UNIT 1- INORGANIC CHEMISTRY

CHEMICAL PERIODICITY

1. Modern Periodic Law

Definition: The properties of elements are periodic functions of their atomic number (Z).

Basis: Atomic number (not atomic mass, as in Mendeleev).

Periodicity arises due to the repetition of similar outer electronic configurations at regular intervals.

---

2. Periodicity in Properties

(a) Atomic Radius

Across a Period: ⬇ decreases

Effective nuclear charge (Z_{eff}) increases → pulls electrons closer.

Down a Group: ⬆ increases

New shells added → size increases despite increase in Z_{eff}.

(b) Ionic Radius

Cations (positive ions): Smaller than parent atom (loss of electrons → less repulsion, higher Z_{eff}).

Anions (negative ions): Larger than parent atom (gain of electrons → more repulsion, lower Z_{eff}).

(c) Ionization Potential (IP / IE)

Definition: Energy required to remove the most loosely bound electron.

Across a Period: ⬆ increases (higher Z_{eff}, smaller radius).

Down a Group: ⬇ decreases (larger radius, weaker attraction).

Exceptions: Be, N, Mg, P show slightly higher values due to stable half/full subshells.

(d) Electron Affinity (EA)

Definition: Energy released when an atom gains an electron.

Across a Period: ⬆ generally increases (greater Z_{eff}, easier to add e^-).

Down a Group: ⬇ decreases (larger radius, weaker attraction for extra e^-).

Exceptions: Noble gases (no EA), Be, Mg (filled s), N, P (half-filled p).

3. Effective Nuclear Charge (Z_{eff})

Definition:

Net positive charge experienced by an electron in a multi-electron atom.

Formula: $Z_{eff} = Z - S$

Where,

Z = actual nuclear charge (atomic number),
S = shielding (screening constant).

---

4. Slater's Rules (for finding S)

Steps:

Write electronic configuration in groups:

(1s) (2s,2p) (3s,3p) (3d) (4s,4p) (4d) (4f) (5s,5p)…

For a given electron, shielding constant S is calculated as:

Electrons in the same group (ns, np): each contributes 0.35 (except 1s, where it's 0.30).

Electrons in (n–1) shell: each contributes 0.85.

Electrons in (n–2) or lower shells: each contributes 1.00.

For d and f orbitals:

Same group → 0.35,

All lower groups → 1.00.

Subtract S from Z → gives Z_{eff}

Uses of Slater's Rules:

Explains trends in atomic size, ionization energy, and electron affinity.

Helps predict relative stability of orbitals.

Useful in rationalizing periodic properties and anomalies.

Property	Across Period →	Down Group ↓
Atomic Radius	Decreases ⬇	Increases ⬆
Ionic Radius (cations)	Decreases ⬇	Increases ⬆
Ionic Radius (anions)	Decreases ⬇	Increases ⬆
Ionization Energy	Increases ⬆	Decreases ⬇
Electron Affinity	Increases ⬆ (with exceptions)	Decreases ⬇

STRUCTURE AND BONDING

1. Molecular Orbitals (Homo- vs Heteronuclear)

Homonuclear molecules (e.g. H_2, O_2, N_2):

- Combination of identical AOs.
- MO diagram ordering:
- For $Z < 8$: $\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2px) = \pi(2py) < \sigma(2pz) < \pi^*(2px) = \pi^*(2py) < \sigma^*(2pz)$
- For $Z \geq 8$: $\sigma(2pz)$ comes **before** $\pi(2px)$, $\pi(2py)$.
- Bond order = ½ (bonding – antibonding electrons).
- Explains paramagnetism (e.g., O_2 has 2 unpaired electrons in π^* orbitals).

Heteronuclear molecules (e.g. CO, NO, HF):

- AOs of different atoms mix → MO energies shift toward atom with closer orbital energy.
- Polar bonds due to unequal AO contributions.

---

2. VSEPR Theory (Shapes of Molecules)

- **Basic Rule:** Electron pairs repel → arrange to minimize repulsion.
- **Electron pair geometry (AXE method):**
- A = central atom, X = bonded atoms, E = lone pairs.

Steric No.	Shape (no lone pairs)	Examples
2	Linear (180°)	$BeCl_2$, CO_2
3	Trigonal planar (120°)	BF_3
4	Tetrahedral (109.5°)	CH_4
5	Trigonal bipyramidal (90°,120°)	PCl_5
6	Octahedral (90°)	SF_6
7	Pentagonal bipyramidal	IF_7

Lone pairs reduce angles due to stronger repulsion:
LP–LP > LP–BP > BP–BP.

---

3. Hybridization & LCAO

Linear Combination of Atomic Orbitals (LCAO):

Hybrid orbitals = combinations of s & p (and d) orbitals.
Ensures equivalent bond energies & orientations

Geometry	Hybridization	Example
Linear	sp	$BeCl_2$, CO_2
Trigonal planar	sp^2	BF_3, C_2H_4
Tetrahedral	sp^3	CH_4
Trigonal bipyramidal	sp^3d	PCl_5
Octahedral	sp^3d^2	SF_6
Square planar	dsp^2	$Ni(CN)_4^{2-}$

4. Stereochemistry of Hybrid Orbitals

sp: 2 orbitals → 180° apart (linear).
sp^2: 3 orbitals → 120° apart (planar).
sp^3: 4 orbitals → 109.5° apart (tetrahedral).
sp^3d: 5 orbitals → 3 in plane (120°), 2 axial (90°).
sp^3d^2: 6 orbitals → octahedral (90°).

5. s and p Character Calculations

General Formula:

%s = (no. of s orbitals / total hybrids) × 100
%p = (no. of p orbitals / total hybrids) × 100

Hybridization	%s	%p	Bond Nature
sp	50	50	Short, strong bonds
sp^2	33.3	66.7	Intermediate
sp^3	25	75	Long, weaker bonds
sp^3d	20	80	More p-character
sp^3d^2	16.7	83.3	Mostly p-character

Higher s-character → shorter, stronger bond (more electronegativity).
Non-equivalent hybrids: Sometimes central atom uses different hybrids for different bonds (e.g., SF_4 has axial & equatorial bonds).

MOLECULAR ORBITAL THEORY

1. Homonuclear Diatomic Molecules (A_2)

Key Rules:
Constructed from **LCAO** (Linear Combination of Atomic Orbitals).
MO ordering depends on Z (atomic number)
For $1 \le Z \le 7$ ($Li_2 \rightarrow N_2$):
$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2px) = \pi(2py) < \sigma(2pz) < \pi^*(2px) = \pi^*(2py) < \sigma^*(2pz)$

For $Z \ge 8$ ($O_2 \rightarrow Ne_2$):
$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2pz) < \pi(2px) = \pi(2py) < \pi^*(2px) = \pi^*(2py) < \sigma^*(2pz)$

Examples:

- **H_2 ($2\ e^-$):** BO = 1 → stable.
- **He_2 ($4\ e^-$):** BO = 0 → not stable.
- **N_2 ($14\ e^-$):** BO = 3 → very stable, diamagnetic.
- **O_2 ($16\ e^-$):** BO = 2 → paramagnetic (2 unpaired ↑ in π*).

2. Heteronuclear Diatomic Molecules (AB)

Key Modifications:

- **AOs differ in energy** → MOs are **closer to the atom with lower energy orbital** (more electronegative).
- Bond is **polar** due to unequal contribution.
- Examples:

  CO: Strong bond, BO = 3. Electrons shifted toward O (χ higher).

  NO (odd e^- molecule): BO = 2.5 → paramagnetic.

  HF: H(1s) overlaps with F(2pz) → σ bond, strongly polarized toward F.

---

3. Trinuclear / Triatomic Molecules (ABC or ABA)

Cases:

1. **Linear molecules (CO_2, $BeCl_2$):**

Combine 3 AOs → give 3 MOs: bonding, nonbonding, antibonding.

Example CO_2:

O 2p orbitals combine with C 2p → form σ(2pz), π(2px), π(2py) bonding and corresponding antibonding orbitals.

Nonbonding orbitals remain localized on O atoms.

2. **Bent molecules (H_2O, O_3, NO_2):**

Symmetry lower than linear → mixing leads to **non-equivalent MOs**.

Example O_3 (ozone): delocalized π system (resonance).

3. **Delocalized π systems:**

3-atom chain: gives 3 π-MOs.

ψ_1 (bonding, all in-phase), ψ_2 (1 node), ψ_3 (antibonding, 2 nodes).

Example: **O_3, CO_2 (π-system).**

4. Bond Order Formula (General)

$BO = \frac{1}{2} (N_b - N_a)]$

(N_b) = bonding electrons

(N_a) = antibonding electrons

---

5. Quick Reference Examples

Molecule	e^- count	MO filling	BO	Magnetism
H_2	2	$\sigma(1s)^2$	1	Dia
He_2	4	$\sigma(1s)^2\ \sigma^*(1s)^2$	0	–
Li_2	6	$\sigma(1s)^2\ \sigma^*(1s)^2\ \sigma(2s)^2$	1	Dia
B_2	10	… $\pi(2p_x)^1 = \pi(2p_y)^1$	1	Para (2 unpaired)
C_2	12	… $\pi(2p_x)^2 = \pi(2p_y)^2$	2	Dia
N_2	14	… $\sigma(2p_z)^2$	3	Dia
O_2	16	… $\pi^*(2p_x)^1 = \pi^*(2p_y)^1$	2	Para
F_2	18	… $\pi^*(2p_x)^2 = \pi^*(2p_y)^2$	1	Dia
Ne_2	20	… $\sigma^*(2p_z)^2$	0	–
