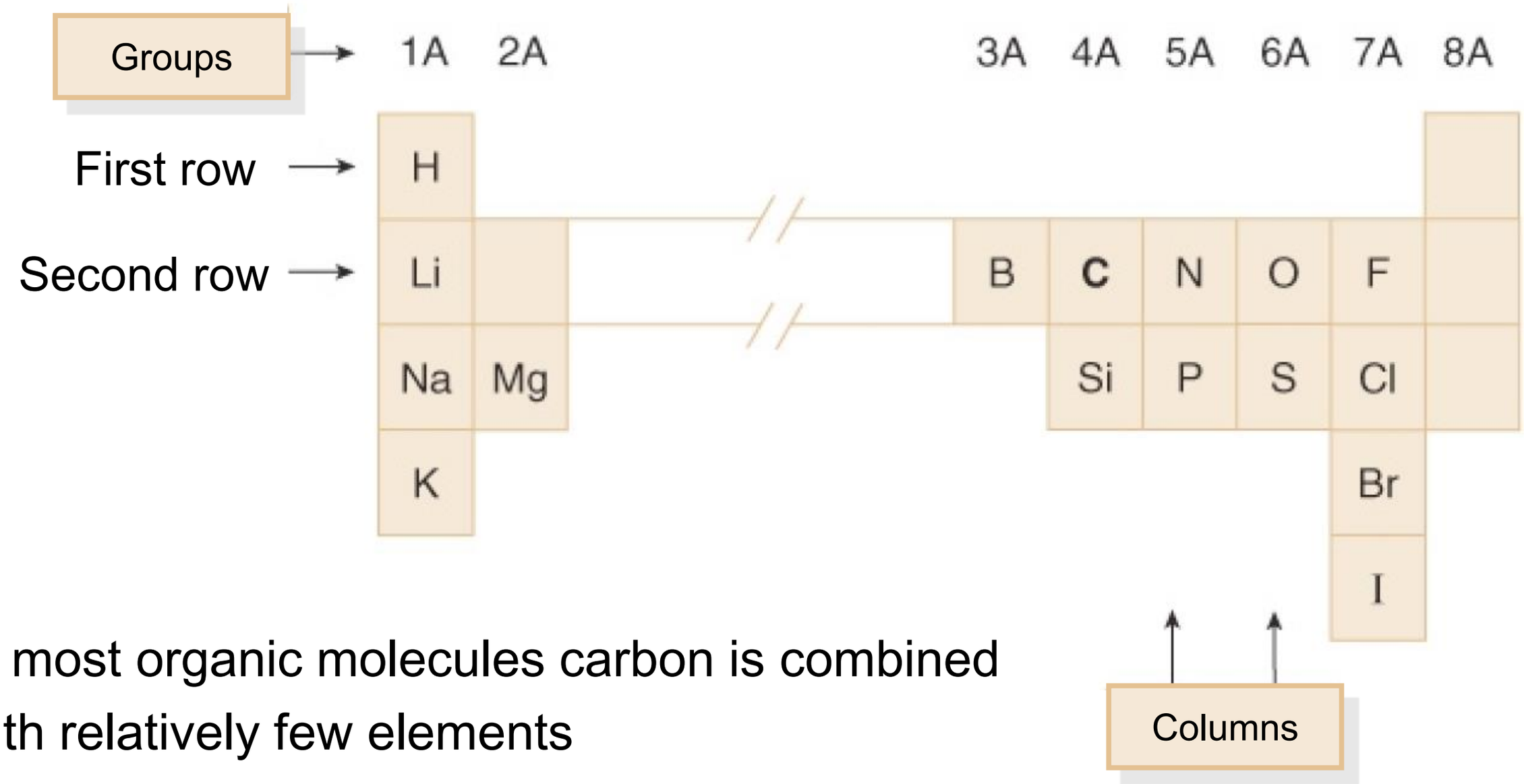
Atomic Structure and Bonding

Chapter 1

Organic Chemistry, *8th Edition*

John McMurry

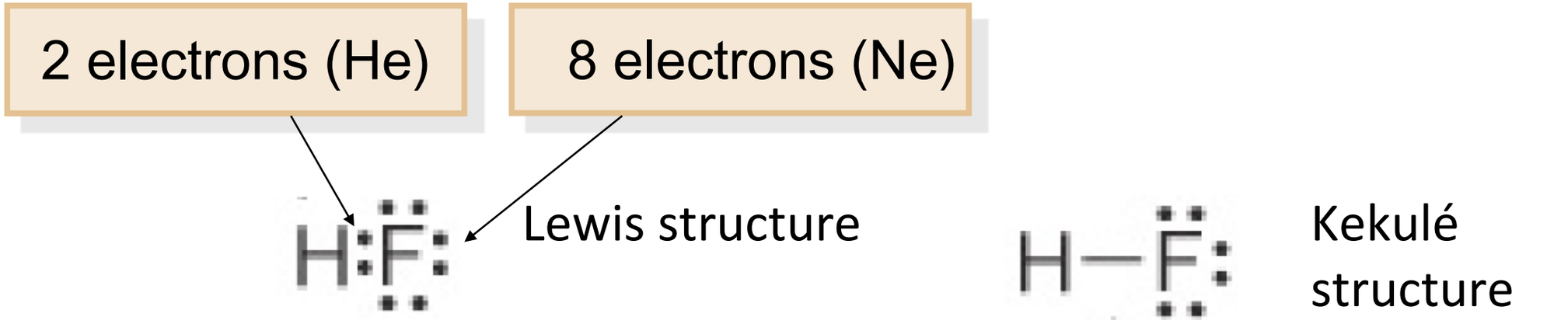
Common Elements



In most organic molecules carbon is combined with relatively few elements

Lewis' Model

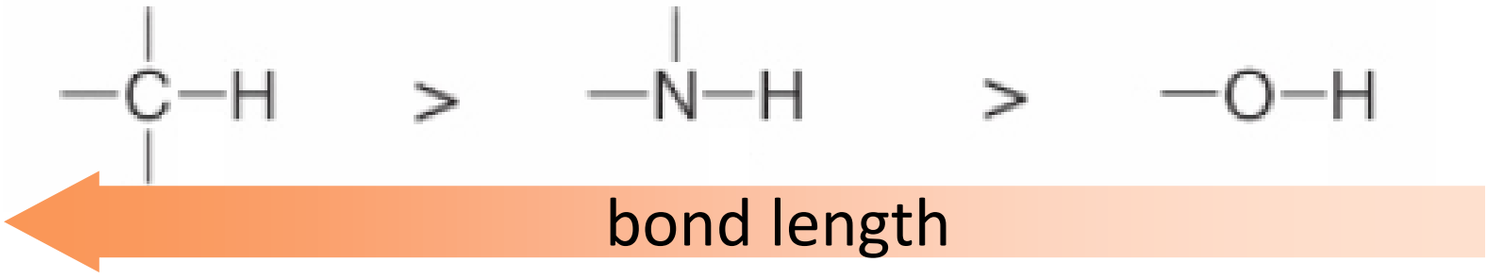
- In Lewis structures electrons are represented as dots.
- Three general rules.
  - Include only valence electrons.
  - If possible, every 2nd raw element should have 8 electrons.
  - Every H atom has 2 electrons.



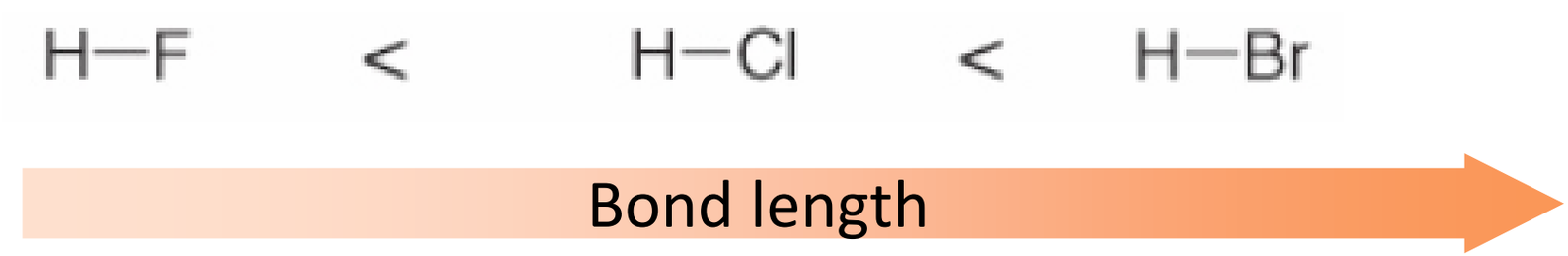
Molecular Shape

- The molecular structure is defined by:
  - bond lengths
  - bond angles

Bond lengths *decrease* along a period.



Bond lengths *increase* along a group



Bond Lengths

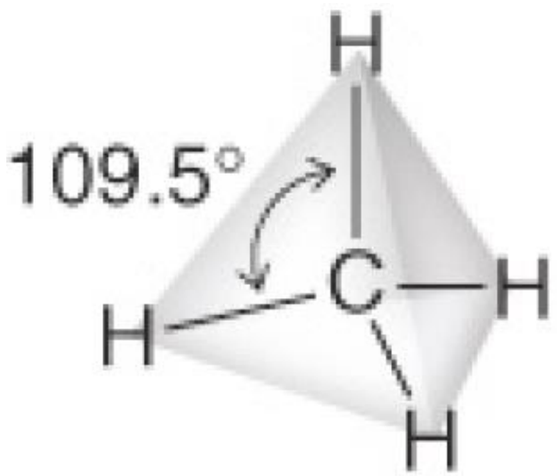
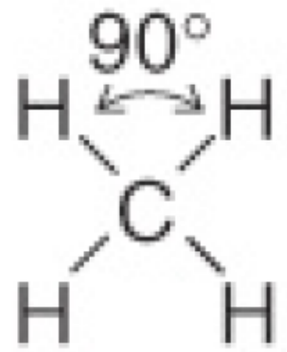
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
H–H	0.74	H–F	0.92	C–F	1.33
C–H	1.09	H–Cl	1.27	C–Cl	1.77
N–H	1.01	H–Br	1.41	C–Br	1.94
O–H	0.96	H–I	1.61	C–I	2.13

Geometry – VSEPR Theory

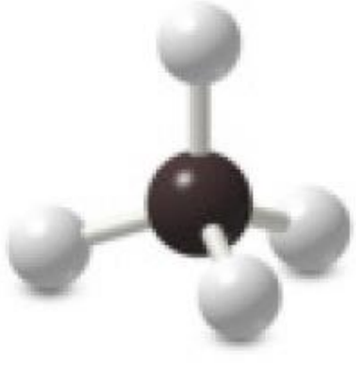
- The number of *Valence Shell Electron Pairs* (groups) around an atom defines the geometry of that atom.
- A group is an atom or a non bonding pair of electrons.
- Groups will tend to be as far apart as possible.

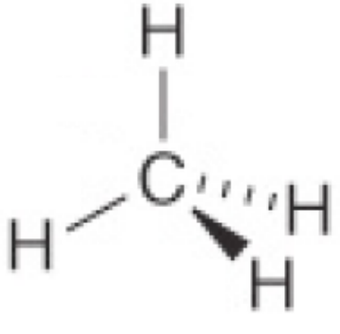
Number of groups	Geometry	Angle
2	linear	180°
3	trigonal planar	120°
4	tetrahedral	109.5°

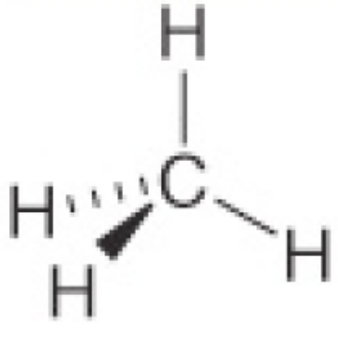
4 groups: CH_4

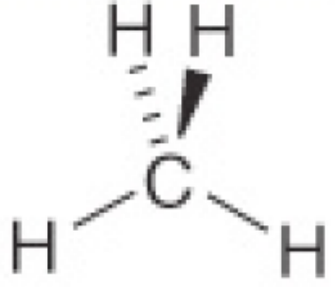
Tetrahedral	Square planar
	
Preferred	Not observed

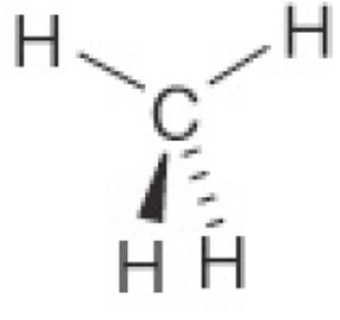
Tridimensional representations of methane





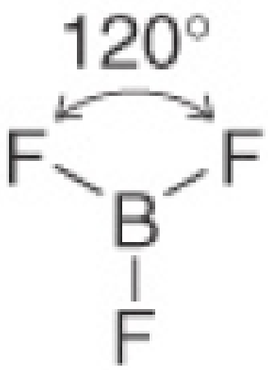






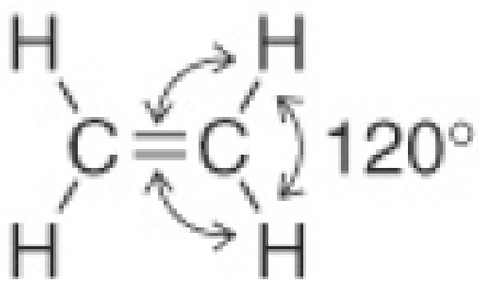
3 groups: BF_3 and C_2H_4

2 trigonal molecules



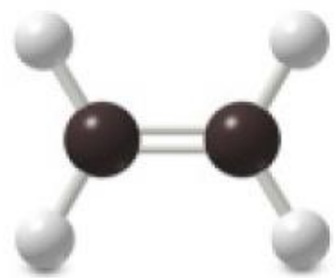
3 atoms around B

All 3 atoms are in the plane

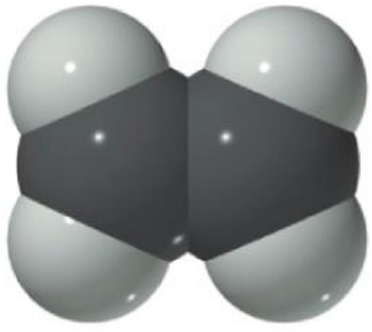


3 atoms around each C

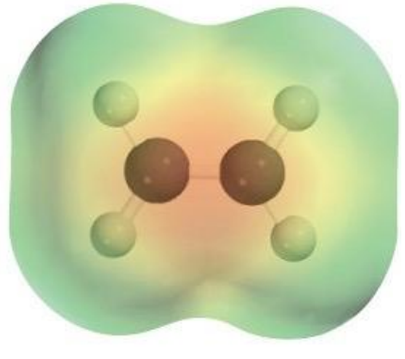
All 6 atoms are in the plane



ball-and-stick model

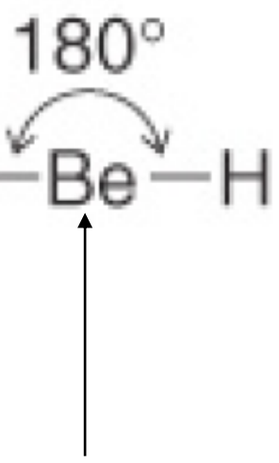


space-filling model

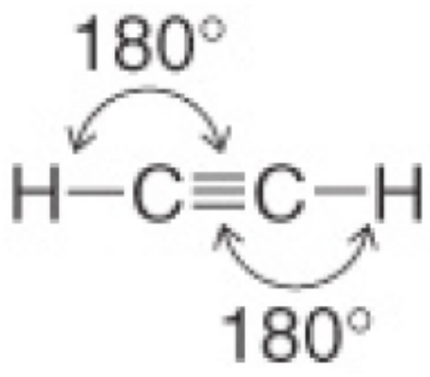


2 groups: BeH_2 and C_2H_2

2 linear molecules



2 atoms around Be



2 atoms around each C

≡

Energies of Multiple Bonds

Bond	Bond Dissociation Energy (kJ/M)
C—C	360
C=C	700
C≡C	950
C—O	400
C=O	750
C—N	360
C=N	700
C≡N	950

The Lewis model is not adequate!

Models for the Chemical Bond

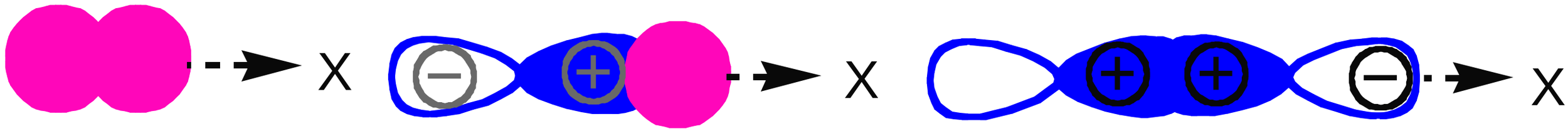
- Valence Orbital theory.
  - Covalent bonds are formed by the overlap of two atomic orbitals and the electron pair is shared by both atoms.
  - A valence bond is localized between two atoms.

- Molecular Orbital theory.
  - n atomic orbitals are combined to give a new set of n molecular orbitals (bonding and antibonding).
  - Molecular orbitals are delocalized on the whole molecule.

Valence Orbitals

- Bonds are formed by the in-phase overlap of two atomic orbitals each contributing one electron.
- The electron pair is localized between two atoms and is shared by both atoms.
- Hydrogen uses the 1s orbital to form σ bonds.
- 2nd row atoms use hybrid orbitals (sp^3, sp^2, sp) to form σ bonds.
- 2nd row atoms use p orbitals to form π bonds that have a nodal plane.
- Atomic orbitals overlap better in σ bonds (co-linear) than in π bonds (parallel).

Strong Bonding Interactions: Axial Overlap

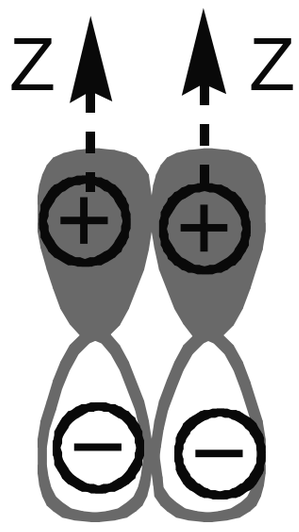


1s(H)-**1s**(H)
H_2

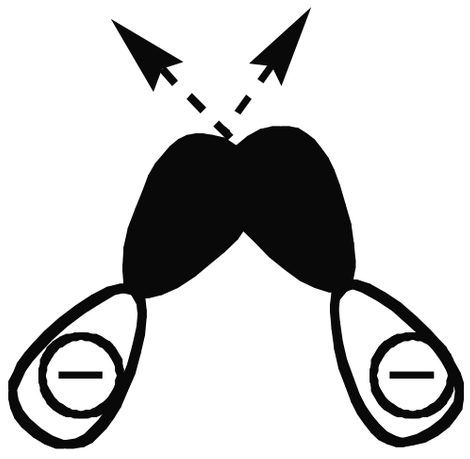
2px(F)-**1s**(H)
F-H

2px(F)-**2px**(F)
F-F

Weak Bonding Interactions: Lateral Overlap

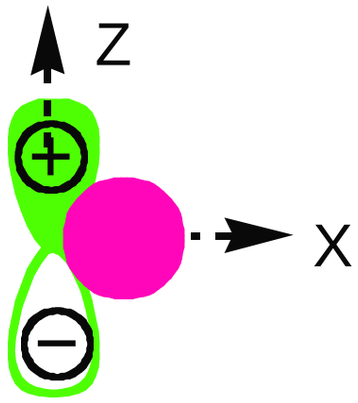


2pz(C)**2pz**(C)
π bond of ethylene

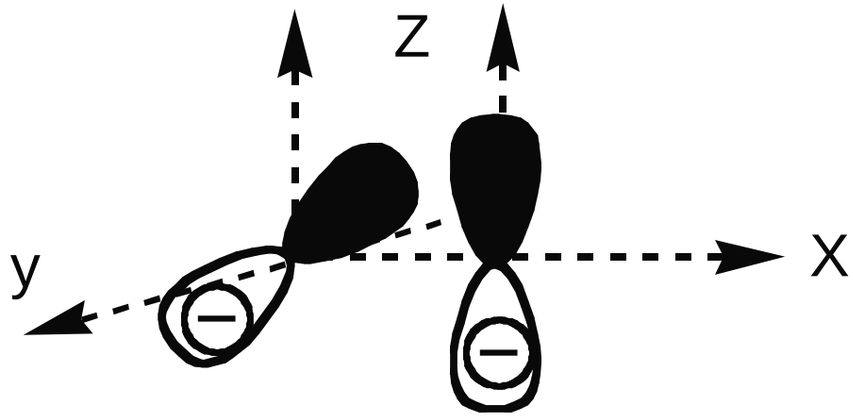


2pz(C)**2pz**(C)
σ bond of cyclopropane

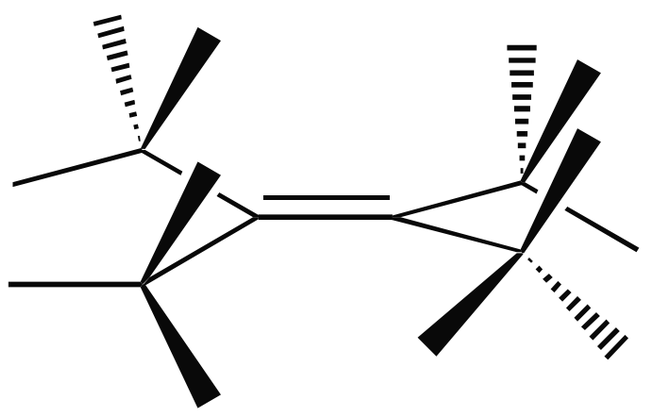
Inexistent Bonding Interactions (0 Overlap)



2px(F)-**1s**(H)
F-H



2pz(C)**2pz**(C)
Bond in tetra-*t*Bu-ethylene

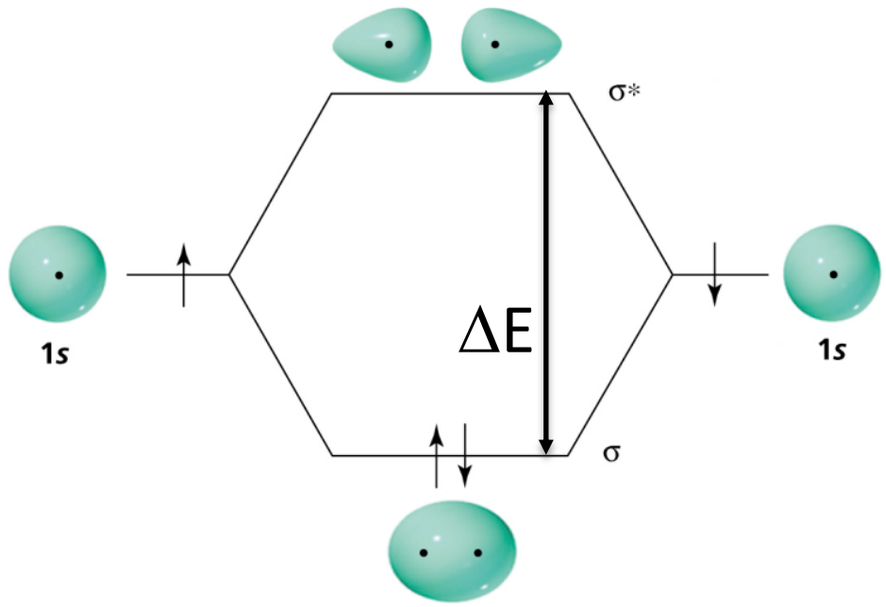


Molecular Orbitals

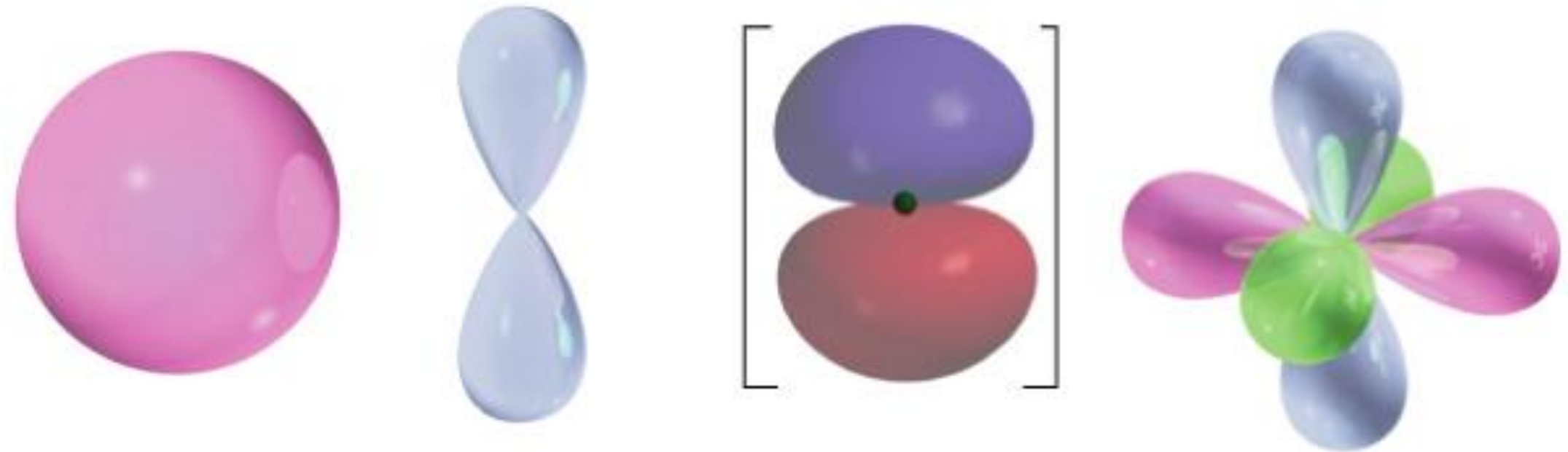
- Valence electrons occupy molecular orbitals delocalized on the whole molecule.
- The combination of *n* atomic orbitals gives *n* new molecular orbitals.
- Bonding orbitals have lower energies and antibonding orbitals have higher energies than the starting atomic orbitals

Robert Mulliken (1896-1986)

The H_2 molecule:



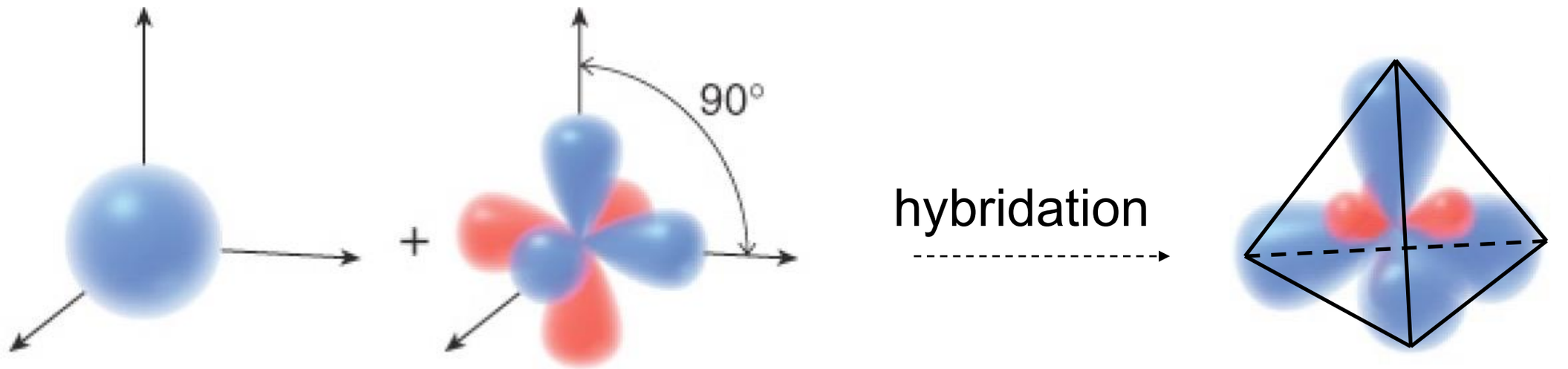
Atomic Orbitals of Carbon



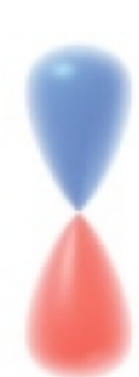
s p 2p 3 x 2p orbitals

sp^3 Hybrids

- The mixing of a spherical 2*s* orbital and three 2*p* orbitals generates four sp^3 orbitals, each with a small and a large lobe.



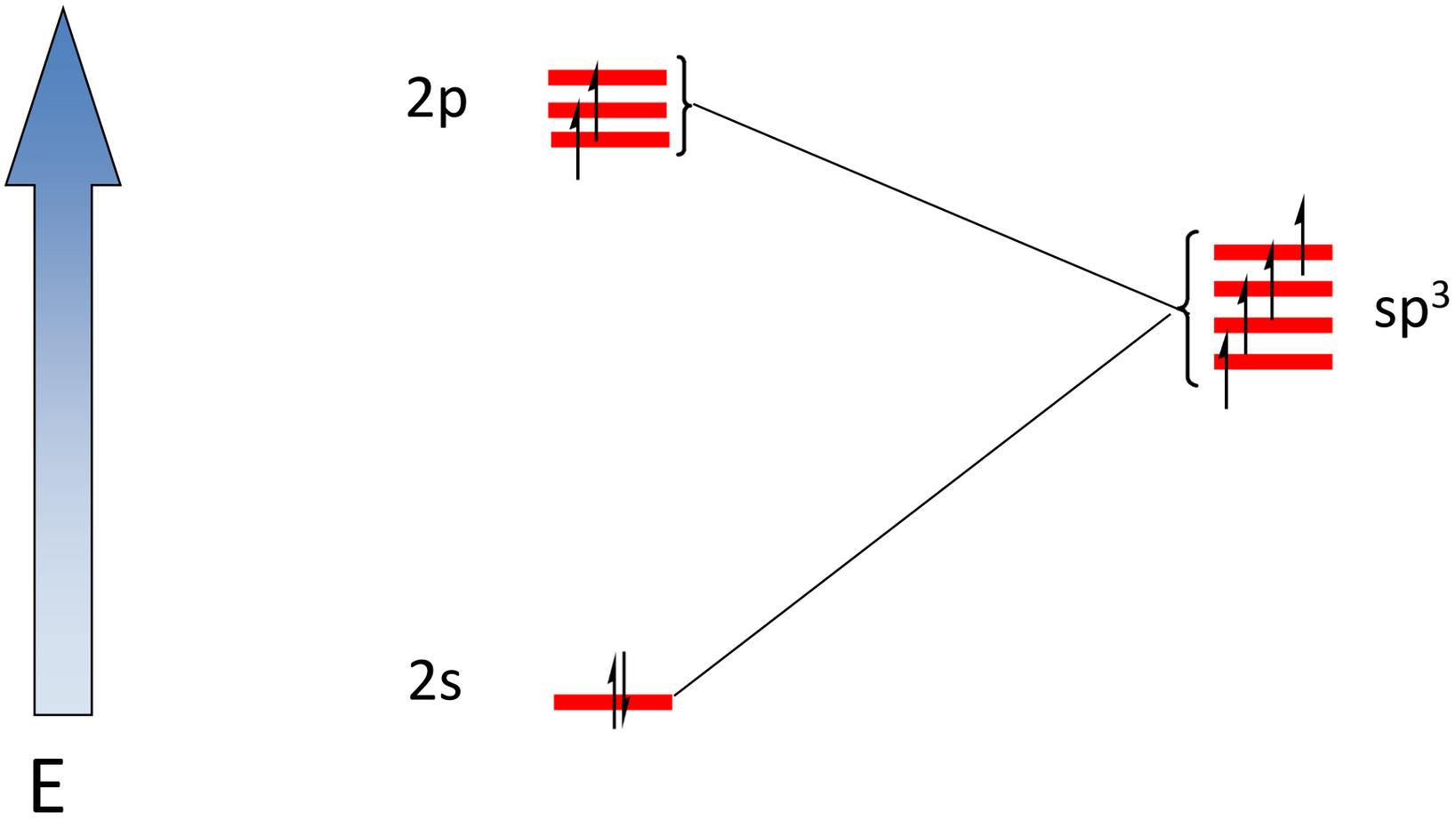
2s 3 x 2p 4 x sp^3 orbitals



p

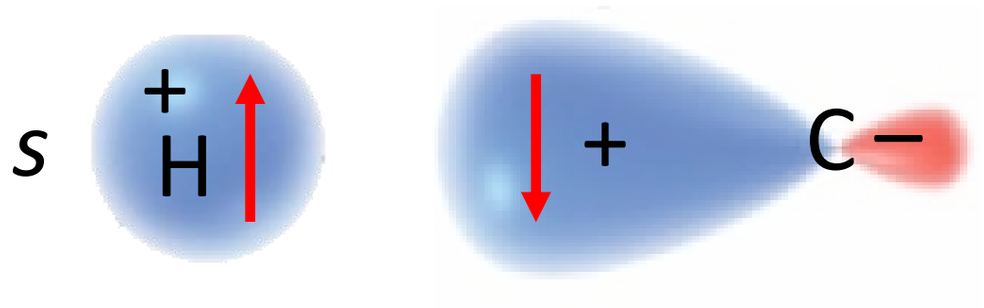
sp^3

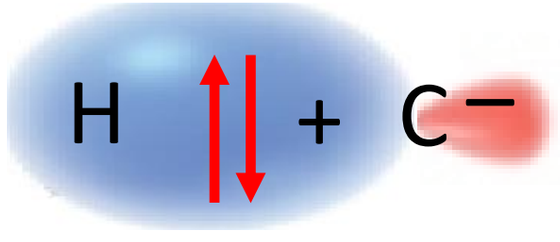
sp^3 Hybrids



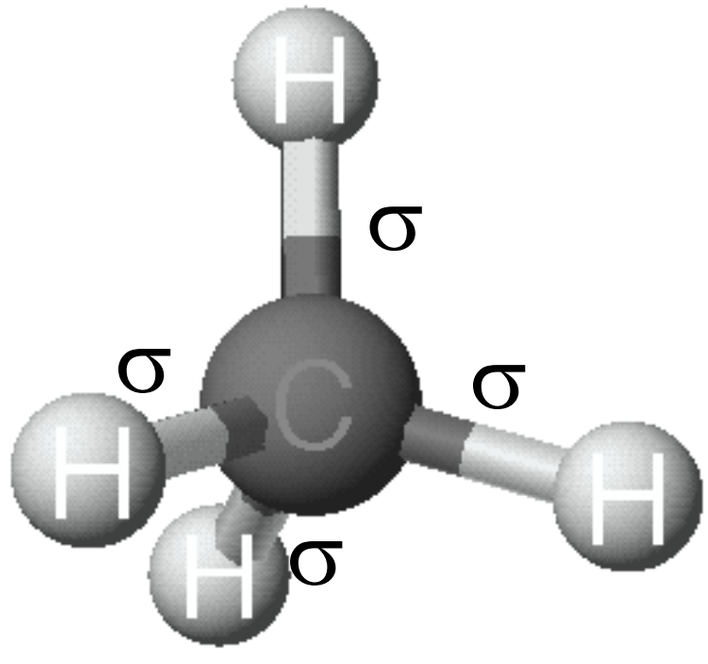
Methane

The overlap of a half-full *1s* orbital of hydrogen with a half-full sp^3 orbital of carbon bond gives a σ orbital.

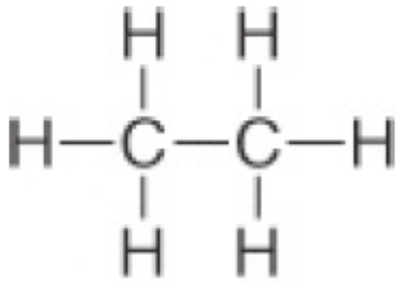




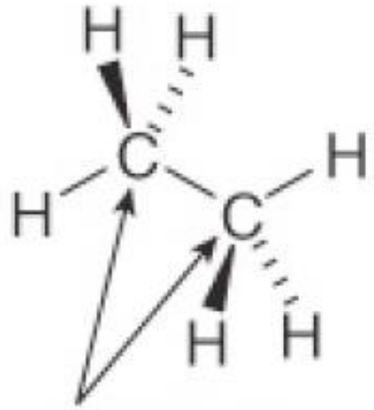
σ C–H



Ethane



ethane



tetrahedral sp^3 C

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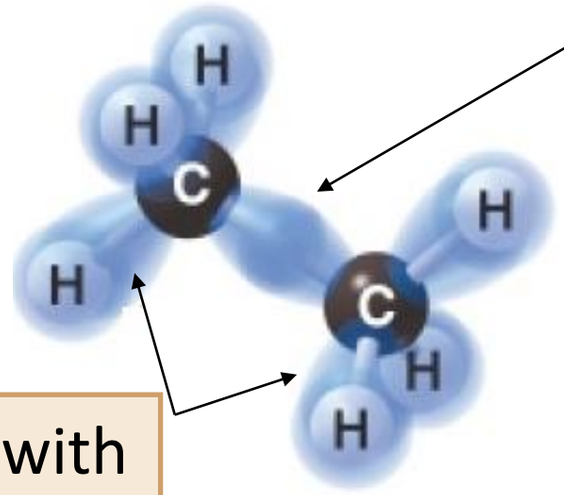
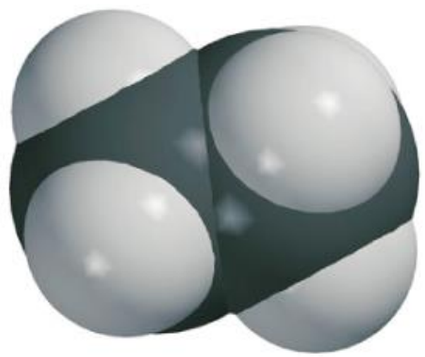
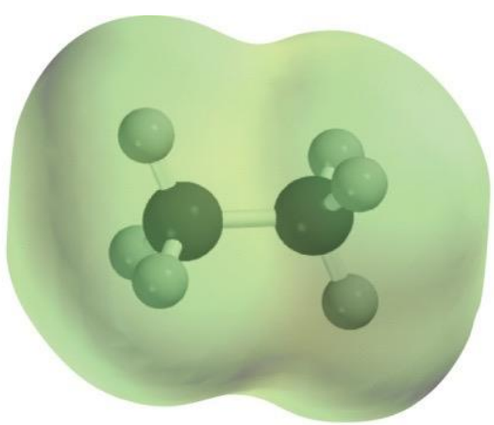
Two sp^3 hybrids overlap giving the C–C σ bond

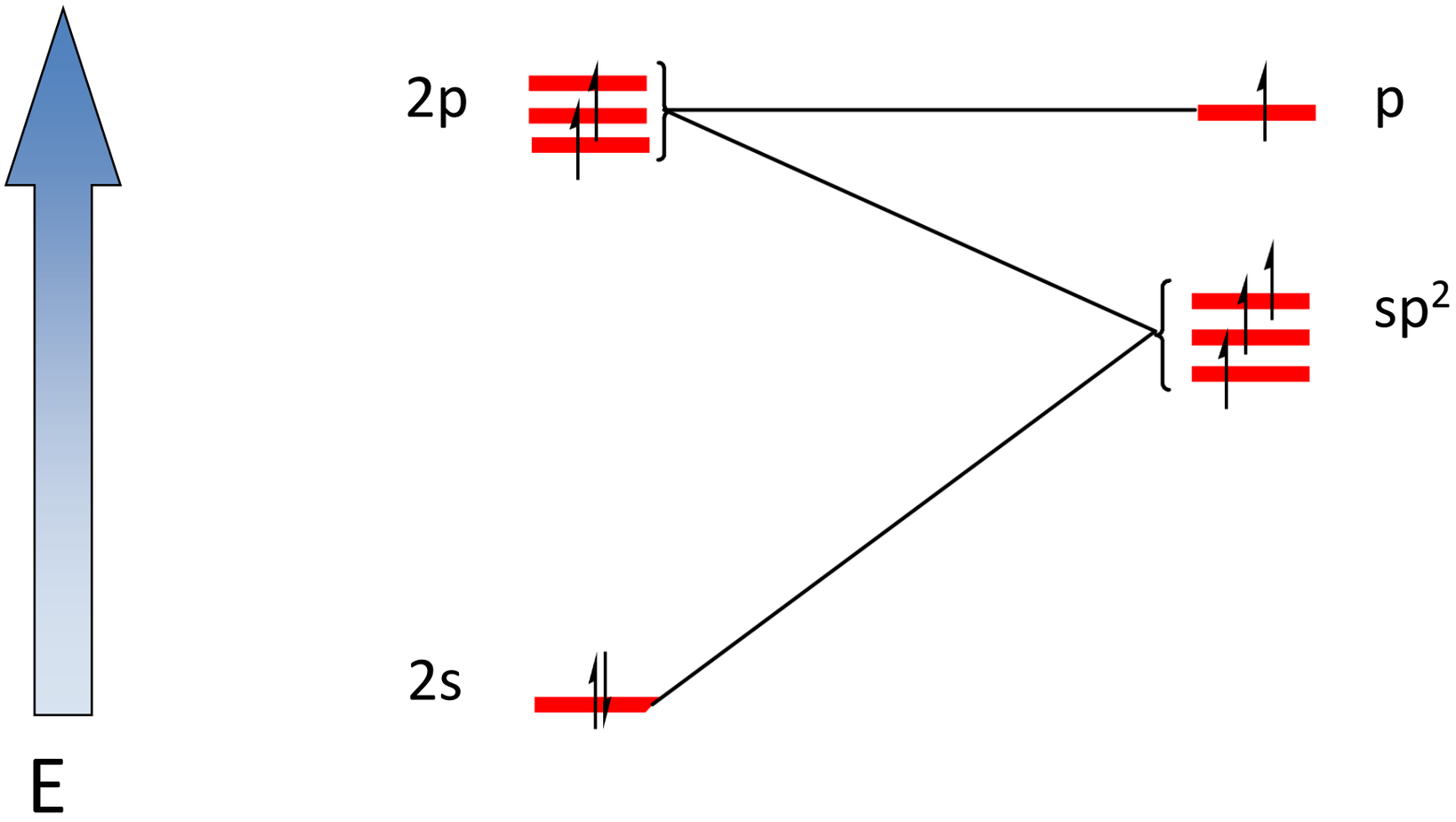


sp^3 hybrids on C overlap with *1s* orbitals on H giving the C-H σ bonds.

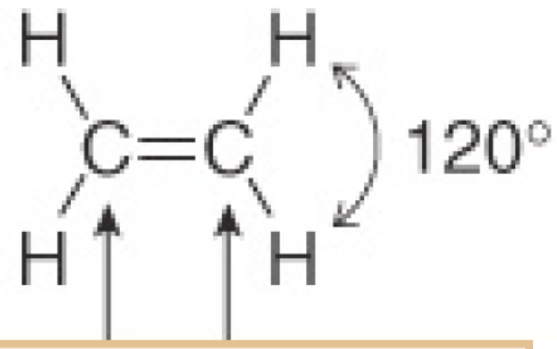




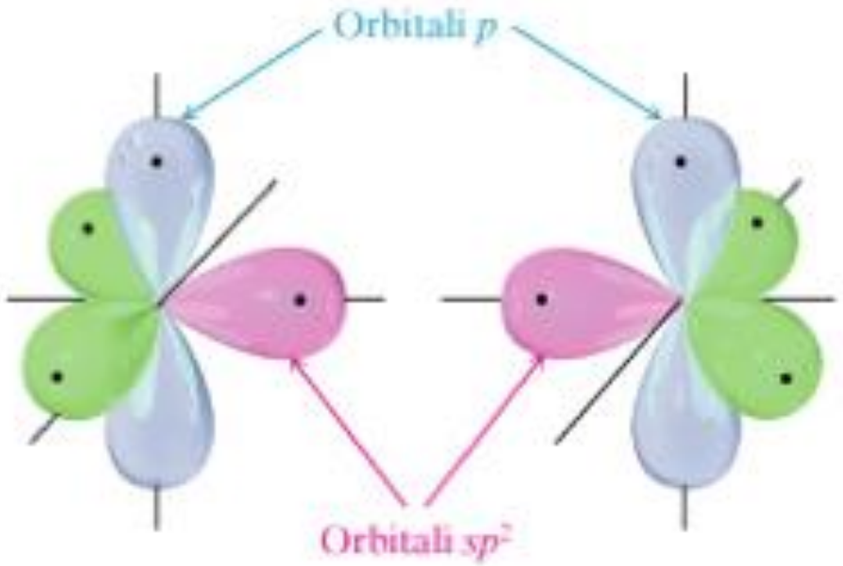
Sp^2 Hybrids

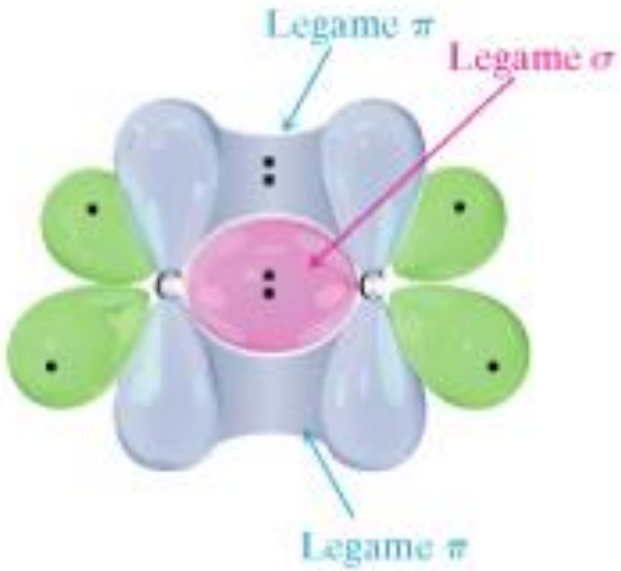


Ethylene C_2H_4

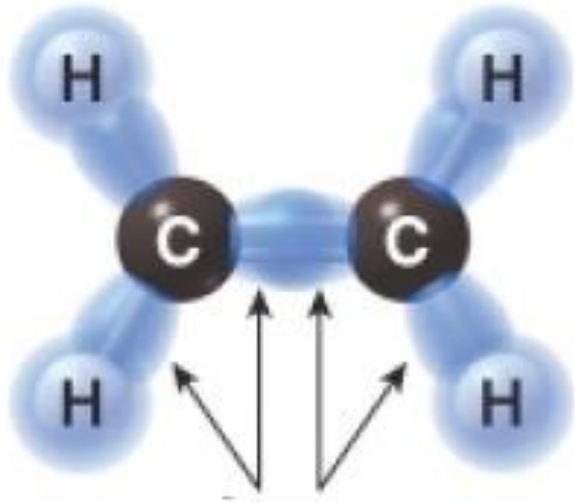


3 groups around C
C atoms are *sp*^{2}



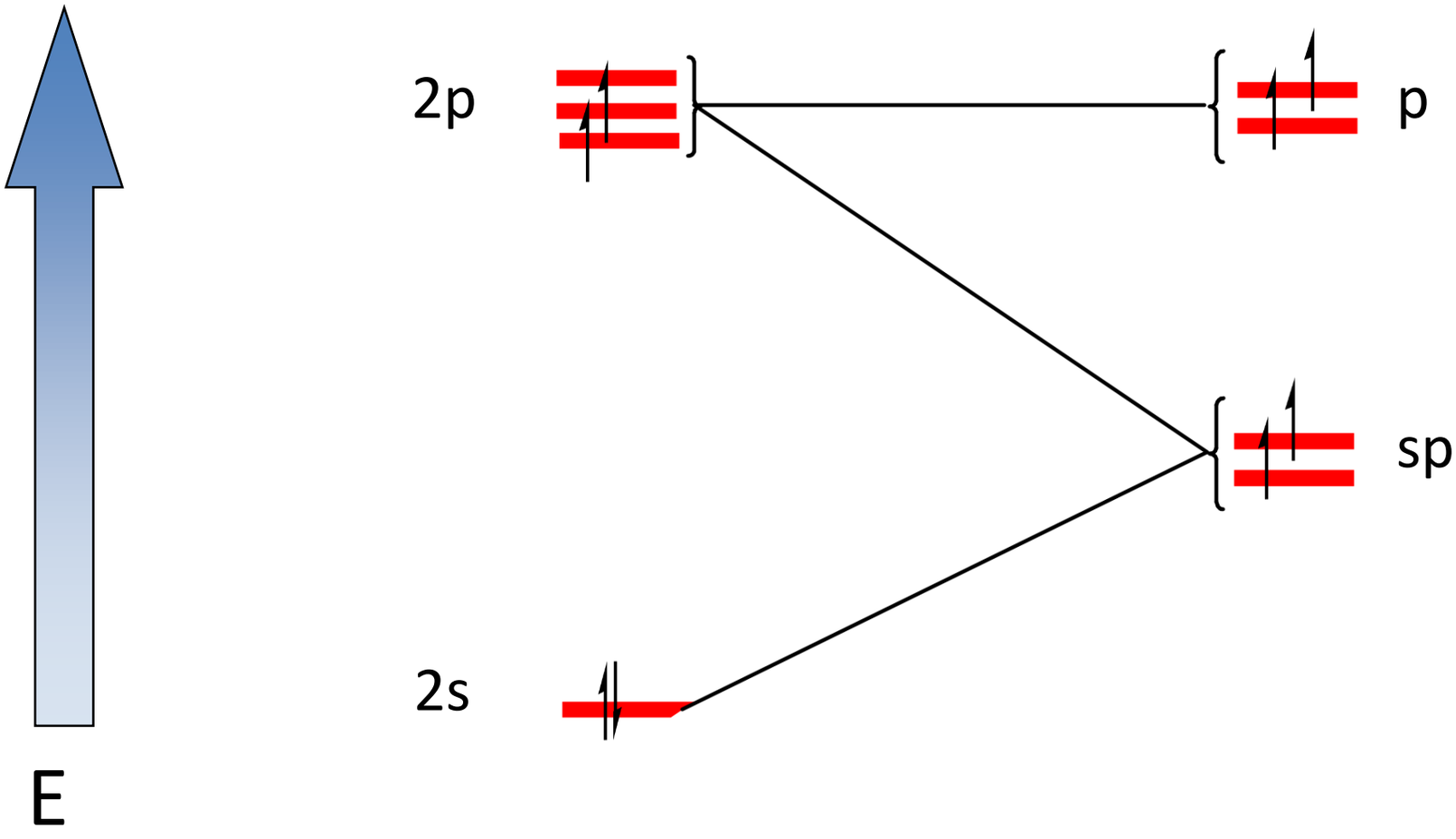


C-C double bond

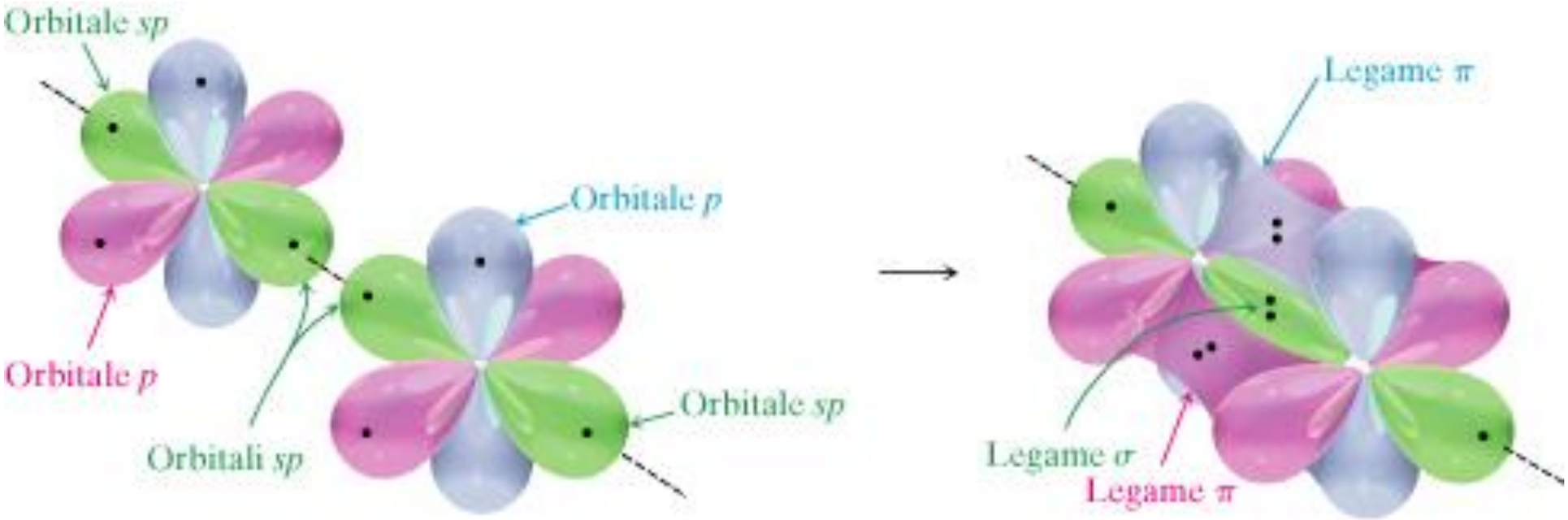


Sp^2 hybrids

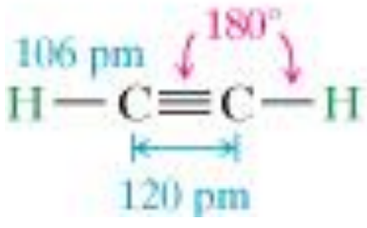
Sp Hybrids



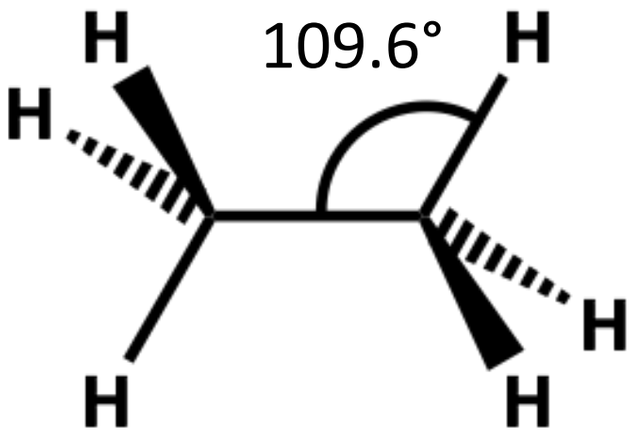
Acetylene C_2H_2

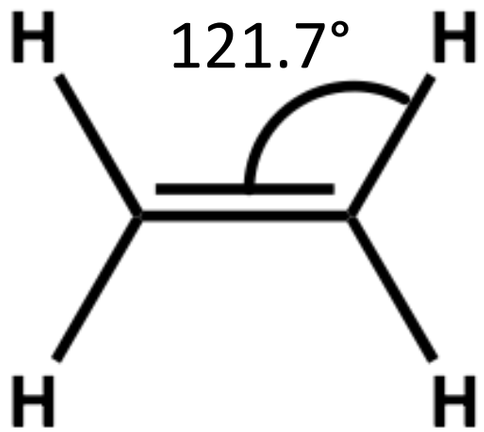


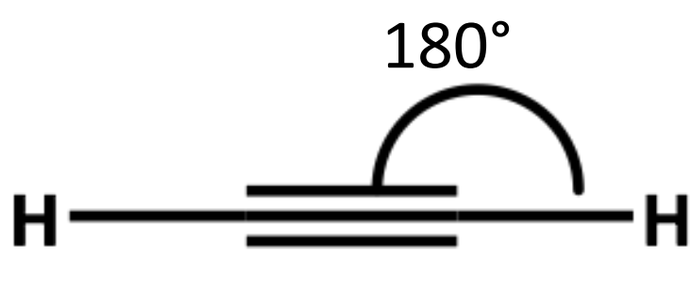
C-C triple bond



Structures of C_2H_6, C_2H_4, C_2H_2

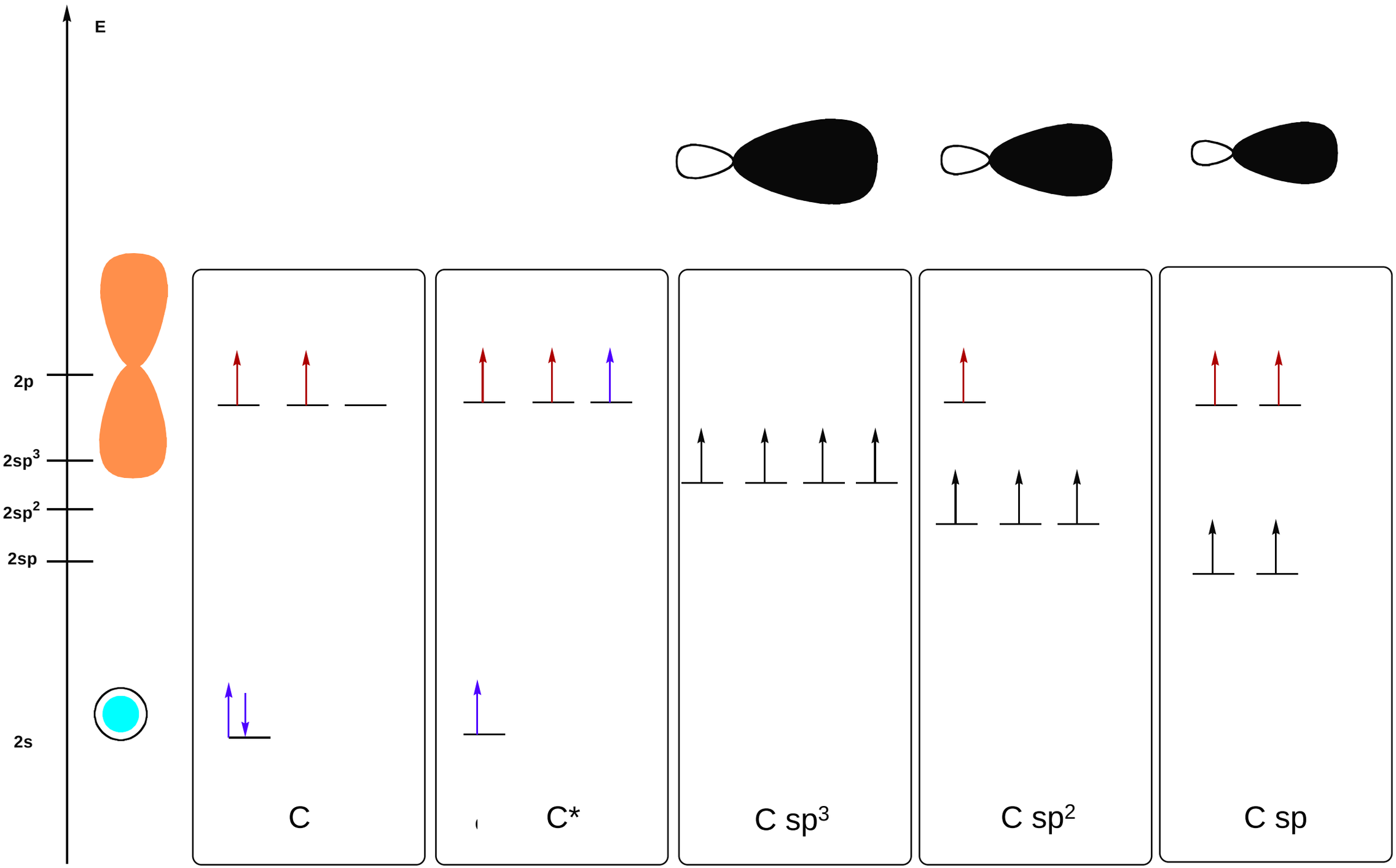




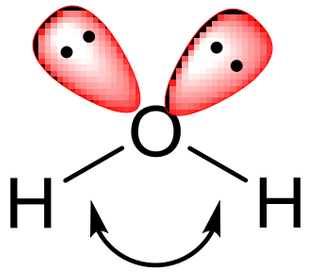


d_{C-C} (pm):	154	133	120
d_{C-H} (pm):	110	107.6	106
E_{C-C} (kJ/M):	376	611	835

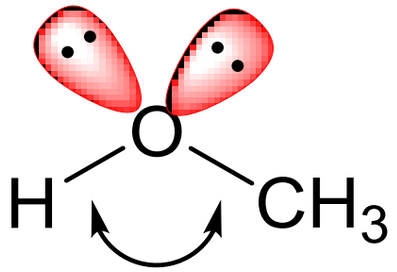
Energy Levels and Orbital Size



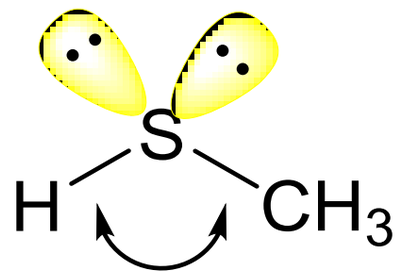
Ibridization of O, S, N



104.5°



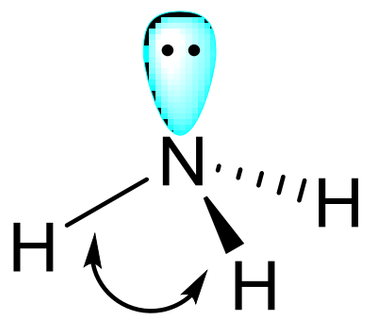
108.5°



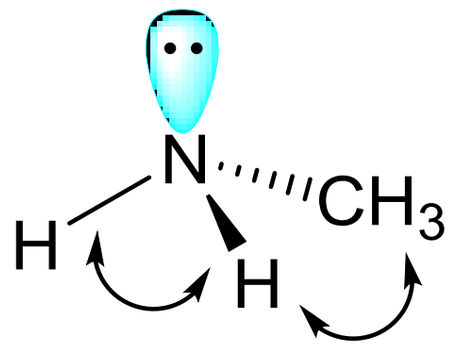
96.5°

$[He]2s^2 2p^4$

$[Ne]3s^2 3p^4$



107°



107.1°

110.3°

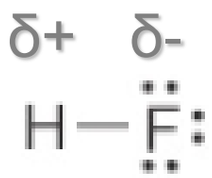
$[He]2s^2 2p^3$

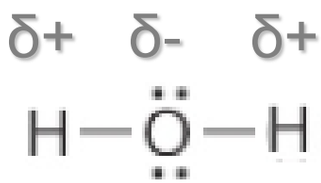
Polar Bonds
Intermolecular Interactions
Delocalised Bonds

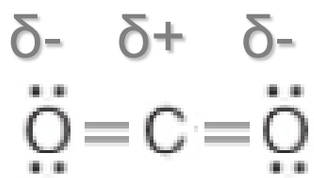
Chapter 2
Organic Chemistry, *8th Edition*
John E. McMurry

Polar Covalent Bonds

- The higher the electronegativy difference, the higher the polar character of a covalent bond.

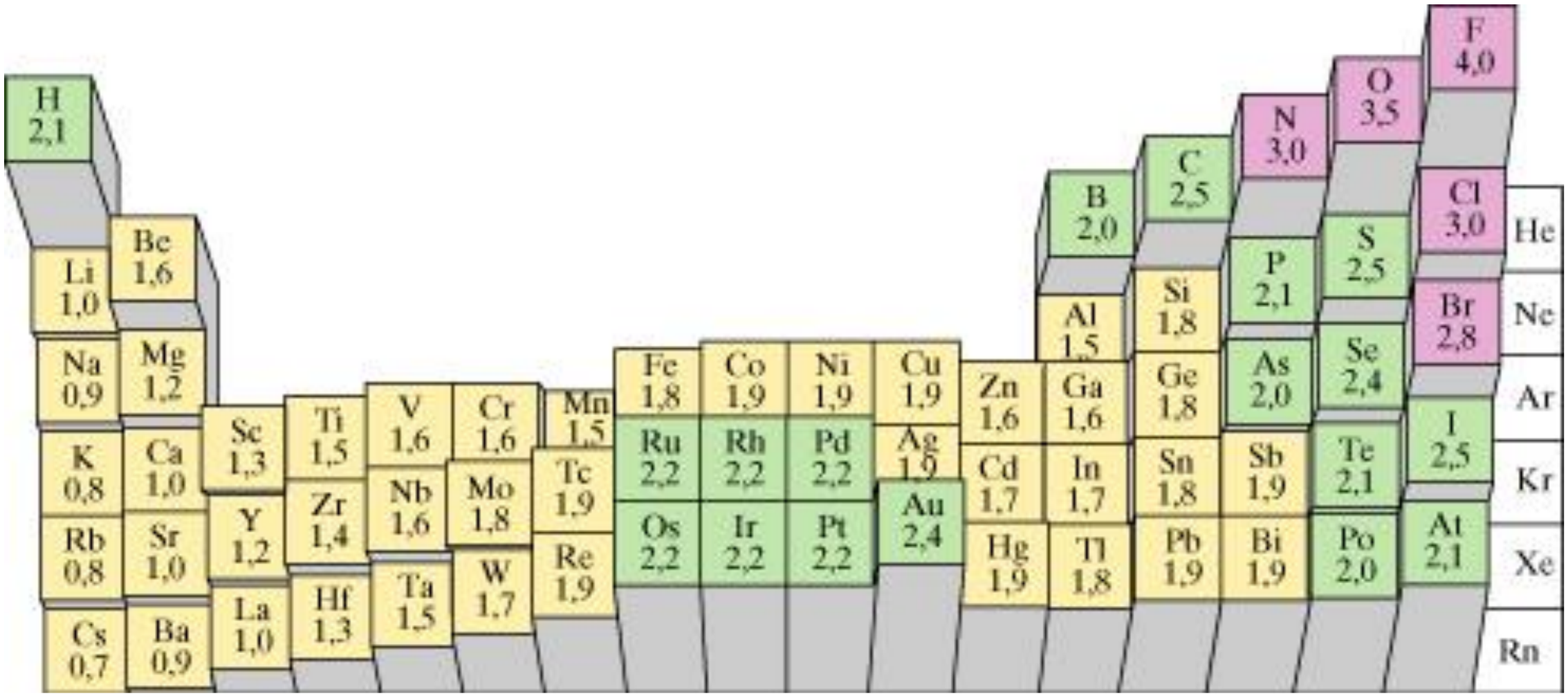






- In polar bonds, bonding electrons are attracted towards the more electronegative atom.
- Generally:
  - ΔX > 1.9 ionic bond
  - ΔX < 0.5 covalent bond
  - ΔX = 0.5 – 1.9 polar covalent bond

Pauling's Electronegativities

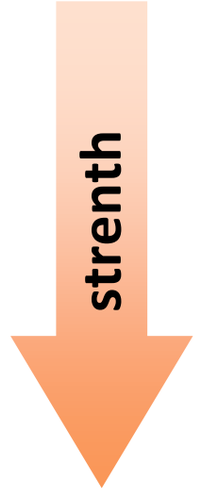


Intermolecular Interactions

- Intermolecular interactions are also called non-covalent and non-bonded interactions.

- Intermolecular interactions depend on the type and number of functional groups.

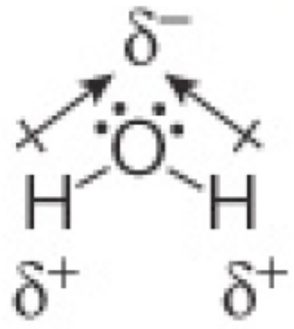
- In neutral molecules there are three main types of intermolecular interactions.
  - Vand der Waals interactions (London dispersion forces) – VDW
  - Dipole-dipole interactions – DD
  - Hydrogen bonds– HB

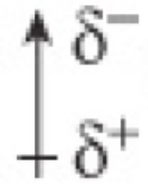


Dipole Moments

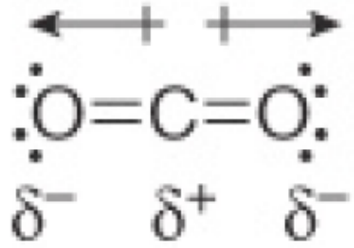
- Polar molecules have one or more polar bonds.

Es. H_2O

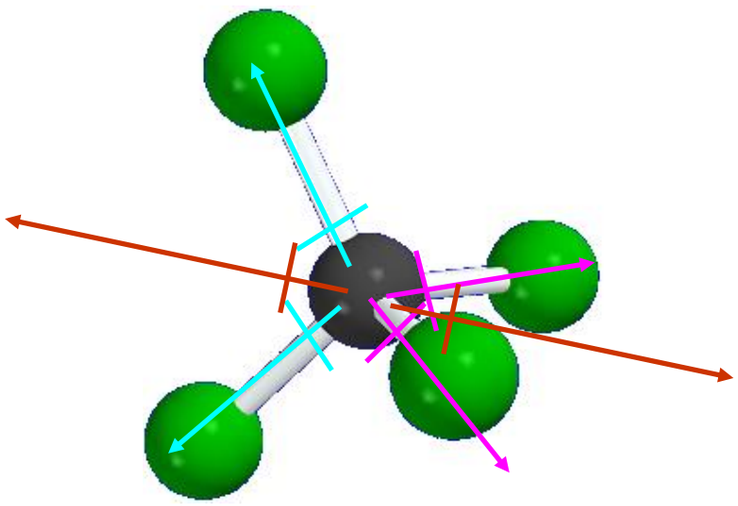




- Apolar molecules either do not have polar bonds or have polar bonds whose dipoles cancell each other. E.g. CO_2

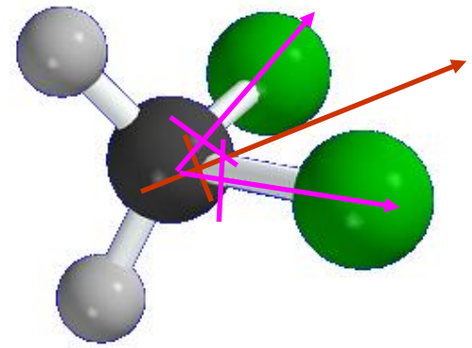


CCl_4 δ = 0 D



Dipoles cancel

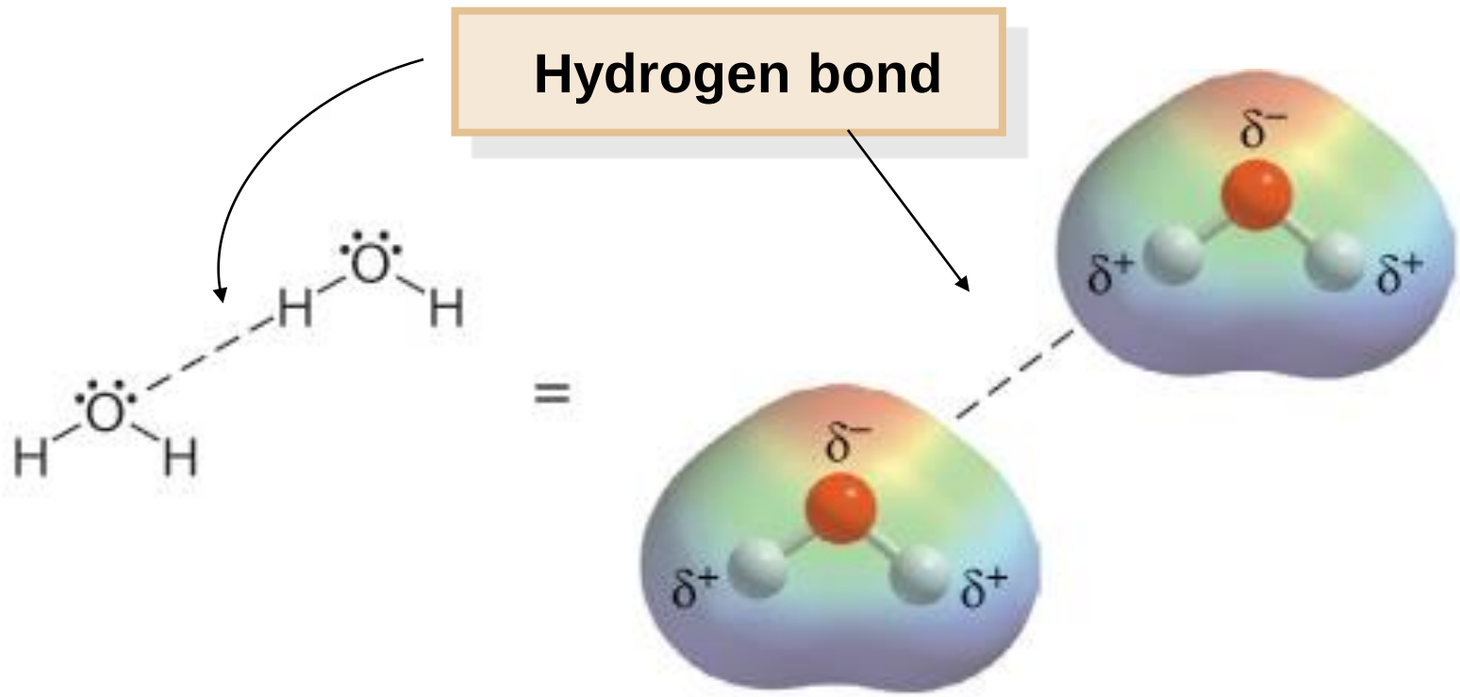
CH_2Cl_2 δ = 1.62 D



Dipoles add

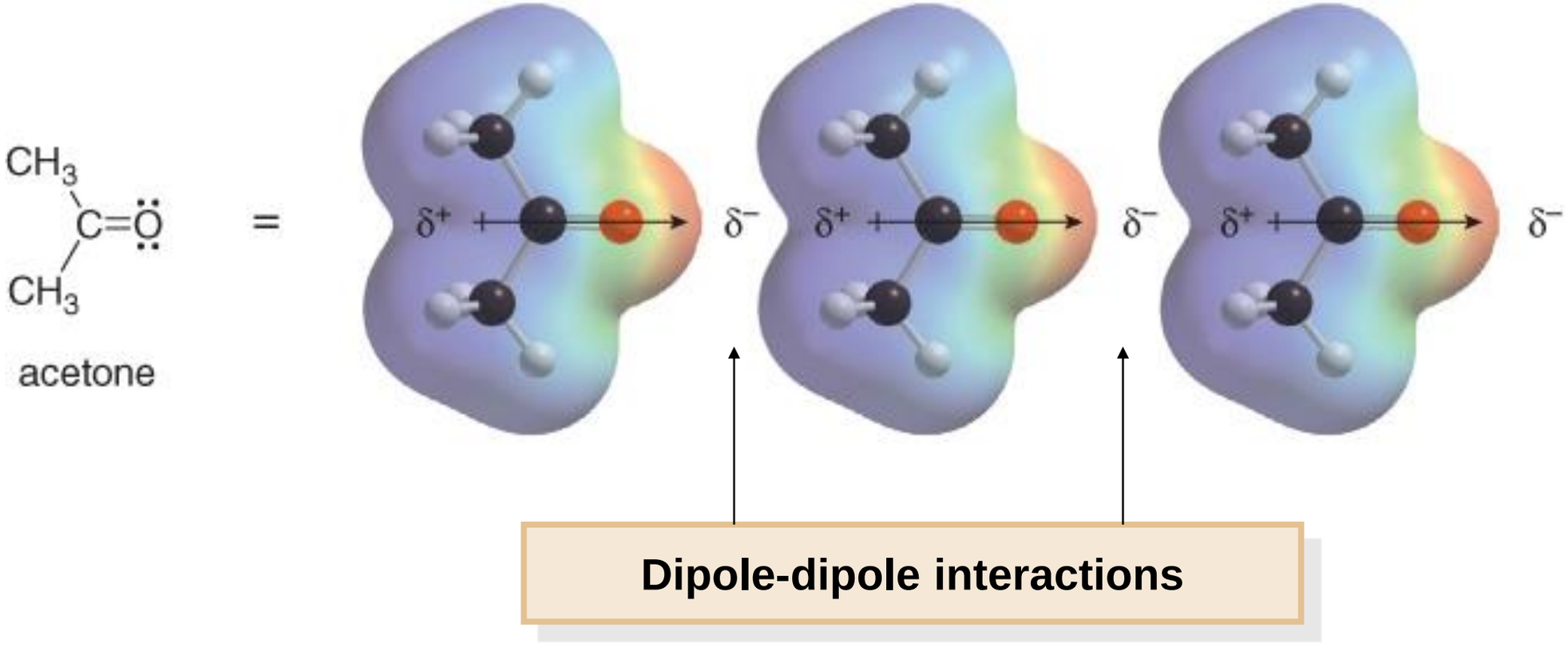
The Hydrogen Bond

The hydrogen bond is an electrostatic interaction between a O-H or N-H group and a lone pair on O or N.



Dipole-Dipole Interactions

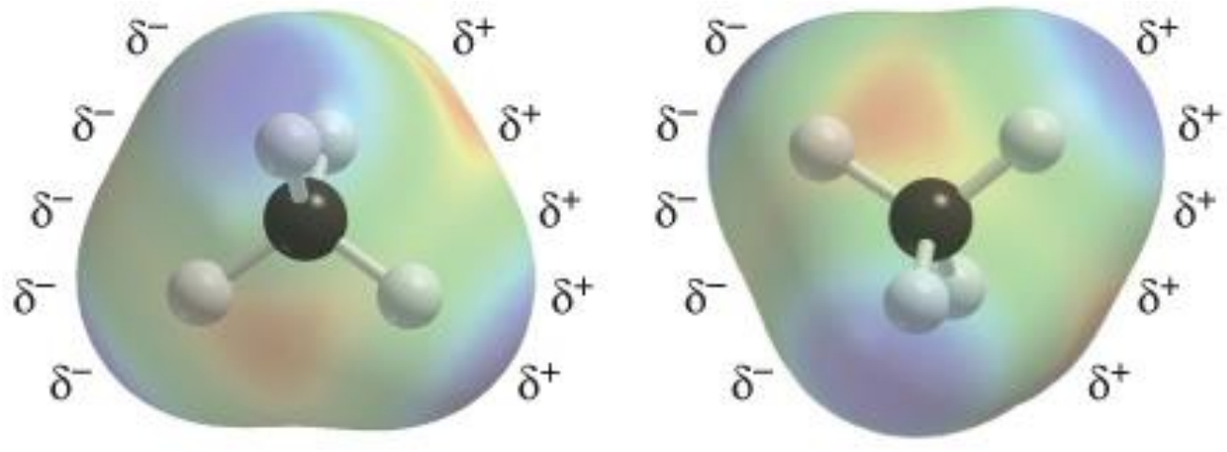
Dipole-dipole interactions are attraction forces between the permanent dipoles of two molecules.



Van der Waals (London) Forces

- VdW forces are weak interactions originating from temporary variations of the molecule's electron density distribution.
- They are the only attractive forces in apolar molecules.

Van der Waals interactions between two CH_4 molecules

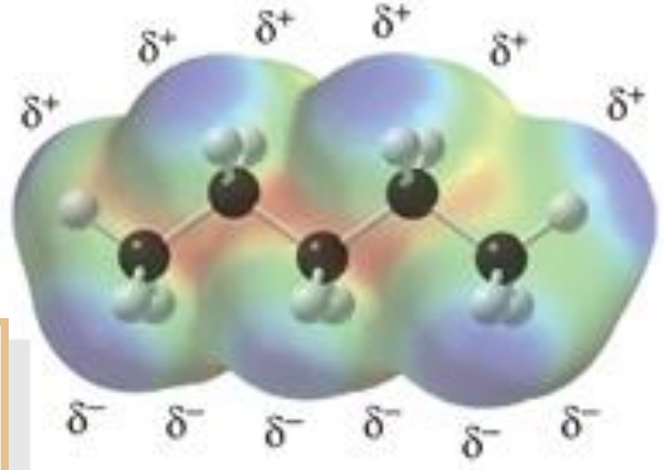


Dipoles generated by a temporay asymmetry in the electron density

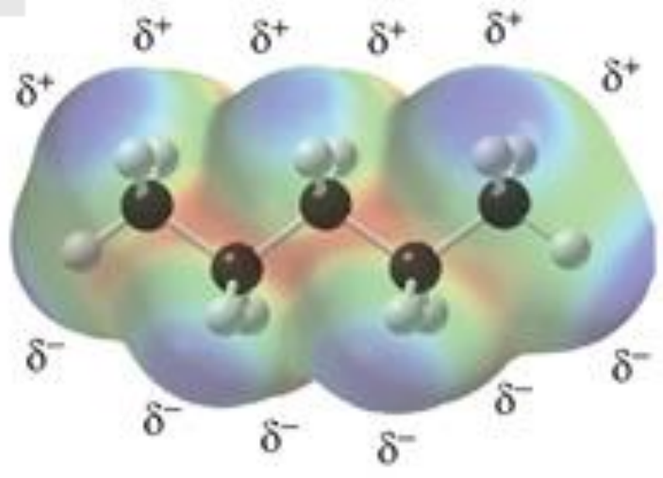
Van der Waals (London) Forces

- Van der Waals interactions are present in all molecules.
- The larger the surface area, the larger the attractive force between two molecules, and the stronger the intermolecular forces.

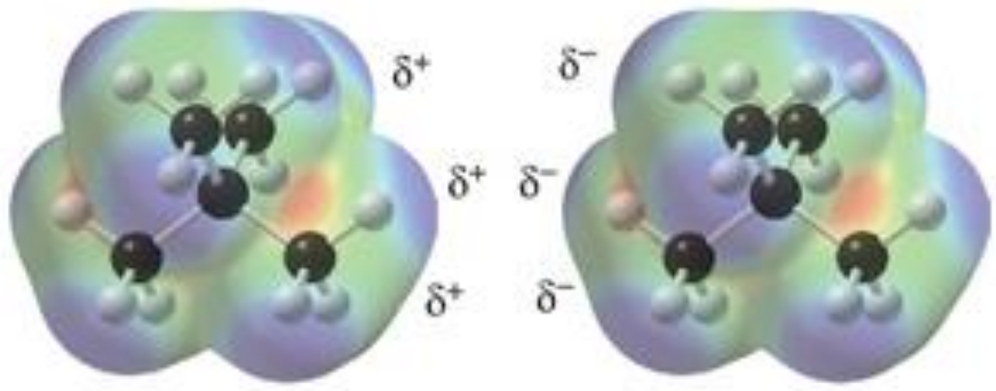
Long, cylindrical molecules:
stronger interactions

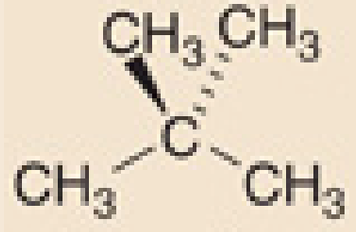


$CH_3CH_2CH_2CH_2CH_3$
***n*-pentane**



Compact, spherical molecules:
weaker interactions





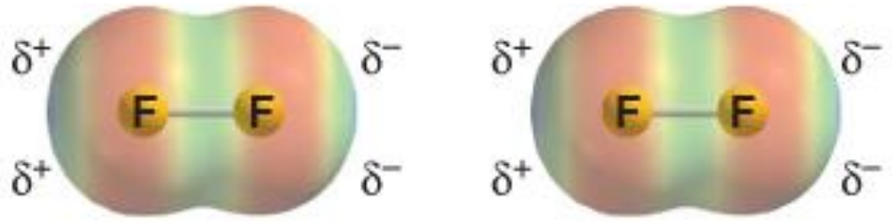
neopentane

Van der Waals (London) Forces

- VdW forces depend on polarizability.
- Larger atoms, like iodine, which have more loosely held valence electrons, are more polarizable than smaller atoms like fluorine, which have more tightly held electrons

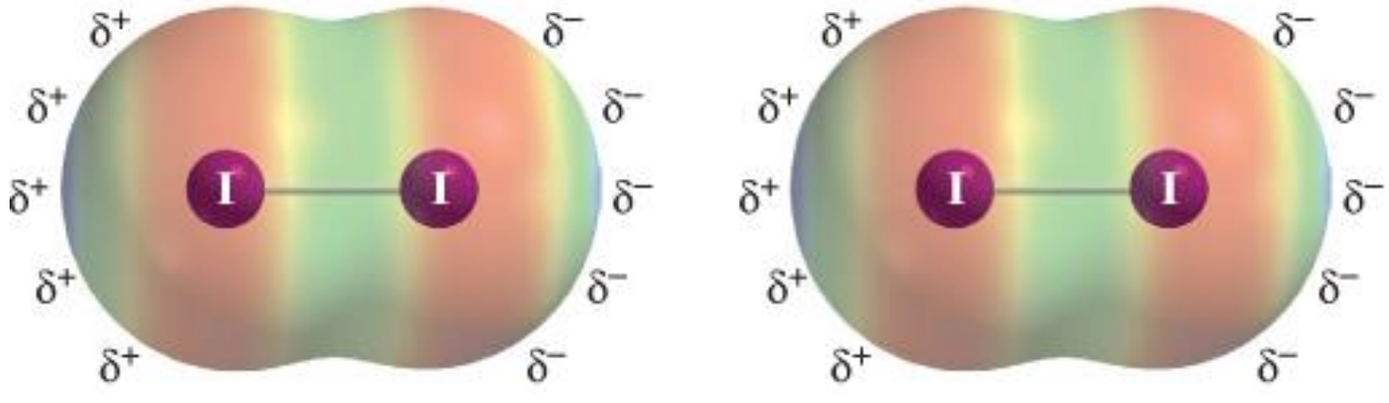
Weak interaction

Small atoms: lower polarizability



Large atoms: higher polarizability

Stronger interaction



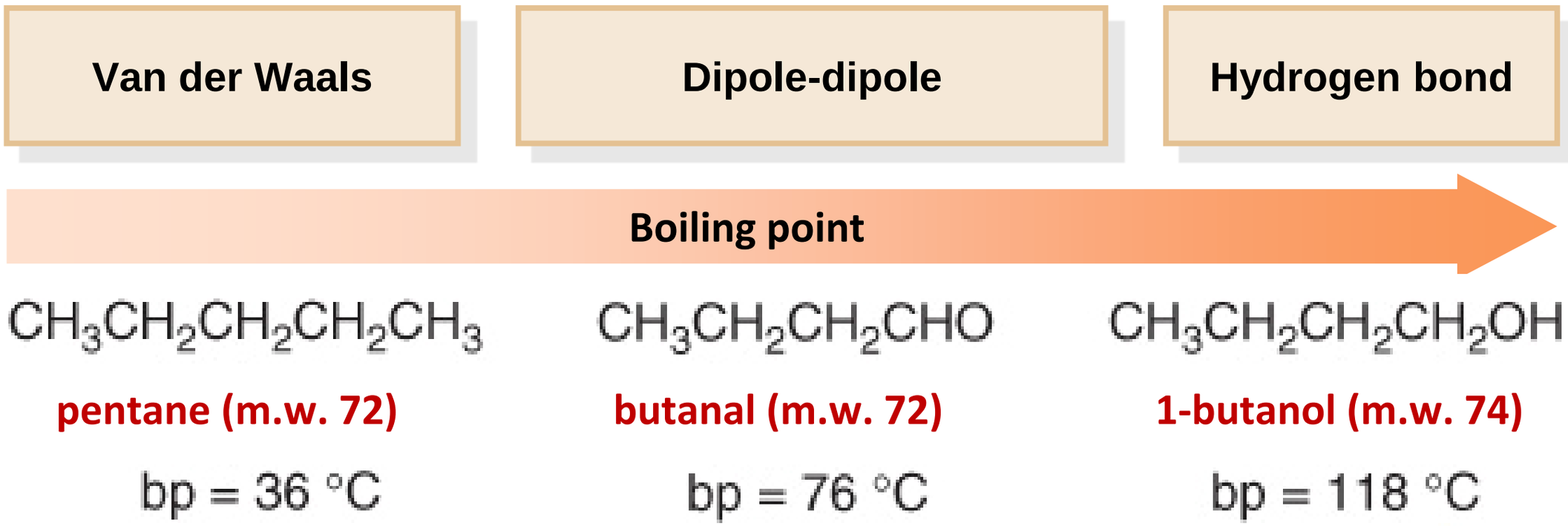
Summary

Interaction	Relative strength	Present in	Examples
Van der Waals VDW	Very weak	All molecules	$CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2CH_2CHO$ $CH_3CH_2CH_2CH_2OH$
Dipole-dipole DD	weak	Permanent dipoles	$CH_3CH_2CH_2CHO$ $CH_3CH_2CH_2CH_2OH$
Hydrogen bond HB	strong	Molecules with OH, NH, FH funct. groups	$CH_3CH_2CH_2CH_2OH$
ionic	Very strong	Ionic compounds	NaCl, LiF

Polar molecules interact strongly than apolar ones.

Boiling Point

- The boiling point is the temperature at which the vapor pressure of a liquid is equal to the external pressure.
- Energy is required to break intermolecular interactions.
- The higher the intermolecular interactions, the higher the b.p..
- Compounds with similar M.W.:



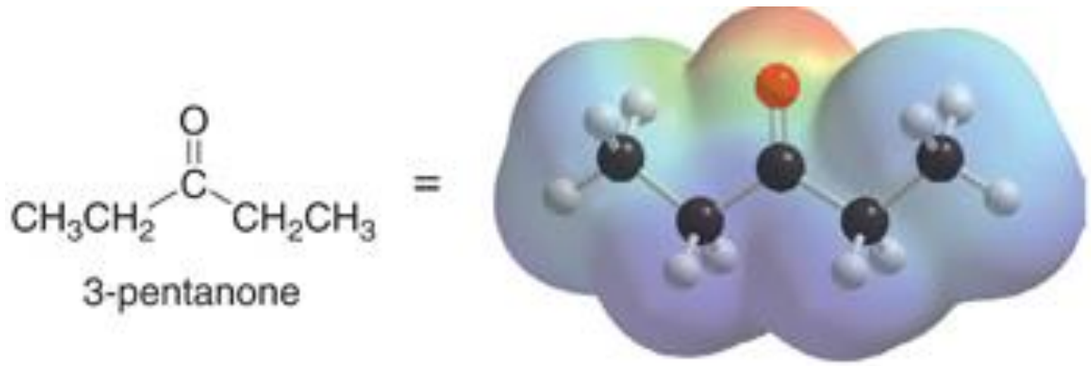
Boiling Point

b.p. = 42 °C

I is more polarizable

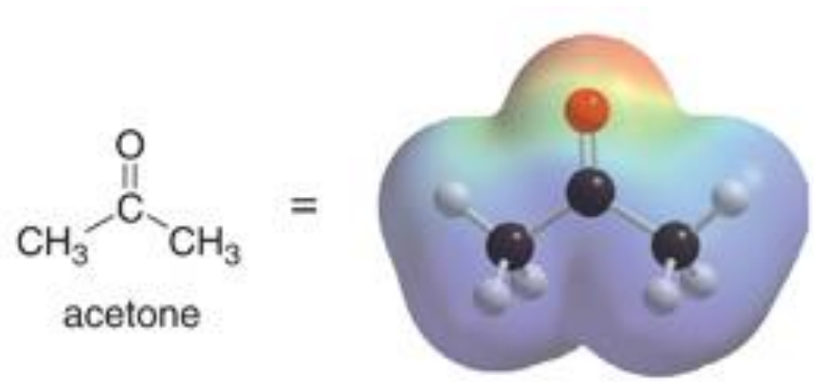
b.p. = –78 °C

Smaller F has a low polarizability



b.p. = 102 °C

Larger surface area



b.p. = 56 °C

Smaller surface area

Melting Point

- M.p. and b.p. follow the same trend.

$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2CH_2OH$
pentane	**butanal**	**1-butanol**
mp = –130 °C	mp = –96 °C	mp = –90 °C

Melting point

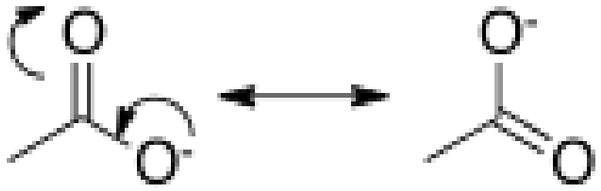
Delocalized Electrons and Bonds. Resonance

- The structure and properties of certain molecules can not be explained by the simple valence orbital model with localized electrons.
- In this case, a single Lewis structure is replaced by a set of Lewis structures: the molecule is said to resonate between these structures and this phenomenon is called resonance.

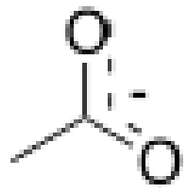
CH_3CH_2OH: pK_a 16

Localized charge
less stabile

CH_3COOH: pK_a 4.75



Resonance structures



Resonance hybrid

Delocalized charge
more stabile

Resonance

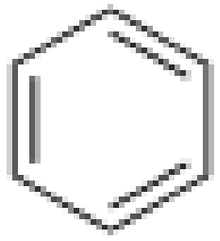
- Resonance structures have the same disposition of atoms but a different arrangement of electrons (π electrons and lone pairs).

- Bond lengths and angles do not change in resonance structures.

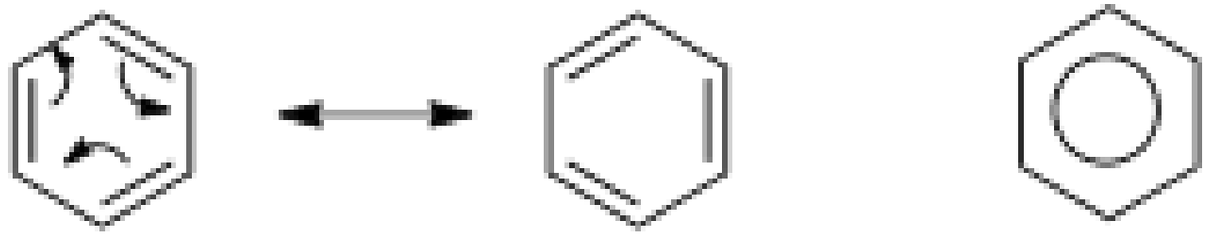
- Resonance is a simple theory to adapt conventional Lewis structures to the representation of molecules with delocalized electrons and bonds.

Resonance

Benzene (C_6H_6)

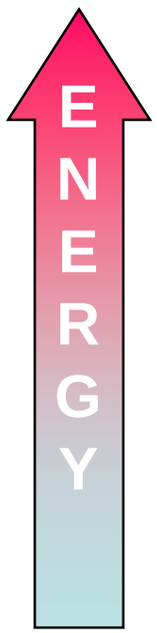


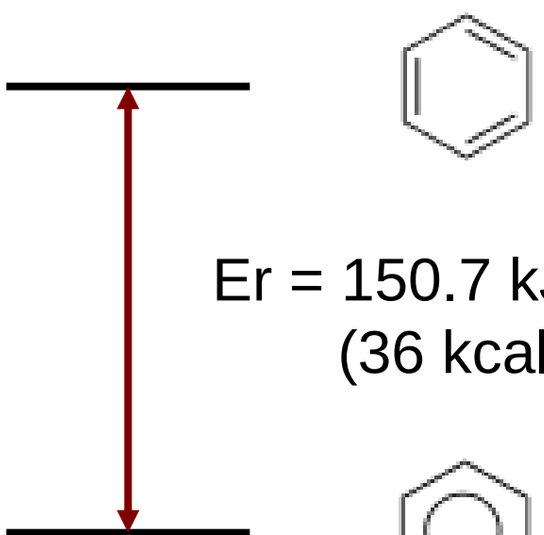
Very stabile
6 identical C-C bonds



Resonance structures

Resonance hybrid



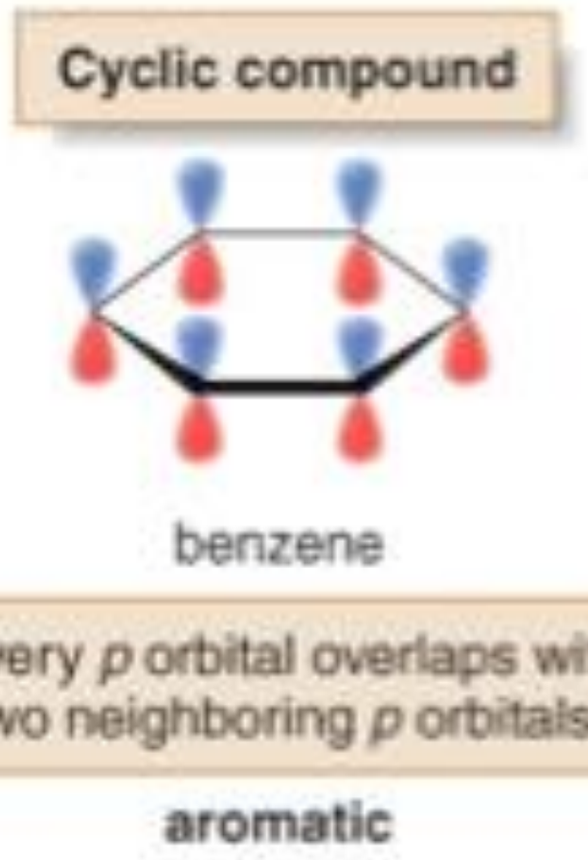


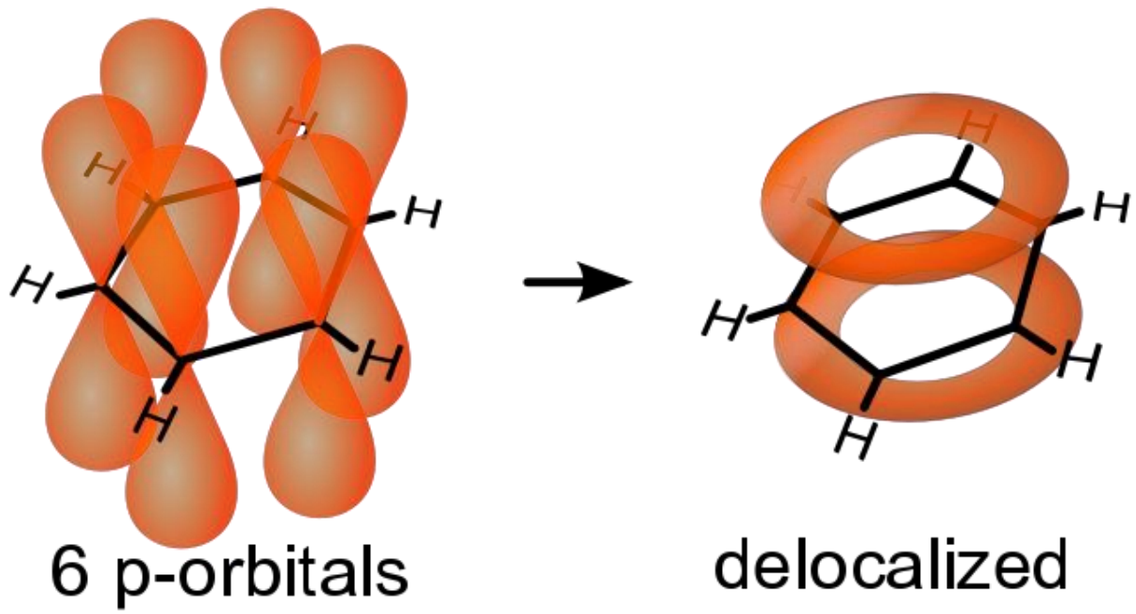
Er = 150.7 kJ/mol
(36 kcal/mol)

6 localized π electrons

6 delocalized π electrons

Resonance


Cyclic compound
benzene
Every p orbital overlaps with two neighboring p orbitals.
aromatic


H
H
H
H
H
H
6 p-orbitals
delocalized

Resonance

1. Resonance structures are not real. No single resonance structure can adequately represent the real structure of a species with delocalized electrons.
2. Resonance structures are not isomers. They only differ in the distribution of electrons not in the disposition of the nuclei.
3. Resonance structures are not in equilibrium.