Théories of Formation of Covalent Bond

Presented by

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Contents of Presentation

- Covalent Bond
- Valence Bond Theory
- Limitations of Valence Bond Theory
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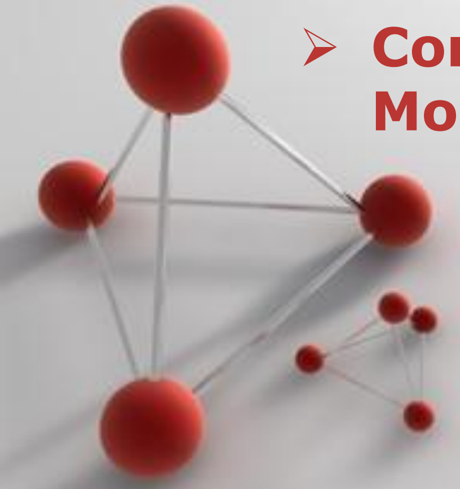
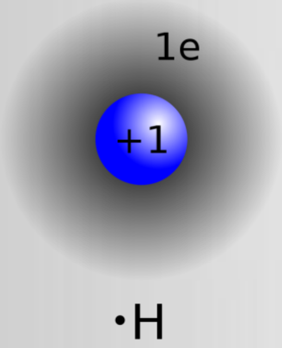
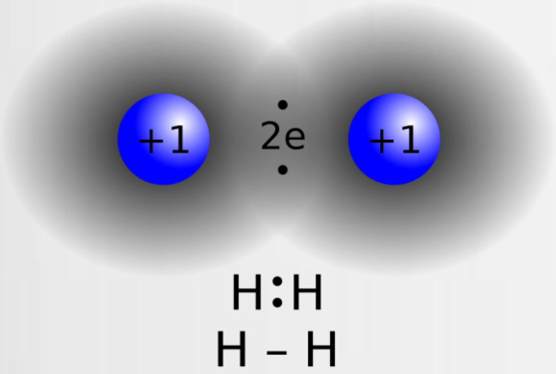
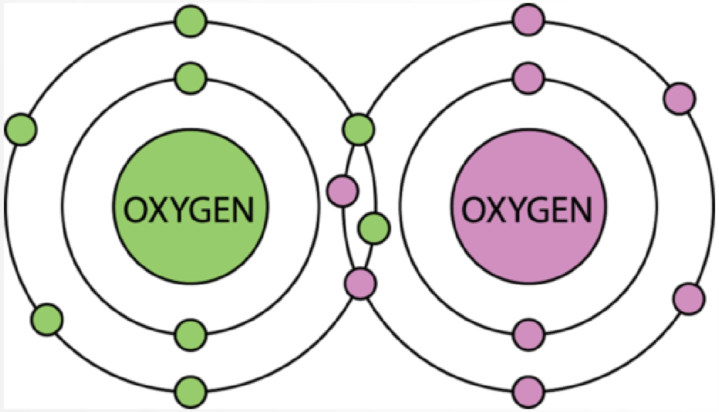


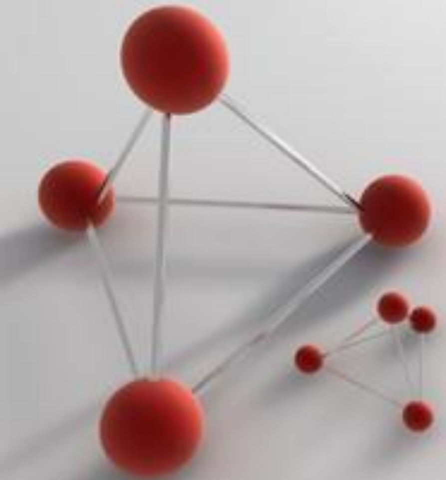
Covalent Bond:

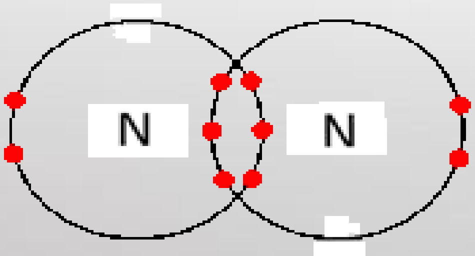
Sharing of electron pairs between atoms

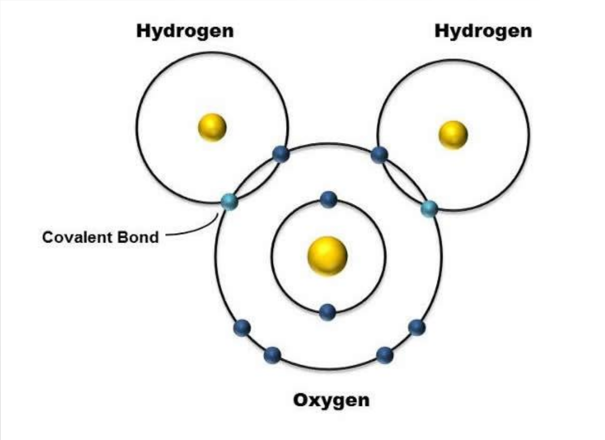












Theories of Covalent Bond

Use the methods of quantum mechanics to explain chemical bonding

(how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds)

VBT

Heitler-London (1927)
Pauling-Slater (1937)

MOT

Hund and Mulliken (1932)

Valence Bond Theory

Postulates:

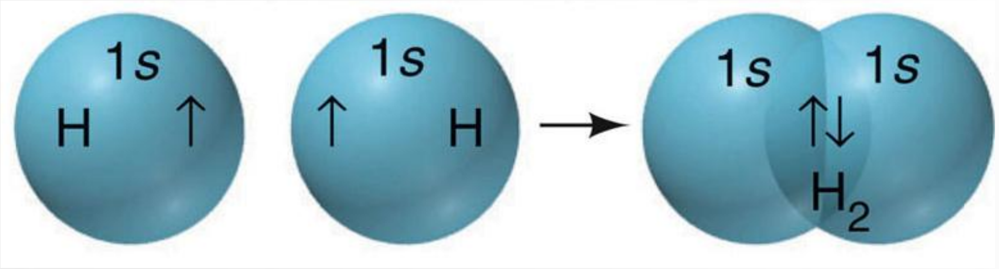
A covalent bond forms when the orbitals of two atoms ***overlap*** and a pair of electrons occupy the overlap region.

The space formed by the overlapping orbitals can accommodate a ***maximum of two electrons*** and these electrons must have ***opposite (paired) spins***.

The greater the orbital overlap, the stronger the bond.

Extent of orbital overlap depends on orbital shape and direction.

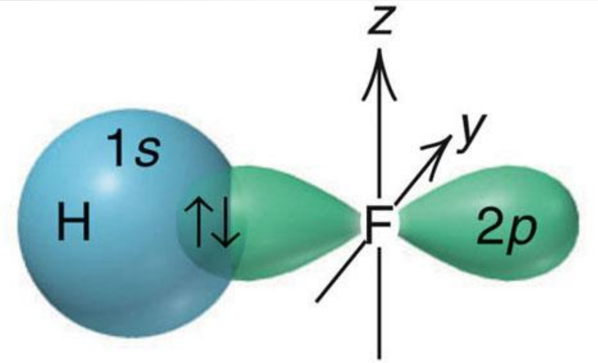
Orbital overlap and spin pairing in H_2.



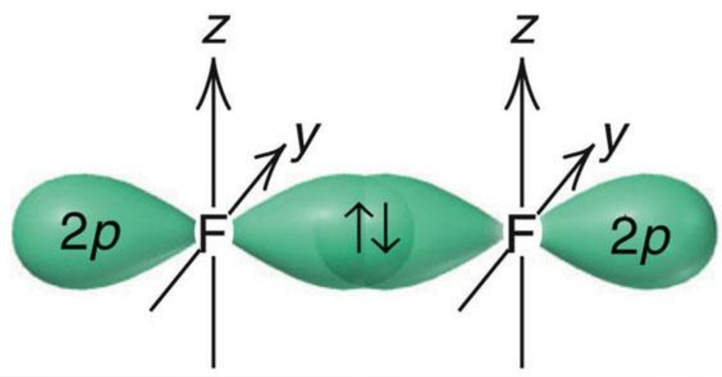
A covalent bond results from the overlap of orbitals from two atoms.

The shared space is occupied by two electrons, which have opposite spins.

Orbital orientation and maximum overlap.



Hydrogen fluoride, HF.



Fluorine, F_2.

The greater the extent of orbital overlap, the stronger the bond.

VB Theory and Orbital Hybridization

The orbitals that form when bonding occurs are ***different*** from the atomic orbitals in the isolated atoms.

If no change occurred, we could not account for the molecular shapes that are observed.

Atomic orbitals “mix” or ***hybridize*** when bonding occurs to form ***hybrid orbitals***.

The spatial orientation of these hybrid orbitals correspond with observed molecular shapes.

Features of Hybrid Orbitals

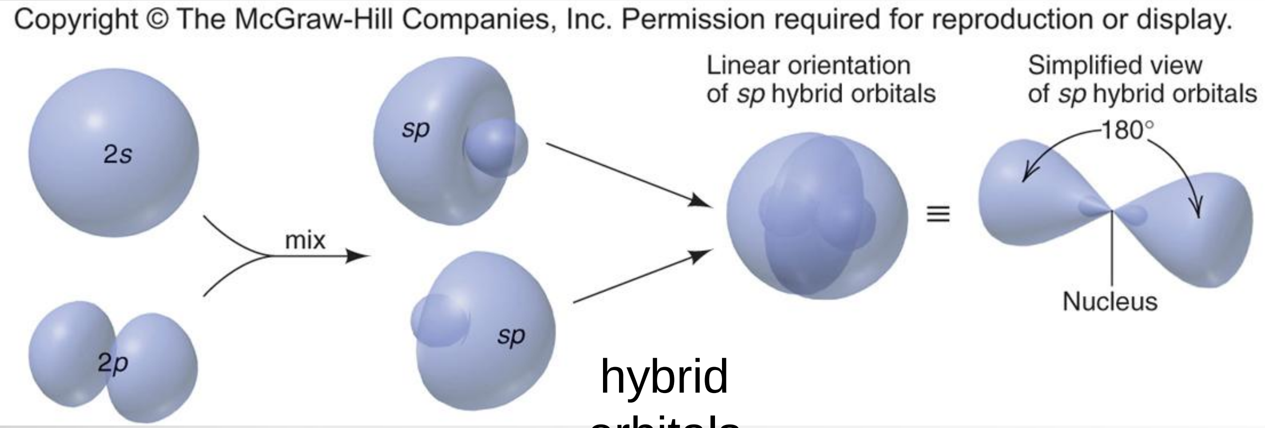
The ***number*** of hybrid orbitals formed ***equals*** the number of atomic orbitals mixed.

The ***type*** of hybrid orbitals formed ***varies*** with the types of atomic orbitals mixed.

The ***shape*** and ***orientation*** of a hybrid orbital ***maximizes*** overlap with the other atom in the bond.

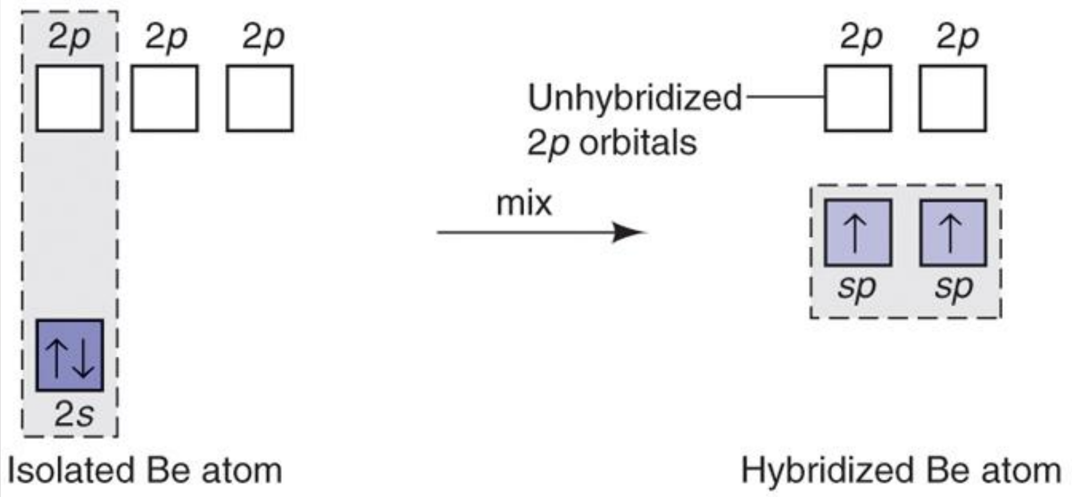
Formation and orientation of *sp* hybrid orbitals and the bonding in $BeCl_2$.

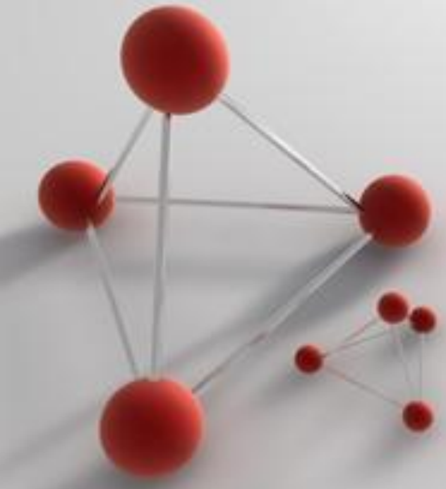
atomic
orbitals



hybrid
orbitals

One 2*s* and one 2*p* atomic orbital mix to form two sp hybrid orbitals.





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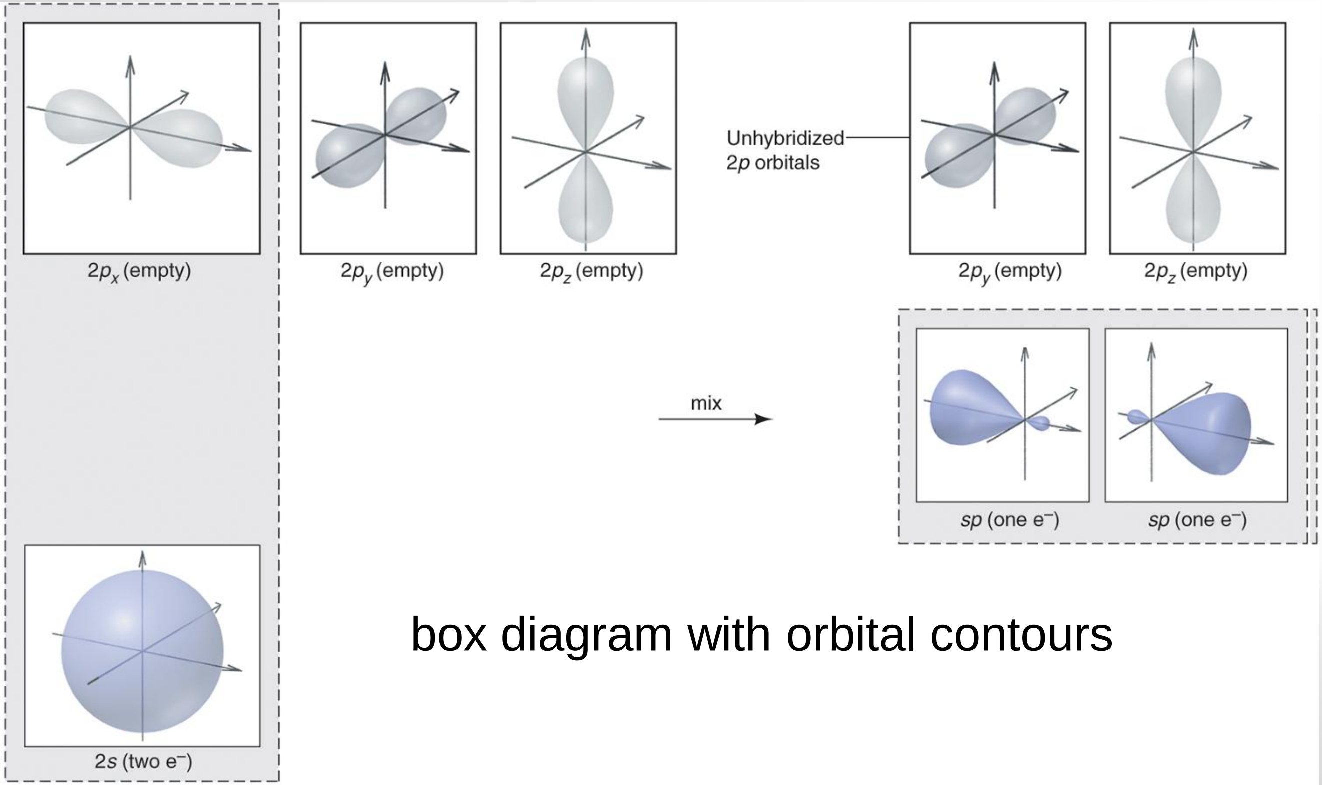
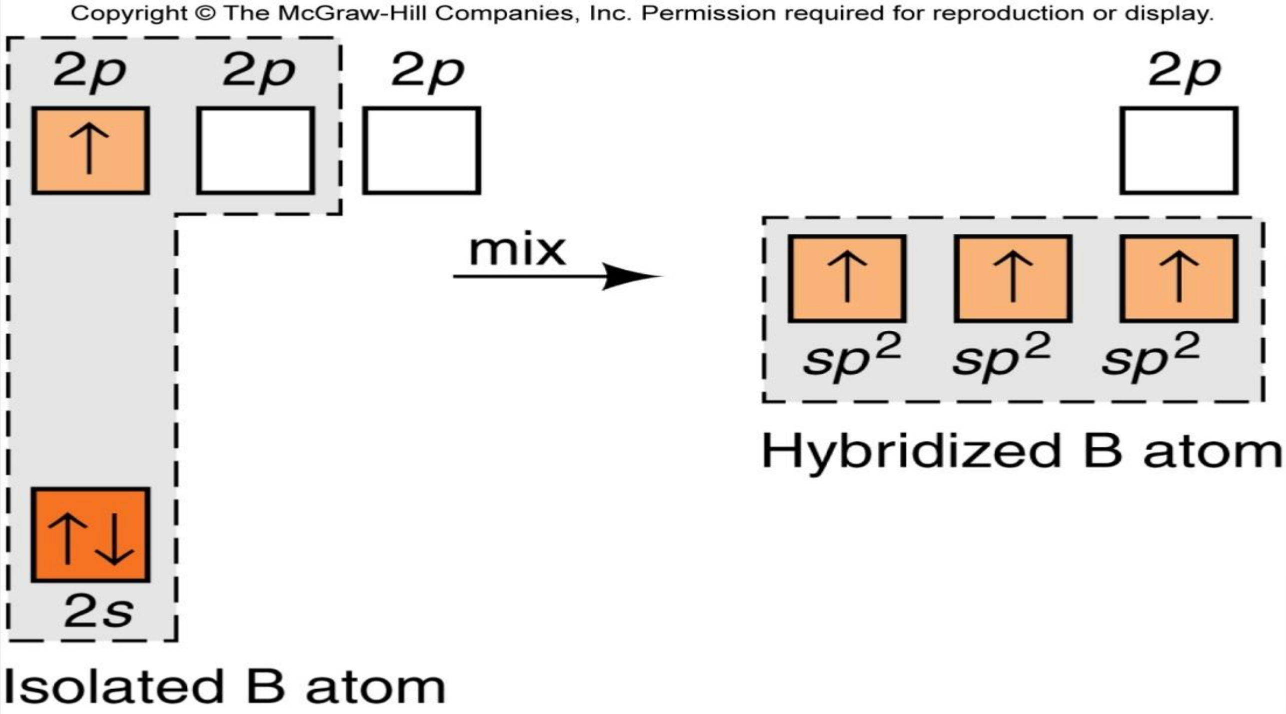


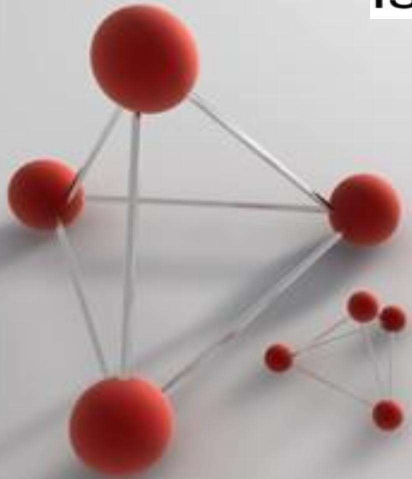
box diagram with orbital contours

Overlap of Be and Cl orbitals to form $BeCl_2$.

The sp^2 hybrid orbitals in BF_3.



Mixing one *s* and two *p* orbitals gives three sp^2 hybrid orbitals. The third 2*p* orbital remains unhybridized.



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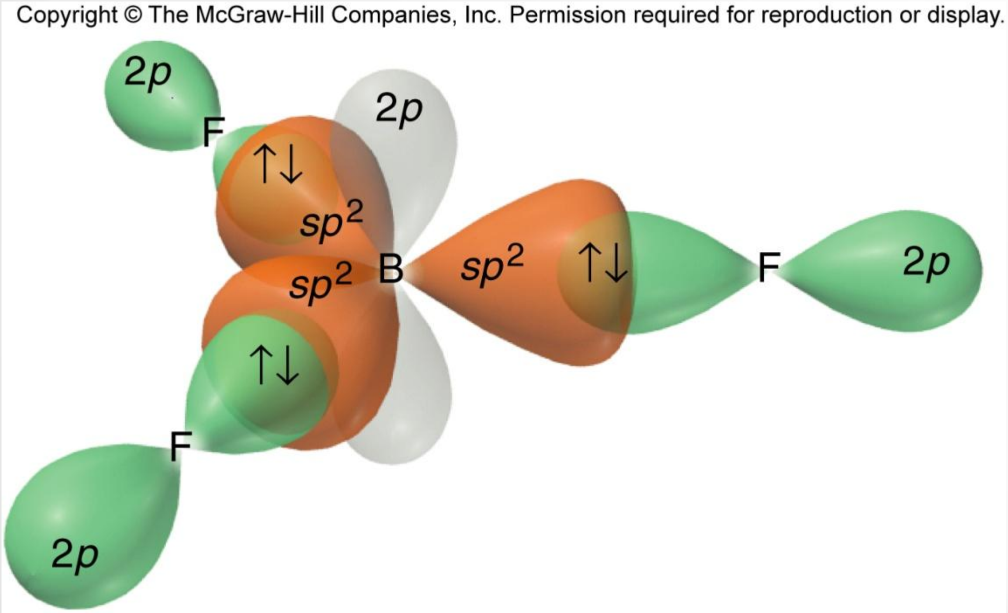
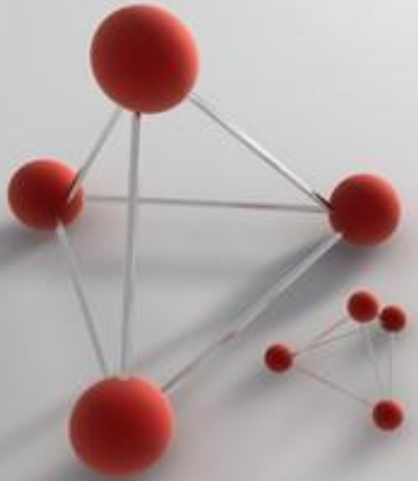
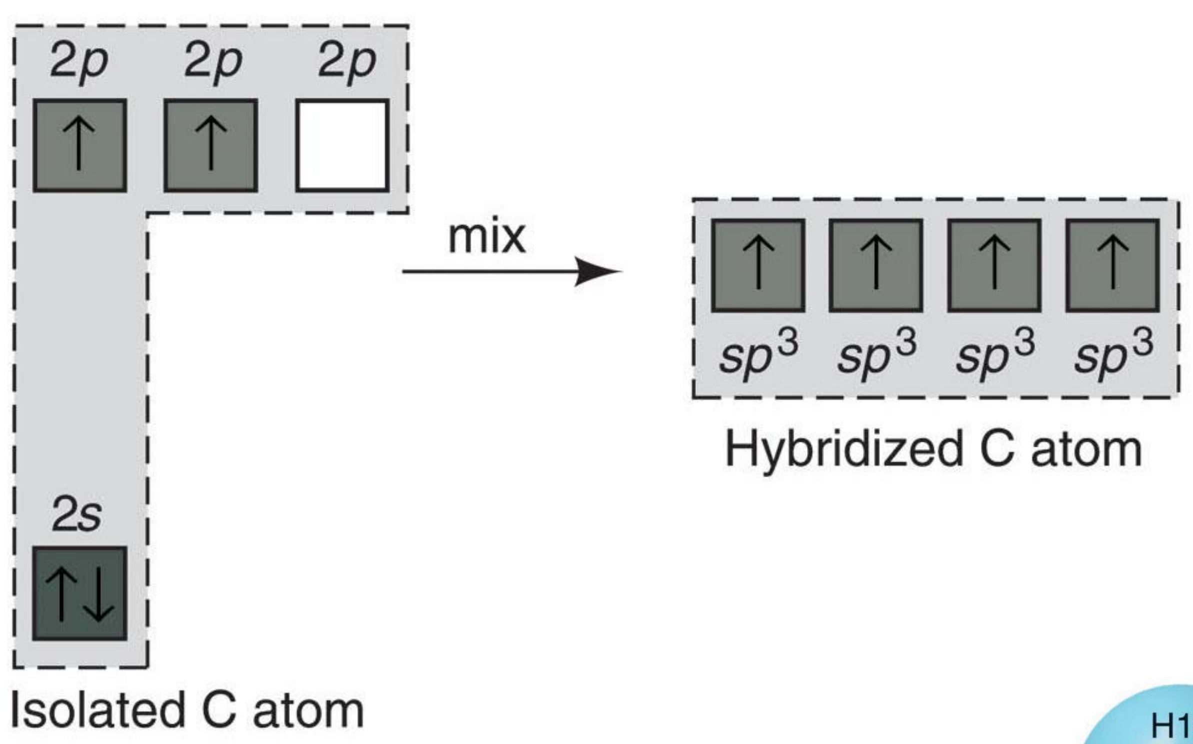


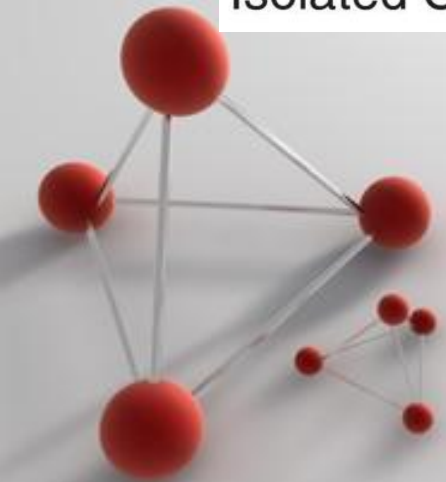


The three sp^2 orbitals point to the corners of an equilateral triangle, their axes 120° apart.

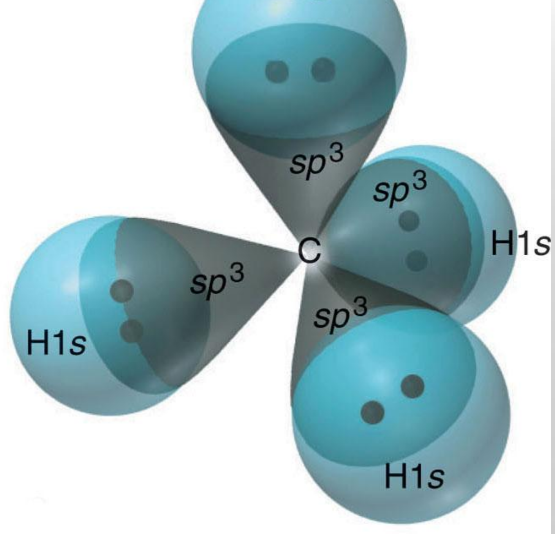
Each half-filled sp^2 orbital overlaps with the half-filled $2p$ orbital of a F atom.

The sp^3 hybrid orbitals in CH_4.

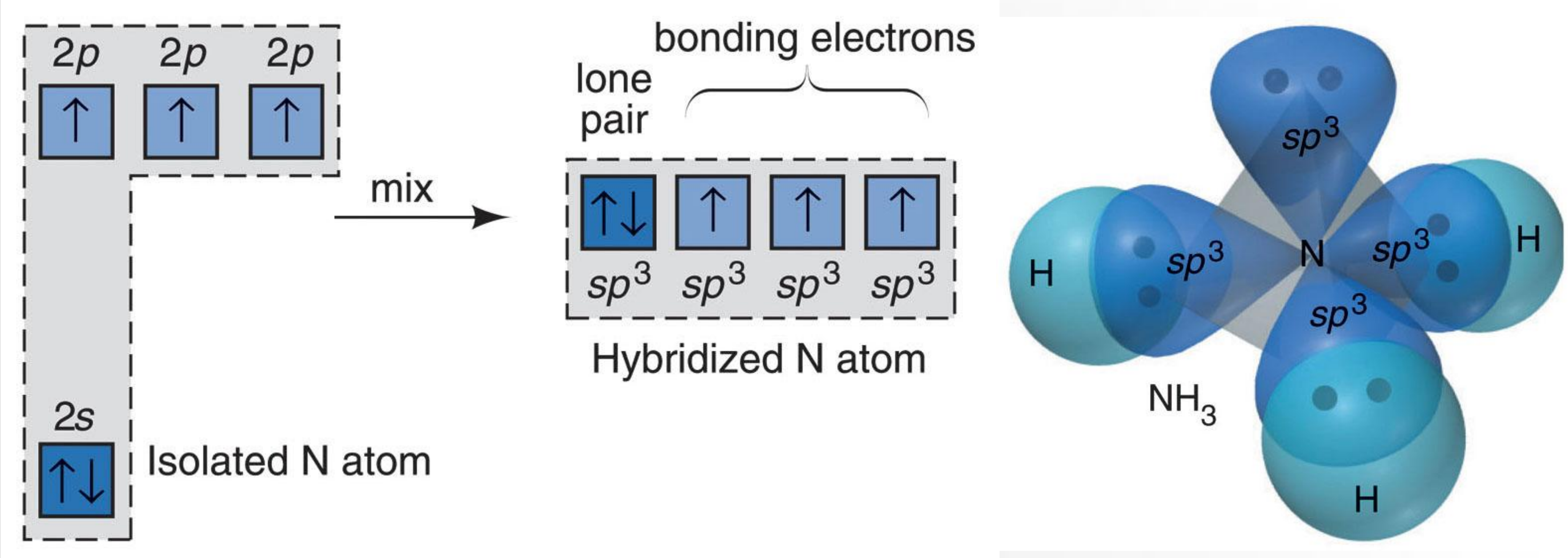


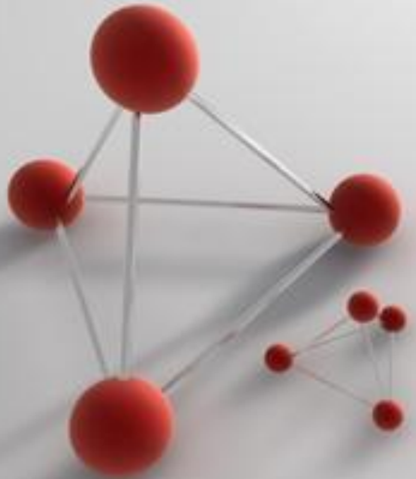


The four sp^3 orbitals adopt a tetrahedral shape.



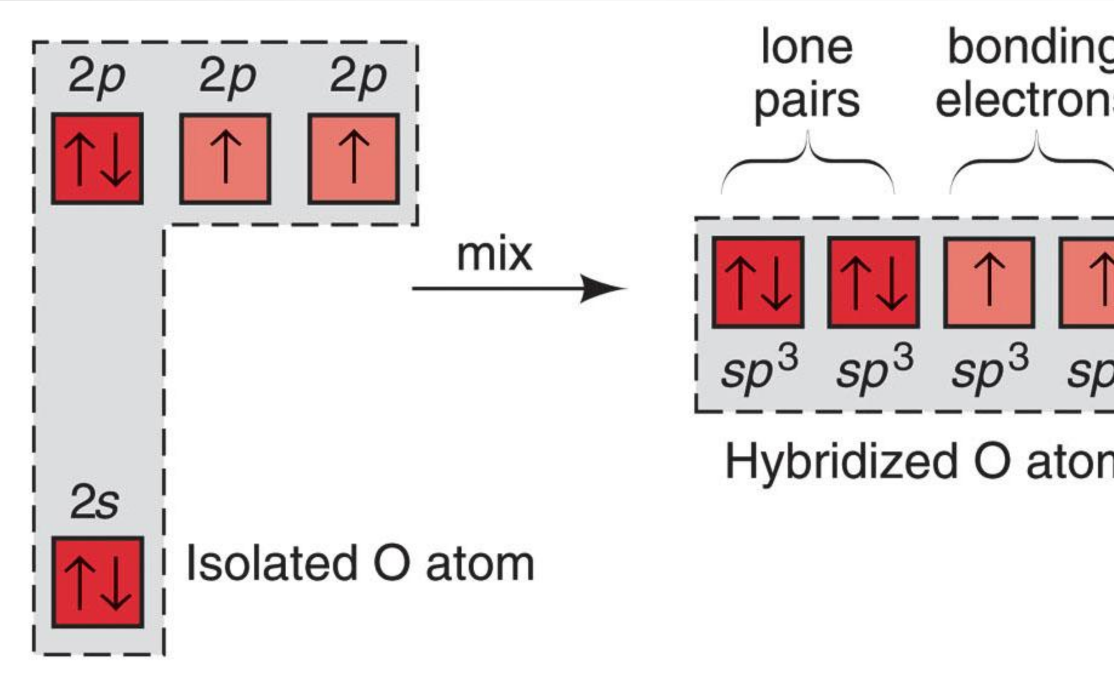
The sp^3 hybrid orbitals in NH_3.

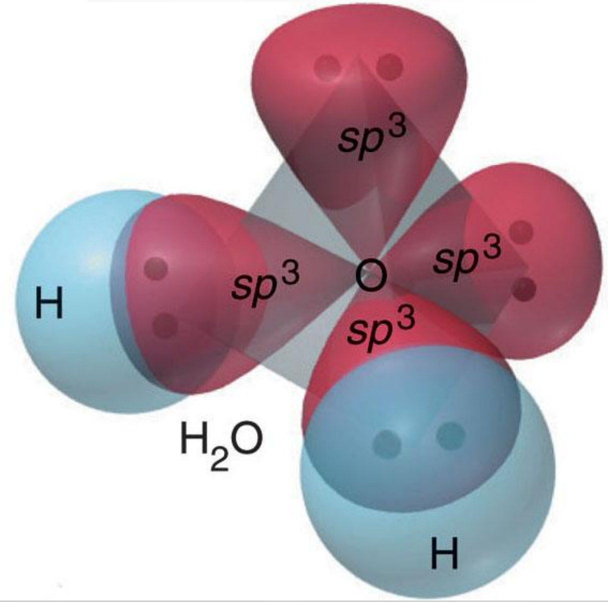




The N lone pair occupies an sp^3 hybrid orbital, giving a trigonal pyramidal shape.

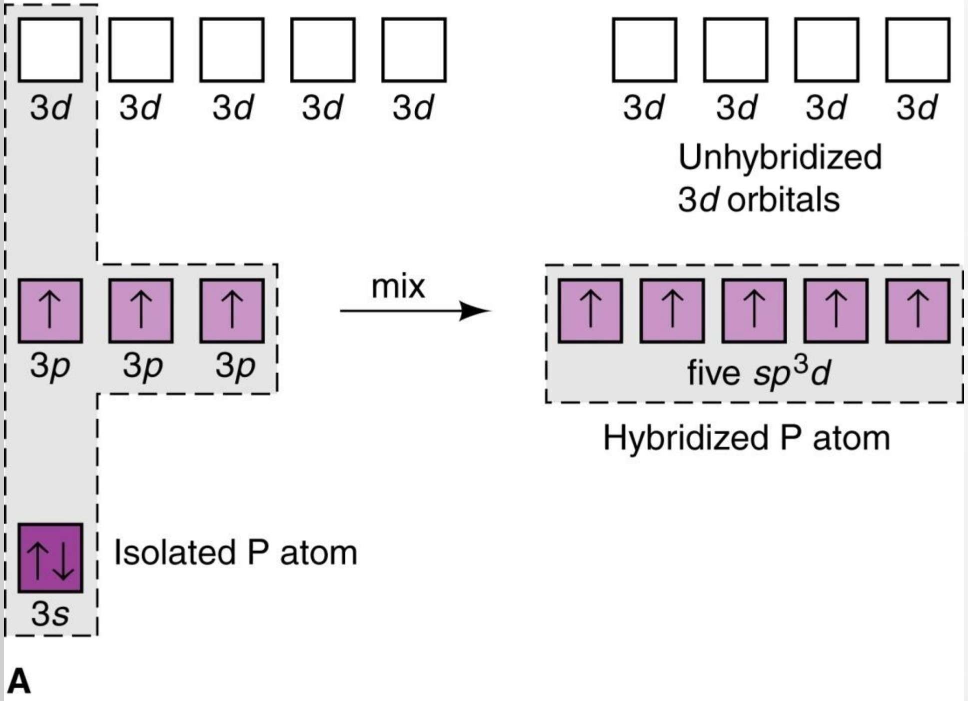
The sp^3 hybrid orbitals in H_2O.

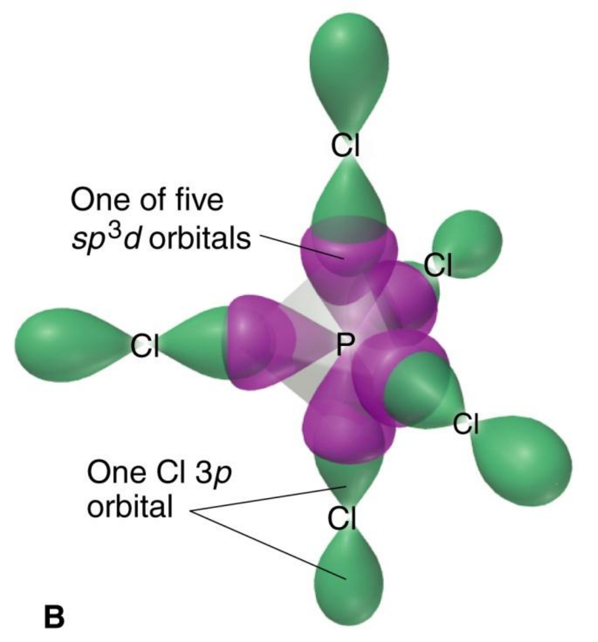


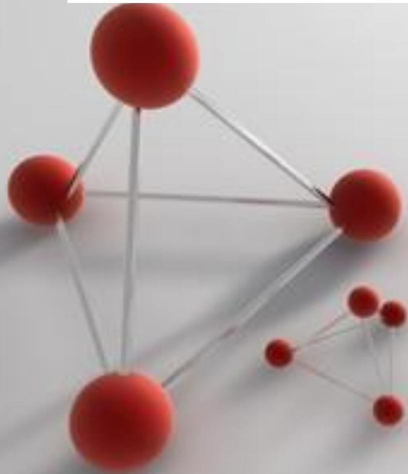


The O lone pairs occupy sp^3 hybrid orbitals, giving a bent shape.

The sp^3d hybrid orbitals in PCl_5.

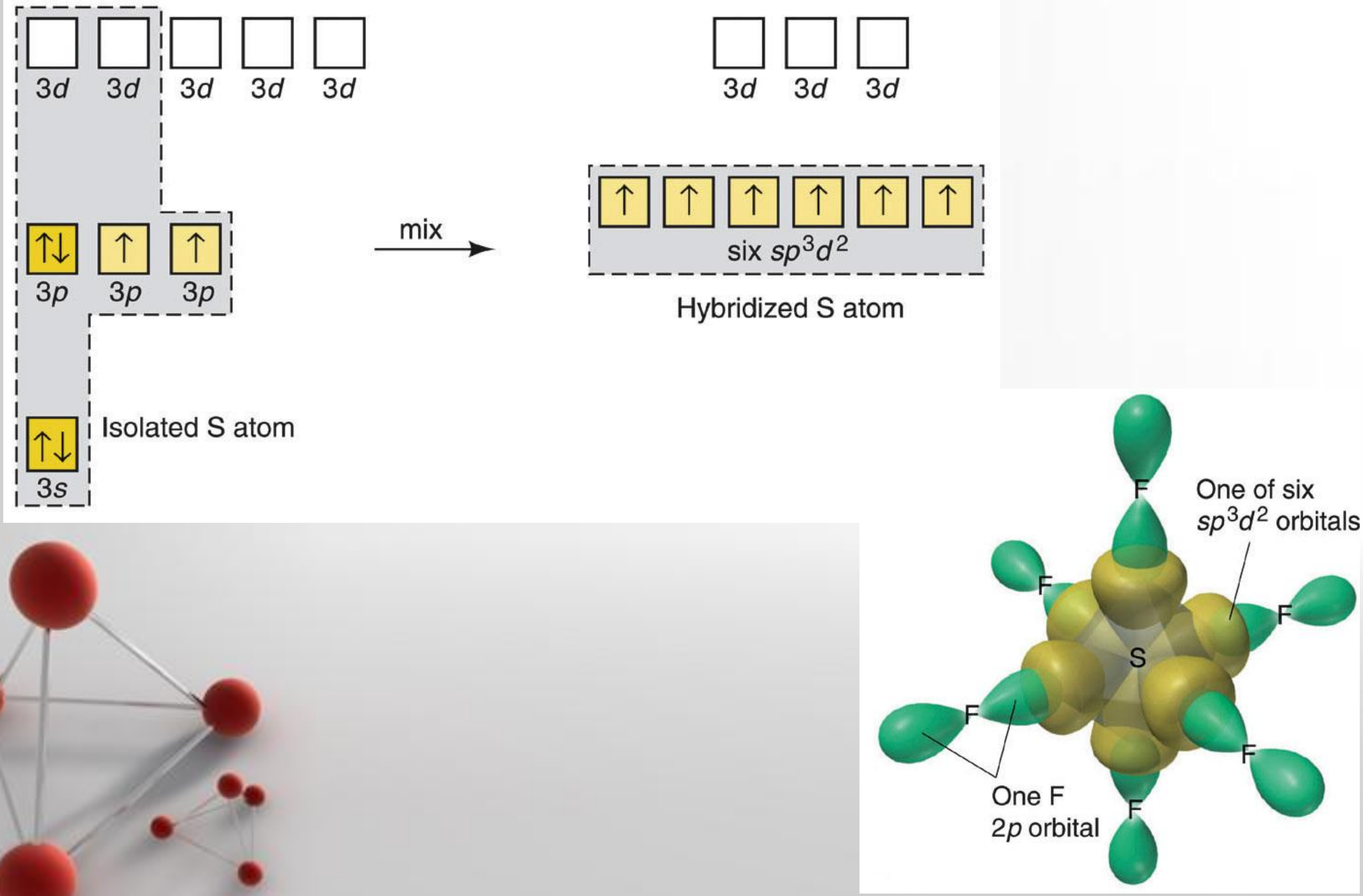




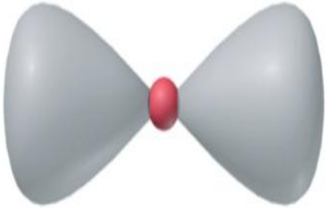
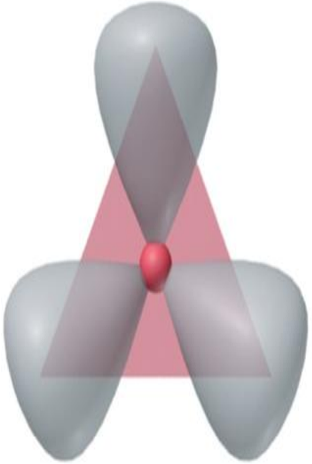
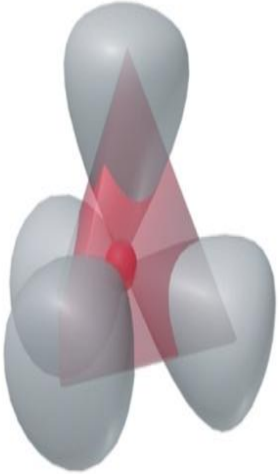
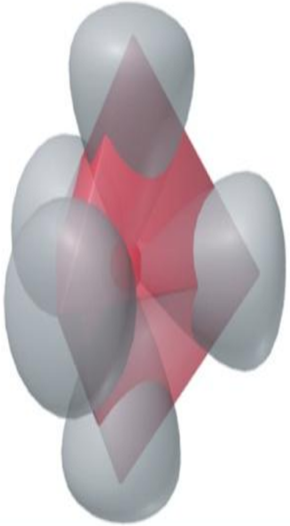
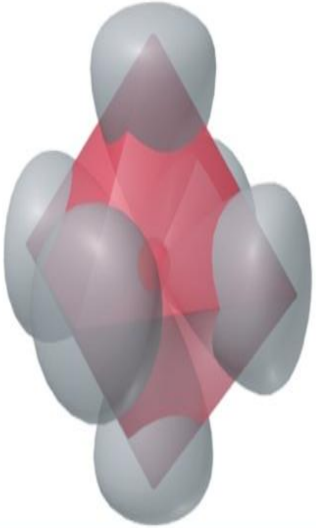


The formation of more than four bonding orbitals requires *d* orbital involvement in hybridization.

The sp^3d^2 hybrid orbitals in SF_6.

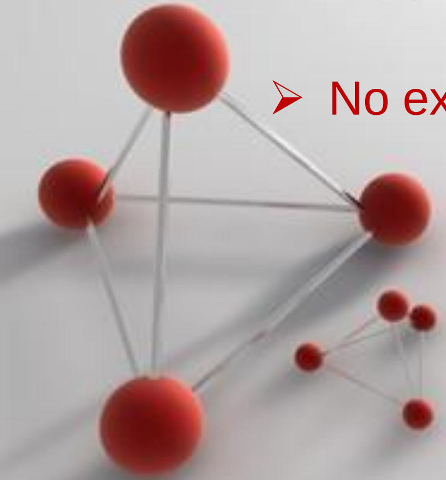


Composition and Orientation of Hybrid Orbitals.

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one s one p	one s two p	one s three p	one s three p one d	one s three p two d
Hybrid orbitals formed	two p	three sp^2	four sp^3	five sp^3d	six sp^3d^2
Unhybridized orbitals remaining	two p	one p	none	four d	three d
Orientation					

Limitations of Valence Bond Theory

- Failure to explain the tetravalency exhibited by carbon
- No insight offered on the energies of the electrons.
- The theory assumes that electrons are localized in specific areas.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- No distinction between weak and strong ligands.
- No explanation for the colour exhibited by coordination compounds.

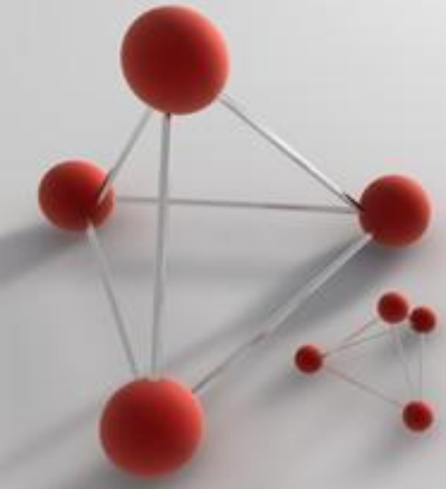


Molecular Orbital (MO) Theory

The combination of orbitals to form bonds is viewed as the combination of ***wave functions***.

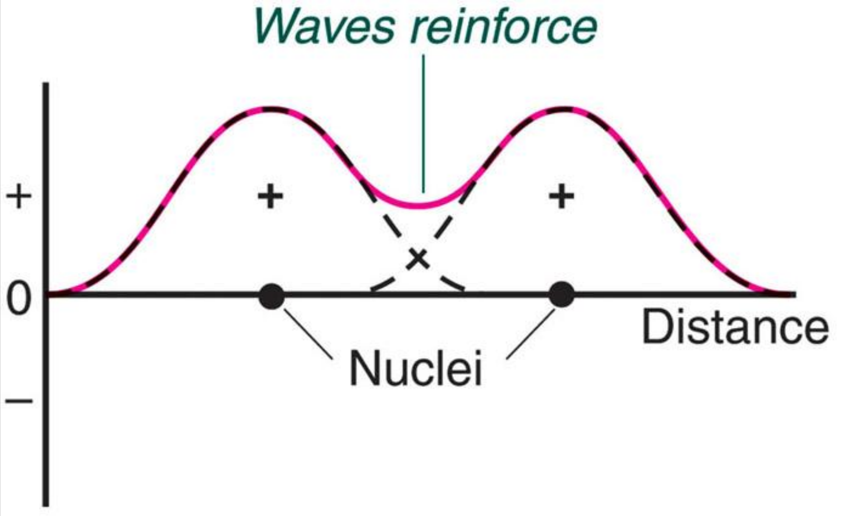
Atomic wave functions (AOs) combine to form ***molecular*** wave functions (MOs).

Addition of AOs forms a ***bonding MO***, which has a region of ***high*** electron density between the nuclei.

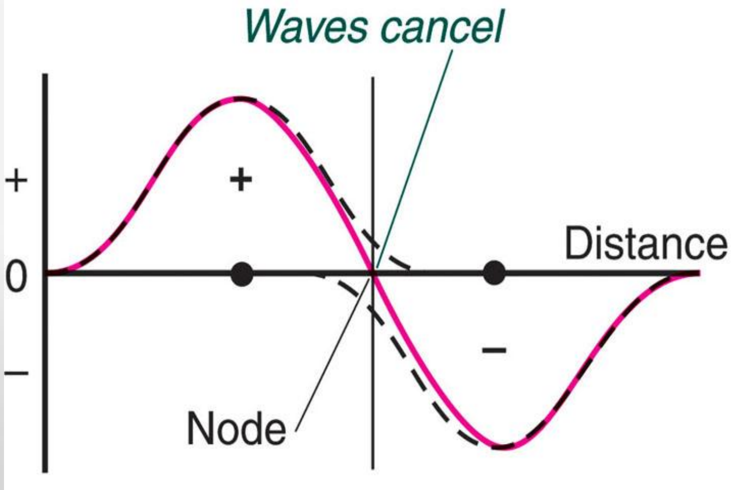


Subtraction of AOs forms an ***antibonding MO***, which has a ***node***, or region of ***zero*** electron density, between the nuclei.

An analogy between light waves and atomic wave functions.

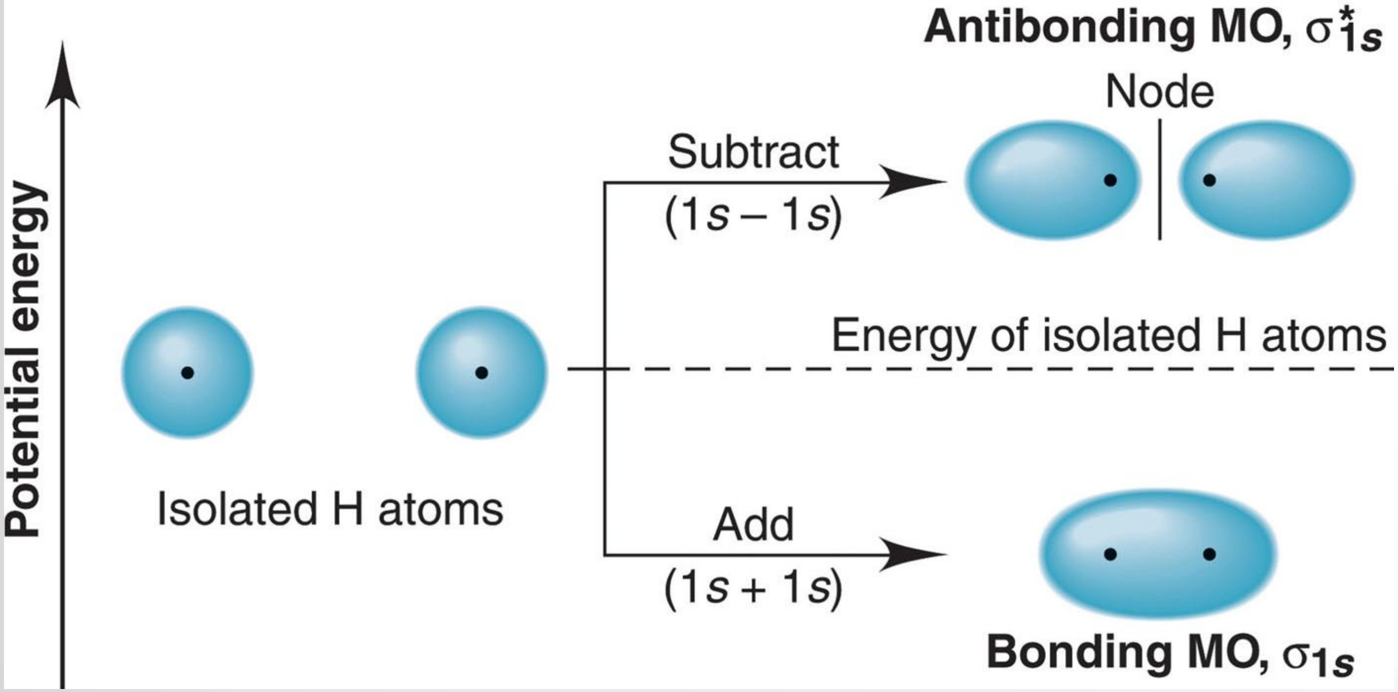


Amplitudes of wave functions added



Amplitudes of wave functions subtracted

Contours and energies of H_2 bonding and antibonding MOs.

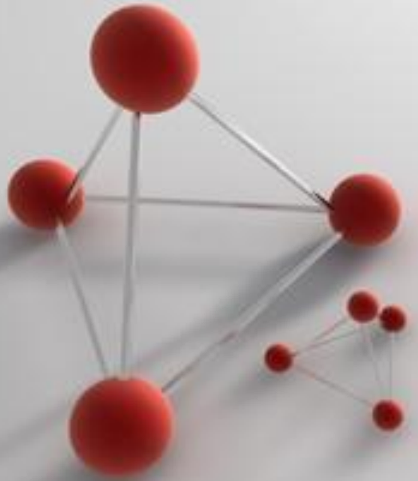


The bonding MO is lower in energy and the antibonding MO is higher in energy than the AOs that combined to form them.

Molecular Orbital Diagrams

An ***MO diagram***, just like an atomic orbital diagram, shows the relative energy and number of electrons in each MO.

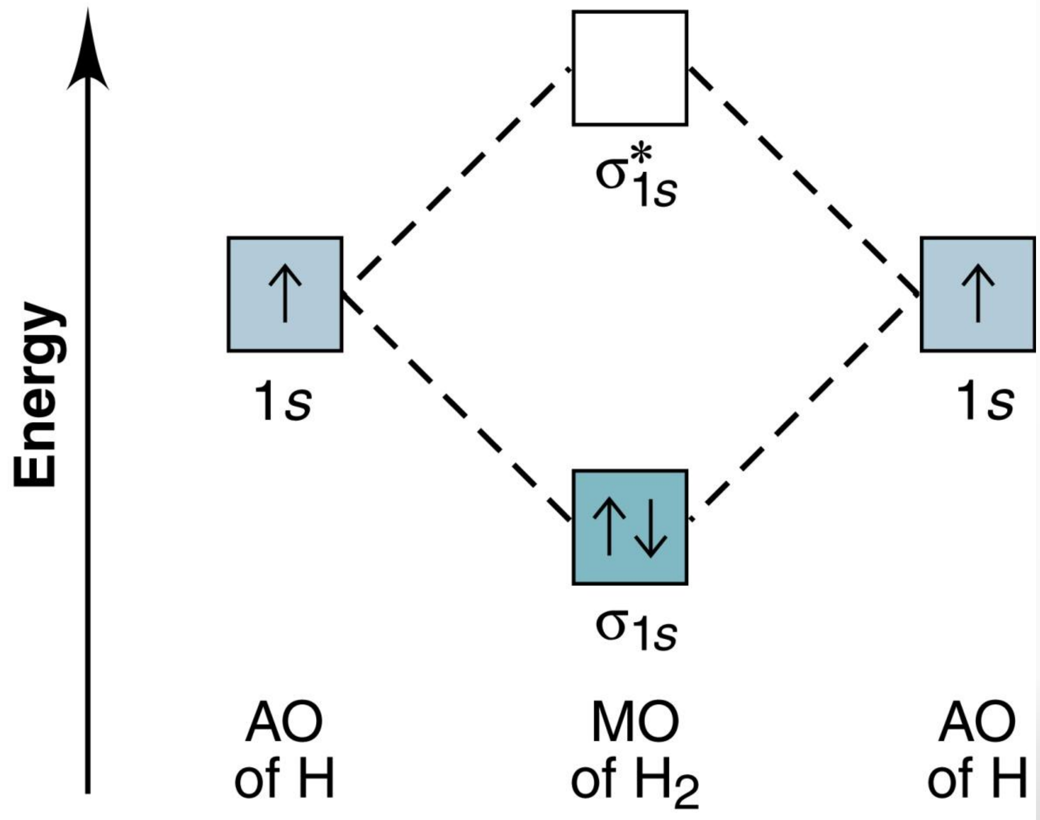
The MO diagram also shows the AOs from which each MO is formed.



Bond order is calculated as follows:
½[(no. of e^- in bonding MO) – (no. of e^- in antibonding MO)]

Bond Order α Bond Energy
Bond Order α 1/ Bond Length

MO diagram for H_2.

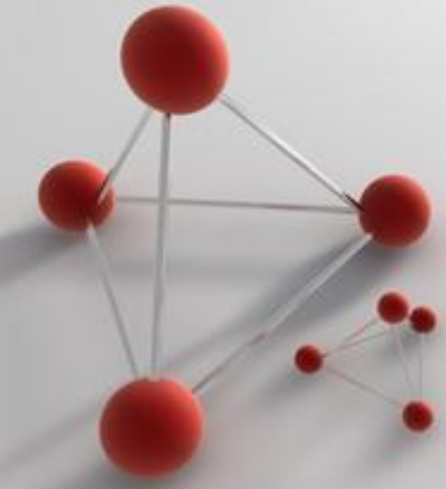


H_2 bond order = ½ (2 − 0) = 1

Electrons in Molecular Orbitals

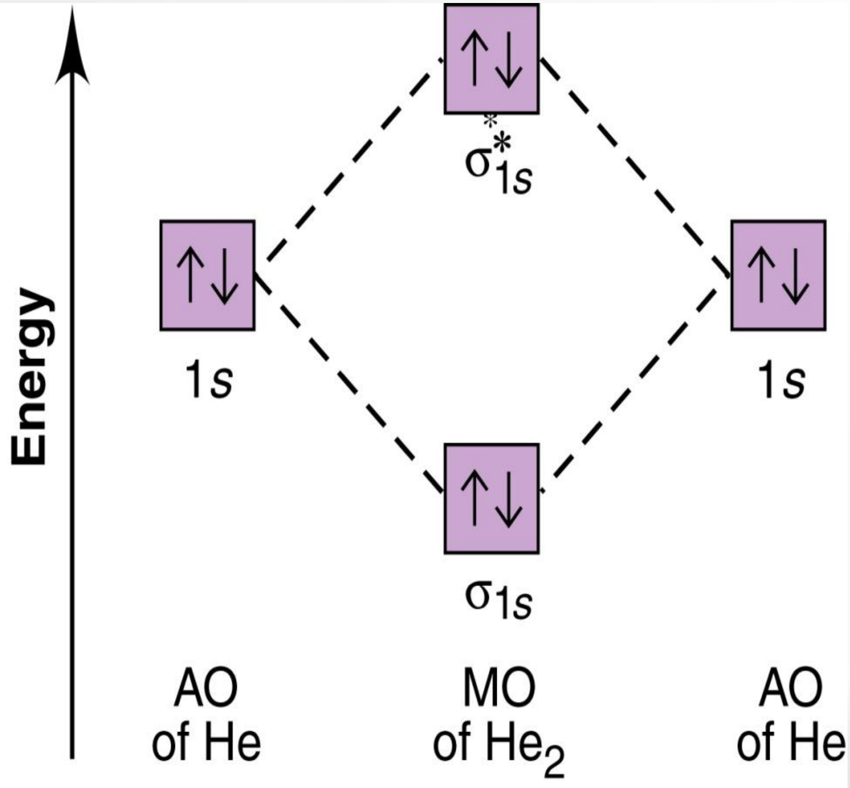
Electrons are placed in MOs just as they are in AOs.

- MOs are filled in order of increasing energy.
- An MO can hold a maximum of 2 e^- with opposite spins.
- Orbitals of equal energy are half-filled, with spins parallel, before pairing spins.



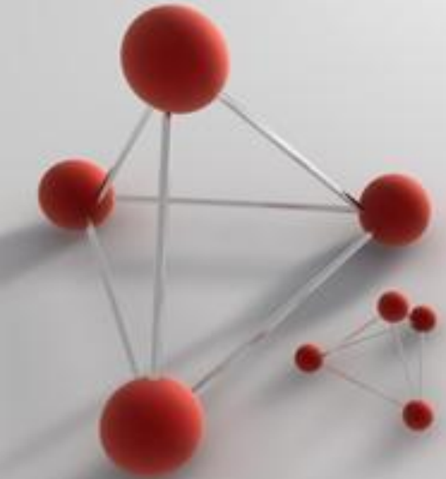
A molecular electron configuration shows the type of MO and the number of e^- each contains. For H_2 the configuration is $(\sigma_{1s})^2$.

MO diagram for He_2.

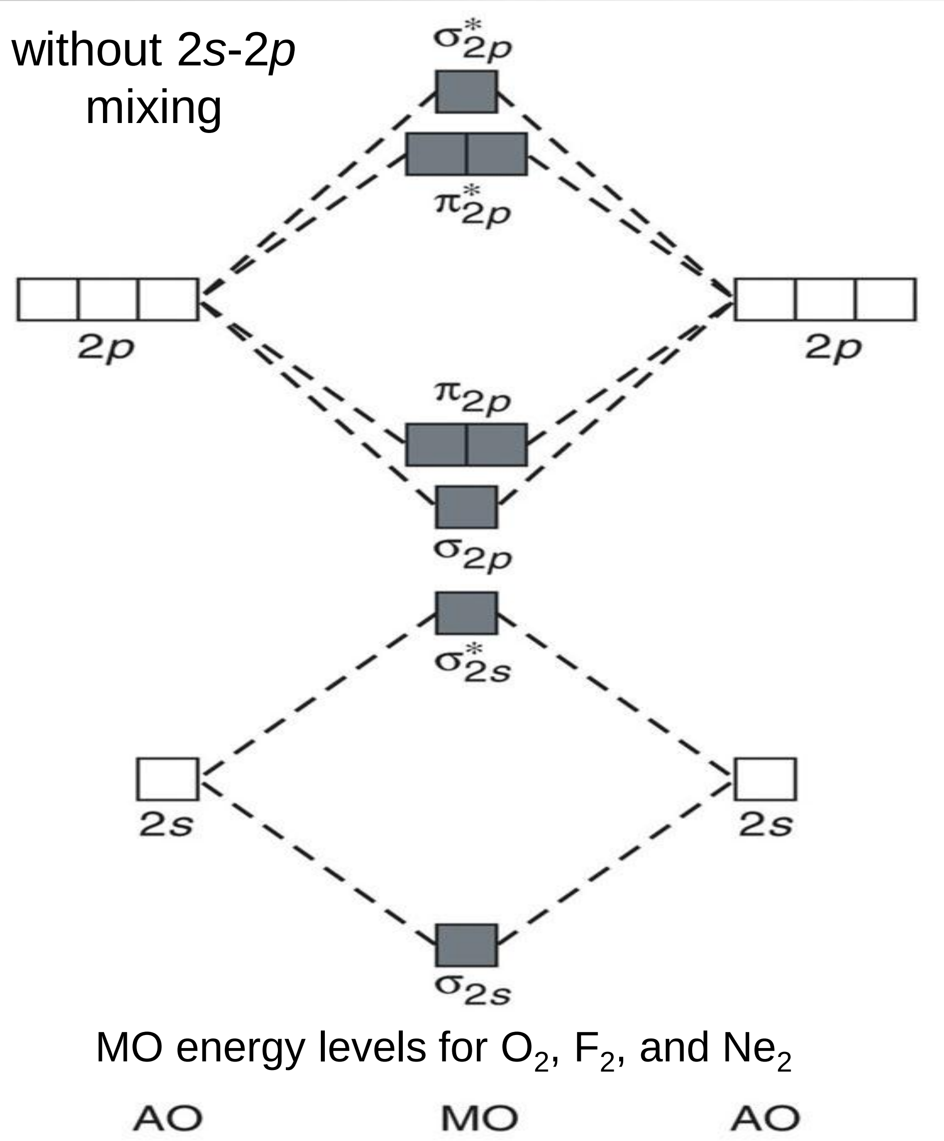


He_2 bond order = ½ (2-2) = 0

$$(\sigma_{1s})^2(\sigma^*_{1s})^2$$

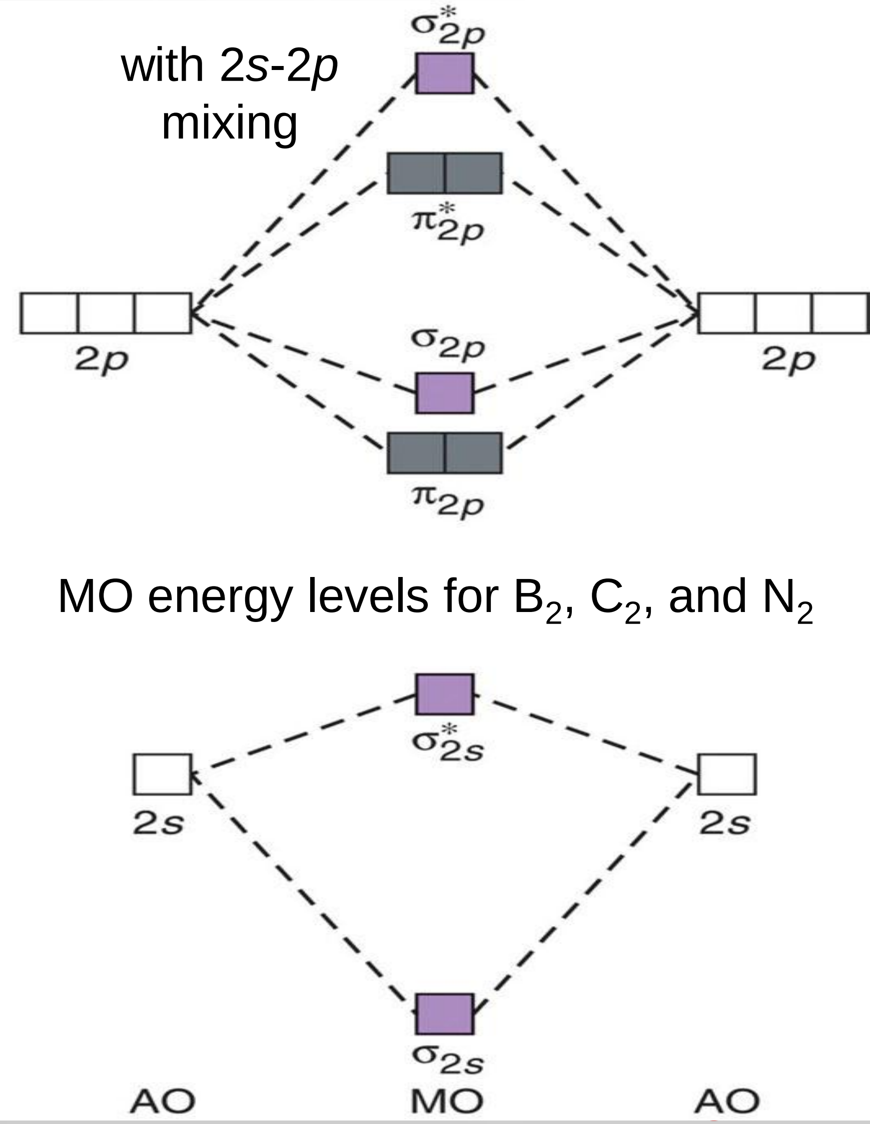


Relative MO energy levels for Period 2 homonuclear diatomic molecules.



without 2*s*-2*p* mixing

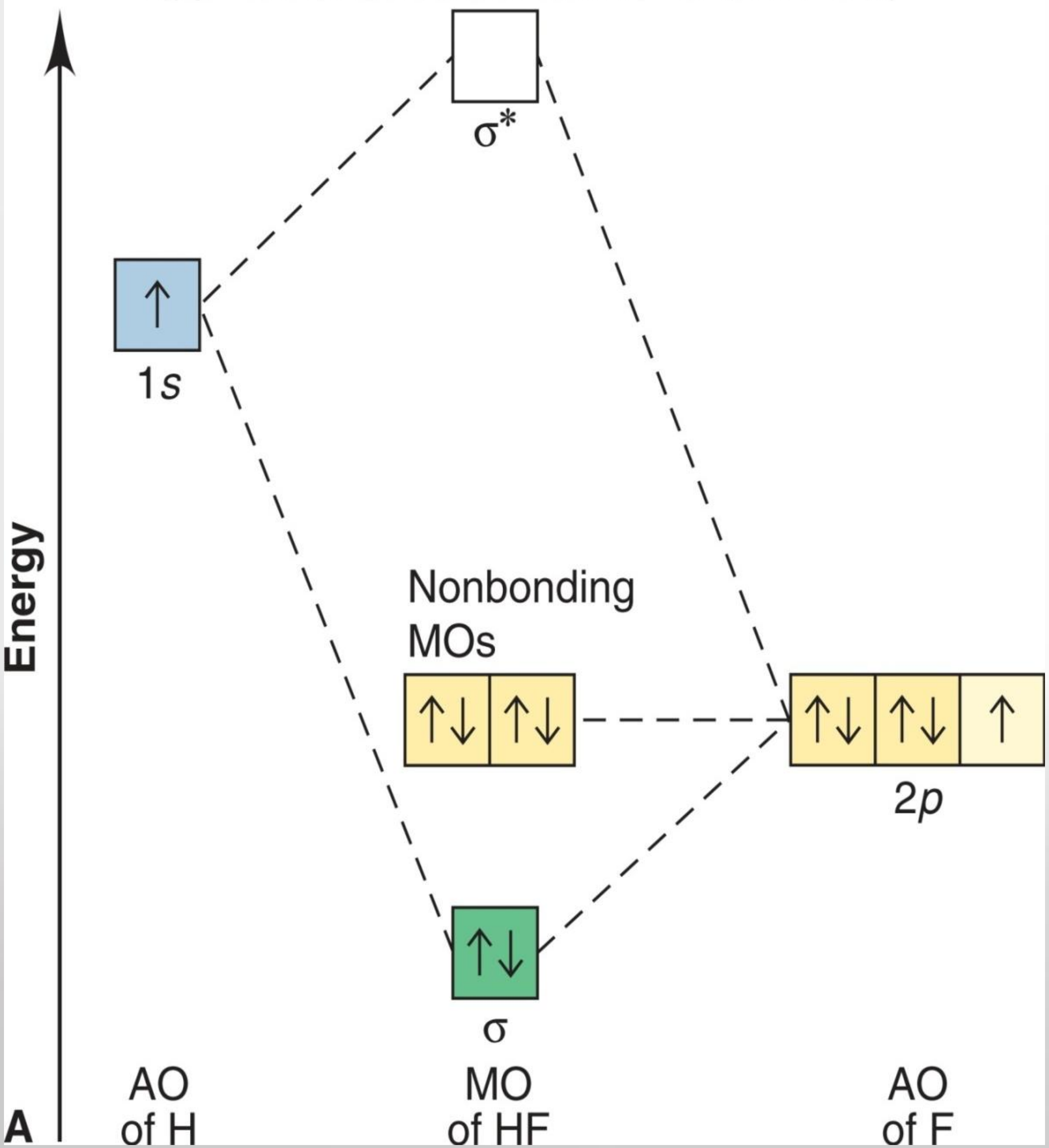
MO energy levels for O_2, F_2, and Ne_2

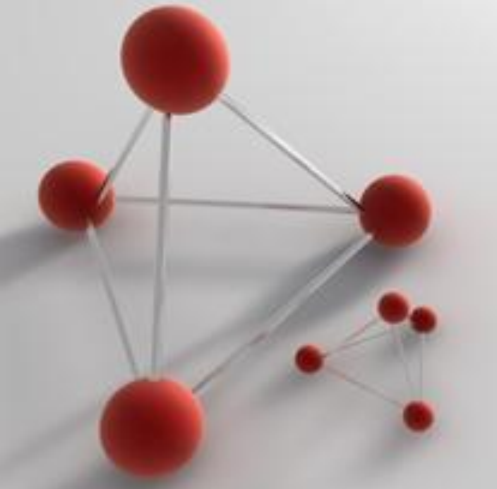


with 2*s*-2*p* mixing

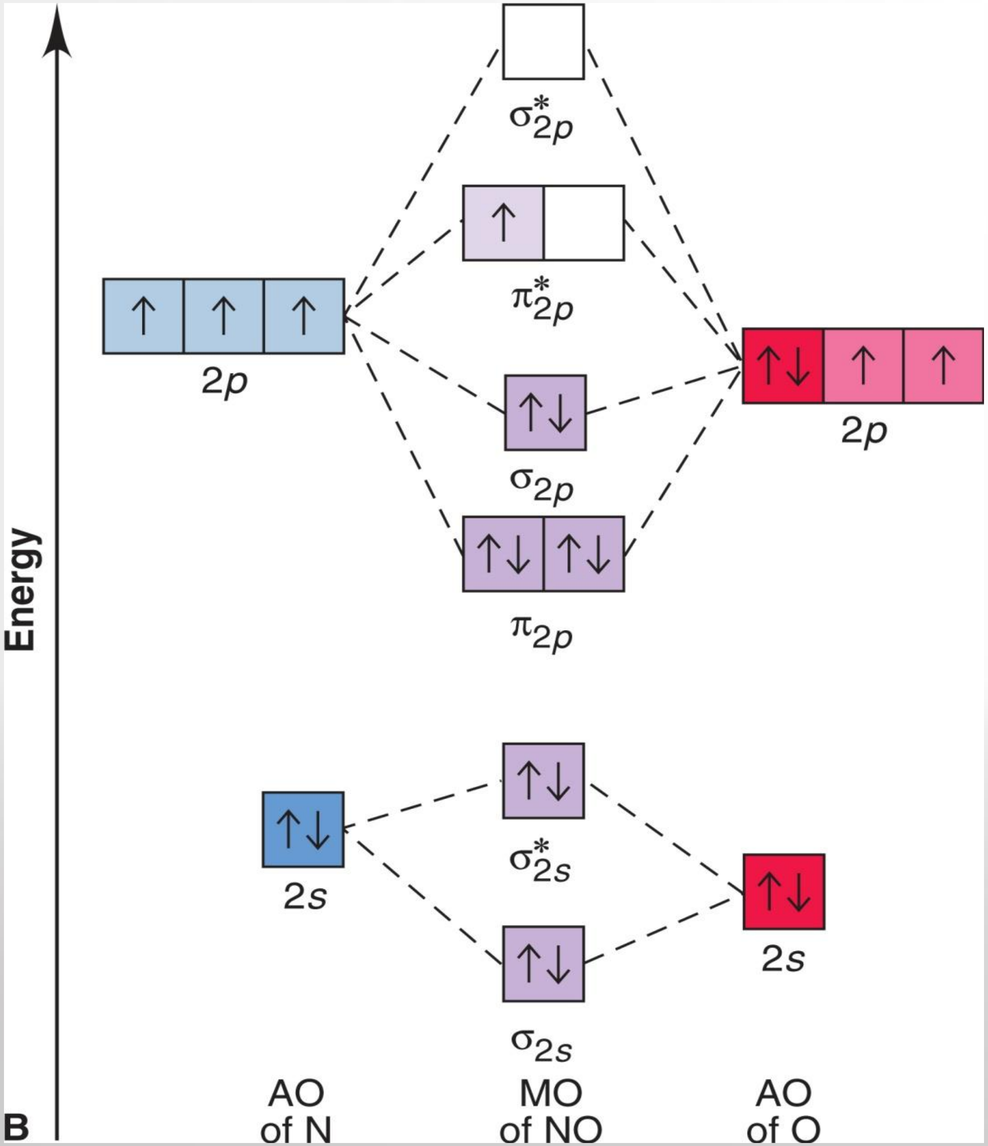
MO energy levels for B_2, C_2, and N_2

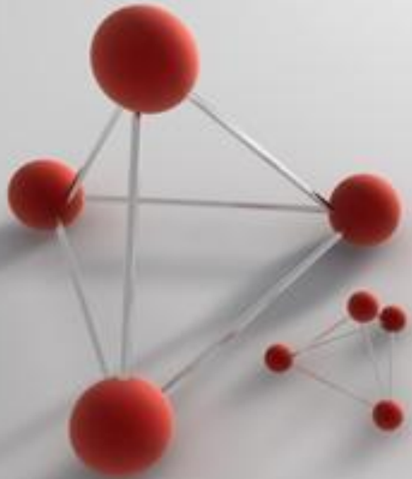
The MO diagram for HF.





The MO diagram for NO.

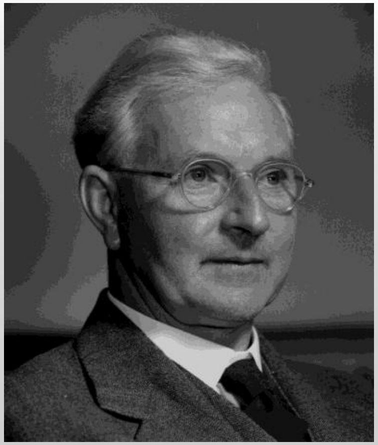




Linear Combination of Atomic Orbitals (LCAO)

A **linear combination of atomic orbitals** or **LCAO** is a quantum superposition of atomic orbitals and a technique for calculating molecular orbitals in quantum chemistry

It was introduced in 1929 by Sir John Lennard-Jones with the description of bonding in the diatomic molecules of the first main row of the periodic table, but had been used earlier by Linus Pauling for H_2^+



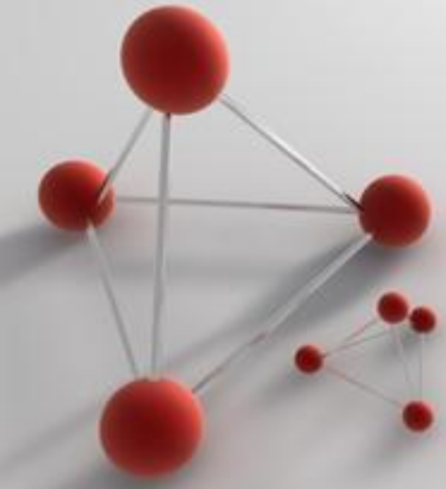
Linear Combination of Atomic Orbitals (LCAO)

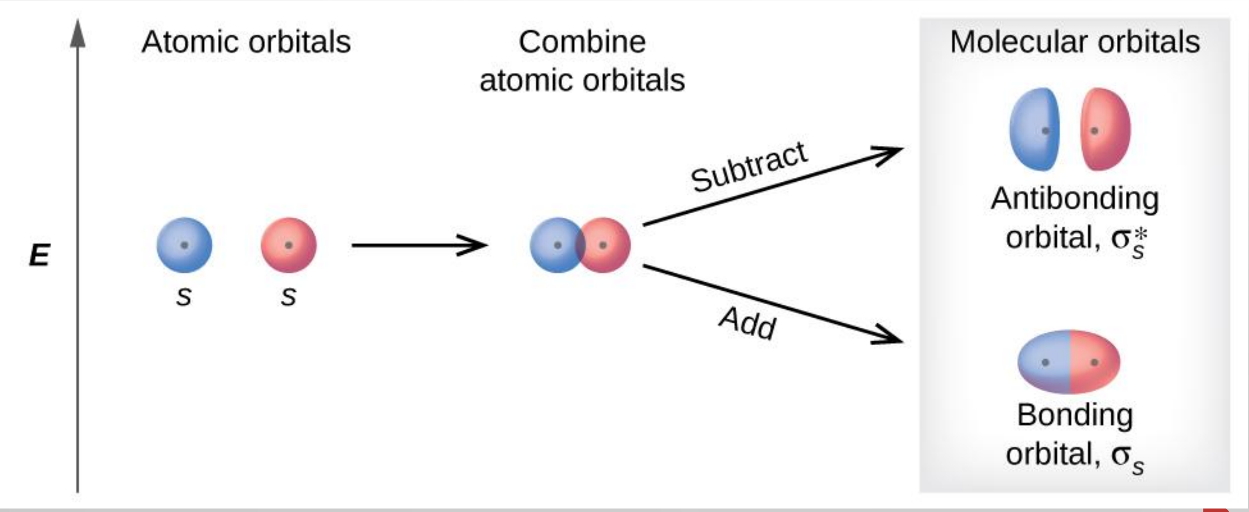
The formation of orbitals is because of Linear Combination (addition or subtraction) of atomic orbitals which combine to form the molecule.

$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

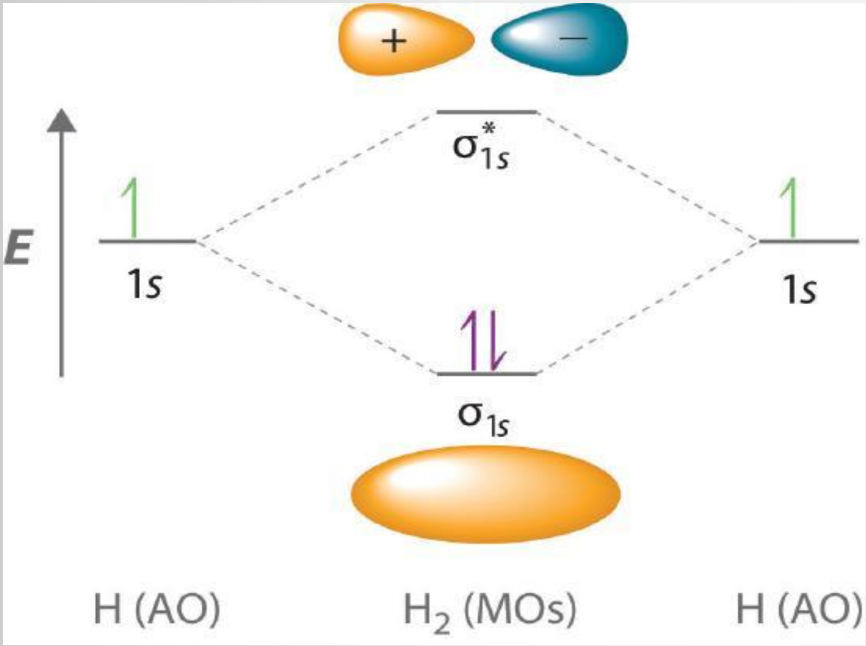
Bonding Molecular Orbitals (BMO) = $\Psi_{MO} = \Psi_A + \Psi_B$.

Anti-Bonding Molecular Orbitals (ABMO) = $\Psi_{MO} = \Psi_A - \Psi_B$



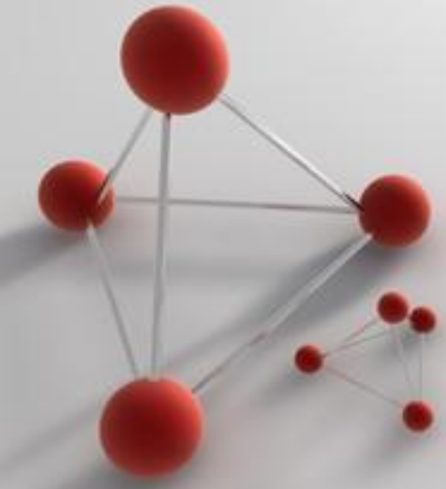


LCAO

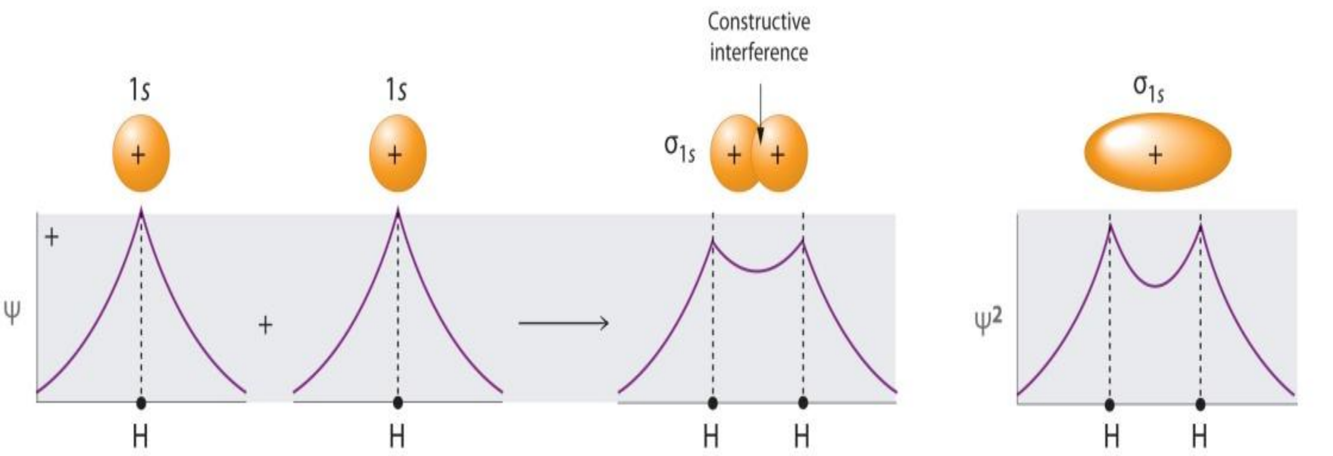


Energy of BMO is less than that of ABMO. This is because of the increase in the attraction of both the nuclei for both the electron of the combining atom

Energy of ABMO is higher than BMO. This is because the electron tries to move away from the nuclei and are in a repulsive state.

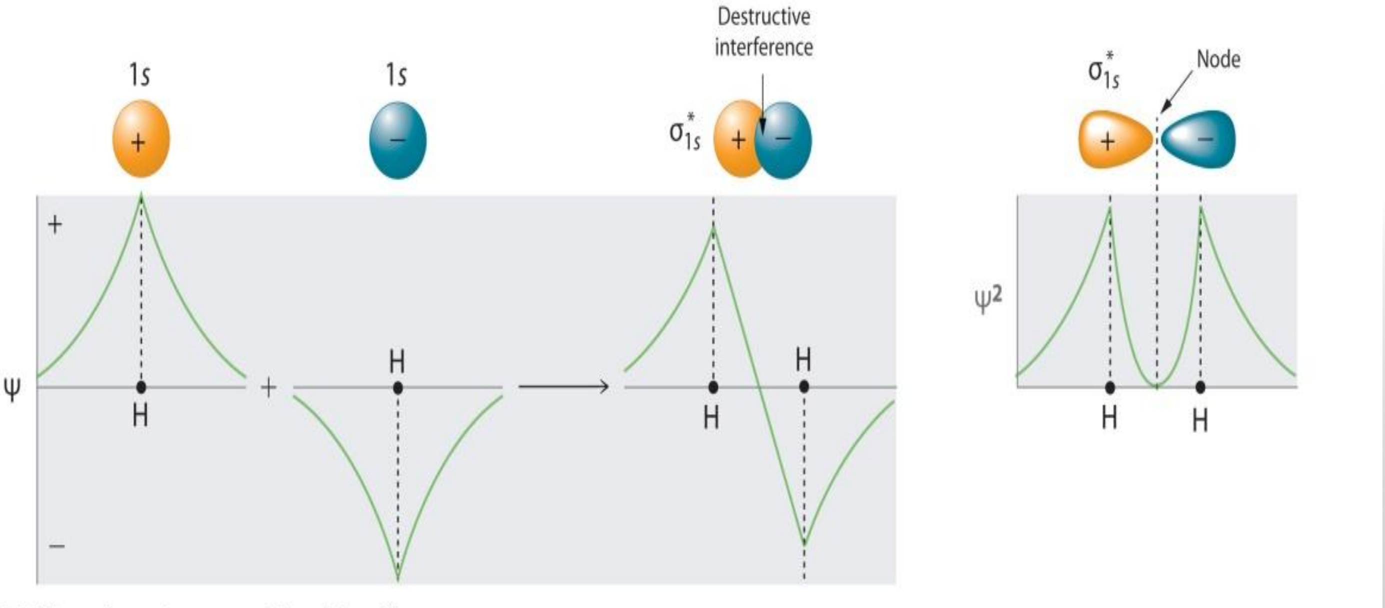


LCAO



(a) Wave functions combined for σ_{1s}

(b) Bonding probability density



(c) Wave functions combined for σ^*_{1s}

(d) Antibonding probability density

Comparison of VBT and MOT

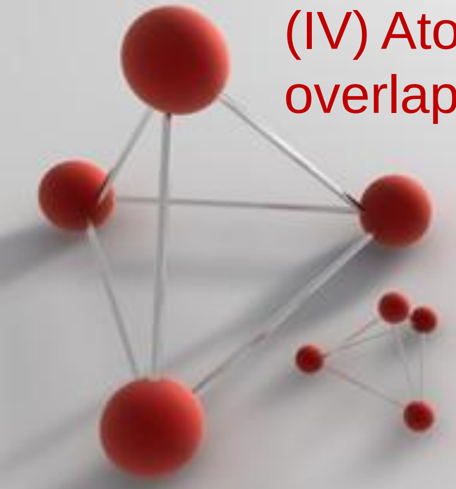
Similarities between VBT and MOT:

(I) They account for the directional nature of the bond.

(II) Bond results by the overlapping of two orbitals of minimum energy.

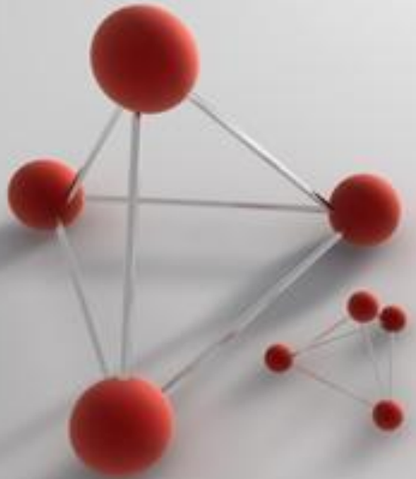
(III) Electronic charge persists in between two atomic nuclei in bond formation.

(IV) Atomic orbitals of same energy, and same symmetry overlap to produce strong bonds.

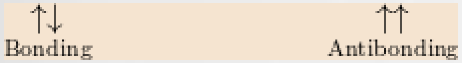
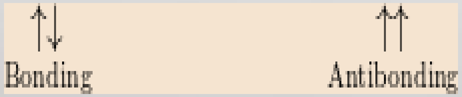


Comparison of VBT and MOT

VBT	MOT
1.Orbitals of bonded atoms cannot lose their identity.	**1**. Orbitals of bonded atoms lose their individual identity.
2.Atomic orbitals monocentric.	**2.** Molecular orbitals are polycentric
3.It explains that inert gases have orbital already spin paired, so they have no tendency to form any linkage.	**3**. Molecular orbital theory explain the non-existence of molecules of inert gases, since number of bonding and antibonding electrons are equal



Comparison of VBT and MOT

VBT	**MOT**
4.Pauli's exclusion principle decides the spin function combination with wave function as 	**4**. It explains how electrons are originally present in atomic orbitals and are distributed in new molecular orbitals.
5.VBT introduces a special form to explain the presence of ionic character in bond.	**5**. MOT is not capable or predicting ionic character in a bond.
6.VBT explains the difference between bonding and antibonding orbitals as following: 	**6**. In MOT both bonding and antibonding orbitals can have electron pairs with opposed spins.

THANK YOU