Organic chemistry background I:

Fundamentals on atoms and molecules

Organic compounds

- **Definition**
  - Any member of compounds containing carbon
  - Exception: carbonates (HCO_3^- and CO_3^{2-}), simple carbon oxides (CO and CO_2), carbides*, cyanides (CN^-)

  ** carbides: compound composed of carbon and a less electronegative element (ex: CaC_2, CSi, WC)*

- **Makeup of organic molecules**
  - Millions of organic compounds exist due to the ability of carbon to form up to four stable carbon-carbon bonds
  - Unlimited kinds of *carbon skeletons* can be made
  - Elemental composition: C, H, O, N, S, P, halogens
  - Heteroatoms: elements in an organic molecule other than C and H

Description of a compound

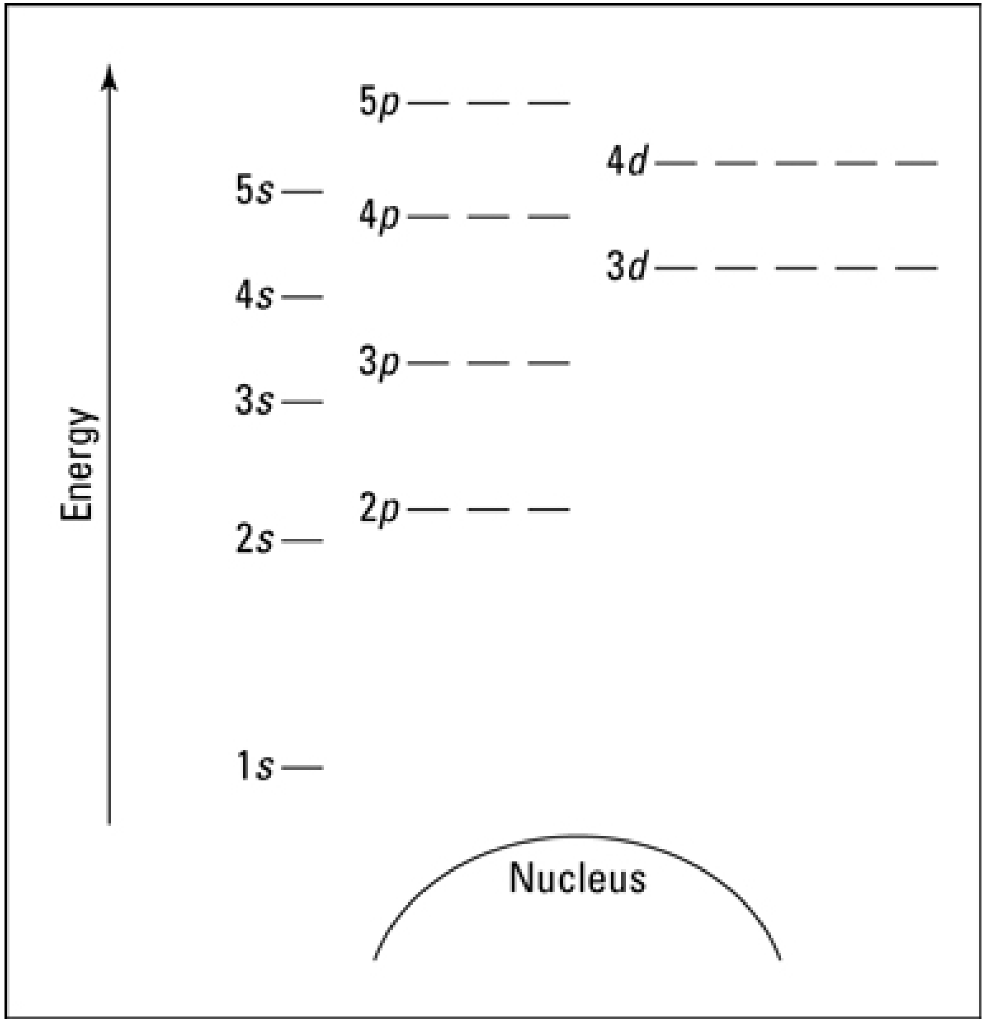
- **Elemental composition**: which elements the compound contains
- **Molecular formula**: how many atoms of each of the elements are present in one molecule
- **Molecular mass**: sum of the masses of all atoms present in the molecule
- **Molecular structure (constitution)**: the exact connection of the atoms constituting the molecule
- **Molecular geometry**: the 3-D arrangement of the atoms

Electron shells of elements

- Atoms containing **“filled shells”** are stable
  - Noble gases: He, Ne, Ar, Kr, Xe, Rn

- Atoms in organic molecules have **tendencies to attain filled-shell conditions** by gaining, losing, or most importantly, **sharing electrons**

Orbital energy levels



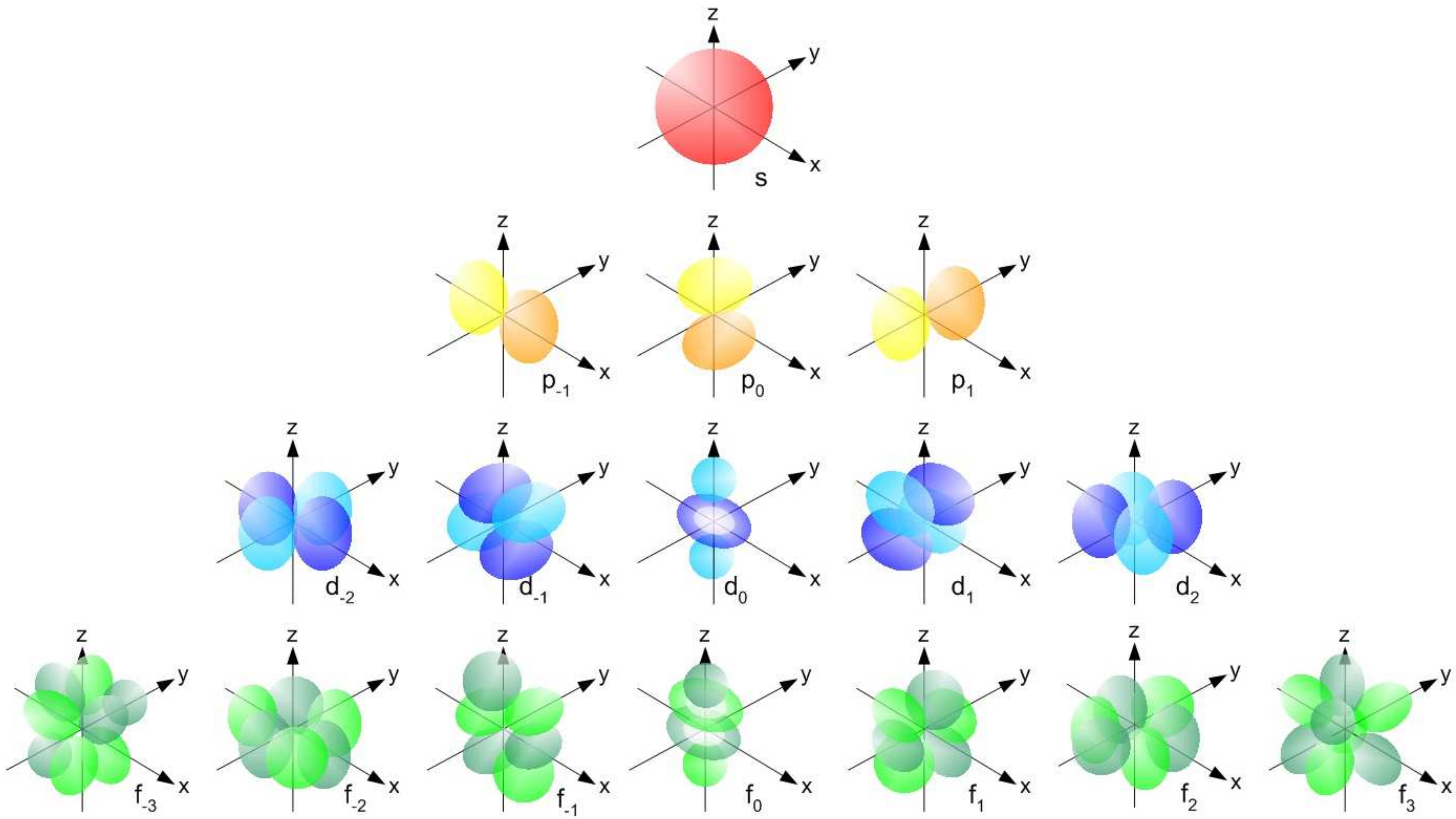
#1

– 1^{st} shell (K-shell): holds 2 electrons ($1s^2$)

– 2^{nd} shell (L-shell): holds 8 electrons ($1s^2\ 2s^2\ 2p^6$)

– 3^{rd} shell (M-shell): holds 18 electrons ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$), but a stable configuration is reached when the shell is filled with 8 electrons ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$)

Orbital diagrams



Electron shells of elements

#3

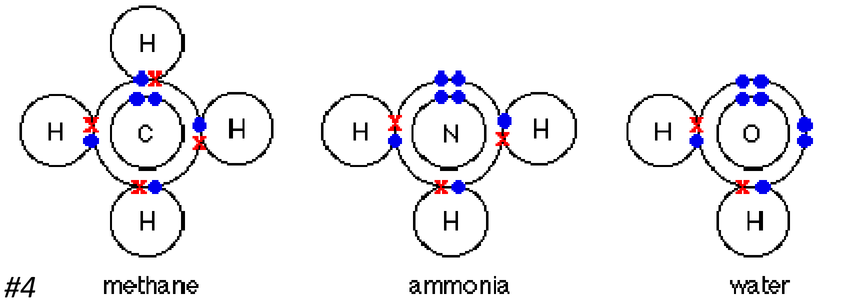
Name	Element[a]		Mass[b] (u)	Number of Electrons in Shell					Net Charge of Kernel[c]	Number of Covalent Bonds Commonly Occurring in Organic Molecules
	Symbol	Number		K	L	M	N	O		
Hydrogen	H	1	1.008	1					1+	1
Helium	He	2		2					0	
Carbon	C	6	12.011	2	4				4+	4
Nitrogen	N	7	14.007	2	5				5+	3,(4)[d]
Oxygen	O	8	15.999	2	6				6+	2,(1)[e]
Fluorine	F	9	18.998	2	7				7+	1
Neon	Ne	10		2	8				0	
Phosphorus	P	15	30.974	2	8	5			5+	3,5
Sulfur	S	16	32.06	2	8	6			6+	2,4,6,(1)[e]
Chlorine	Cl	17	35.453	2	8	7			8+	1
Argon	Ar	18		2	8	8			0	
Bromine	Br	35	79.904	2	8	18	7		7+	1
Krypton	Kr	36		2	8	18	8		0	
Iodine	I	53	126.905	2	8	18	18	7	7+	1
Xenon	Xe	54		2	8	18	18	8	0	

[a] The underlined elements are the noble gases. [b] Based on the assigned atomic mass constant of u=atomic mass of ^{12}C/12; abundance-averaged values of the naturally occurring isotopes. [c] Kernel: the portion of an atom excluding the outer shell electrons. [d] Positively charged atom. [e] Negatively charged atom.

Covalent bond

- Octet rule: atoms tend to combine in such a way that each atom has 8 electrons in its outer (valence) shell

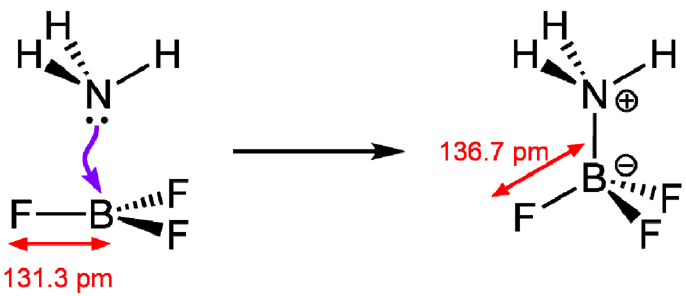
- Covalent bond
  - Atoms complete their outer-shell octet by sharing a pair of electrons, in most cases one electron contributed by each of the two bonded atoms
  - Each atom feels it has both of the shared electrons
  - The electron pairs are localized between the two positive atomic nuclei; the electrostatic attraction of these nuclei to these electrons holds the atoms together



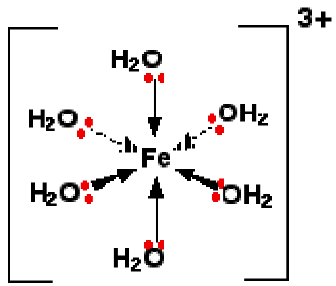
#4

Covalent bond

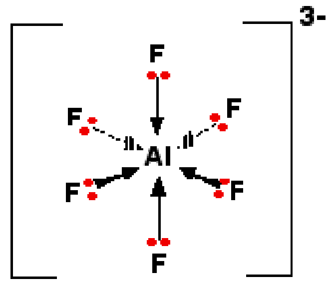
- Coordinate bond
  - A kind of a covalent bond in which the two electrons derive from the same atom
  - One atom donates a lone pair of electrons (Lewis base) and the other atom accepts the electron pair (Lewis acid)



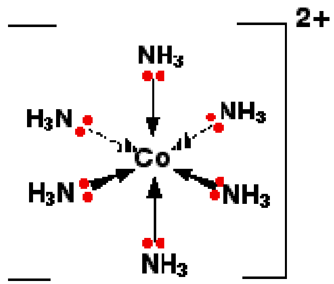
#5



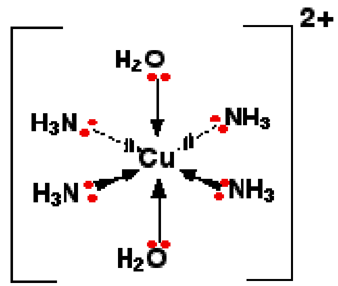
$[Fe(H_2O)_6]^{3+}$



$[AlF_6]^{3-}$



$[Co(NH_3)_6]^{2+}$



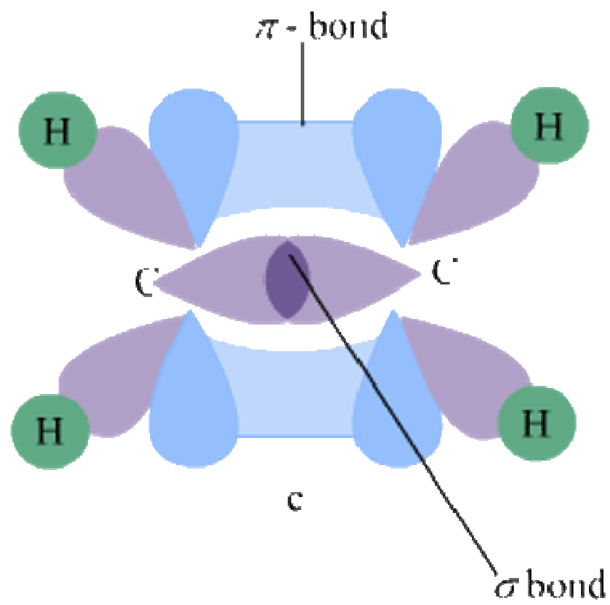
$[Cu(NH_3)_4(H_2O)_2]^{2+}$

#6

Drawing molecular structures

Double and triple bonds

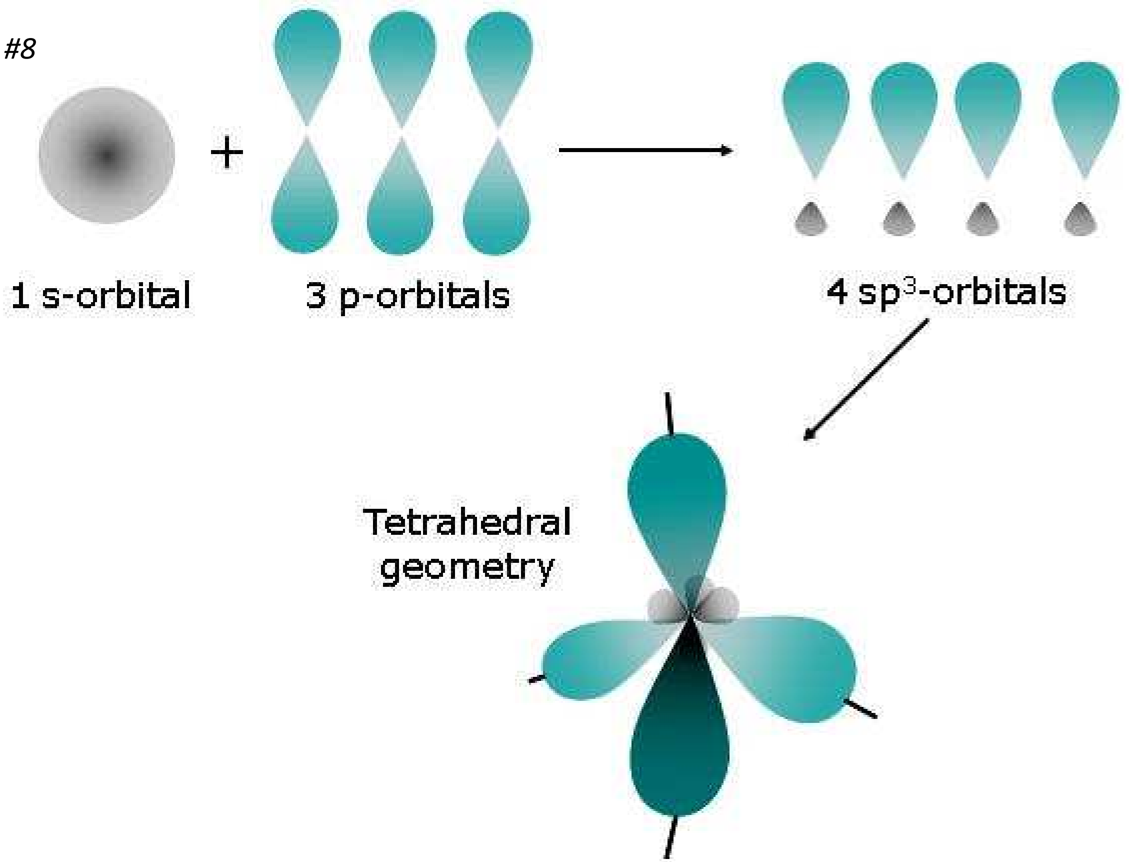
- Atoms with more than one missing electrons in their outer shells may form double or triple bonds
- Single covalent bond is a sigma (σ) bond; double and triple bonds contain one σ bond and π bond(s)
  - σ bond: a covalent bond in which orbital overlap of the bond is concentrated along the axis joining the two nuclei
  - π bond: a covalent bond formed by overlap of parallel p orbitals (generally weaker than the σ bonds)



#7

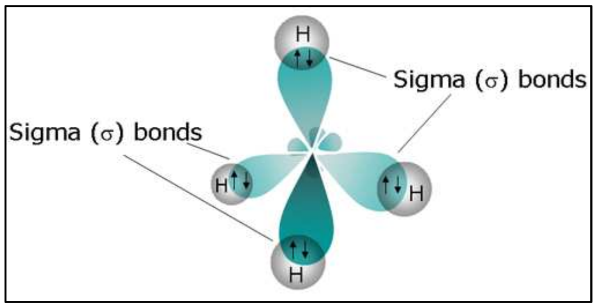
Orbital hybridization

#8



sp3 hybridization

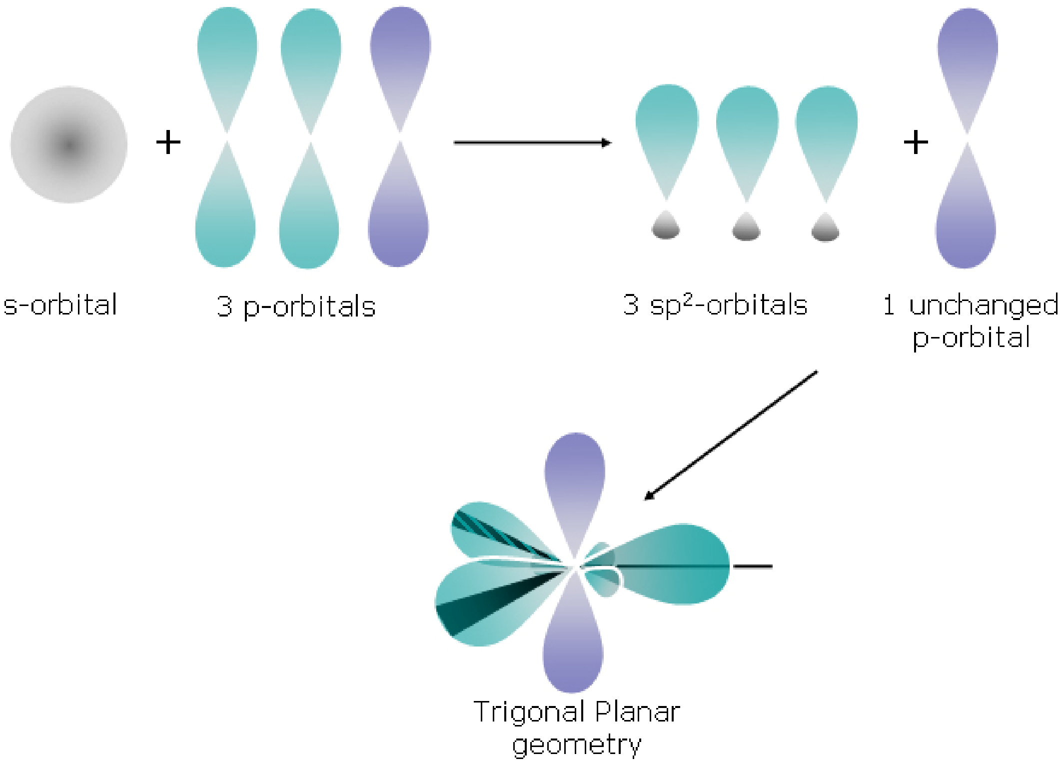
methane



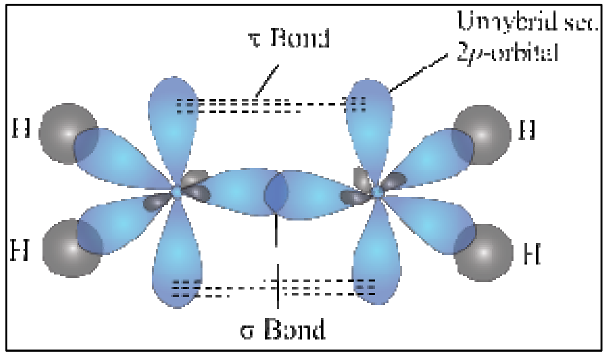
#9

Orbital hybridization

#8



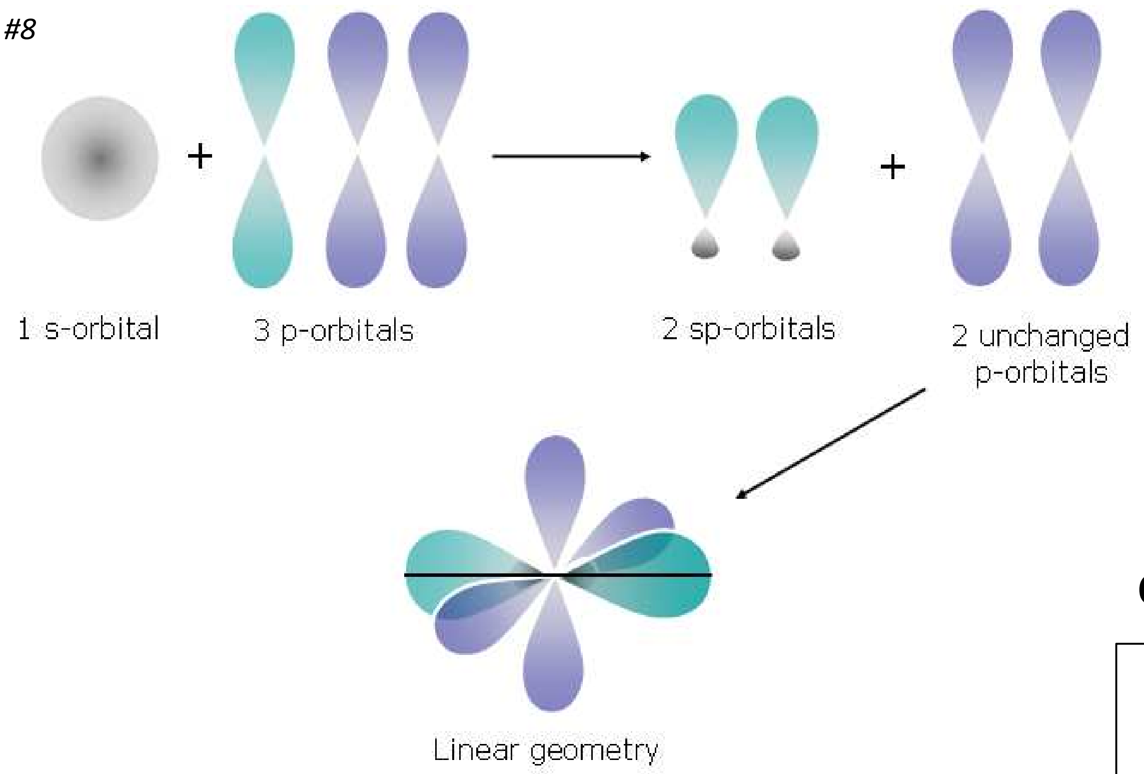
ethene (ethylene)



#10

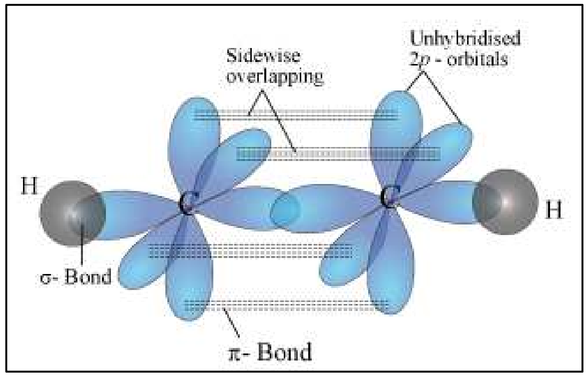
Orbital hybridization

#8



sp hybridization

ethyne (acetylene)



#11

References

#1) https://www.dummies.com/education/science/chemistry/how-to-represent-electrons-in-an-energy-level-diagram/

#2) https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Quantum_Mechanics/09._The_Hydrogen_Atom/Atomic_Theory/Electrons_in_Atoms/Electronic_Orbitals

#3) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, p. 16.

#4) https://www.chemguide.co.uk/atoms/bonding/covalent.html

#5) https://en.wikipedia.org/wiki/Coordinate_covalent_bond

#6) https://www.chemguide.co.uk/inorganic/complexions/shapes.html

#7) https://vakir.wordpress.com/category/cl-xi-chemistry/chapter-4-chemical-bonding-and-molecular-structure/

#8) https://www.askiitians.com/iit-study-material/iit-jee-physics/chemical-bonding/hybridization/

#9) https://socratic.org/questions/does-methane-have-a-sigma-bond

#10) http://www.chem.ucla.edu/~harding/ec_tutorials/tutorial04.pdf

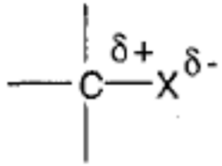
#10) https://www.meritnation.com/ask-answer/question/what-are-the-bond-angles-and-shape-of-ethane-ethene-and-eth/chemistry/5308746

Organic chemistry background II:

Makeup of organic compounds

Electronegativity

- The "electron cloud" or averaged electron position located between the two nuclei is, in general, distorted toward the atom that has the higher attraction for the electrons (the atom that is more ***electronegative***)
  - ex: carbon-halogen bond



- Electronegativity increases with increasing kernel size within a row in the Periodic Table and decreases with increasing kernel size within a column

Electronegativity

#1

H 2.1																	He ---
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0	Ar ---
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn ---
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

Oxidation state

- For convenience, assign the possession of the electron pair in a covalent bond to the more electronegative atom

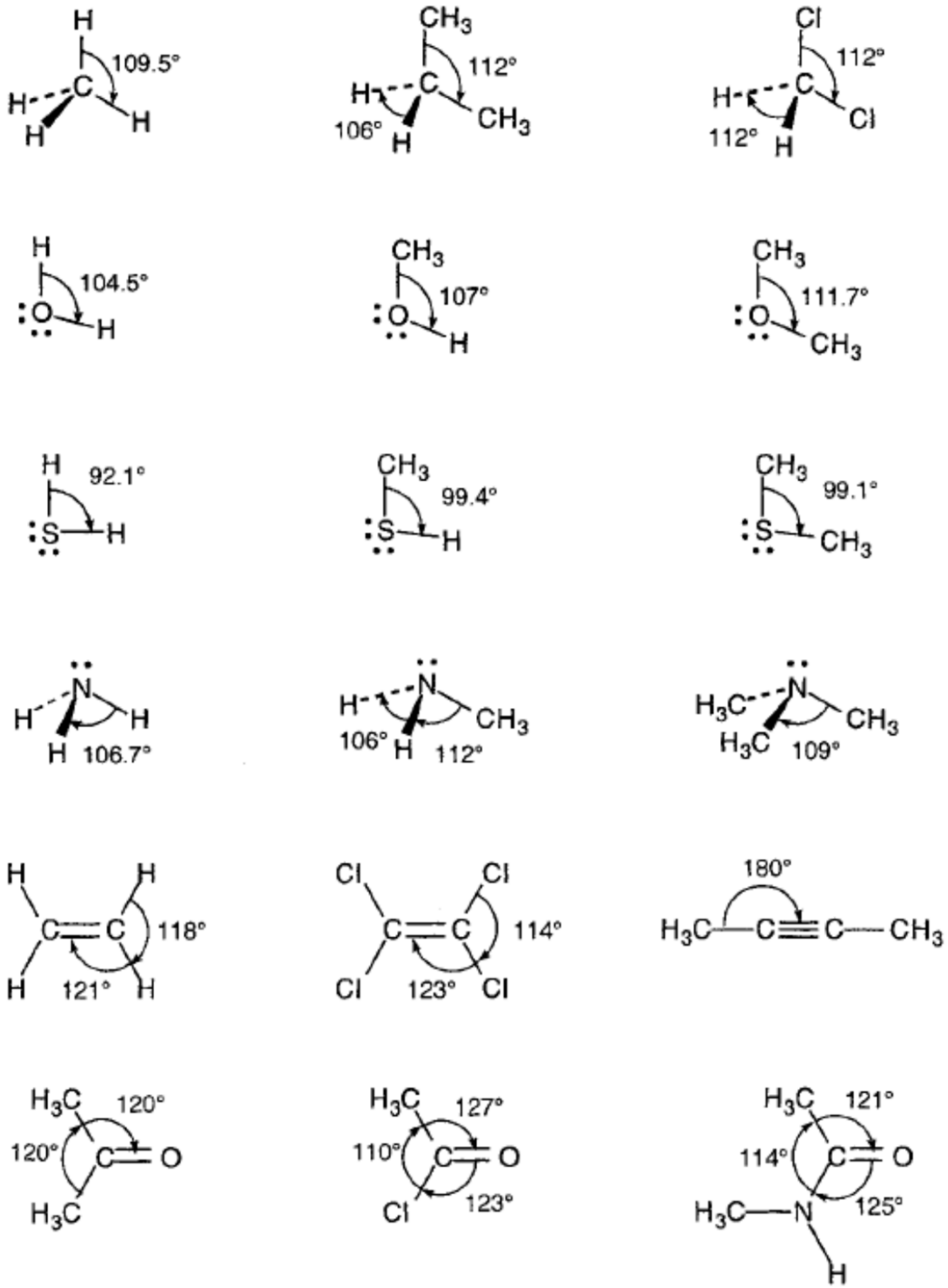
- Add 0 for each bond to an identical atom; -1 for each bond to a less electronegative atom or for each negative charge on the atom; +1 for each bond to a more electronegative atom or for each positive charge on the atom

Oxidation state

Q: Determine the oxidation state of each atom in acetate (CH_3COO^-).

Spatial arrangement of atoms

- Each pair of electrons, shared or unshared, wants to stay as far as possible from one another
  - For a carbon atom with four single bonds will form a tetrahedron
  - When carbon is bound to four identical atoms or groups (ex: CH_4), the bond angles should be 109.5°
  - The difference of the atoms or groups bound to a carbon leads to minor variations in the bond angles



109.5°
112°
106°
112°
112°
104.5°
107°
111.7°
92.1°
99.4°
99.1°
106.7°
106°
112°
109°
118°
121°
114°
123°
180°
120°
120°
127°
110°
123°
121°
114°
125°

#2

Isomers

- **(Structural) Isomers**: the set of compounds whose molecular formula is identical, but the molecular structures are different

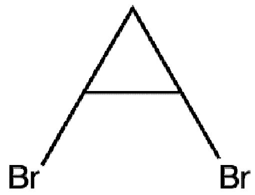
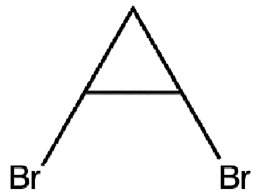
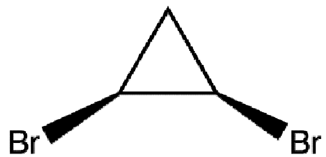
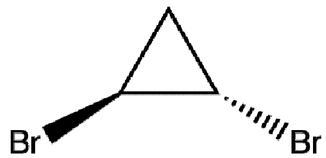
- **Stereoisomers**: the set of compounds whose molecular structure is identical, but the spatial arrangements are different

Isomers

Q: How many (structural) isomers are there for monochlorinated butane (C_4H_9Cl)? Draw the chemical structures of all isomers.

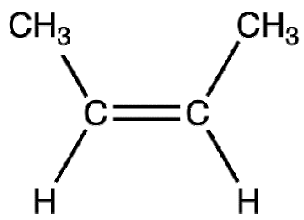
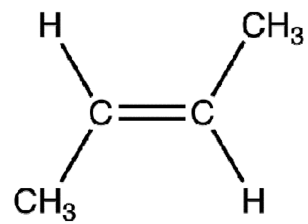
Stereoisomers

#3

	cis–1,2–dibromo cyclopropane **(1)**	*trans*–1,2–dibromo cyclopropane **(2)**
molecular formula	$C_3H_4Br_2$	$C_3H_4Br_2$
structural formula		
configuration		

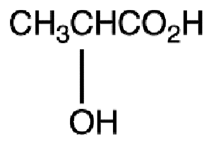
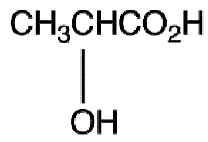
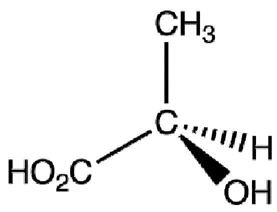
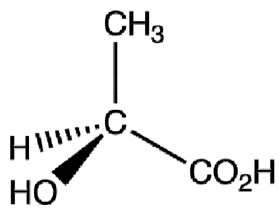
Stereoisomers

#3

	cis–2–butene **(1)**	*trans*–2–butene **(2)**
molecular formula	C_4H_8	C_4H_8
structural formula	$CH_3CH{=}CHCH_3$	$CH_3CH{=}CHCH_3$
configuration		

Stereoisomers

#3

	(R)–lactic acid (**1**)	(S)–lactic acid (**2**)
molecular formula	$C_3H_6O_3$	$C_3H_6O_3$
structural formula		
configuration		

Stereoisomers

Q: Are there any pair of stereoisomers among structural isomers of monochlorinated butane?

References

#1) http://www.chem.ucla.edu/~harding/IGOC/E/electronegativity.html

#2) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, p. 25.

#3) http://www.ochempal.org/index.php/alphabetical/s-t/stereoisomers/