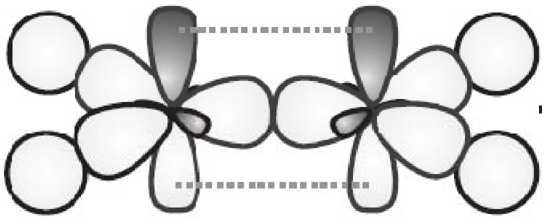
Topic 7

Valence Bond Theory (Hybridization)



7.1 Contents in Brief

- Understanding hybrid atomic orbitals
- sp, sp^2, sp^3, sp^3d and sp^3d^2 hybridization
- Compounds involving lone pairs in hybrid orbitals
- The relationship between VSEPR and hybridization at the central atom

7.2 Introduction

7.3 Hybrid Atomic Orbitals

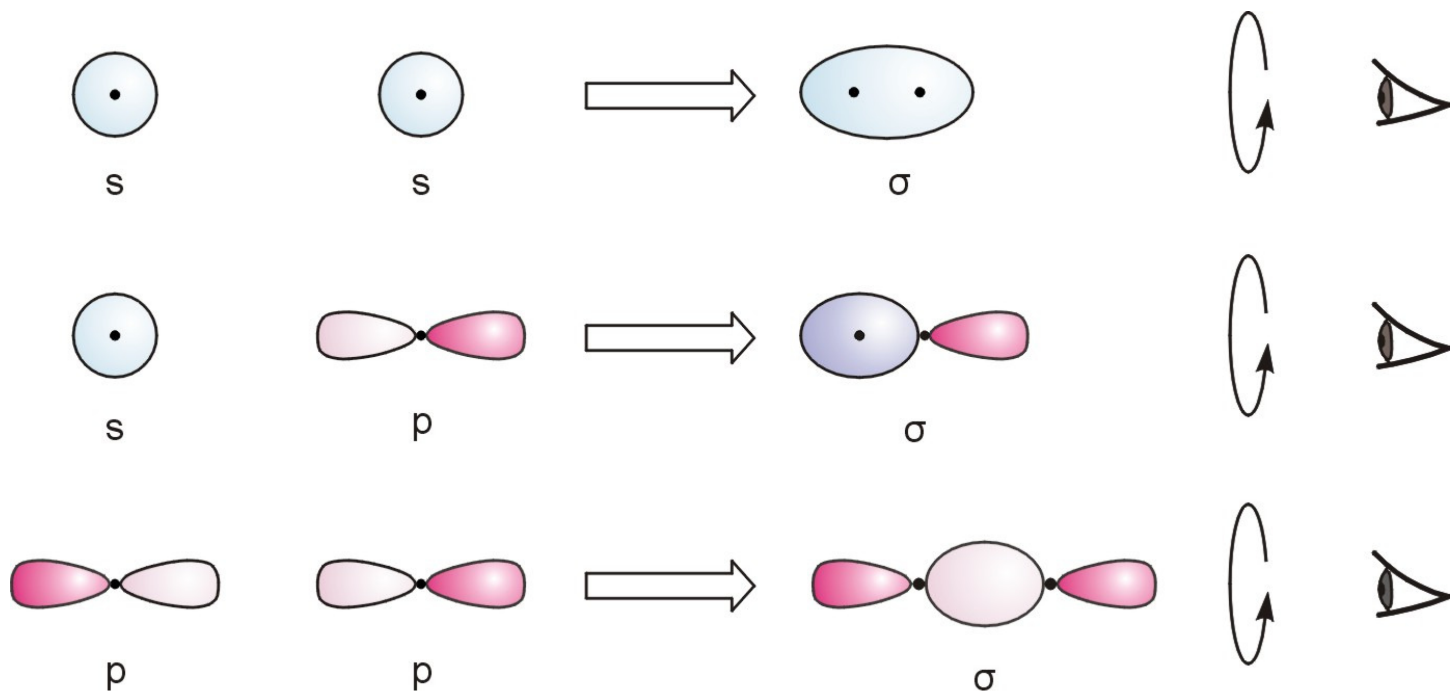


Figure 7.1: Overlap of s and p atomic orbitals to form σ-bonds. Dots represent the positions of the nuclei. Shading (light or dark) denotes the relative sign of the wave function.

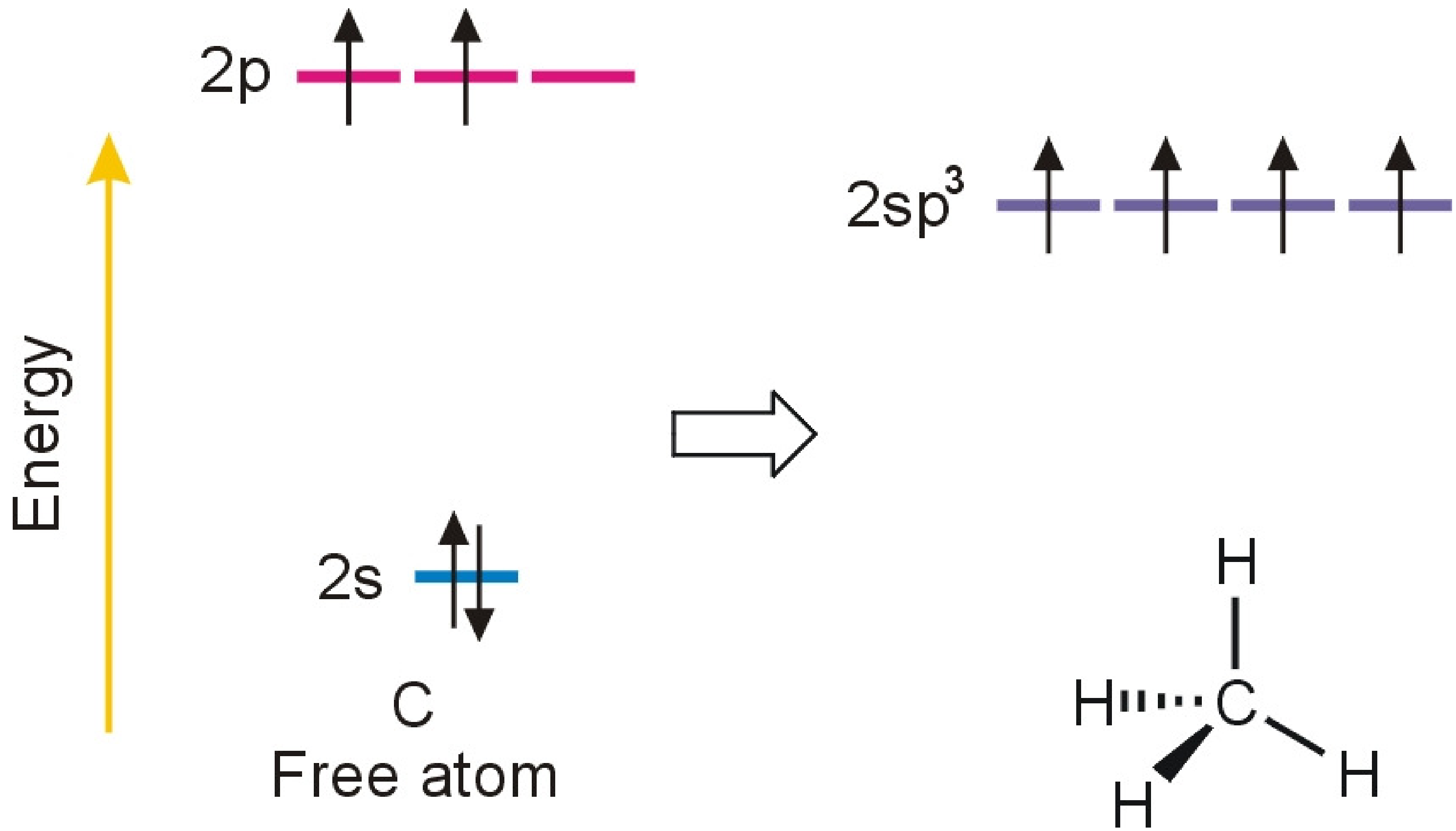


Figure 7.2: Energy levels of 2s and 2p atomic orbitals of carbon and the corresponding four degenerate $2sp^3$ hybrid orbitals in methane.

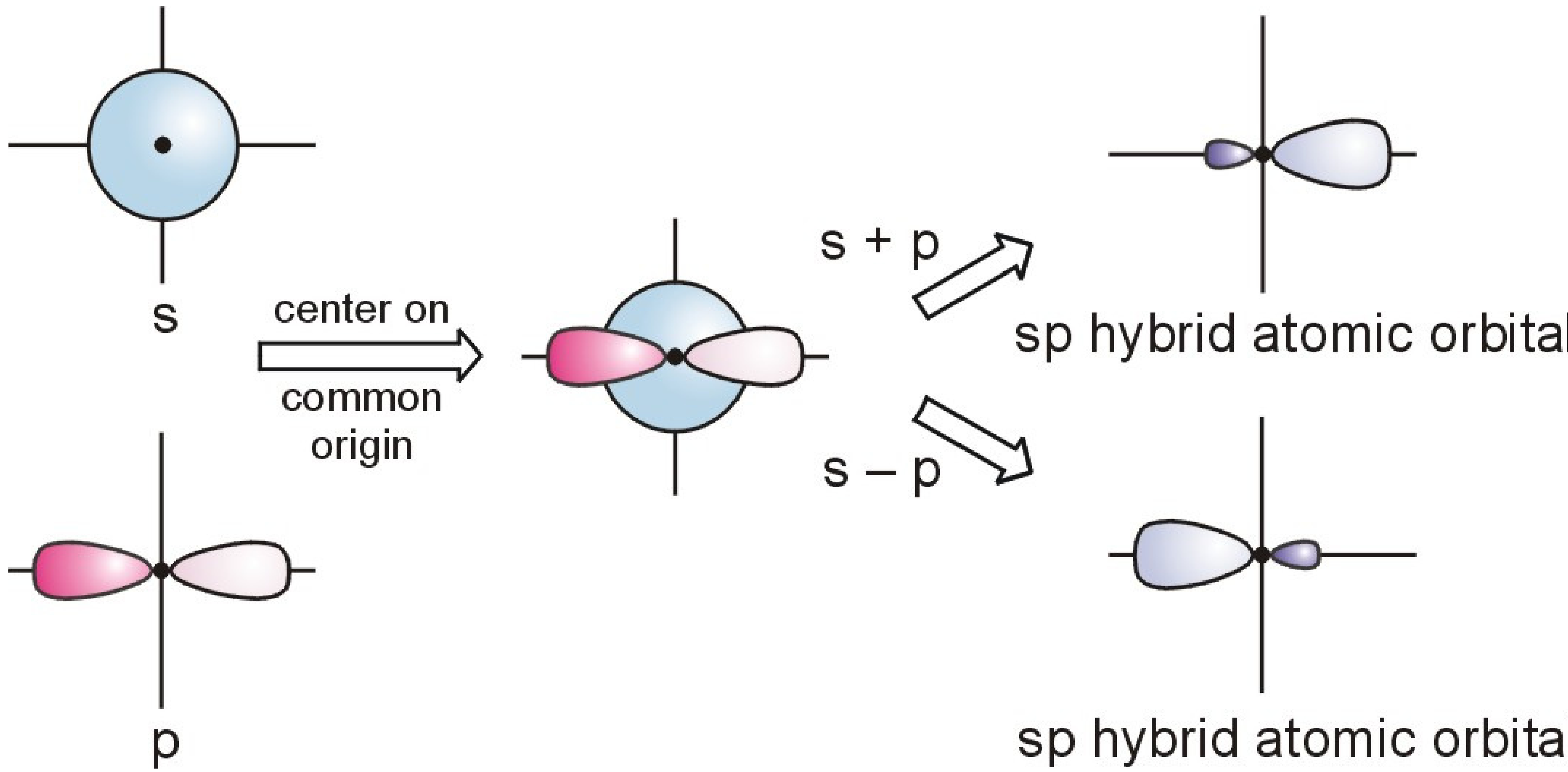


Figure 7.3: Visualizing hybridization of an s and p orbital.

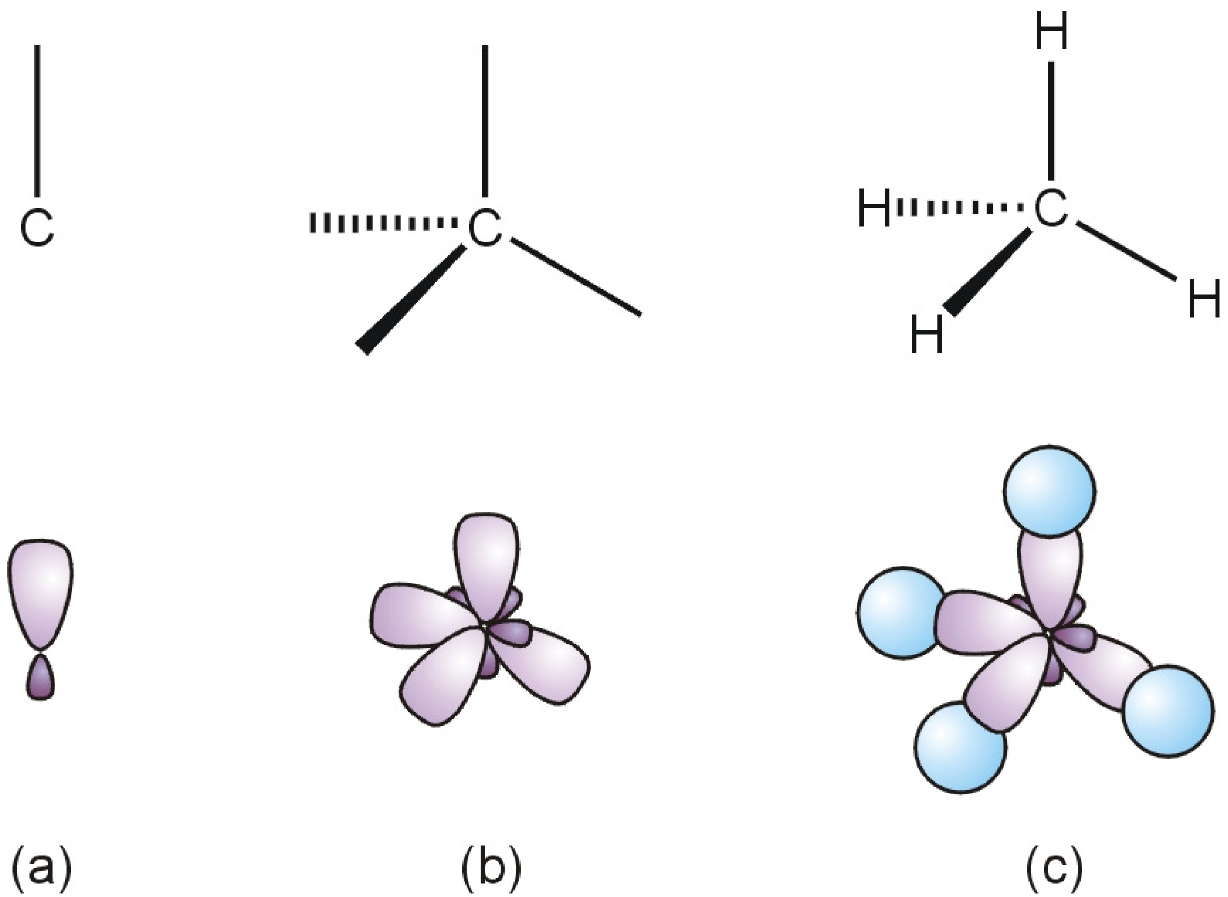


Figure 7.4: (a) Shape of a $2sp^3$ orbital of carbon (b) tetrahedral arrangement of four $2sp^3$ orbitals (c) overlap of four $2sp^3$ orbitals with four H 1s orbitals in methane.

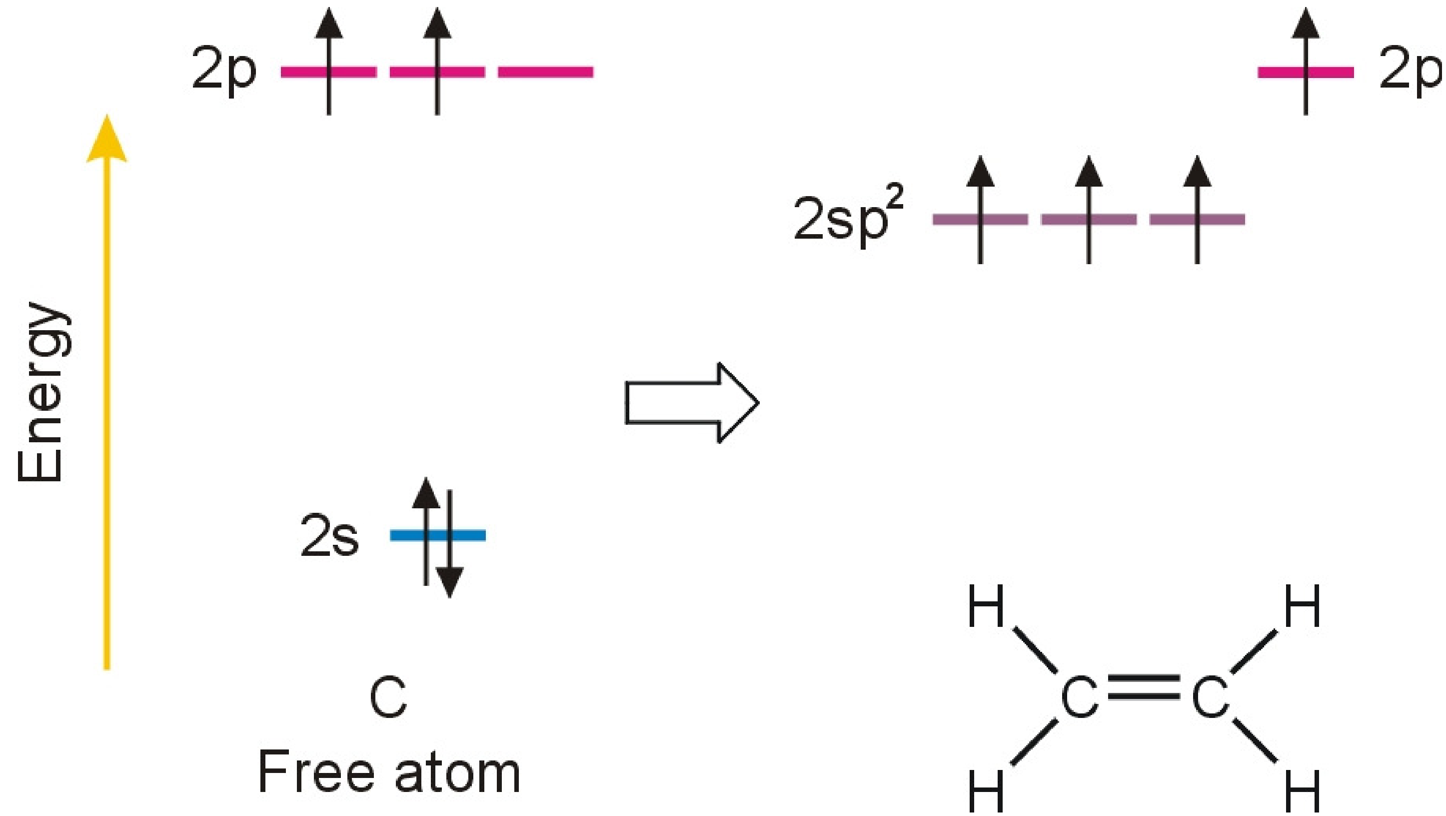


Figure 7.5: Hybridization of one 2s and two 2p atomic orbitals of each carbon atom in ethene to form three $2sp^2$ hybrid orbitals. One unhybridized 2p orbital is used to form a π bond with the unhybridized 2p orbital of the neighbouring carbon atom.

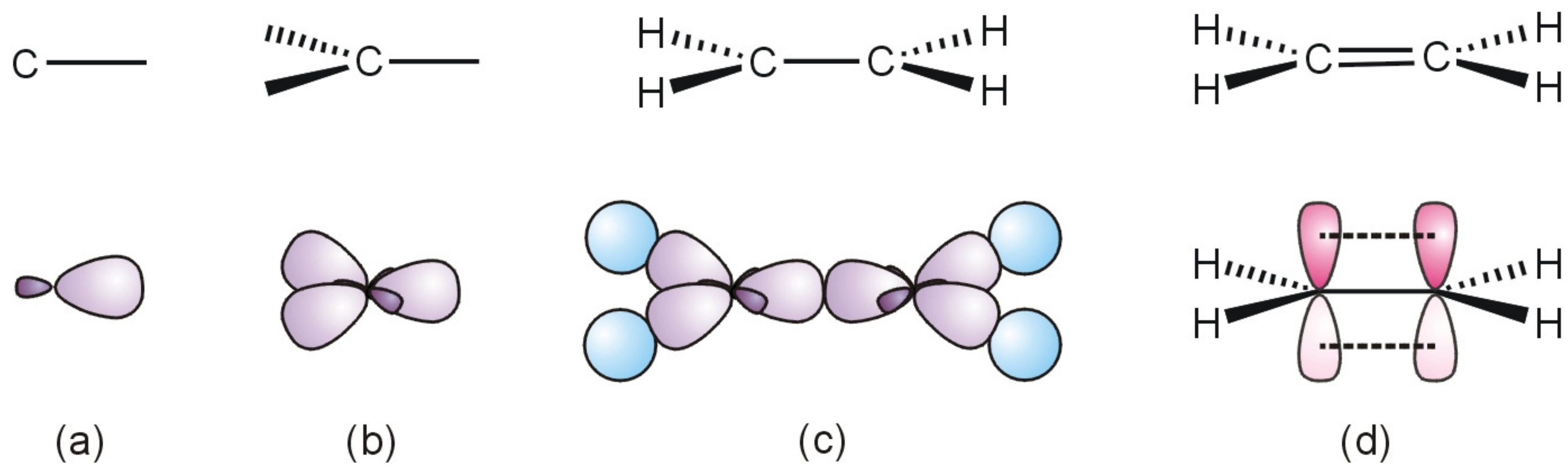


Figure 7.6: (a) Shape of a $2sp^2$ orbital of carbon (b) trigonal planar arrangement of three $2sp^2$ orbitals at each carbon atom in ethene (c) σ-overlap between two carbon atoms and σ-overlap of four terminal $2sp^2$ orbitals with four H 1s orbitals (d) π-overlap of two unhybridized 2p orbitals on neighbouring carbon atoms.

concepts in chemistry

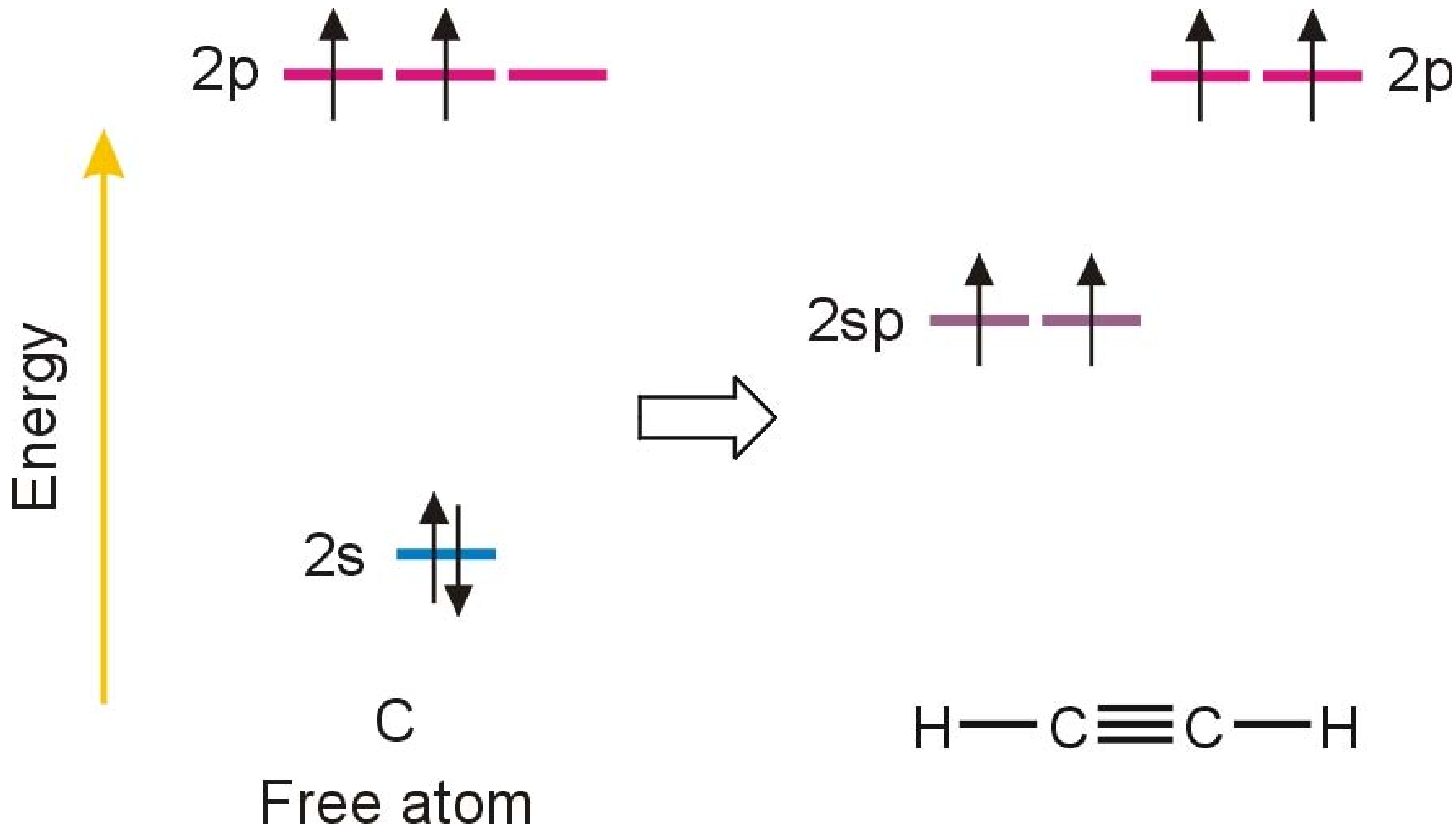


Figure 7.7: Hybridization of one 2s and one 2p atomic orbital of each carbon atom to form two degenerate sp hybrid orbitals on carbon in ethyne. Unhybridized 2p orbitals are used to form π overlap with unhybridized 2p orbitals on the neighboring carbon atom.

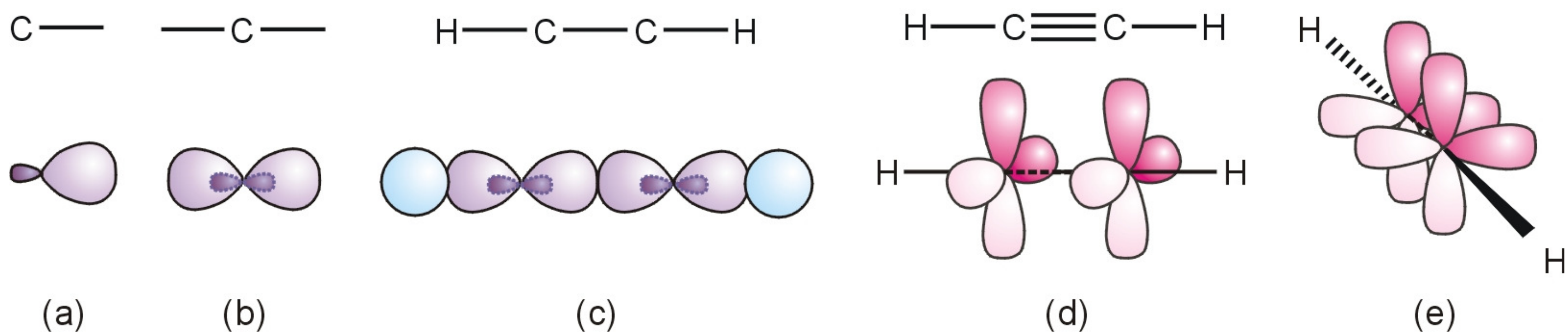


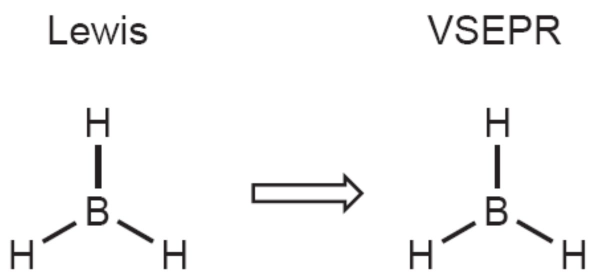
Figure 7.8: (a) Shape of a 2sp orbital of carbon (b) linear arrangement of two sp orbitals at each carbon atom in ethyne (c) σ overlap between two carbon atoms and σ overlap of two sp orbitals with two H 1s orbitals (d) π overlap of two pairs of unhybridized 2p orbitals on neighbouring carbon atoms (e) end-on view of π overlap in (d).

Table 7.1: Relationship between VSEPR number and hybridization.

VSEPR formula	Example	No. of VSEPR pairs, n + m	VSEPR shape (polygon)	Hybridization at A
AX_2	$BeCl_2$	2	linear	sp
AXE	CO	2	linear	sp
AX_3	BF_3	3	trigonal planar	sp^2
AX_2E	NO_2^-	3	trigonal planar	sp^2
AXE_2	O_2	3	trigonal planar	sp^2
AX_4	NH_4^+	4	tetrahedral	sp^3
AX_3E	NH_3	4	tetrahedral	sp^3
AX_2E_2	H_2O	4	tetrahedral	sp^3
AXE_3	HF	4	tetrahedral	sp^3
AX_5	PF_5	5	trigonal bipyramidal	sp^3d
AX_4E	$BrCl_4^+$	5	trigonal bipyramidal	sp^3d
AX_3E_2	ClF_3	5	trigonal bipyramidal	sp^3d
AX_2E_3	XeF_2	5	trigonal bipyramidal	sp^3d
AX_6	SF_6	6	octahedral	sp^3d^2
AX_5E	ICl_5	6	octahedral	sp^3d^2
AX_4E_2	XeF_4	6	octahedral	sp^3d^2

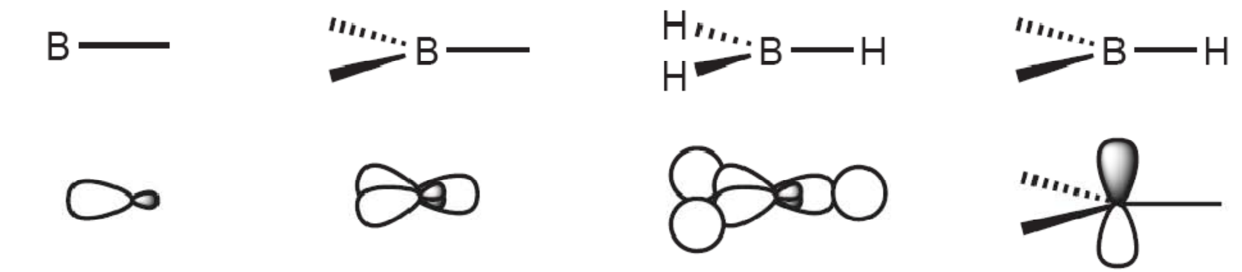
Example 7.1: Drawing hybrid orbitals

Describe the hybridization at B in BH_3.



AX_3
3 VSEPR pairs
trigonal planar
angles: 120°

For Lewis procedures, see Topic 5.4, for VSEPR procedures, see Topic 6.4. The trigonal planar VSEPR geometry is modeled by sp^2 hybridization, a mixing of one 2s and two 2p orbitals on B that gives three energy-equivalent (degenerate) $2sp^2$ orbitals with an angle of 120° between them. This leaves one unhybridized 2p orbital perpendicular to the trigonal plane. Following the same process as that illustrated in Figure 7.5 for the hybrid orbitals of the carbon centers in ethene, the three $2sp^2$ orbitals of B will each contain one electron and will overlap with the 1s orbitals from each of the three hydrogen centers (each containing one electron) to form three σ bonds, as illustrated in Figure 7.6 for the orbitals of carbon in ethene. The unhybridized 2p orbital is perpendicular to the trigonal plane of the molecule and is vacant.



$2sp^2$ hybrid

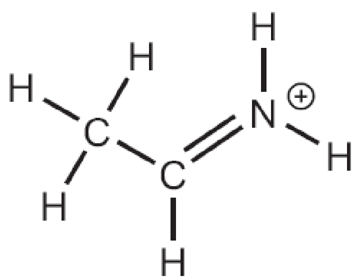
3 x $2sp^2$ hybrids in trigonal planar arrangement

3 x σ bonds

unhybridized 2p orbital on B

Exercise 7.1

For the Lewis structure shown below, describe the hybridization at nitrogen and carbon.

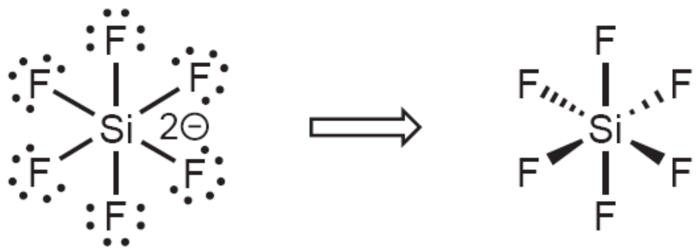


7.4 Hybridization in Compounds Containing the Heavy Elements

Example 7.2: Hybrid orbitals in compounds containing the heavy elements

Describe the hybridization in SiF_6^{2-}.

Lewis VSEPR



AX_6 (octahedral)
6 VSEPR pairs
octahedral
angles: 90°

For Lewis procedures see Topic 5.4, for VSEPR procedures, see Topic 6.4. The octahedral VSEPR geometry is modeled by sp^3d^2 hybridization, a mixing of one 3s, three 3p orbitals and two 3d orbitals on Si to give six degenerate $3sp^3d^2$ orbitals with an angle of 90° between them.

Exercise 7.2

Describe the hybridization at phosphorus in:

(a) PCl_4^+

(b) PCl_5

7.5 Compounds Involving Lone Pairs in Hybrid Orbitals

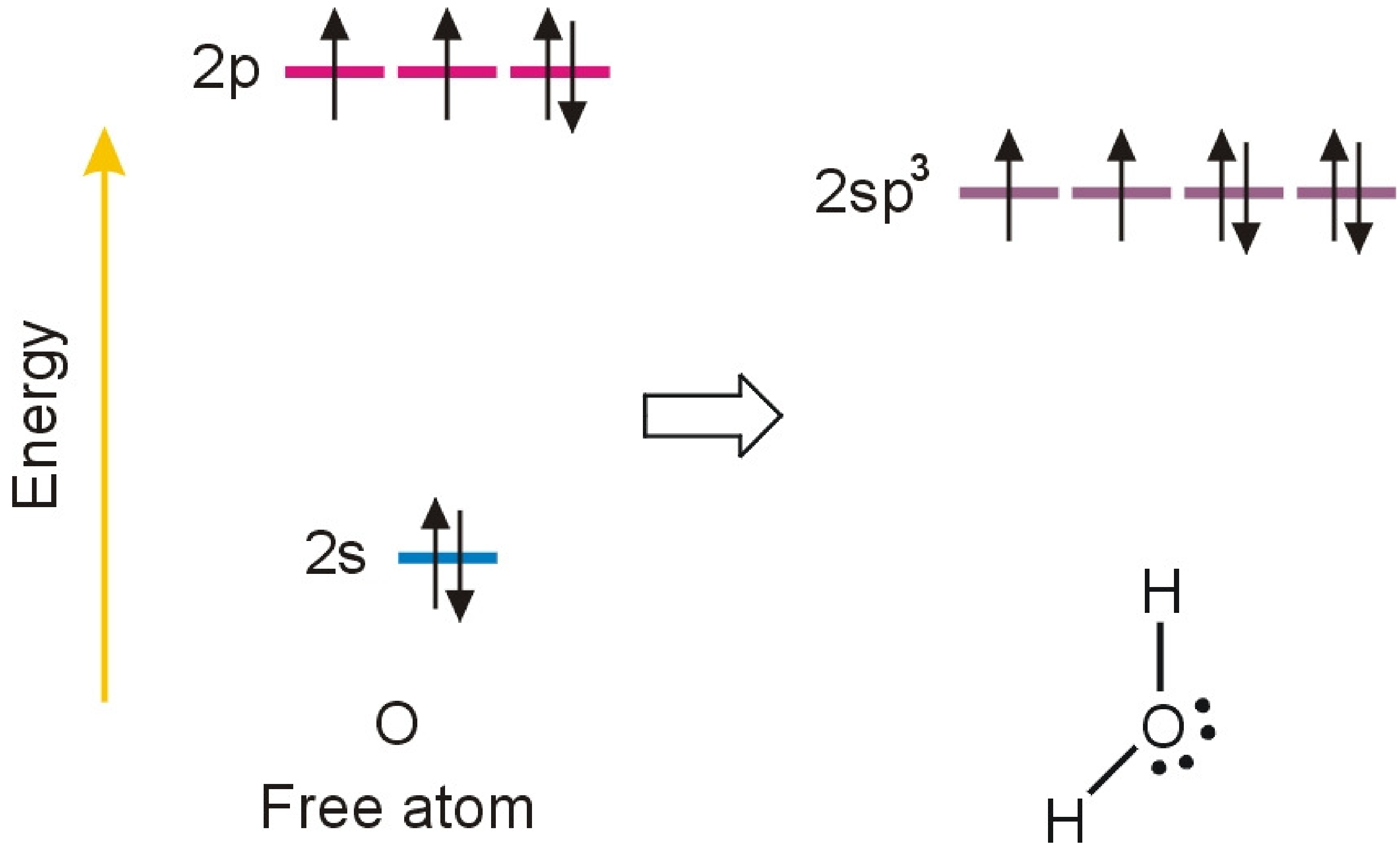
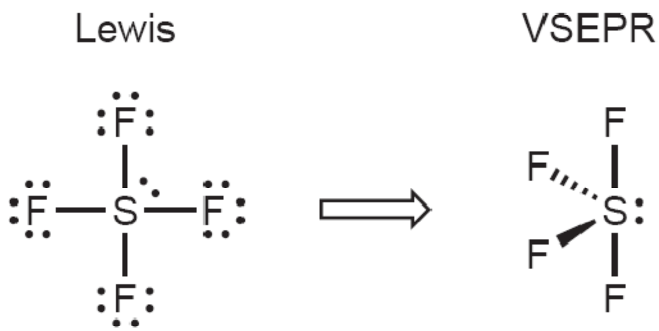


Figure 7.9: Hybridization of oxygen atomic orbitals in water.

Example 7.3: Hybrid orbitals containing lone pairs

Describe the hybridization in SF_4.



AX_4E (see-saw)
5 VSEPR pairs
trigonal bipyramidal
angles: 90° and 120°

For Lewis procedures see Topic 5.4, for VSEPR procedures, see Topic 6.4. The trigonal bipyramidal VSEPR geometry is modeled by sp^3d hybridization, a mixing of one 3s, three 3p orbitals and one 3d orbital on S to give five degenerate $3sp^3d$ orbitals with angles of 90° and 120° between them. The five degenerate $3sp^3d$ orbitals have an energy that is an average of the 3s, 3p and 3d orbitals involved.

Exercise 7.3

Describe the hybridization at xenon in XeF_2.

Exercise 7.4

Draw the best Lewis structure and determine the hybridization of the underlined atom in each of the following molecules.

(a) H<u>C</u>N

(b) <u>P</u>H_3

(c) <u>C</u>HCl_3

(d) <u>N</u>H_4^+

(e) <u>B</u>F_4^-

(f) <u>Se</u>F_2

(g) $\underline{P}OCl_3$

(h) $\underline{S}O_4^{2-}$

(i) $\underline{Xe}O_4$

(j) $\underline{P}O_4^{3-}$

(k) $\underline{Cl}O_3^-$

(l) $\underline{N}O_2^-$

(m) $H\underline{N}O_2$

(n) $H\underline{N}O_3$

(o) $\underline{C}_2N_2$ $(N\underline{CC}N)$

(p) $\underline{C}O_2$

(q) $\underline{Br}F_5$

(r) $\underline{Kr}F_4$

(s) $\underline{C}H_4O$ ($\underline{C}H_3OH$)

(t) $\underline{S}O_3^{2-}$

(u) $\underline{P}O_3^{3-}$

(v) $\underline{Cl}O_2^{-}$

(w) $\underline{P}Cl_2^-$

(x) $\underline{Xe}OF_3^+$

(y) $\underline{Sb}Cl_4^+$

(z) $\underline{S}F_3^+$