

Molecular Orbital Theory (MOT)

S-7: Introduction and LCAO method

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Dt. 24/9/2021

Molecular Orbital Theory (MOT)

- ❖ MOT was developed by F. Hund, R.S. Mulliken and J.E. Lennard-Jones
- ❖ As the atomic orbitals are the solutions of the time-independent Schrodinger wave equation for atoms, molecular orbitals are the corresponding solutions for molecules.
- ❖ Atomic orbitals represent the regions around the nuclei where there is a high probability of finding the electrons
- ❖ When atomic orbitals come close together, they overlap forming Molecular orbitals (MO)
- ❖ When two atomic orbitals overlap to form two MOs, one of them lies at a lower energy level than the overlapping orbitals, and is called a **bonding molecular orbital** (BMO)
- ❖ The other one lies at a higher energy level, called as **antibonding molecular orbital** (ABMO)

- ❖ The goal of molecular orbital theory is to describe molecules in a similar way as we describe atoms, that is, in terms of orbitals, orbital diagrams, and electron configurations.
- ❖ According to **Born-Oppenheimer approximation**, the nuclei being so much heavier than electrons, can be treated as stationary and the electrons move relative to them
- ❖ The Schrödinger wave equation can be solved for the electronic wave function
- ❖ In the LCAO-MO method, the MO can be written as,

$$\psi = c_1 \phi_1 + c_2 \phi_2 + \dots \quad (1)$$
 where ϕ_1 and ϕ_2 are atomic orbitals

- ❖ The energy E of the MO can be obtained by solving the Schrödinger wave Equation: $\hat{H}\psi = E\psi$
where \hat{H} is the Hamiltonian operator

The energy E is given by,

$$E = \int \psi^* \hat{H} \psi \, d\tau / \int \psi^* \psi \, d\tau \dots\dots\dots (2)$$

Substituting Eq. 1 into Eq. 2, we have

$$\begin{aligned} E &= \int (c_1\phi_1 + c_2\phi_2) \hat{H} (c_1\phi_1 + c_2\phi_2) \, d\tau / \int (c_1\phi_1 + c_2\phi_2)^2 \, d\tau \\ &= c_1\phi_1 \hat{H} c_1\phi_1 + c_1\phi_1 \hat{H} c_2\phi_2 + c_2\phi_2 \hat{H} c_1\phi_1 + c_2\phi_2 \hat{H} c_2\phi_2 \, d\tau / \int (c_1^2\phi_1^2 + 2c_1c_2\phi_1\phi_2 + c_2^2\phi_2^2) \, d\tau \dots\dots\dots (3) \end{aligned}$$

$$\begin{aligned} \text{Let } H_{11} &= \int \phi_1 \hat{H} \phi_1 d\tau \\ H_{12} &= H_{21} = \int \phi_1 \hat{H} \phi_2 d\tau = \int \phi_2 \hat{H} \phi_1 d\tau \\ H_{22} &= \int \phi_2 \hat{H} \phi_2 d\tau \\ S_{11} &= \int \phi_1^2 d\tau ; S_{22} = \int \phi_2^2 d\tau ; \\ S_{12} &= S_{21} = \int \phi_1 \phi_2 d\tau \end{aligned}$$

Now Eq. 3 can be written as,

$$E = c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22} / c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22} \dots\dots\dots (4)$$

The ground state energy is given by $dE/dc_i = 0$

Hence we have

$$c_1 H_{11} + c_2 H_{12} = (c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22}) (c_1 S_{11} + c_2 S_{12}) / (c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22})$$

$$\text{Or, } c_1 H_{11} + c_2 H_{12} = E (c_1 S_{11} + c_2 S_{12})$$

$$\text{Or, } c_1 (H_{11} - ES_{11}) + c_2 (H_{12} - ES_{12}) = 0 \dots\dots\dots(5)$$

$$\text{Similarly, } c_1 (H_{21} - ES_{21}) + c_2 (H_{22} - ES_{22}) = 0 \dots\dots\dots (6)$$

The essential condition for these equations to have a non-trivial solution is that the determinant of coefficients of c_1 and c_2 should vanish, i.e.,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \dots\dots\dots(7)$$

where H_{ii} (Coulomb integral) = $\int \phi_i H \phi_i d\tau$ represents the energy of electron in the AO of atom i

H_{ij} (Exchange integral) = $\int \phi_i H \phi_j d\tau$ represents the energy of interaction of electrons in atoms i and j

S_{ij} (overlap integral) = $\int \phi_i \phi_j d\tau$ represents overlap of orbitals centered on atoms i and j

Eq. 7 can be solved to obtain the energies of the molecular orbitals.

For a **diatomic molecule**,

$$\Psi_g = 1 (\phi_a + \phi_b) / [2 (1+s)]^{1/2}$$

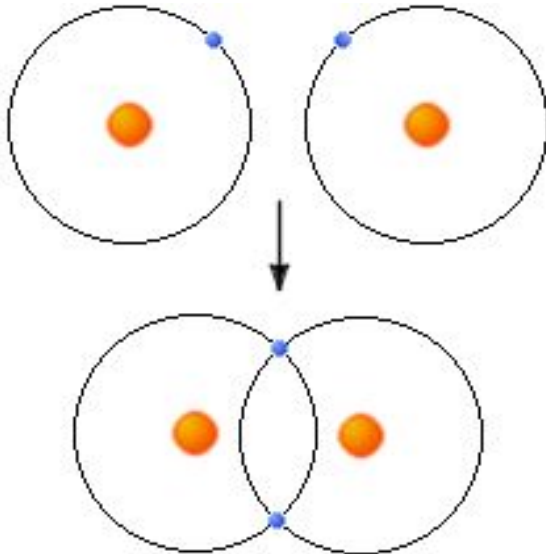
$$\text{and } \Psi_u = 1 (\phi_a - \phi_b) / [2 (1- s)]^{1/2}$$

where Ψ_g is **bonding MO** and Ψ_u is **anti-bonding MO**.

Atomic and Molecular Orbitals

• Orbital Mixing

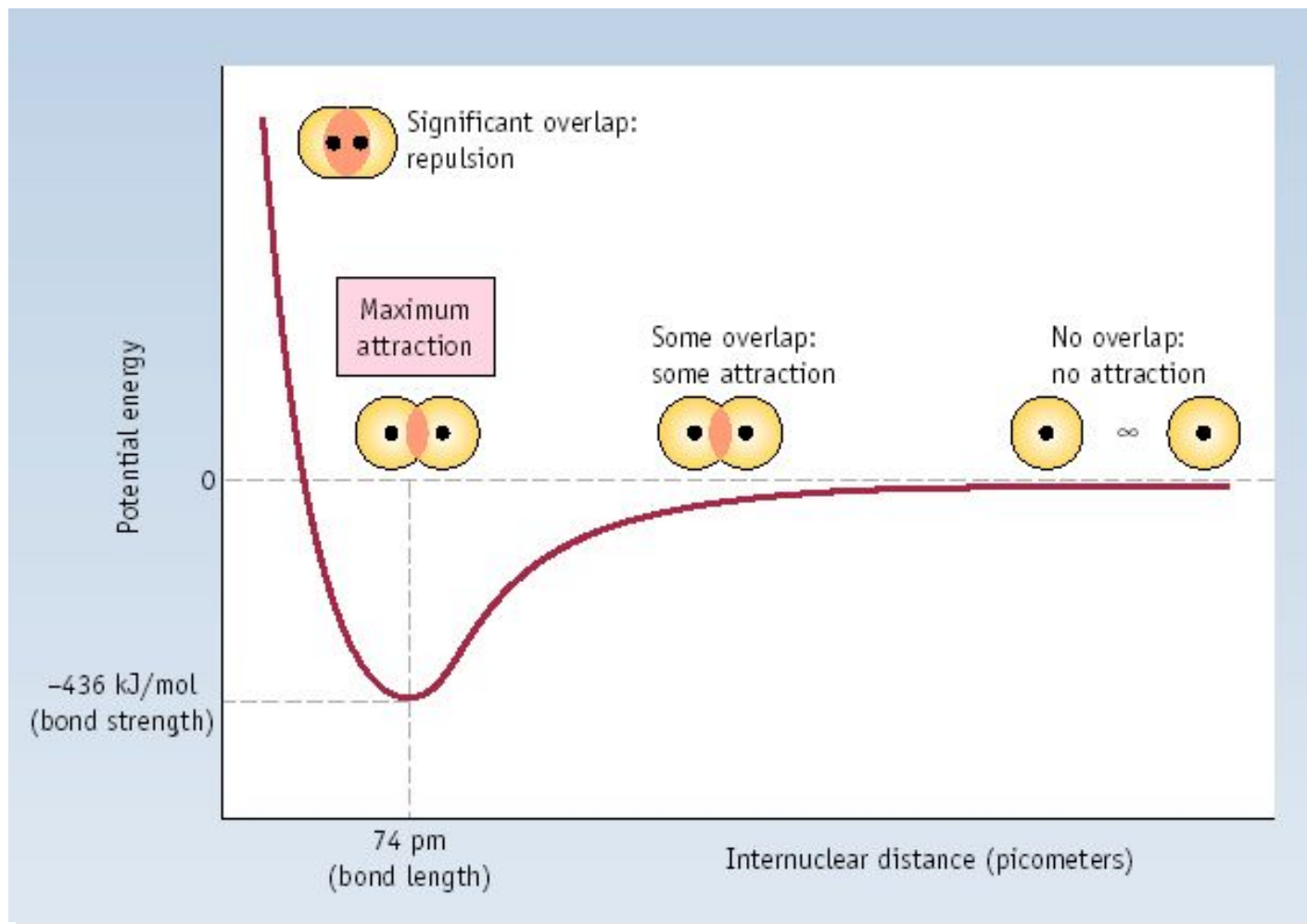
- When atoms share electrons to form a bond, their atomic orbitals mix to form molecular orbitals. In order for these orbitals to mix they must:
 - Have similar energy levels
 - Overlap well
 - Be close together

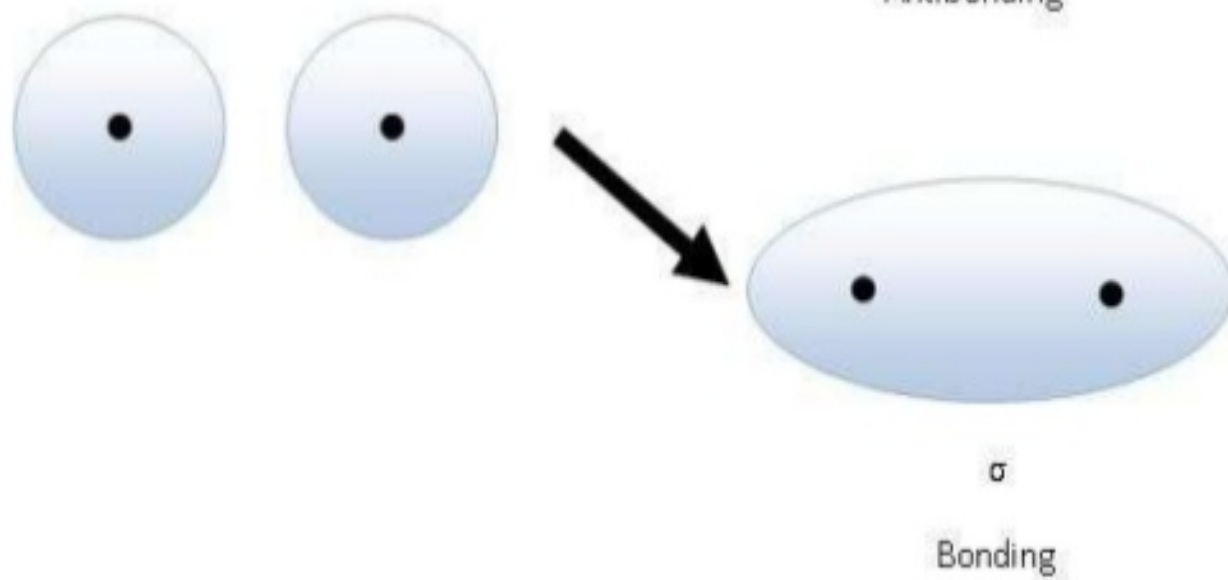
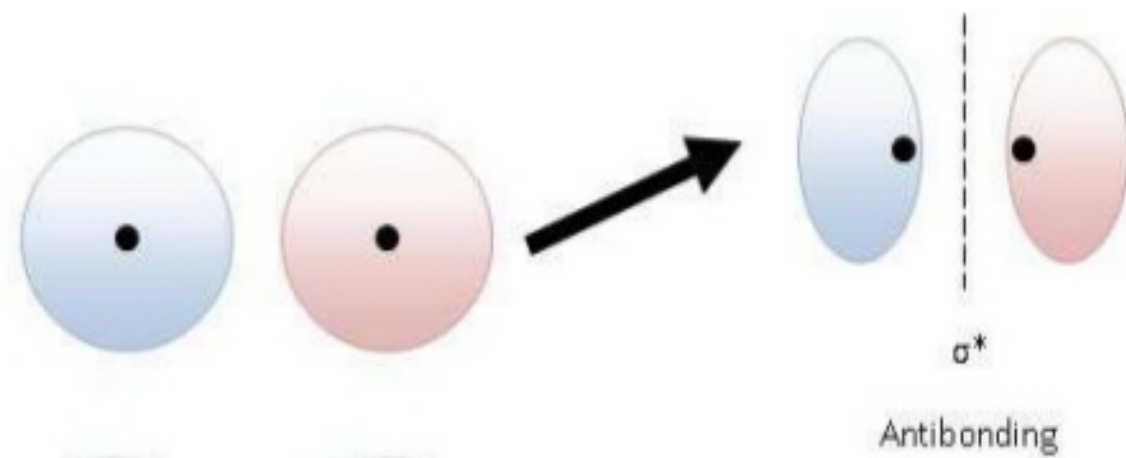


This is an example of orbital mixing. The two atoms share one electron each from their outer shell.

In this case, both 1s orbitals overlap and share their valence electrons.

Energy Diagram of Sigma Bond Formation by Orbital Overlap





Difference between Bonding and antibonding molecular orbitals

Bonding MO	Antibonding MO
Formed by addition overlap of Atomic orbitals	Formed by subtraction overlap of atomic orbitals
Wave function of a BMO is given by $\psi_{MO} = \psi_A + \psi_B$	Wave function of an ABMO is given by $\psi_{MO}^* = \psi_A - \psi_B$
Its formation takes place when lobes of atomic orbitals have same signs	Its formation takes place when lobes of atomic orbitals have different signs
The energy of BMO is lower than the atomic orbitals from which it is formed	The energy of ABMO is higher than the atomic orbitals from which it is formed
The electron density is high in the region between the nuclei of bonded atoms	The electron density is low in the region between the nuclei of bonded atoms

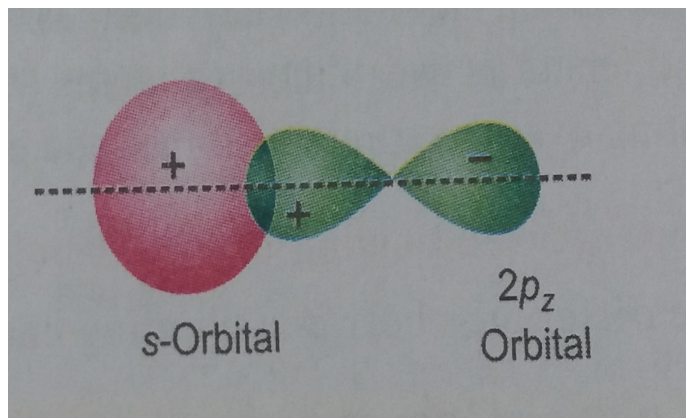
Conditions for the combination of atomic orbitals

- ❖ The energies of atomic orbitals should be comparable
e.g., 1s orbital of one atom combines with 1s orbital of other atom
- ❖ The extent of overlapping between the two atomic orbitals should be to a considerable extent
 - Greater the overlap between the atomic orbitals, greater is the charge density between the nuclei
- ❖ The symmetry of the combining atomic orbitals should be the same

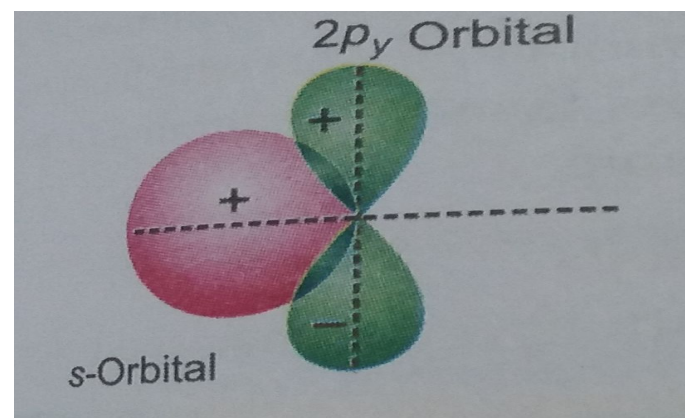
The atomic orbitals should have the same symmetry about the internuclear axis. For ex: 2s orbital of one atom can combine with 2s or $2p_z$ orbital of another atom, but not with $2p_x$ or $2p_y$ orbital

Allowed combination of atomic orbitals

1 st orbital	2 nd orbital	Type of MO formed
s-orbital	s-orbital	σ (sigma)
s-orbital	p_z -orbital	σ (sigma)
p_z -orbital	p_z -orbital	σ (sigma)
p_y -orbital	p_y -orbital	π (Pi)
p_x -orbital	p_x -orbital	π (Pi)

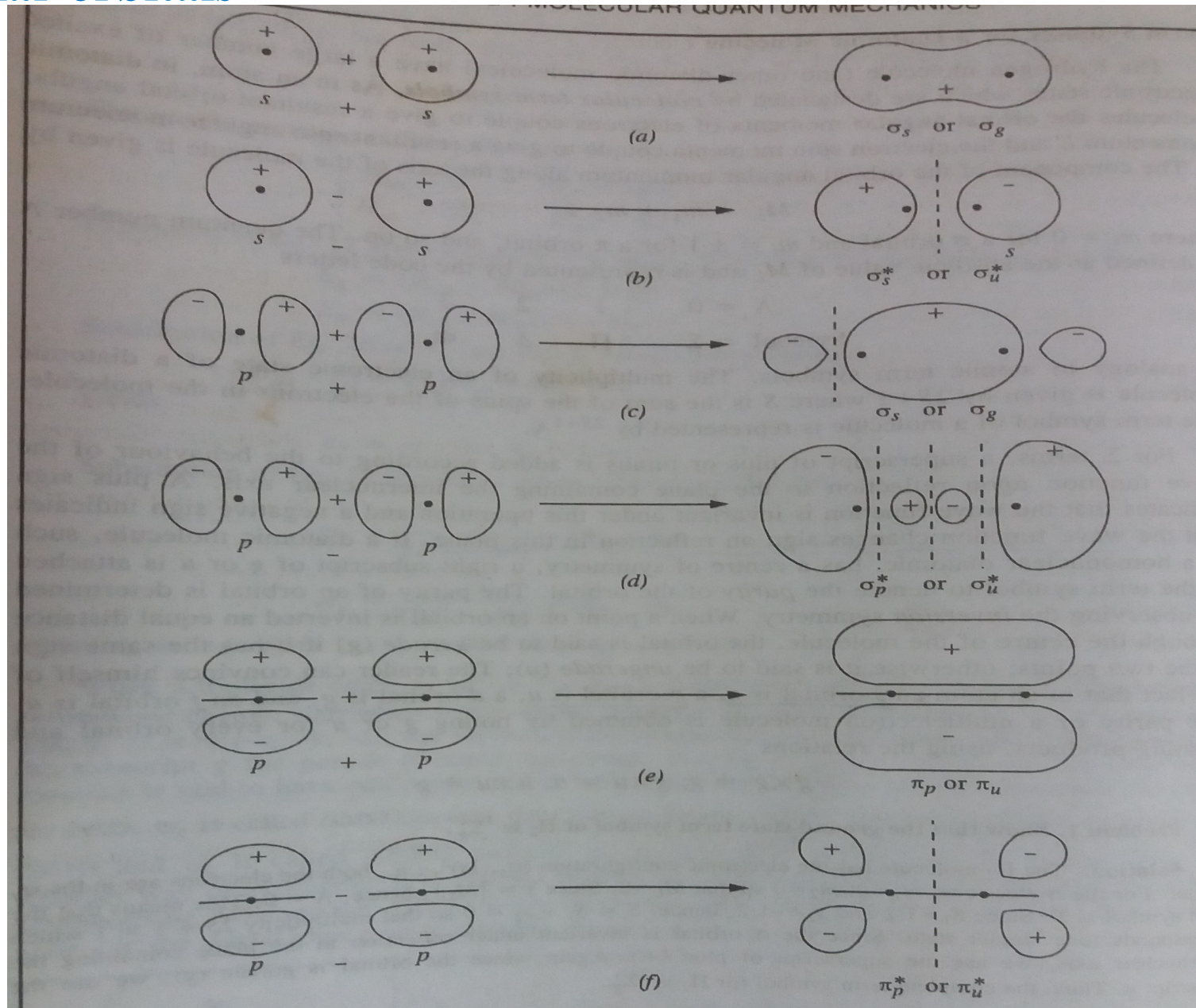


Allowed because of similar symmetry

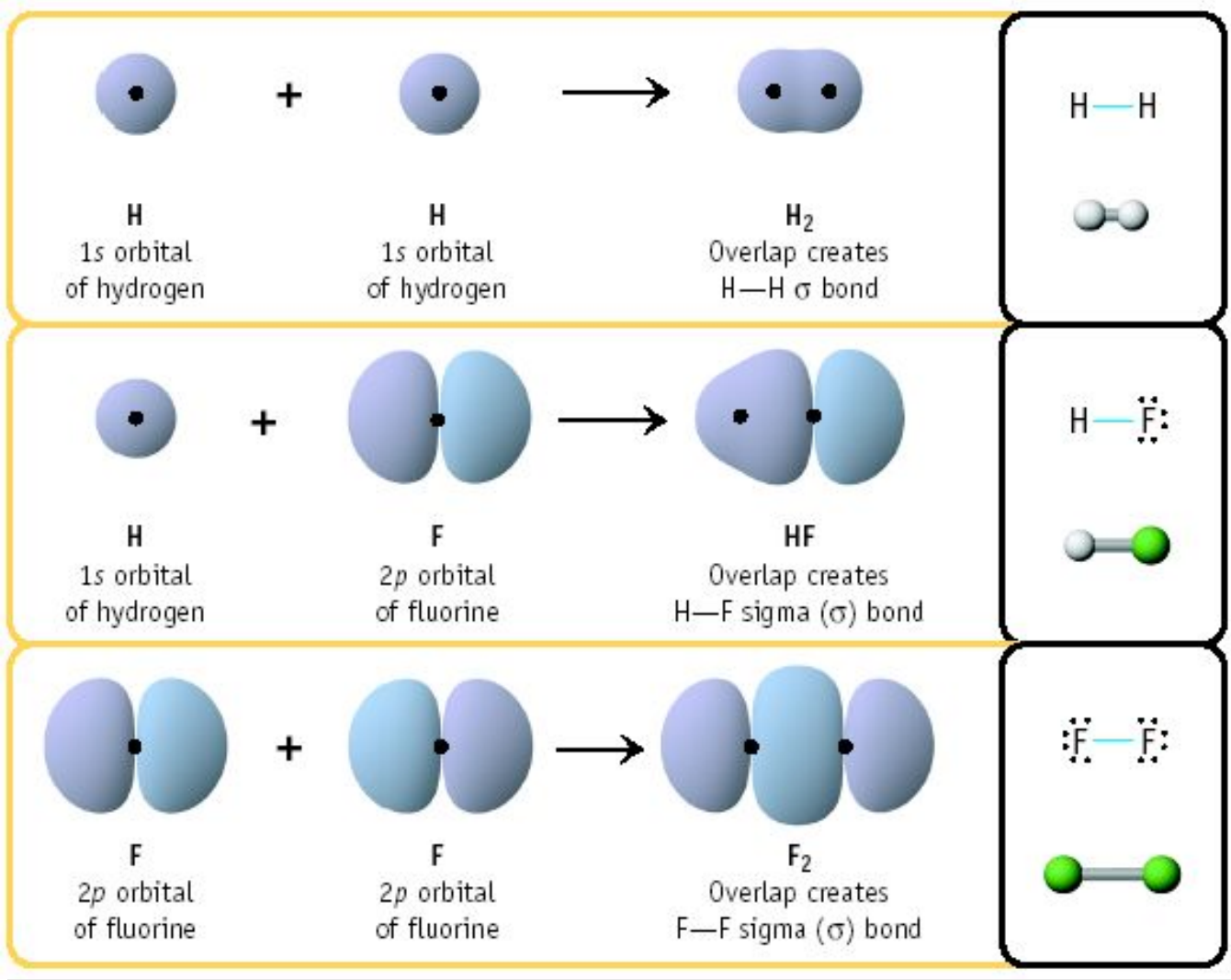


Not Allowed because of different symmetry

Different combinations of s, s and p, p atomic orbitals to form molecular orbitals



Examples of Sigma Bond Formation



**Thank
You**