KTH Information and Communication Technology

IM2665 Chemistry of Nanomaterials

Atomic Structure and Bonding

Assoc. Prof. Muhammet Toprak

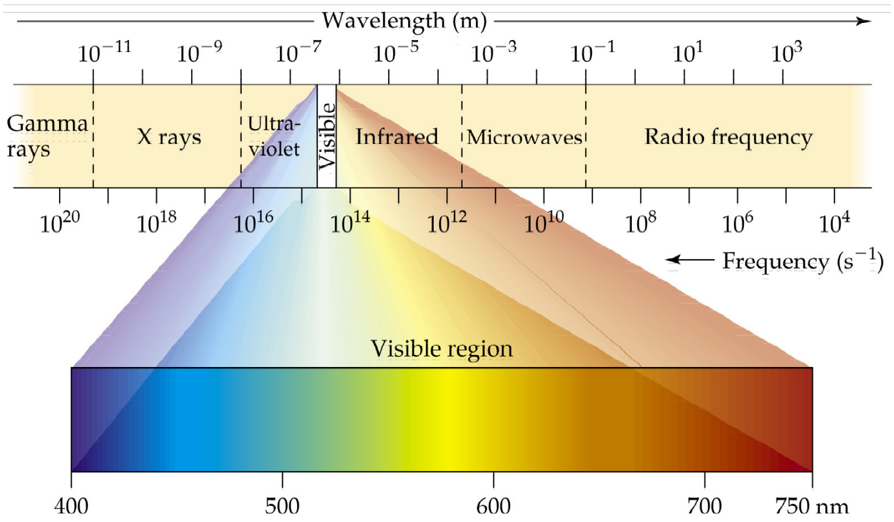
Division of Functional Materials
KTH Royal Institute of Technology

Background

- Electromagnetic waves
- Quantified energy and photons
  - Max Planck (1858-1947)
  - Albert Einstein (1879-1955)
- Bohr's atom model
  - Niels Bohr (1885-1962)
- Materials wave motion,
  - Louis de Broglie (1892-1987)
- Uncertainity principle
  - Werner Heisenberg (1901-1976)
- Schrödinger equation
  - Erwin Schrödinger (1887-1961)

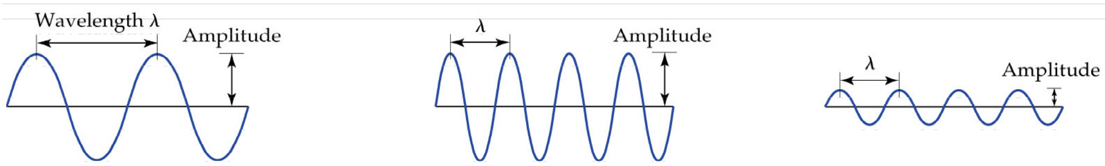
Electromagnetic Spectrum

Visible light is only a small part of the Electromagnetic Spectrum



Electromagnetic Waves

- Wavemotion is defined by
  - ν = Frequency (Hz)
  - λ = wavelength (m)
- Calculations
  - $c = \nu \times \lambda$
  - $c = 3{,}00 \times 10^8$ m/s (speed of light)



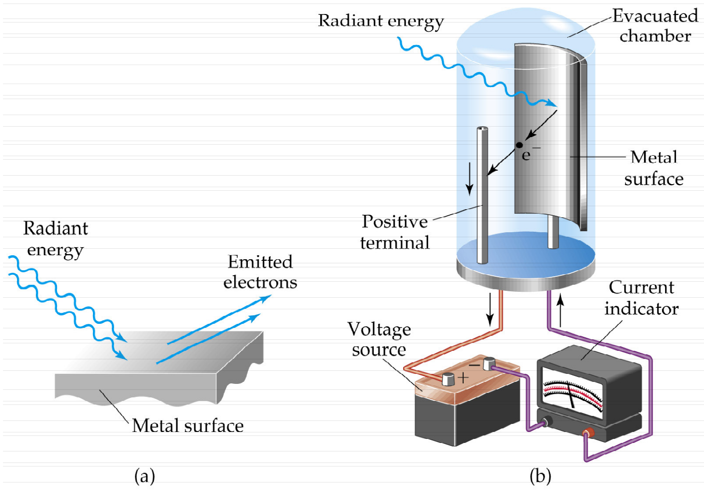
(a) Two complete cycles of wavelength λ

(b) Wavelength half of that in (a); frequency twice as great as in (a)

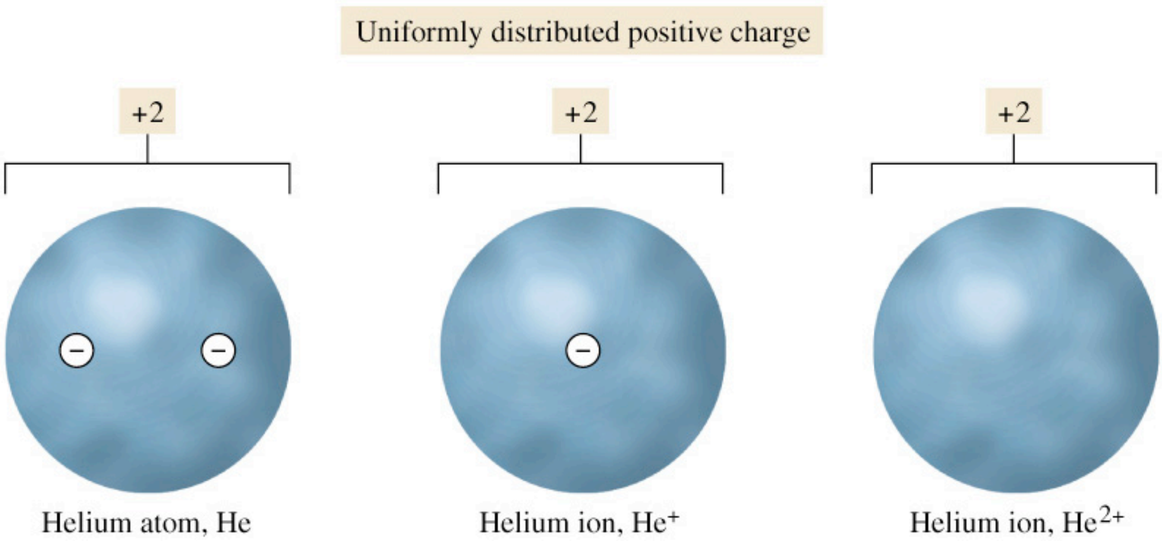
(c) Same frequency as (b), smaller amplitude

Quantified Energy and Photons

- $E = h \times \nu$; where $h = 6{,}63 \times 10^{-34}$ J s (Planck's constant)
- Photoelectric Effect (1905)

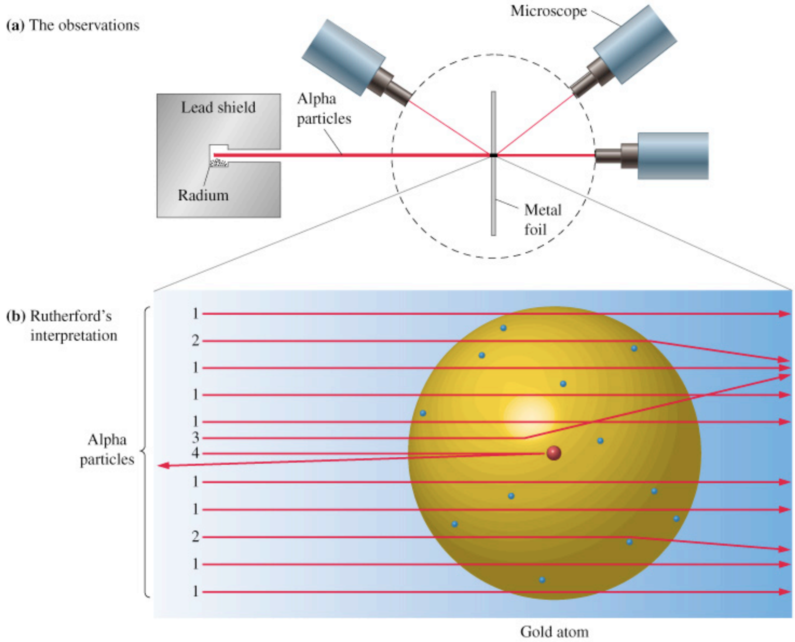


Thomson´s Pudding Model



For a helium atom, the model proposes a large spherical cloud with two units of positive charge. Th e two electrons lie on a line through the center of the cloud. The loss of one electron produces the He+1 ion, with the remaining electron at the center of the cloud. The loss of a second electron prod uces He+2 , in which there is just a cloud of positive charge. ♪

Rutherford's Experiment



The notion that atoms consist of very small nuclei containing protons and neutrons surrounded by a much larger cloud of electrons was developed from an α particle scattering experiment.

Bohr Atomic Model

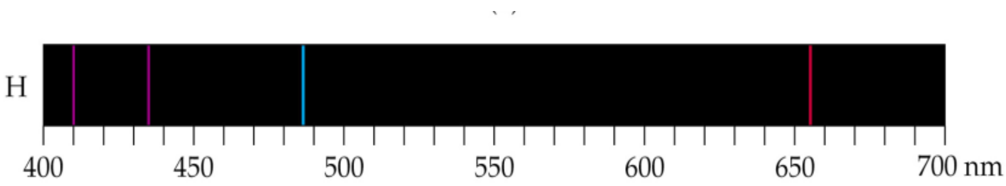
Explained H atoms line spectrum (1913)

OBS! Discrete lines with certain wavelengths

Equation:

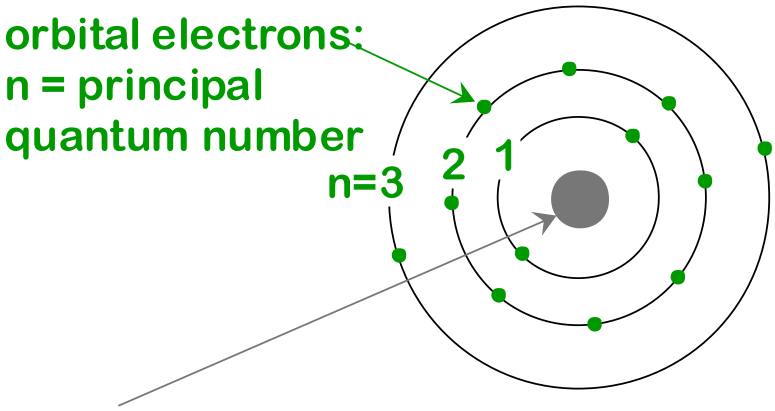
Rydberg's formula; $\nu = R_H \times (1/n_1^2 - 1/n_2^2)$ where

$R_H = 3{,}29 \times 10^{15}$ Hz



(b)

BOHR ATOM



Adapted from Fig. 2.1, *Callister 6e.*

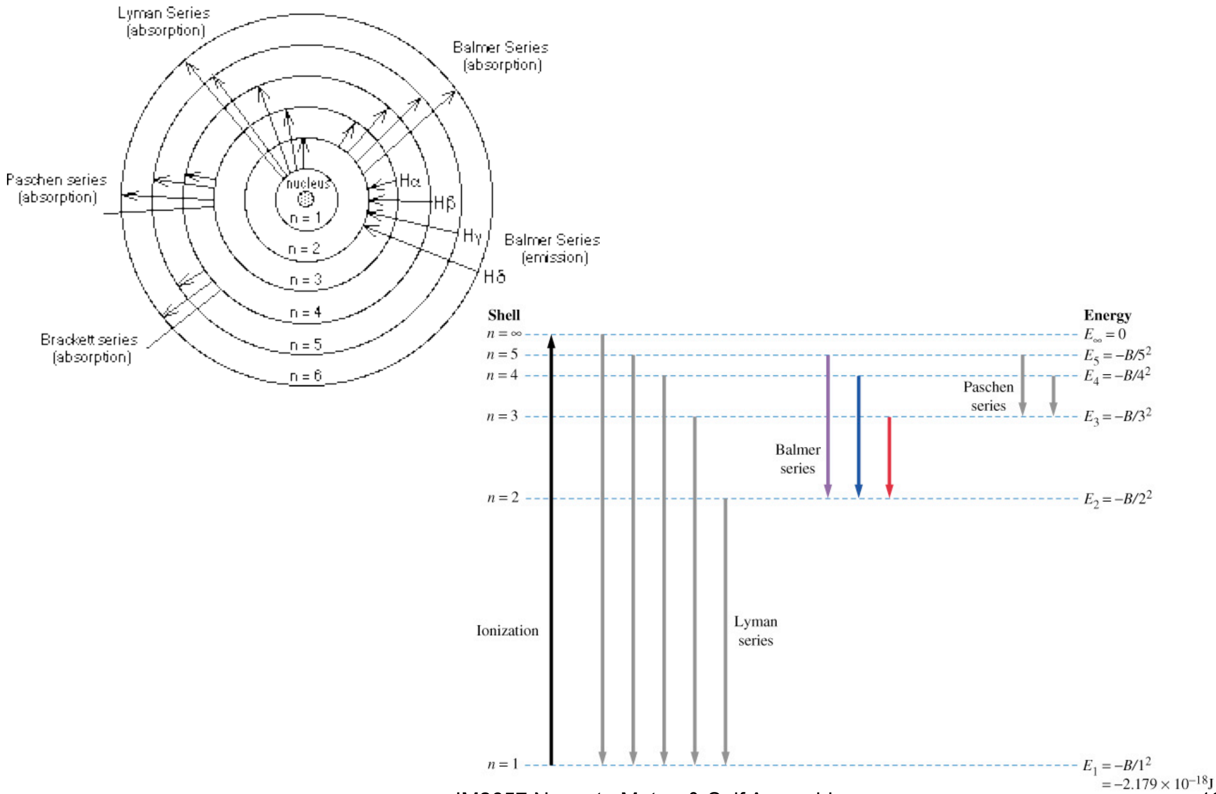
Nucleus: Z = # protons

= 1 for hydrogen to 94 for plutonium

N = # neutrons

Atomic mass A ≈ Z + N

Emission Spectrum



Material's Wavemotion

de Broglie Relation (1924)

$\lambda = h / (m \times v)$ where v = velocity

Uncertainity Principle

$$\Delta x . \Delta p \geq \frac{\hbar}{2} \qquad \Delta x . \Delta mv \geq \frac{h}{4\pi}$$

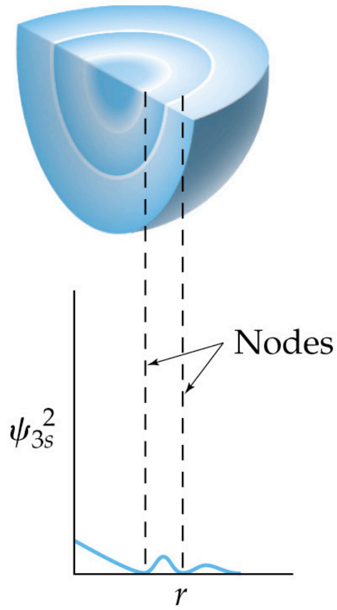
Schrödinger Equation

$$H \psi = E \psi$$

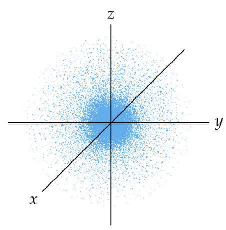
where ψ is electron wavefunction and E the energy level (1926)

Atomic Orbitals

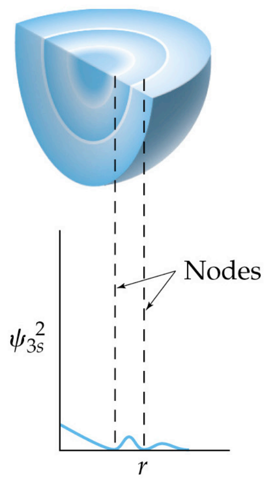
- Wavefunction for an electron = ato -mic orbital
- Wavefunction square gives the pro bability of finding an electron at a given space
- Tight electroncloud ⇒ higher prob ability
- Every orbital has a specific energy ($E = -hR_H/n^2$)



Atomic Orbitals

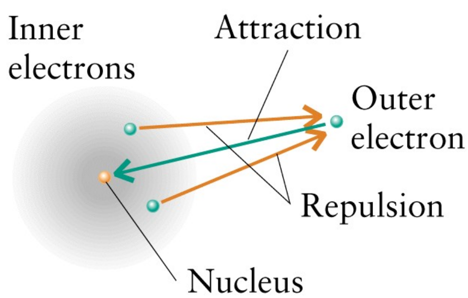


- Atomic Orbitals are wavefunctions which are solutions to Schrödinger's equation
- Atomic orbitals are defined as $\psi(n,l,m_l)$
- Electrons wavefunction is defined as $\psi(n,l,m_l,m_s)$
- n,l,m_l and m_s are quantum numbers



Energy Levels

- Energy levels can be divided into
  - main levels (corresponding to electr on shell)
  - sublevels (orbital groups)



Quantum Numbers

- Solving Schrödinger's Equation, yields a set of wave fu nction for an electron with 3 quantum numbers

- All electrons can be identified with four quantum numbers

  n - principle quantum number - shell- energy

  l - orbital quantum no - subshell - shape

  m_l – magnetic quantum no - orbitals - orientation

  m_s – spin quantum number

Definitions of Quantum Numbers and Constraints

- Principle quantum number n

  $n = 1, 2, 3, \ldots$

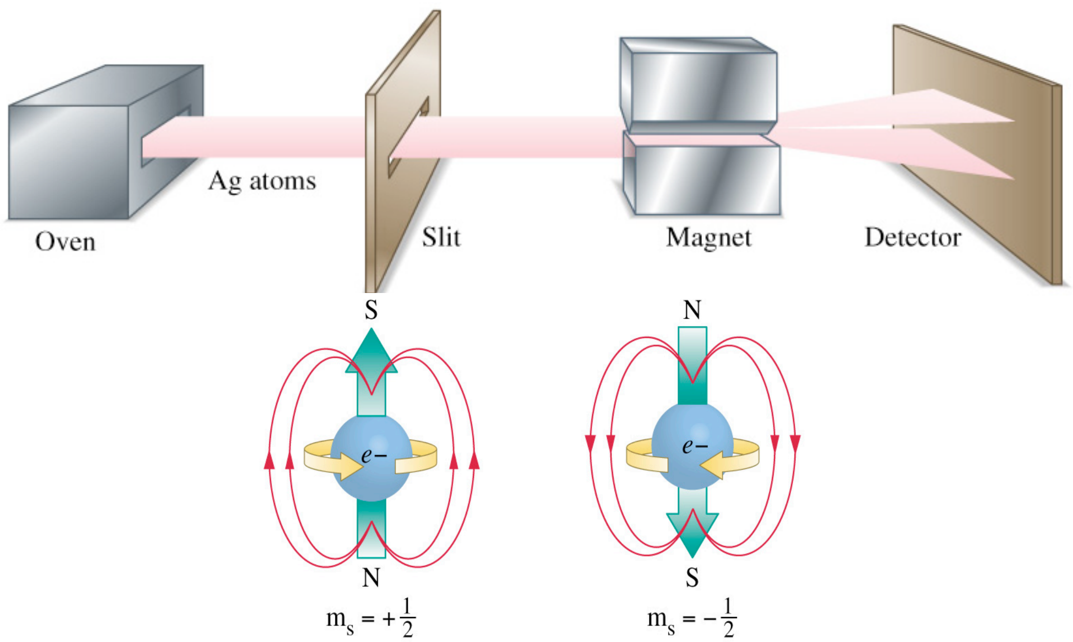
- Orbital angular momentum quantum number l

  $l = 0, 1, 2, \ldots (n\text{-}1)$

- Magnetic quantum number ml

  $ml = -l, -l + 1, -l + 2, \ldots 0 \ldots l - 2, l - 1, l$

Spin of Electron



Using Quantum Numbers

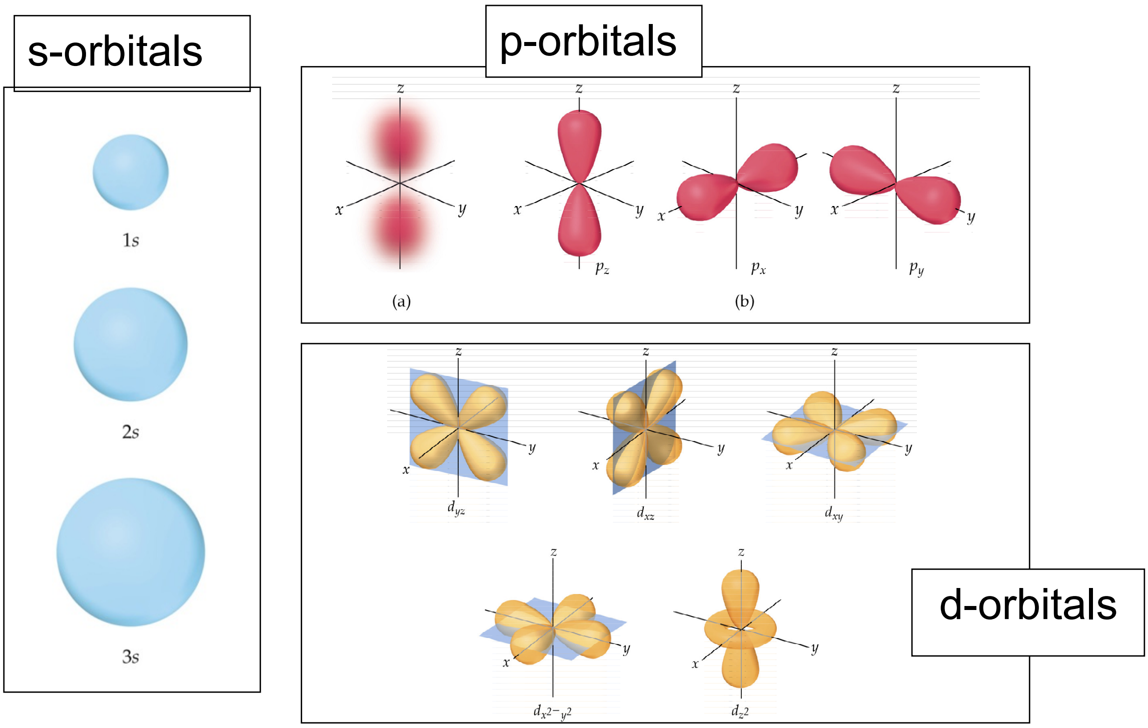
- $n = 1, 2, 3.....$
- $l = 0, 1, 2, n\text{-}1,....$
- $m_l = +l, +l\text{-}1, ..., 0, ..., -l$
- $m_s = +½, -½$

- No of Orbitals = n^2
- No of orbitals in a s ubshell = $2 \times l + 1$

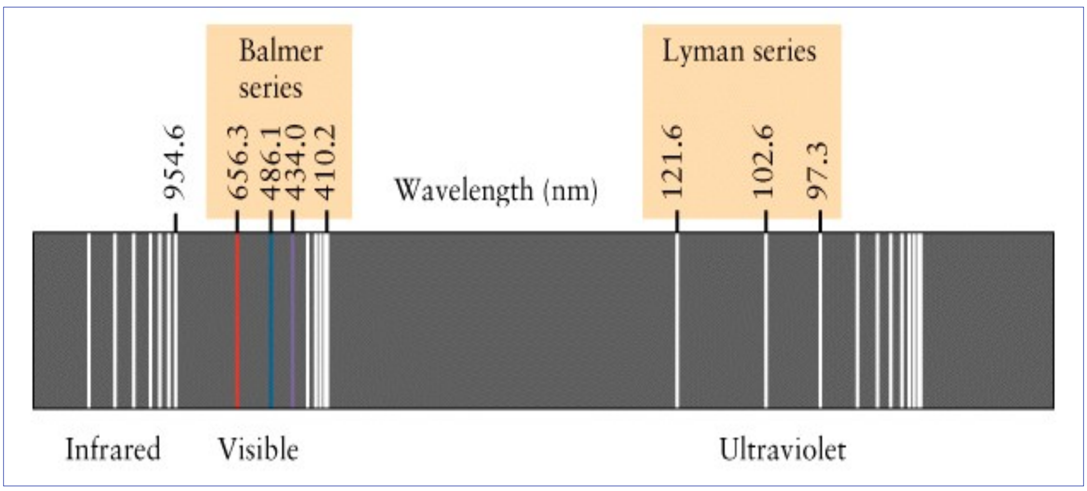
Shells and Subshells

- l = 0 gives 1 s-orbital
- l = 1 gives 3 p-orbitaler
- l = 2 gives 5 d-orbitaler
- l = 3 gives 7 f-orbitaler

Different Atomic Orbitals

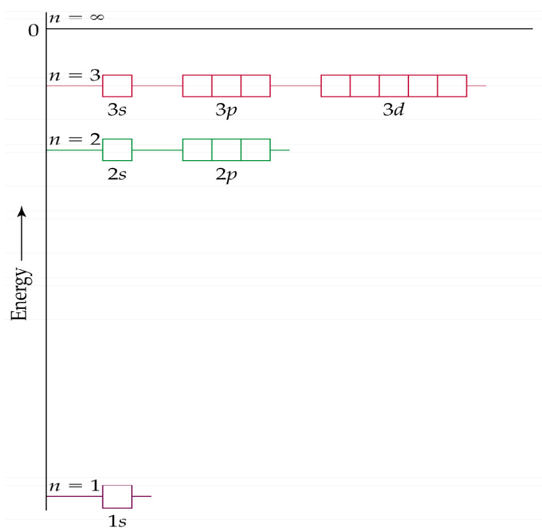


Hydrogen Spectrum

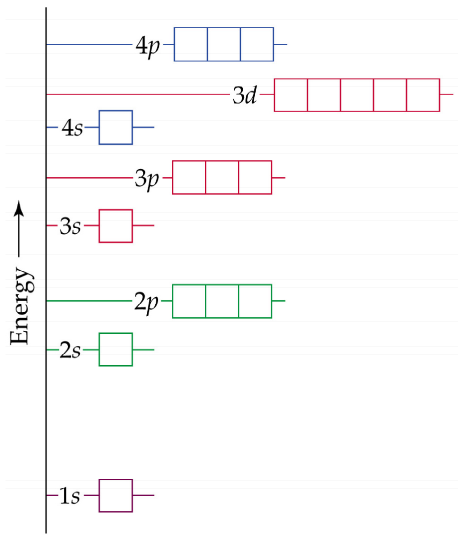


Energy Levels

Energy Levels for Hydrogen atom



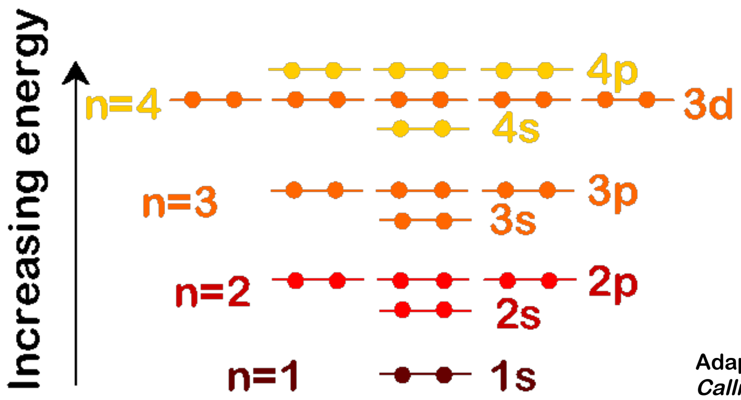
Energy Levels for atoms with many electrons



ELECTRON ENERGY STATES

Electrons...

- have discrete energy states
- tend to occupy lowest available energy state.



Adapted from Fig. 2.5, *Callister 6e.*

STABLE ELECTRON CONFIGURATIONS

Stable electron configurations...

- have complete s and p subshells
- tend to be unreactive.

Z	Element	Configuration
2	He	$1s^2$
10	Ne	$1s^2 2s^2 2p^6$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Adapted from Table 2.2, *Callister 6e.*

SURVEY OF ELEMENTS

- **Most elements: Electron configuration not stable.**

Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4^6$	(stable)

Adapted from Table 2.2, *Callister 6e.*

- **Why? Valence (outer) shell usually not filled completely.**

Chemical Bonding

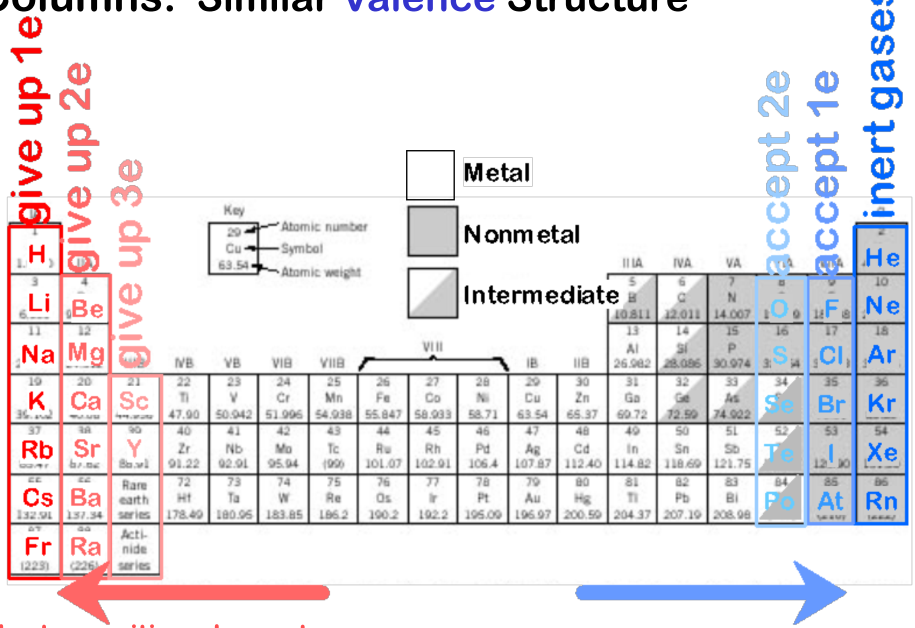
Ionic Bonding

Covalent Bonding

Metallic Bonding

THE PERIODIC TABLE

- **Columns: Similar Valence Structure**



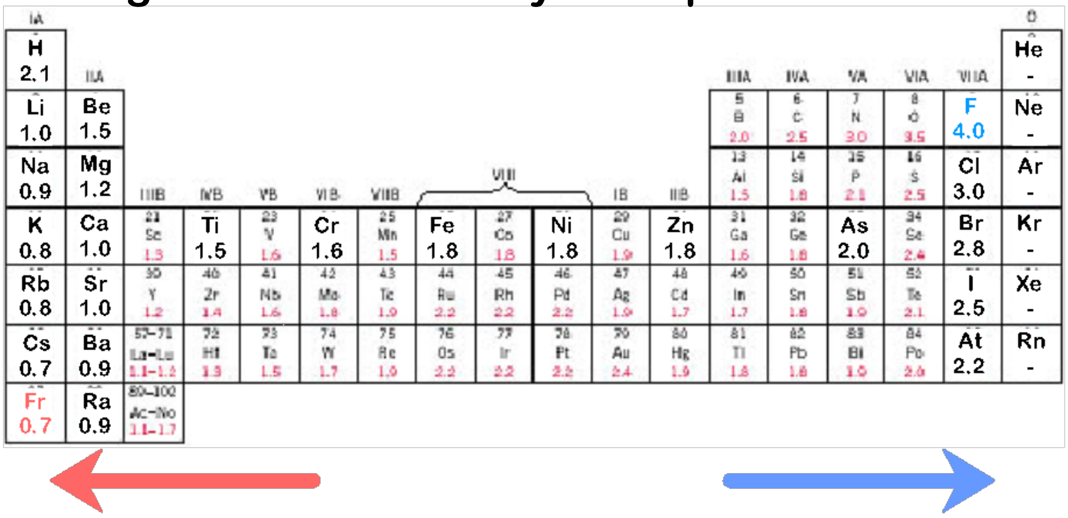
Adapted from Fig. 2.6, *Callister 6e.*

Electropositive elements: Readily give up electrons to become "+" ions.

Electronegative elements: Readily acquire electrons to become "-" ions.

ELECTRONEGATIVITY

- **Ranges from 0.7 to 4.0,**
- **Large values: tendency to acquire electrons.**



Smaller electronegativity **Larger electronegativity**

Adapted from Fig. 2.7, *Callister 6e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

What is a Chemical Bond?

- Intermolecular forces holding the atoms toget her
- Different types of bonding are
  - Ionic bonds
  - covalent bonds
    - polar covalent bonds
  - Metallic bonds

Ionic Bonds

- Electrostatic attraction forces between ions
- Coulombs law

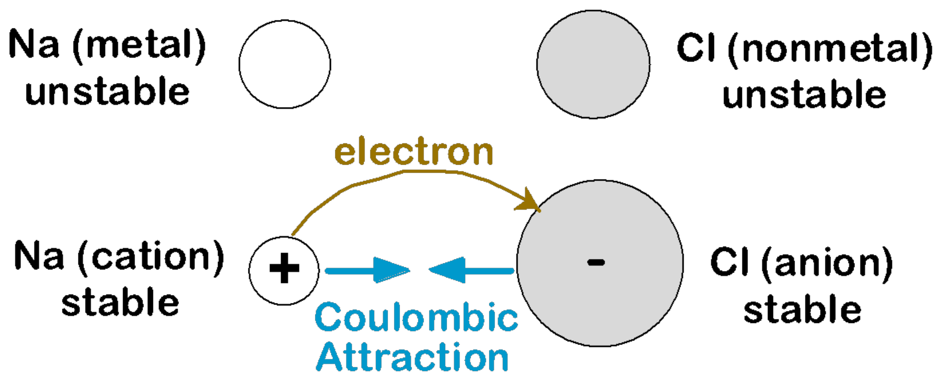
  $F = k \times (Q_1 \times Q_2)/ d^2$

  i.e. The strength depends on the charge and the dist

  ance

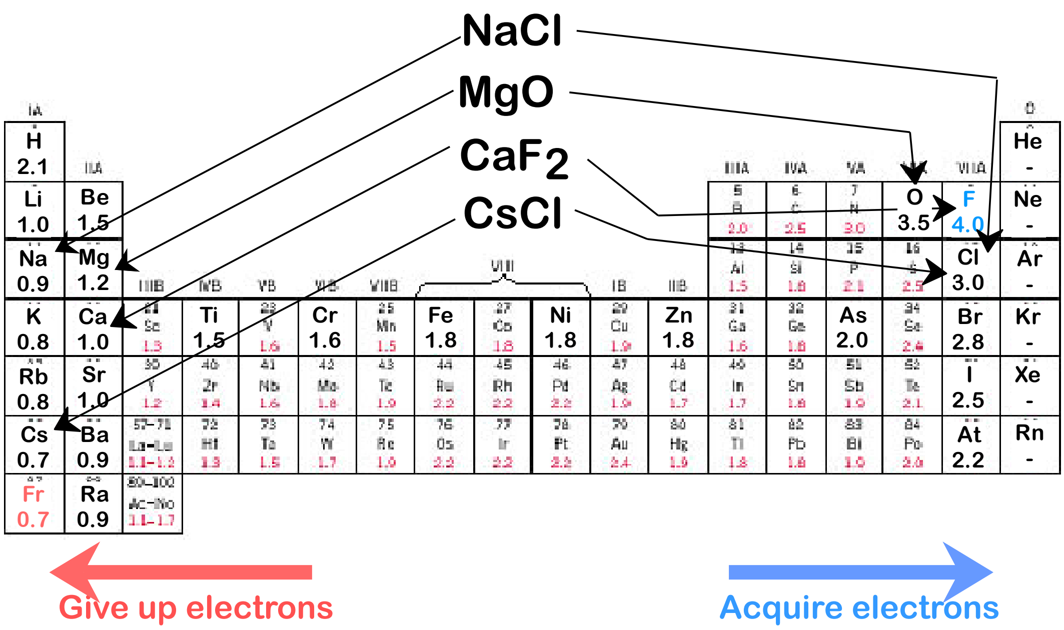
IONIC BONDING

- Occurs between "+" and "-" ions.
- Requires electron transfer.
- Large difference in electronegativity required.
- Example: NaCl



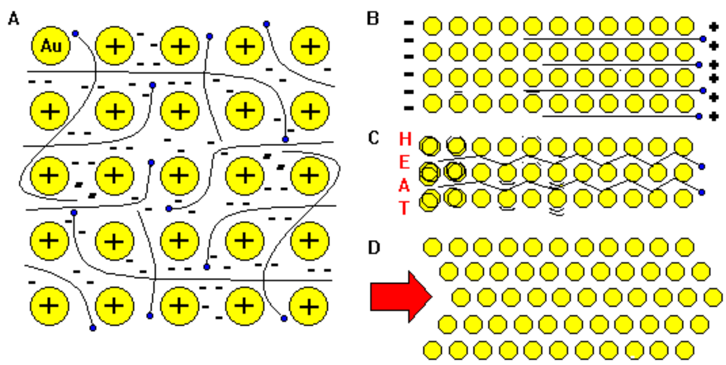
EXAMPLES: IONIC BONDING

- **Predominant bonding in Ceramics**



Adapted from Fig. 2.7, *Callister 6e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Metallic Bonding



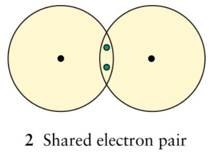
A: Outermost electrons wander freely through metal. Metal consists of cations held together by negatively-charged electron "glue."

B: Free electrons can move rapidly in response to electric fields, hence metals are a good conductor of electricity.

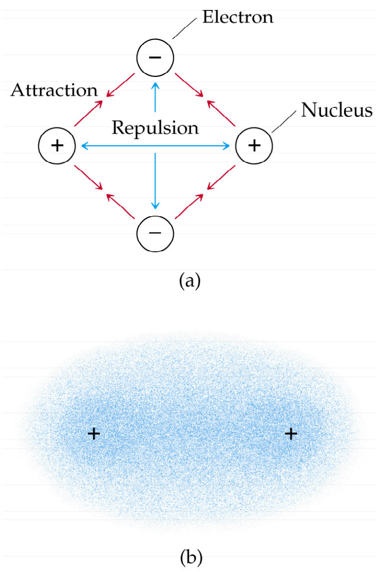
C: Free electrons can transmit kinetic energy rapidly, hence metals are good conductors of heat.

D: The layers of atoms in metal are hard to pull apart because of the electrons holding them together, hence metals are tough. But individual atoms are not held to any other specific atoms, hence atoms slip easily past one another. Thus metals are ductile. **Metallic Bonding is the basis of our industrial civilization.**

Covalent Bonding



- Forms between non-metals and non -metals
- Two atoms share an electron pair
- Octet rule is valid
- Directional bonds
- Strength depends on the no of elect ron pairs participating in the bonding



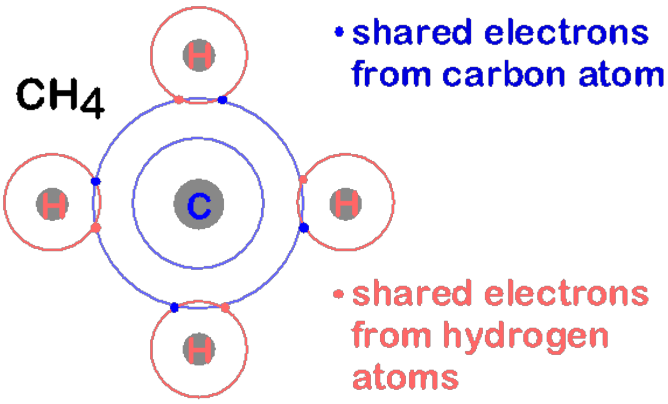
COVALENT BONDING

- Requires shared electrons
- Example: CH_4

C: has 4 valence e^-, needs 4 more

H: has 1 valence e^-, needs 1 more

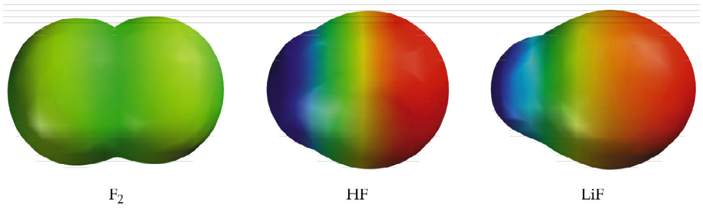
Electronegativities are comparable.



Adapted from Fig. 2.10, *Callister 6e.*

Polar Covalent Bond

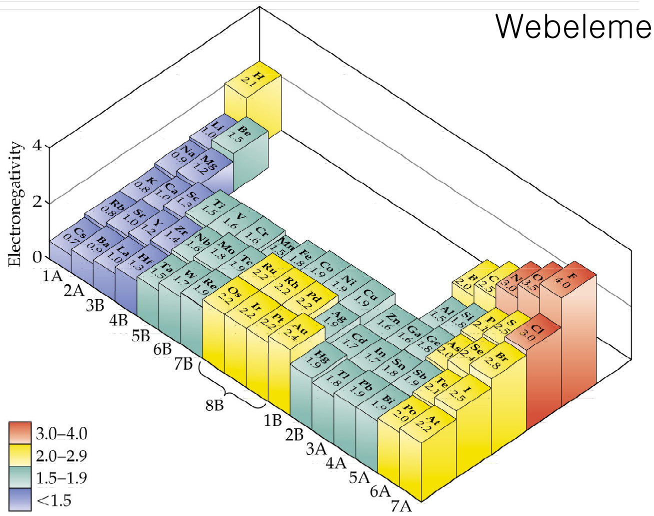
- A covalent bond which has charge distribution o ver the bond
  - Electronegativity is the ability of an atom to attract ele ctrons



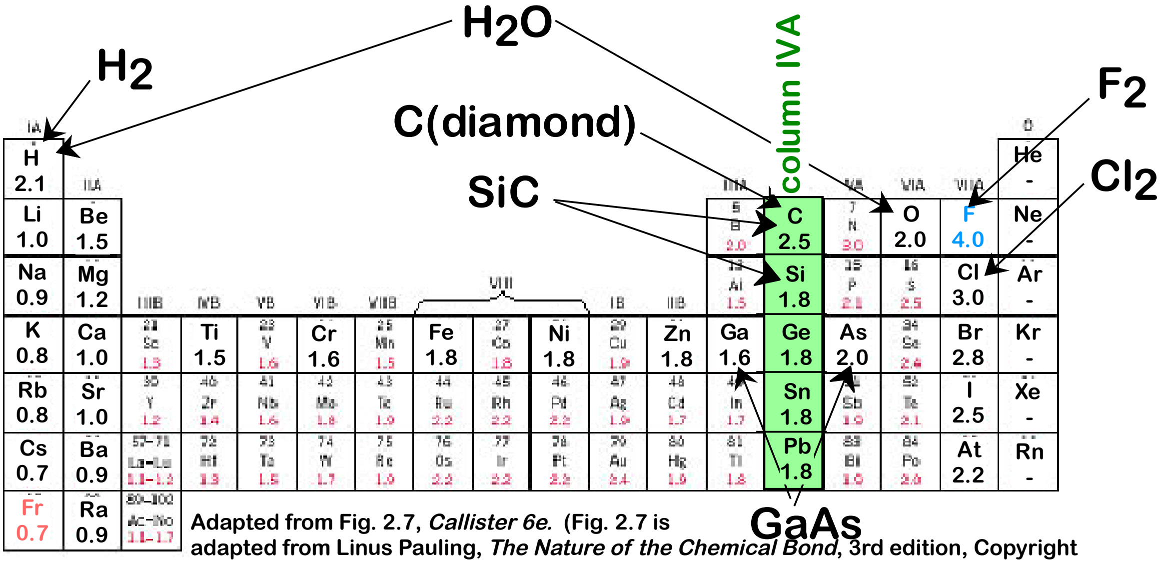
Electronegativity

- Atoms having very high ionization energy and very negative electron affinity will have high el ectronegativity

Webelements.com♪



EXAMPLES: COVALENT BONDING

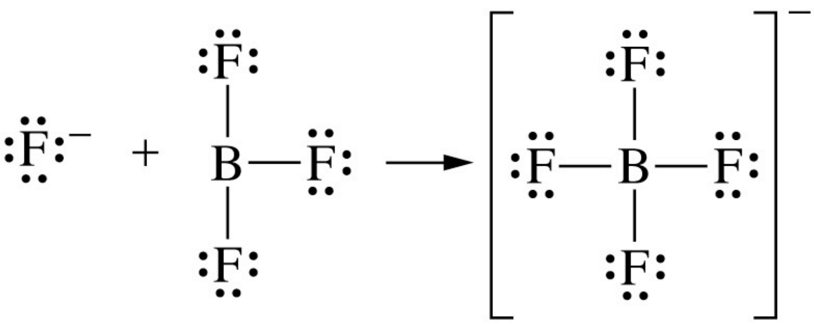


Adapted from Fig. 2.7, *Callister 6e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

- Molecules with nonmetals
- Molecules with metals and nonmetals
- Elemental solids (RHS of Periodic Table)
- Compound solids (about column IVA)

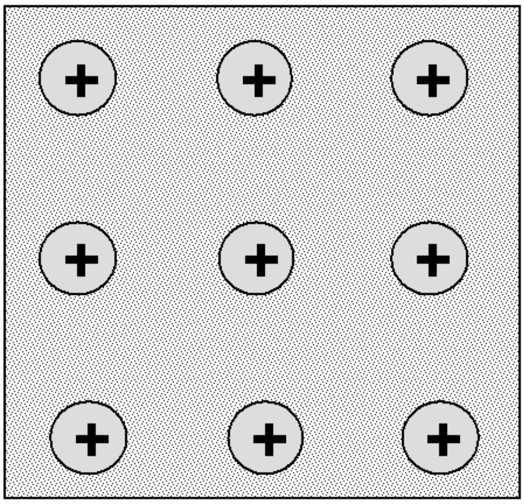
Coordinate/Dative Covalent Bond

- One of the atoms provide both of the bonding electrons.



METALLIC BONDING

- Arises from a sea of donated valence electrons (1, 2, or 3 from each atom).



Adapted from Fig. 2.11, *Callister 6e.*

- Primary bond for metals and their alloys

Lewis Structures

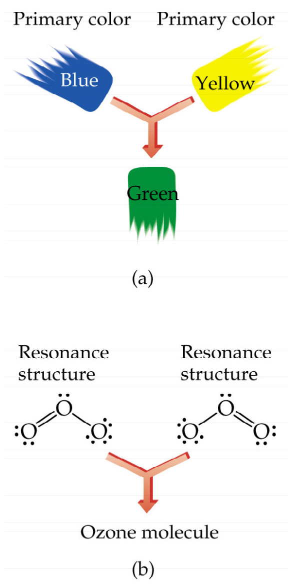
- Molecule Forms
- Polarity
- Intermolecular interactions
- Hybridization

Lewis Structures

- Find out the no of valence electrons around the central atom
- Place atoms in a symmetric way around the atom
- Place electron pairs between every atom
- Form octets, double triple bonds.

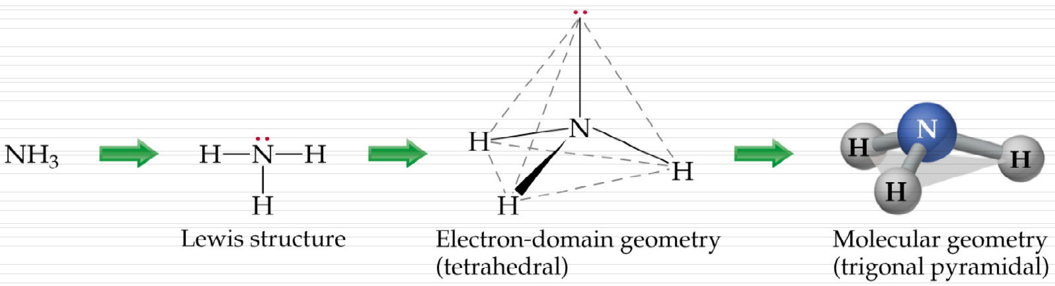
Lewis structures

- Formal Charge
  - No of valence e – no of unshar ed electrons - electrons which were shared in the Lewis structure
- Resonance
  - Where a molcule can be descri bed by different arrangement of bonding electrons in Lewis structure
- Expanded valence
  - When empty d-orbitals are available



Molecule form

- Lewis structures
  - Shows 2D structures with e sharing
- VSEPR (Valence Shell Electron Pair Repulsion Model)
  - Shows 3-D structures with free e pairs



Geometries

- Eletronic structure

  2 VSEPR pair ⇒ linear

  3 VSEPR pair ⇒ triangel

  4 VSEPR pair ⇒ tetrahedral

  5 VSEPR pair ⇒ trigonal bipyram
  id

  6 VSEPR pair ⇒ octahedral

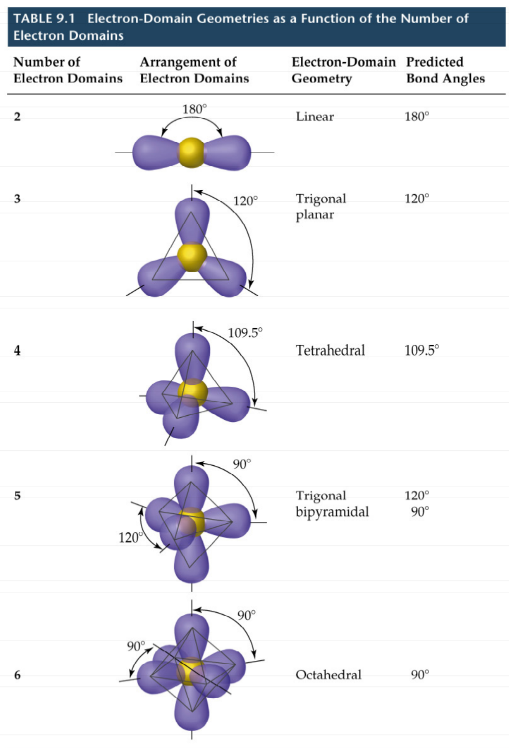
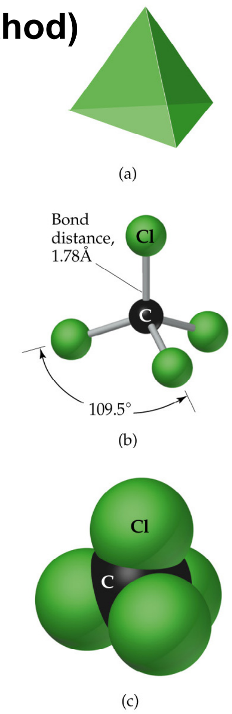


TABLE 9.1 Electron-Domain Geometries as a Function of the Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2	180°	Linear	180°
3	120°	Trigonal planar	120°
4	109.5°	Tetrahedral	109.5°
5	90°, 120°	Trigonal bipyramidal	120° 90°
6	90°, 90°	Octahedral	90°

VSEPR

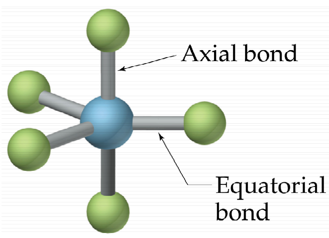
(Valence Shell Electron Pair Repulsion method)

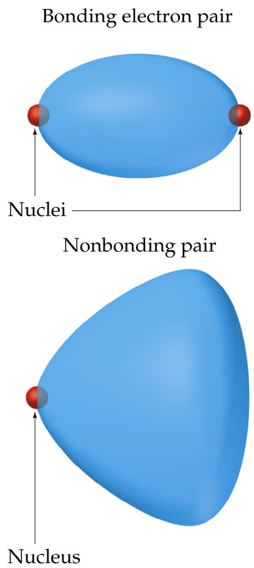


- Draw Lewis structure
- Count VSEPR-pairs around central atom
- Decide electron structure
- Determine the shape of the molecule

Free electron pairs

- They take place but do not show





- Strength of repulsion
  - Electron pair-electron pair > electronpair-bond pair>bond pair-bond pair

Shape of Molecules

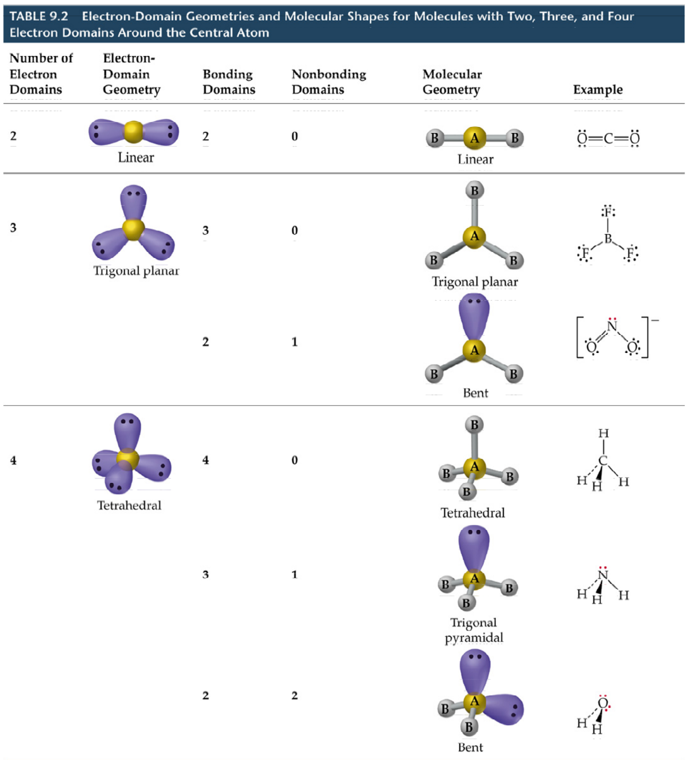


TABLE 9.2 Electron-Domain Geometries and Molecular Shapes for Molecules with Two, Three, and Four Electron Domains Around the Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	O=C=O
3	Trigonal planar	3	0	Trigonal planar	BF_3
		2	1	Bent	$[NO_2]^-$
4	Tetrahedral	4	0	Tetrahedral	CH_4
		3	1	Trigonal pyramidal	NH_3
		2	2	Bent	H_2O

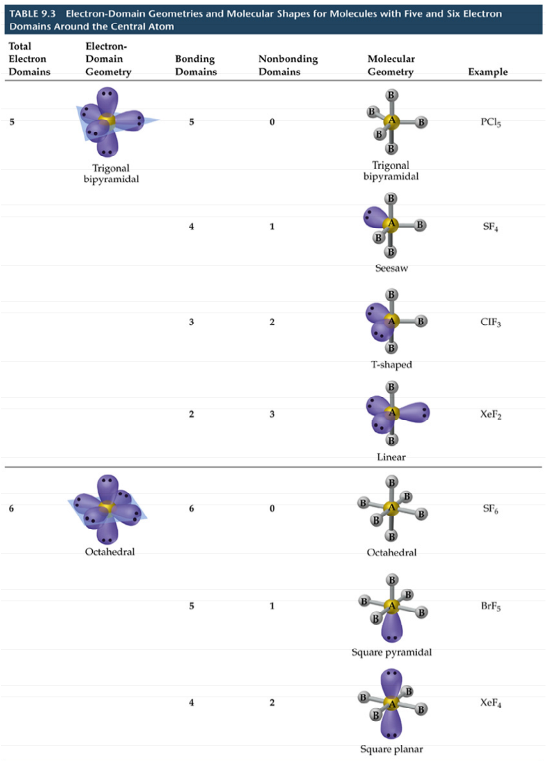
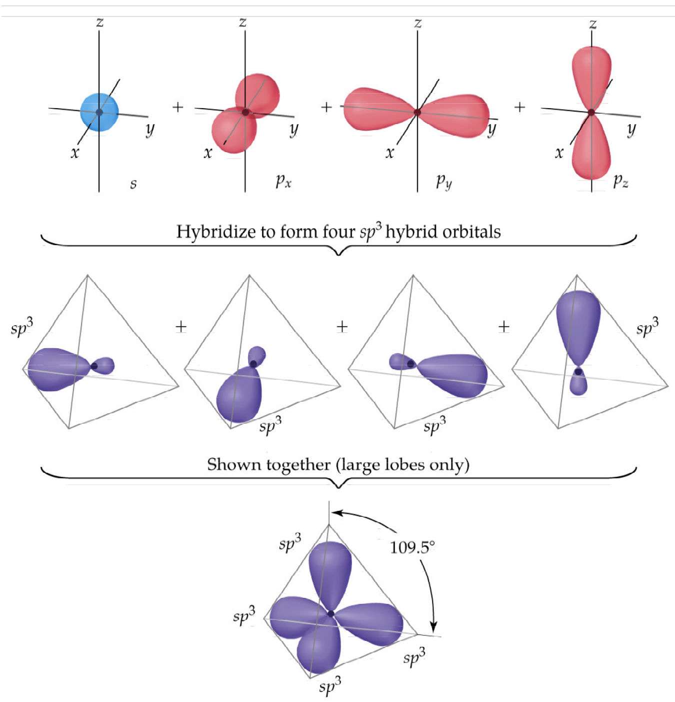


TABLE 9.3 Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	Seesaw	SF_4
		3	2	T-shaped	ClF_3
		2	3	Linear	XeF_2
6	Octahedral	6	0	Octahedral	SF_6
		5	1	Square pyramidal	BrF_5
		4	2	Square planar	XeF_4

Hybridisation

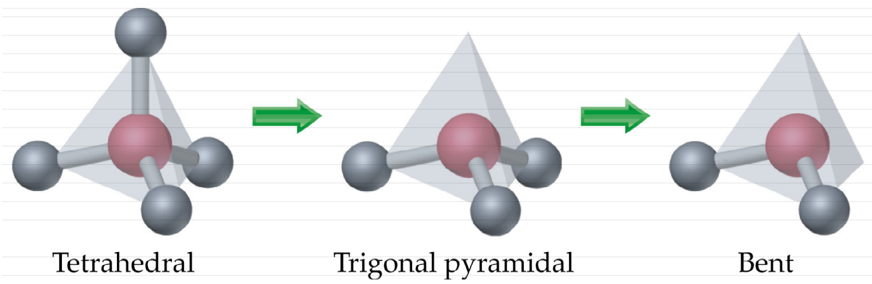


- sp^3 orbital

Shape of the Molecule

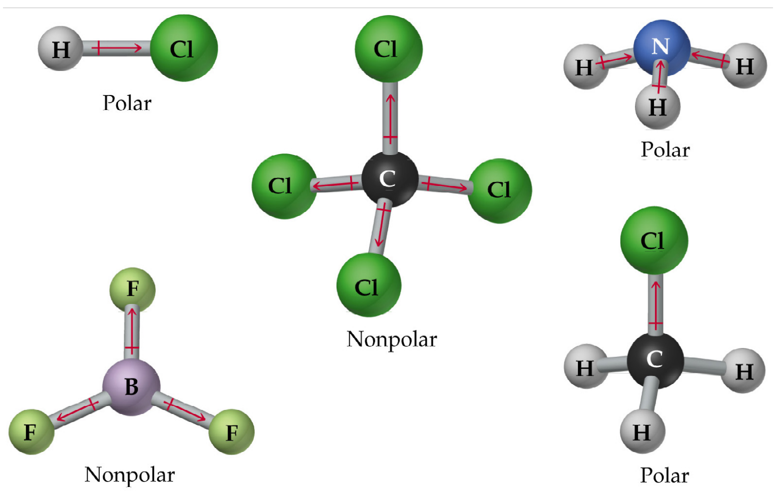
- Strength of repulsion
  - Electron pair-electron pair > electronpair-bond pair>bond pair-bond pair

♪



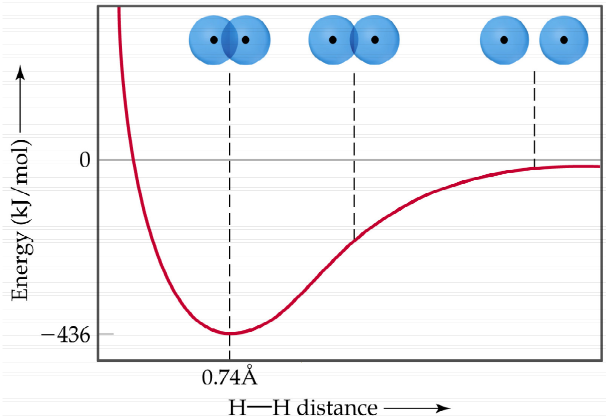
Dipoles

- Dipoles have a char ge separation within the molecule,
  - Polar covalent bonds , i.e. Charge distributi on within the bond
  - convenient geometry



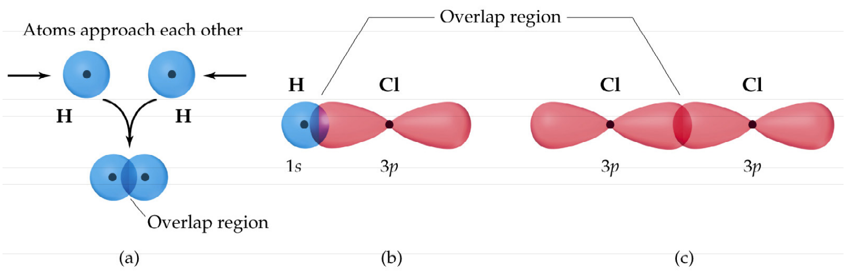
Valence Bond Theory

- Lewis theory
  - Bonding where the two atoms share an electron pair♪
- Valence Bond Theory
  - Bonding where two a tomic orbitals overlap



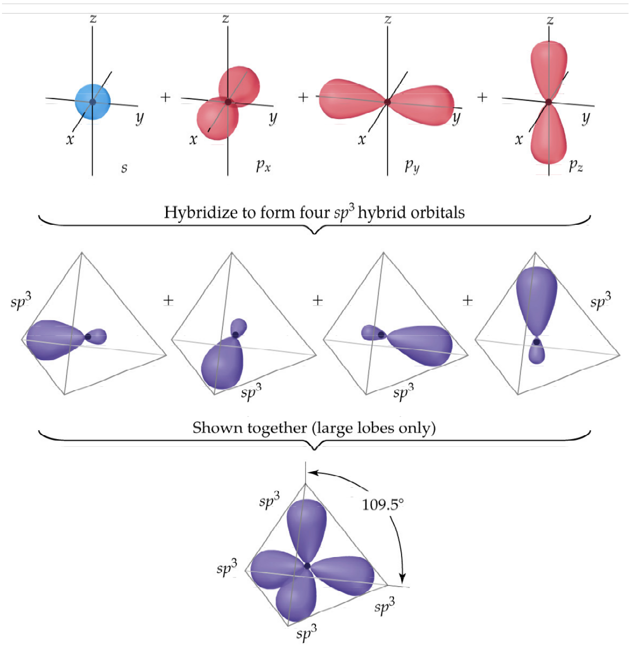
Type of Bonding

- σ- bonds
  - Overlap accross the two nuclei♪



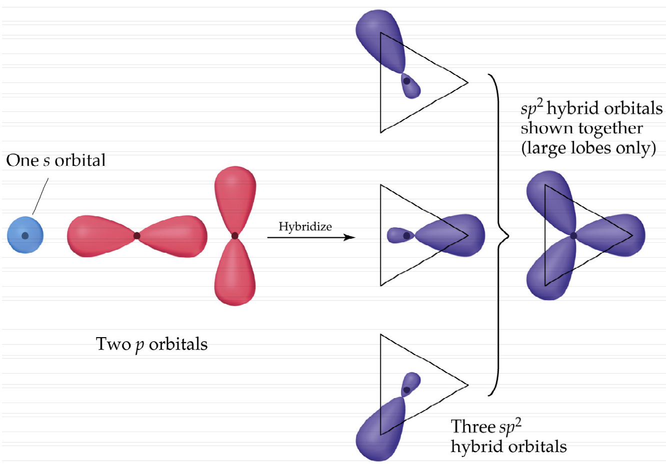
- π -bonding
  - Overlap above and under the axis between the two nuclei

Why CH_4 is tetrahedral?



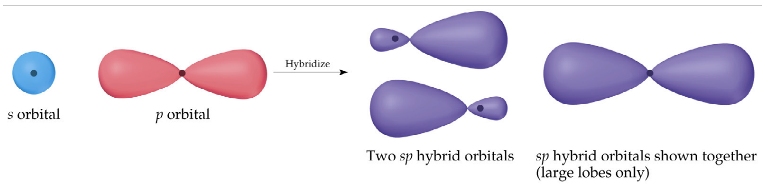
- sp^3 hybrid orbital

Hybridisation

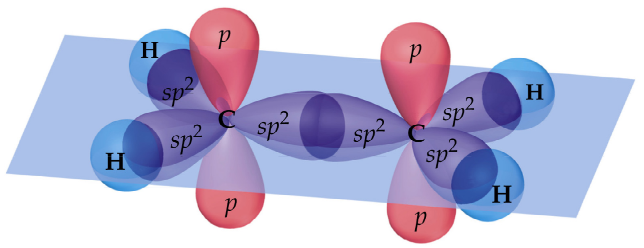


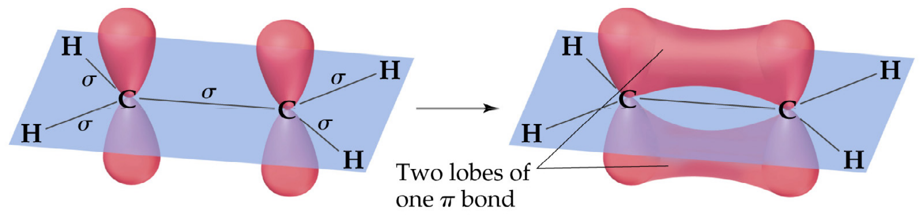
sp^2-hybrid orbital

sp-hybrid orbital

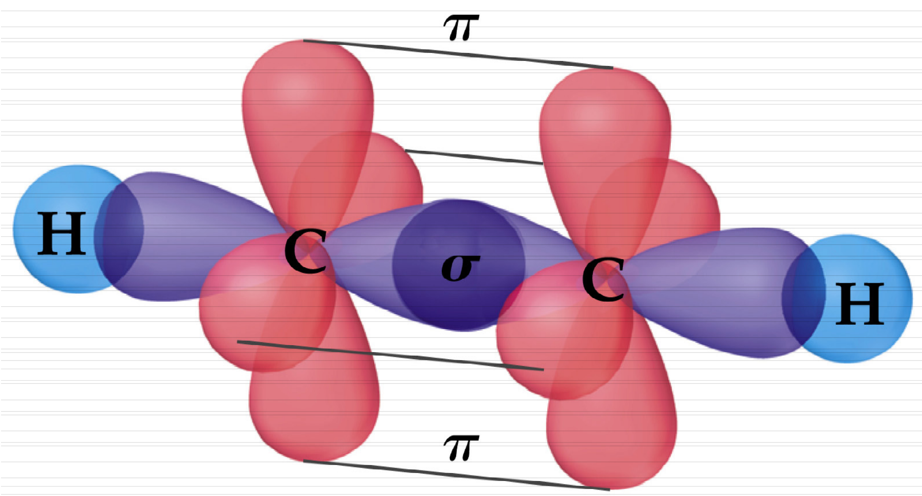


Bonding in CH_2CH_2

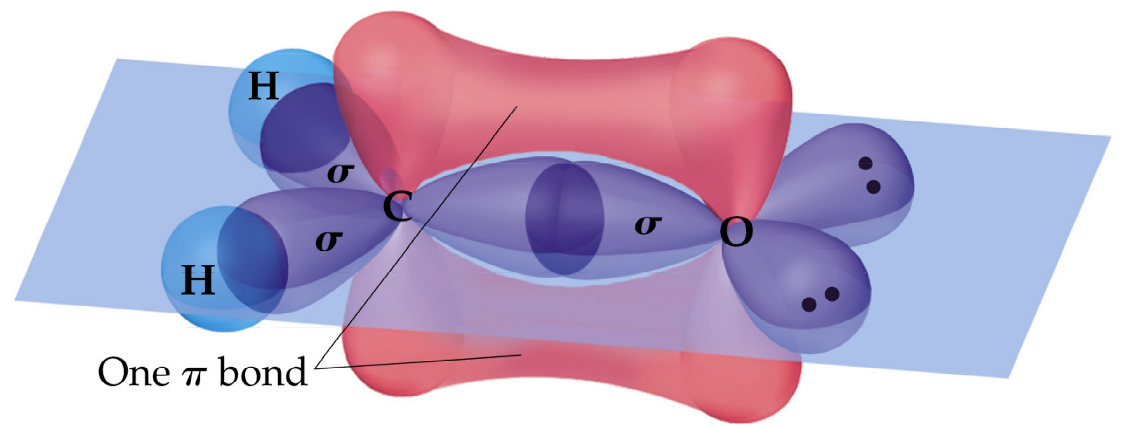




Bonding in CHCH

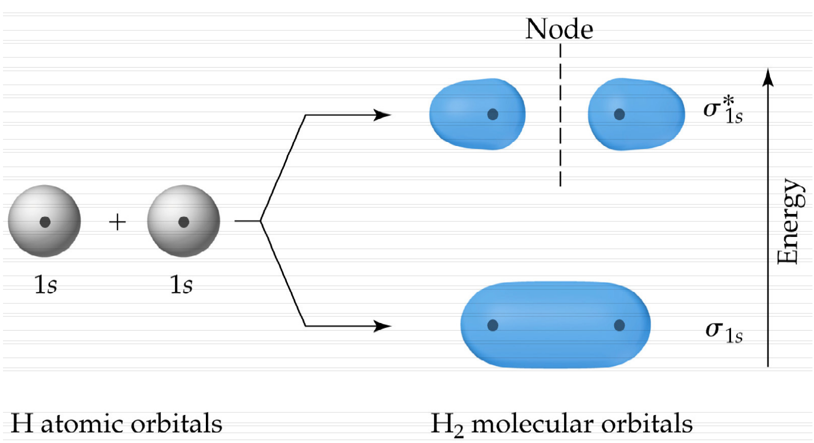


Which molecule is this?

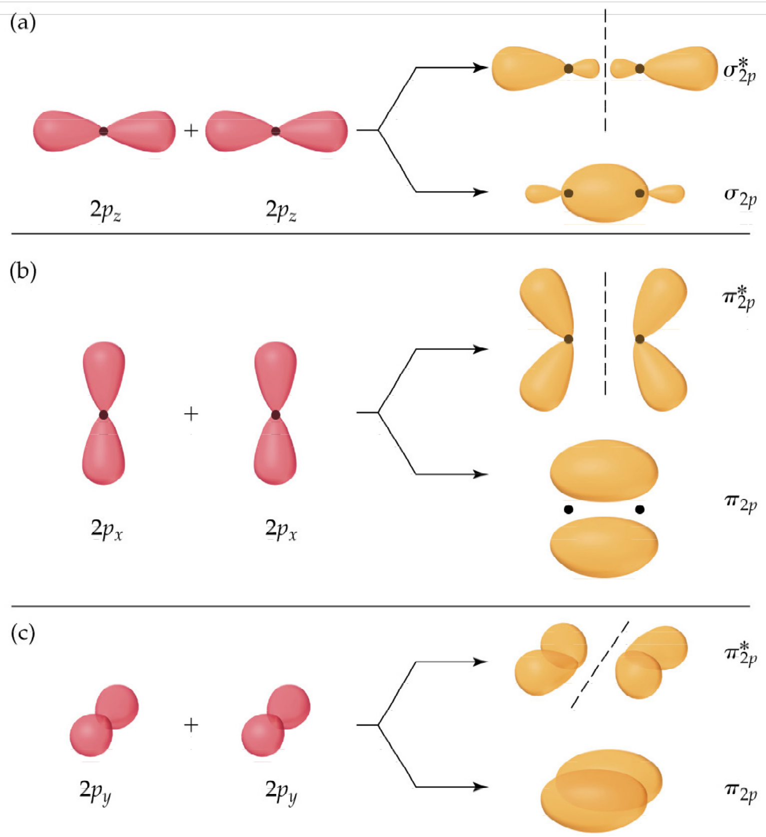


Molecule Orbital Model

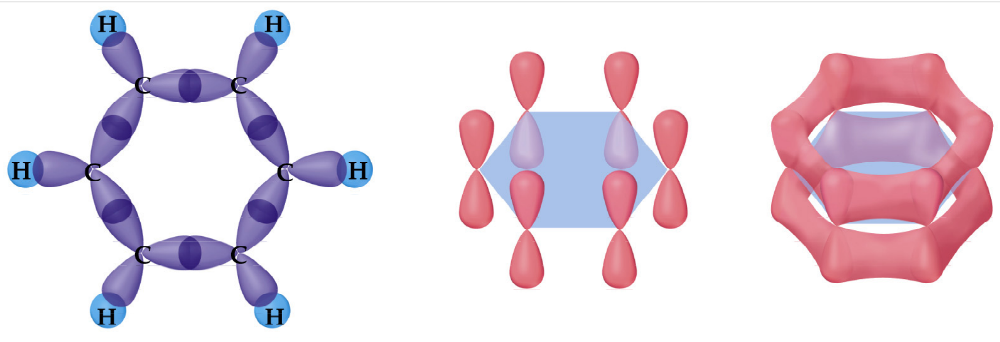
A molecular orbital (MO) is a linear combination of atomic orbitals



MO:s from p-orbitals

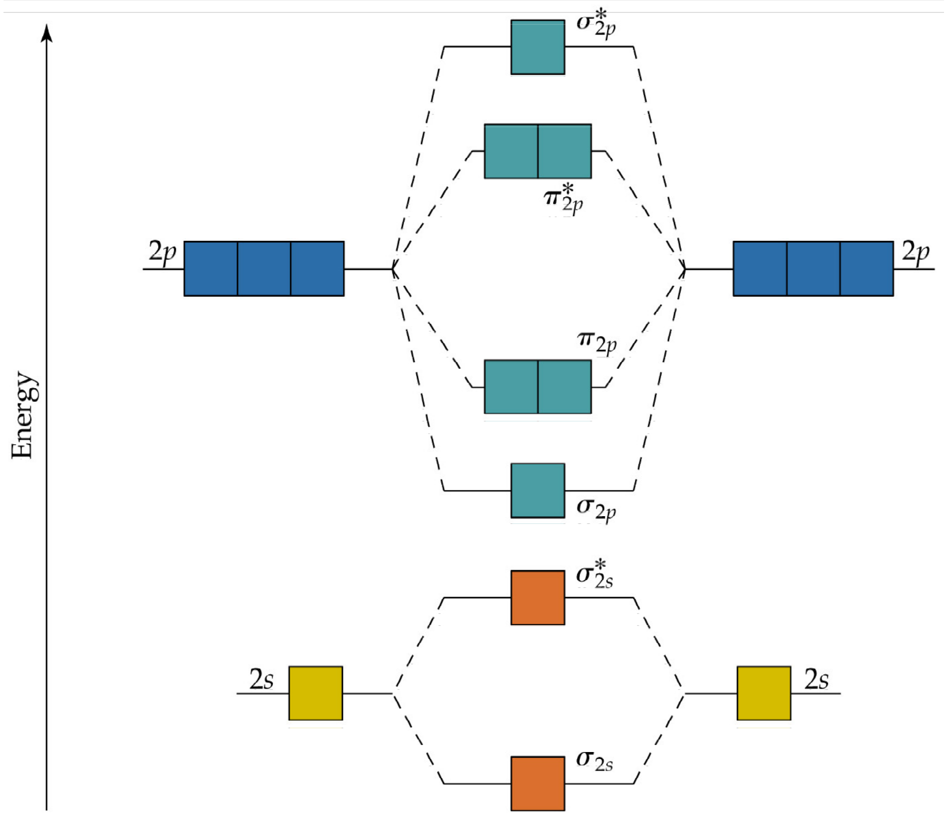


Bonding in benzene

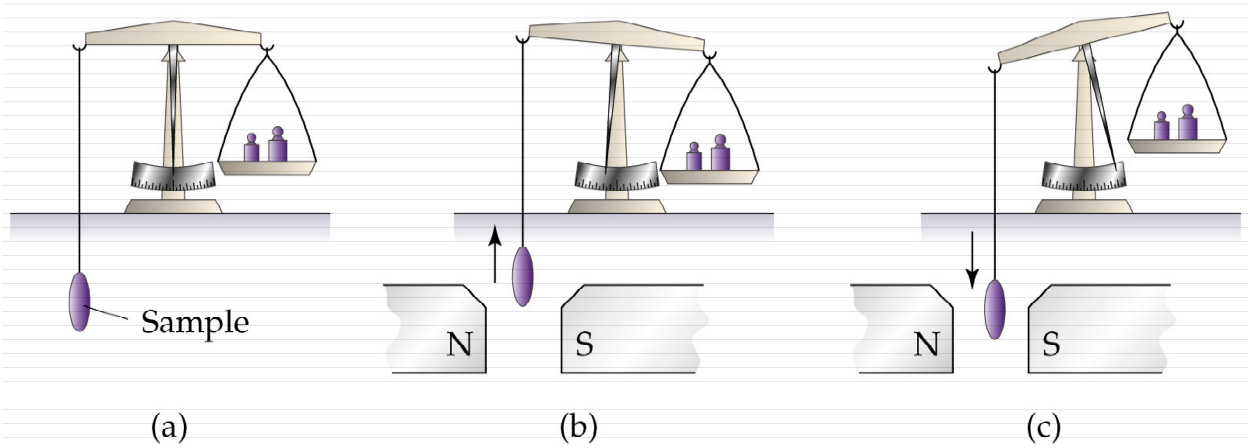


(a) σ bonds (b) $2p$ atomic orbitals (c) Delocalized π bonds

Valence Bond Theory can explain the resonance



	Large $2s$-$2p$ interaction				Small $2s$-$2p$ interaction		
	B_2	C_2	N_2		O_2	F_2	Ne_2
σ^*_{2p}				σ^*_{2p}			↑↓
π^*_{2p}				π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}			↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓	↑↓
Bond order	1	2	3		2	1	0
Bond enthalpy (kJ/mol)	290	620	941		495	155	—
Bond length (Å)	1.59	1.31	1.10		1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic		Paramagnetic	Diamagnetic	—



Diamagnetic **Parmagnetic**

Summary

- Atomic Orbitals
- Electron distributions
- Molecular Orbitals
- Intermolecular forces
  - Bonding (Ionic, Covalent, Metallic)
  - Lewis Structures
    - Form/Shape of molecules
    - Dipole Forces - Polarity
- Behavior in Magnetic Field