

CY121

Inorganic & Physical Chemistry

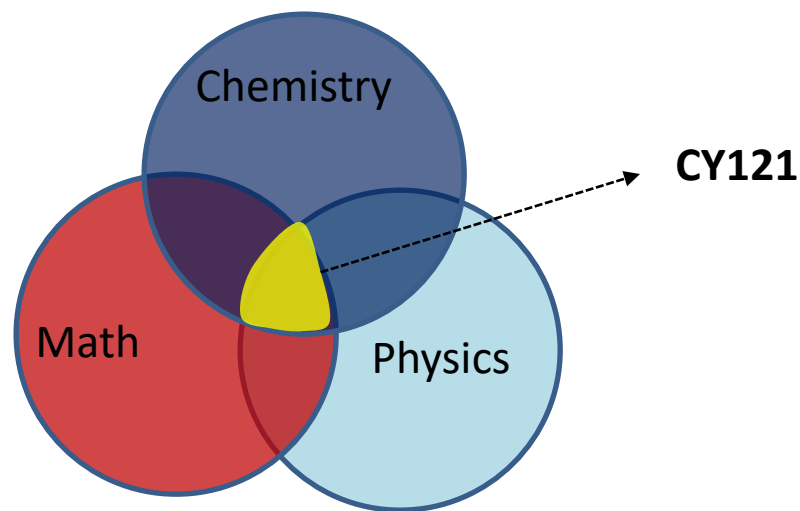
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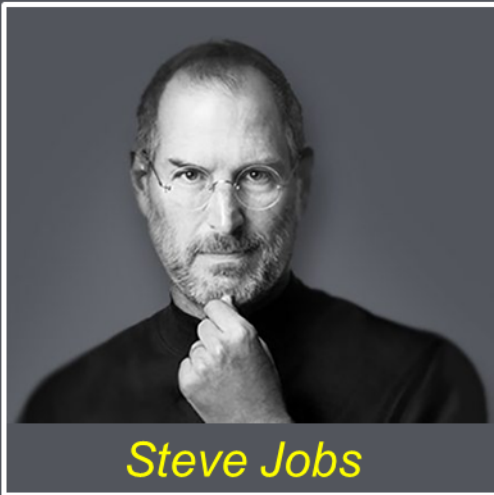


Unit I:

Chemical Bonding

- Bonding Theory :
 - Valence Bond Theory &
 - Molecular Orbital Theory;
- Symmetries in Molecular Orbitals.
- MO Diagrams of Homonuclear Nuclei- N_2 , C_2 , B_2 .
- MO Diagrams of NH_3 , H_2O , CH_4 and Metal Complexes,

Organization of Teaching Material



Steve Jobs

1955 –2011

The most powerful person in the world is the storyteller. The storyteller sets the vision, values and agenda of an entire generation that is to come.

CHEMISTRY

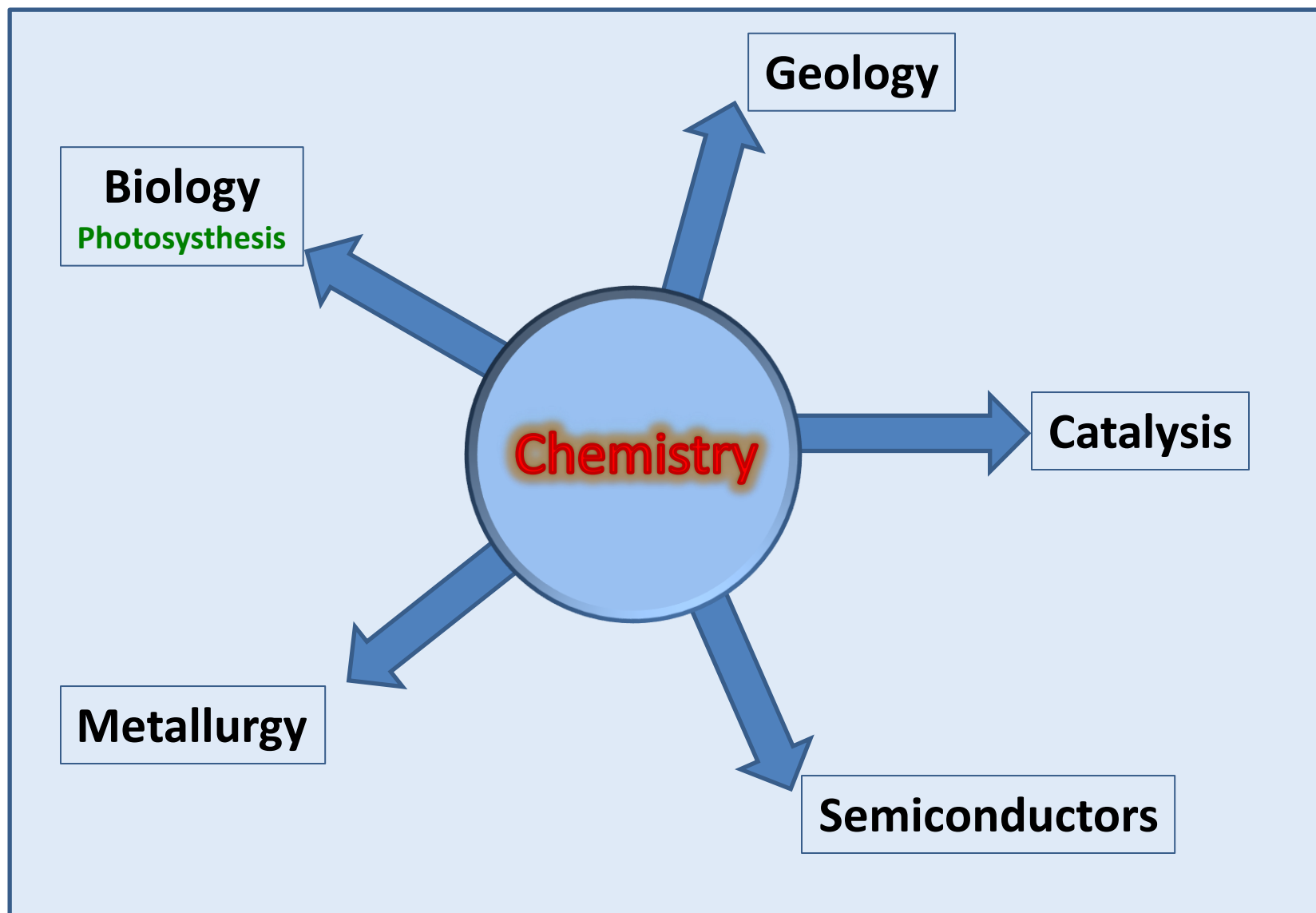


Antoine-Laurent de Lavoisier

Father of Modern Chemistry

Lavoisier discovered that water is made from hydrogen and oxygen and that air is made from oxygen and nitrogen.

Why should you learn Chemistry ?



Why should you learn Chemistry ?

"In inorganic chemistry everything is super"

Prof. W. Beck, Munich, 1986

| | |
|-------------------|--|
| super-expensive | <ul style="list-style-type: none">• Gold• Platinum• Diamonds• Promethium |
| super-corrosive | <ul style="list-style-type: none">• Ozone (O_3) ignites organic materials immediately. Very toxic• Fluorine• ClF_3 |
| super-explosive | <ul style="list-style-type: none">• NI_3• Fulminates• XeO_3 forms, whenever Xenon fluorides are hydrolyzed. It explodes violently in a very unpredictable fashion. |
| super-complicated | <ul style="list-style-type: none">• Structure and Bonding Inorganic compounds are examples of unusual bonding situations. Delocalized bonding such as in clusters, semiconductors and metals is the rule rather than the exception. |
| super-coordinated | High coordination numbers (organic carbon: 1-5) are common: <ul style="list-style-type: none">• IF_7 (CN = 7)• $[ReH_9]^{2-}$ (CN = 9)• $U(COT)_2$ (CN = 16) |

Why should you learn Chemistry ?

"In inorganic chemistry everything is super"

Prof. W. Beck, Munich, 1986

| | |
|--------------------|--|
| super-acidic | <ul style="list-style-type: none">• Magic Acid $\text{HF} + \text{SbF}_5 \rightarrow [\text{H}_2\text{F}]^+ + [\text{SbF}_6]^-$ protonates methane and is probably the strongest acid known. |
| super-conducting | <ul style="list-style-type: none">• Hg• Nb_3Ge• $\text{YBa}_2\text{La}_3\text{CuO}_7$• Most "high-tech" materials (semiconductors, superconductors, wave guides optoelectronic materials etc.) are inorganic |
| super-hard | <ul style="list-style-type: none">• Diamond (5600 Vickers hardness)• Cubic boron nitride• Ti-B-C-N, Vickers Hardness = 6000) |
| super high-melting | <ul style="list-style-type: none">• TaC, m. p. = 3780 °C There is an unabated race for materials that can withstand extreme temperatures and / or corrosive environment. Applications are the coating of cutting tools, motor parts, ball bearings etc. |
| super-clean | <ul style="list-style-type: none">• Si 99.999999 %• Semiconductors |
| super-selective | <ul style="list-style-type: none">• Catalysts (homogeneous and heterogeneous) |

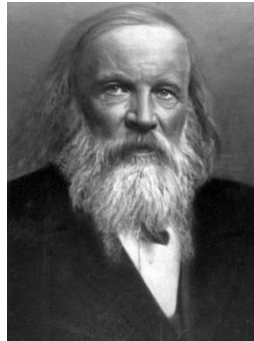
Periodic Table

Systematic variation of the properties of chemical elements depend upon the electronic structure of the atom.


The diagram illustrates the periodic table with the following features:

- Groups:** Labeled at the top as I, II, III, IV, V, VI, VII, VIII (18).
- Periods:** Labeled on the right as 1, 2, 3, 4, 5, 6, 7.
- Blocks:**
 - s block:** Groups 1 and 2.
 - d block:** Groups 3 through 10.
 - p block:** Groups 13 through 18.
 - f block:** Lanthanides and Actinides series shown below the main table.
- Labels:**
 - Transition metals:** Indicated in green text above the d-block.
 - Main group elements (s,p):** Indicated in black text above the s and p blocks.
 - Non-metal:** Indicated in red text above the top-right portion of the p-block.
 - Elements:** Specific elements are labeled in blue: H, B, Al, Si, Ge, As, Sb, Te, Po, At.
 - Lanthanides/Actinides:** Labeled on the right side of the f-block.

Periodic Table



Dimitrii Mendeleev

| | | | | | | | | | | | | | | | | | | | |
|--|---|--|--|---|---|--|---|---|--|---|--|---|--|---|---|--|---|---|--|
| <div>hydrogen 1 H 1.0079</div> | | <div></div> <div>Dimitrii Mendeleev</div> | | | | | | | | | | | | | | | | <div>helium 2 He 4.0026</div> | |
| <div>lithium 3 Li 6.941</div> | <div>beryllium 4 Be 9.0122</div> | | | | | | | | | | | <div>boron 5 B 10.811</div> | <div>carbon 6 C 12.011</div> | <div>nitrogen 7 N 14.007</div> | <div>oxygen 8 O 15.999</div> | <div>fluorine 9 F 18.998</div> | <div>neon 10 Ne 20.180</div> | | |
| <div>sodium 11 Na 22.990</div> | <div>magnesium 12 Mg 24.305</div> | | | | | | | | | | | <div>aluminium 13 Al 26.982</div> | <div>silicon 14 Si 28.086</div> | <div>phosphorus 15 P 30.974</div> | <div>sulfur 16 S 32.065</div> | <div>chlorine 17 Cl 35.453</div> | <div>argon 18 Ar 39.948</div> | | |
| <div>potassium 19 K 39.098</div> | <div>calcium 20 Ca 40.078</div> | <div>scandium 21 Sc 44.956</div> | <div>titanium 22 Ti 47.867</div> | <div>vanadium 23 V 50.942</div> | <div>chromium 24 Cr 51.996</div> | <div>manganese 25 Mn 54.938</div> | <div>iron 26 Fe 55.845</div> | <div>cobalt 27 Co 58.933</div> | <div>nickel 28 Ni 58.693</div> | <div>copper 29 Cu 63.546</div> | <div>zinc 30 Zn 65.39</div> | <div>gallium 31 Ga 69.723</div> | <div>germanium 32 Ge 72.61</div> | <div>arsenic 33 As 74.922</div> | <div>selenium 34 Se 78.96</div> | <div>bromine 35 Br 79.904</div> | <div>krypton 36 Kr 83.80</div> | | |
| <div>rubidium 37 Rb 85.468</div> | <div>strontium 38 Sr 87.62</div> | <div>yttrium 39 Y 88.906</div> | <div>zirconium 40 Zr 91.224</div> | <div>niobium 41 Nb 92.906</div> | <div>molybdenum 42 Mo 95.94</div> | <div>technetium 43 Tc [98]</div> | <div>ruthenium 44 Ru 101.07</div> | <div>rhodium 45 Rh 102.91</div> | <div>palladium 46 Pd 106.42</div> | <div>silver 47 Ag 107.87</div> | <div>cadmium 48 Cd 112.41</div> | <div>indium 49 In 114.82</div> | <div>tin 50 Sn 118.71</div> | <div>antimony 51 Sb 121.76</div> | <div>tellurium 52 Te 127.60</div> | <div>iodine 53 I 126.90</div> | <div>xenon 54 Xe 131.29</div> | | |
| <div>caesium 55 Cs 132.91</div> | <div>barium 56 Ba 137.33</div> | <div>57-70 ★</div> | <div>lutetium 71 Lu 174.97</div> | <div>hafnium 72 Hf 178.49</div> | <div>tantalum 73 Ta 180.95</div> | <div>tungsten 74 W 183.84</div> | <div>rhenium 75 Re 186.21</div> | <div>osmium 76 Os 190.23</div> | <div>iridium 77 Ir 192.22</div> | <div>platinum 78 Pt 195.08</div> | <div>gold 79 Au 196.97</div> | <div>mercury 80 Hg 200.59</div> | <div>thallium 81 Tl 204.38</div> | <div>lead 82 Pb 207.2</div> | <div>bismuth 83 Bi 208.98</div> | <div>polonium 84 Po [209]</div> | <div>astatine 85 At [210]</div> | <div>radon 86 Rn [222]</div> | |
| <div>francium 87 Fr [223]</div> | <div>radium 88 Ra [226]</div> | <div>89-102 ★ ★</div> | <div>lawrencium 103 Lr [262]</div> | <div>rutherfordium 104 Rf [261]</div> | <div>dubnium 105 Db [262]</div> | <div>seaborgium 106 Sg [266]</div> | <div>bohrium 107 Bh [264]</div> | <div>hassium 108 Hs [269]</div> | <div>meitnerium 109 Mt [268]</div> | <div>ununnitium 110 Uun [271]</div> | <div>unununium 111 Uuu [272]</div> | <div>ununbium 112 Uub [277]</div> | <div>ununquadium 114 Uuq [289]</div> | | | | | | |

| | | | | | | | | | | | | | |
|--|--------------------------------------|---|--|--|---------------------------------------|---------------------------------------|---|---------------------------------------|---|---|--------------------------------------|--|--|
| lanthanum 57 La 138.91 | cerium 58 Ce 140.12 | praseodymium 59 Pr 140.91 | neodymium 60 Nd 144.24 | promethium 61 Pm [145] | samarium 62 Sm 150.36 | europium 63 Eu 151.96 | gadolinium 64 Gd 157.25 | terbium 65 Tb 158.93 | dysprosium 66 Dy 162.50 | holmium 67 Ho 164.93 | erbium 68 Er 167.26 | thulium 69 Tm 168.93 | ytterbium 70 Yb 173.04 |
| actinium 89 Ac [227] | thorium 90 Th 232.04 | protactinium 91 Pa 231.04 | uranium 92 U 238.03 | neptunium 93 Np [237] | plutonium 94 Pu [244] | americium 95 Am [243] | curium 96 Cm [247] | berkelium 97 Bk [247] | californium 98 Cf [251] | einsteinium 99 Es [252] | fermium 100 Fm [257] | mendelevium 101 Md [258] | nobelium 102 No [259] |

* Lanthanide series

** Actinide series

Periodic Table

**In 1871 Mendeleev predicted
Existence of Eka-aluminium (because of its proximity to Al)
actual characteristics of Gallium**

| Property | Eka-aluminium | Gallium |
|------------------------------|---|--|
| atomic mass | 68 | 69.72 |
| density (g/cm ³) | 6.0 | 5.904 |
| melting point (°C) | Low | 29.78 |
| oxide's formula | Ea ₂ O ₃ (density: 5.5 g/cm ³) (soluble in both alkalis and acids) | Ga ₂ O ₃ (density: 5.88 g/cm ³) (soluble in both alkalis and acids) |
| chloride's formula | Ea ₂ Cl ₆ (volatile) | Ga ₂ Cl ₆ (volatile) |

IUPAC Nomenclature of Elements

with atomic number above 100

| Digit | Name | Abbreviation |
|-------|------|--------------|
| 0 | nil | n |
| 1 | un | u |
| 2 | bi | b |
| 3 | tri | t |
| 4 | quad | q |
| 5 | pent | p |
| 6 | hex | h |
| 7 | sept | s |
| 8 | oct | o |
| 9 | enn | e |

For example:

114 → Un-un-quad-ium → Uuq

118 → Un-un-oct-ium → Uuo

Building Up the Periodic Table: The Basis

1. Various quantum numbers

2. Hund's Rule:

When more than one orbital has the same energy (e.g. p_x , p_y , p_z), electrons occupy separate orbitals and do so with parallel spins.

3. Pauli (Exclusion) Principle

No more than two electrons shall occupy a single orbital and, if two do occupy a single orbital, then their spins must be paired. or

"no two electrons can have the same four quantum numbers"

4. The order of orbitals for a given quantum number depends on

Shielding Effects (Z^*)

Penetration of orbitals

$$3s < 3p < 3d$$

Electronic Configuration

| | |
|-------|------------------|
| H | $1s^1$ |
| He | $1s^2$ |
| Li | $1s^2 2s^1$ |
| | |
| F | $1s^2 2s^2 2p^5$ |
| Ne | $1s^2 2s^2 2p^6$ |

Four Quantum Numbers

The principal quantum number, $n = 1, 2, \dots$,
determines the energy E of the electron in the atom.

The angular momentum quantum number, $\ell = 0, 1, 2, \dots, n-1$,
determines the orbital angular momentum of the electron.

| | | |
|------------|---|-----------------------|
| $\ell = 0$ | s | “sharp” |
| $\ell = 1$ | p | “principal” |
| $\ell = 2$ | d | “diffuse” |
| $\ell = 3$ | f | “fundamental or fine” |

The magnetic quantum number, $m = 0, \pm 1, \dots, \pm \ell$
determines the amount of angular momentum of the
electron around a particular axis.

The Spin quantum number, $s = \pm 1/2$

Orbit *and* Orbital

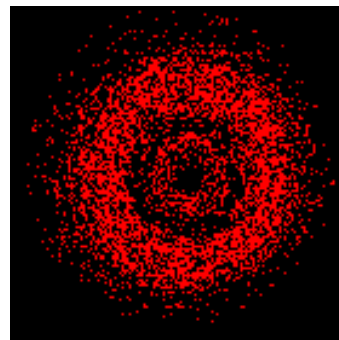
An **Orbit** is the path of an electron around the nucleus of an atom.

When a planet moves around the sun, you can plot a definite path for it which is called an orbit.

The impossibility of drawing orbits for electrons

The ***Heisenberg Uncertainty Principle*** says - that you can't know with certainty both where an electron is and where it's going next.

An **Orbital** is the three dimensional space where the probability of finding an electron around the nucleus is maximum. In other words, 'Orbital' refers to an electron's probable location.



Schrodinger equation for Hydrogen-like Atom

$$\left[-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hbar^2}{2mr^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + V(r) \right] \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

$$\psi(r, \theta, \phi) = R(r) \cdot P(\theta) \cdot F(\phi)$$

↑
Radial part

$Y_{l,m_l}(\theta, \phi)$ ← Angular part

$R(r)$

Solution exists iff

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

$P(\theta)$

Solution exists iff

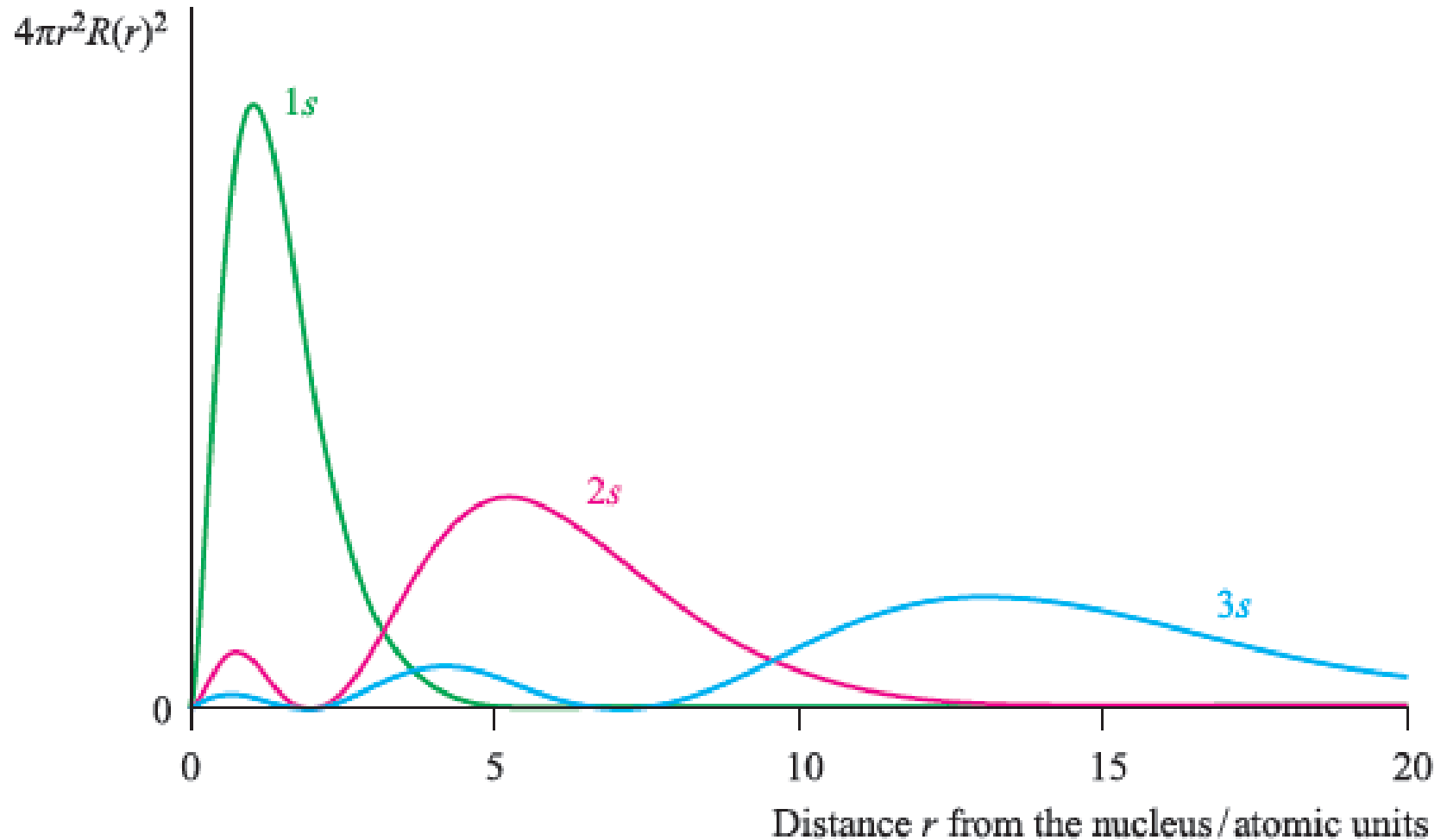
$\ell = 0, 1, 2, \dots, n-1$

$F(\phi)$

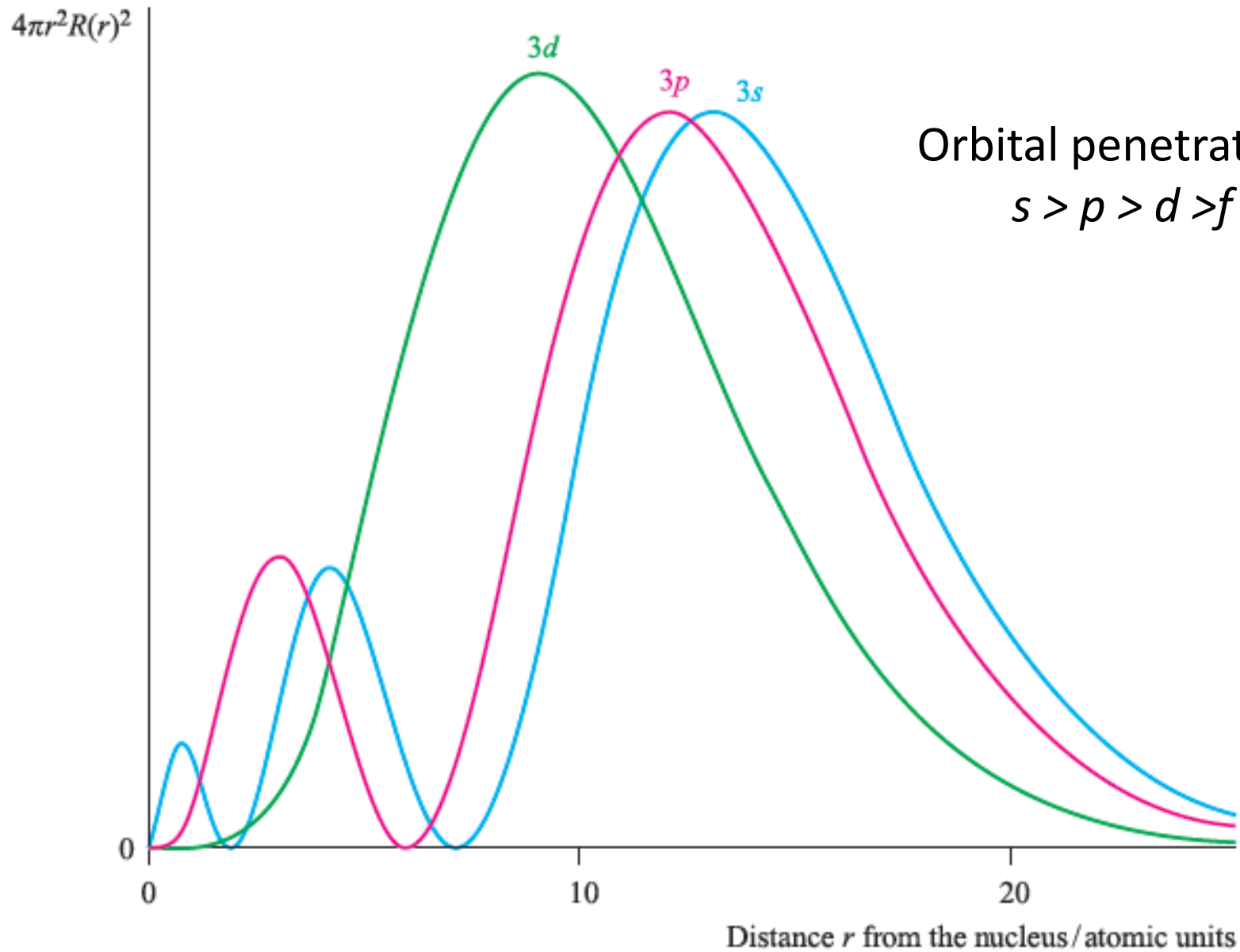
Solution exists iff

$m_l = -\ell, -\ell + 1, \dots, +\ell$

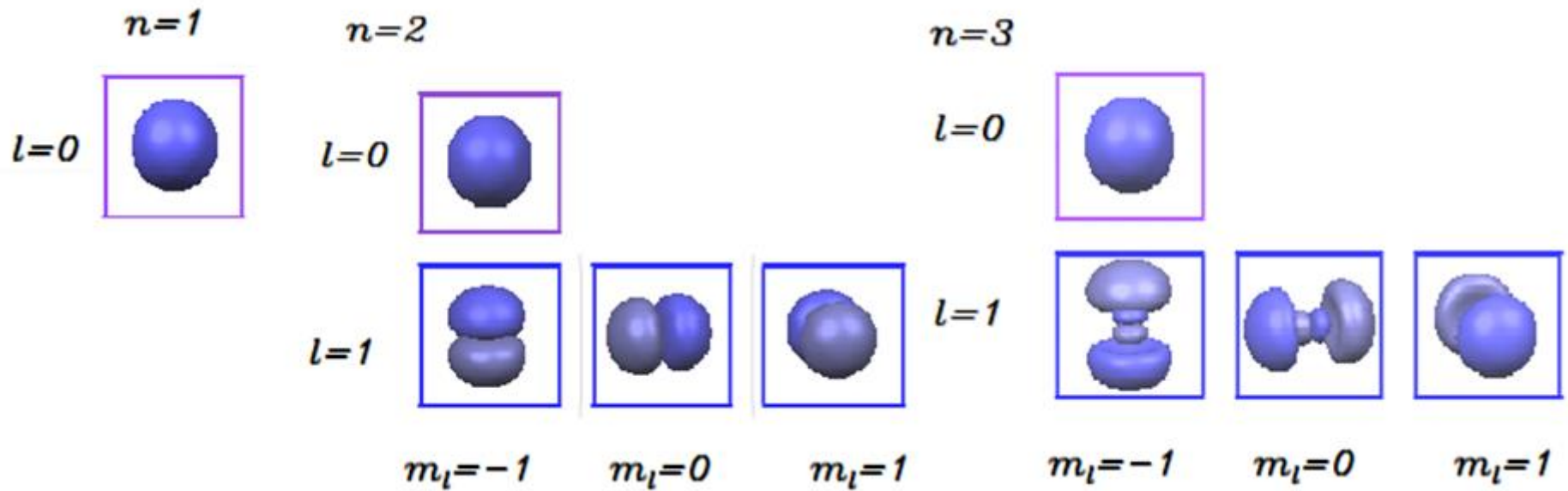
Distribution of Radial Probability density



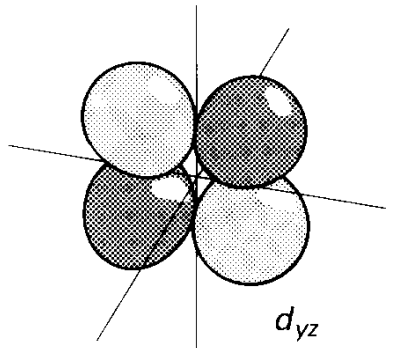
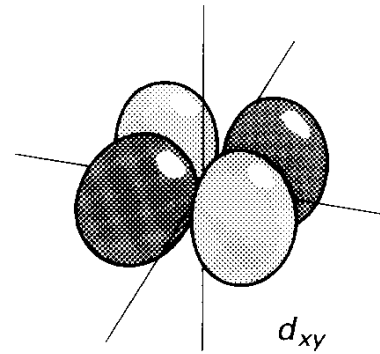
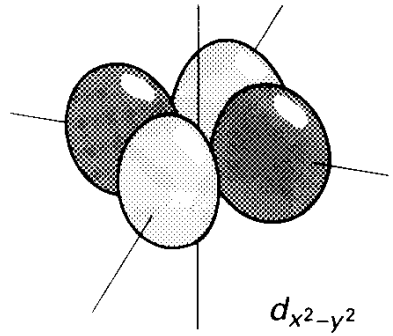
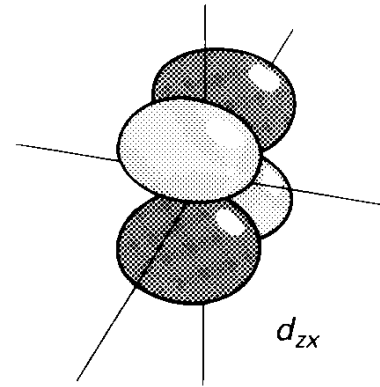
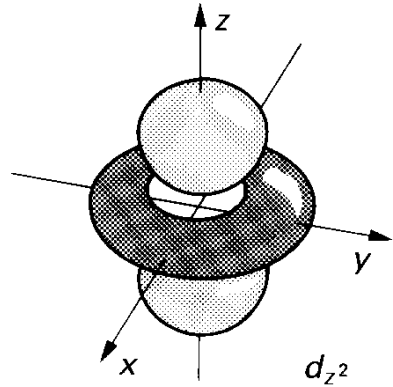
Distribution of Radial Probability density



s & p-type Orbitals

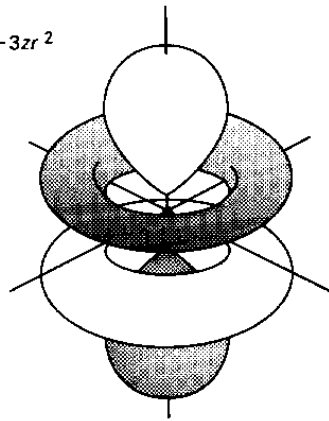


d -type Orbitals

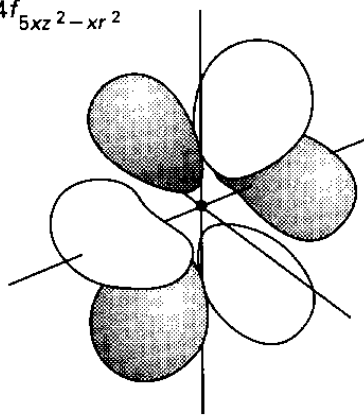


f-type Orbitals

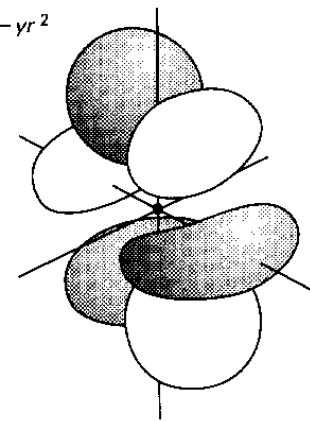
$$4f_{5z^3-3zr^2}$$



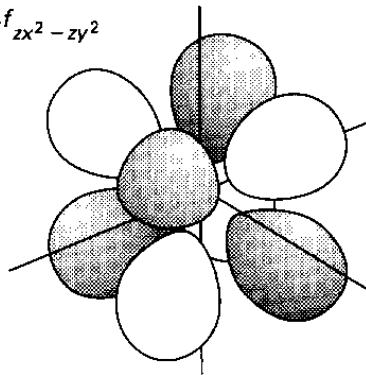
$$4f_{5xz^2-xr^2}$$



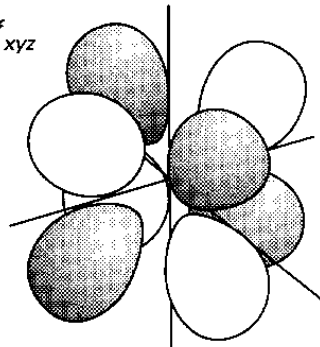
$$4f_{5yz^2-yr^2}$$



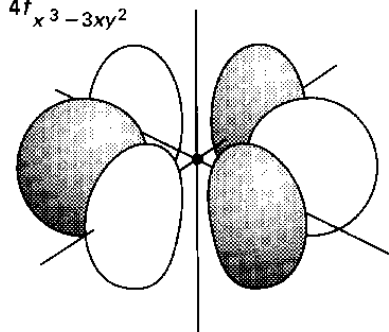
$$4f_{zx^2-zy^2}$$



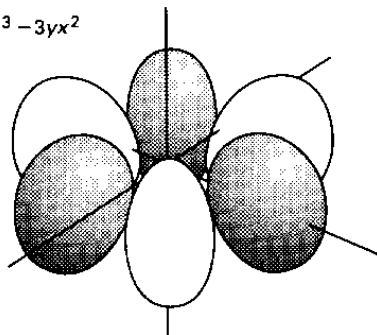
$$4f_{xyz}$$



$$4f_{x^3-3xy^2}$$



$$4f_{y^3-3yx^2}$$



Madelung's Rule

Energy increases with increasing $n + l$

For identical values of $n + l$, *energy* increases with increasing n

$$\begin{array}{ccccccccccc} 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < \dots \\ 1 & 2 & 3 & 3 & 4 & 4 & 5 & 5 & : (n + l) \end{array}$$

Reason: Shielding of the nuclear charge by the innermost electrons

Orbital penetration:

$$s > p > d > f$$

Slater's rules

Effective nuclear charges, Z_{eff} , experienced by electrons in different atomic orbitals may be estimated using *Slater's rules*. These rules are based on experimental data for electron promotion and ionization energies, and Z_{eff} is determined from the equation:

$$Z_{\text{eff}} = Z - S$$

where Z = nuclear charge, Z_{eff} = effective nuclear charge, S = screening (or shielding) constant.

Values of S may be estimated as follows:

1. Write out the electronic configuration of the element in the following order and groupings: $(1s)$, $(2s, 2p)$, $(3s, 3p)$, $(3d)$, $(4s, 4p)$, $(4d)$, $(4f)$, $(5s, 5p)$ etc.
2. Electrons in any group higher in this sequence than the electron under consideration contribute nothing to S .
3. Consider a particular electron in an ns or np orbital:
 - (i) Each of the other electrons in the (ns, np) group contributes $S = 0.35$.
 - (ii) Each of the electrons in the $(n - 1)$ shell contributes $S = 0.85$.
 - (iii) Each of the electrons in the $(n - 2)$ or lower shells contributes $S = 1.00$.
4. Consider a particular electron in an nd or nf orbital:
 - (i) Each of the other electrons in the (nd, nf) group contributes $S = 0.35$.
 - (ii) Each of the electrons in a lower group than the one being considered contributes $S = 1.00$.

An example of how to apply Slater's rules

Question: Confirm that the experimentally observed electronic configuration of K, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, is energetically more stable than the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$.

For K, $Z = 19$.

Applying Slater's rules, the effective nuclear charge experienced by the $4s$ electron for the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ is:

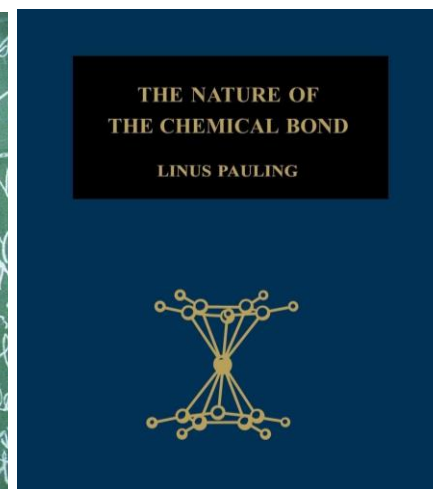
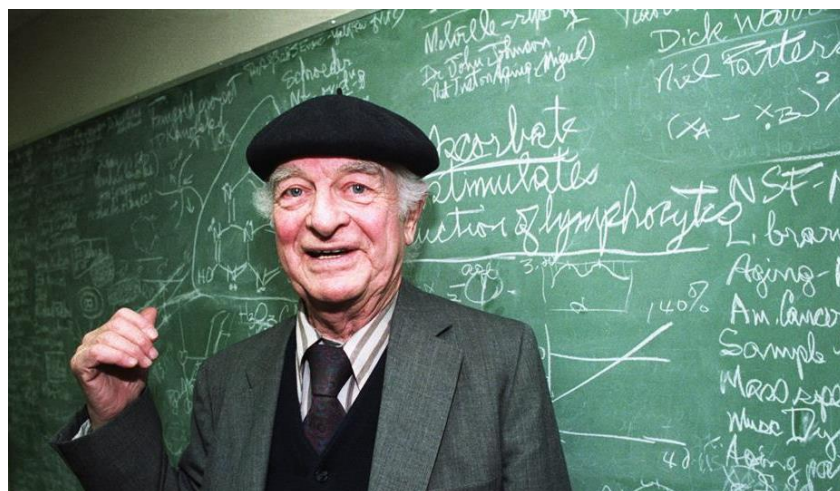
$$\begin{aligned}Z_{\text{eff}} &= Z - S \\&= 19 - [(8 \times 0.85) + (10 \times 1.00)] \\&= 2.20\end{aligned}$$

The effective nuclear charge experienced by the $3d$ electron for the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ is:

$$\begin{aligned}Z_{\text{eff}} &= Z - S \\&= 19 - (18 \times 1.00) \\&= 1.00\end{aligned}$$

Thus, an electron in the $4s$ (rather than the $3d$) atomic orbital is under the influence of a greater effective nuclear charge and in the ground state of potassium, it is the $4s$ atomic orbital that is occupied.

Chemical Bonding



Linus Carl Pauling

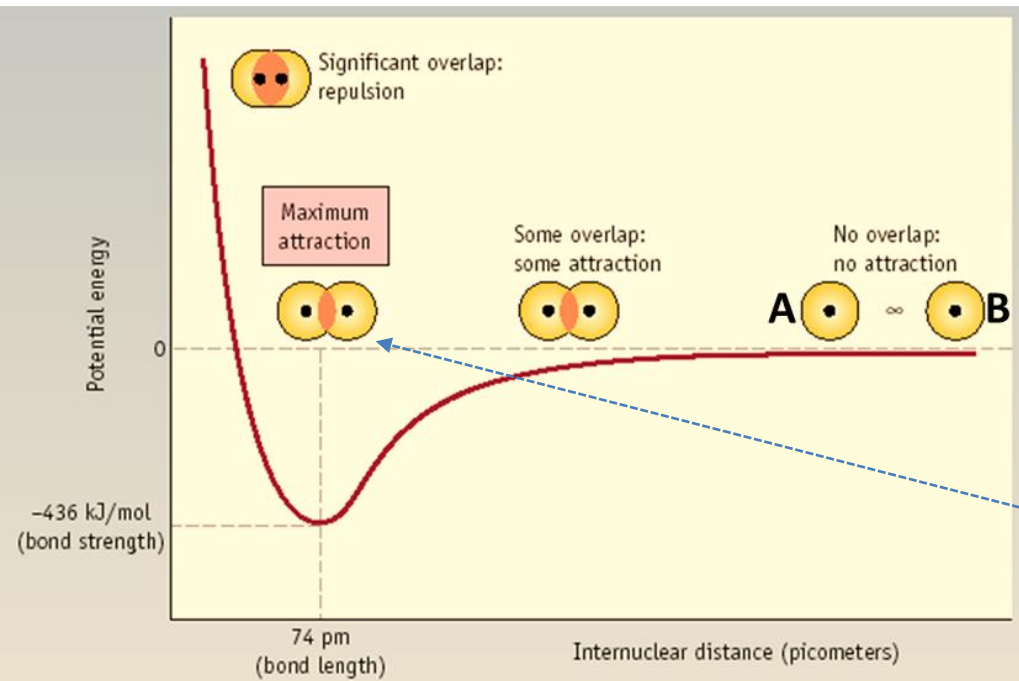
1901 –1994

Nobel Prize in Chemistry (1954)

Nobel Peace Prize (1962)

Valence Bond Theory

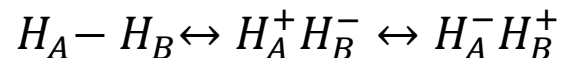
1,2 designate electrons number 1 & 2.



$$\psi = \psi_{A(1)}\psi_{B(2)}$$

Exchange Energy

$$\psi = \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}$$



$$\psi = \underbrace{\psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}}_{\text{Covalent}} + \underbrace{\lambda\psi_{A(1)}\psi_{A(2)} + \lambda\psi_{B(1)}\psi_{B(2)}}_{\text{Ionic}}$$

$$\psi = \psi_{cov} + \lambda\psi_{H^+H^-} + \lambda\psi_{H^-H^+} \quad \Rightarrow \quad \psi = (1 - \lambda)\psi_{cov} + \lambda\psi_{ion}$$

Linear Combination of ionic & covalent functions

Elementary Concepts

OCTET RULE: In forming compounds, atoms gain, lose, or share electrons to give a stable electron configuration characterized by 8 valence electrons.

FORMAL CHARGE: *is the charge calculated for an atom in a Lewis structure on the basis of an equal sharing of bonded electron pairs*

$$\text{Formal charge} = \text{Valence shell electrons} - \text{number of bonds} - \text{number of unshared electrons}$$

Resonance: Same atomic positions But differ in electron positions

- Resonance structures are not real.
- Resonance structures are not in equilibrium with each other.
- Resonance structures are not isomers.

Every Atom has electronic configuration



Atoms are the building-blocks of molecule

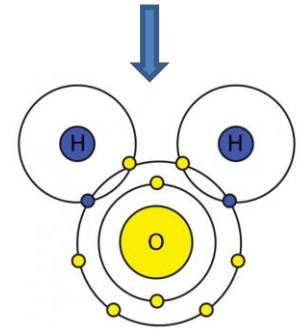
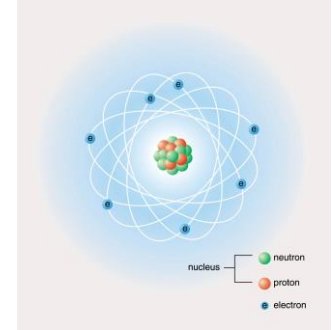


Molecules are the building block of materials

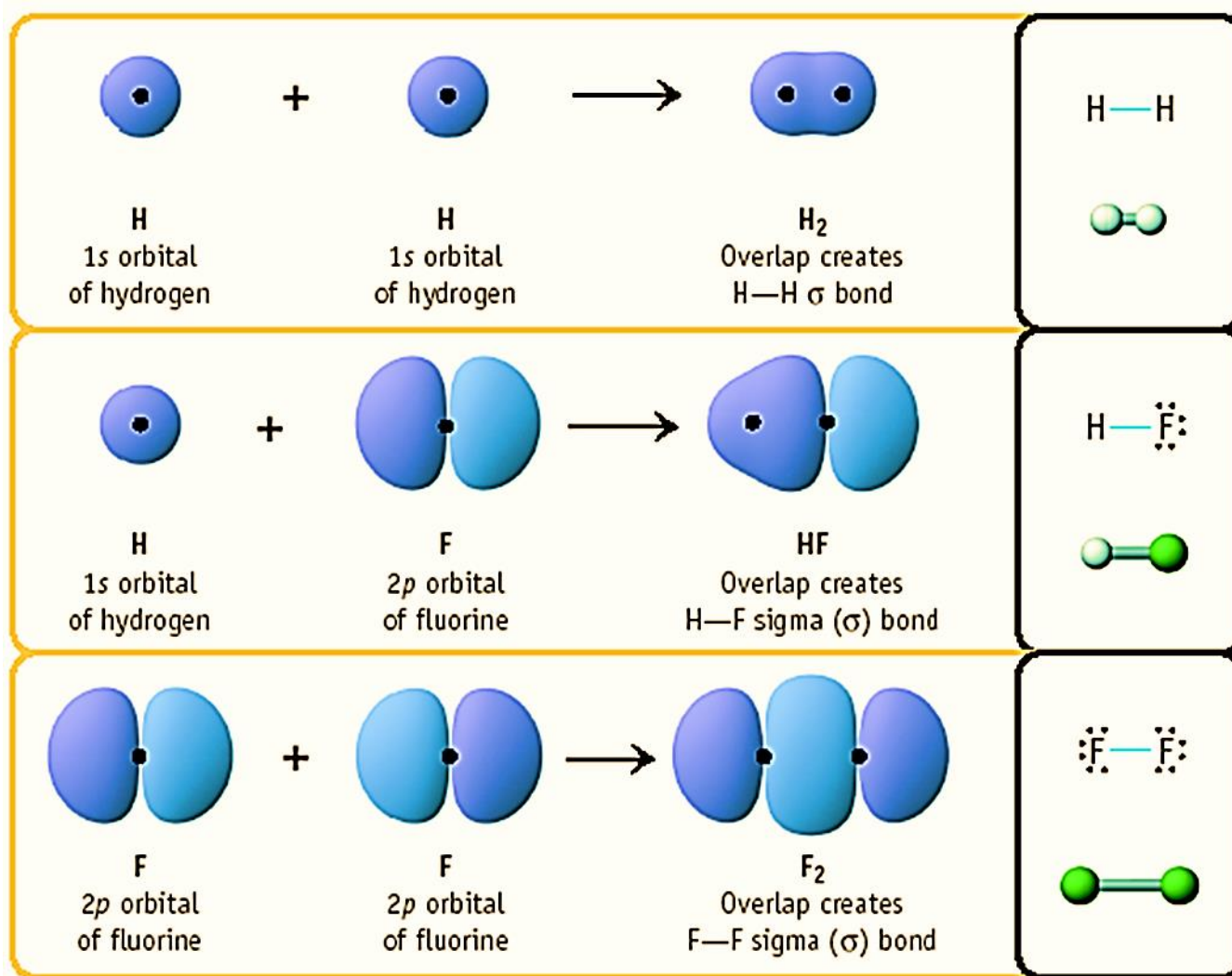


Electronics

Computer



Sigma bond formation



HYBRIDIZATION

Linear Combination of s and p orbital wave functions

$$\psi = a\psi_s + b\psi_p$$

sp hybrid $\left\{ \begin{array}{l} \psi_1 = N(\psi_s + \psi_{p_x}) \\ \psi_2 = N(\psi_s - \psi_{p_x}) \end{array} \right.$ N= Normalization Constant

sp² hybrid $\left\{ \begin{array}{l} \psi_1 = \frac{1}{\sqrt{3}}\psi_s + \sqrt{\frac{2}{3}}\psi_{p_x} \\ \psi_2 = \frac{1}{\sqrt{3}}\psi_s - \frac{1}{\sqrt{6}}\psi_{p_x} + \frac{1}{\sqrt{2}}\psi_{p_y} \\ \psi_3 = \frac{1}{\sqrt{3}}\psi_s - \frac{1}{\sqrt{6}}\psi_{p_x} - \frac{1}{\sqrt{2}}\psi_{p_y} \end{array} \right.$

sp³ hybrid $\left\{ \begin{array}{l} \psi_1 = 0.5(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}) \\ \psi_2 = 0.5(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}) \\ \psi_3 = 0.5(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z}) \\ \psi_4 = 0.5(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z}) \end{array} \right.$

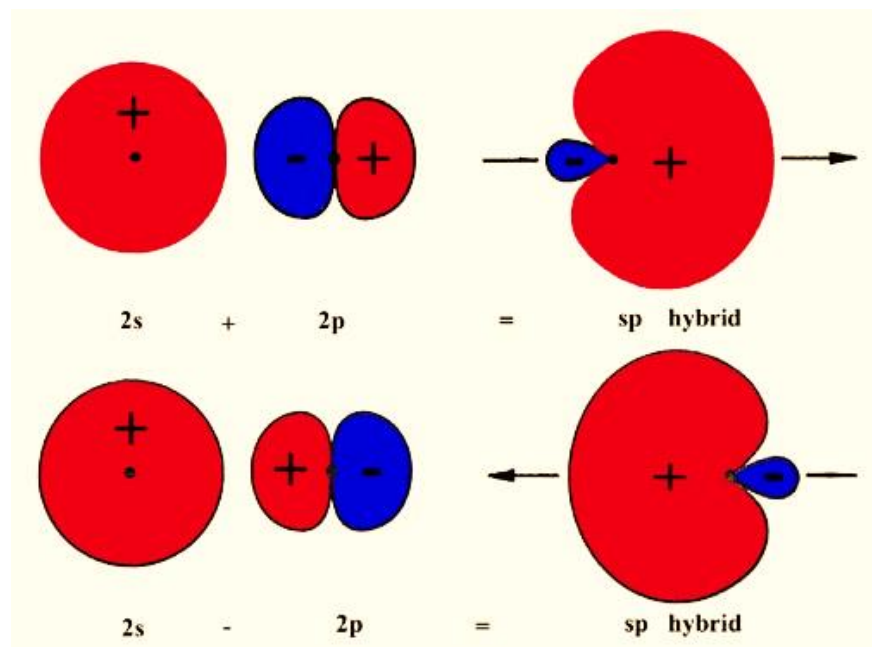
HYBRIDIZATION

Linear Combination of s and p orbital wave functions

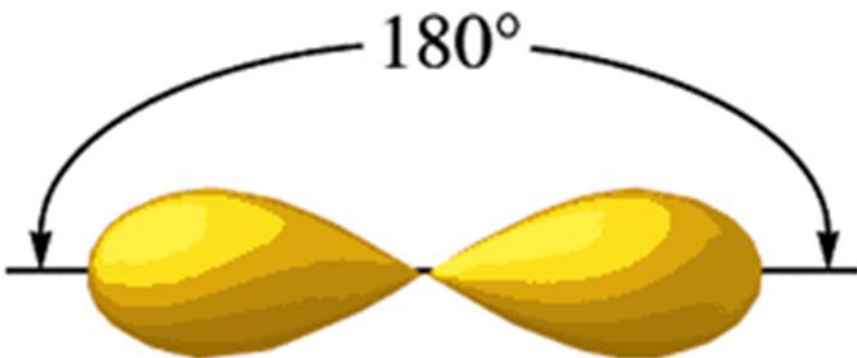
sp hybrid

$$\psi_1^{sp} = \frac{1}{\sqrt{2}} (\psi_s + \psi_{p_x})$$

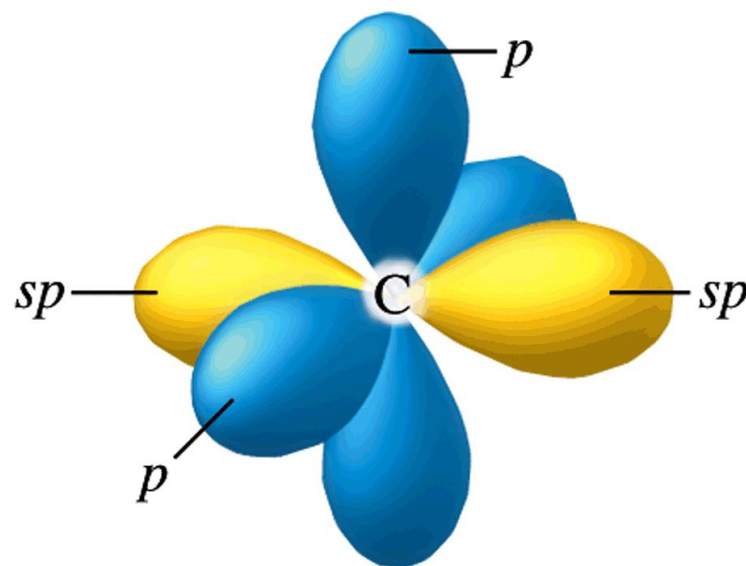
$$\psi_2^{sp} = \frac{1}{\sqrt{2}} (\psi_s - \psi_{p_x})$$



sp HYBRIDIZATION



The Orbitals of an sp hybridized carbon atom

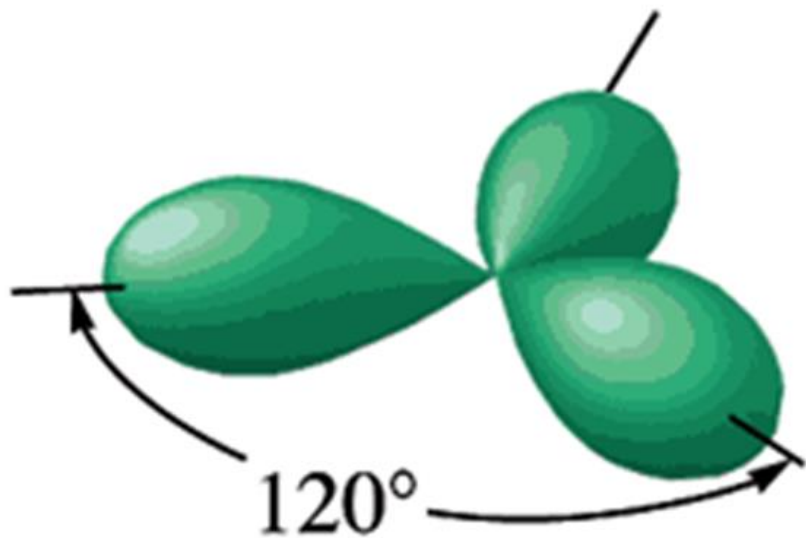


Electron Pair Geometry:

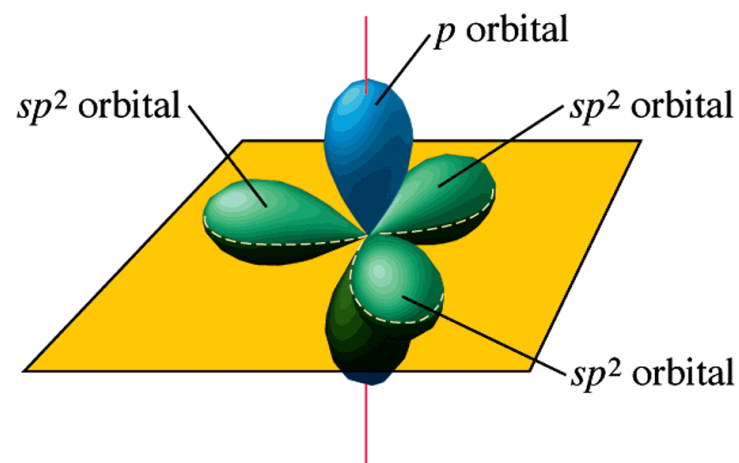
Linear



sp^2 HYBRIDIZATION

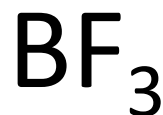


The Orbitals of an sp^2 hybridized carbon



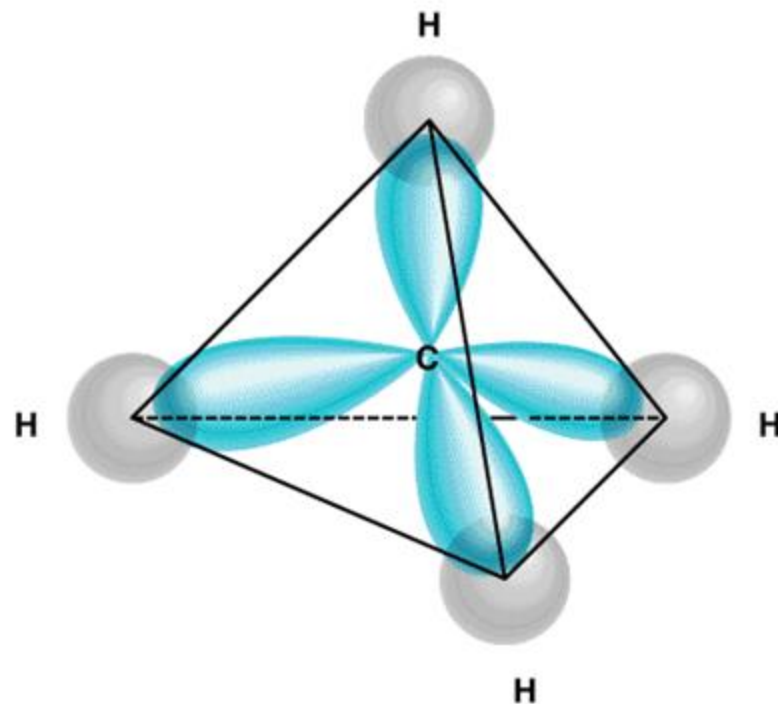
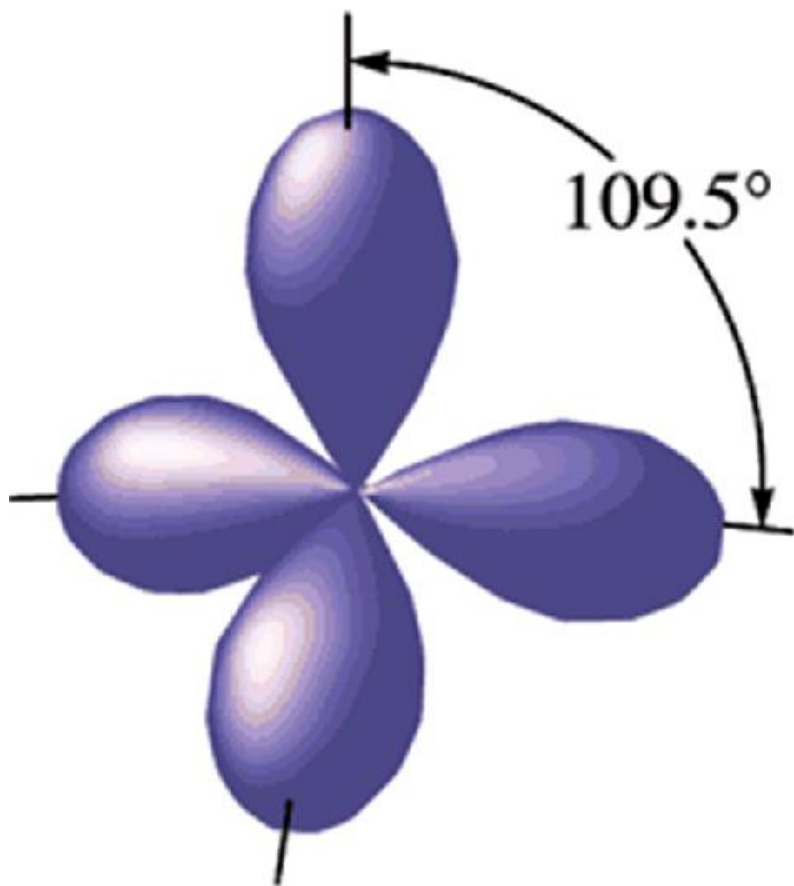
Electron Pair Geometry:

Trigonal Planar



sp^3 HYBRIDIZATION

The Orbitals of an sp^3 hybridized carbon

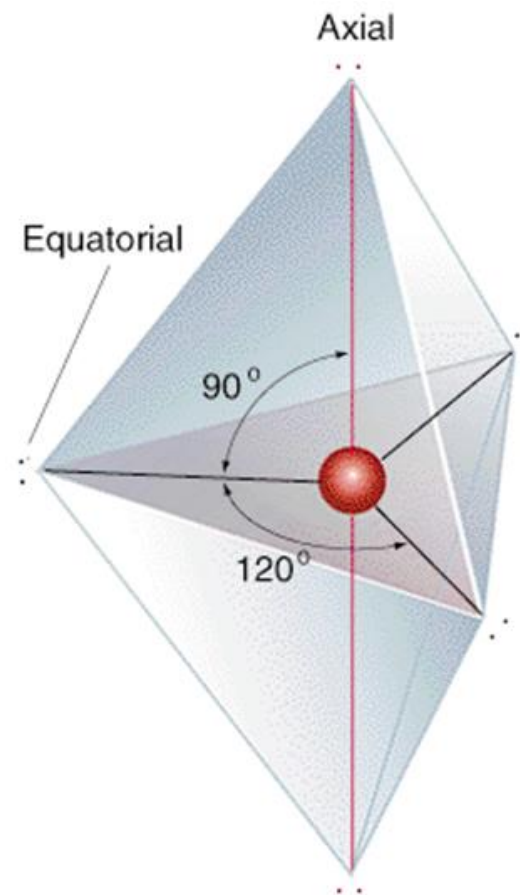
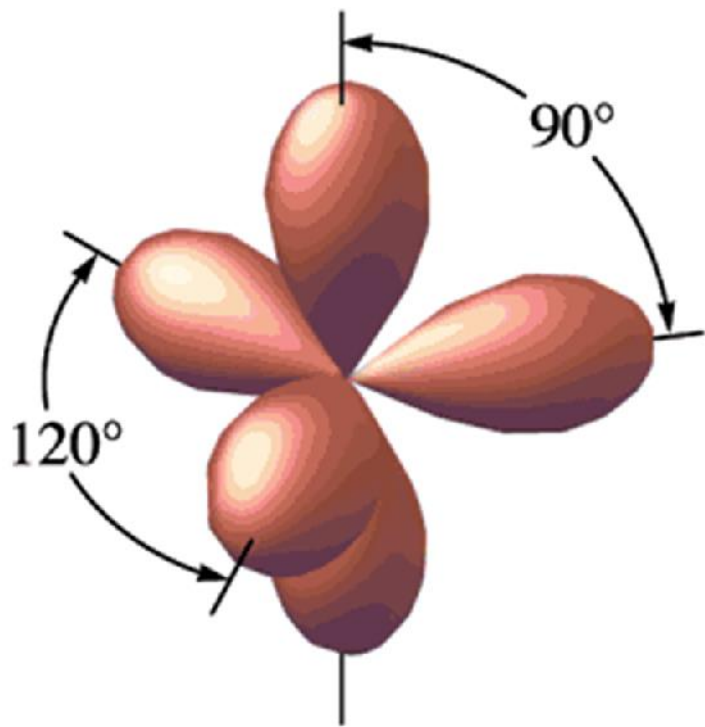


Electron Pair Geometry:

Tetrahedral



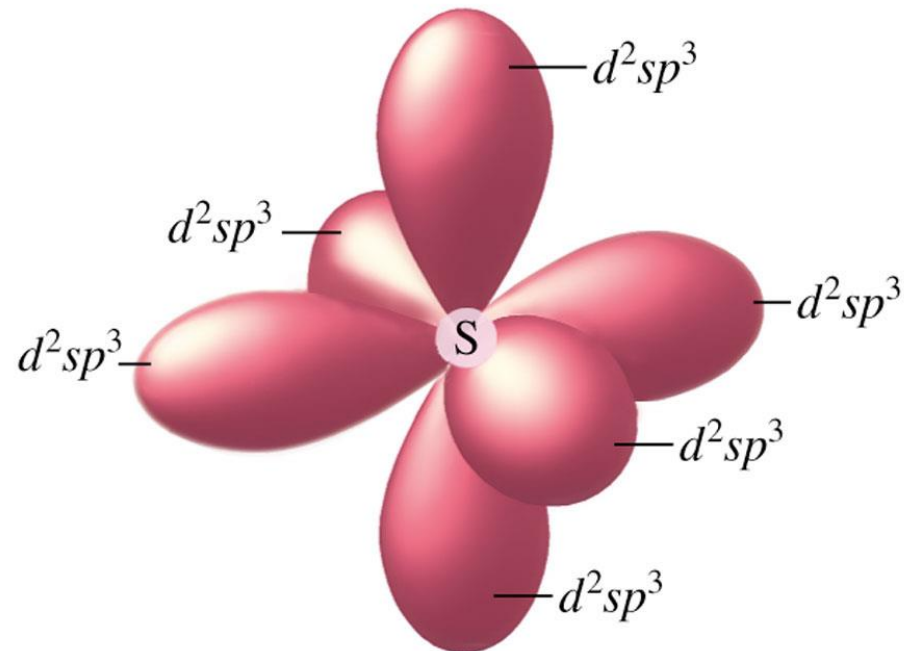
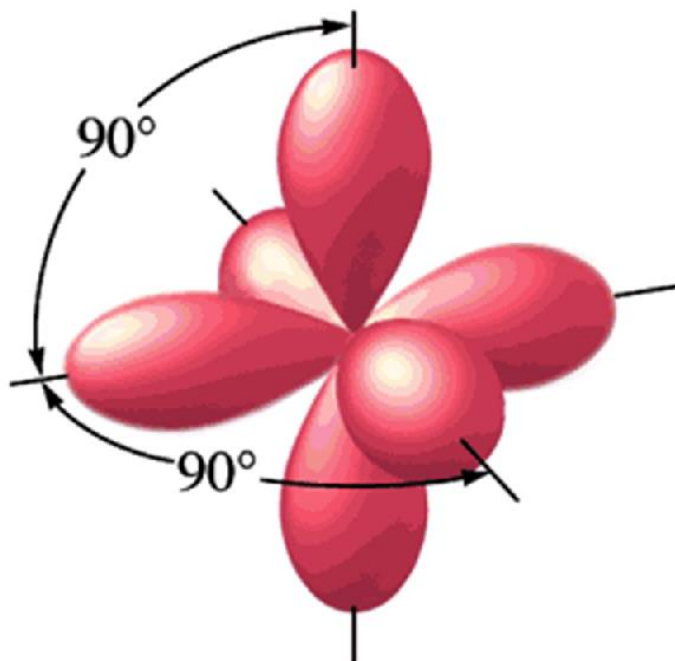
sp^3d HYBRIDIZATION



Electron Pair Geometry:
Trigonal bipyramidal



sp^3d^2 HYBRIDIZATION



Electron Pair Geometry:
Octahedral



Summary on Electron-pair Geometry

| No. of orbitals | Hybridization | Electron-pair Geometry | Example |
|-----------------|--------------------------------|------------------------|-------------------|
| 2 | sp | Linear | BeCl ₂ |
| 3 | sp ² | Trigonal Planar | BF ₃ |
| 4 | sp ³ | Tetrahedral | CH ₄ |
| 5 | sp ³ d | Trigonal Pyramidal | PCl ₅ |
| 6 | sp ³ d ² | Octahedral | SF ₆ |

VSEPR THEORY

Valence Shell Electron Pair Repulsion

How do we determine the shapes of molecules ?

- (1) Electron pairs repel each other and try to remain as far apart from one another as possible.

Repulsion strengths

lone pair -lone pair > lone pair e-bond pair > bond pair-bond pair

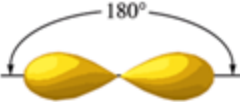
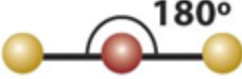
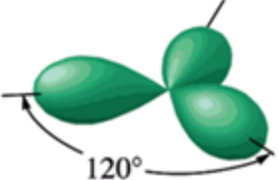
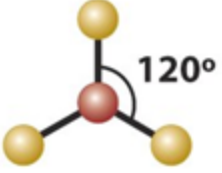
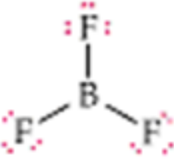
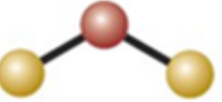
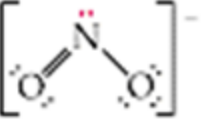
- (2) Molecular geometry is determined by the relative positions that electron pairs achieve after taking repulsions into account.
- (3) The arrangement of pairs about a central atom depends on the number of pairs that exist about the atom.

VSEPR Theory--Molecular Shapes

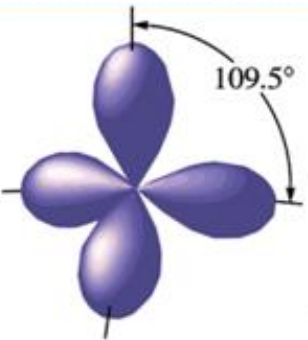
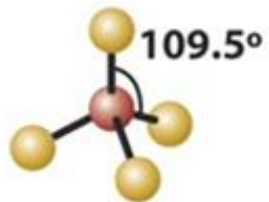
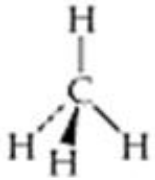


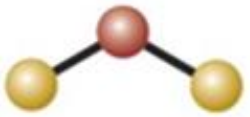

Rules for Predicting Molecular Geometry

1. Sketch the Lewis structure of the molecule or ion
2. Count the electron pairs and arrange them in the way that minimizes electron-pair repulsion.
3. Determine the position of the atoms from the way the electron pairs are shared.
4. Determine the name of the molecular structure from the position of the atoms.
5. Double or triple bonds are counted as one bonding pair when predicting geometry.

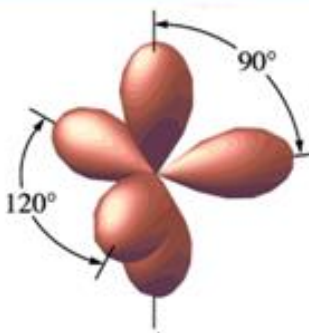
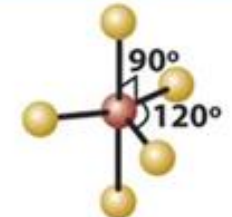
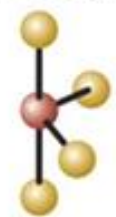
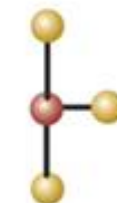

VSEPR THEORY : Molecular Geometry

| Hybridization | Bonding Pairs | Nonbonding Pairs | Molecular Geometry | Example |
|---|---------------|------------------|---|--|
|  Linear | 2 | 0 |  Linear | $\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$ |
|  Trigonal planar | 3 | 0 |  Trigonal planar |  |
| | 2 | 1 |  Bent |  |

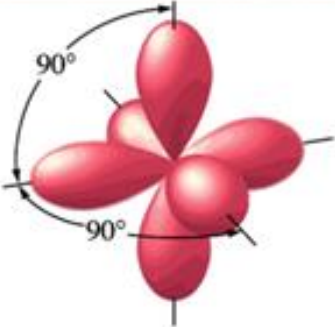
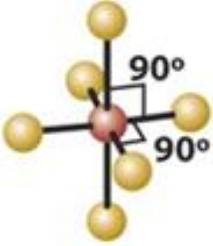
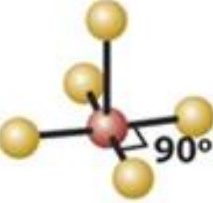
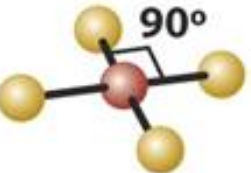
VSEPR THEORY : Molecular Geometry

| Hybridization | Bonding Pairs | Nonbonding Pairs | Molecular Geometry | Example |
|--|---------------|------------------|---|---|
|  Tetrahedral | 4 | 0 |  Tetrahedral |  |
| | 3 | 1 |  Trigonal pyramidal |  |
| | 2 | 2 |  |  |

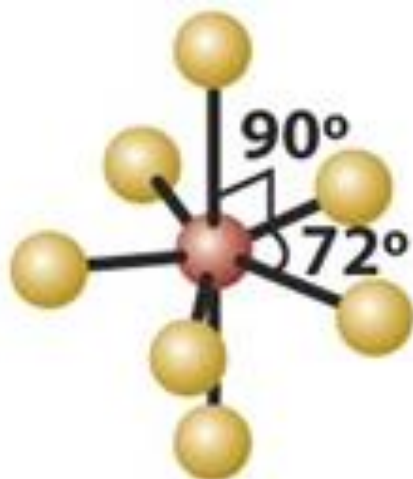
VSEPR THEORY : Molecular Geometry

| Hybridization | Bonding Pairs | Nonbonding Pairs | Molecular Geometry | Example |
|---|---------------|------------------|---|----------------|
|  <p>Trigonal bipyramidal</p> | 5 | 0 |  <p>Trigonal bipyramidal</p> | PCl_5 |
| | 4 | 1 |  <p>Seesaw</p> | SF_4 |
| | 3 | 2 |  <p>T-shaped</p> | ClF_3 |
| | 2 | 3 |  <p>Linear</p> | XeF_2 |

VSEPR THEORY : Molecular Geometry

| Hybridization | Bonding Pairs | Nonbonding Pairs | Molecular Geometry | Example |
|---|---------------|------------------|---|----------------|
|  <p>Octahedral</p> | 6 | 0 |  <p>Octahedral</p> | SF_6 |
| | 5 | 1 |  <p>Square pyramidal</p> | BrF_5 |
| | 4 | 2 |  <p>Square planar</p> | XeF_4 |

VSEPR THEORY : Molecular Geometry



**Pentagonal
bipyramidal**

Iodine heptafluoride (IF₇)
with 7 bonding groups

VSEPR Theory--Molecular Shapes : Summary

| No. e ⁻ pairs | Geometrical arrangement | Types of e ⁻ pairs | Molecular shapes | Examples |
|--------------------------|---|--|--|---|
| 2 | linear, 180° | 2 bp | linear | BH ₂ |
| 3 | trigonal planar, 120° | 3 bp 2bp, 1lp | trigonal planar bent | BF ₃ O ₃ |
| 4 | tetrahedral 109° 28' | 4 bp 3 bp, 1 lp 2 bp, 2 lp | tetrahedral trigonal pyramidal bent | CH ₄ NH ₃ H ₂ O |
| 5 | trigonal bipyramidal 120° e-e, 90° a-e | 5 bp 4 bp, 1 lp 3 bp, 2 lp 2 bp, 3 lp | trigonal bipyramidal see saw T-shape linear | PF ₅ SF ₄ ICl ₃ I ₃ ⁻ |
| 6 | octahedral, 90° | 6 bp 5 bp, 1lp 4 bp, 2 lp | Octahedral square pyramidal square planar | SF ₆ IF ₅ XeF ₄ |

Chemical Bonding...

- Why shouldn't you write H_2O as HHO ?
- Can you able to predict the bond length?
- What is the origin of molecular magnetism?

Molecular Orbital Theory

Linear Combination of ionic & covalent functions

$$\psi = (1 - \lambda)\psi_{cov} + \lambda\psi_{ion}$$

Valence Bond Theory

Linear Combination of s and p orbital wave functions

$$\psi = a\psi_s + b\psi_p$$

Linear Combination of Atomic Orbitals (LCAO)

Bonding MO $\psi_b = \psi_A + \psi_B$

Antibonding MO $\psi_b = \psi_A - \psi_B$

ψ_A & ψ_B are atomic orbitals of atom A and atom B respectively

Molecular Orbital Theory

Molecular Orbital Theory

ψ_A & ψ_B are atomic orbitals of atom A and atom B respectively

for H_2^+ ion:

Bonding MO $\psi = \psi_{b(1)} = \psi_{A(1)} + \psi_{B(1)}$

for H_2 molecule:

Total wave function is the product of wavefunctions for each electron

$$\psi = \psi_{b(1)}\psi_{b(2)} = [\psi_{A(1)} + \psi_{B(1)}] [\psi_{A(2)} + \psi_{B(2)}]$$

$$\psi = \psi_{A(1)}\psi_{A(2)} + \psi_{B(1)}\psi_{B(2)} + \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}$$



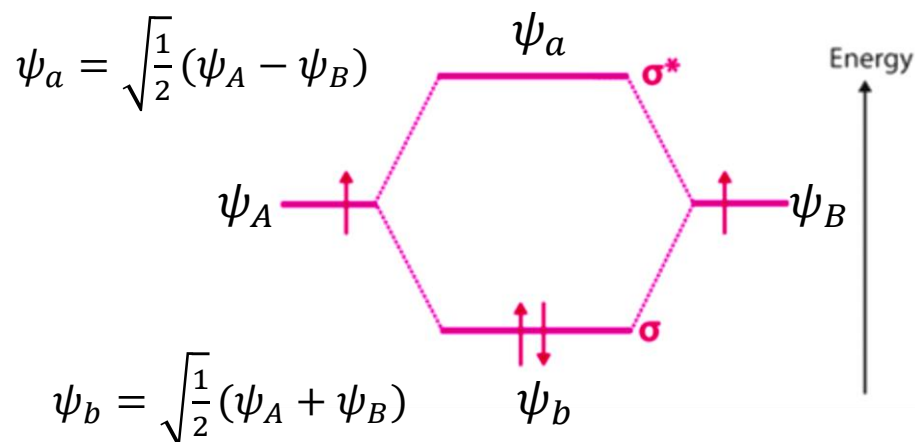
Ionic



Covalent

Molecular Orbital Theory

ψ_A & ψ_B are atomic orbitals of atom A and atom B respectively



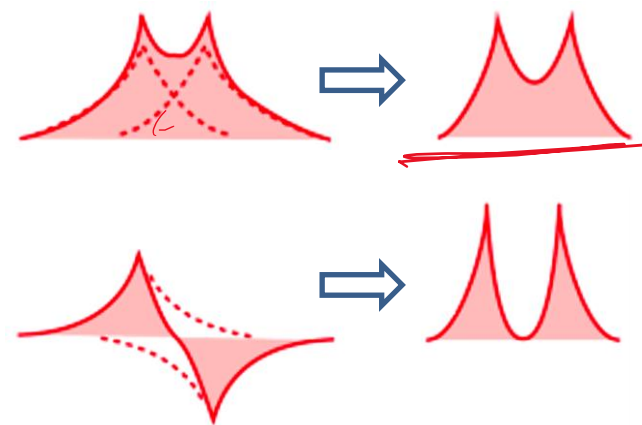
$$\text{Bond Order} = \frac{1}{2} (N_b - N_a)$$

Probability density
of Bonding MO

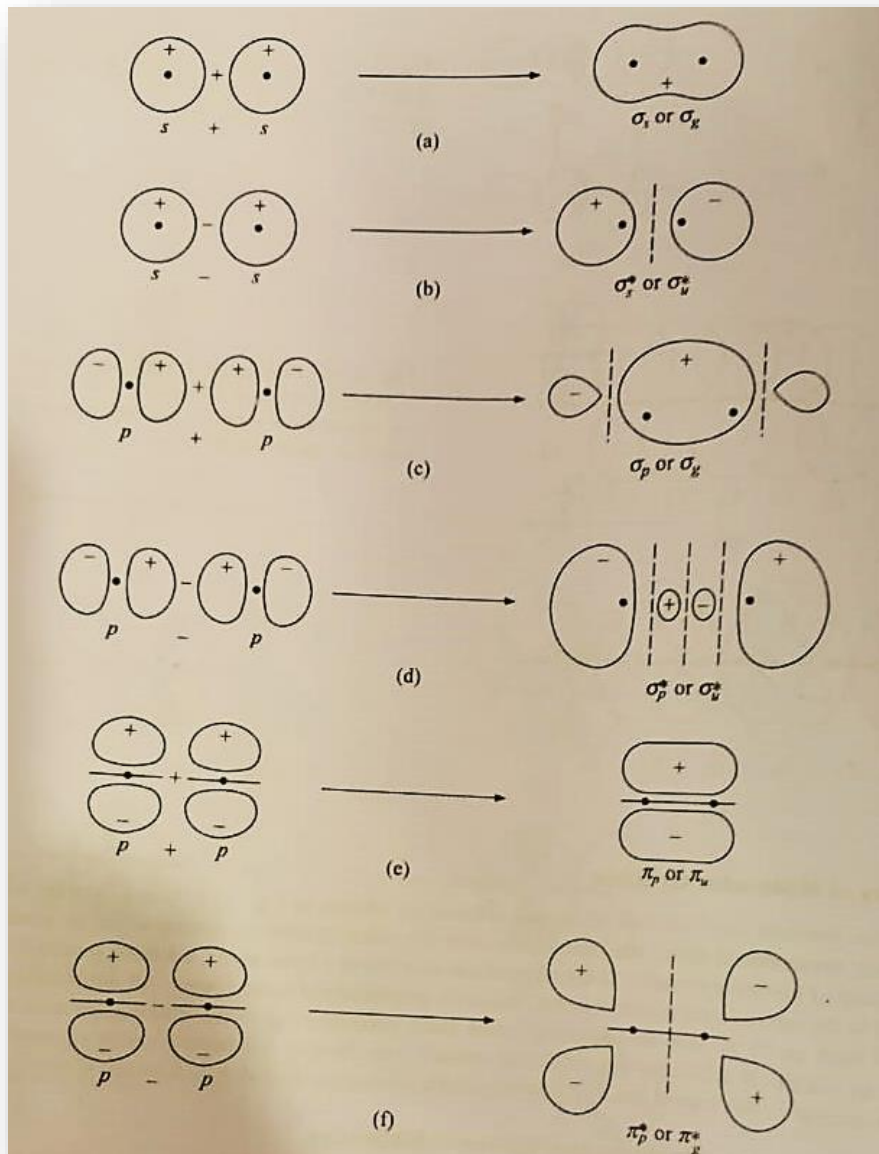
$$|\psi_b|^2 = \psi_A^2 + 2\psi_A\psi_B + \psi_B^2$$

Probability density
of Antibonding MO

$$|\psi_a|^2 = \psi_A^2 - 2\psi_A\psi_B + \psi_B^2$$



Symmetry & Overlap



$$\sigma_{1s} = 1s_A + 1s_B$$

$$\sigma_{1s}^* = 1s_A - 1s_B$$

$$\sigma_{2s} = 2s_A + 2s_B$$

$$\sigma_{2s}^* = 2s_A - 2s_B$$

$$\sigma_{2p} = 2p_{zA} + 2p_{zB}$$

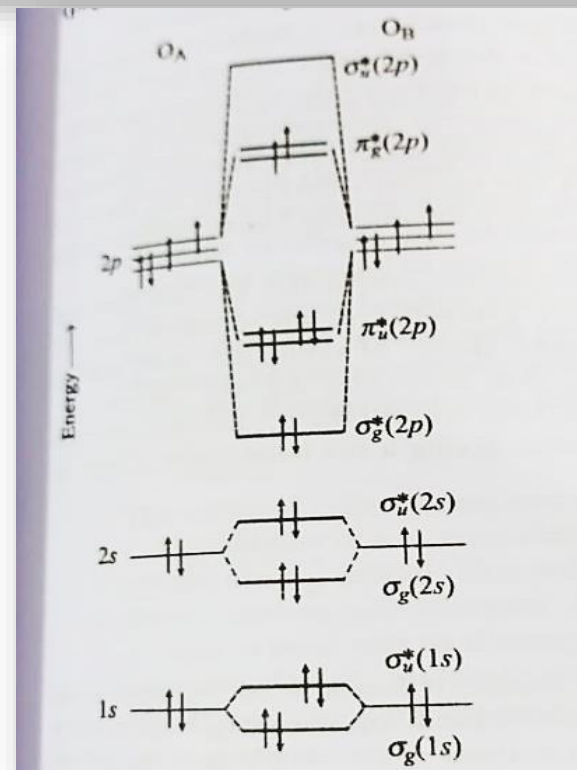
$$\sigma_{2p}^* = 2p_{zA} - 2p_{zB}$$

$$\pi_{2p_y} = 2p_{yA} + 2p_{yB}$$

$$\pi_{2p_x} = 2p_{xA} + 2p_{xB}$$

$$\pi_{2p_y}^* = 2p_{yA} - 2p_{yB}$$

$$\pi_{2p_x}^* = 2p_{xA} - 2p_{xB}$$



Symmetry Operations

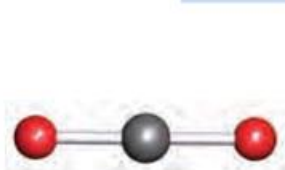
Centre of Symmetry (i)

or, Centre of Inversion (i)

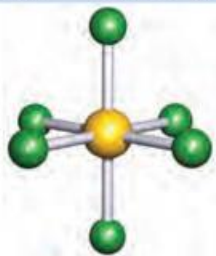
If reflection of all parts of a molecule through **the centre of the molecule** produces an indistinguishable configuration, **the centre is a centre of symmetry**.

A point at the center of the molecule.

$$(x, y, z) \longrightarrow (-x, -y, -z).$$



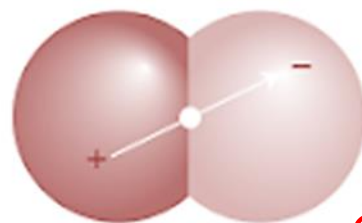
CO₂



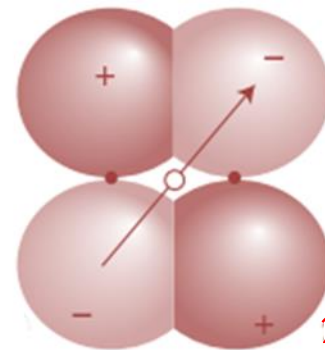
SF₆



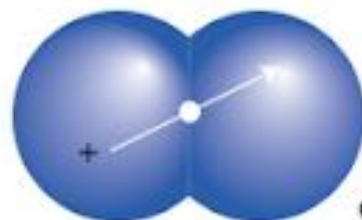
H₂S



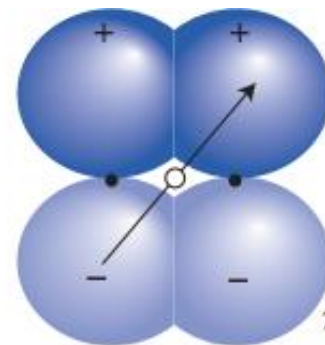
σ_u^*



π_g^*



σ_g



π_u

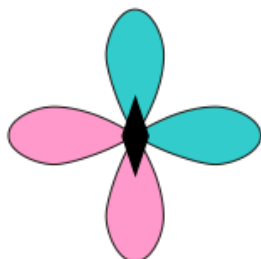
Symmetry Operations

Depends on the specific group

| <u>by symmetry:</u> | Principal rotation axis (C_n) | Center of inversion (i) | plane to princip. axis (σ_v) | plane \perp to princip. axis (σ_h) |
|---------------------|-----------------------------------|-------------------------|--|---|
| symmetric | A | g | 1 | ' |
| antisymmetric | B | u | 2 | " |

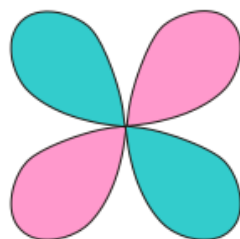
C_2 :

$p_x \rightarrow -p_x$
 $p_y \rightarrow -p_y$
 $\Rightarrow B$



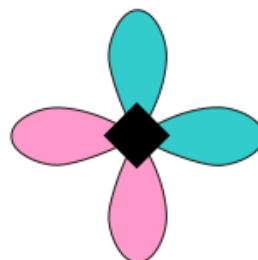
i:

$d_{xy} \rightarrow d_{xy}$
 (similarly all d)
 $\Rightarrow g$



C_4 :

$p_x \rightarrow p_y$
 $p_y \rightarrow -p_x$
 $\Rightarrow E$



by

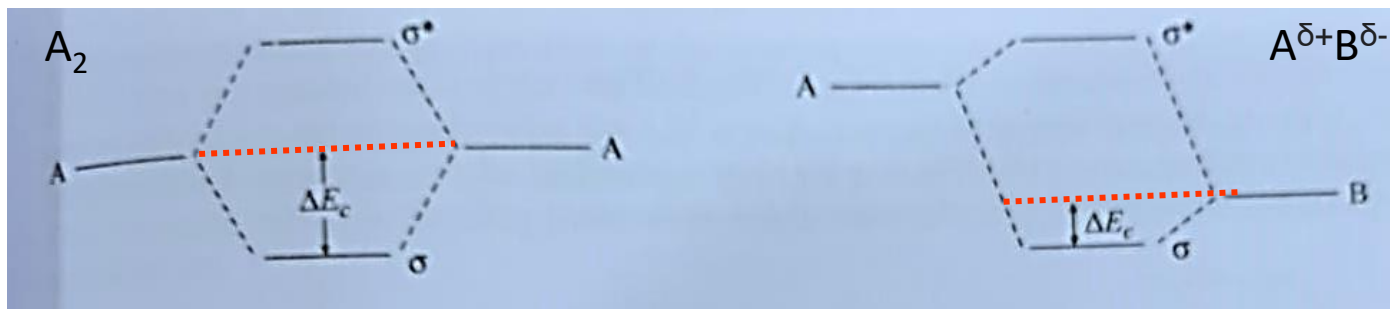
degeneracy:

1: A,B

2: E

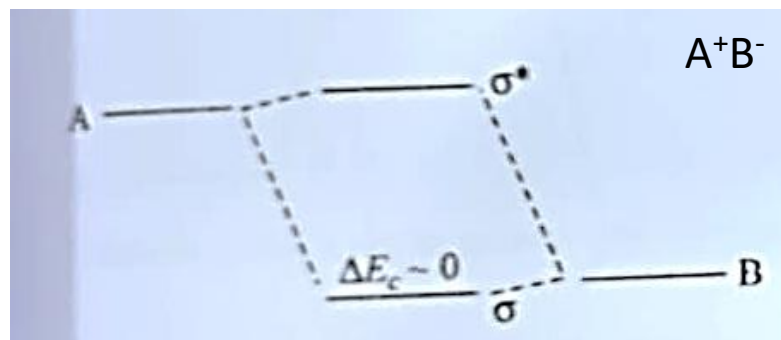
3: T

Molecular Orbital Theory

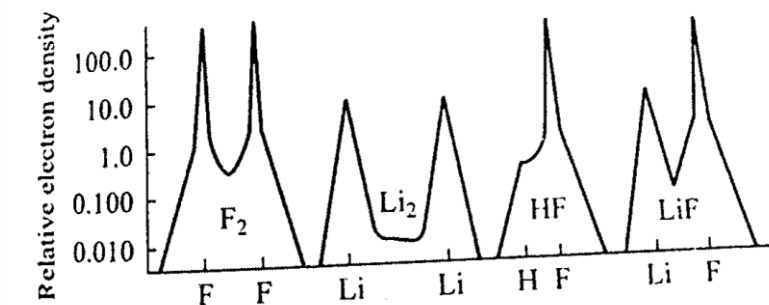


Homonuclear diatomic molecule, A_2

Heteronuclear diatomic molecule, AB
(with small electronegativity difference)



Heteronuclear diatomic molecule, AB
(with LARGE electronegativity difference)



The Rules of Molecular Orbital Theory:

First principle: The number of molecular orbitals produced is always equal to the number of atomic orbitals brought by the atoms that have combined.

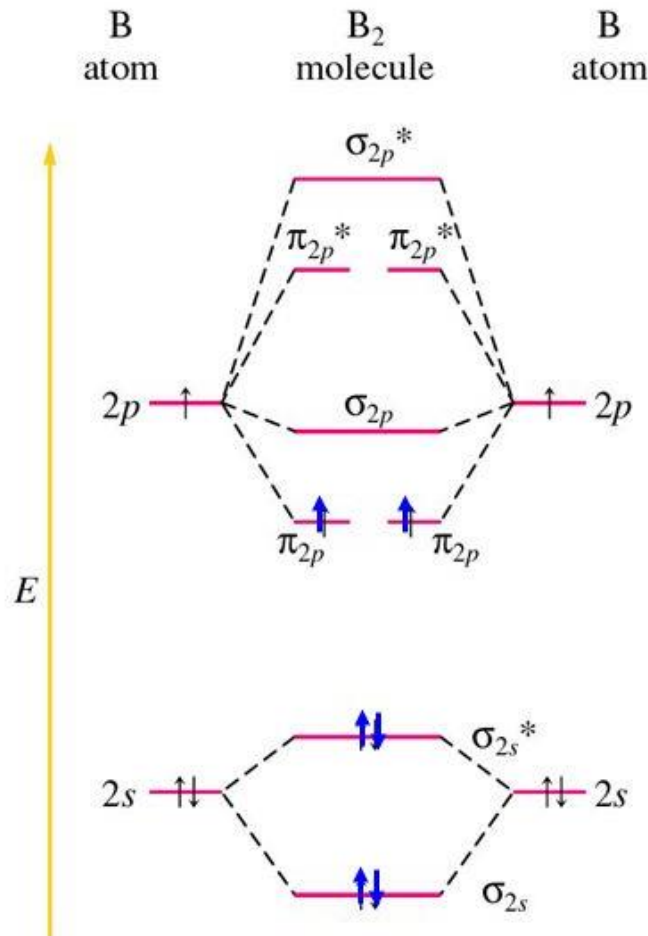
Second principle: Bonding molecular orbitals are lower in energy than the parent orbitals, and the antibonding orbitals are higher in energy.

Third principle: Electrons of the molecule are assigned to orbitals from lowest to successively higher energy

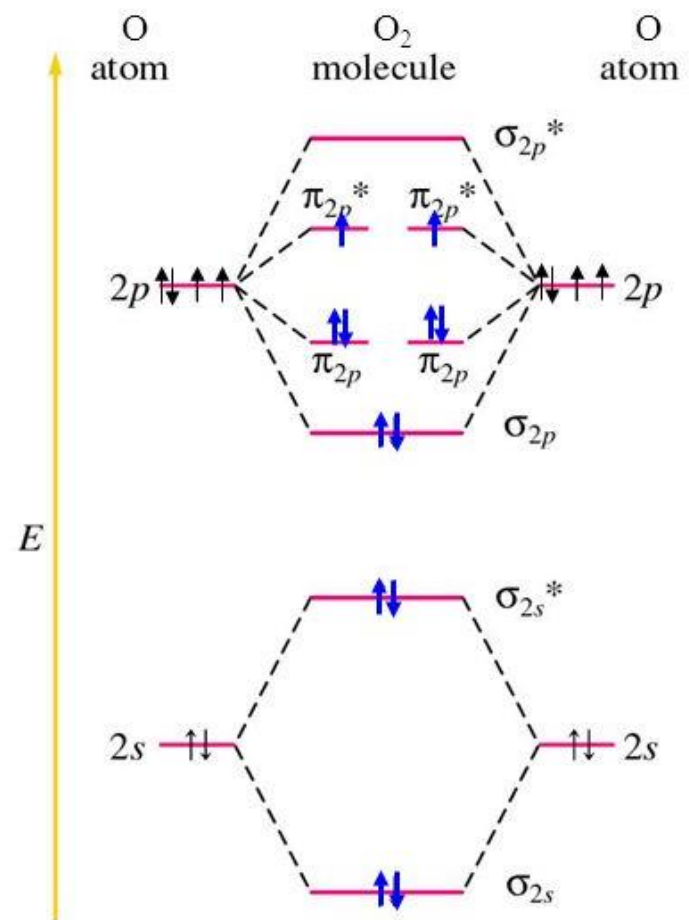
Fourth principle: Atomic orbitals combine to form molecular orbitals most effectively when the atomic orbitals are of similar energy.

MO Diagrams for Diatomic Molecules

M.O. Diagram for B_2
(similar for C_2 and N_2)



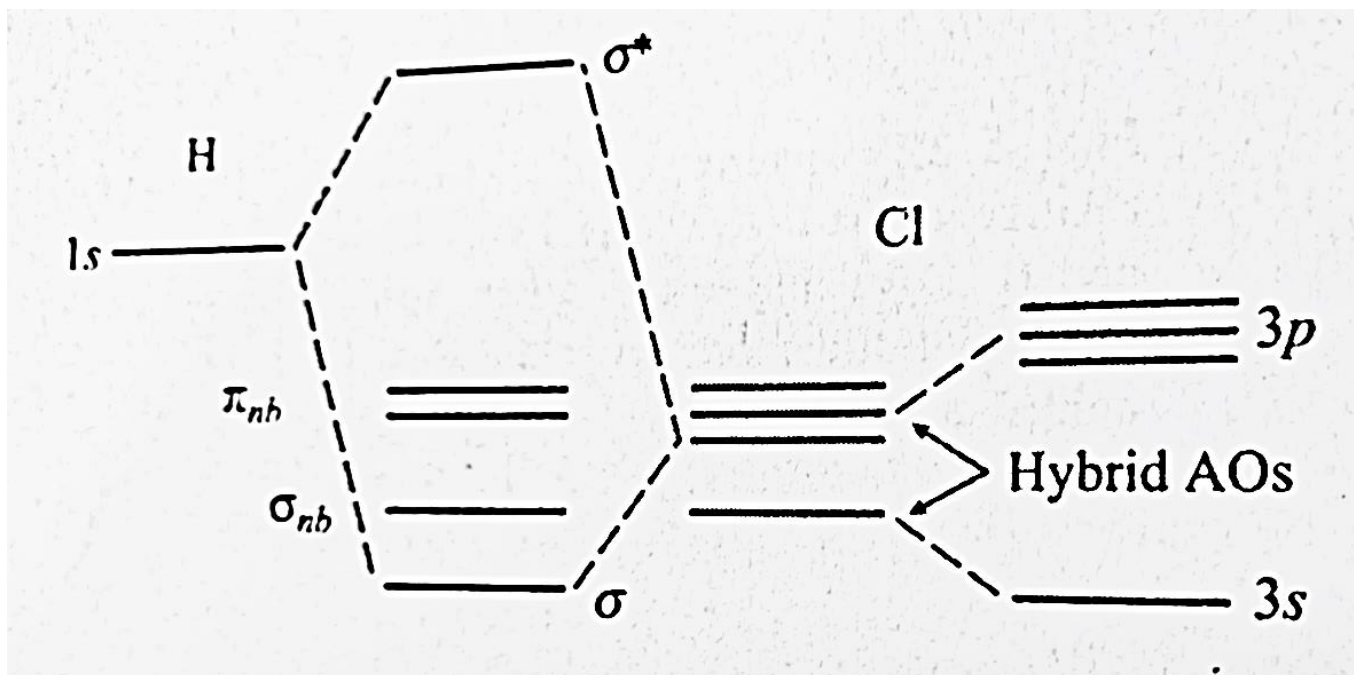
M.O. Diagram for O_2
(similar for F_2 and Xe_2)



MO Diagrams for Heteronuclear Diatomic Molecules

- Only atomic orbitals of about same energy can combine effectively.
- Orbitals should have maximum overlap.
- They must have the same symmetry.

MO Diagram for HCl

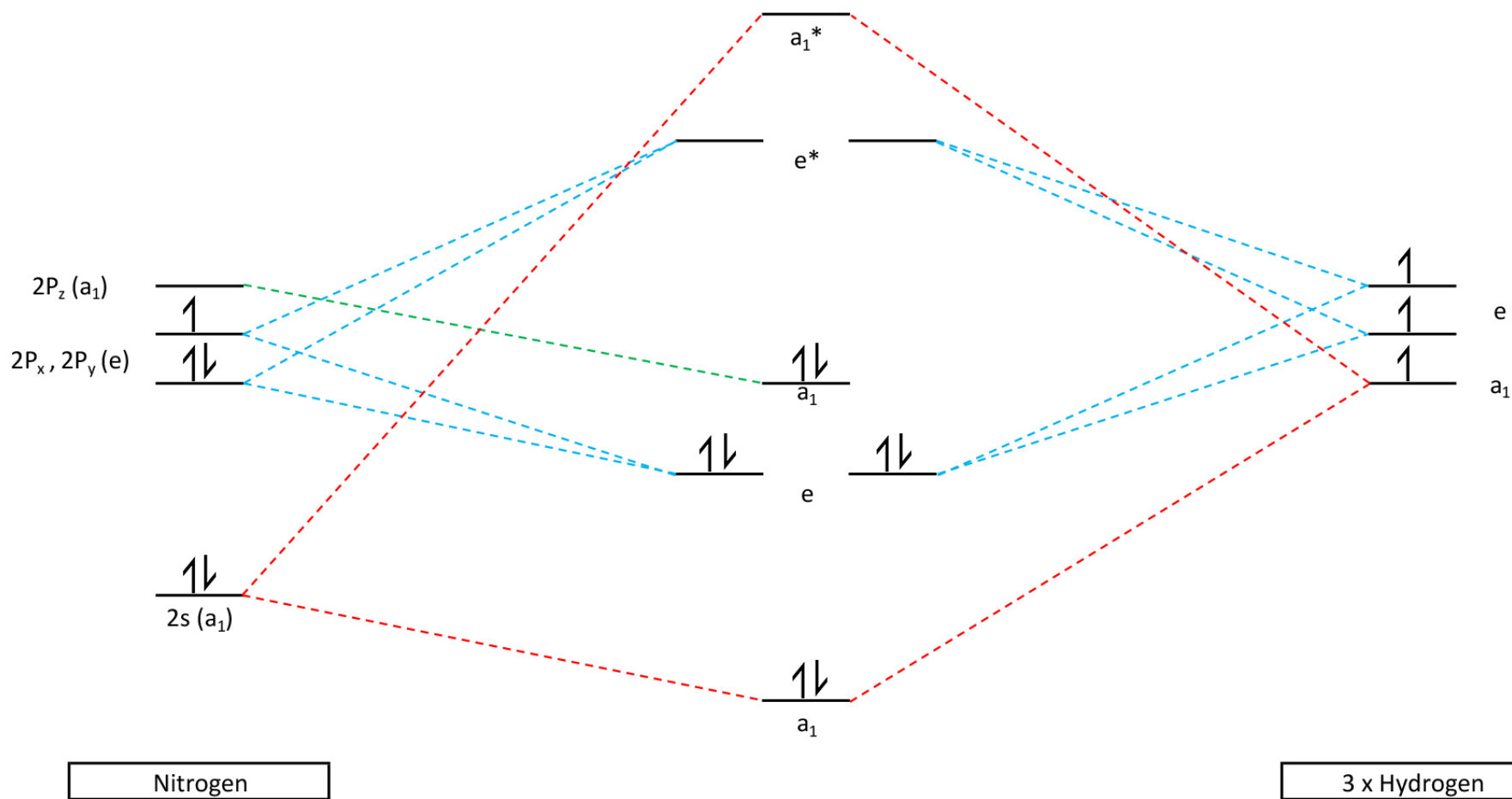


Orbital Energies

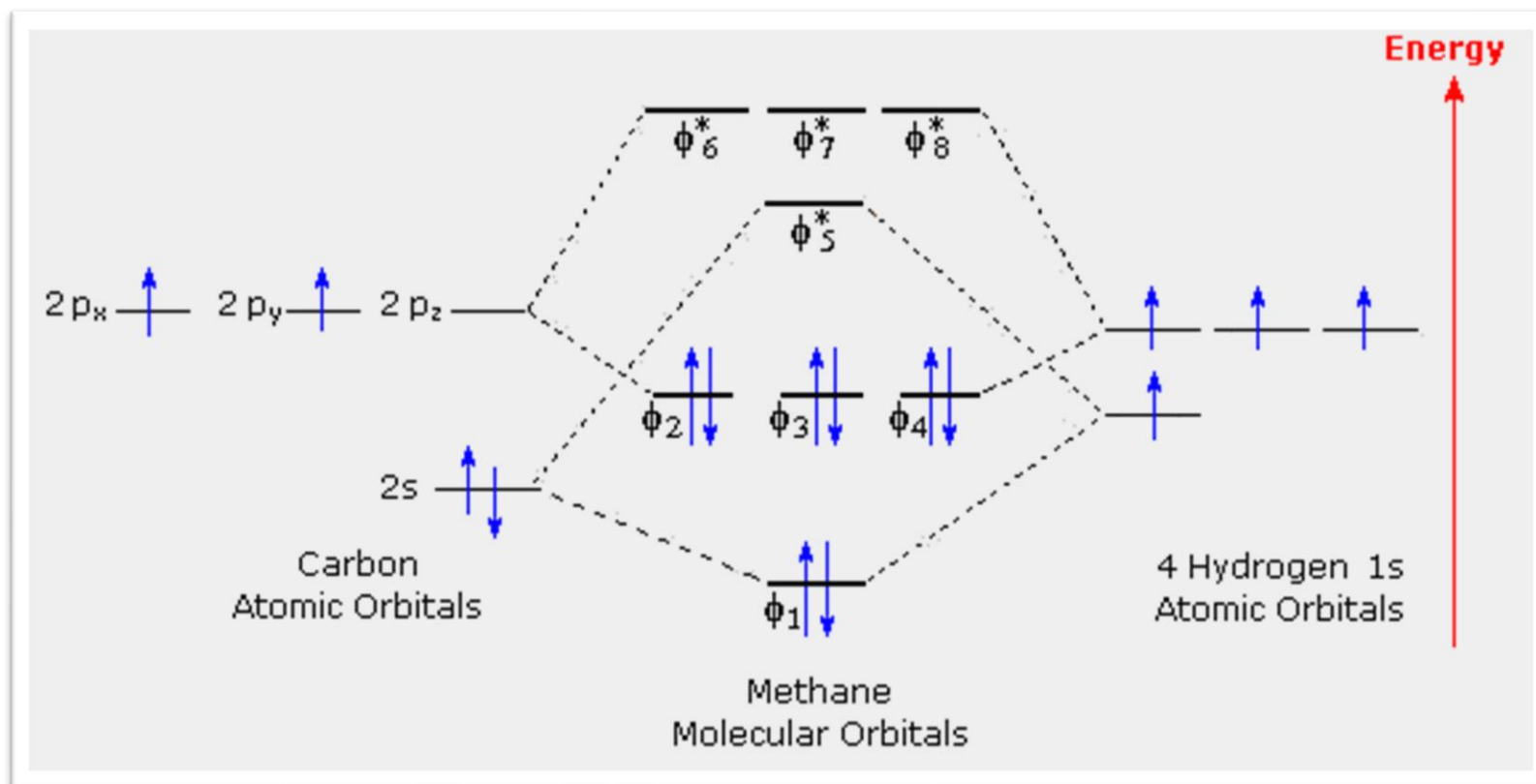
$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

| Atom | Valence orbitals | E (eV) |
|------|------------------|----------|
| H | 1s ¹ | - 13.595 |
| Be | 2s ¹ | - 9.323 |
| C | 2p ¹ | - 11.260 |
| O | 2p ¹ | - 13.618 |

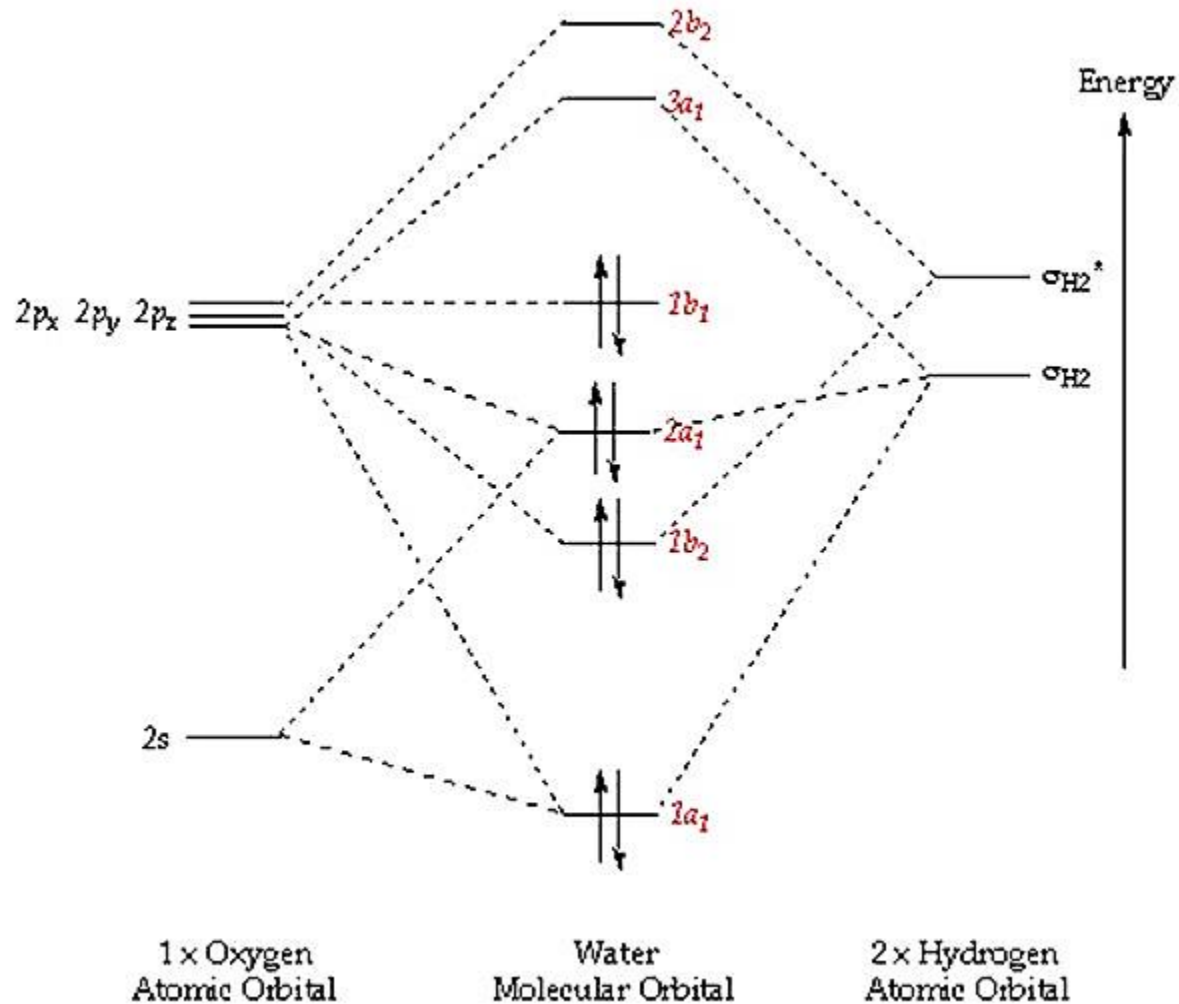
MO Diagram for NH₃



MO Diagram for CH₄



MO Diagram for H₂O



MO Diagram for CO

