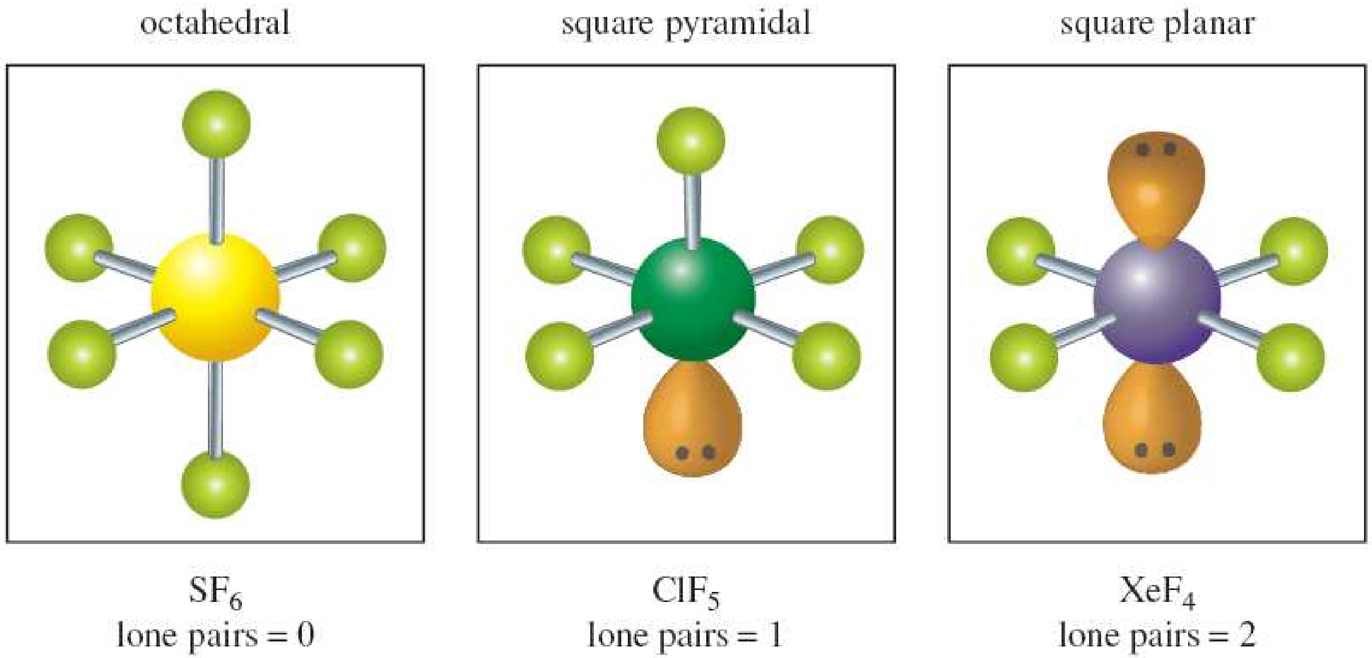
ClF_3
lone pairs = 2

I_3^-
lone pairs = 3

5 BP | 4BP+1LP | 3BP+2LP | 2BP+3LP

5.4 VSEPR Theory

Six sets of electron pairs → octohedral geometry



6 BP 5BP+1LP 4BP+2LP

5.4 VSEPR Theory

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Worked Example 5.4:

Determine the shape of the hydronium ion, H_3O^+, using VSEPR theory. Make a sketch of the ion that shows the three-dimensional shape, including any lone pairs that may be present.

5.5 Properties of Covalent Bonds

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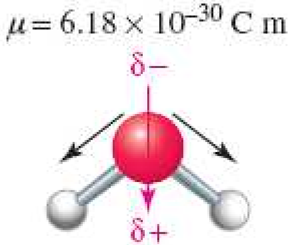
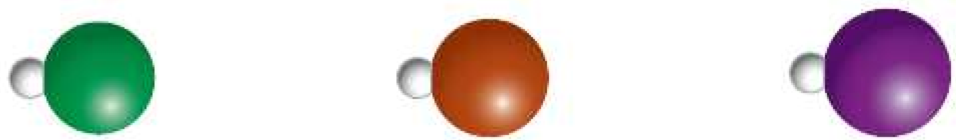
Dipole moment

- Most chemical bonds are polar (one end slightly positive, the other slightly negative)
- Bond polarities can lead to molecules with dipole moment
- Dipole moment depend on bond polarities ($\Delta\chi$) and on molecular shape

(a) CO_2



(b) H_2O



HCl $\Delta\chi = 1.9$ $\mu = 3.57 \times 10^{-30}$ C m

HBr $\Delta\chi = 0.7$ $\mu = 2.64 \times 10^{-30}$ C m

HI $\Delta\chi = 0.4$ $\mu = 1.27 \times 10^{-30}$ C m

5.5 Properties of Covalent Bonds

Worked Example 5.5:

Does either ClF_5 or XeF_4 have a dipole moment?

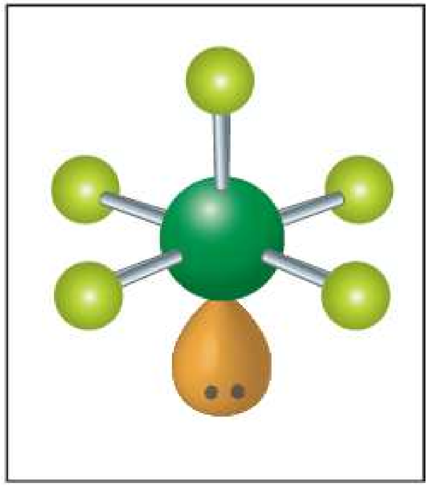
Interactive Problem

Does ClF_5 have a dipole moment?

A. Yes

B. No

square pyramidal



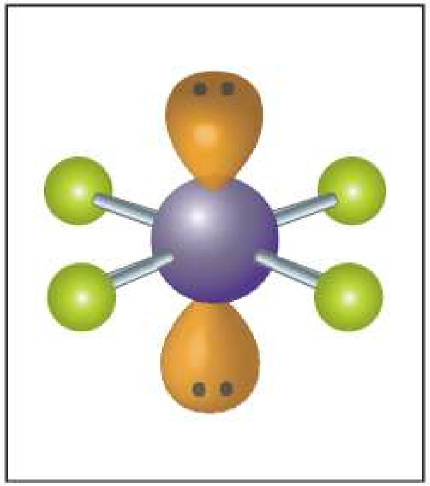
ClF_5
lone pairs = 1

Does XeF_4 have a dipole moment?

A. **Yes**

B. **No**

square planar



XeF_4
lone pairs = 2

5.5 Properties of Covalent Bonds

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Bond length

- Bond length of a covalent bond is the nuclear separation distance at which the molecule is most stable
- At this distance, attractive interactions are maximised relative to repulsive interactions
- Bond lengths vary between 70 and 250 pm ($1pm = 10^{-12}m$)

5.5 Properties of Covalent Bonds

Bond energy

- It is the amount of energy that must be supplied to break a chemical bond
- Bond energies increase as more electrons are shared between the atoms
- Bond energies increase as the electronegativity difference ($\Delta\chi$) between bonded atoms increases
- Bond energies decrease as bonds become longer

5.6 Valence Bond Theory

Two ways to think about chemical bonding :

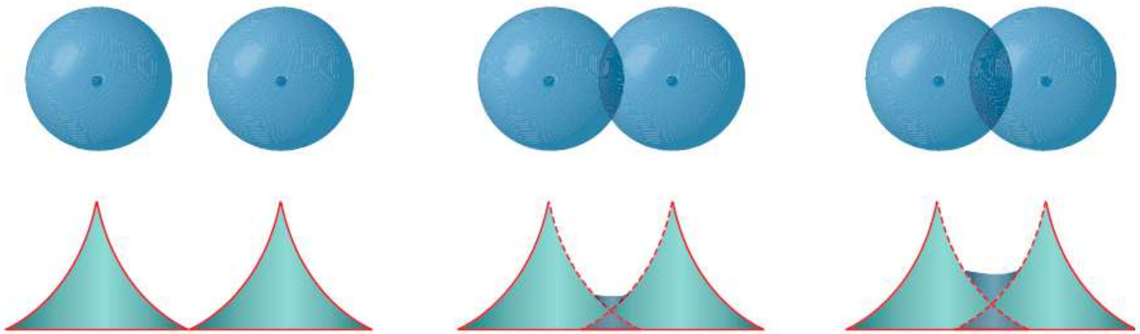
- Valence bond theory (localised bonds)
- Molecular orbital theory (delocalised bonds)

Delocalisation requires a more complicated analysis but explain chemical properties that localised bonds cannot

5.6 Valence Bond Theory

Orbital overlap

- Bonding orbitals are created by combining atomic orbitals
- Example : H_2, as 2 hydrogen atoms approach each other, the overlap of their 1s orbitals increases



5.6 Valence Bond Theory

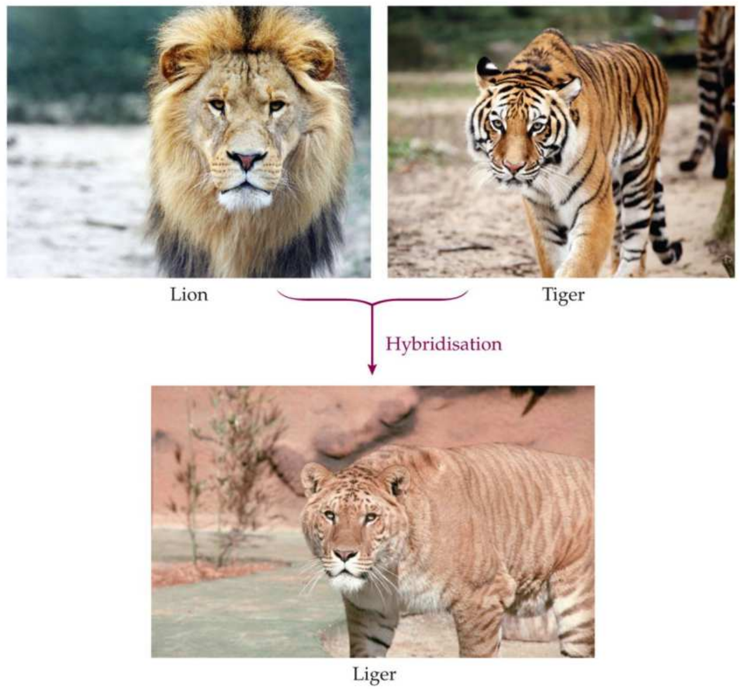
Conventions of the orbital overlap model

- Each electron in a molecule is assigned to a specific orbital
- No two electrons in a molecule have identical descriptions (Pauli exclusion principle; Ch 4)
- The electrons in molecules occupy the lowest energy orbital available (Aufbau principle; Ch 4)
- Only the valence orbitals are needed to describe bonding

5.6 Valence Bond Theory

Hybridisation of atomic orbital

- Hybrid orbitals are combinations of atomic orbitals
- The process by which we combine them is called hybridisation



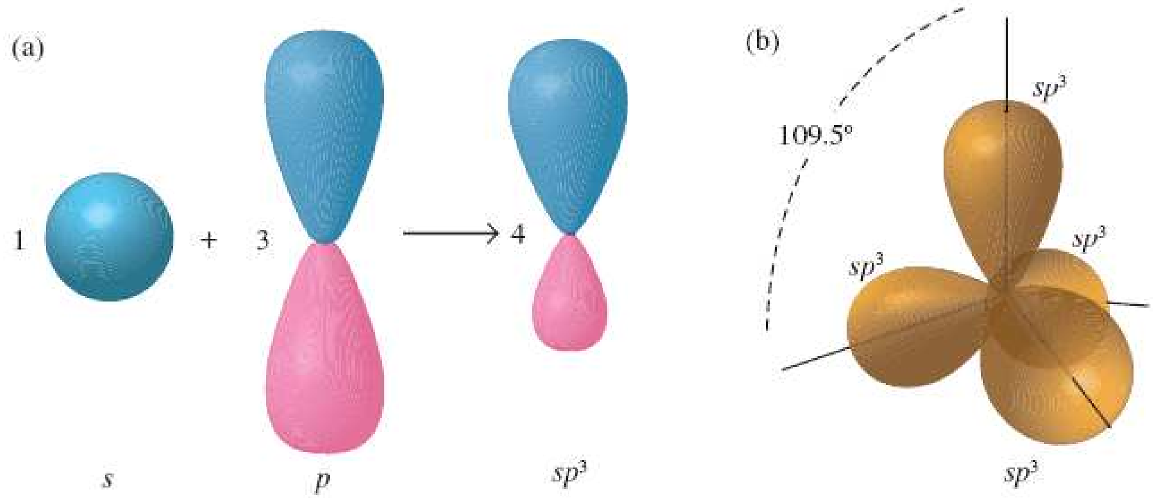
5.6 Valence Bond Theory

sp^3 hybrid orbital (example of methane CH_4)

Electron configuration of carbon $1s^2 2s^2 2p^2$

Valence orbitals are 2*s* and 2*p* orbitals

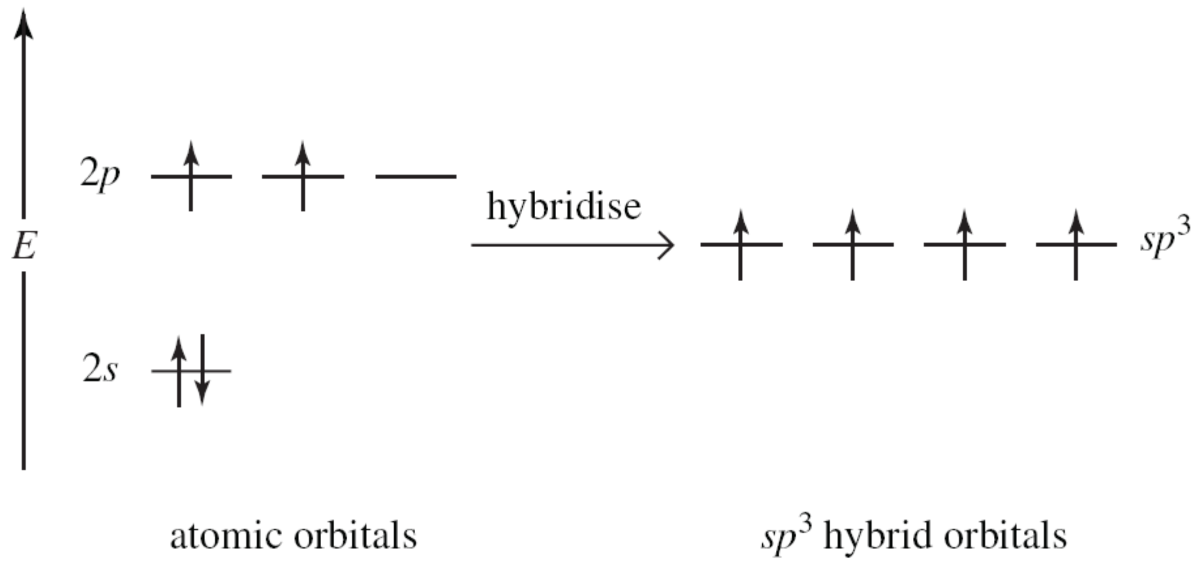
They are mixed to form a new hybrid orbital sp^3 (¼*s* character – ¾*p* character)



5.6 Valence Bond Theory

sp^3 hybrid orbital (example of methane)

In terms of energy of *sp*^{3} hybrid orbital must be $\frac{1}{4}\,E_{2s} + \frac{3}{4}\,E_{2p}$



5.6 Valence Bond Theory

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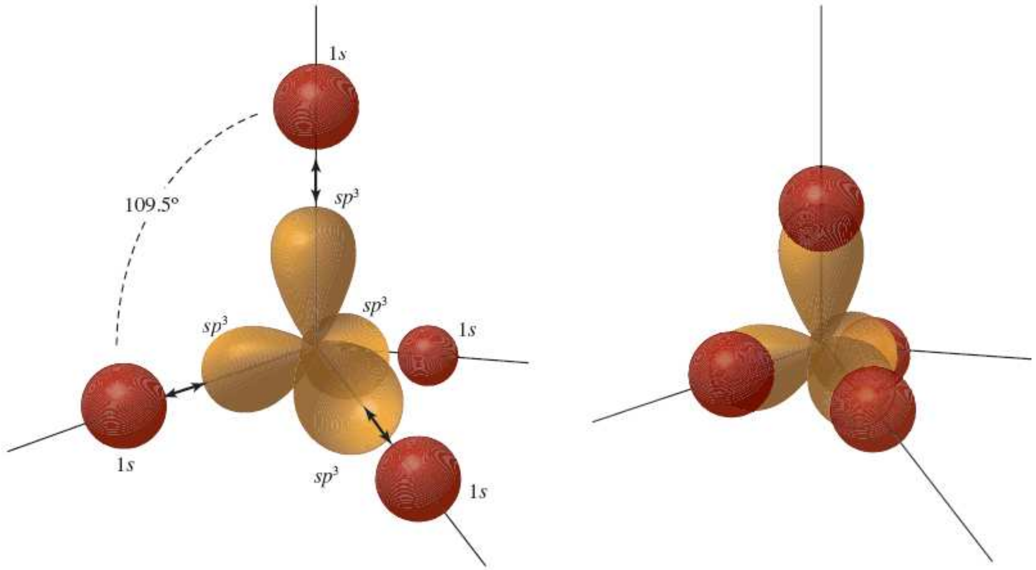
sp^3 hybrid orbital (example of methane)

Methane forms from orbital overlap between the hydrogen 1*s* orbitals and the *sp*^{3} hybrid orbital of carbon atom



sp^3 hybridisation is not limited to carbon

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Worked Example 5.7:

Describe the bonding of the hydronium ion, H_3O^+, in terms of hybrid orbitals

5.6 Valence Bond Theory

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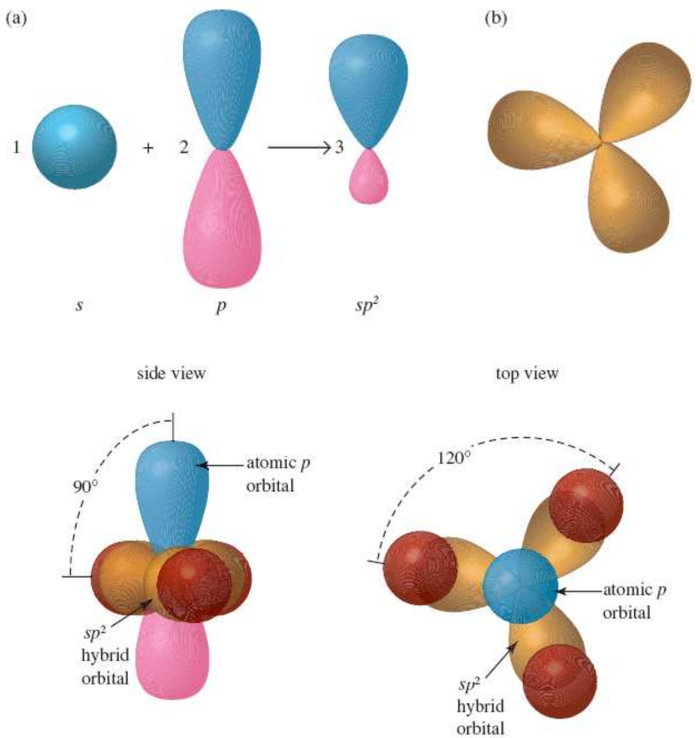
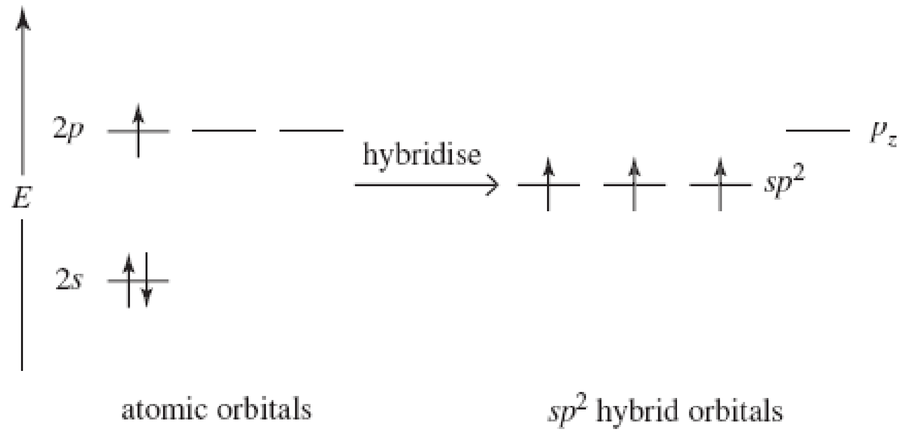
sp^2 hybrid orbital (example of BF_3)

Electron configuration of boron $1s^2 2s^2 2p^1$

(1/3 *s* character – 2/3 *p* character)



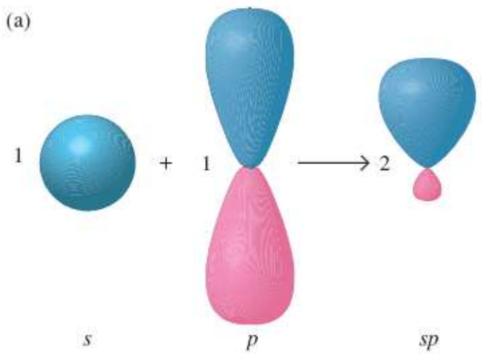


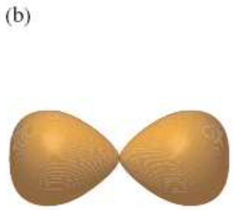
5.6 Valence Bond Theory

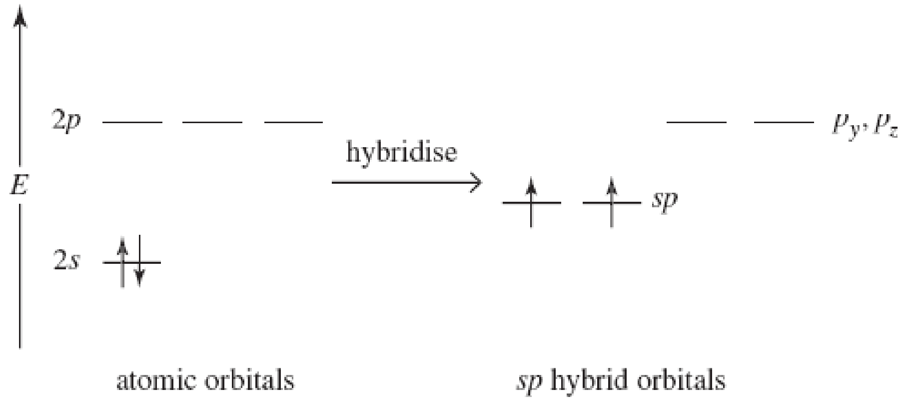
sp hybrid orbital (example of BeH_2)

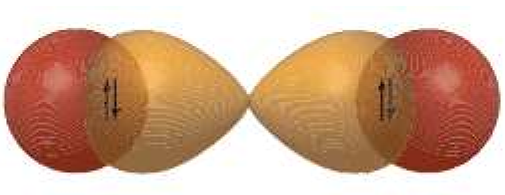
Electron configuration of berylium $1s^2 2s^2 2p^0$

(½*s* character – ½*p* character)









5.6 Valence Bond Theory

Multiple bonds

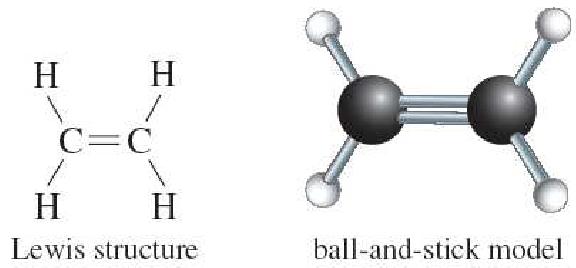
Procedure :

- Determine the Lewis structure
- Use the Lewis structure to determine the type of hybridisation
- Construct the σ bond framework
- Add the π bonds

5.6 Valence Bond Theory

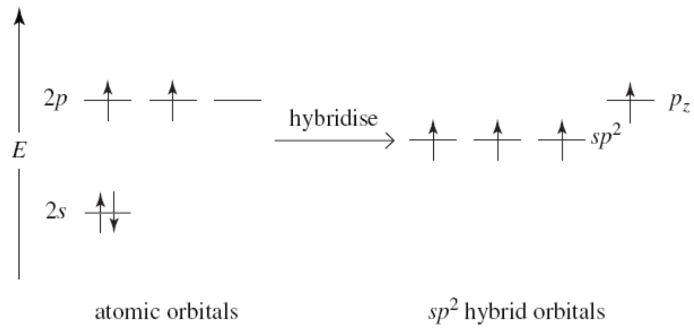
Multiple bonds – example of ethene

Double bond



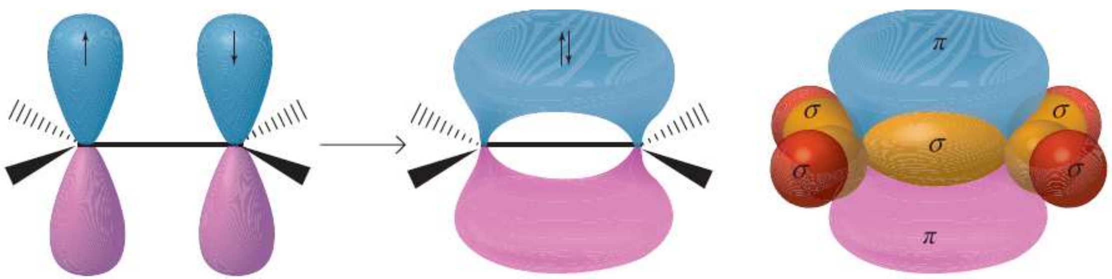
Carbon atoms

sp^2 hybridised



Orbital picture of bonding

one σ bond and one π bond



5.6 Valence Bond Theory

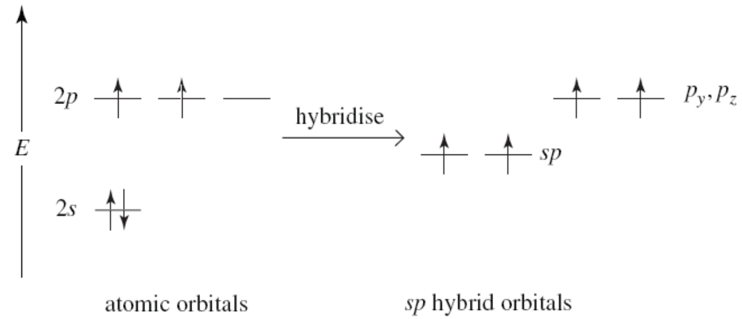
Multiple bonds-example of ethyne

Triple bond

$H-C\equiv C-H$

Carbon atoms

sp hybridised

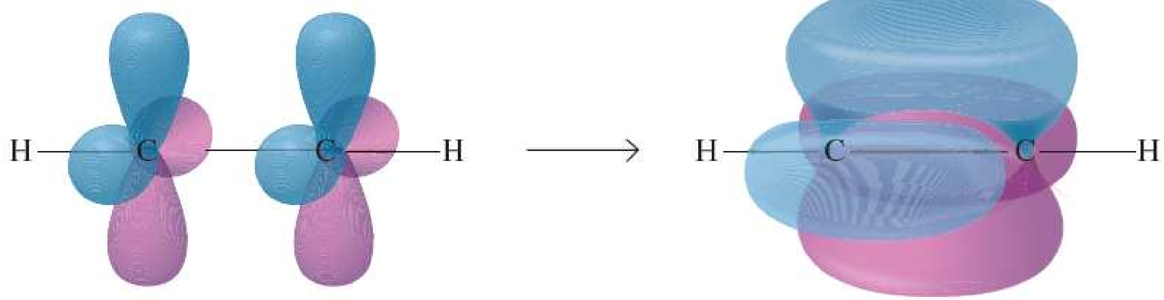


Orbital picture

of bonding

one σ bond

and two π bonds



5.6 Valence Bond Theory

Worked Example 5.7:

Hydrogen cyanide, HCN, is an extremely poisonous gas. Approximately half a million tonnes of HCN is produced each year, most of which is used to prepare starting materials for polymers. Construct a complete bonding picture for HCN and sketch various orbitals.