HOMO–LUMO Theory

□ Basic Concept:

In molecular chemistry, we study the electron configuration in molecules through molecular orbitals.

Each molecule has orbitals filled with electrons and orbitals that are empty.

The two most important of these are:

HOMO = Highest Occupied Molecular Orbital

□ The highest orbital occupied by electrons.

LUMO = Lowest Unoccupied Molecular Orbital

□ The lowest orbital that is empty and has not yet been occupied by an electron.

□ Concept:

Electron transitions (light absorption, chemical reactions) often occur from the HOMO to the LUMO.

The difference between the energy of the HOMO and LUMO is called the energy gap.

Importance of the theory:

1. Chemical reactivity:

The smaller the HOMO–LUMO gap, the more easily the electron transfers, and the more reactive the molecule.

The larger the gap, the more stable and less reactive the molecule.

2. Photochemistry:

The absorption of light excites an electron from the HOMO to the LUMO.

For example, in dyes and semiconductors.

3. Electrical conductivity:

In conductive and semiconductor materials, the HOMO–LUMO gap determines their conductivity.

□ Simplified example:

In the ethylene molecule (C_2H_4):

The HOMO is a π orbital (occupied).

The LUMO is a π* orbital (antibonding, empty).

Any addition reaction (such as H_2 or Br_2) occurs through the overlap of the HOMO with the LUMO.

Ill explain it visually (imagine a simple energy diagram):

↑ High energy

|-------- LUMO (empty orbital)

| Energy gap

|-------- HOMO (highest occupied orbital)

↓ Low energy

□ Process:

The electron is in the HOMO.

When light or energy is absorbed, it jumps to the LUMO.

The difference between the two energies = the gap size.

□ Result:

If the gap is small → the transition is easier → the molecule is chemically active (e.g., colored dyes).

If the gap is large → the transition is difficult → the molecule is stable (e.g., noble gases or saturated molecules).

Explaining the hydrogen molecule H_2 using the HOMO-LUMO concept:

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1. Formation of the H_2 Molecule

Each hydrogen atom has one electron in its 1s orbital.

When two atoms come close together, the 1s + 1s orbitals fuse → forming two molecular orbitals:

1. σ (bonding orbital) = bonding orbital (lowest energy) → electrons are concentrated between the two nuclei.

2. σ (antibonding orbital)* = antibonding orbital (highest energy).

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2. Filling Electrons

H_2 has two electrons.

These two electrons fill the σ (bonding) orbital.

The σ* orbital remains empty.

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3. HOMO–LUMO Relationship

HOMO (highest occupied orbital) = σ (bonding).

LUMO (lowest empty orbital) = σ* (antibonding).

The gap between them is large → therefore, the H_2 molecule is very stable.

Let's take a second example other than H_2 for comparison:

□ Example: Oxygen molecule O_2

1. Electron configuration of single atoms (O):

Atomic number = 8

Distribution: $1s^2\ 2s^2\ 2p^4$

2. When forming an O_2 molecule:

The 2p orbitals of the two atoms combine → molecular orbitals are formed:

σ(2px), π(2py), π(2pz) (bonds)

σ*(2px), π*(2py), π*(2pz) (antibonding)

3. Electron filling:

O_2 has 16 electrons.

After filling the orbitals: Two single electrons remain in the π* orbitals (antibonding).

4. HOMO–LUMO:

HOMO = occupied π* (antibonding) orbital.

LUMO = empty π* orbital.

5. Conclusion:

The presence of electrons in antibonding orbitals explains why oxygen is less stable than H_2.

More importantly, this explains its paramagnetic property (attracts magnets) because it has unpaired electrons.

Comparison:

H_2: All electrons in bonding orbitals → very stable.

O_2: Has electrons in antibonding orbitals → less stable + paramagnetic.

We explain the nitrogen molecule N_2 using the same logic as molecular orbitals (MO) and HOMO–LUMO:

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1. Electron configuration of a single atom (N)

Atomic number = 7

Configuration: $1s^2\ 2s^2\ 2p^3$

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2. Formation of the N_2 molecule

When two nitrogen atoms combine → we have 14 electrons.

The orbitals combine to form:

Bonding orbitals: σ(1s), σ(2s), π(2px), π(2py), σ(2pz)

Anti-bonding orbitals: σ*(1s), σ*(2s), π*(2px), π*(2py), σ*(2pz)

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3. Filling the electrons

We distribute 14 electrons:

σ(1s) → 2 electrons

σ*(1s) → 2 electrons

σ(2s) → 2 electrons

σ*(2s) → 2 electrons

π(2px), π(2py) → 4 electrons

σ(2pz) → 2 electrons

 Result: All electrons are filled in bonding orbitals, and no electrons are in anti-bonding (2p*) orbitals.

4. HOMO – LUMO

HOMO (Highest Occupied Orbital) = σ(2pz)

LUMO (Lowest Empty Orbital) = π*(2px) or π*(2py)

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5. Stability

The bond in N_2 is very strong because:

There are no electrons in antibonding orbitals.

Bond order = (10 bonding electrons – 4 antibonding) ÷ 2 = 3 (triple bond).

 This explains why N_2 is a very inert molecule (difficult to react; it requires high energy to break, for example, in the Haber process to produce ammonia).

 Quick comparison:

H_2 → Simple bond (σ), large gap → Stable.

N_2 → Very strong triple bond → Inert.

O_2 → Has electrons in antibonding orbitals → Less stable + paramagnetic.

This is a comparison table between H_2, N_2, and O_2 in terms of molecular orbitals, HOMO–LUMO, and bond order:

Molecule Number of electrons HOMO (highest occupied orbital) LUMO (lowest empty orbital) Bond order Stability/Properties

H_2 2 σ(1s) σ*(1s) 1 (single bond) Very stable, large energy gap

N_2 14 σ(2pz) π*(2px, 2py) 3 (triple bond) Very stable and inert, very strong bond

O_2 16 π*(2px, 2py) (partially occupied) π*(2px, 2py) (partially empty) 2 (double bond) Less stable than N_2, paramagnetic (attracts magnets)

 Summary:

H_2: Very simple, strong, and stable single bond.

N_2: Strongest triple bond between atoms → Inert and difficult to react.

O_2: Double bond + lone electrons in anti-orbitals → More reactive + paramagnetic.

We explain the concept of the HOMO–LUMO gap and its relationship to color:

1. The principle of light absorption

The molecule absorbs a photon (light) → bounces an electron from the HOMO → LUMO.

The amount of energy required = the energy gap (ΔE).

Relationship:

ΔE = h\cdot ν = \frac{hc} {λ}

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2. If the gap is large, it requires high energy (ultraviolet radiation).

The molecule absorbs in the UV (invisible).

Result: The substance is transparent or colorless to the eye (such as H_2 or N_2).

3. If the gap is small, it requires less energy (visible light 400–700 nm).

The molecule absorbs a specific color from the visible spectrum.

What we see is the complementary color of the absorbed color.

For example:

If the molecule absorbs green light, it appears red.

If it absorbs blue, it appears orange/yellow.

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4. Examples from Daily Life

O_2: Medium bandgap, absorbs little in a specific area, but is nearly transparent.

Organic pigments (such as β-carotene in carrots): Small bandgap → absorbs blue/green → appears orange.

Transition metals (such as Cu^{2+} or Fe^{3+} ions): Small d-d or HOMO–LUMO transitions → give distinct colors (blue, green, etc.).