Organic Chemistry Concepts LOKT.09.051

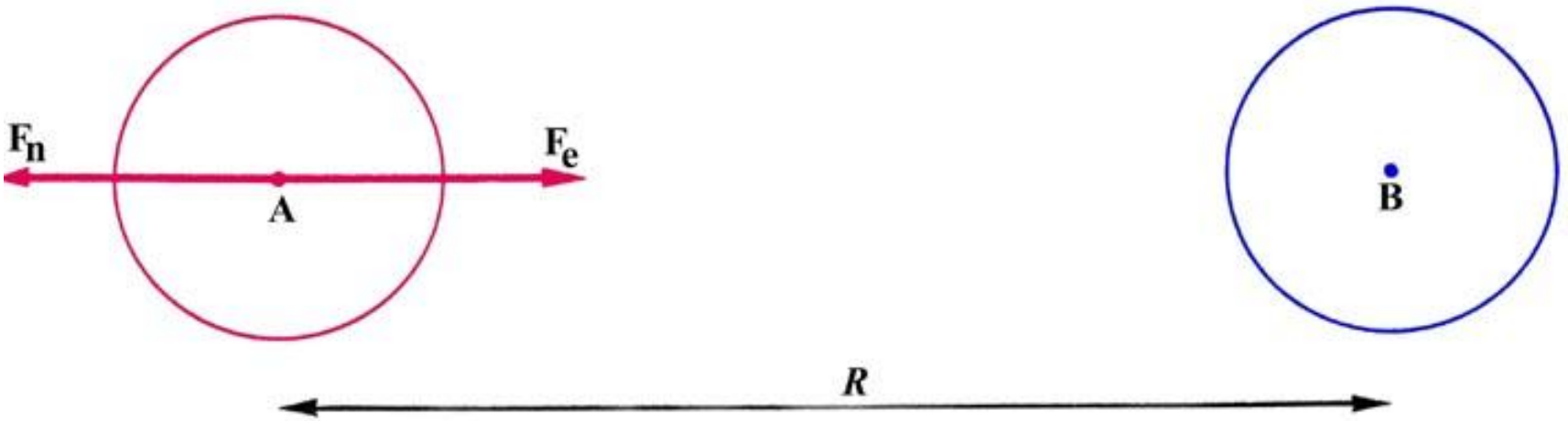
Organic molecules 1

CHAPTER 4

Organic molecules

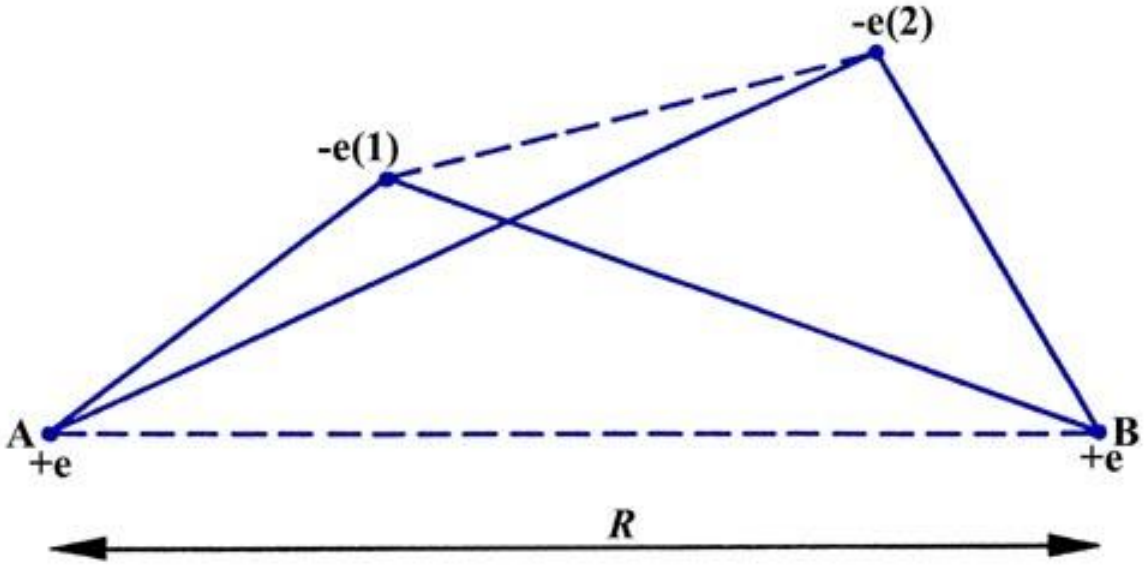
- Molecule is a group of bonded atoms
- Molecular structure – position of bonded atoms in space
- Chemical bond – interaction between two atoms via shared valence shell electrons
- Bond properties: length, valence angles, bond polarity, bond energy

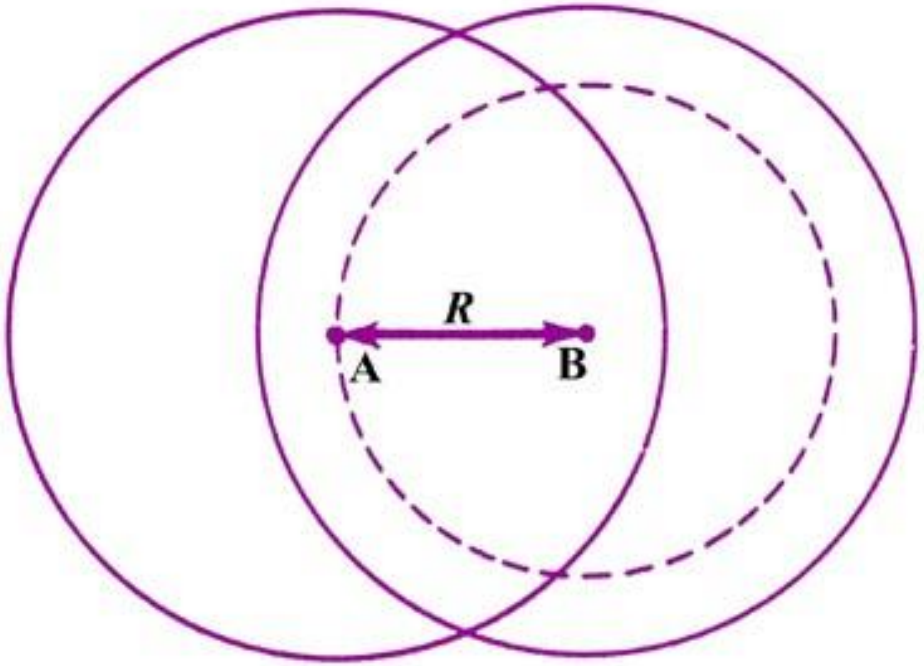
Chemical bond formation



$$F_n = (+e)(+e)/R^2 = e^2/R^2$$

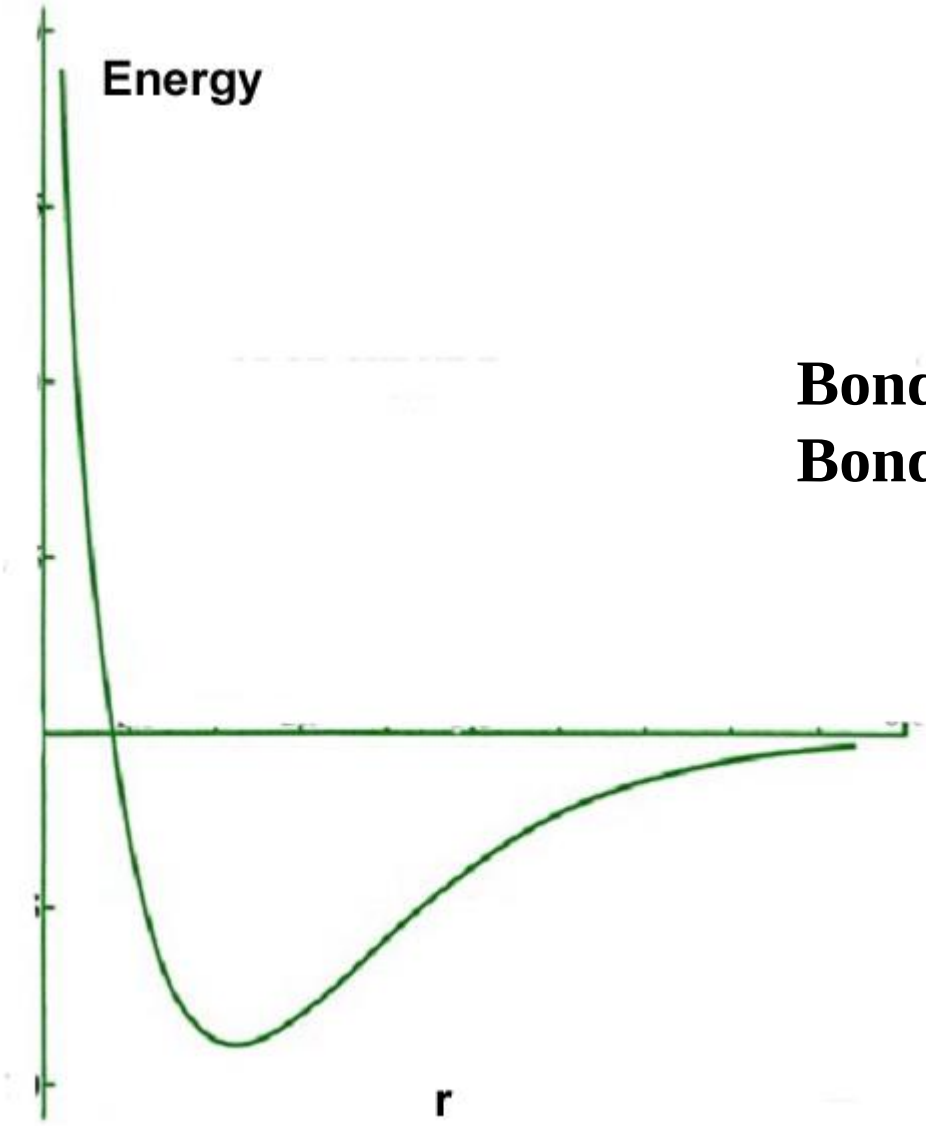
$$F_e = \frac{(-e)(+e)}{R^2} = -e^2/R^2$$


-e(2)
-e(1)
A
+e
B
+e
R


R
A
B

H_2
74 pm
or 0.74 Å

HI
161 pm
or 1.61



Bond length
Bond energy

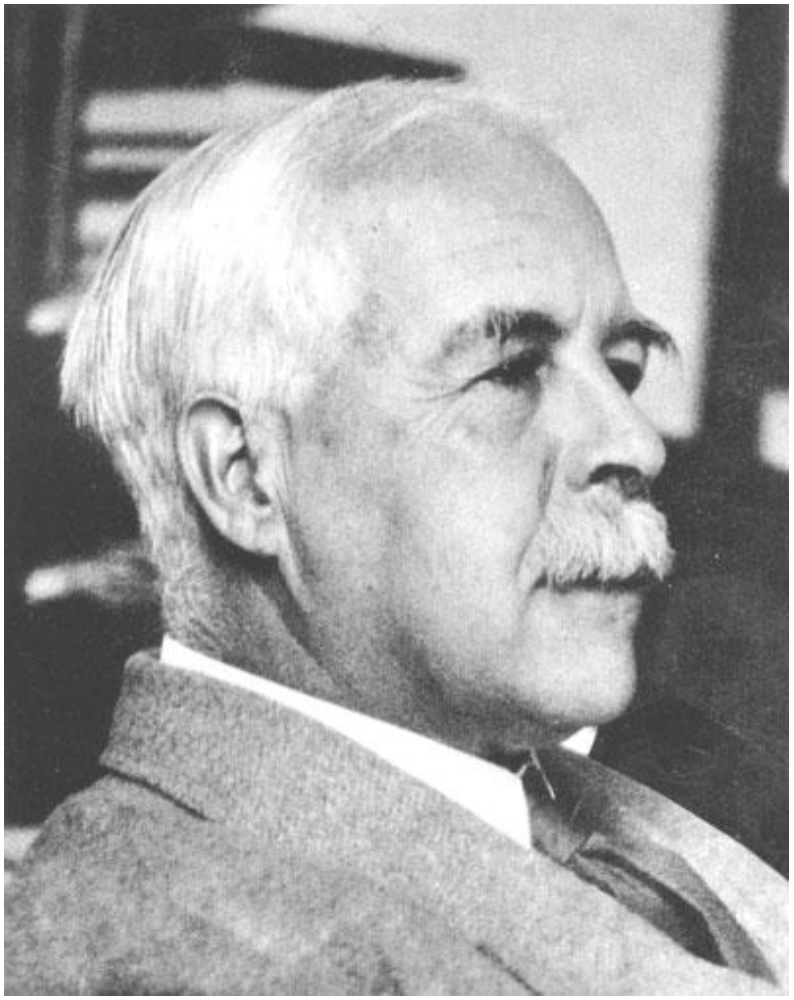
Chemical bond between two atoms

- Common pair of electrons (from valence shell)
- Bond length
- Bond energy
- Bond polarity
- Angle between bonds, if two or more bonds are formed

Gilbert N. Lewis (1916)

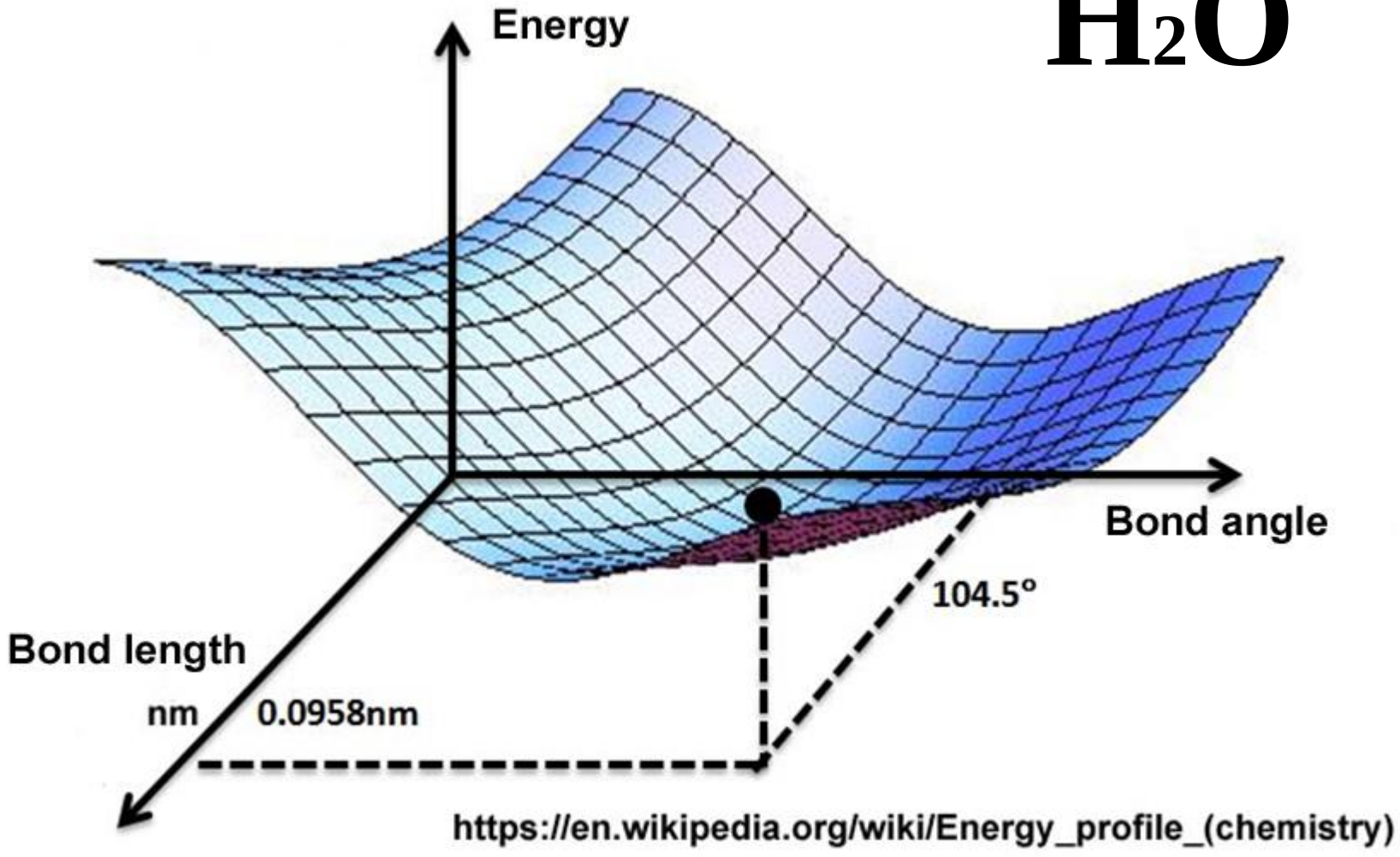
The Atom and the Molecule

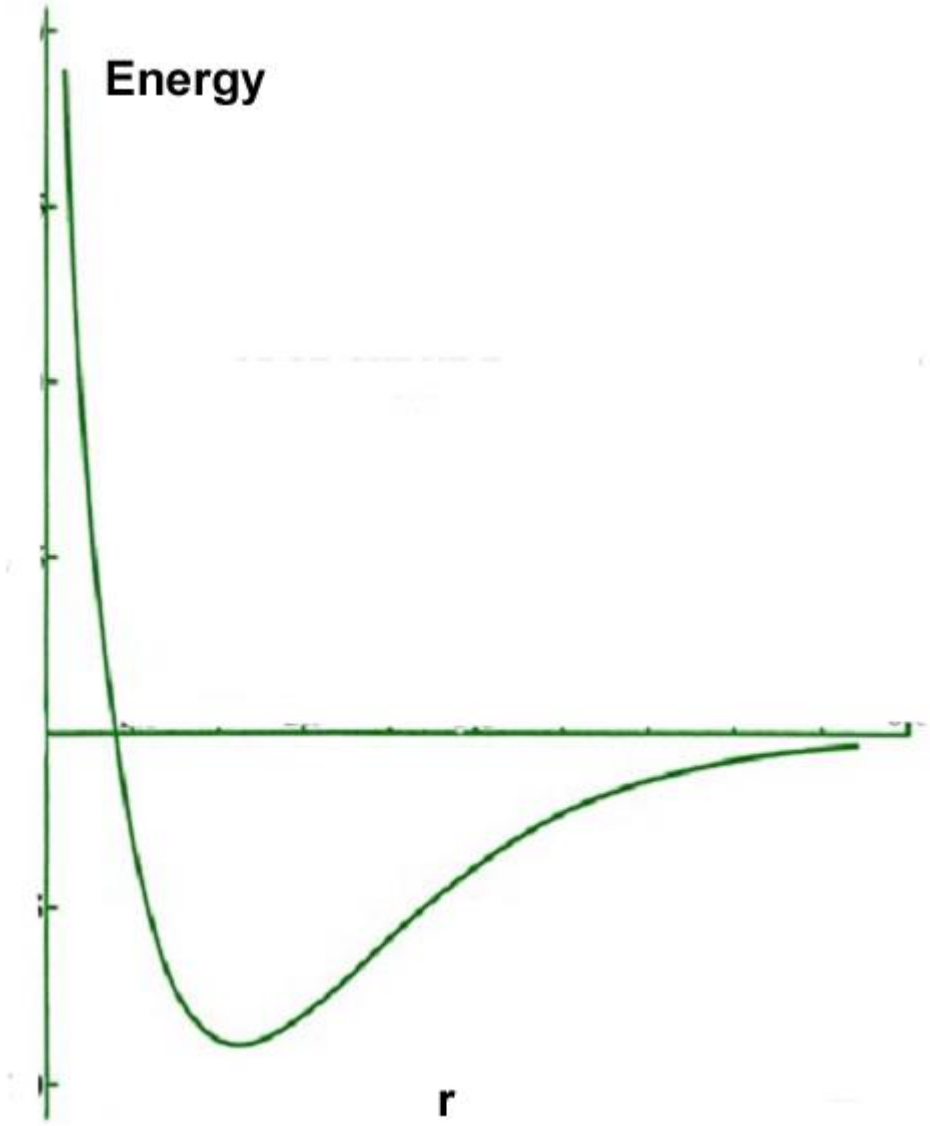
JACS, 38, 762-786



Gilbert N. Lewis
1875-1946

H_2O


Energy
Bond angle
104.5°
Bond length
nm
0.0958nm
https://en.wikipedia.org/wiki/Energy_profile_(chemistry)



Bond length
Bond energy

Bond length (pm) and energy (kJ/mol)

Bond	Length	Energy	Bonde	Length	Energy
H-H	74	436	H-C	109	413
C-C	154	348	H-N	101	391
N-N	145	170	H-O	96	366
O-O	148	145	H-F	92	568
F-F	142	158	H-Cl	127	432
Cl-Cl	199	243	H-Br	141	366
Br-Br	228	193	H-I	161	298
I-I	267	151			

Some rules

- Bond length and energy are correlated
- Bonds are weaker if elements are in different periods

  C-O 85 kcal/mol, C-S 61 kcal/mol

- Double bonds are shorter and stronger, but not additively
  - C = C 148.8 kcal/mol
  - C – C 79.1 kcal/mol

C – C bond lengths

- Diamond 1.544 Å
- C_2H_6 1.5324 Å
- C_2H_5Cl 1.5495 Å
- cyclohexane 1.540 Å
- iso-butane 1.535 Å

C – C bond energy

- **Ethane: 79.1 kcal/mol**
- **Propane: 80.3 kcal/mol**
- **Iso-buthane: 81.6 kcal/mol**

Bond polarity

- How the common pair of electrons is located between two atoms
- Electronegativity scale

Electronegativity scale

H						
2.1						
Li	**Be**	**B**	**C**	**N**	**O**	**F**
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca					Br
0.8	1.0					2.8

Proposed by L. Pauling

Linus Carl Pauling
1901-1994

Bonds

- If atoms have similar electronegativity, the valence electrons are shown in the middle between atoms and this is a **nonpolar covalent bond.**

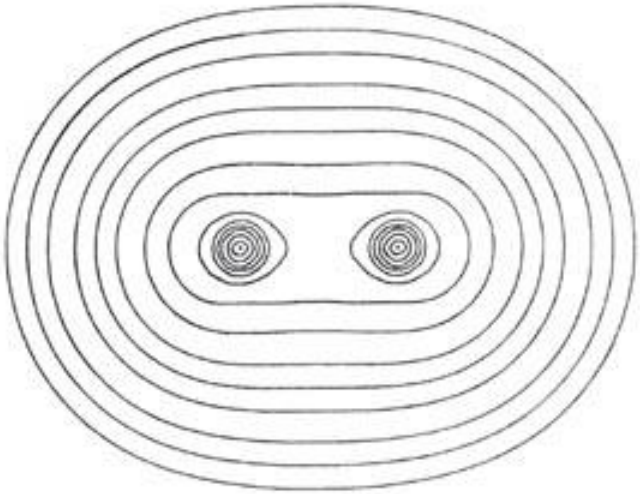
$$H – H \; ; \; Cl – Cl$$

- If atoms have different electronegativity the electron pair is shifted and this is **polar covalent bond.**

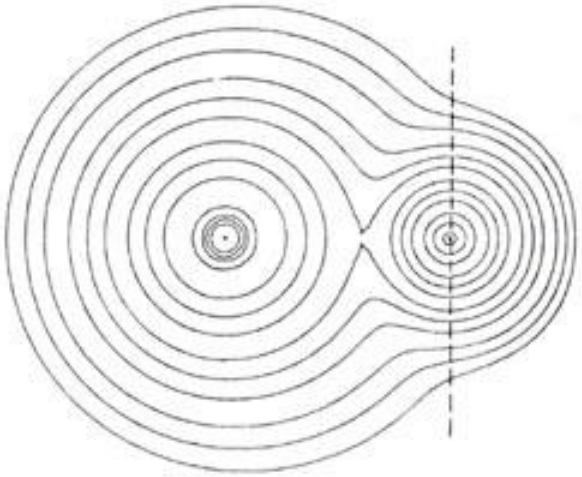
$$H^{\delta+} \rightarrow F^{\delta-} \qquad CH_3^{\delta+} \rightarrow Cl^{\delta-}$$

- In extreme case the electron pair is close to one of the atoms and this is **ionic bond**

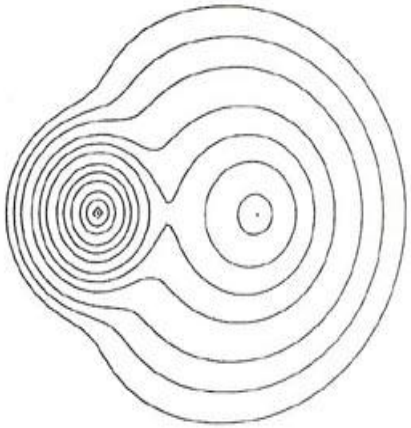
$$Na^+ \; Cl^-$$



N_2

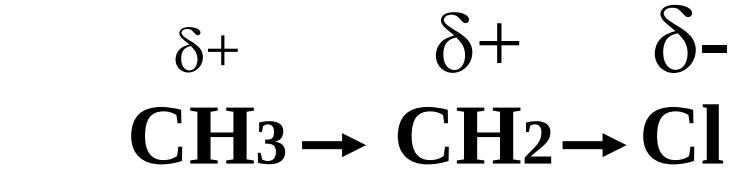


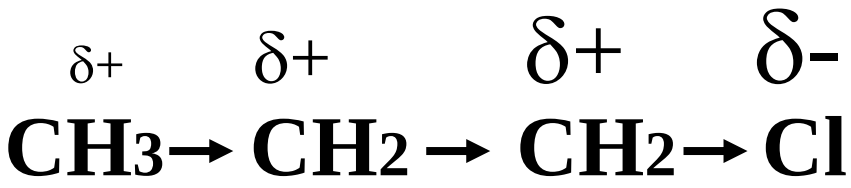
F Li



LiH

Polarization of covalent bonds and inductive effect





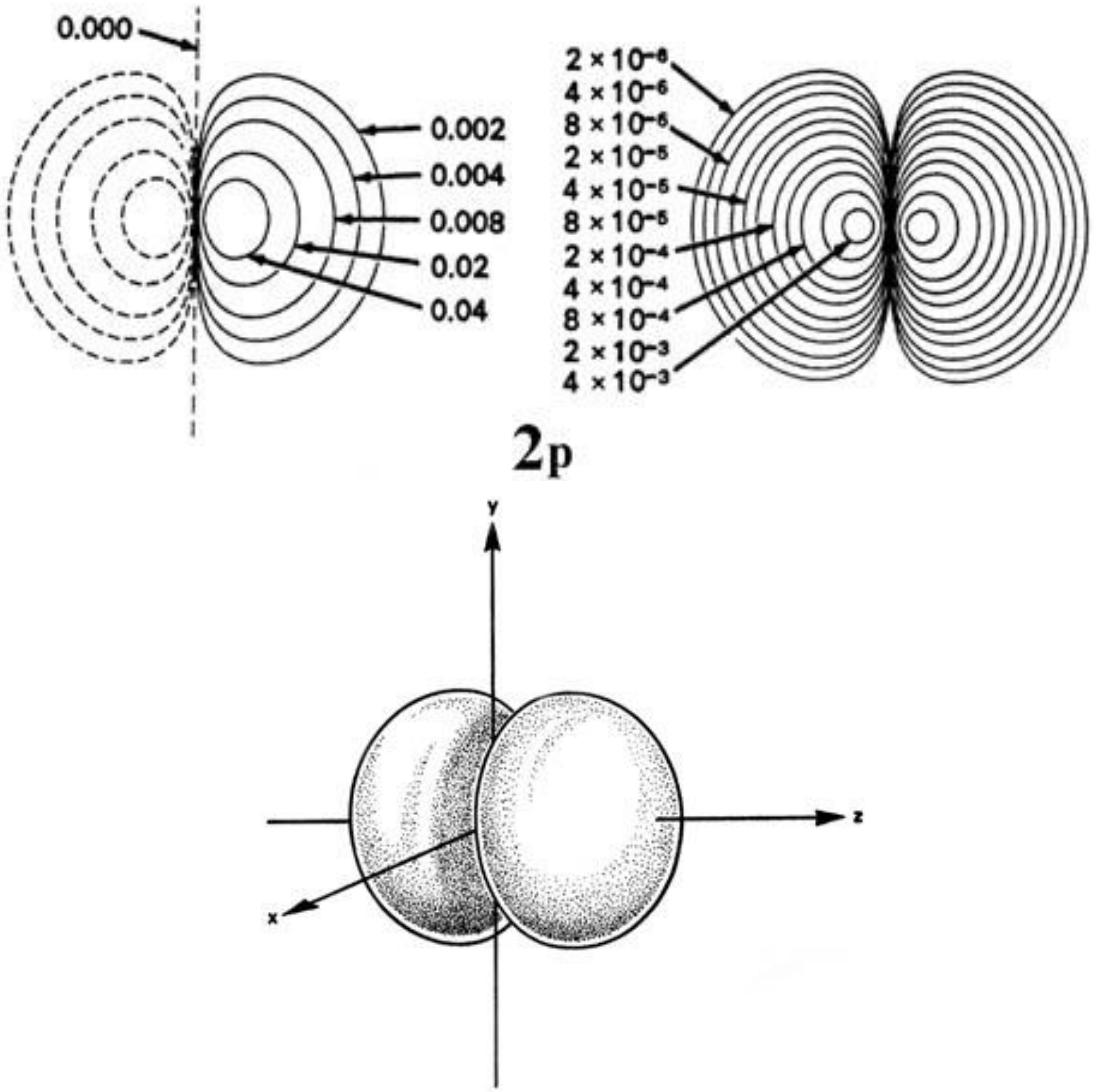
Sir Christopher (Kelk) Ingold

1893-1970 **

Portrait: 58
Location - Floor: Fifth - Zone: Elevator area - Wall: West - Sequence: 1
Source: John D. Roberts
Sponsors: Chung-yin Lai
E. F. Houghton Company

Bond angles depend on orbital configuration in atom

- **H atom has s orbital**
- **C, N and O atoms have s and p orbitals**
- https://en.wikipedia.org/wiki/Electron_configuration
- ***www.orbitals.com/orb/ov.htm***

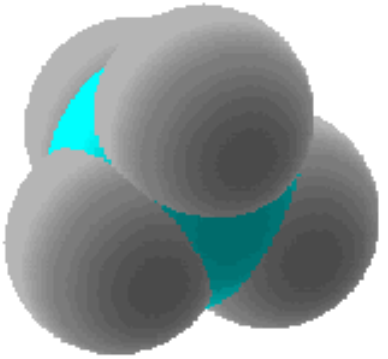

0.000
0.002
0.004
0.008
0.02
0.04
2 × 10⁻⁶
4 × 10⁻⁶
8 × 10⁻⁶
2 × 10⁻⁵
4 × 10⁻⁵
8 × 10⁻⁵
2 × 10⁻⁴
4 × 10⁻⁴
8 × 10⁻⁴
2 × 10⁻³
4 × 10⁻³
2p
y
z
x

Carbon atom

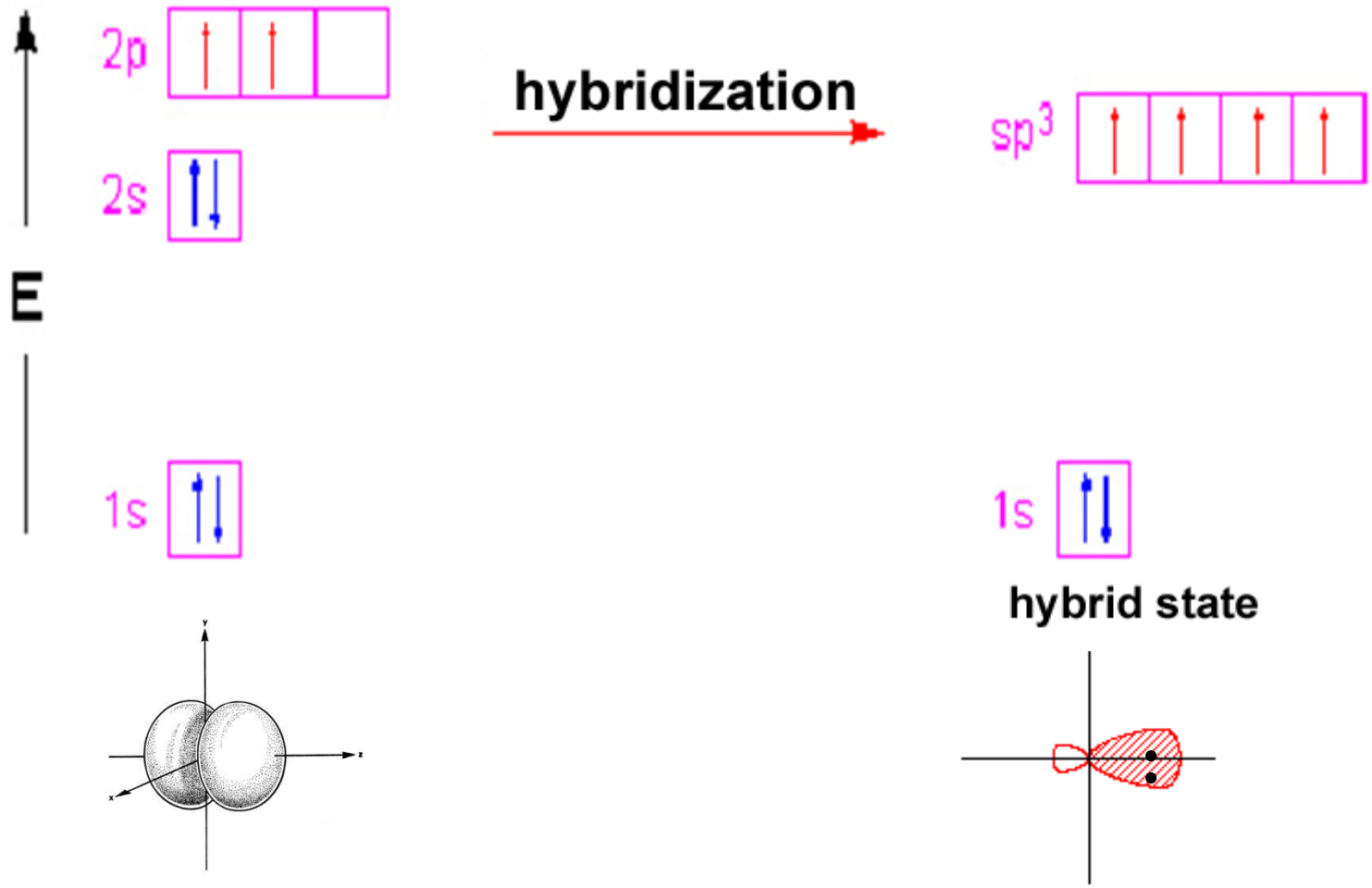
- Carbon atom has 6 electrons on two orbitals:

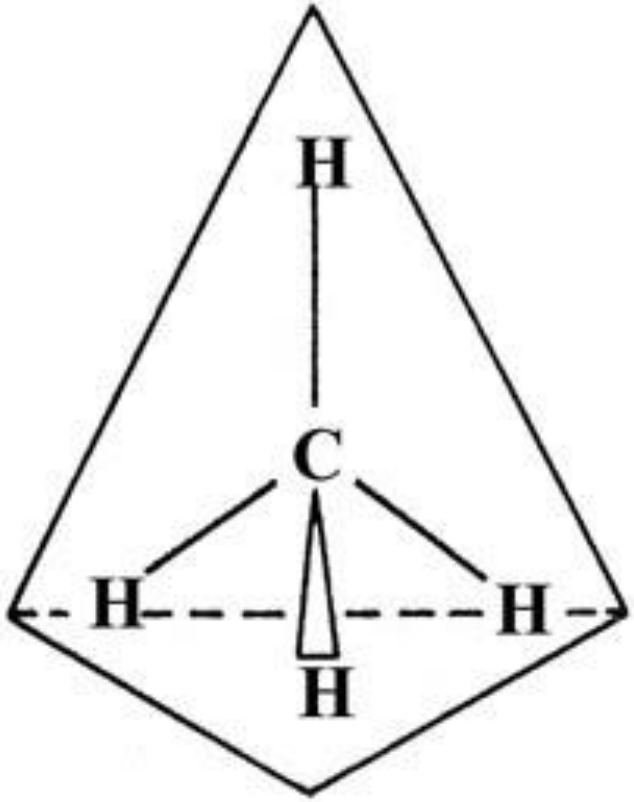
$$\mathbf{1s^2\ 2s^2\ 2p^2}$$

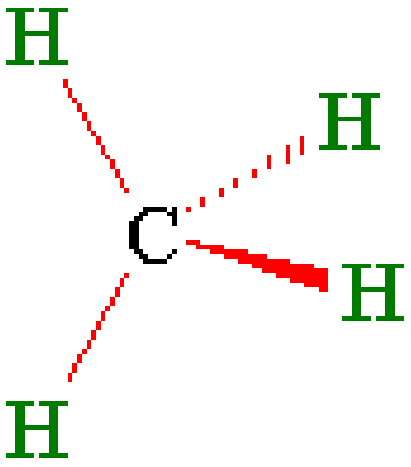
- In fact, carbon atom can form four equal bonds as in CH_4

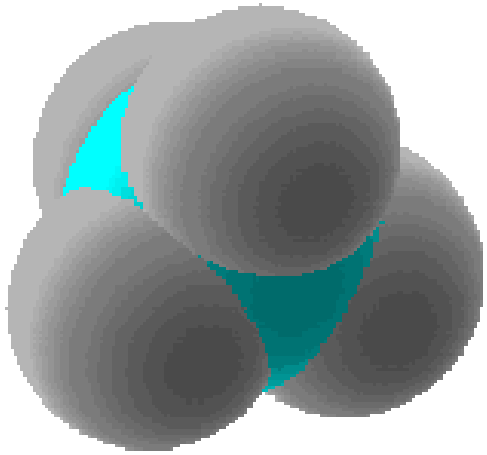


Electron configuration sp^3 in a carbon atom



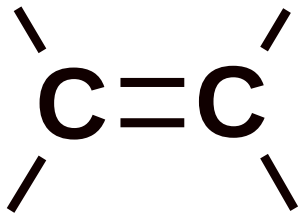

H
C
H
H
H


H
H
C
H
H

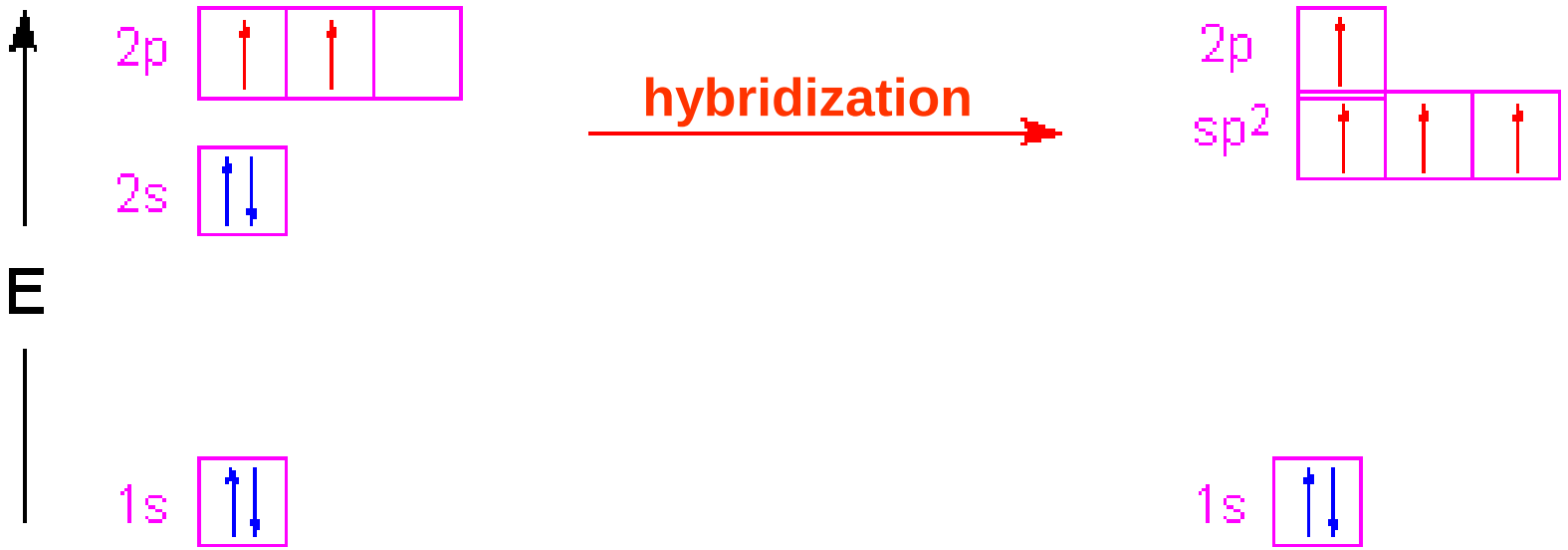


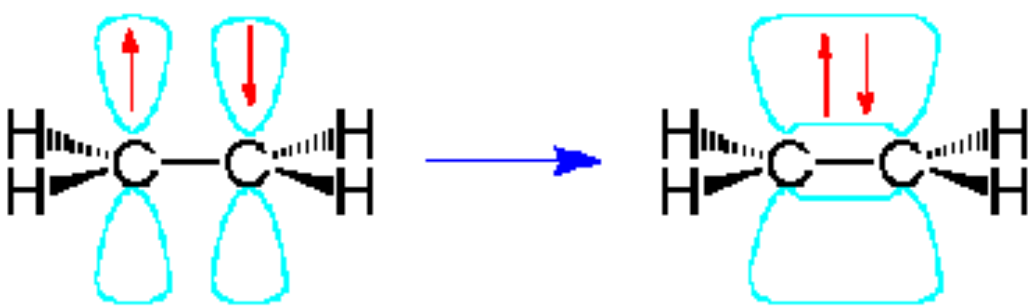
Still problems with carbon atom

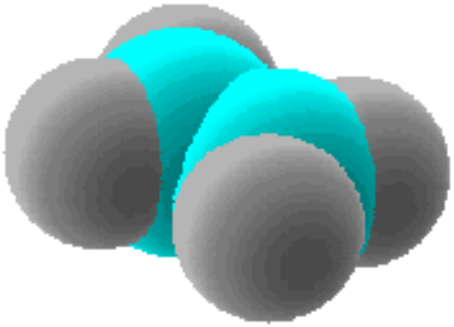
- Electron configuration should explain double and triple bonds between carbon atoms



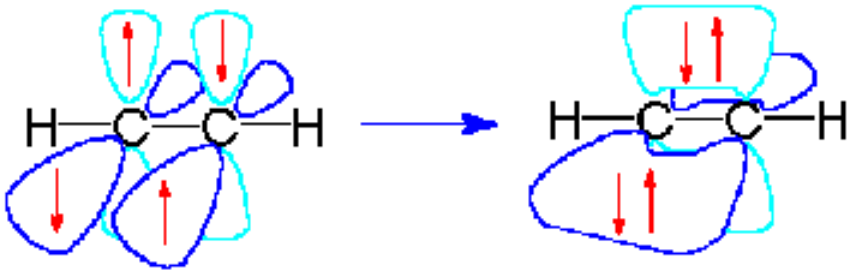
sp^2

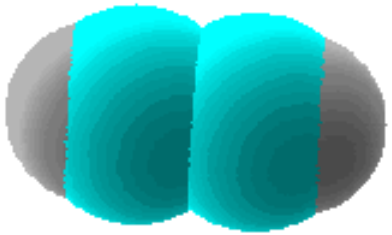


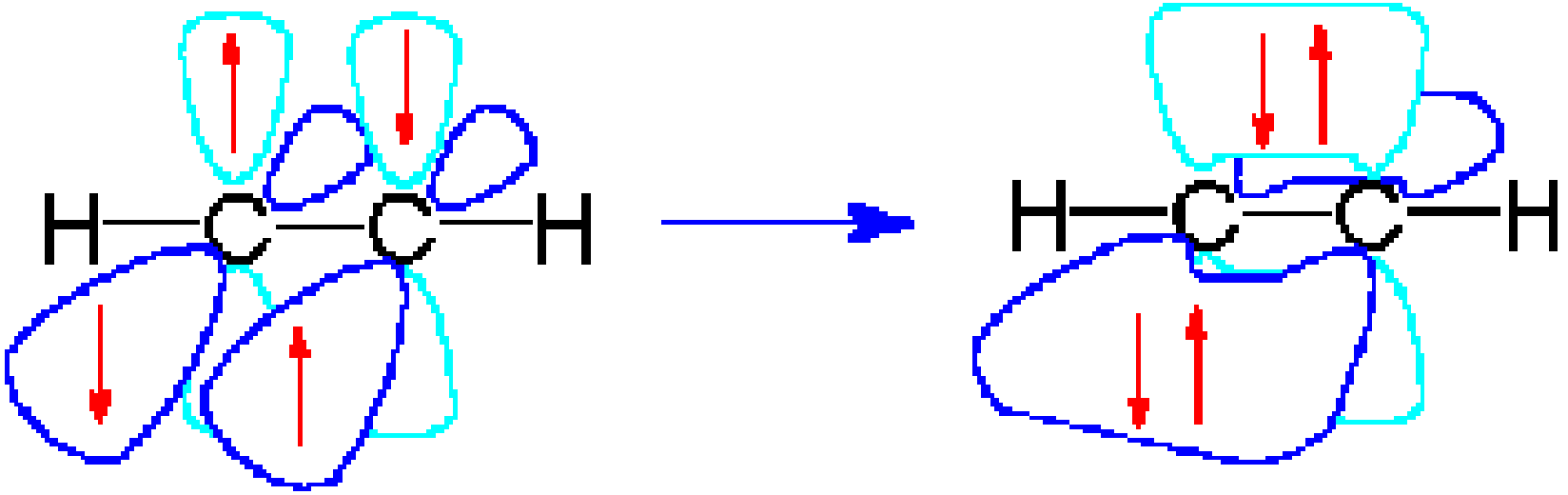




sp





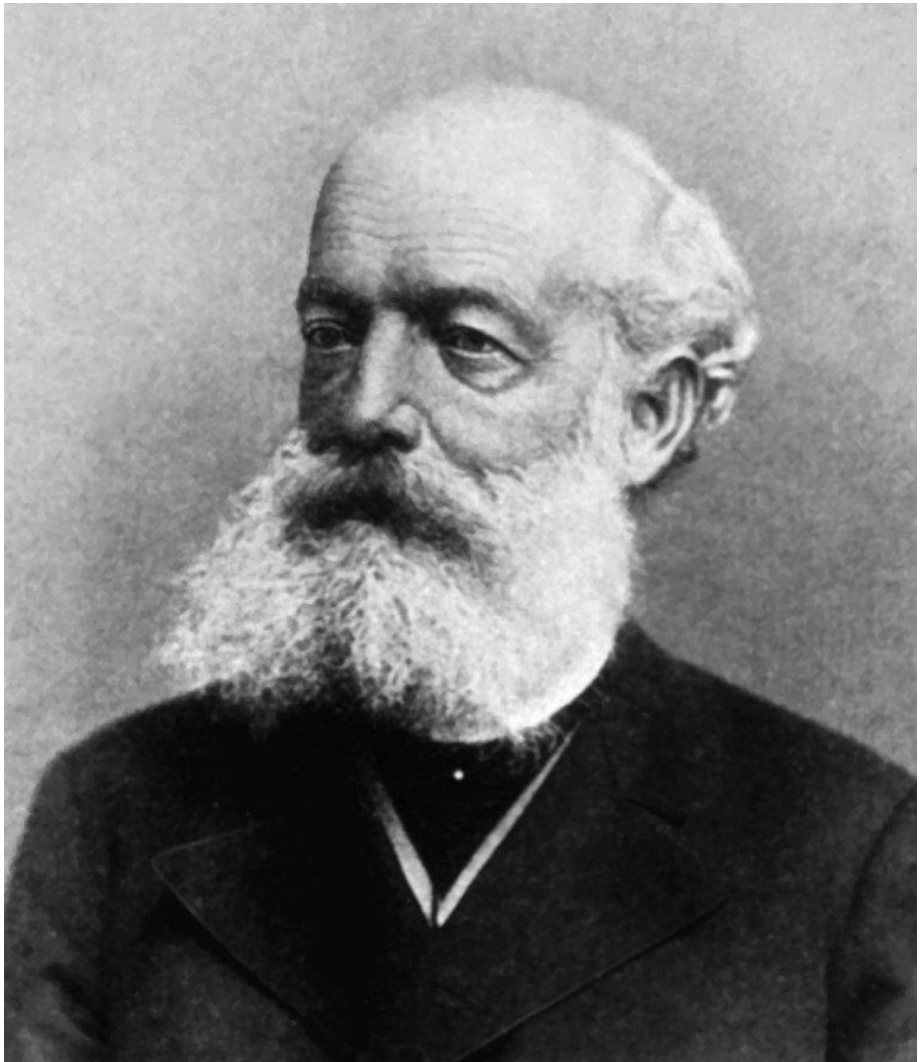

H
C
C
H
H
C
C
H

Geometry	Hybrid orbitals	Hybrid name
LINEAR	**2**	***sp***
PLANAR	**3**	***sp*^{2}**
TETRAHEDRAL	**4**	***sp*^{3}**

Carbon-carbon bond coding

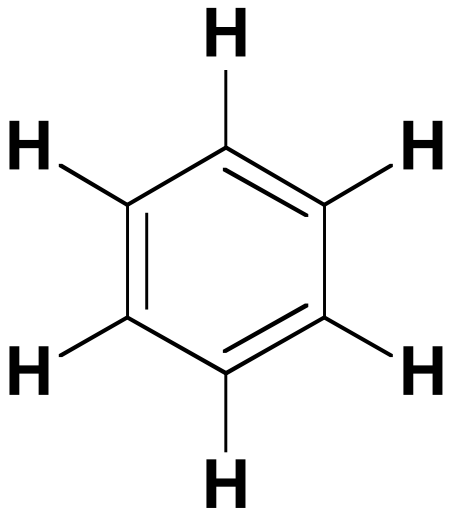
Bond type	code
Single bond (σ bond)	-ane
Double bond ($\sigma + \pi$ bonds)	-ene
Triple bond ($\sigma + 2\pi$ bonds)	-yne

Cyclic structure of benzene C_6H_6

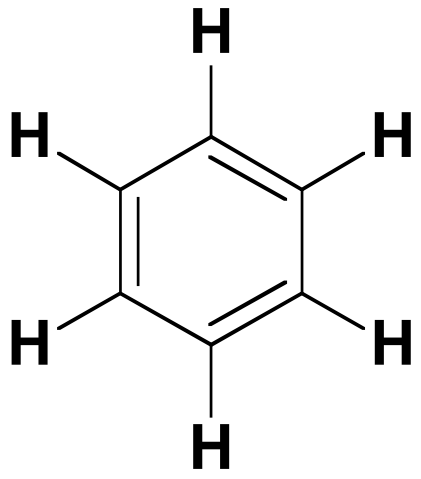


Friedrich August Kekulé von Stradonitz

More problems with carbon



- Three single bonds and three double bonds
  - C = C 148.8 kcal/mol
  - C – C 79.1 kcal/mol



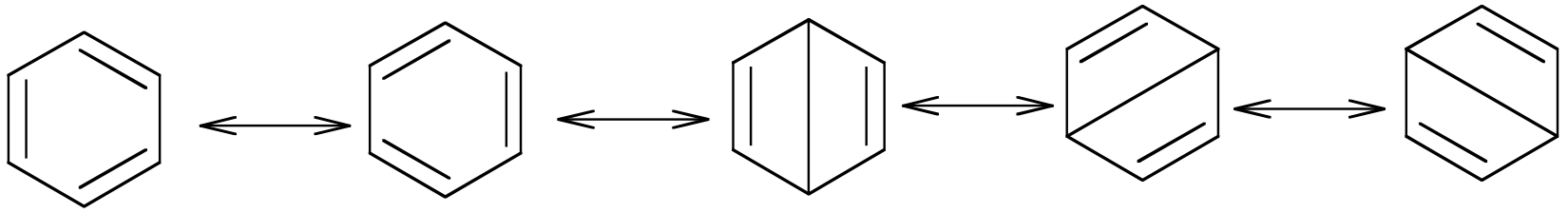
C_6H_6

Calculated formation energy **1289** kcal/mol

Experimental formation energy **1323** kcal/mol

Difference: -34 kcal/mol

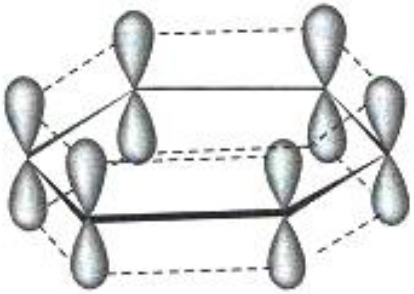
Benzene



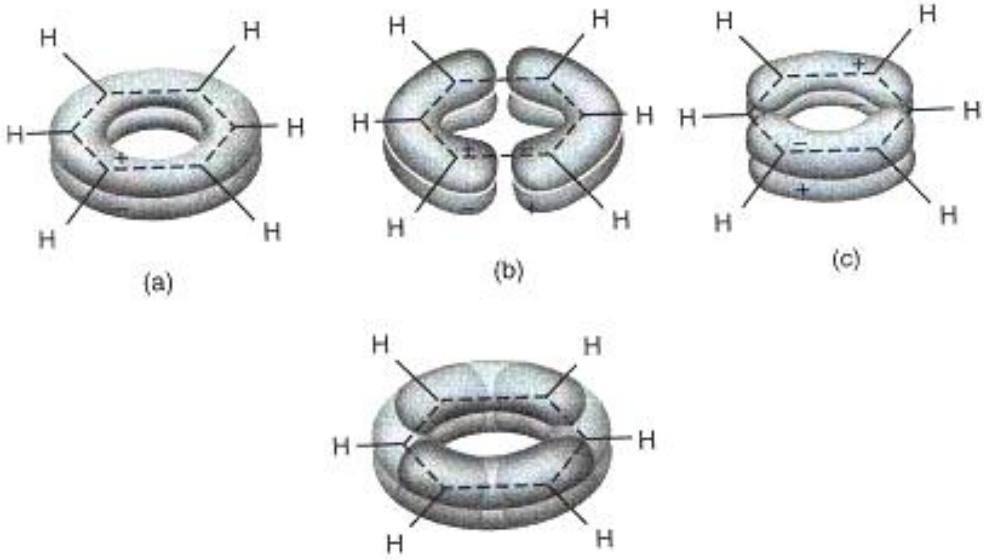
39% 39% 7.3% 7.3% 7.3%

These structures **are not in equilibrium**

https://en.wikipedia.org/wiki/Benzene

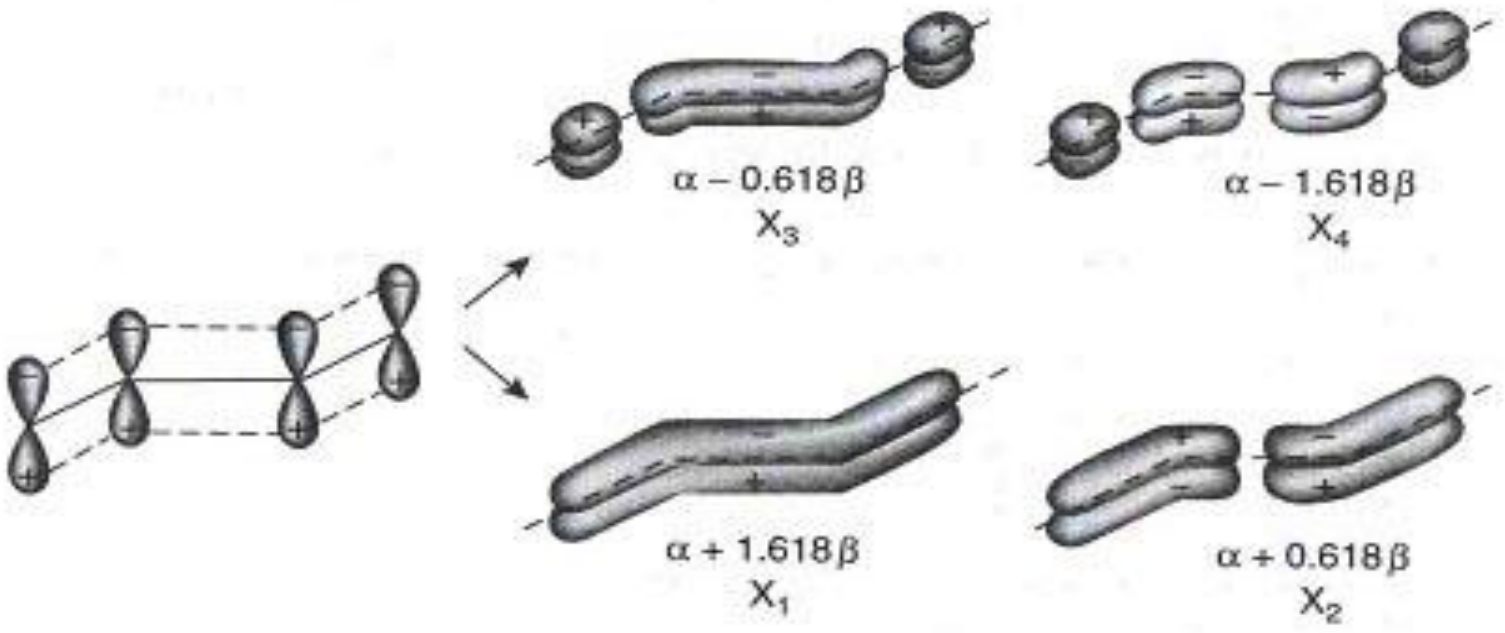


1.667



Electron pair (double bond) delocalization

CH_2=CH-CH=CH_2



CH_2=CH-CH=CH_2 $\longleftrightarrow^{+}$ CH_2-CH=CH-CH_2^{-}

Analogs of $CH_2=CH-CH=CH_2$

>C=C-C=O

$>C=CH-CH=O \leftrightarrow {}^{+}{>}C-CH=CH-O^{-}$

>C=C-C=N-

RESONANCE or CONJUGATION

- Describes **redistribution of electrons in a molecule**
- Can be depicted by writing resonance structures or using curly arrows
- Presence of p-orbitals is needed in conjugated positions
- All rules for writing canonic formulas are in force

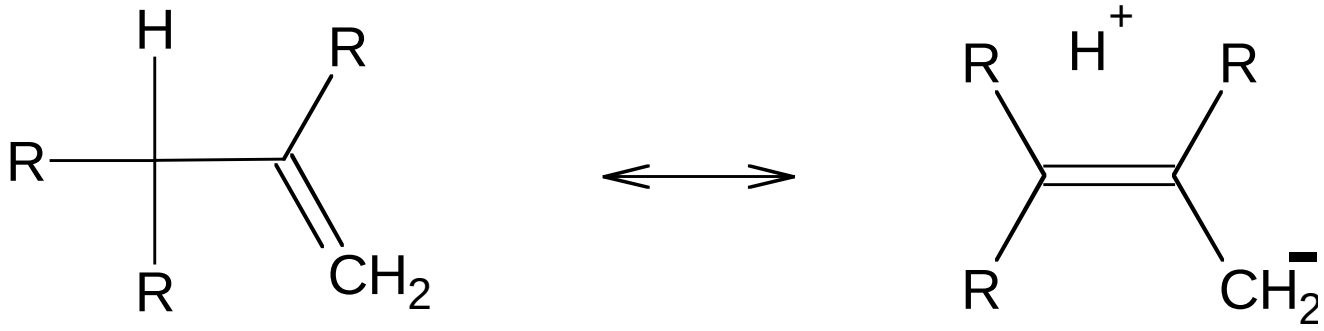
RESONANCE or CONJUGATION

- **Electron delocalization stabilizes molecule**
- Stabilization effect depends on number of p-orbitals involved
- Delocalization may cause charge separation in molecule, but no repositioning of atoms

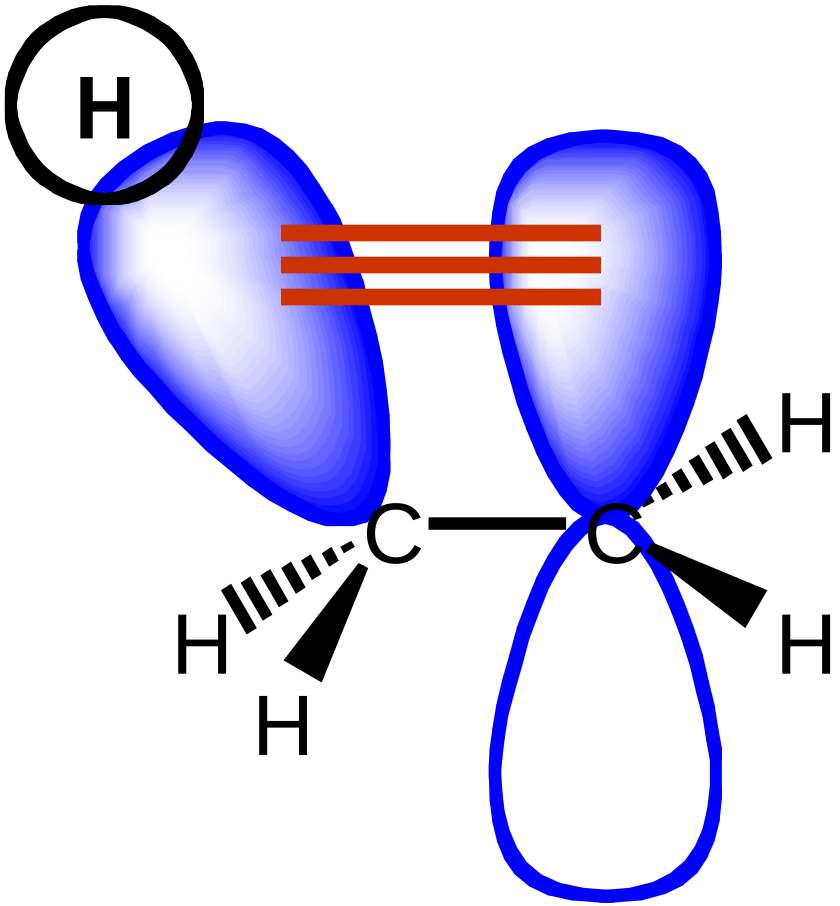
- **Chapter 4 in the main textbook**. Prepare for test

Hyperconjugation

- C-H σ-bond electrons interact with C-C π-bond electrons

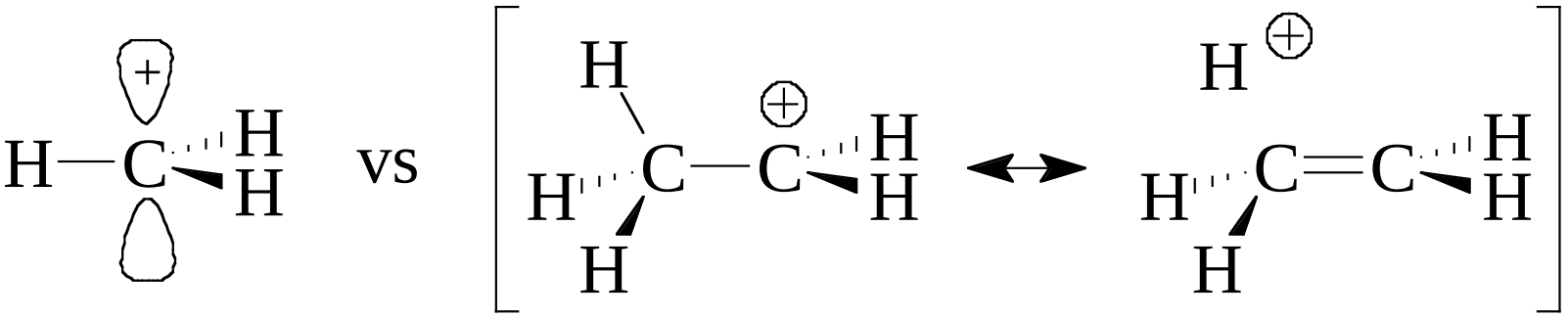


Hyperconjugation



Hyperconjugation and stability of cations

CH_3^+ and $CH_3\text{-}CH_2^+$



hyperconjugation

Alkyl groups are electron donors

HOMEWORK

CHAPTER 4

ROOS, G, ROOS, C, ORGANIC CHEMISTRY CONCEPTS, ACADEMIC PRESS 2015,