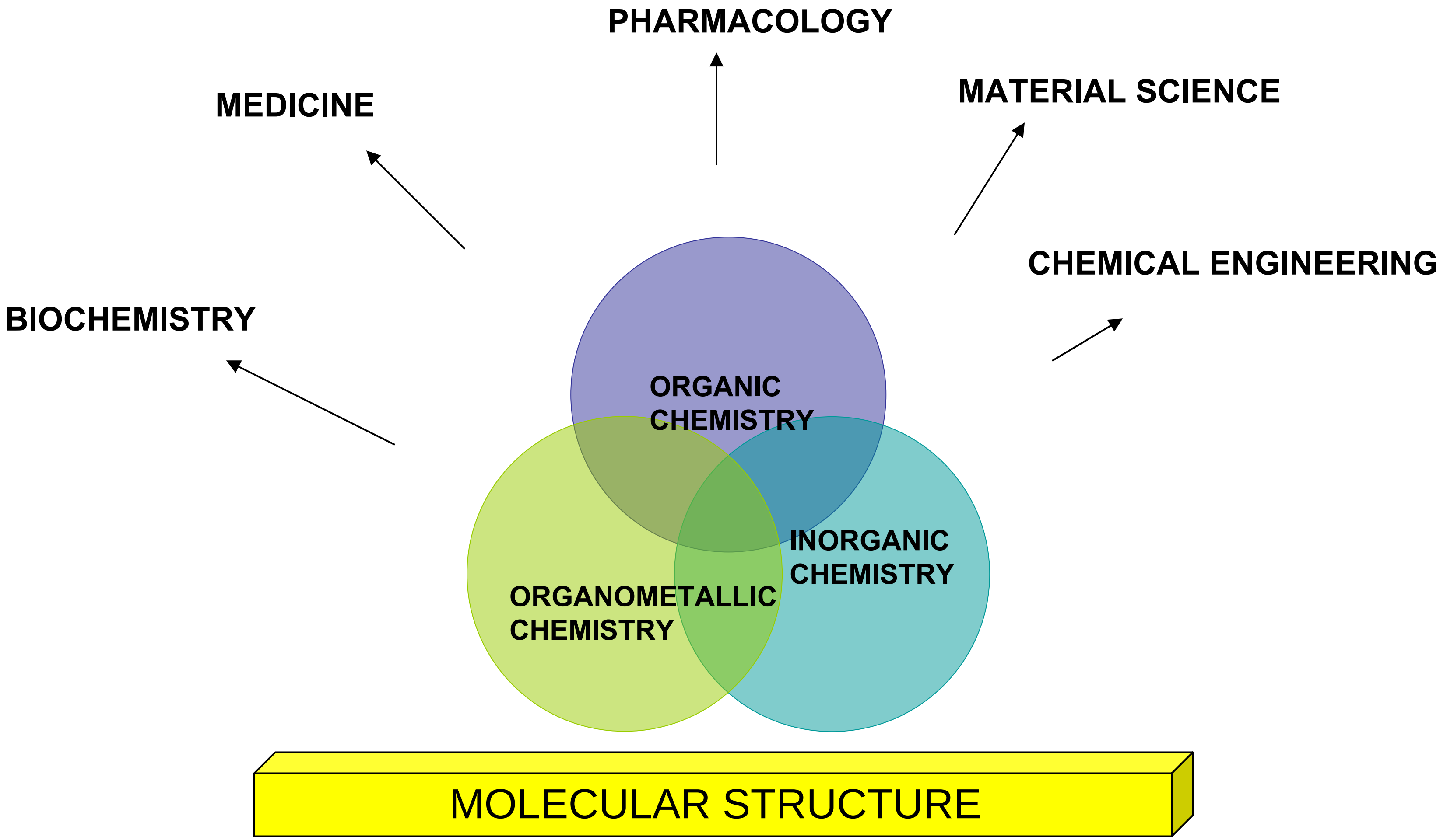
CHEM421

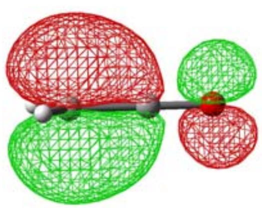
FROM MOLECULAR STRUCTURE TO FUNCTION



ORGANIC CHEMISTRY

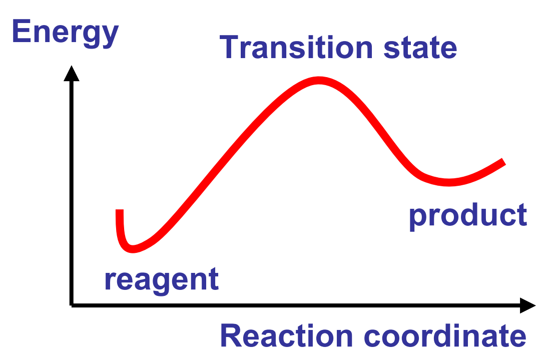
STRUCTURE

Geometries
Electronic structure
bonding



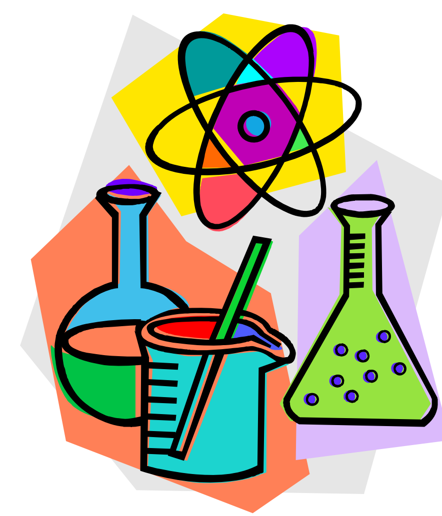
REACTION MECHANISM

Thermodynamics, kinetics, reagents, pre-reaction complex, transition state structure, intermediate, post-reaction complex, products



SYNTHESIS

Knowing the structure and reaction mechanism- make the substance



Solving Schrödinger equation gives quantum numbers, describing electrons

$$-i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\,\Psi$$

n- principle number (energy), l- orbital angular momentum (shape of the electron cloud, s, p, d, f,), m_l- magnetic quantum number (maximum possible number of similar shapes of the same energy: 1 for s,, 3 for p, 5 for d, 7 for f)

s- spin magnetic momentum must be introduced for non-relativistic Schrödinger equation

ELECTRONIC STRUCTURES OF ATOMS

•Principal Quantum Number n (1,2, 3, N)

orbital angular momentum $\ell = 0, 1, \quad n-1$

Magnetic Quantum Number, $m_\ell. = -\ell, 0, \quad +\ell$

Spin magnetic momentum m_s, (+1/2 and -1/2)

s-orbitals (1) , p-orbitals (3) , d-orbitals (5) , f-orbitals (7)

•electrons fill orbitals starting with lowest *n* and moving upwards

•no two electrons can fill one orbital with the same spin (Pauli)

•for degenerate orbitals (same energy), electrons fill each orbital singly before any orbital gets a second electron. Total spin should be maximum possible. (Hund’s rule).

Sample

Which set of n , l , and m_l is incorrect

1. 2, 1, 0

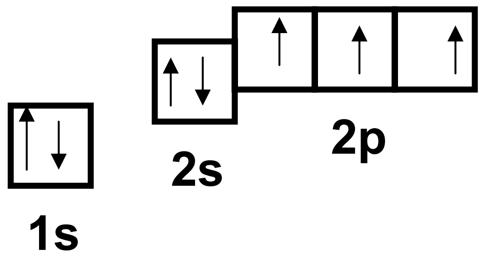
2. 3, 2, -2

3. 2, 2, 1

4. 2, 0, -1

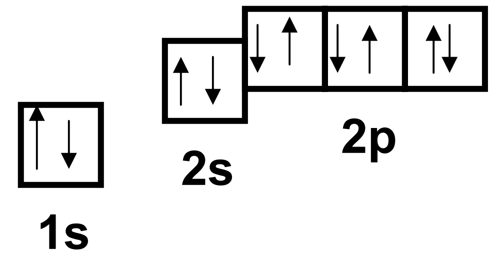
5. 3, 2, 3

N



$1s^22s^22p^3$

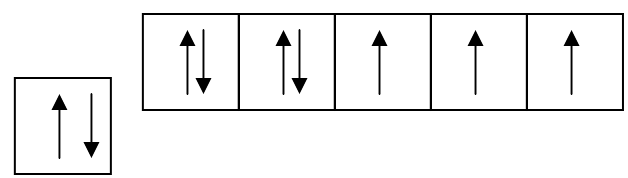
Ne



$1s^22s^22p^6$

- ***Core electrons***: electrons in [Noble Gas].
- ***Valence electrons***: electrons outside of [Noble Gas].

Co [Ar]



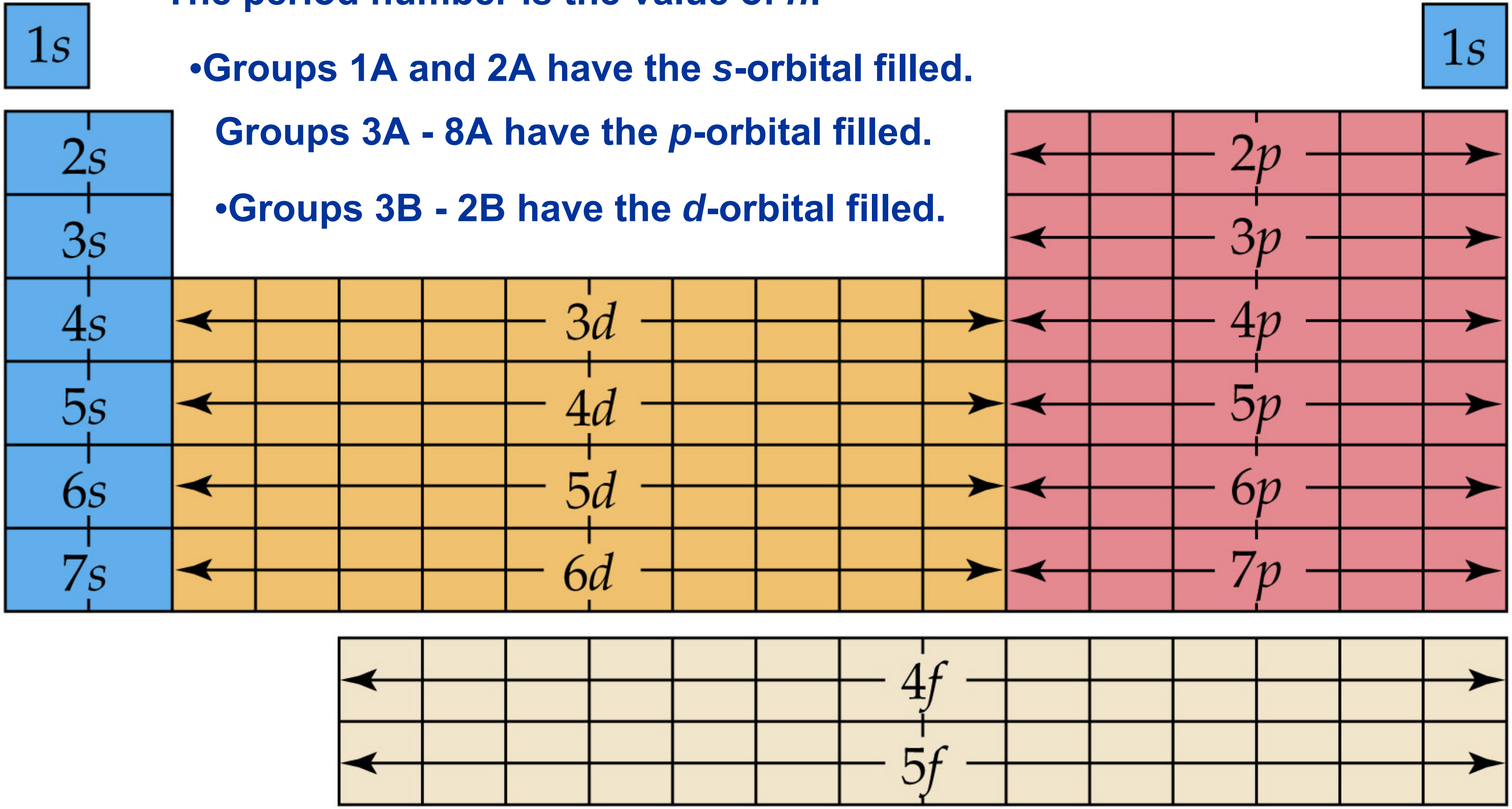
Excited states: C* $1s^2\ 2s^1\ 2p^3$

•The period number is the value of *n*.

•Groups 1A and 2A have the *s*-orbital filled.

Groups 3A - 8A have the *p*-orbital filled.

•Groups 3B - 2B have the *d*-orbital filled.



The lanthanides and actinides have the *f*-orbital filled.

Core	1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
	1 **H** $1s^1$																	2 **He** $1s^2$
[He]	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
[Ne]	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$
[Ar]	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^1 4s^2$	22 **Ti** $3d^2 4s^2$	23 **V** $3d^3 4s^2$	24 **Cr** $3d^5 4s^1$	25 **Mn** $3d^5 4s^2$	26 **Fe** $3d^6 4s^2$	27 **Co** $3d^7 4s^2$	28 **Ni** $3d^8 4s^2$	29 **Cu** $3d^{10} 4s^1$	30 **Zn** $3d^{10} 4s^2$	31 **Ga** $3d^{10} 4s^2 4p^1$	32 **Ge** $3d^{10} 4s^2 4p^2$	33 **As** $3d^{10} 4s^2 4p^3$	34 **Se** $3d^{10} 4s^2 4p^4$	35 **Br** $3d^{10} 4s^2 4p^5$	36 **Kr** $3d^{10} 4s^2 4p^6$
[Kr]	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^1 5s^2$	40 **Zr** $4d^2 5s^2$	41 **Nb** $4d^3 5s^2$	42 **Mo** $4d^5 5s^1$	43 **Tc** $4d^5 5s^2$	44 **Ru** $4d^7 5s^1$	45 **Rh** $4d^8 5s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10} 5s^1$	48 **Cd** $4d^{10} 5s^2$	49 **In** $4d^{10} 5s^2 5p^1$	50 **Sn** $4d^{10} 5s^2 5p^2$	51 **Sb** $4d^{10} 5s^2 5p^3$	52 **Te** $4d^{10} 5s^2 5p^4$	53 **I** $4d^{10} 5s^2 5p^5$	54 **Xe** $4d^{10} 5s^2 5p^6$
[Xe]	55 **Cs** $6s^1$	56 **Ba** $6s^2$	71 **Lu** $4f^{14} 5d^1 6s^2$	72 **Hf** $4f^{14} 5d^2 6s^2$	73 **Ta** $4f^{14} 5d^3 6s^2$	74 **W** $4f^{14} 5d^4 6s^2$	75 **Re** $4f^{14} 5d^5 6s^2$	76 **Os** $4f^{14} 5d^6 6s^2$	77 **Ir** $4f^{14} 5d^7 6s^2$	78 **Pt** $4f^{14} 5d^9 6s^1$	79 **Au** $4f^{14} 5d^{10} 6s^1$	80 **Hg** $4f^{14} 5d^{10} 6s^2$	81 **Tl** $4f^{14} 5d^{10} 6s^2 6p^1$	82 **Pb** $4f^{14} 5d^{10} 6s^2 6p^2$	83 **Bi** $4f^{14} 5d^{10} 6s^2 6p^3$	84 **Po** $4f^{14} 5d^{10} 6s^2 6p^4$	85 **At** $4f^{14} 5d^{10} 6s^2 6p^5$	86 **Rn** $4f^{14} 5d^{10} 6s^2 6p^6$
[Rn]	87 **Fr** $7s^1$	88 **Ra** $7s^2$	103 **Lr** $5f^{14} 6d^1 7s^2$	104 **Rf** $5f^{14} 6d^2 7s^2$	105 **Db** $5f^{14} 6d^3 7s^2$	106 **Sg** $5f^{14} 6d^4 7s^2$	107 **Bh** $5f^{14} 6d^5 7s^2$	108 **Hs** $5f^{14} 6d^6 7s^2$	109 **Mt** $5f^{14} 6d^7 7s^2$	110	111	112		114		116		

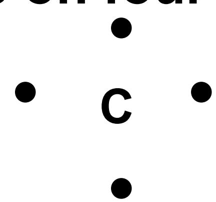
[Xe]	Lanthanide series	57 **La** $5d^1 6s^2$	58 **Ce** $4f^1 5d^1 6s^2$	59 **Pr** $4f^3 6s^2$	60 **Nd** $4f^7 6s^2$	61 **Pm** $4f^5 6s^2$	62 **Sm** $4f^6 6s^2$	63 **Eu** $4f^7 6s^2$	64 **Gd** $4f^7 5d^1 6s^2$	65 **Tb** $4f^9 6s^2$	66 **Dy** $4f^{10} 6s^2$	67 **Ho** $4f^{11} 6s^2$	68 **Er** $4f^{12} 6s^2$	69 **Tm** $4f^{13} 6s^2$	70 **Yb** $4f^{14} 6s^2$
[Rn]	Actinide series	89 **Ac** $6d^1 7s^2$	90 **Th** $6d^2 7s^2$	91 **Pa** $5f^2 6d^1 7s^2$	92 **U** $5f^3 6d^1 7s^2$	93 **Np** $5f^4 6d^1 7s^2$	94 **Pu** $5f^6 7s^2$	95 **Am** $5f^7 7s^2$	96 **Cm** $5f^7 6d^1 7s^2$	97 **Bk** $5f^9 7s^2$	98 **Cf** $5f^{10} 7s^2$	99 **Es** $5f^{11} 7s^2$	100 **Fm** $5f^{12} 7s^2$	101 **Md** $5f^{13} 7s^2$	102 **No** $5f^{14} 7s^2$

Metals | Metalloids | Nonmetals

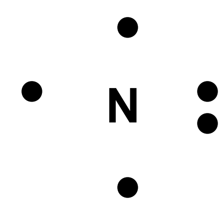
Lewis Symbols

- the valence electrons are in an out electron shell of an atom. we represent the valence electrons as dots around the symbol for the element.

- The number of electrons available for bonding are indicated by unpaired dots.
- These symbols are called Lewis symbols.
- We generally place the electrons on four sides of a square around the element symbol.



If an atom has more than 4 electrons, we form electron pairs

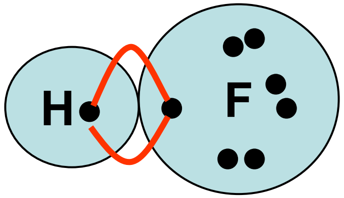


The Octet (8) Rule

All noble gases except He have an s^2p^6 configuration (8 electrons).

All atoms try to get configuration of a nearest noble gas

- ***<u>Octet rule</u>***: atoms tend to gain, lose, or share electrons until they are surrounded by 8 valence electrons (4 electron pairs).



•**<u>Caution: there are many exceptions to the octet rule starting from the 3 period.</u>**

Special rule for hydrogen

For hydrogen- duet (2 electrons)

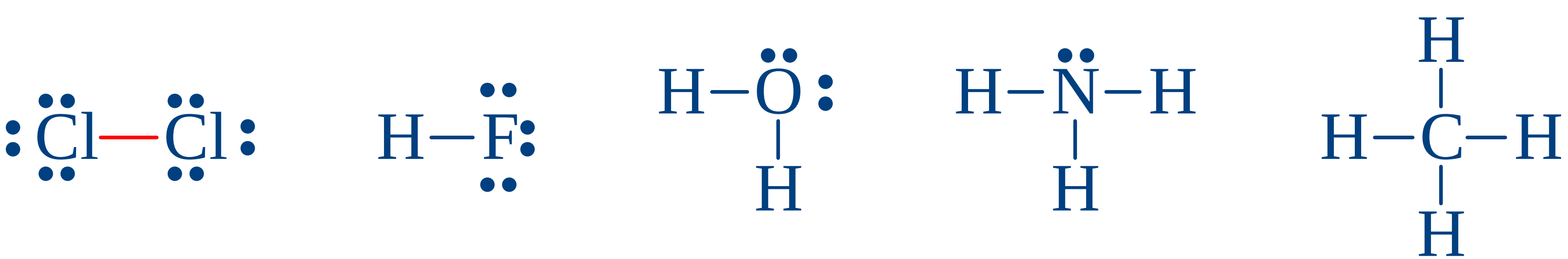
Nearest noble gas to H is He ($1s^2$)

So, hydrogen tends to achieve electron configuration on He

Lewis Structures

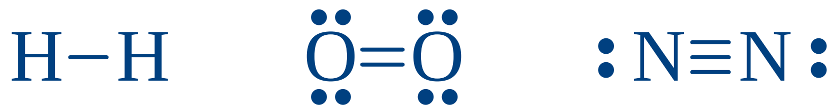
- **Covalent bonds can be represented by the Lewis symbols of the elements:**

- **In Lewis structures, each pair of electrons in a bond is represented by a single line:**



Multiple Bonds

- It is possible for more than one pair of electrons to be shared between two atoms (multiple bonds):



  - One shared pair of electrons = single bond (e.g. H_2);
  - Two shared pairs of electrons = double bond (e.g. O_2);
  - Three shared pairs of electrons = triple bond (e.g. N_2).

- Generally, bond distances decrease as we move from single through double to triple bonds.

The pair of electrons which is not involved in bonding is called a LONE PAIR

Drawing Lewis Structures

Our goals are to predict:

a) the lowest energy structure (most thermodynamically stable)

b) its properties (bond lengths, atomic charges, dipole moment, chemical reactivities)

General rules:

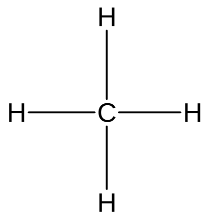
1. Show ALL the valence electrons with dots

2. Provide octet (8 electrons) for each atom.
For hydrogen- duet (2 electrons)

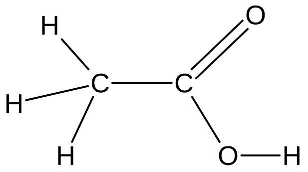
3. Sometimes, multiple bonds are needed for octet.
Multiple bonds are typical of C, N, O, P, S. Hydrogen NEVER forms multiple bonds

Skeletal Structures:

Atoms are in order in which they are bonded



CH_4, methane

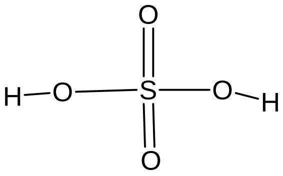


Acetic acid

H – always a terminal atom

C – always a central atom

Atoms with lower electronegativity are usually central



H_2SO_4

H and Halogens (F, Cl, Br, I) do not form multiple bonds

A strategy for writing Lewis structures from formulas

1. Calculate the number of valence electrons

PO_4^{3-} :   5 (P) + 4x6 (O) + 3 (from charge) = 32 e

NH_4^+ : 5 (N) + 4x1 (H) -1 (from charge = 8e

2. Identify the central atom(s) and terminal atoms

3. Write a plausible skeletal structure(s) using single covalent bonds
(A ——B, —— represents 2 electrons)

4. The remaining valence electrons form lone pairs

5. Use lone pairs first to complete octet for terminal atoms, then, if possible, for central atoms

Sample:

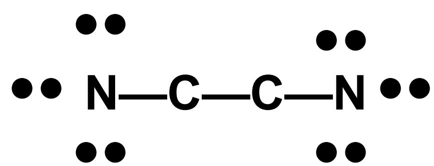
C_2N_2

1. **Total number of valence electrons: 2x4(fromC) + 2x5(fromN)=18**

2. **Skeletal structure (less electronegative- in the middle):**

N—C—C—N

3. **Complete octet for terminal atoms (6e are used for 3 single bonds, 12 are left)**



4. **Carbon atoms do not have octet: use lone pairs to form multiple bonds**