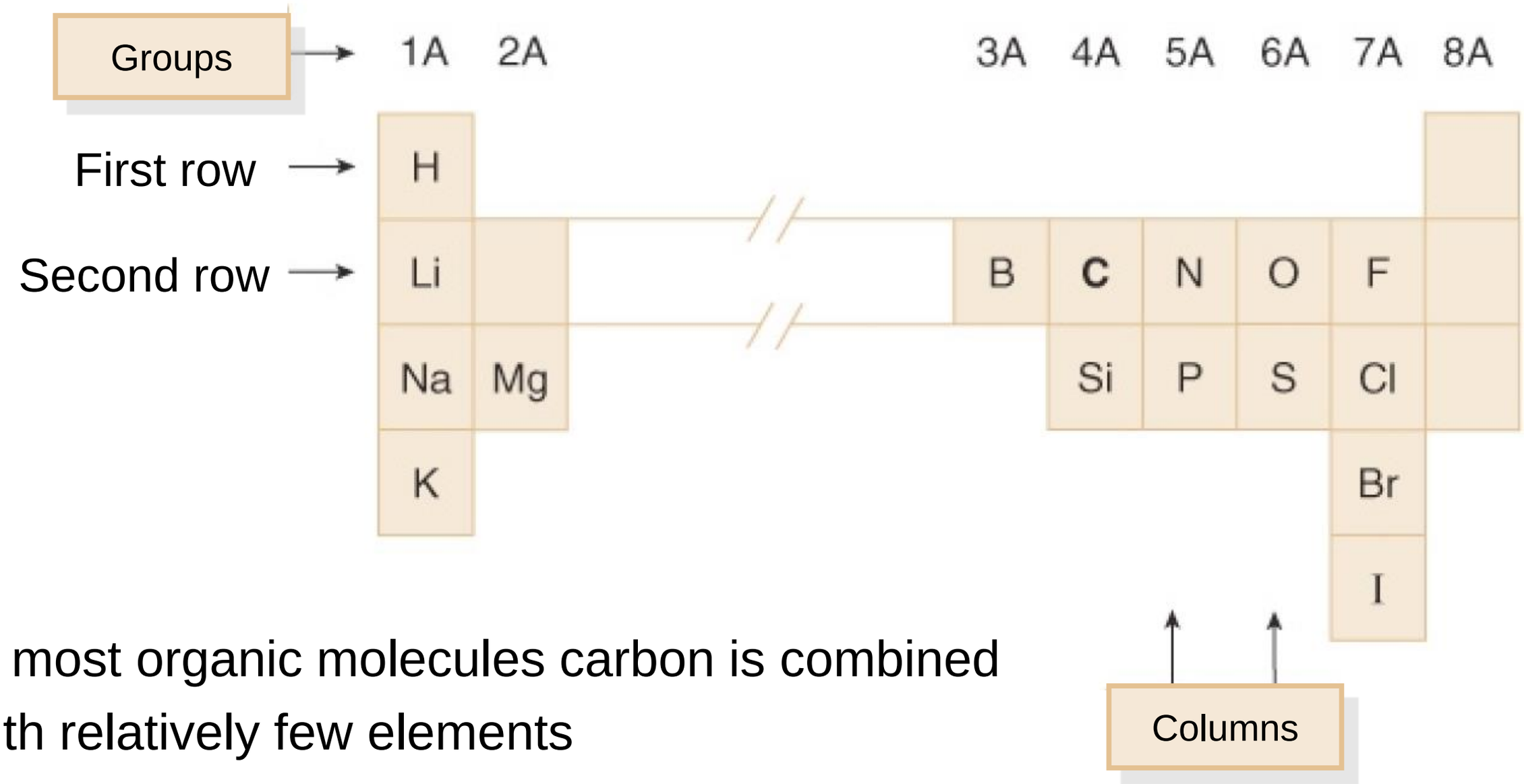
# Atomic Structure and Bonding

Chapter 1

Organic Chemistry, *8th Edition*

John McMurry

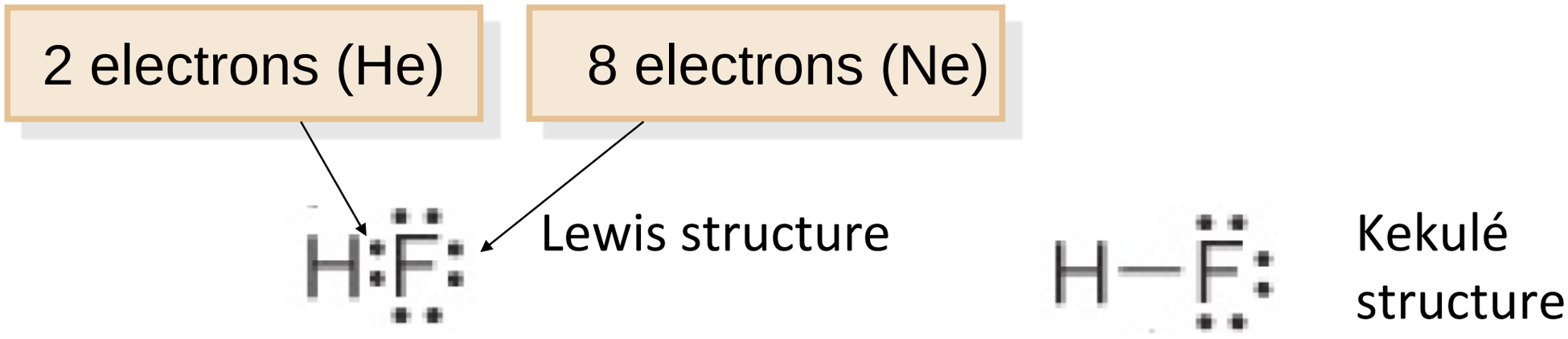
# Common Elements




In most organic molecules carbon is combined with relatively few elements

# Lewis' Model

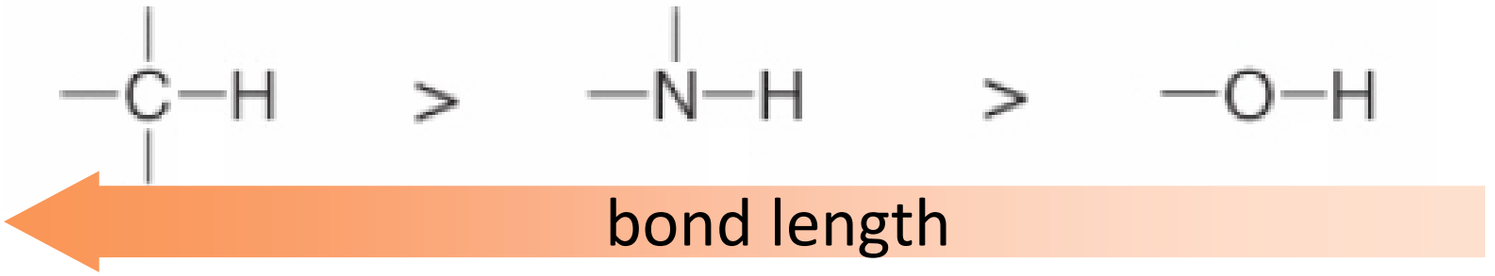
- In Lewis structures electrons are represented as dots.
- Three general rules.
  - Include only valence electrons.
  - If possible, every 2nd raw element should have 8 electrons.
  - Every H atom has 2 electrons.



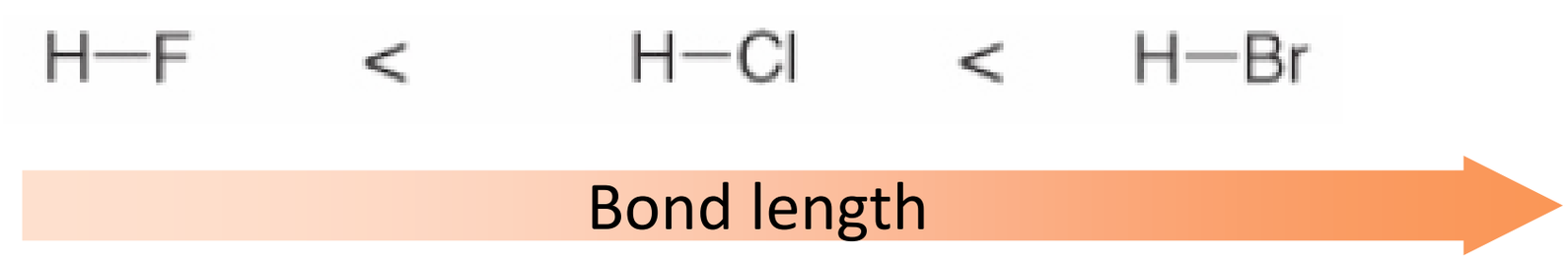
# Molecular Shape

- 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 |

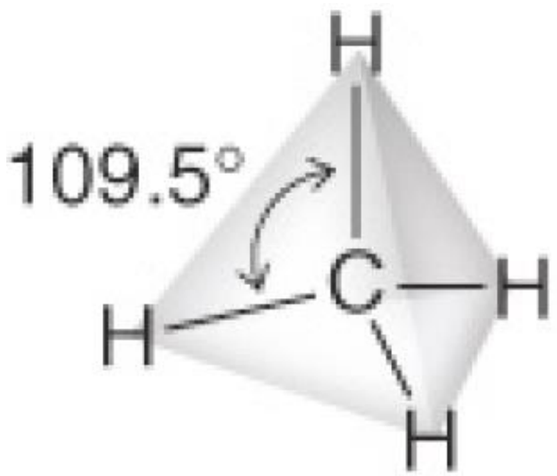
# Geometry – VSEPR Theory

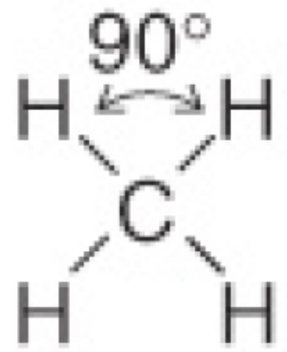
- The number of *Valence Shell Electron Pairs* (groups) around an atom defines the geometry of that atom.
- A group is an atom or a non bonding pair of electrons.
- Groups will tend to be as far apart as possible.

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

# 4 groups: $CH_4$

| Tetrahedral | Square planar |
|---|---|

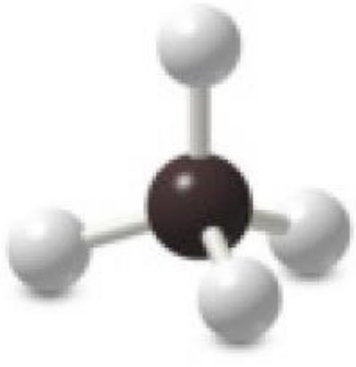


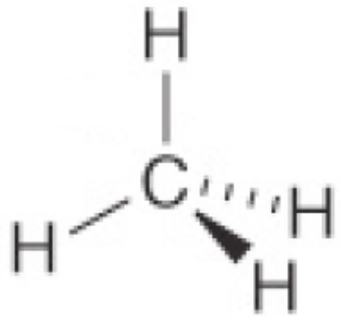



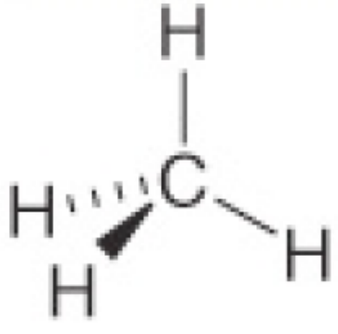

Preferred

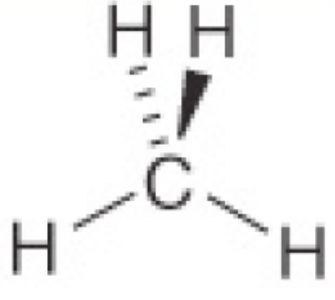
Not observed

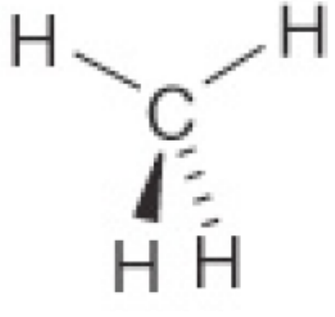
Tridimensional representations of methane





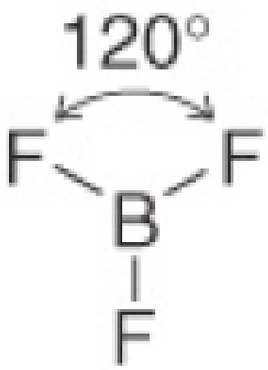



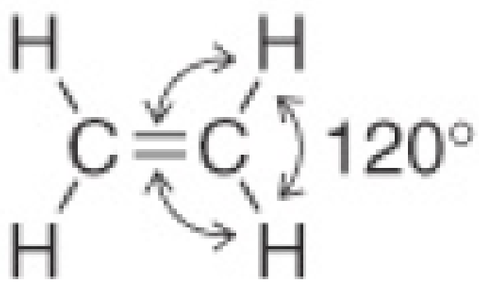
# 3 groups: $BF_3$ and $C_2H_4$

2 trigonal molecules



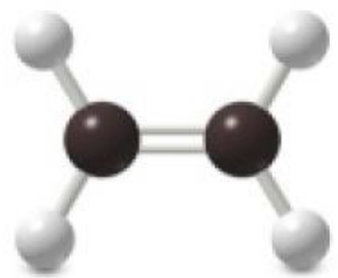

3 atoms around B

All 3 atoms are in the plane

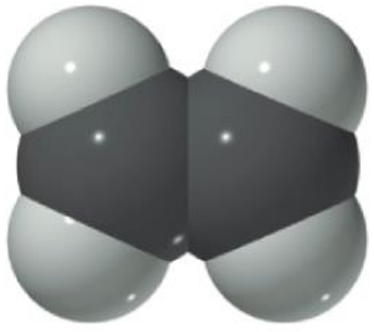



3 atoms around each C

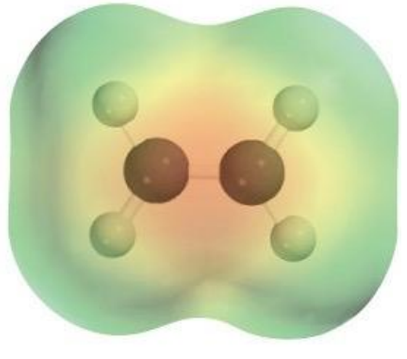
All 6 atoms are in the plane



ball-and-stick model

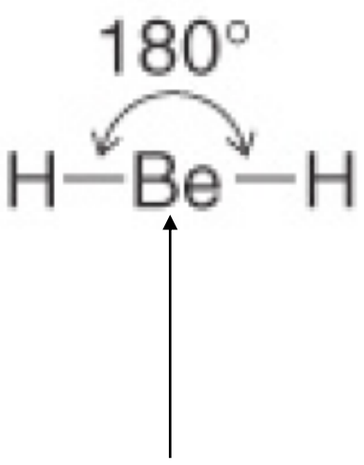


space-filling model

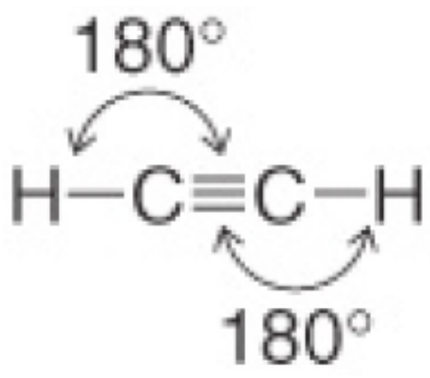


# 2 groups: $BeH_2$ and $C_2H_2$

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

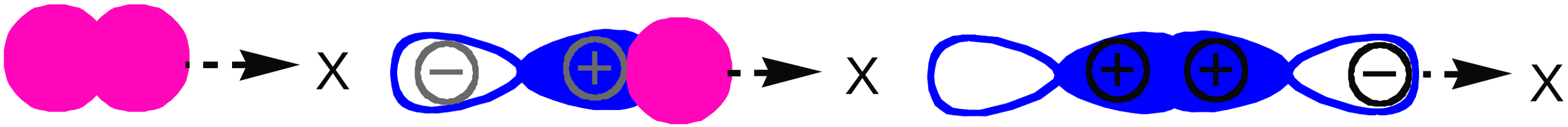
- Valence Orbital theory.
  - Covalent bonds are formed by the overlap of two atomic orbitals and the electron pair is shared by both atoms.
  - A valence bond is localized between two atoms.

- 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 $\sigma$ bonds.
- 2nd row atoms use hybrid orbitals ($sp^3$, $sp^2$, $sp$) to form $\sigma$ bonds.
- 2nd row atoms use p orbitals to form $\pi$ bonds that have a nodal plane.
- Atomic orbitals overlap better in $\sigma$ bonds (co-linear) than in $\pi$ bonds (parallel).

## Strong Bonding Interactions: Axial Overlap

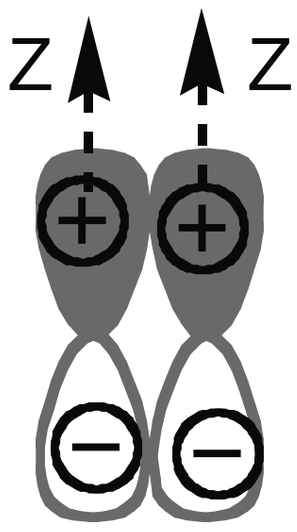


**1s**(H)-**1s**(H)
$H_2$

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

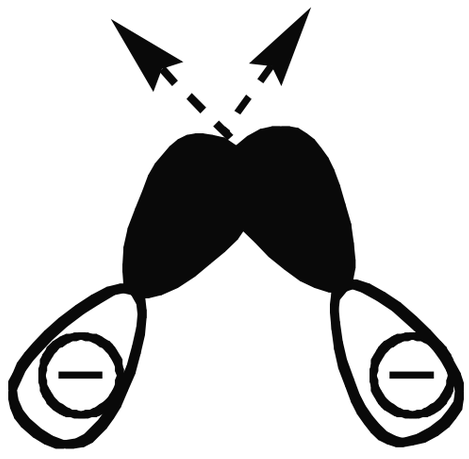
**2px**(F)-**2px**(F)
F-F

## Weak Bonding Interactions: Lateral Overlap



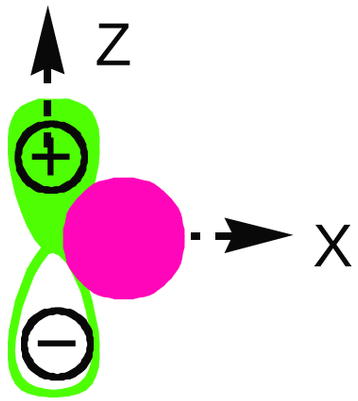

**2pz**(C)**2pz**(C)
$\pi$ bond of ethylene

..

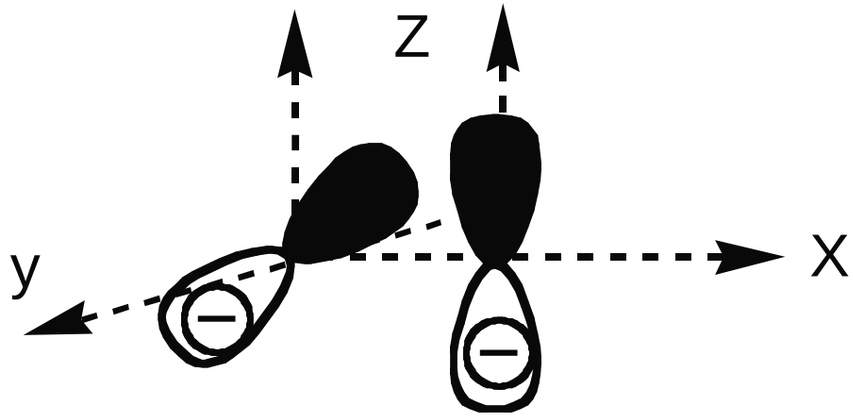


**2pz**(C)**2pz**(C)
$\sigma$ bond of cyclopropane

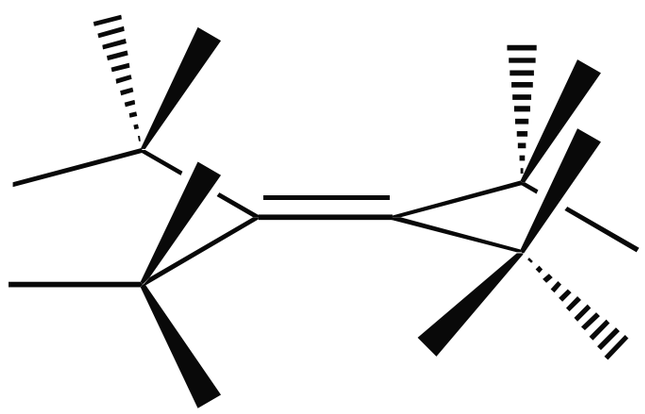
# Inexistent Bonding Interactions (0 Overlap)




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




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

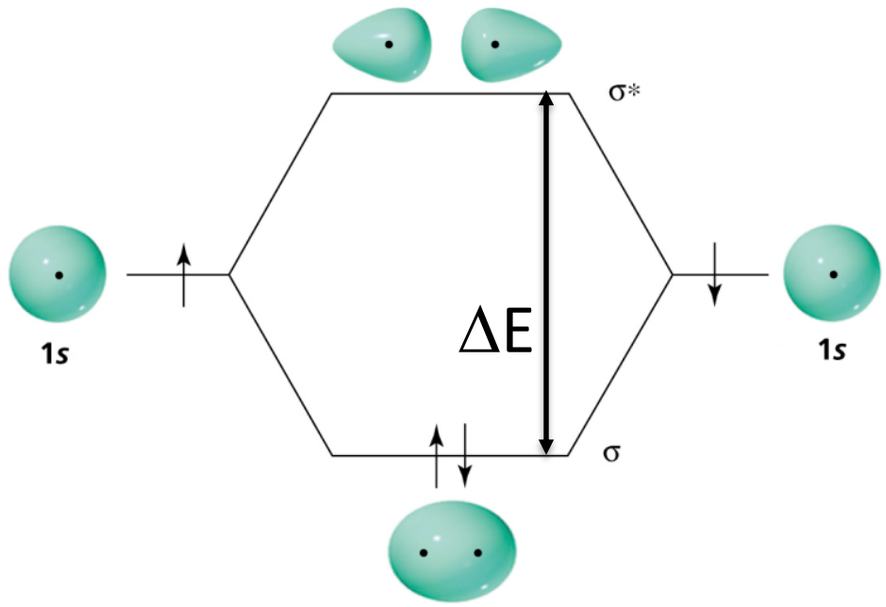


# Molecular Orbitals

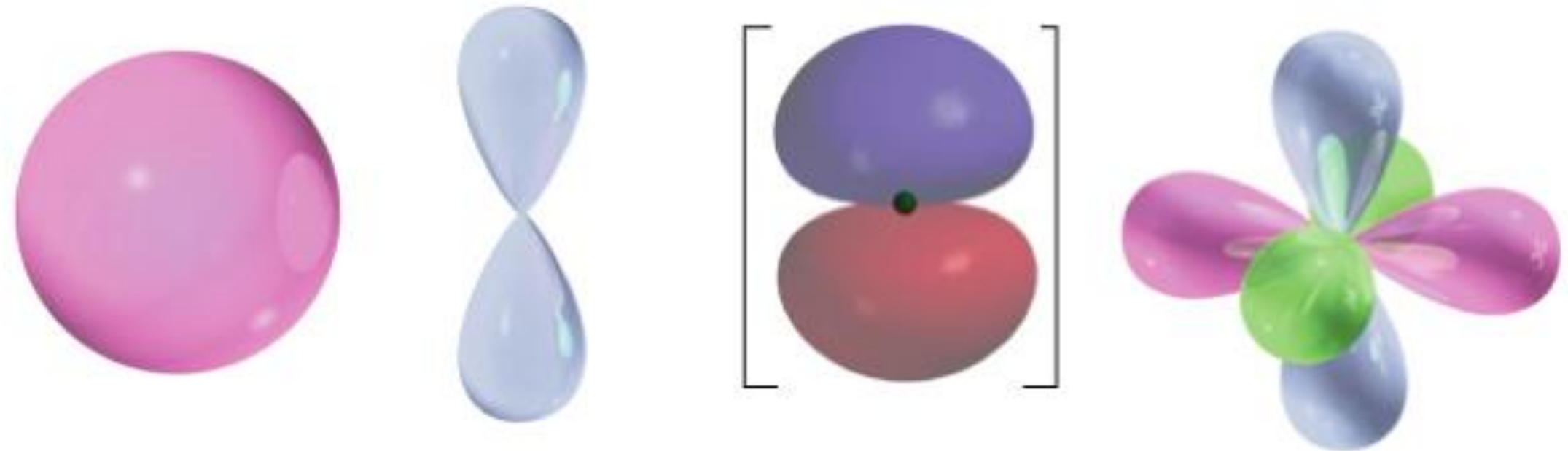
- Valence electrons occupy molecular orbitals delocalized on the whole molecule.
- The combination of *n* atomic orbitals gives *n* new molecular orbitals.
- Bonding orbitals have lower energies and antibonding orbitals have higher energies than the starting atomic orbitals

Robert Mulliken (1896-1986)

The $H_2$ molecule:



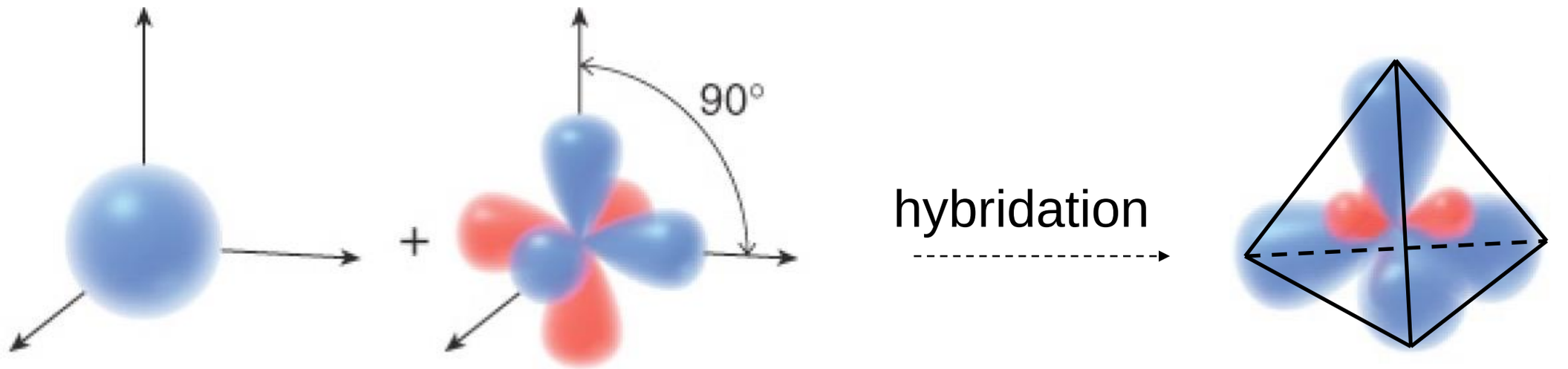
# Atomic Orbitals of Carbon



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.

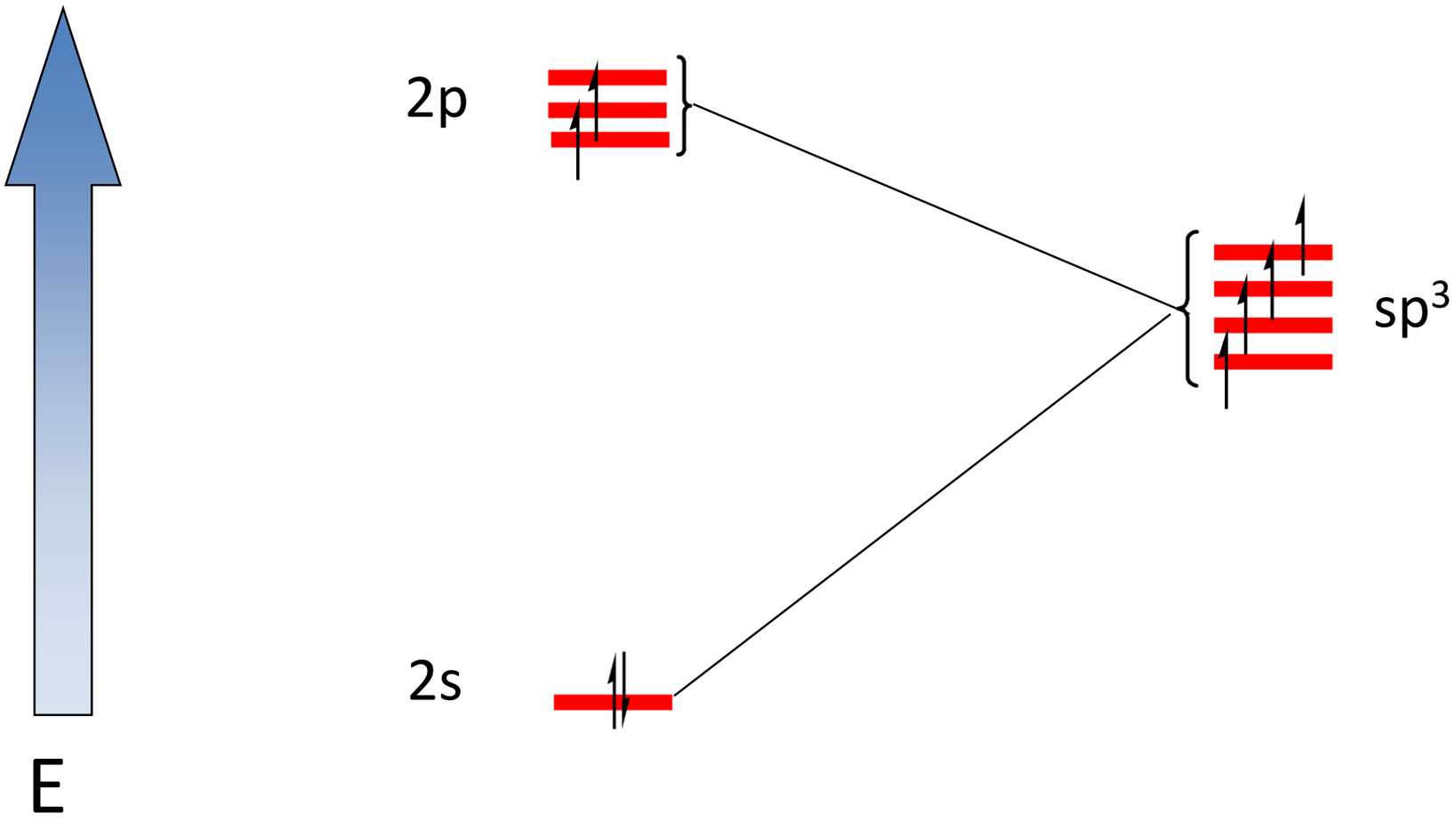



2s 3 x 2p 4 x $sp^3$ orbitals

*p*

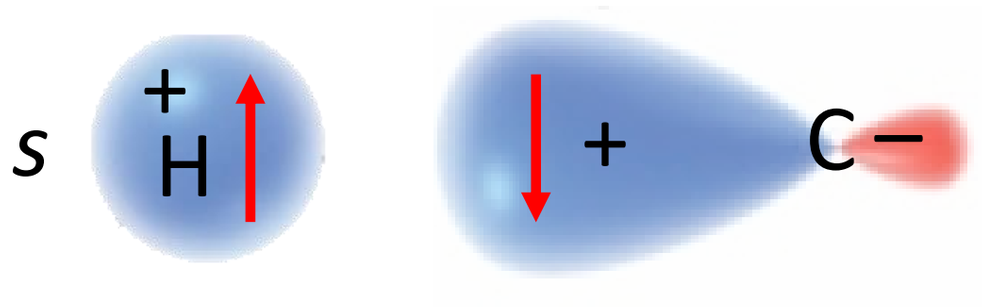
$sp^3$

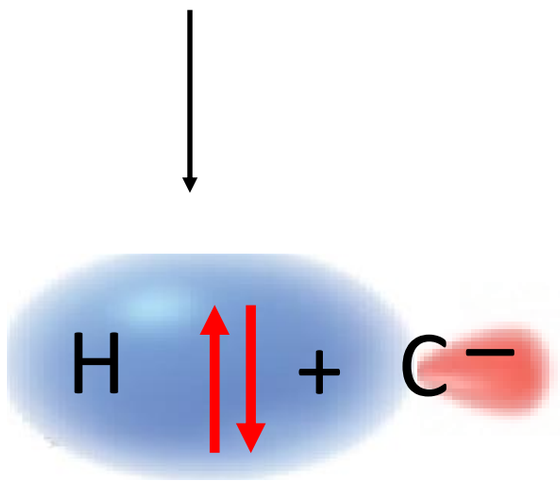
# $sp^3$ Hybrids

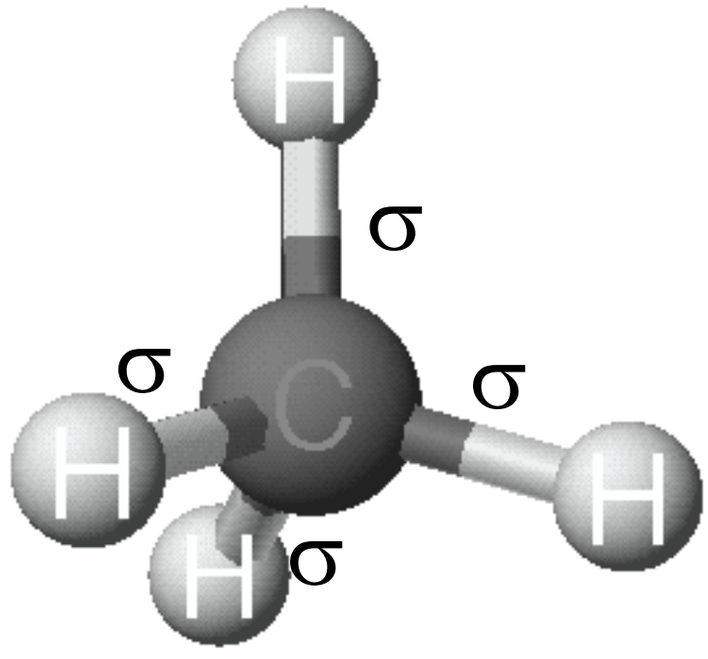


# Methane

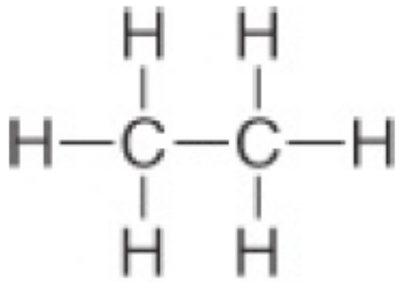
The overlap of a half-full *1s* orbital of hydrogen with a half-full $sp^3$ orbital of carbon bond gives a σ orbital.



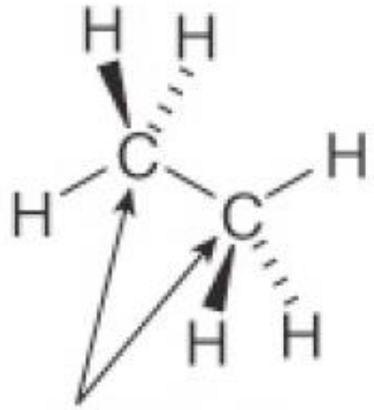



# Ethane



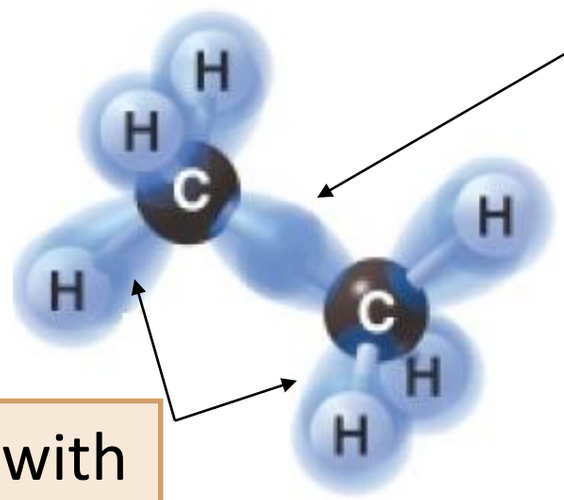

ethane



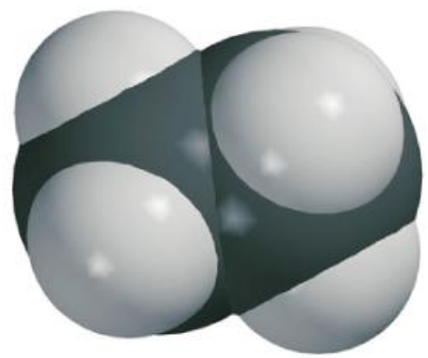

tetrahedral $sp^3$ C

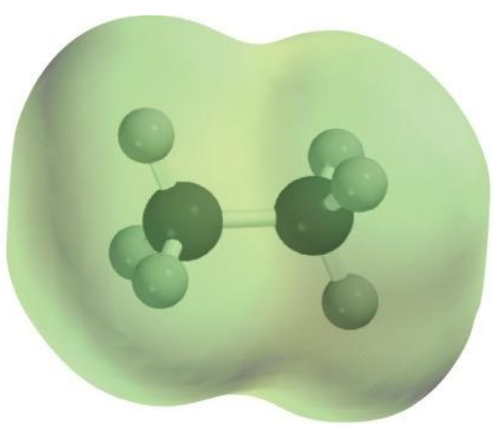
=

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

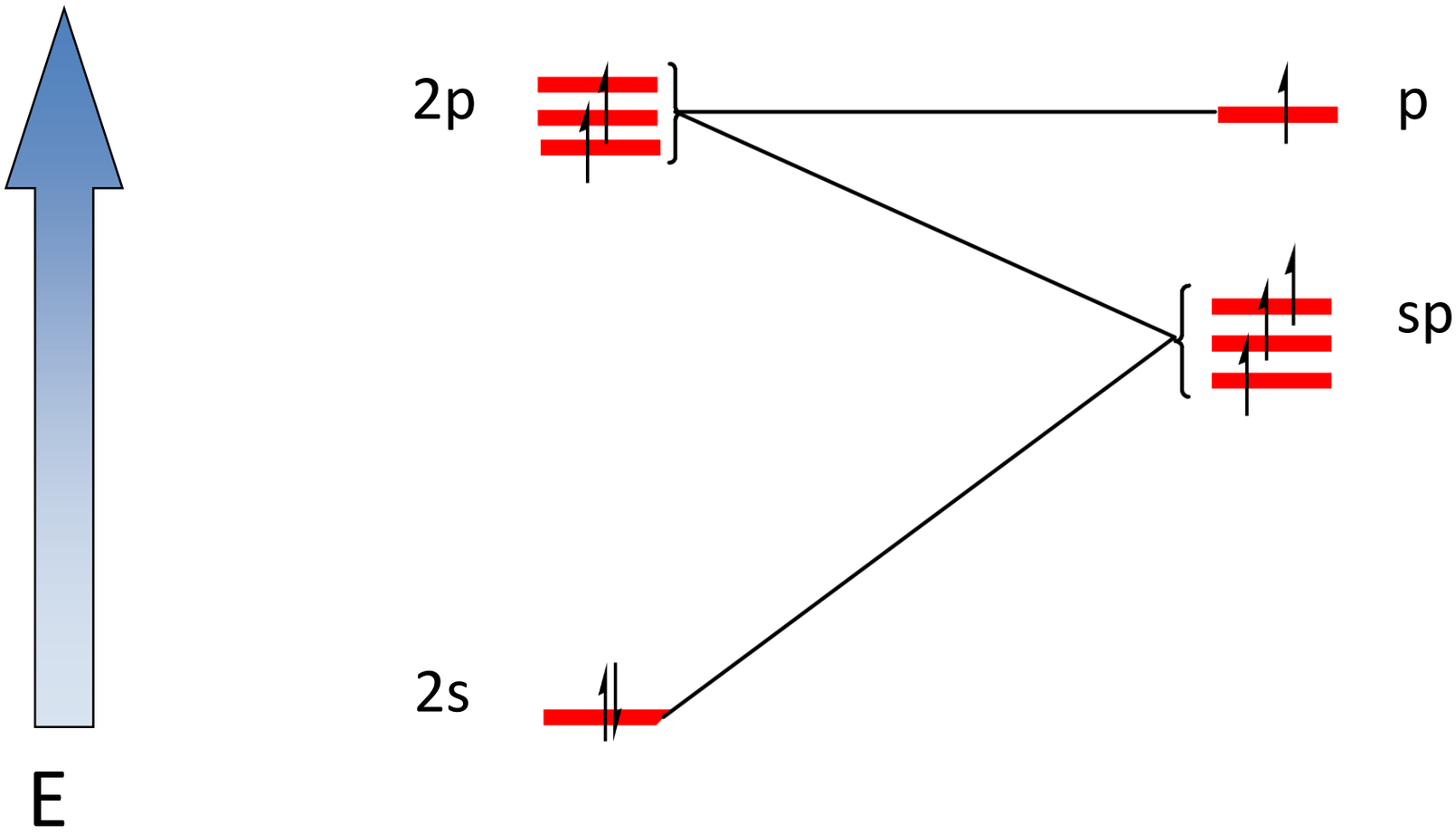



$sp^3$ hybrids on C overlap with *1s* orbitals on H giving the C-H σ bonds.

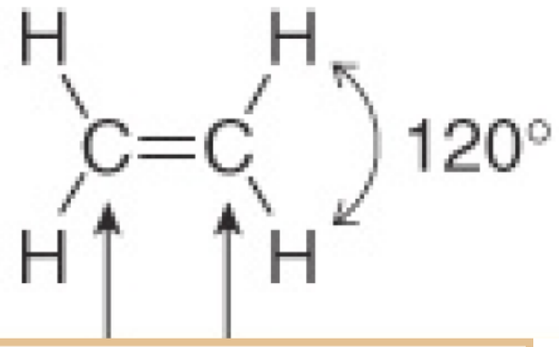




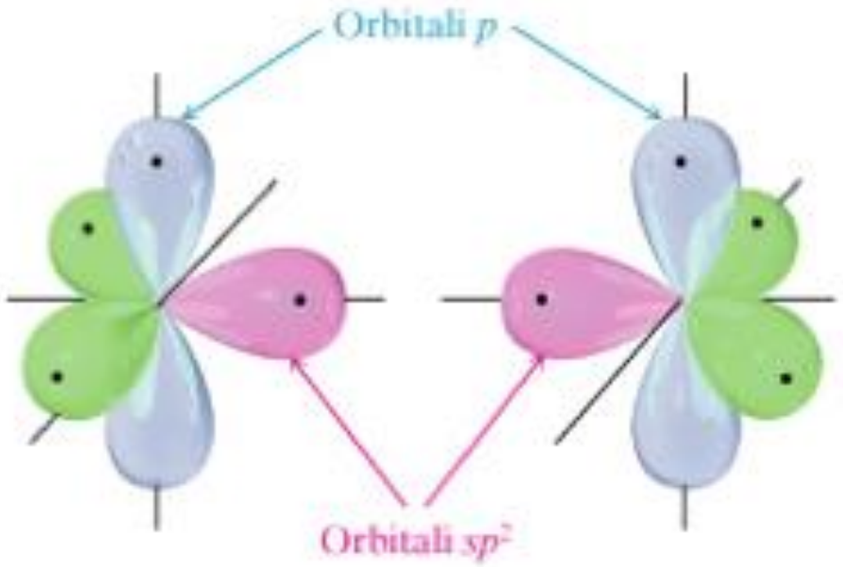
# $Sp^2$ Hybrids

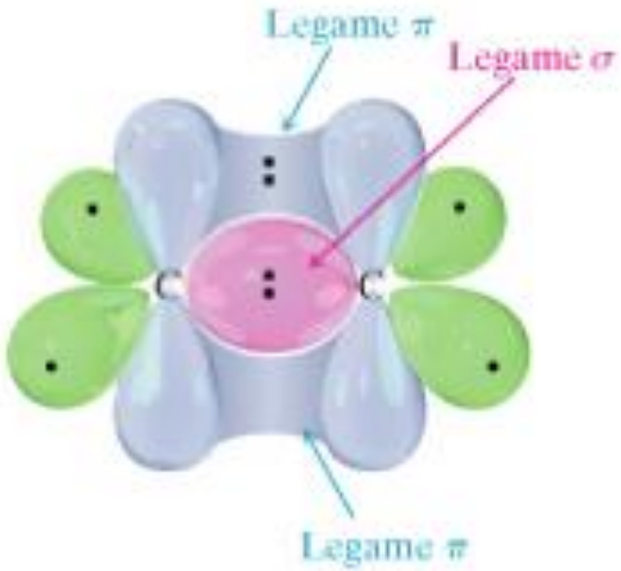


# Ethylene $C_2H_4$

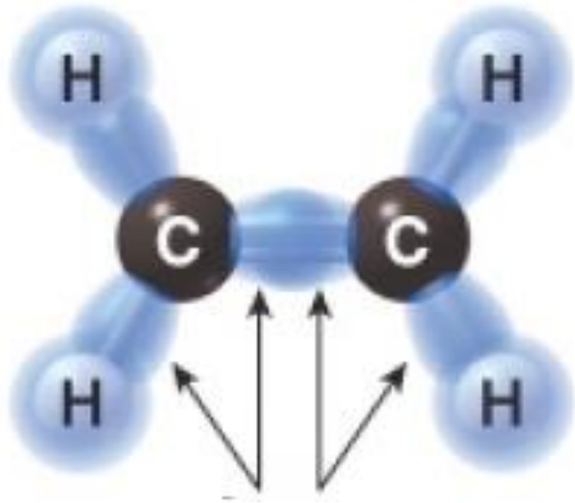



3 groups around C
C atoms are *sp*$^2$



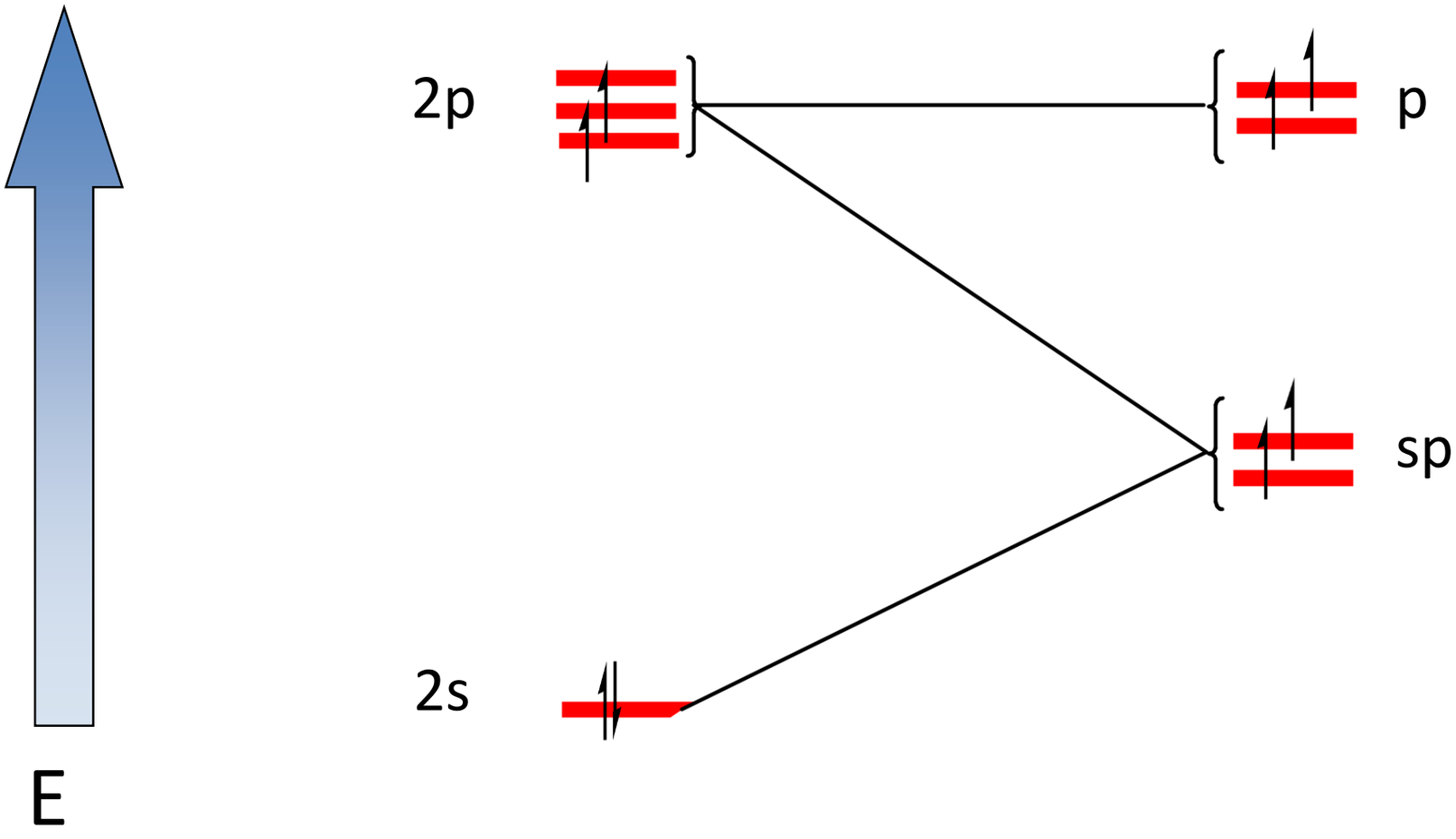




C-C double bond

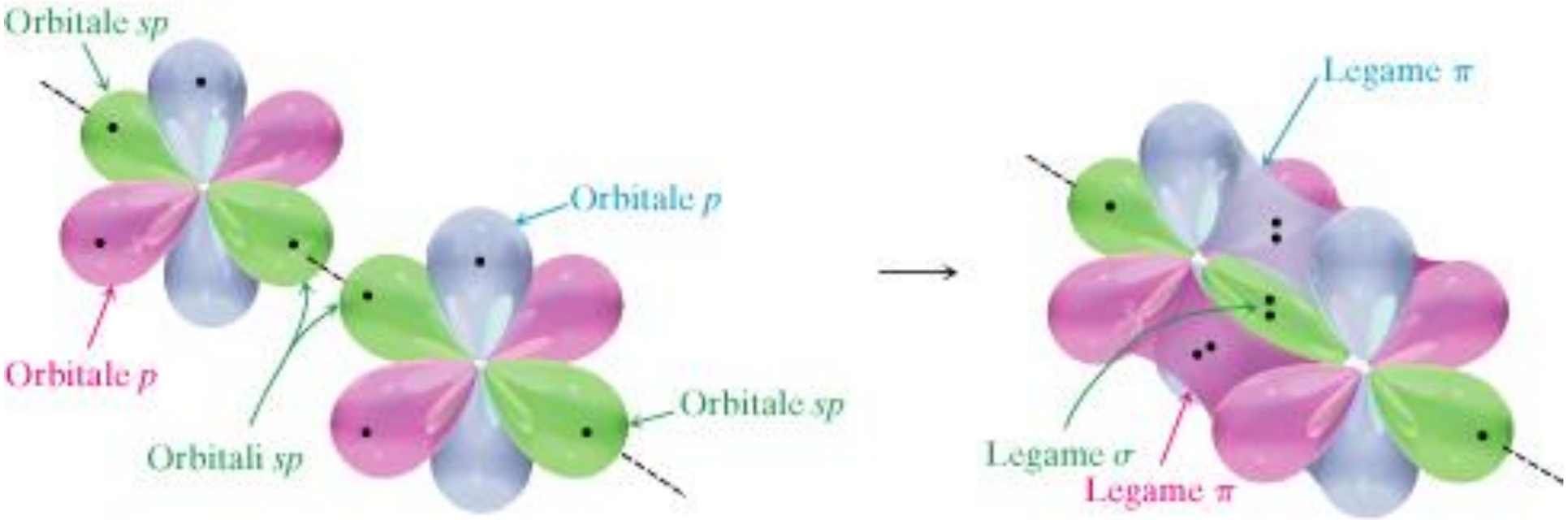



*Sp*$^2$ hybrids

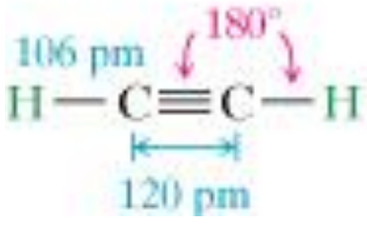
# Sp Hybrids



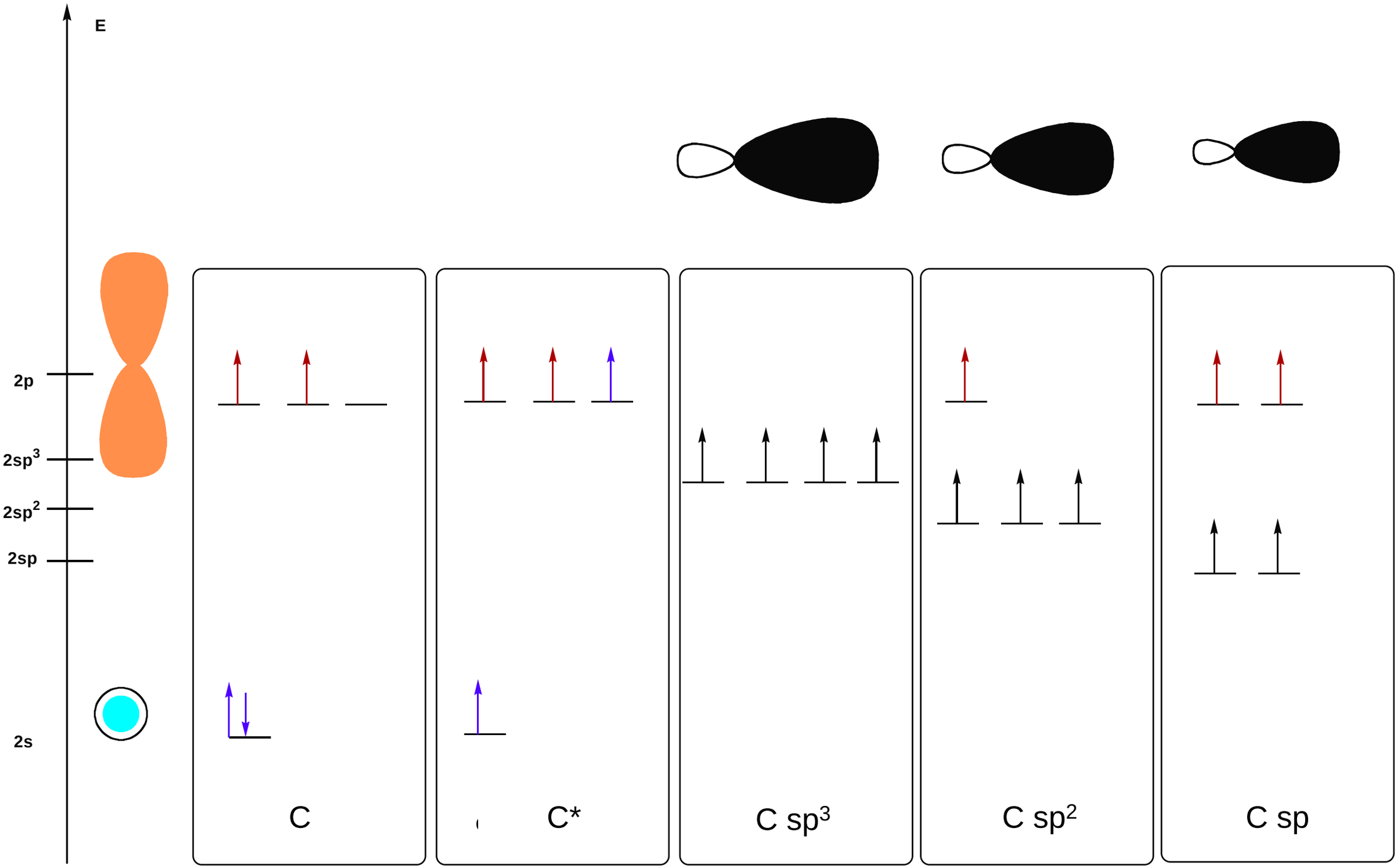
# Acetylene $C_2H_2$



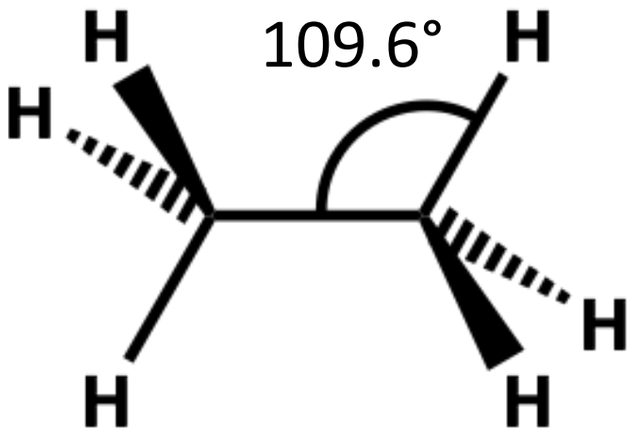

C-C triple bond

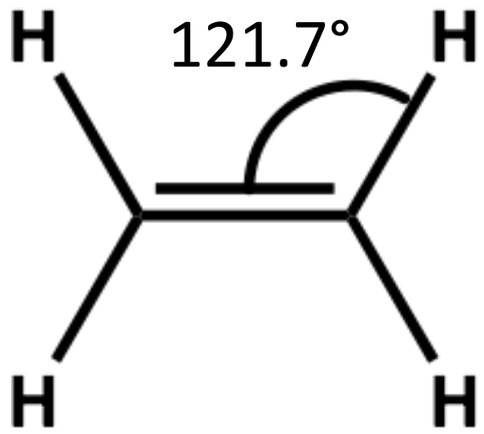


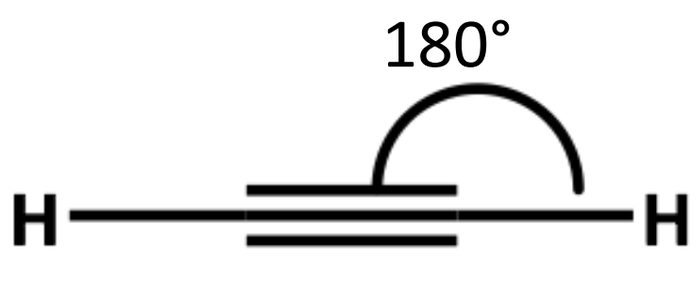

# Energy Levels and Orbital Size



# Structures of $C_2H_6$, $C_2H_4$, $C_2H_2$

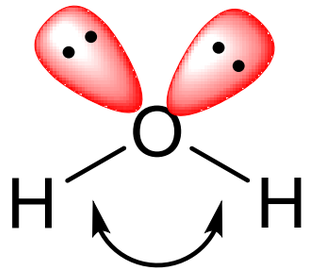


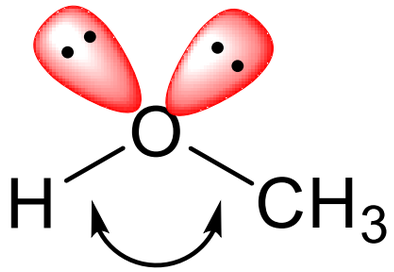




| | | | |
|---|---|---|---|
| $d_{C-C}$ (pm): | 154 | 133 | 120 |
| $d_{C-H}$ (pm): | 110 | 107.6 | 106 |
| $E_{C-C}$ (kJ/M): | 376 | 611 | 835 |

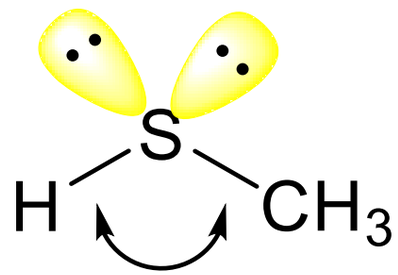
# Ibridization of O, S, N




104.5°



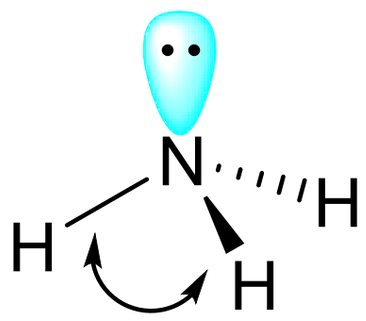

108.5°



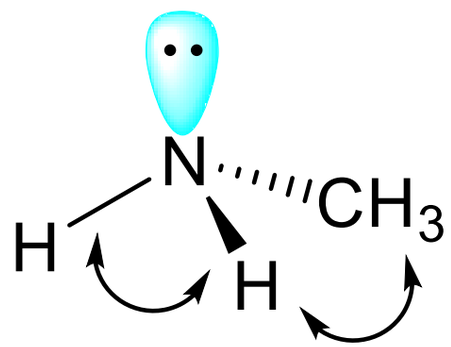

96.5°

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

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




107°




107.1°

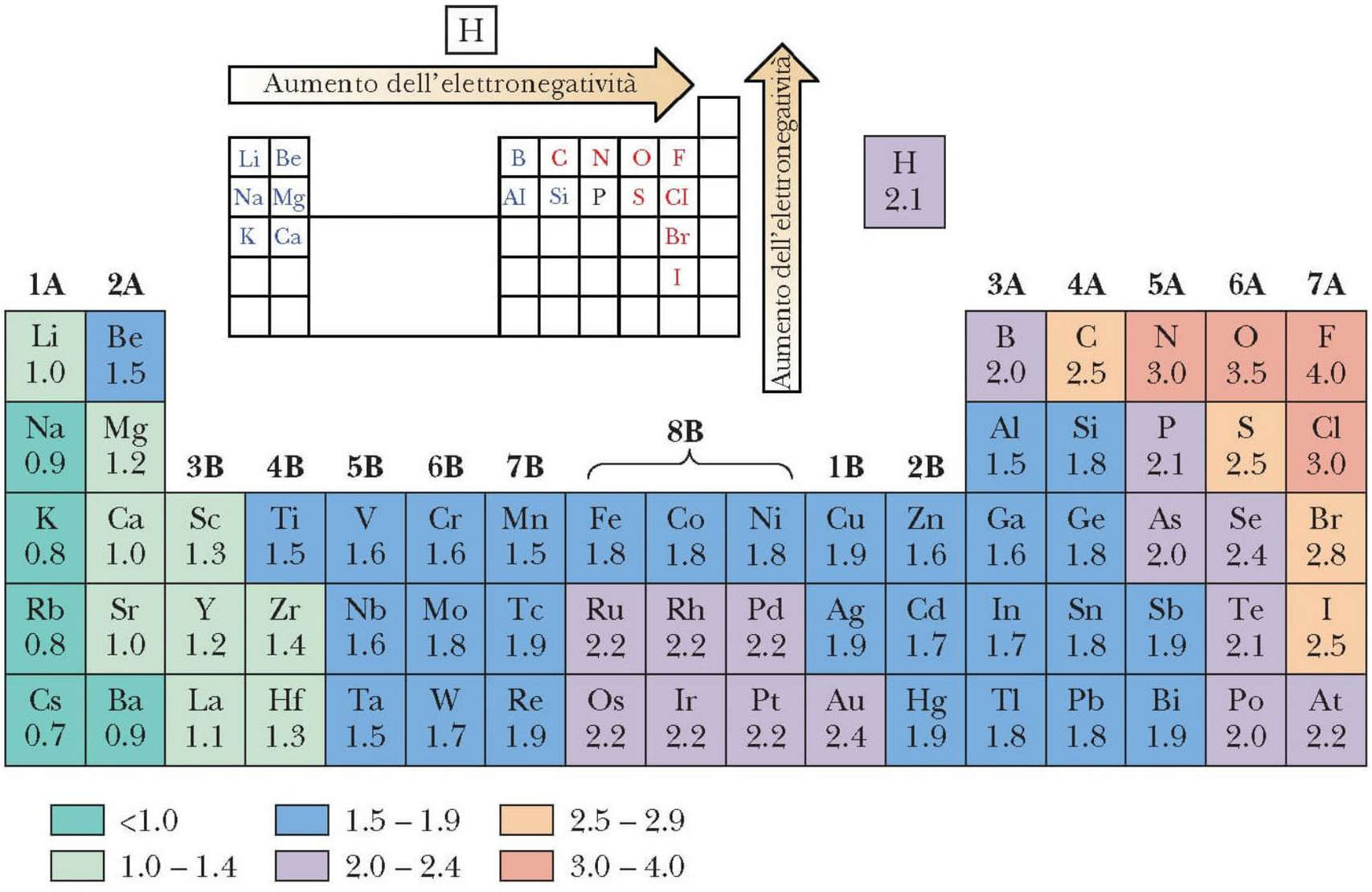
110.3°

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

# Polar Bonds
# Intermolecular Interactions
# Delocalised Bonds

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

# Legami covalenti e ionici

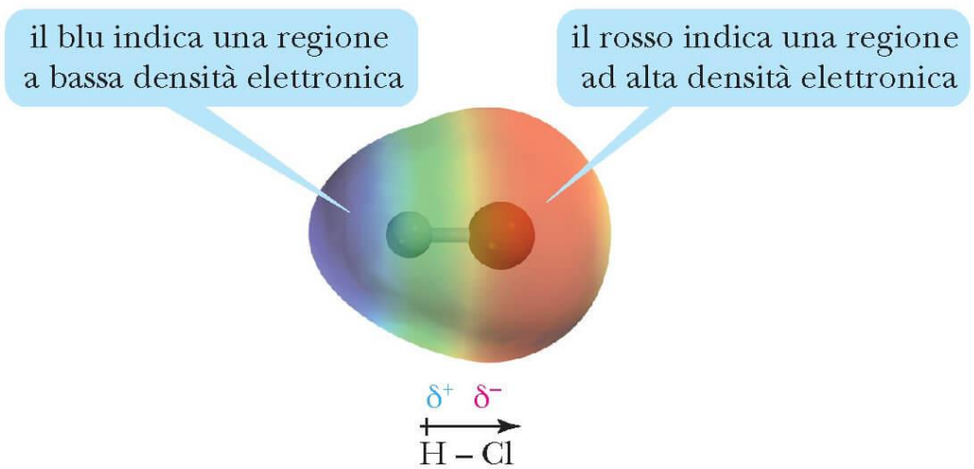


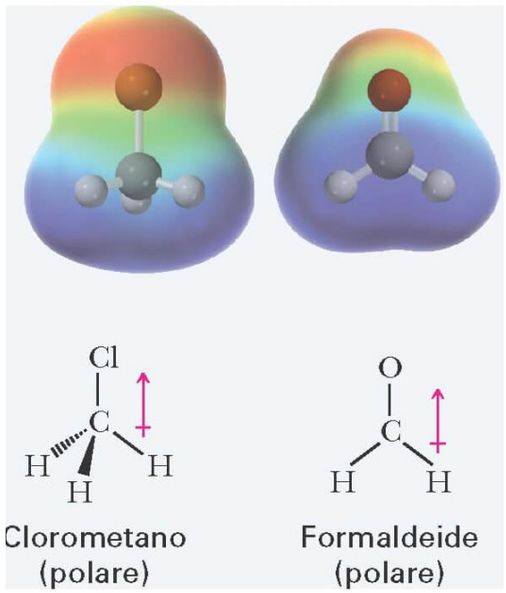
# Legami covalenti e ionici

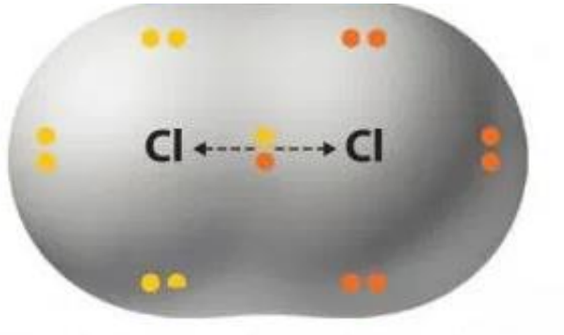
**ΔX = differenza di elettronegatività**

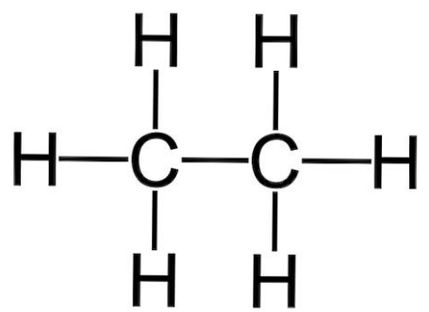
- ΔX > 1.9 legame ionico
- ΔX < 0.5 legame covalente
- ΔX = 0.5 – 1.9 legame covalente polare

| Legame | Differenza di elettronegatività | Tipo di legame |
|---|---|---|
| (a) O — H | 3.5 – 2.1 = 1.4 | Covalente polare |
| (b) N — H | 3.0 – 2.1 = 0.9 | Covalente polare |
| (c) Na — F | 4.0 – 0.9 = 3.1 | Ionico |
| (d) C — Mg | 2.5 – 1.2 = 1.3 | Covalente polare |



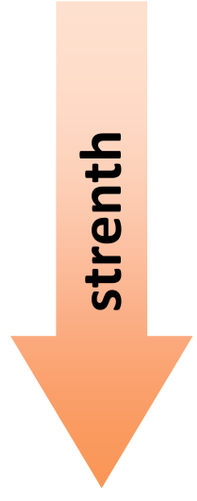



# Intermolecular Interactions

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

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

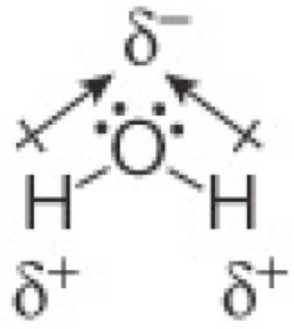
- In neutral molecules there are three main types of intermolecular interactions.
  - Van der Waals interactions (London dispersion forces) – VDW
  - Dipole-dipole interactions – DD
  - Hydrogen bonds– HB

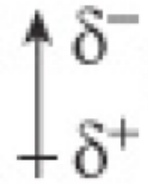


# Dipole Moments

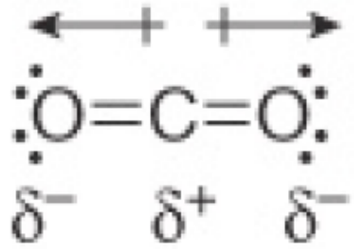
- Polar molecules have one or more polar bonds.

Es. $H_2O$

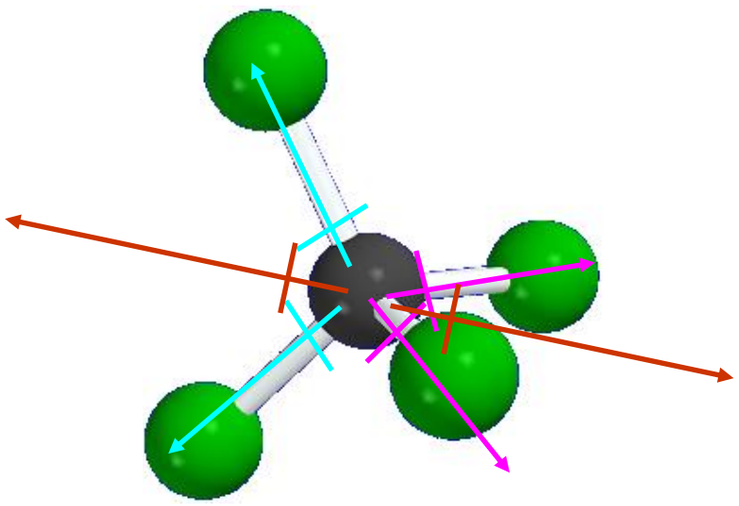



- Apolar molecules either do not have polar bonds or have polar bonds whose dipoles cancell each other. E.g. $CO_2$

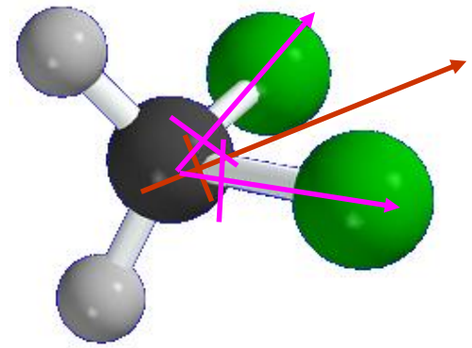



$CCl_4$ $\delta$ = 0 D



Dipoles cancel

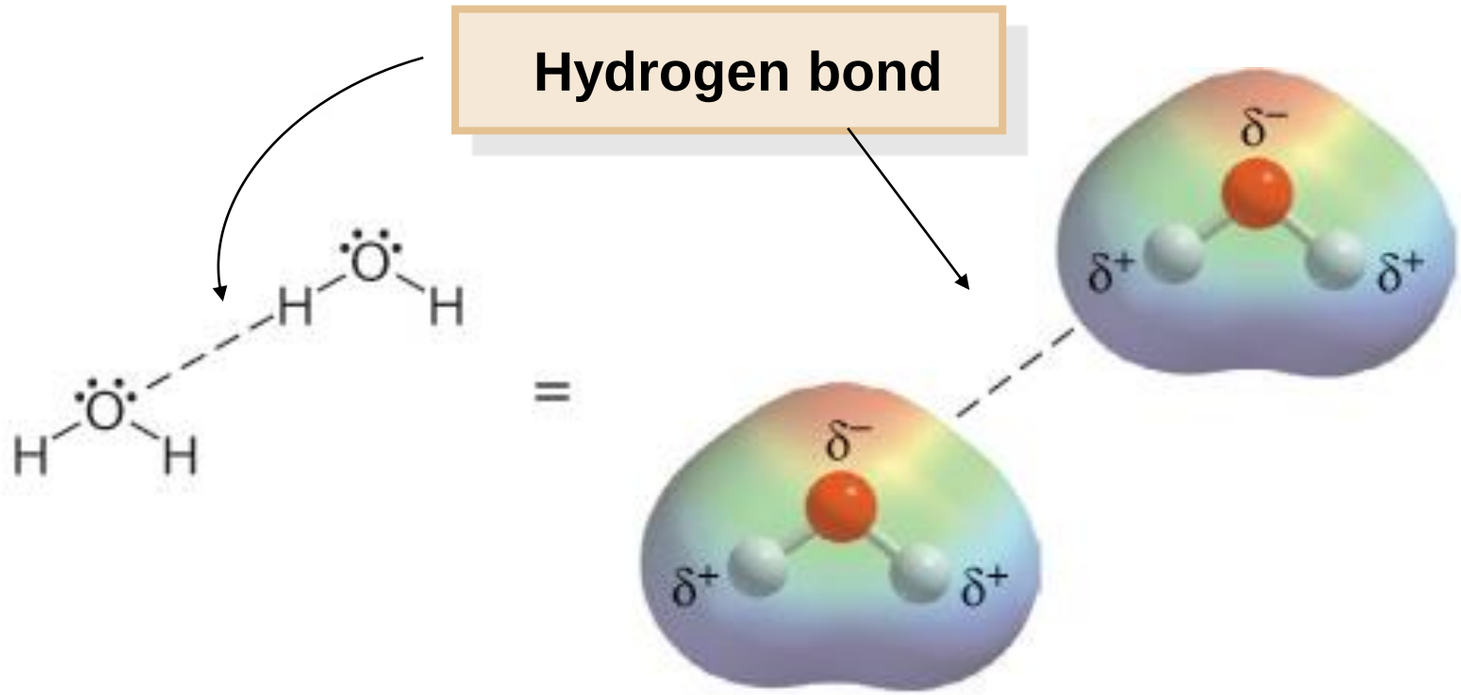
$CH_2Cl_2$ $\delta$ = 1.62 D

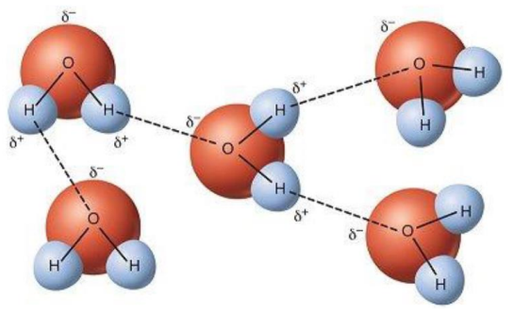


Dipoles add

# The Hydrogen Bond

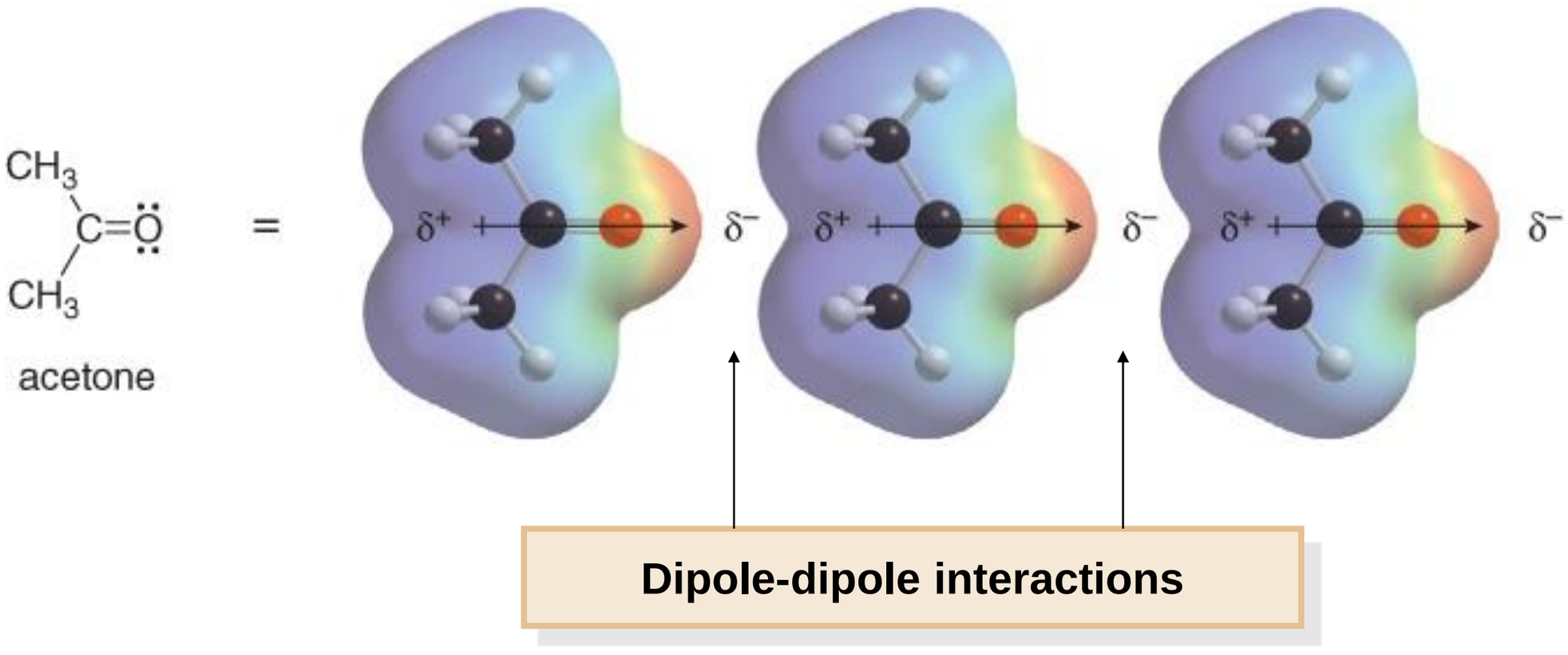
The hydrogen bond is an electrostatic interaction between a O-H or N-H group and a lone pair on O or N.



# Dipole-Dipole Interactions

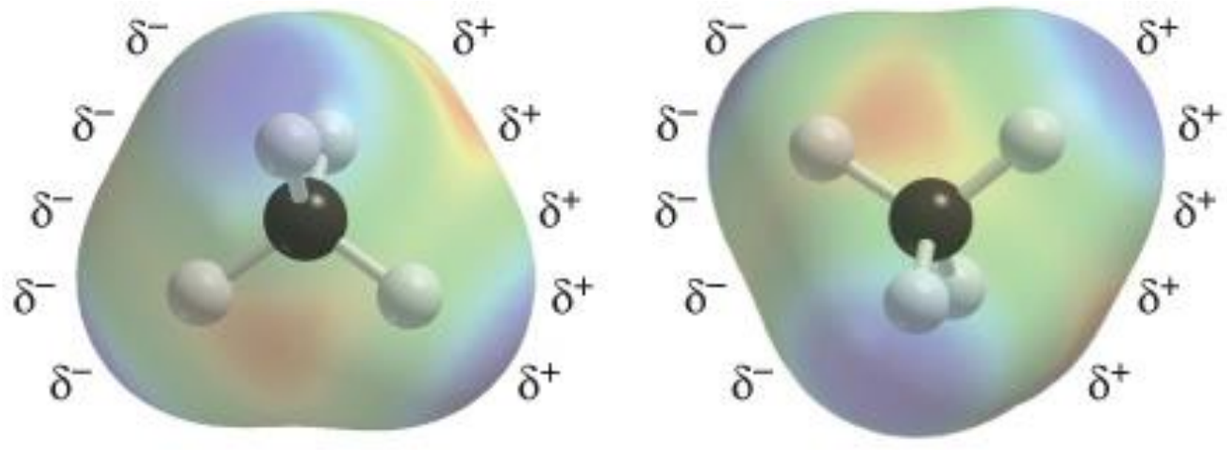
Dipole-dipole interactions are attraction forces between the permanent dipoles of two molecules.



# 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**

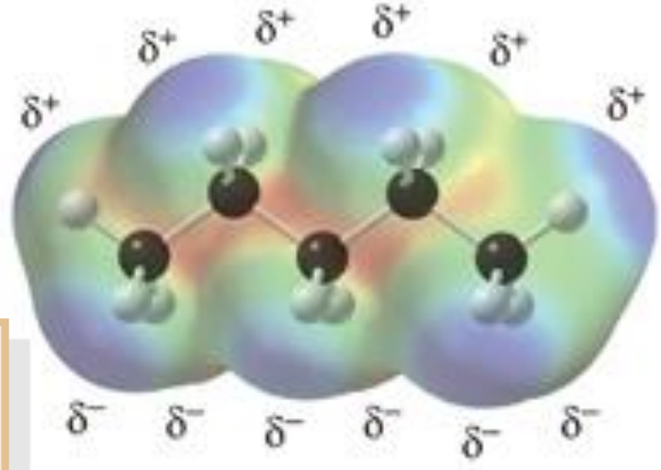



**Dipoles generated by a temporay asymmetry in the electron density**

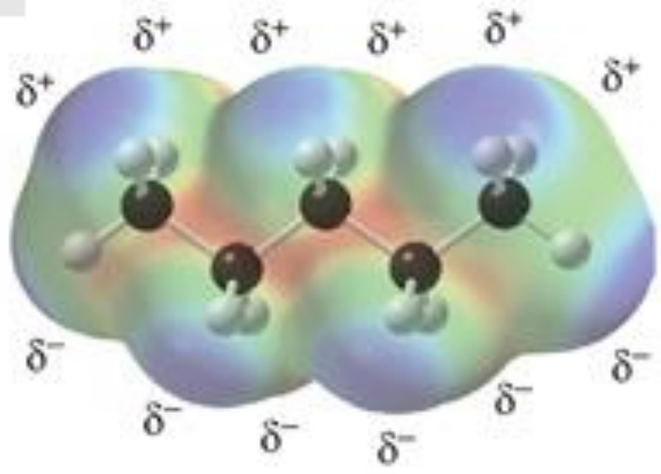
# Van der Waals (London) Forces

- 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.

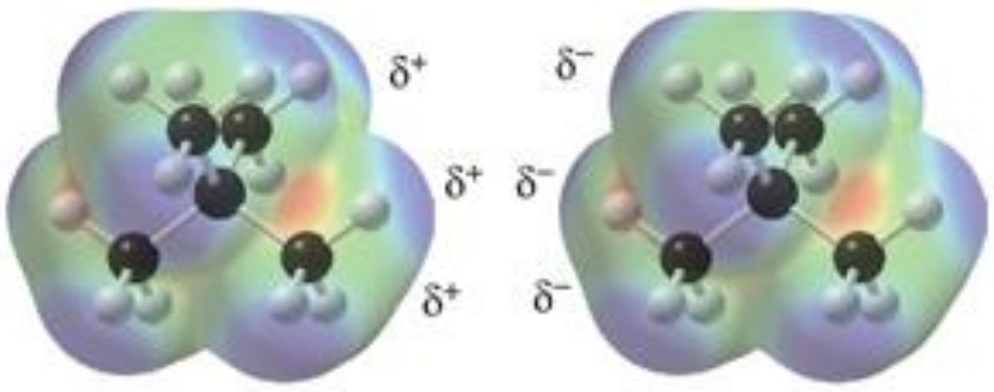
**Long, cylindrical molecules:**
**stronger interactions**

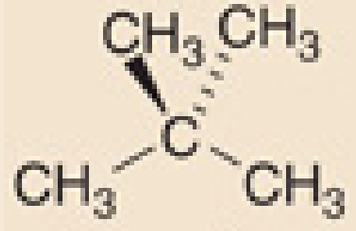



$CH_3CH_2CH_2CH_2CH_3$
***n*-pentane**




**Compact, spherical molecules:**
**weaker interactions**



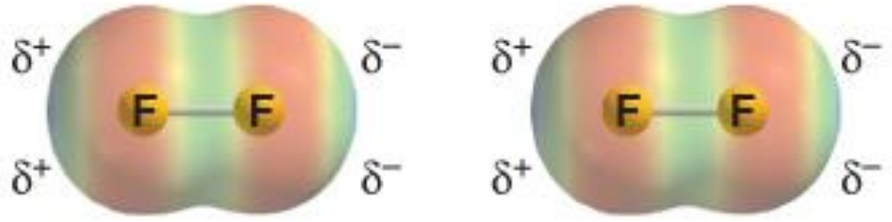

**neopentane**

# 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

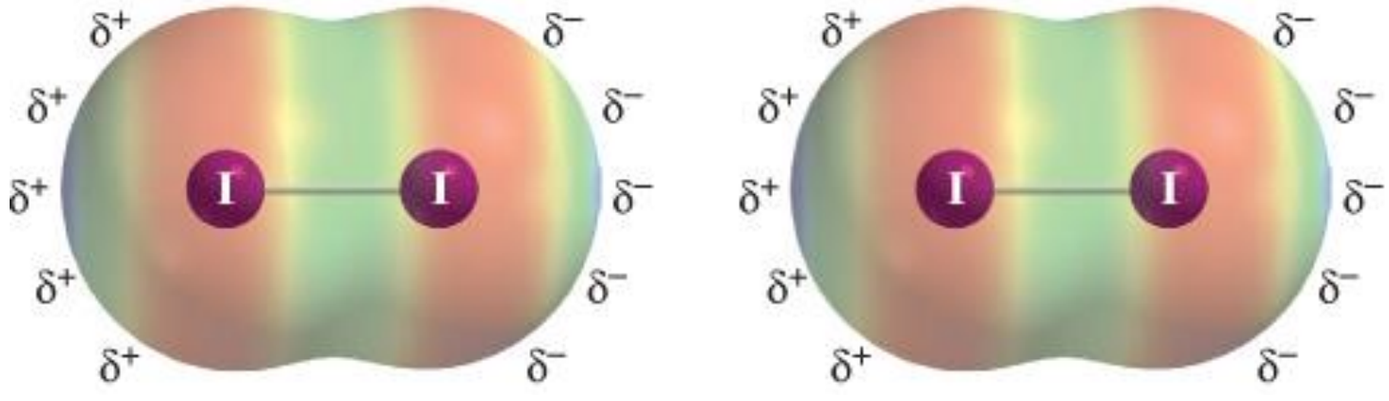
**Weak interaction**

**Small atoms: lower polarizability**




**Large atoms: higher polarizability**

**Stronger interaction**



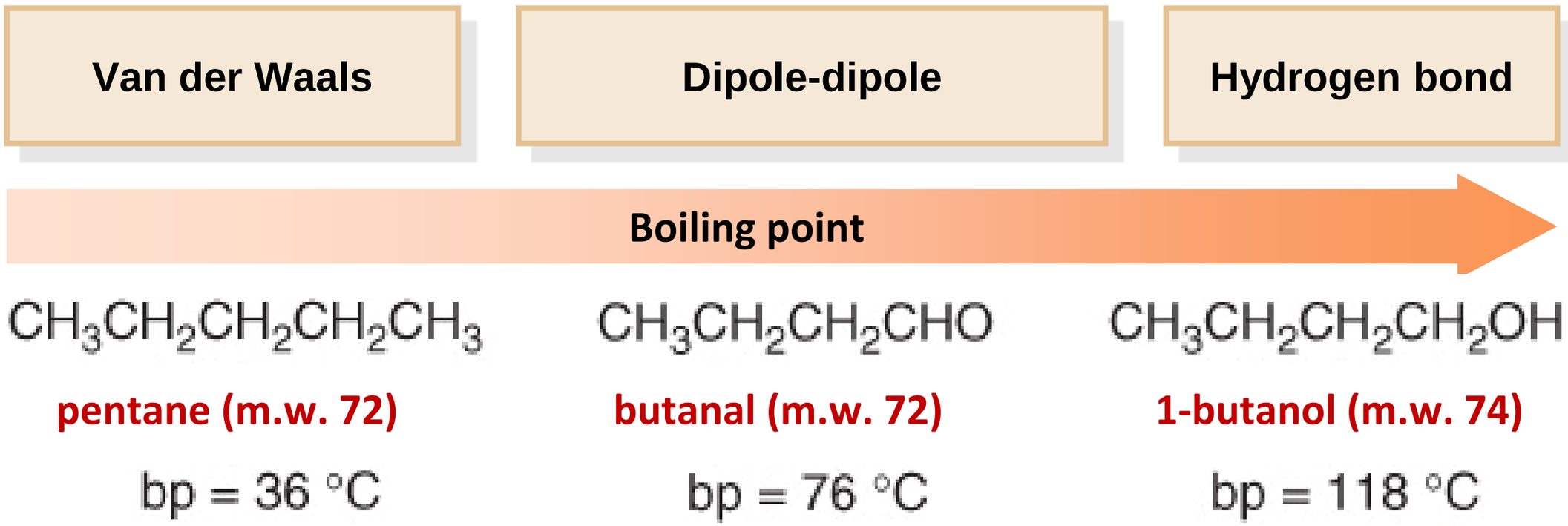
# Summary

| Interaction | Relative strength | Present in | Examples |
|---|---|---|---|
| Van der Waals<br>VDW | Very weak | All molecules | $CH_3CH_2CH_2CH_2CH_3$<br>$CH_3CH_2CH_2CHO$<br>$CH_3CH_2CH_2CH_2OH$ |
| Dipole-dipole<br>DD | weak | Permanent dipoles | $CH_3CH_2CH_2CHO$<br>$CH_3CH_2CH_2CH_2OH$ |
| Hydrogen bond<br>HB | strong | Molecules with OH,<br>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.:



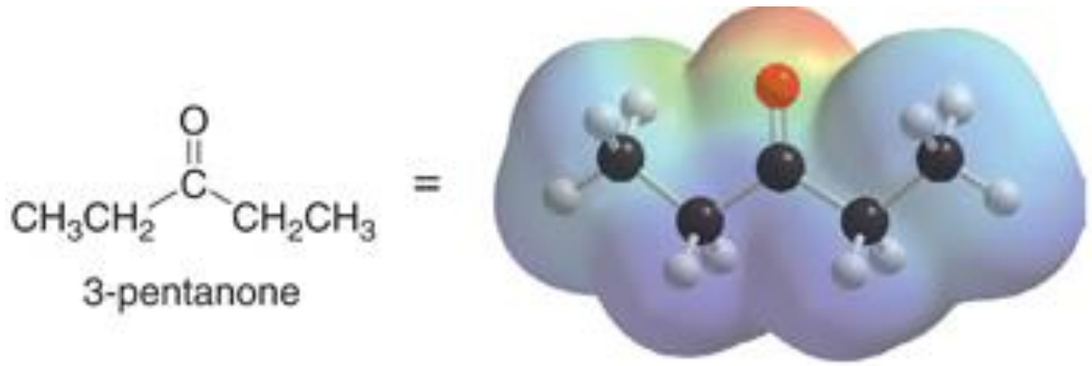
# Boiling Point

**b.p. = 42 °C**

**I is more polarizable**

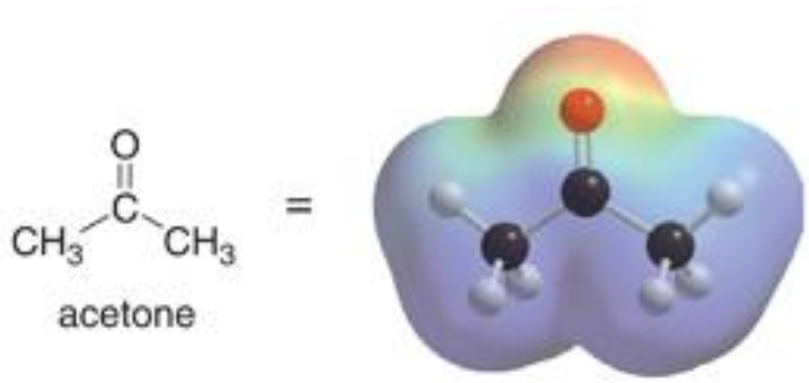
**b.p. = –78 °C**

**Smaller F has a low polarizability**




**b.p. = 102 °C**

**Larger surface area**




**b.p. = 56 °C**

**Smaller surface area**

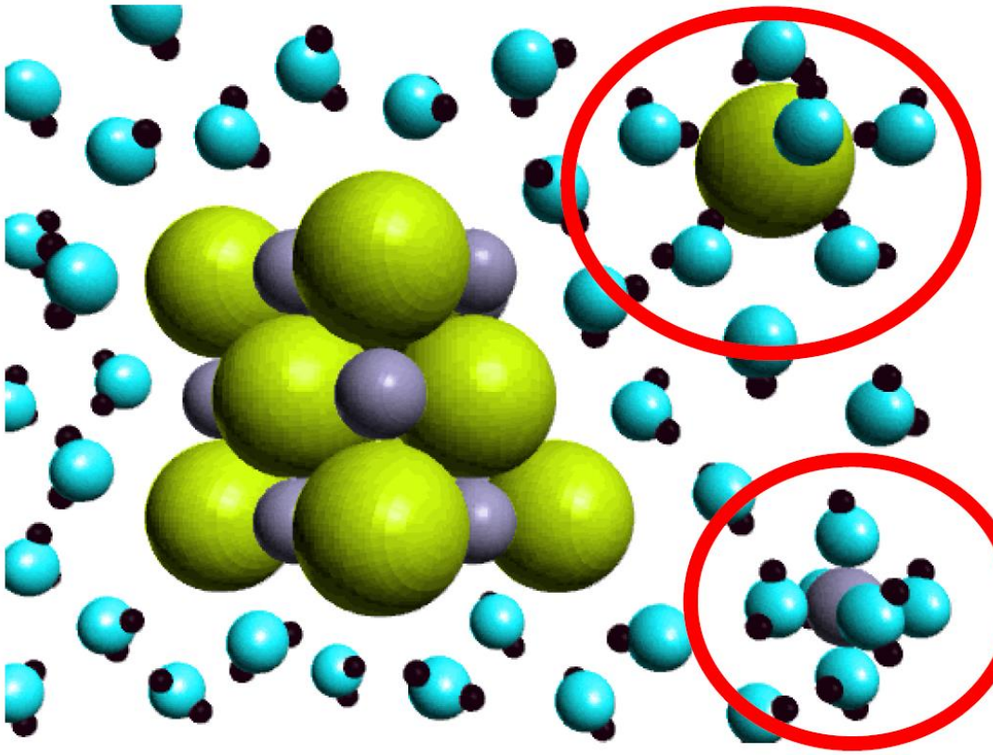
# Melting Point

- 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 |

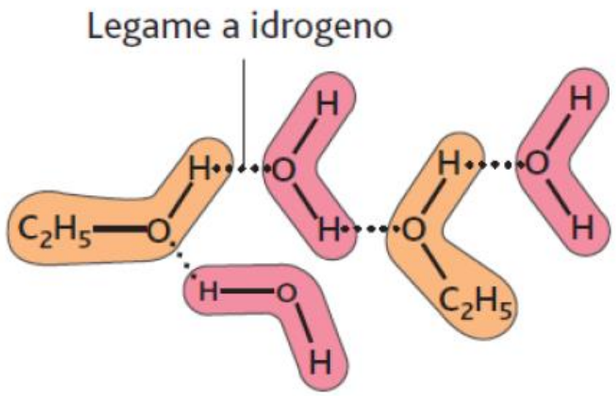
**Melting point**

# Solubilità

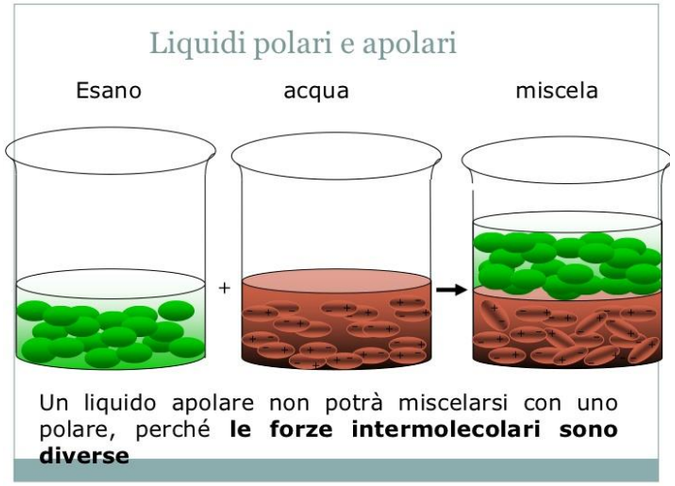


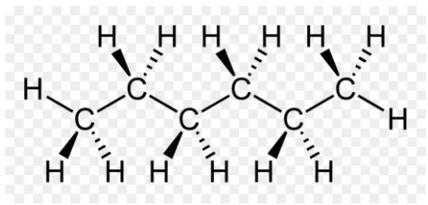
L'immagine mostra un cristallo di Cloruro di sodio che viene dissolto da molecole d'acqua. Il polo negativo delle molecole d'acqua circonda gli ioni $Na^+$, mentre il polo positivo gli ioni $Cl^-$.

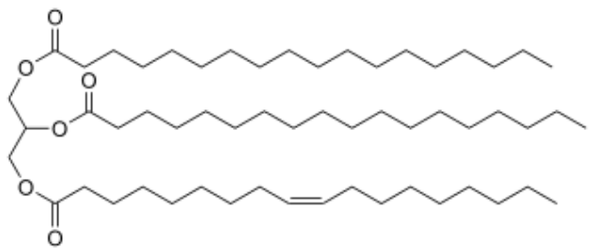
Per solubilizzare un composto il solvente deve interagire mediante interazioni non covalenti con il soluto compensando le interazioni tra molecole di soluto che sono presenti allo stato solido (**solvatazione**).

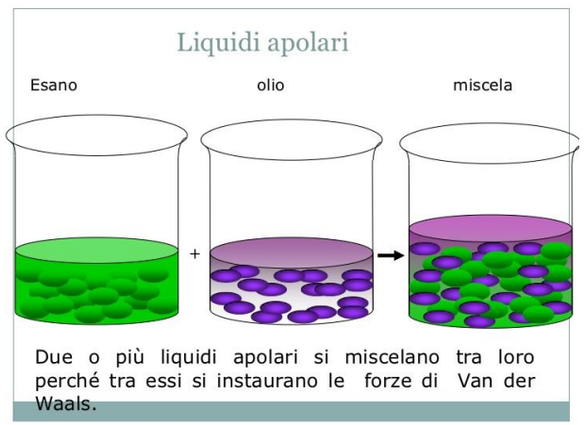


# Solubilità


Liquidi polari e apolari
Esano
acqua
miscela
Un liquido apolare non potrà miscelarsi con uno polare, perché **le forze intermolecolari sono diverse**

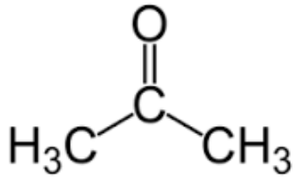




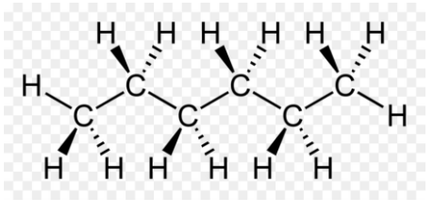

Liquidi apolari
Esano
olio
miscela
Due o più liquidi apolari si miscelano tra loro perché tra essi si instaurano le forze di Van der Waals.

# Solubilità: il simile scioglie il simile

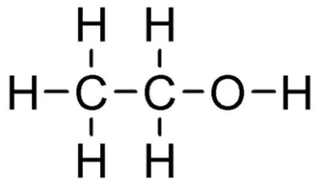
| | NaCl (ionico) | Alcol etilico (HB) | Etere etilico (dipolo) | Benzene (apolare) |
|---|---|---|---|---|
| Acqua (HB) | SI | SI | poco | NO |
| Acetone (dipolo) | NO | SI | SI | SI |
| Esano (apolare) | NO | NO | SI | SI |



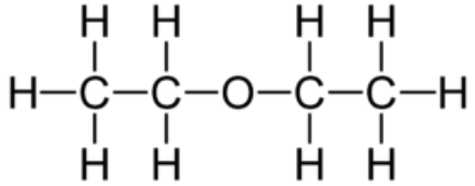

acetone



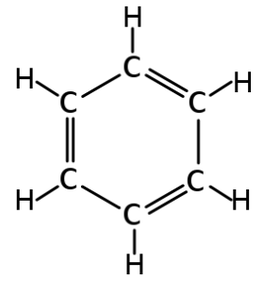
esano




etanolo



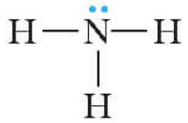
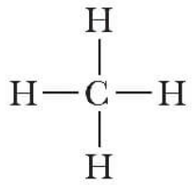
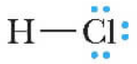
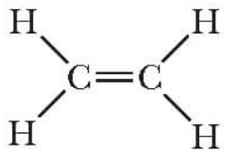
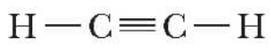
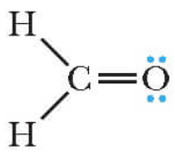
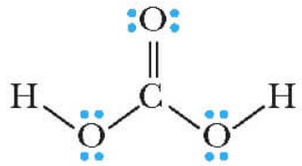

dietiletere



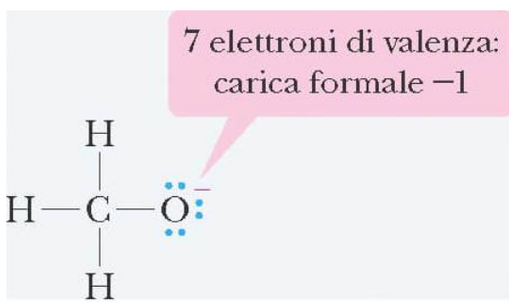

benzene

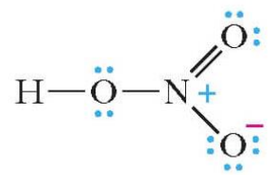
# Lewis structures

**TABELLA 1.6** **Strutture di Lewis di diverse molecole. Il numero degli elettroni di valenza in ciascuna molecola è indicato in parentesi dopo la formula molecolare**

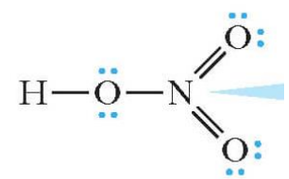
| | | | |
|---|---|---|---|
|  |  |  |  |
| $H_2O$ (8)<br>Acqua | $NH_3$ (8)<br>Ammoniaca | $CH_4$ (8)<br>Metano | HCl (8)<br>Acido cloridrico |
|  |  |  |  |
| $C_2H_4$ (12)<br>Etilene | $C_2H_2$ (10)<br>Acetilene | $CH_2O$ (12)<br>Formaldeide | $H_2CO_3$ (24)<br>Acido carbonico |

$$\text{Carica formale} = \begin{array}{l}\text{Numero di elettroni}\\ \text{di valenza nell'atomo}\\ \text{neutro non legato}\end{array} - \left(\begin{array}{l}\text{Tutti gli}\\ \text{elettroni non}\\ \text{condivisi}\end{array} + \begin{array}{l}\text{Metà degli}\\ \text{elettroni}\\ \text{condivisi}\end{array}\right)$$

Struttura di Lewis accettabile

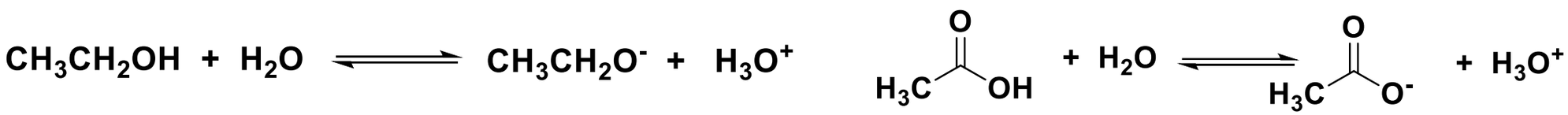


Struttura di Lewis non accettabile

$HNO_3$

# Delocalizzazione di legami ed elettroni: Risonanza

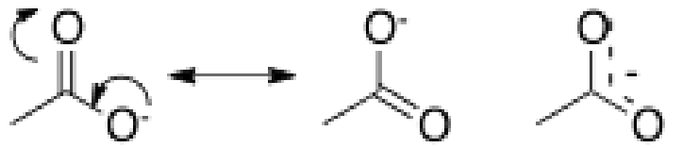
- La struttura e le proprietà di alcune molecole non possono essere spiegate dal semplice modello dell'orbitale di valenza con gli elettroni localizzati.
- In questo caso, una singola struttura di Lewis viene sostituita da un insieme di strutture di Lewis: **si dice che la molecola risuoni tra queste strutture e questo fenomeno è chiamato risonanza**.




**$CH_3CH_2OH$: $pK_a$ 16**

**$CH_3COOH$: $pK_a$ 4.75**

**Carica localizzata**
**meno stabile**



**Strutture di risonanza**

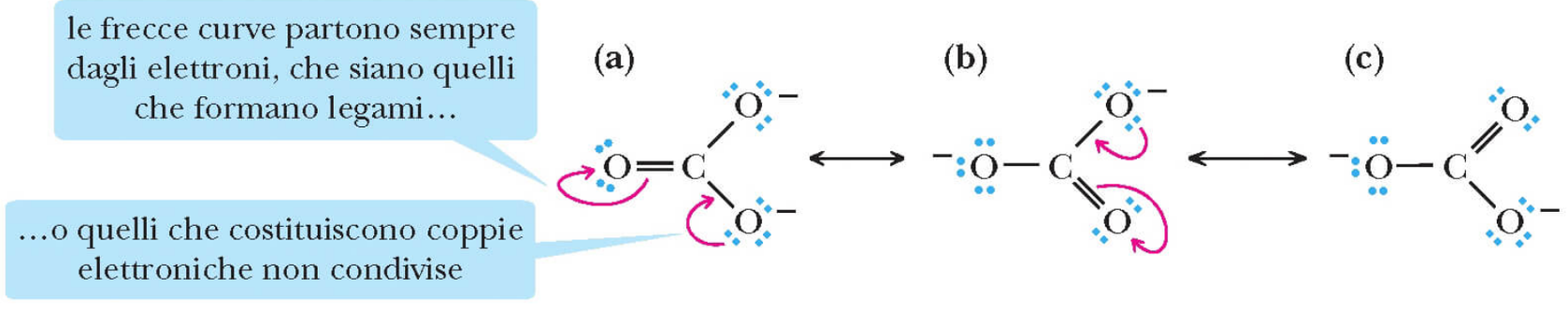
**Ibrido di risonanza**

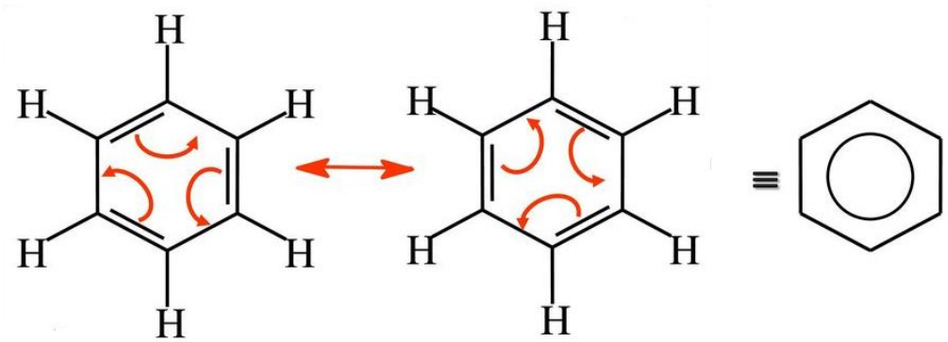
**Carica delocalizzata**
**più stabile**

# RISONANZA

- Le strutture di risonanza hanno la stessa disposizione degli atomi ma una diversa disposizione degli elettroni (elettroni π e coppie solitarie).
- Le lunghezze e gli angoli dei legami non cambiano nelle strutture di risonanza.
- Le strutture di risonanza devono rispettare le regole di Lewis (ottetto)
- La risonanza è una semplice teoria per adattare le strutture convenzionali di Lewis alla rappresentazione di molecole con elettroni e legami delocalizzati.
- **Le strutture di risonanza non sono reali.** Nessuna singola struttura di risonanza può rappresentare adeguatamente la struttura reale di una specie con elettroni delocalizzati.
- Le strutture di risonanza **non sono isomeri**. Esse differiscono solo nella distribuzione degli elettroni e non nella disposizione dei nuclei.
- Le strutture di risonanza **non sono in equilibrio**.

# Risonanza



benzene