Valence Bond Theory

History:

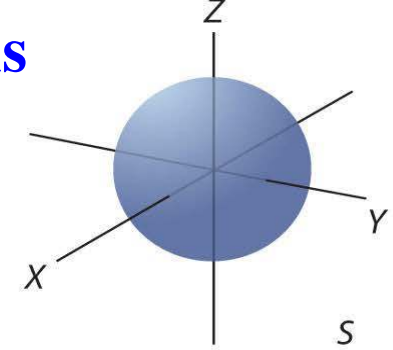
- 1916: G. N. Lewis proposed that the chemical bond forms by the interaction of two shared bonding electrons and are represented as "—" between the two atoms →Called the "Lewis structure"
- 1927: Heitler and London showed using Schrödinger's wave equation (1926) how two H atom wave functions can be joined together by +, - and exchange terms to form a covalent bond.
- 1928: Linus Pauling formulated the basis of Valence Bond Theory and coined the terms Resonance (1928) and Orbital Hybridization (1930)

Basis of Valance Bond Theory (VBT)

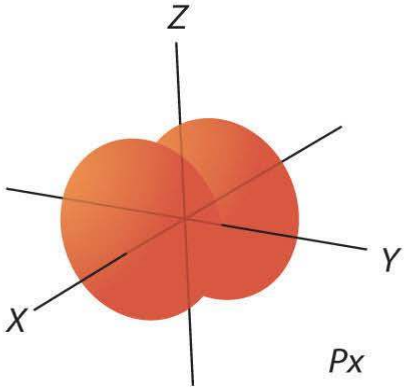
Overlap of Atomic Orbitals

- *A covalent bond* is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron
- The sharing of electrons between atoms is viewed as an overlap of atomic orbitals of the bonding atoms
- Mixing of atomic orbitals to form bonding orbital is termed as *HYBRIDIZATION*

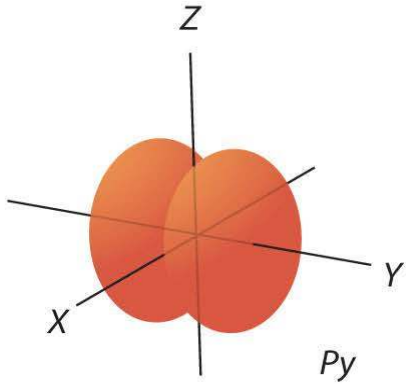
Shapes of atomic orbitals



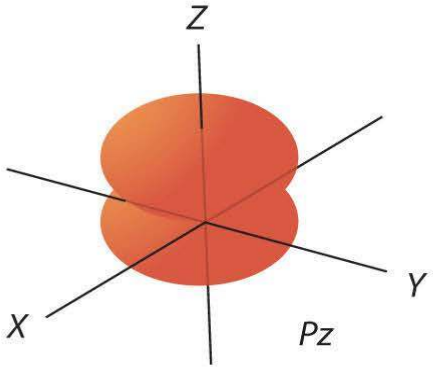
(a) *S*



Px

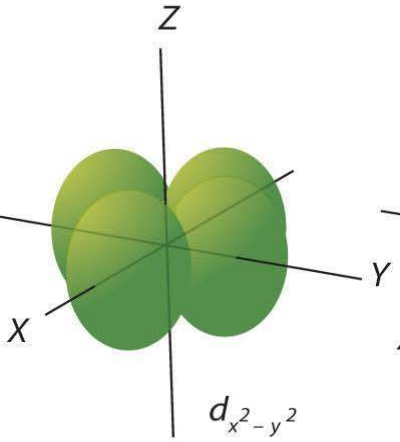


Py

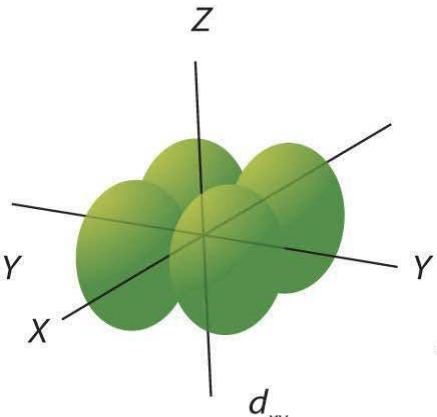


Pz

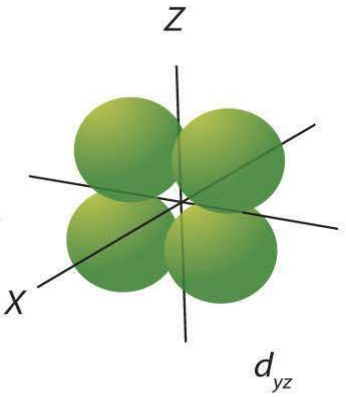
(b)



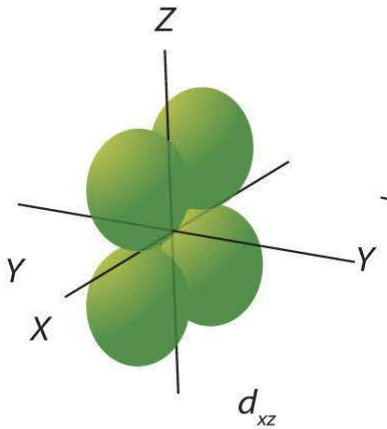
$d_{x^2-y^2}$



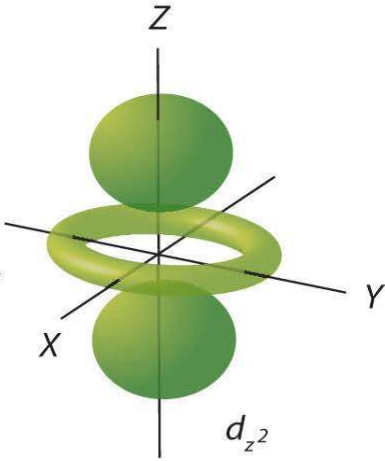
d_{xy}



d_{yz}

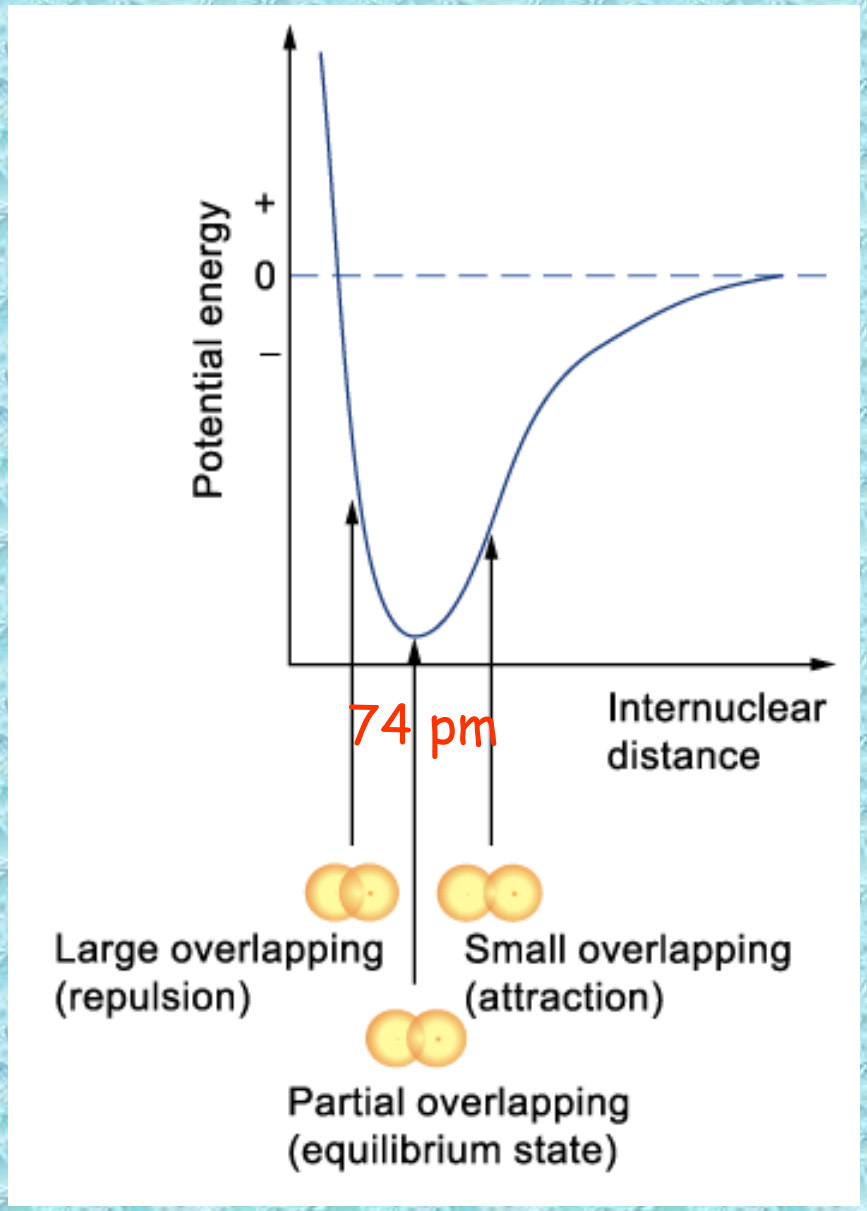


d_{xz}



d_{z^2}

Bonding in H_2 molecule



When H – H distance = 74 pm,

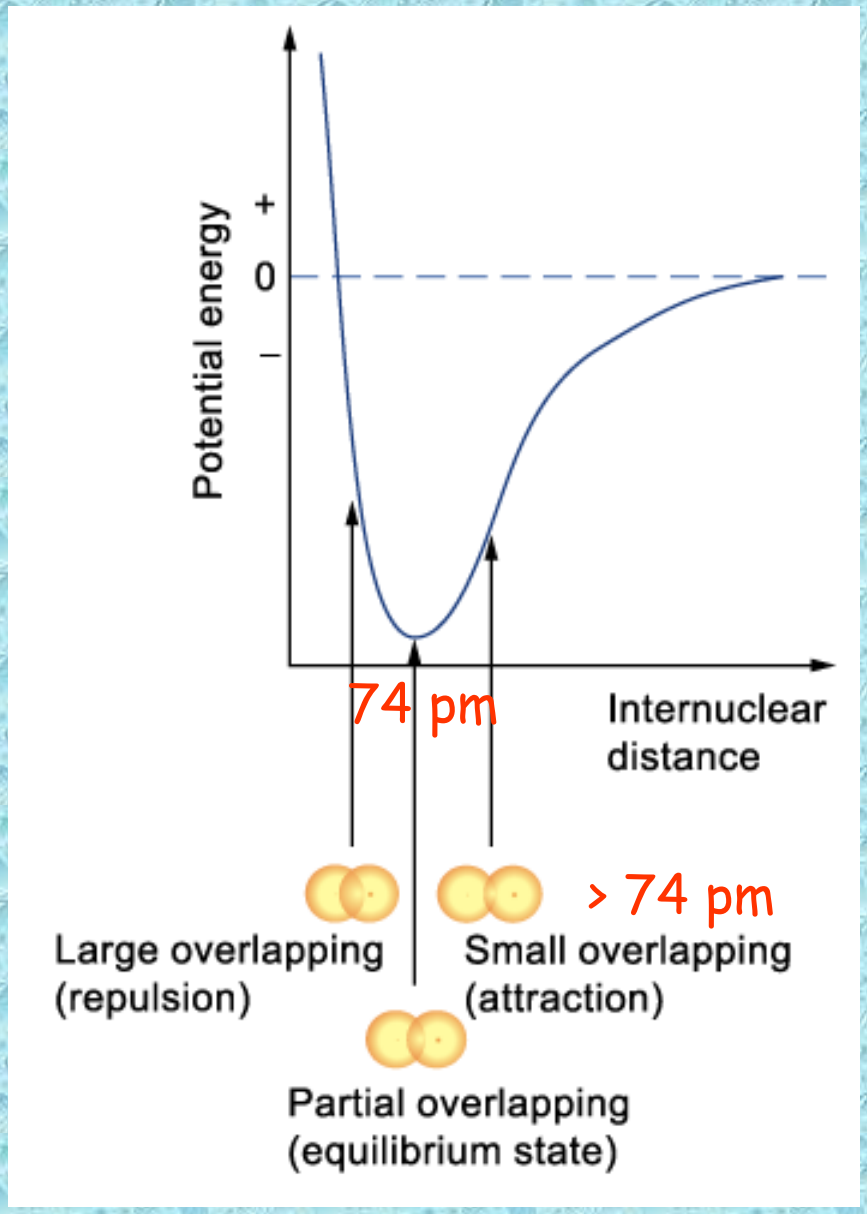
Repulsion = Attraction

→ strongest bond

→ optimal overlap

→ lowest energy

Bonding in H_2 molecule



At H – H distance > 74 pm,

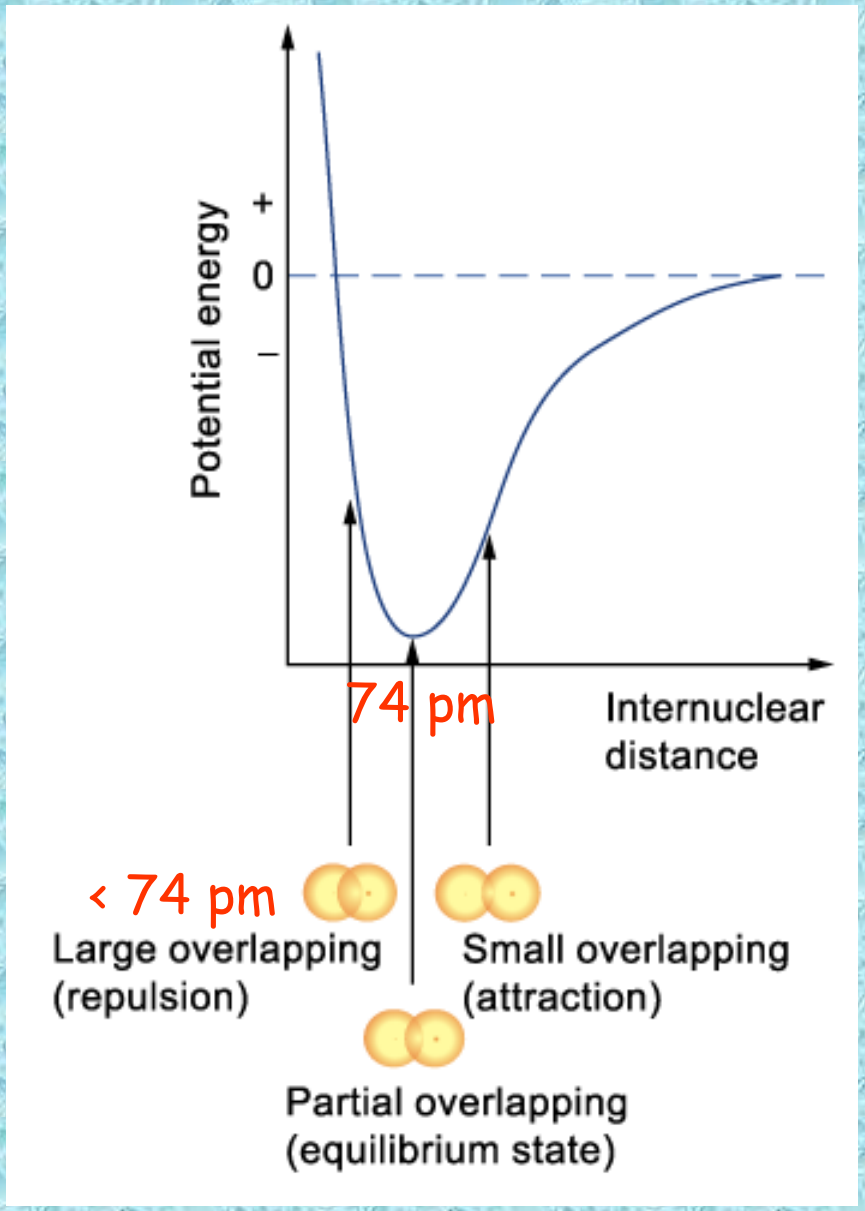
Repulsion < Attraction

→ weaker bond

→ too little overlap

→ atoms come closer

Bonding in H_2 molecule



At H – H distance < 74 pm,

Repulsion > Attraction

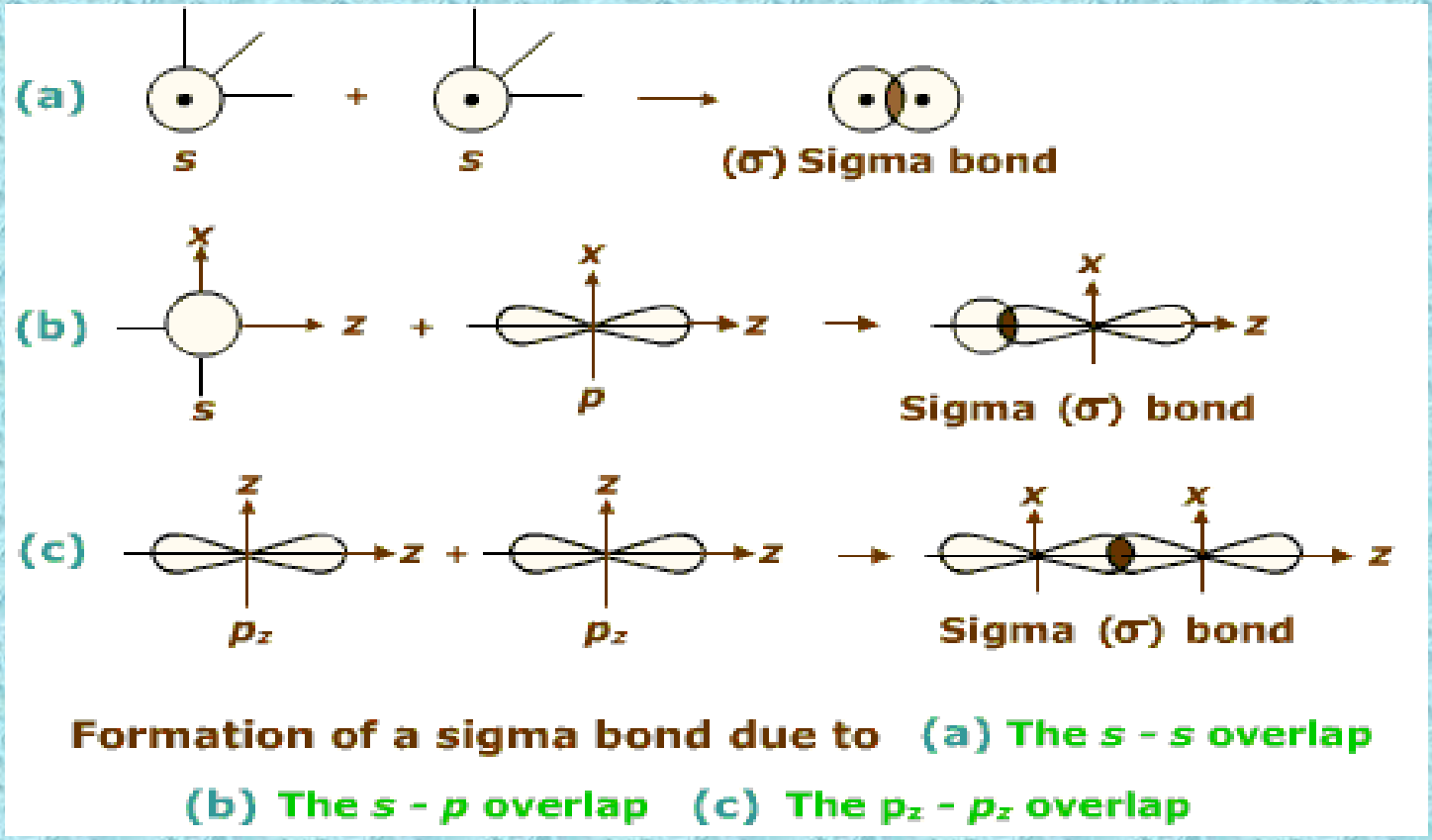
→ weaker bond

→ too much overlap

→ atoms get further apart

Because of orbital overlap, the bonding electrons localize in the region between the bonding nuclei such that

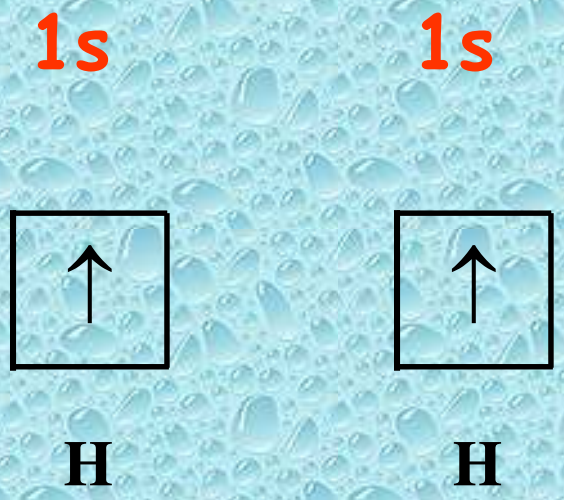
There is a high probability of finding the electrons in the region between the bonding nuclei.



Formation of a sigma bond due to (a) The *s* - *s* overlap

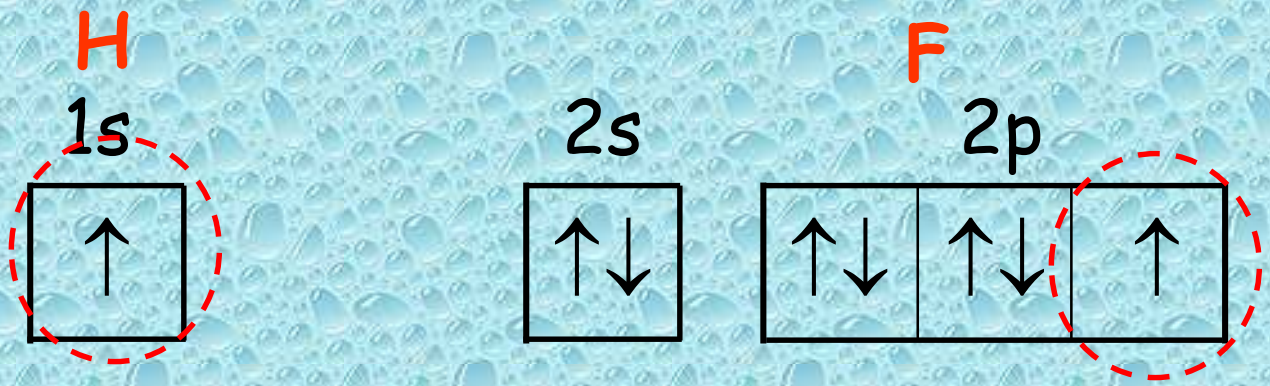
(b) The *s* - *p* overlap (c) The p_z - p_z overlap

Overlap of two **half-filled** orbitals leads to the formation of a covalent bond.



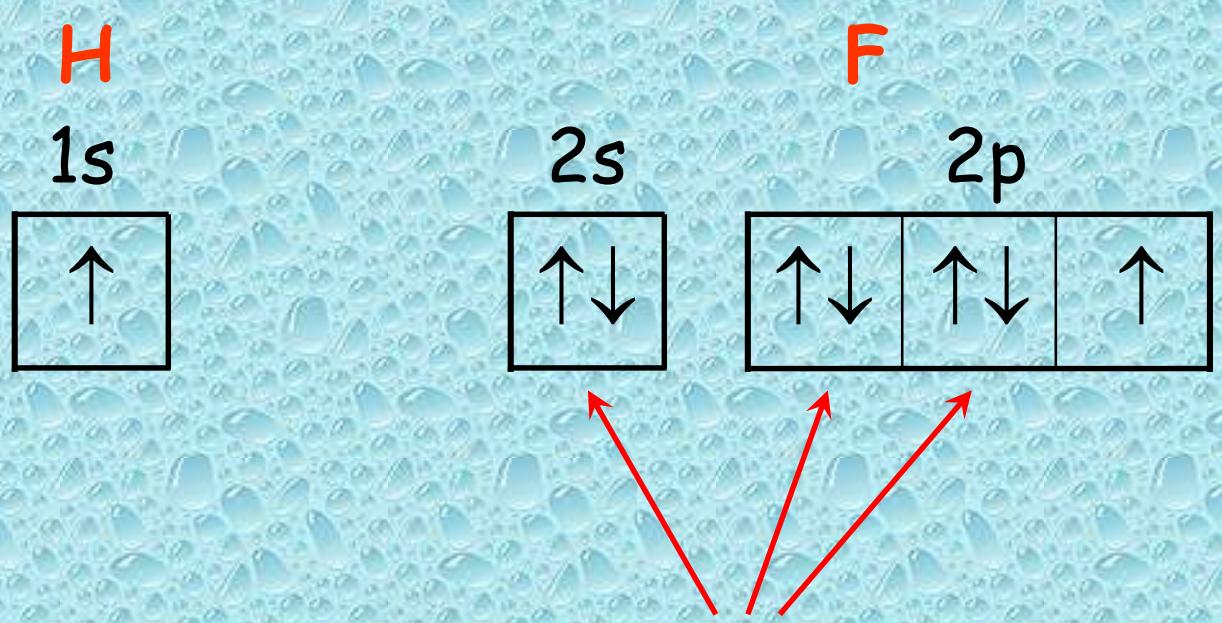
1s-1s overlap gives a H – H single bond

Formation of H_2 molecule



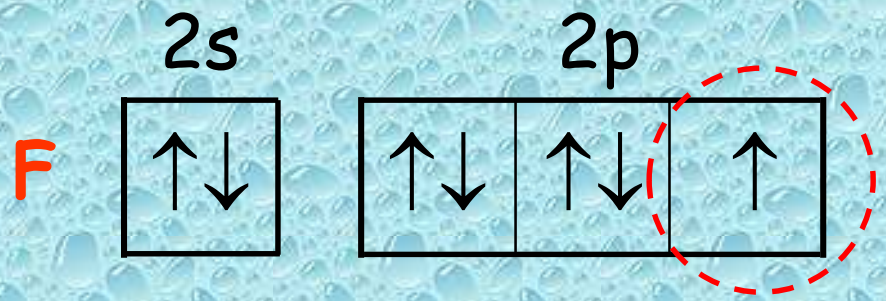
The 1s-2p overlap gives a H – F single bond

Formation of HF molecule

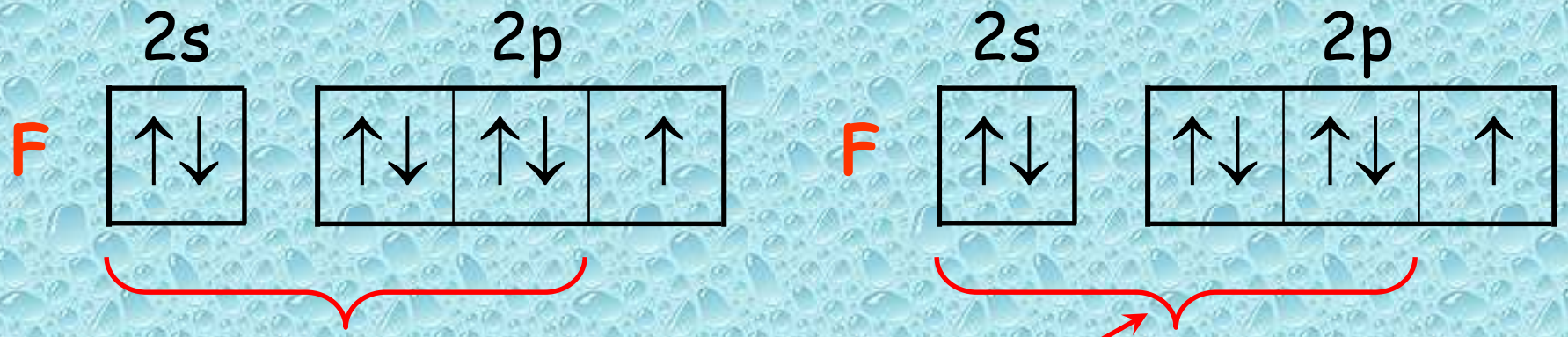


Non-bonding electrons

H–F:



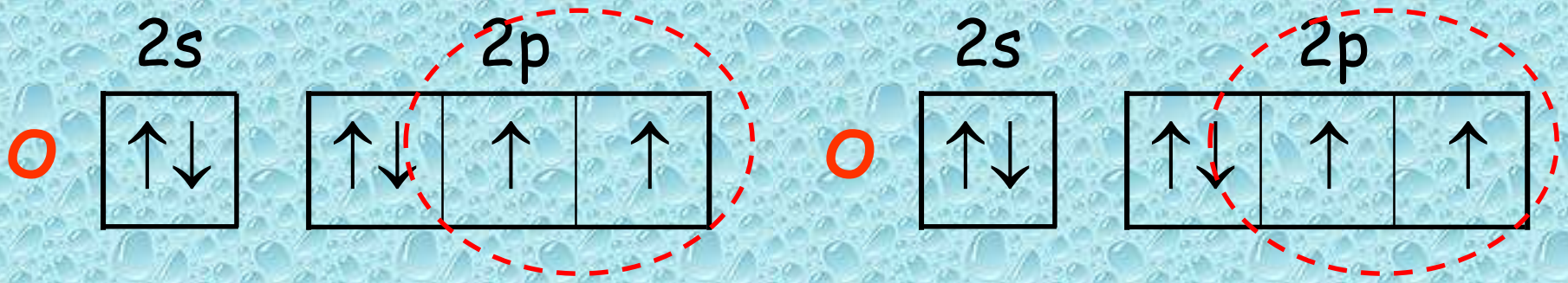
The 2p-2p overlap gives a F – F single bond



Non-bonding electrons

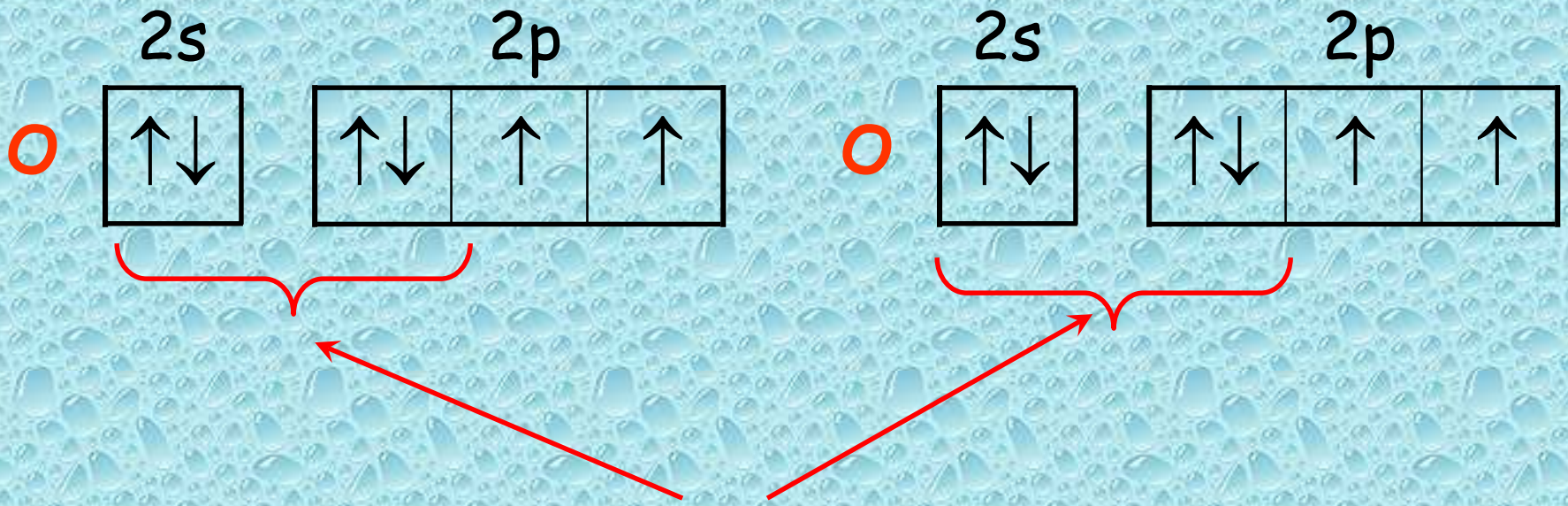
Each F atom has three pairs of non-bonding electrons.

Identify the non-bonding electrons in O_2 molecules.



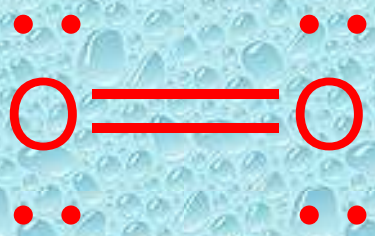
Two 2p-2p overlaps give a O=O double bond

Q.23 Identify the non-bonding electrons in O_2 molecules.

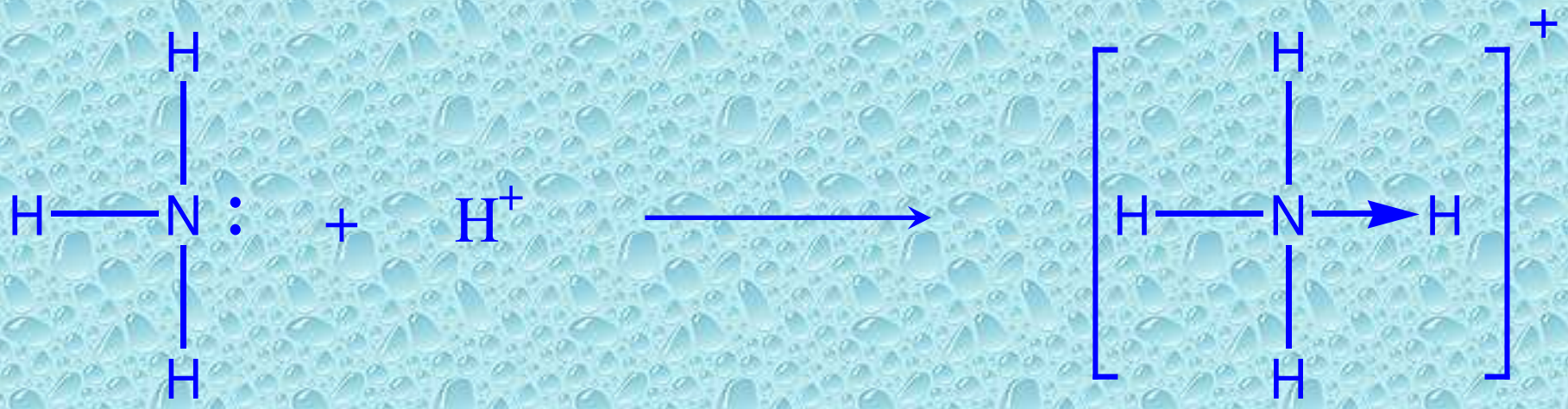


Non-bonding electrons

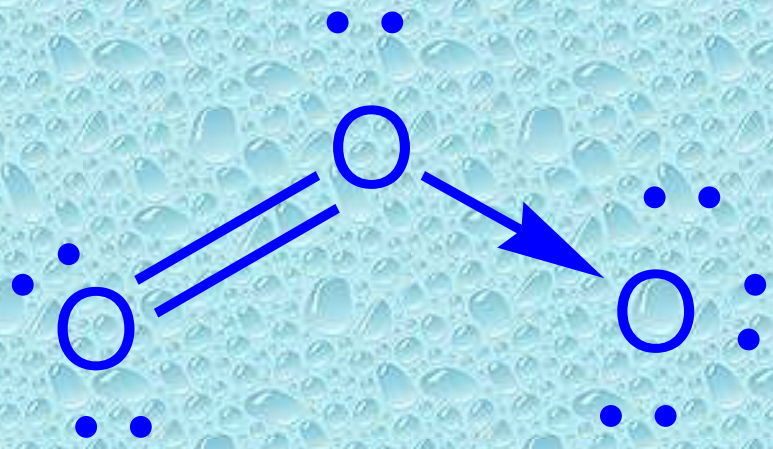
Each O atom has two pairs of non-bonding electrons.

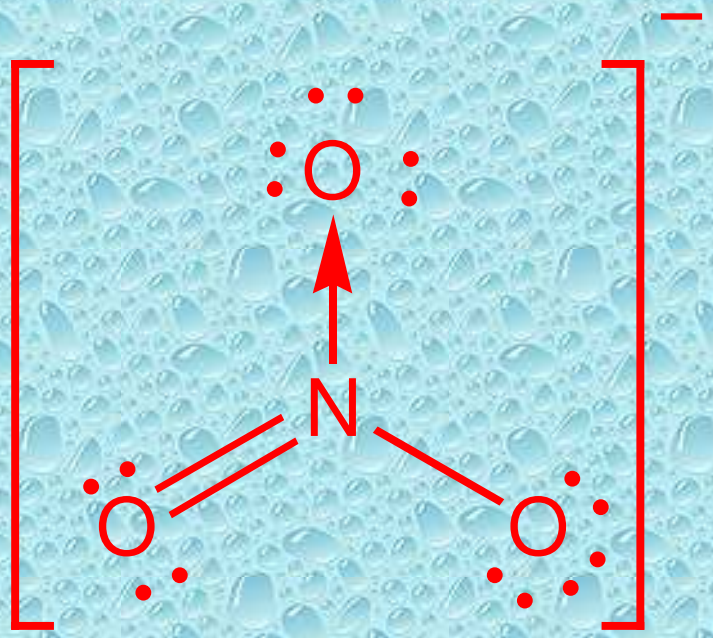


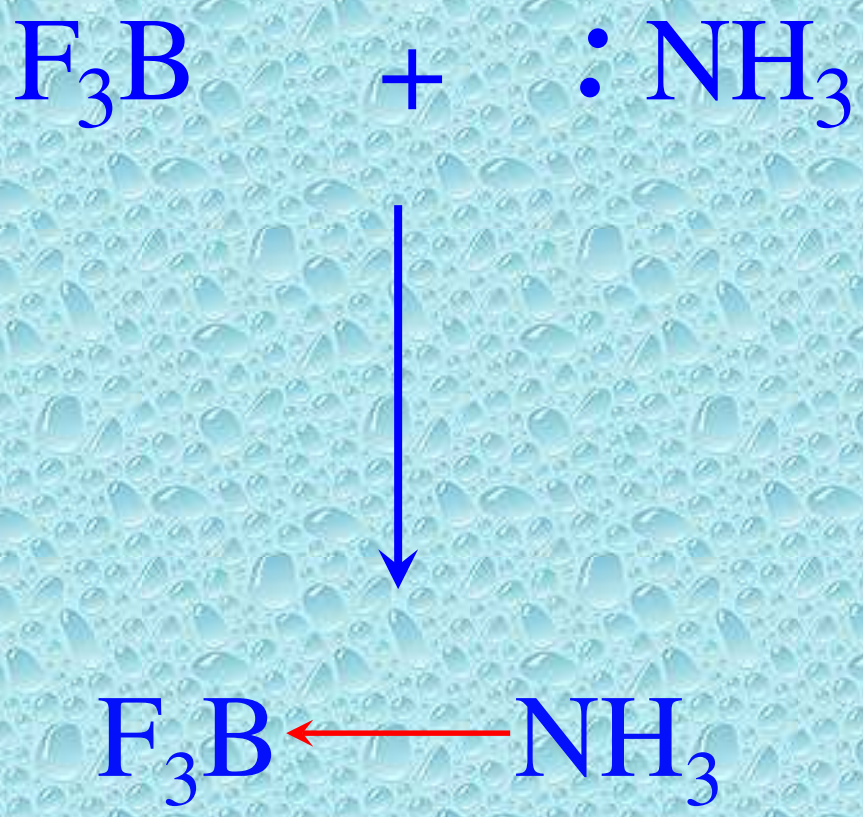
Overlap of an **empty orbital** with a **fully-filled orbital** leads to the formation of a **co-ordinate covalent bond** or **dative bond**



Represented by an arrow → pointing from the electron pair **donor** to the electron pair **acceptor**.



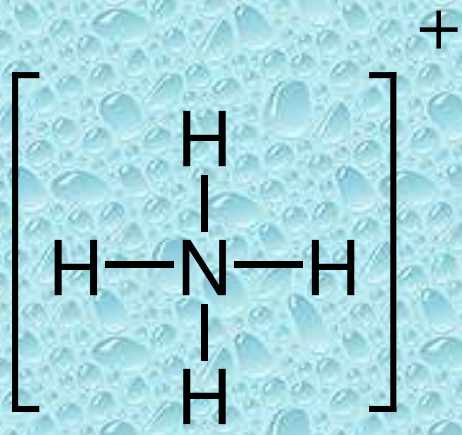

O
N
O
O
−


F3B + :NH3
F3B NH3

Interpretation of the Formation of Covalent Bonds in terms of Valence Bond Theory

(a) NH_4^+

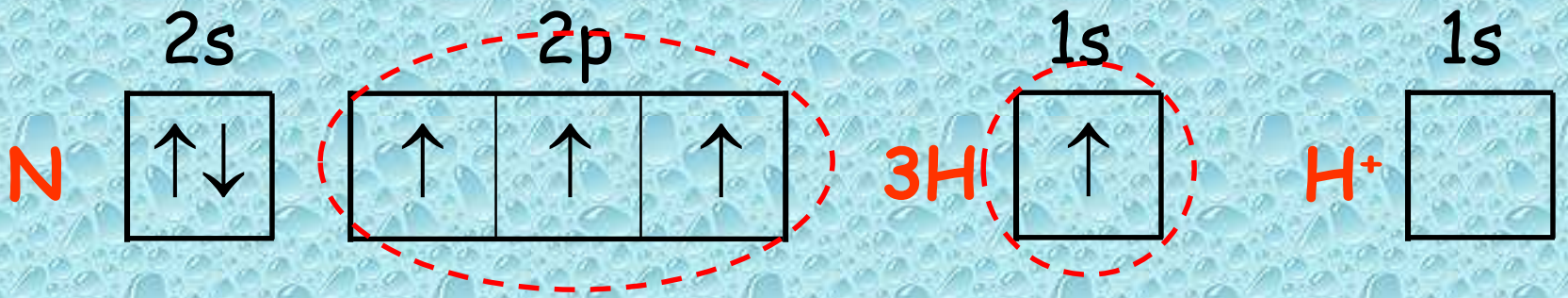
By Lewis model, the structure is



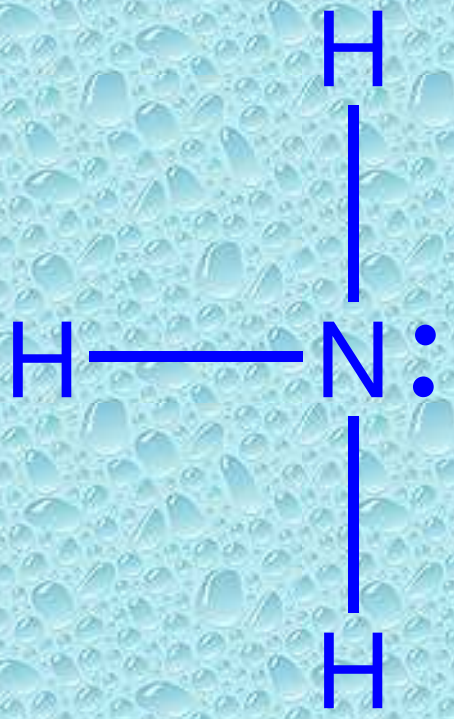
⇒ 4 single bonds are formed,

one of them is a dative bond.

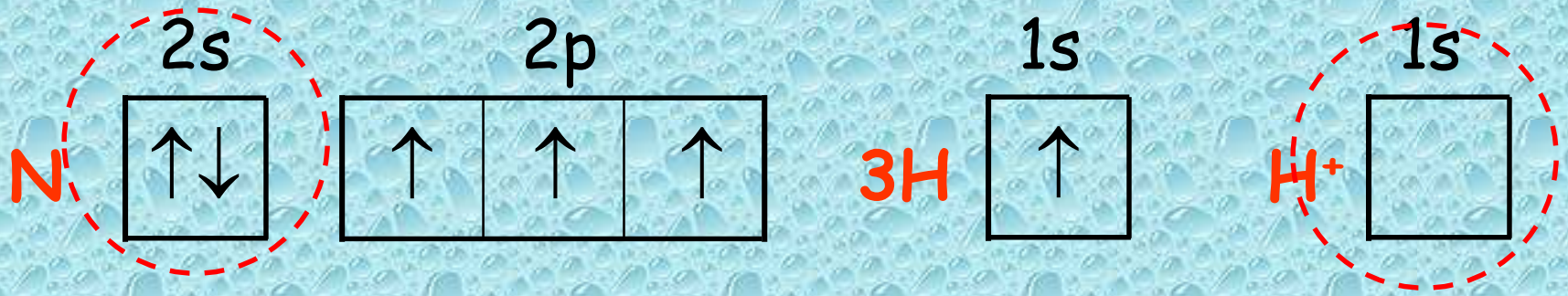
By VB Theory,



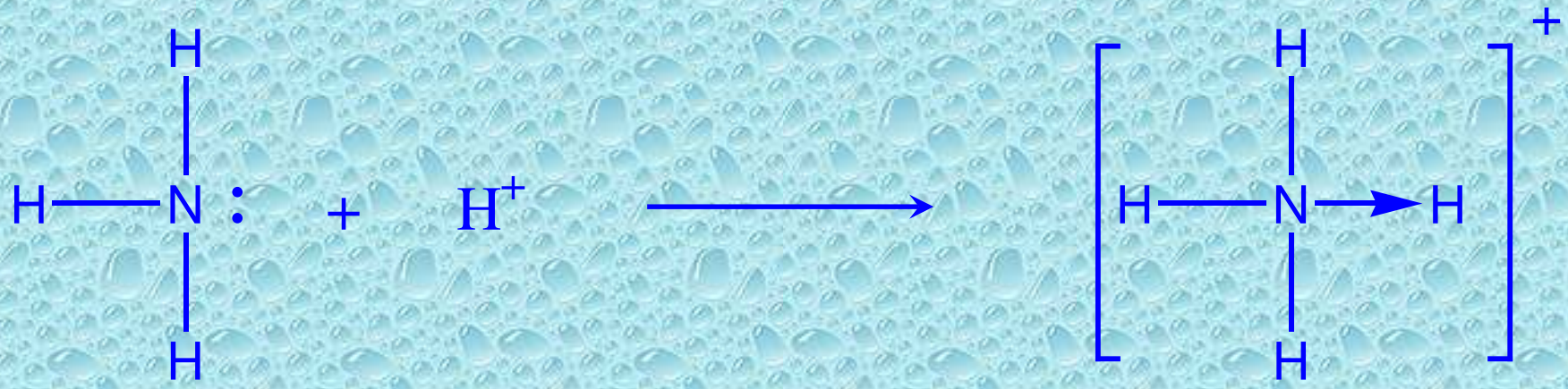
Three 2p-1s(half-filled) overlaps lead to the formation of three N – H single bonds.



By VB Theory,



One 2s(fully-filled)-1s(vacant) overlap leads to the formation of one N → H dative bond.

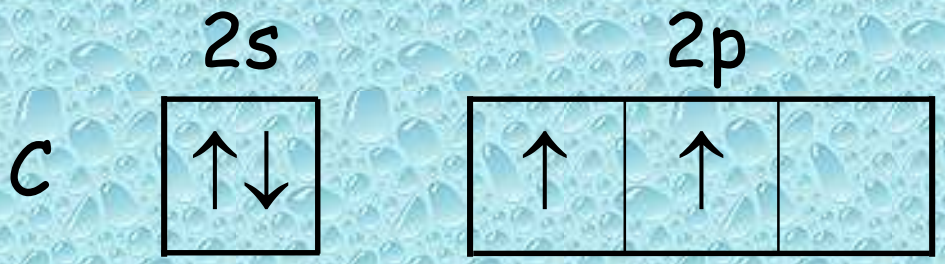


(b) HCN

By Lewis model, the structure is H-C≡N

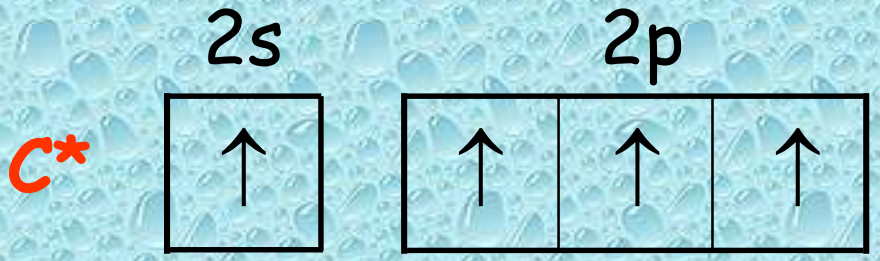
⇒ one H-C single bond (σ bond) and one C≡N triple bond (one σ and two π bonds) .

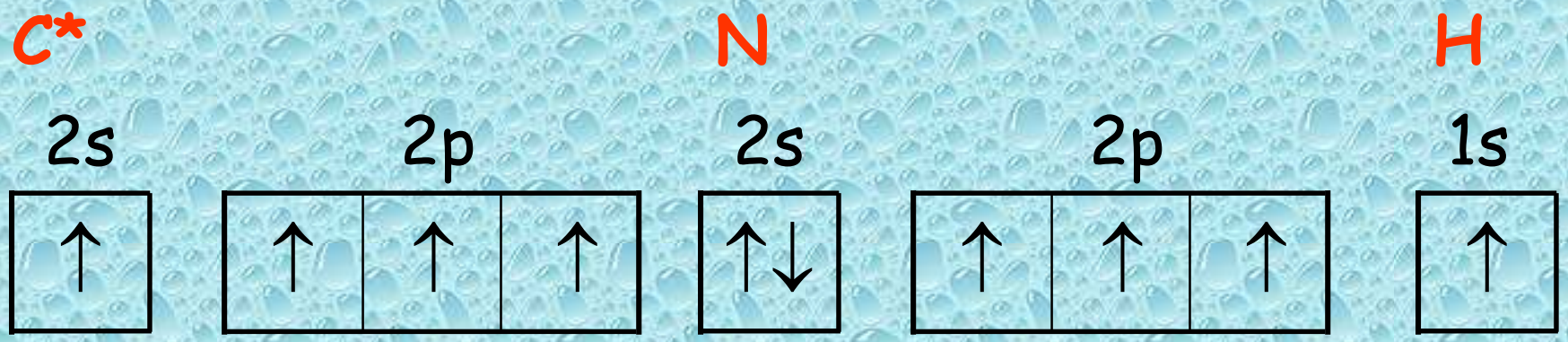
By VB Theory,



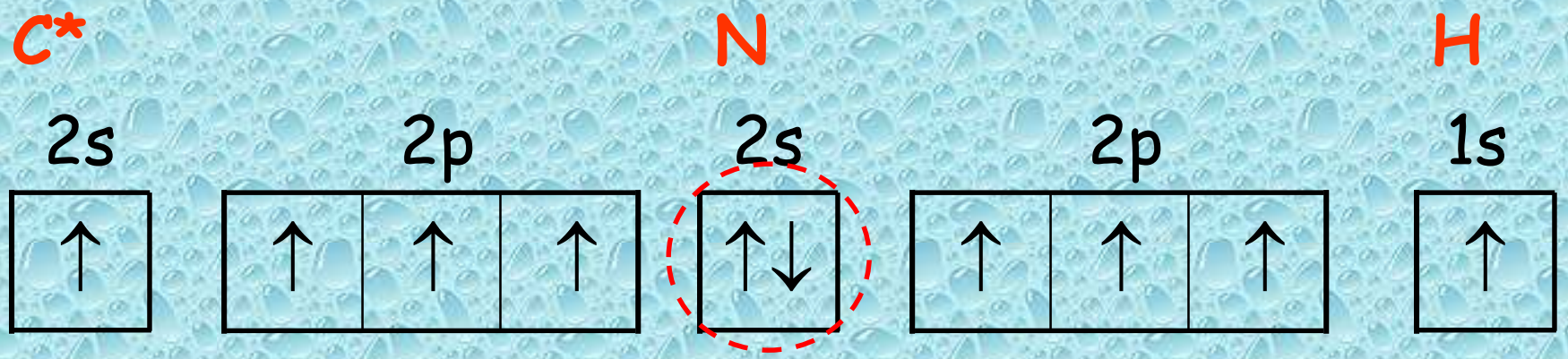
⇒ Only 2 single bonds can be formed.

⇒ Promotion of a 2s electron to a 2p orbital.

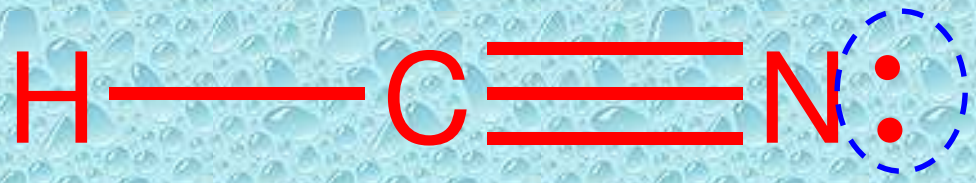




- The overlap of one orbital (?) of *C** with an 1s orbital of H gives the C-H single bond.
- Overlaps of three orbitals (???) of *C** with three 2p orbitals of N give the C≡N triple bond.



☞ The 2s electrons on N are non-bonding electrons.

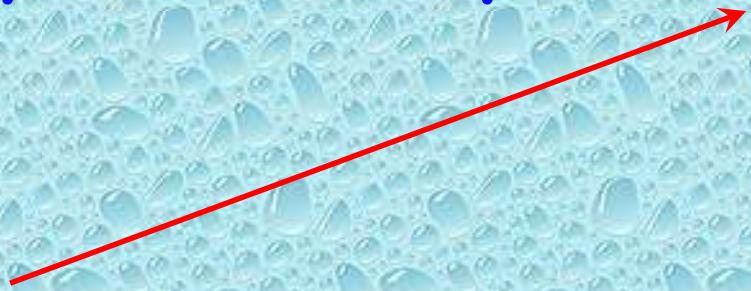


☞ The energy released by forming a stronger triple bond outweighs the energy required for promoting an electron from a 2s orbital to a 2p orbital.

(c) SO_2

By Lewis model, the three possible structures are

$O \leftarrow S = O$, $O = S \rightarrow O$, $O = S = O$

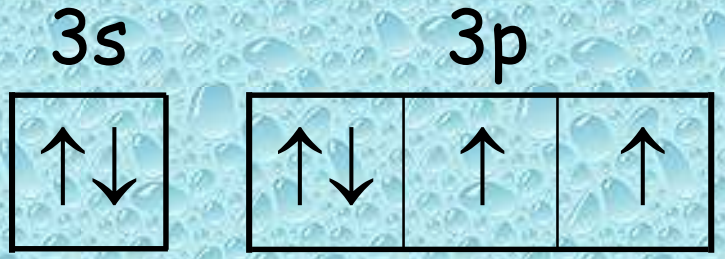


Most stable

$\because$ no separation of opposite formal charges.

By VB Theory,

S

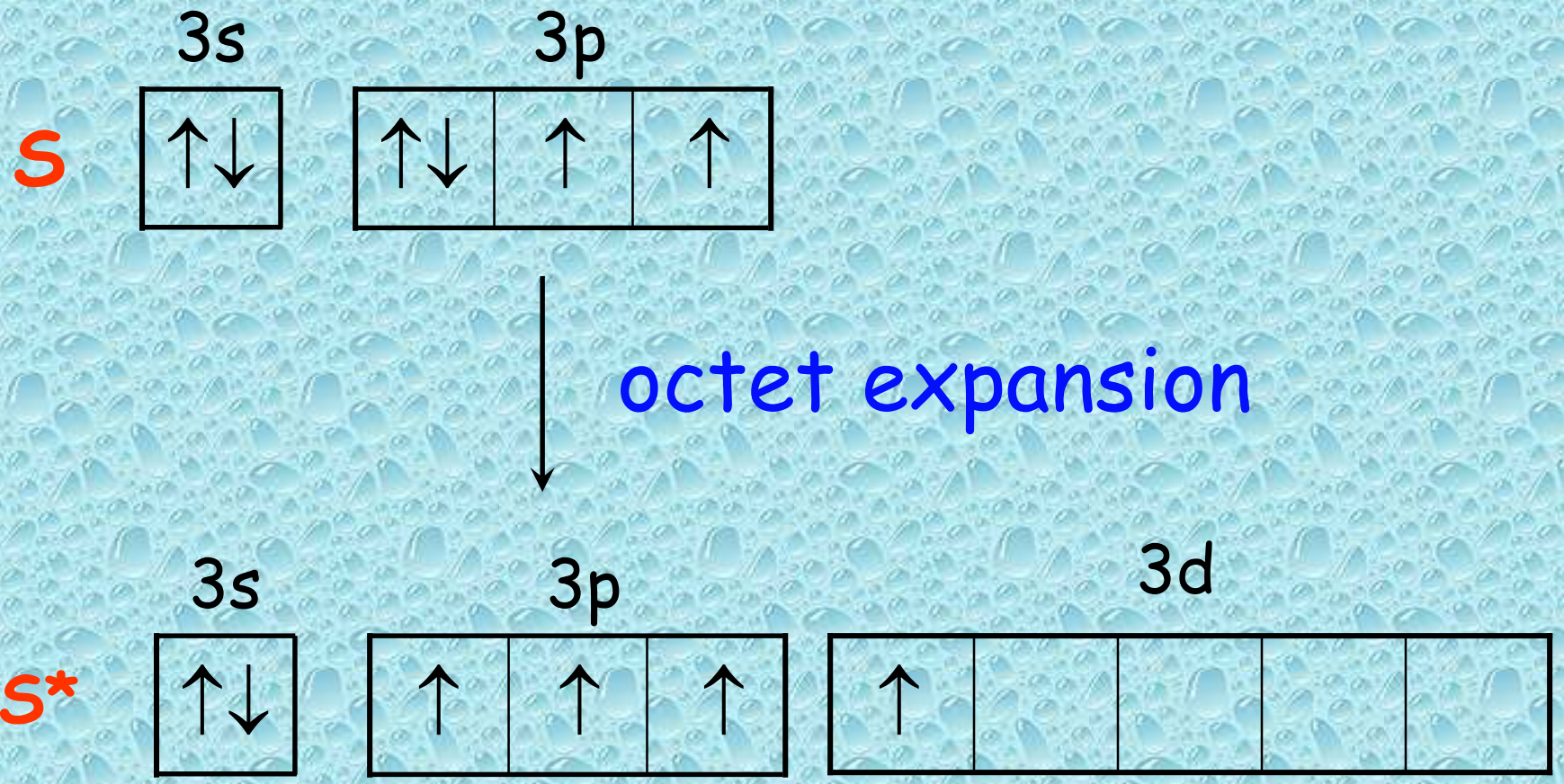


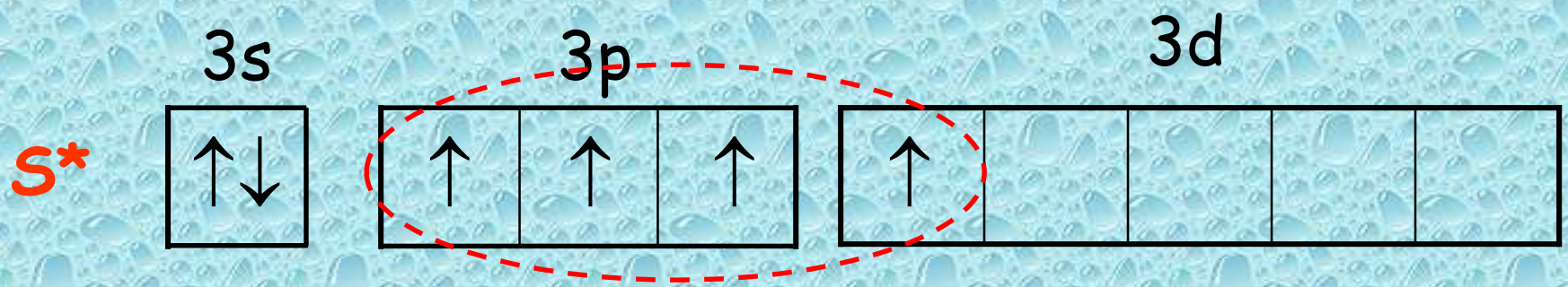
⇒ Only two single bonds can be formed.

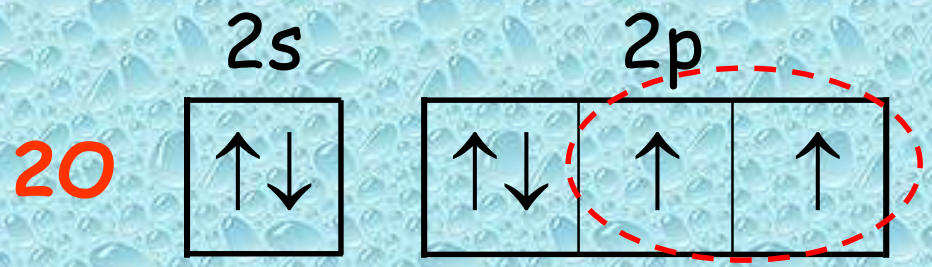
⇒ One 3p electron has to be promoted to a 3d orbital.

⇒ Expansion of Octet.

By VB Theory,

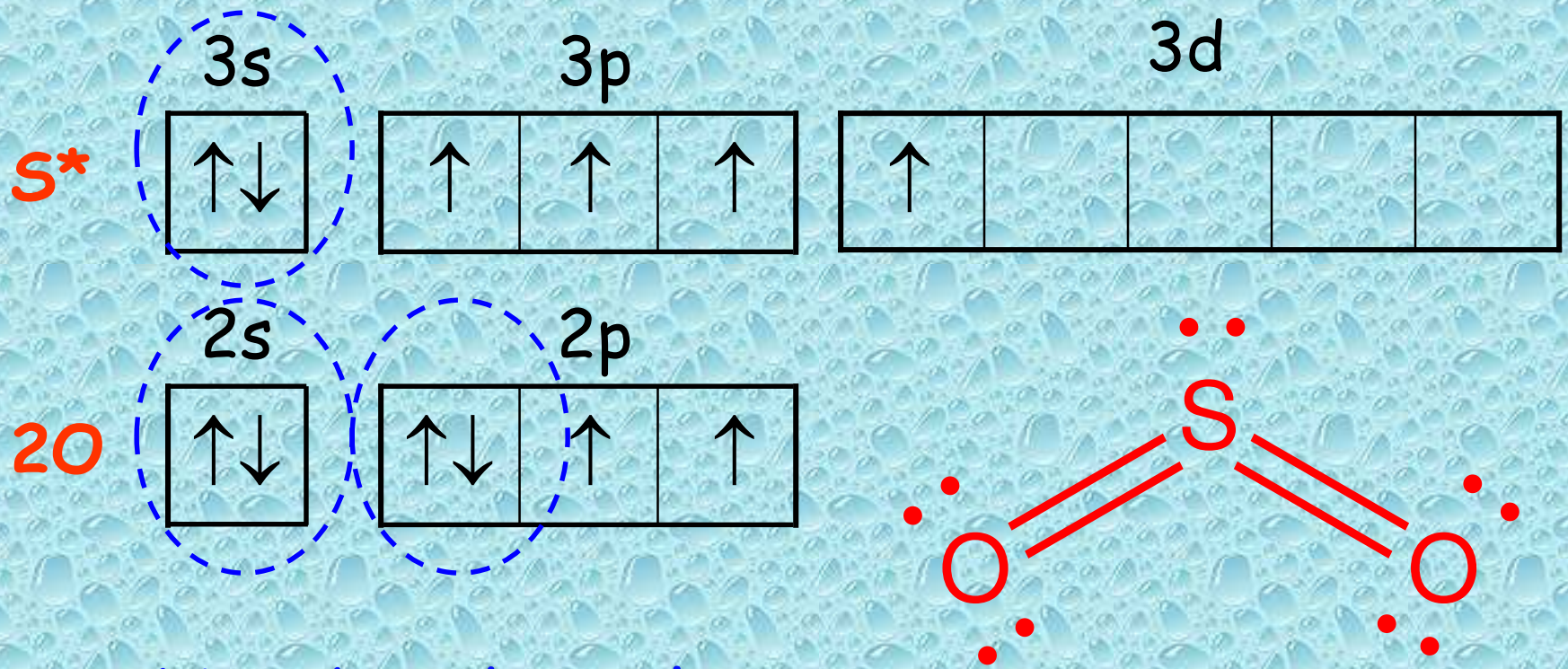






☞ Overlaps of two half-filled orbitals (??) of S* with two half-filled 2p orbitals of an oxygen atom give a S=O double bond.

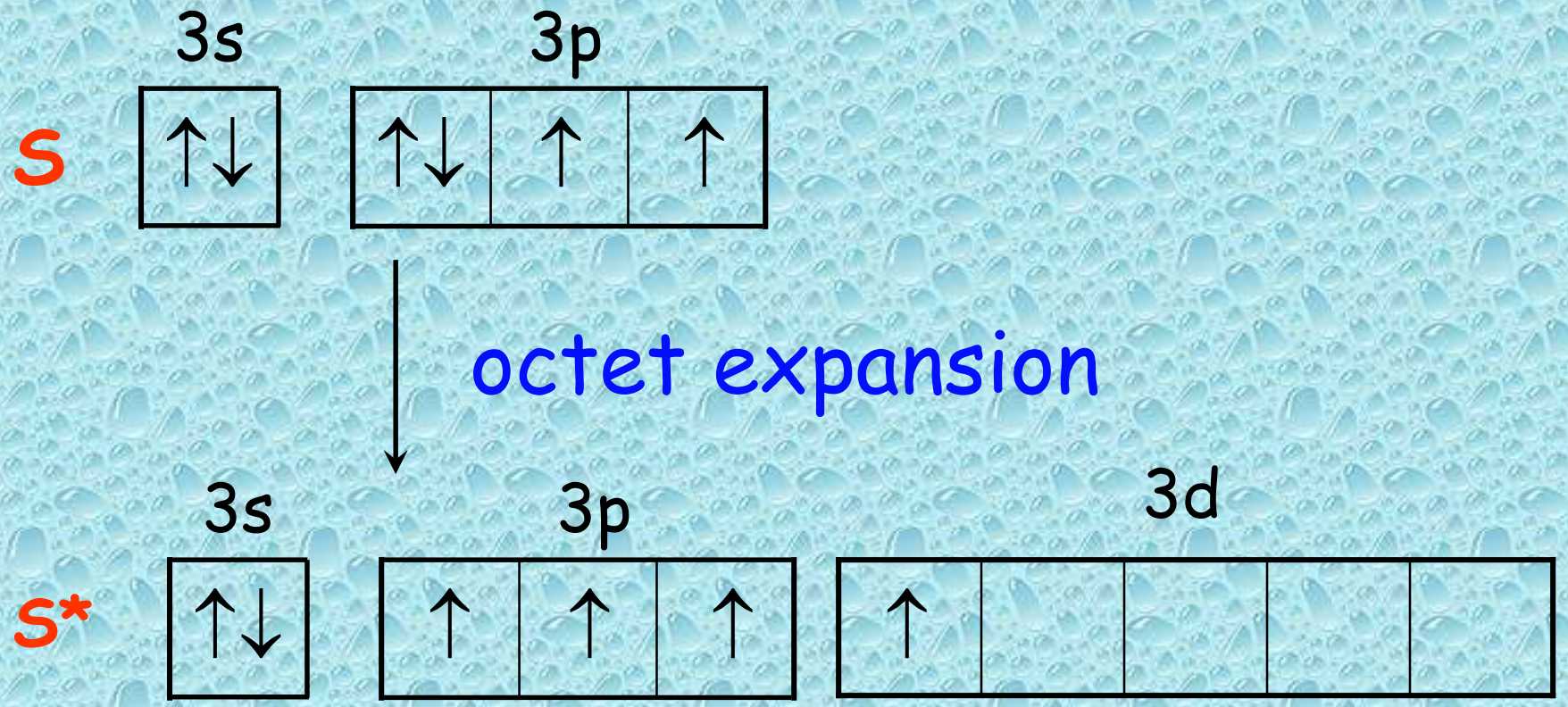
A total of two S=O bonds are formed with two O atoms



Non-bonding electrons :

S* $3s^2$;

O $2s^2$ and $2p^2$



The energy released by forming of two stronger double bonds outweighs the energy required for promoting an electron from a 3p orbital to a 3d orbital.

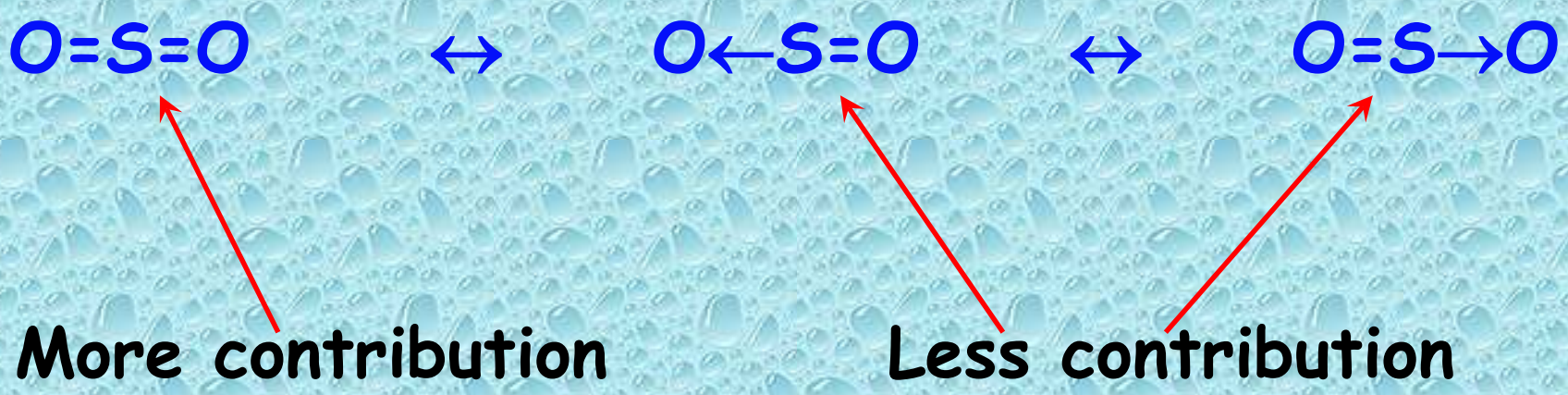
The Concept of Resonance

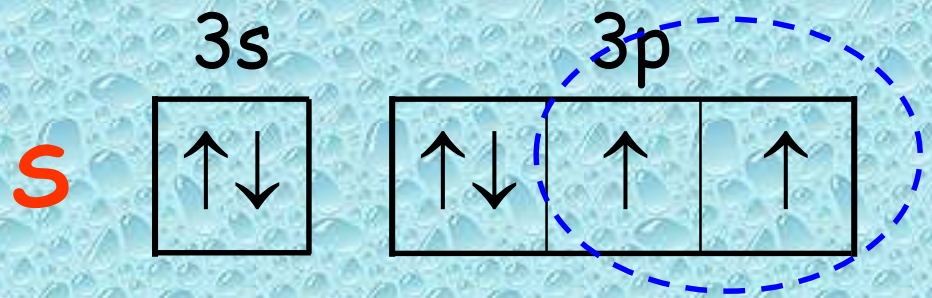
According to VB theory, the two less stable structures of SO_2,

$O \leftarrow S=O$ and $O=S \rightarrow O$ do 'exist'.

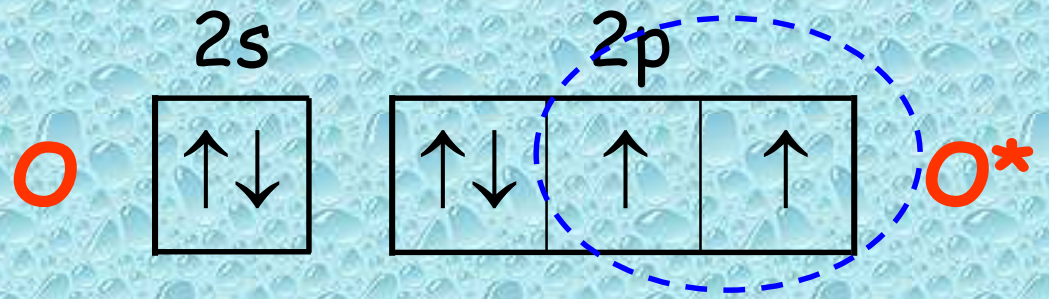
Each of these structures contributes in certain extent to the real structure of SO_2.

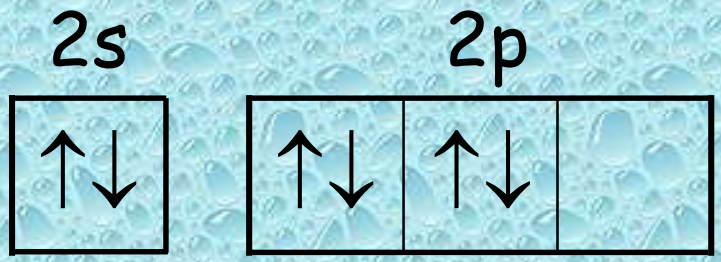
In other words, the real structure of SO_2 is the resonance hydrid of the three possible structures.



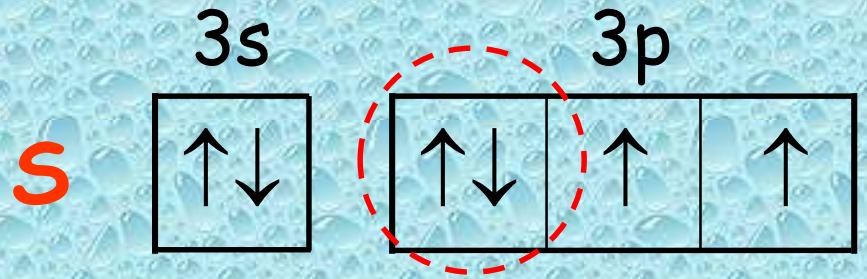


$O=S\rightarrow O$

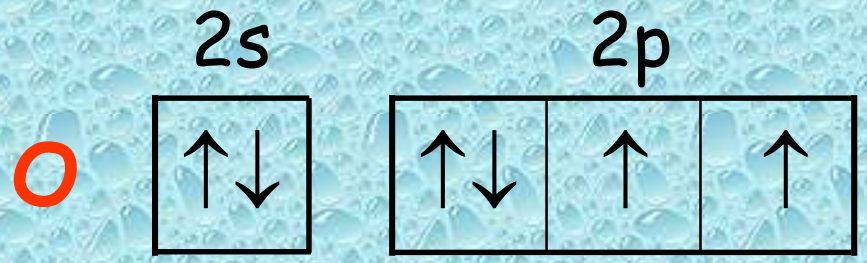


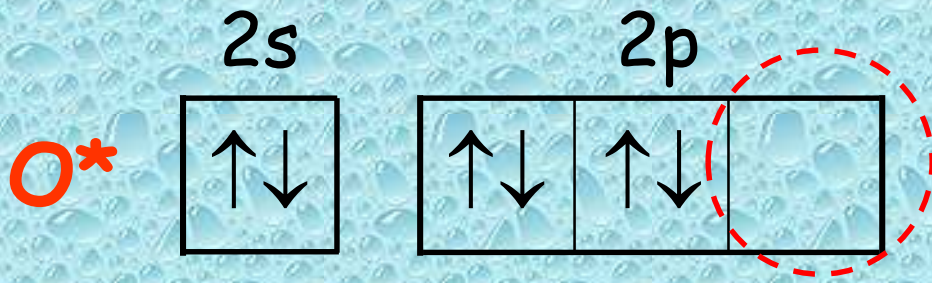


A S=O double bond is formed by 3p(half-filled)-2p(half-filled) overlaps between S and O.

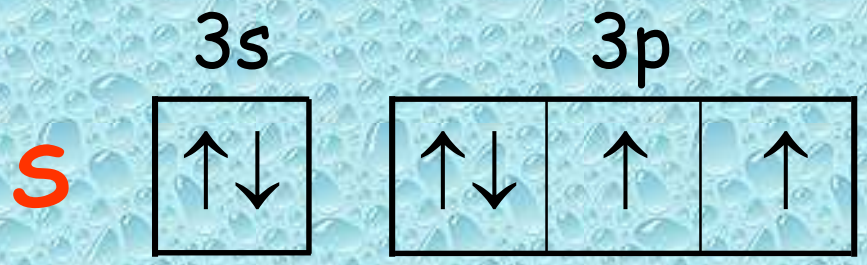


$O=S\rightarrow O$

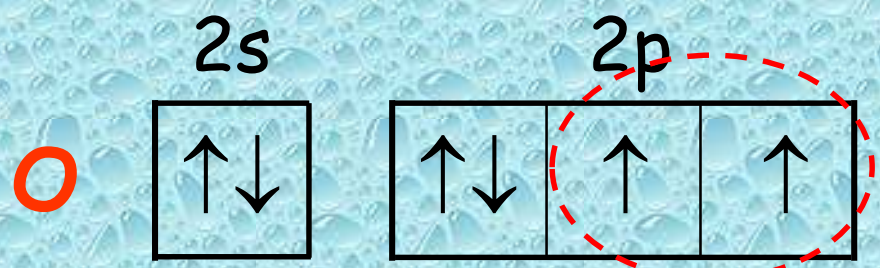


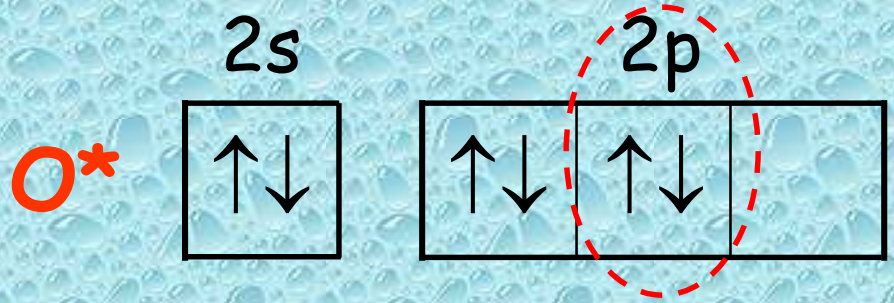


A O←S dative bond is formed by 3p(fully-filled)-2p(empty) overlap between S and O*



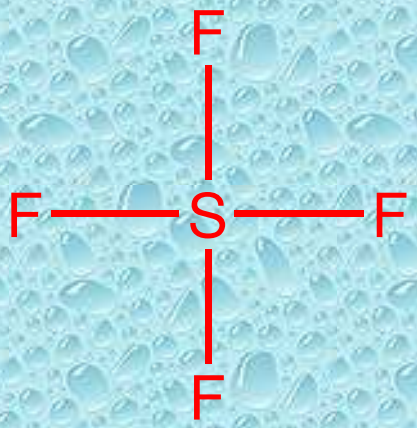
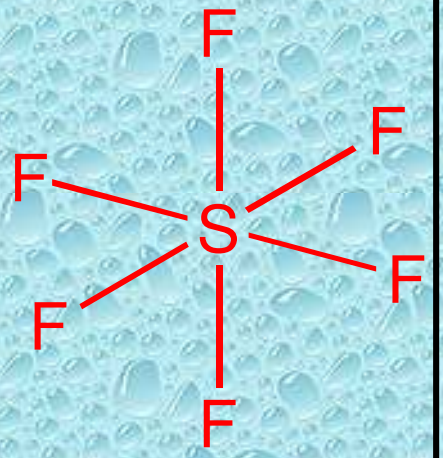
$O=S\rightarrow O$



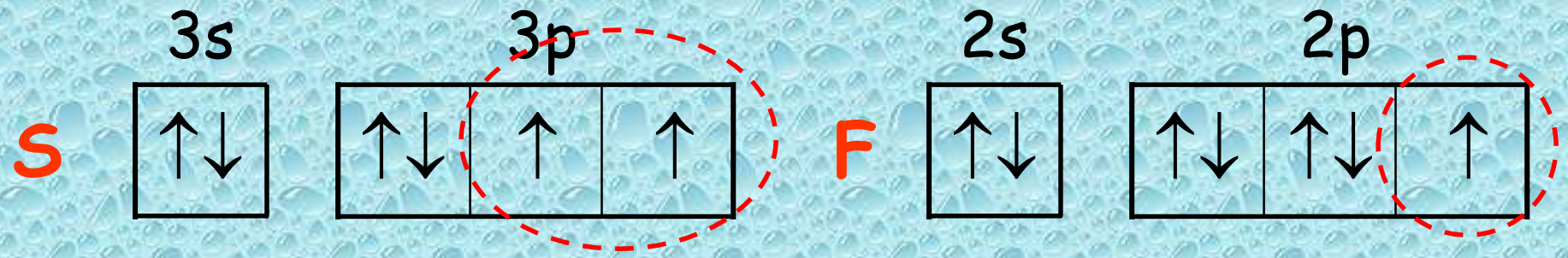


Formation of dative bond is <u>not favourable</u> because the two unpaired 2p electrons in O are forced to pair up to give O*

SF_2, SF_4, SF_6

Molecule	SF_2	SF_4	SF_6
Most stable Lewis Structure	F-S-F		

By VB Theory,

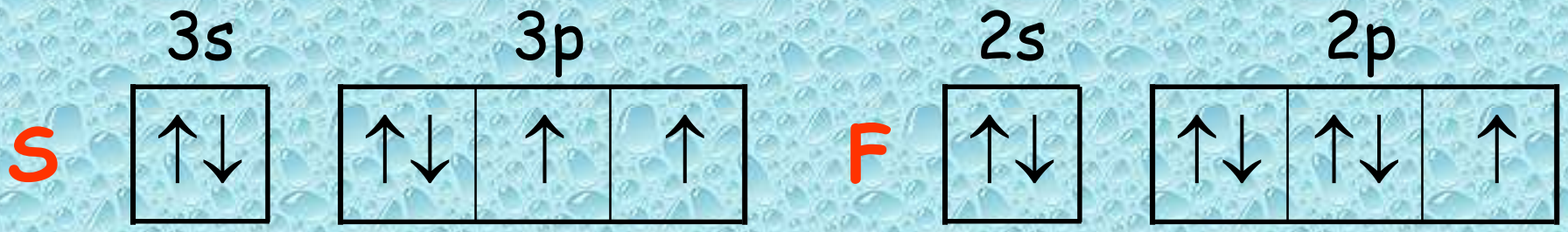


Only two S-F single bonds can be formed by 3p-2p overlaps between one S atom and two F atoms

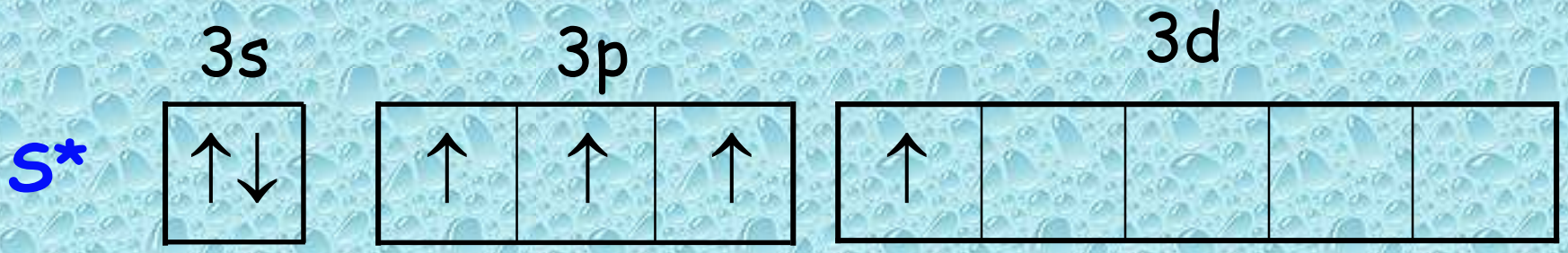
$\Rightarrow SF_2$ is formed.

F-S-F

By VB Theory,

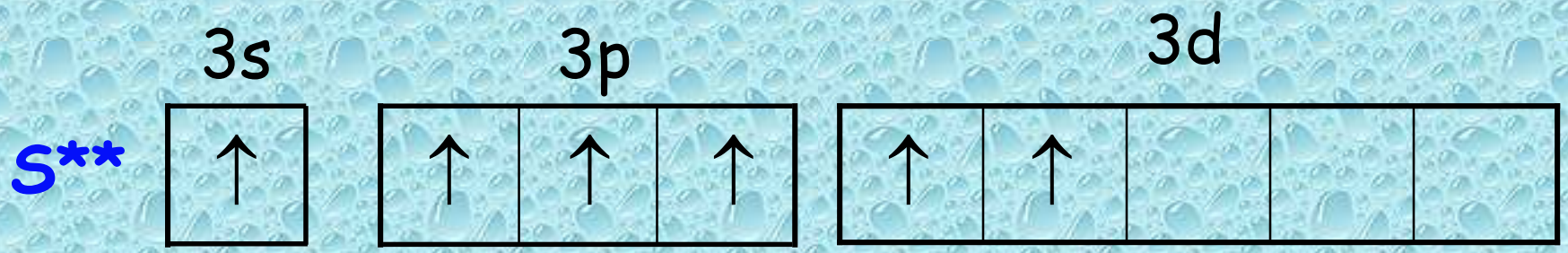


To form four S-F single bonds in SF_4, a 3p electron in S has to be promoted to a 3d orbital.

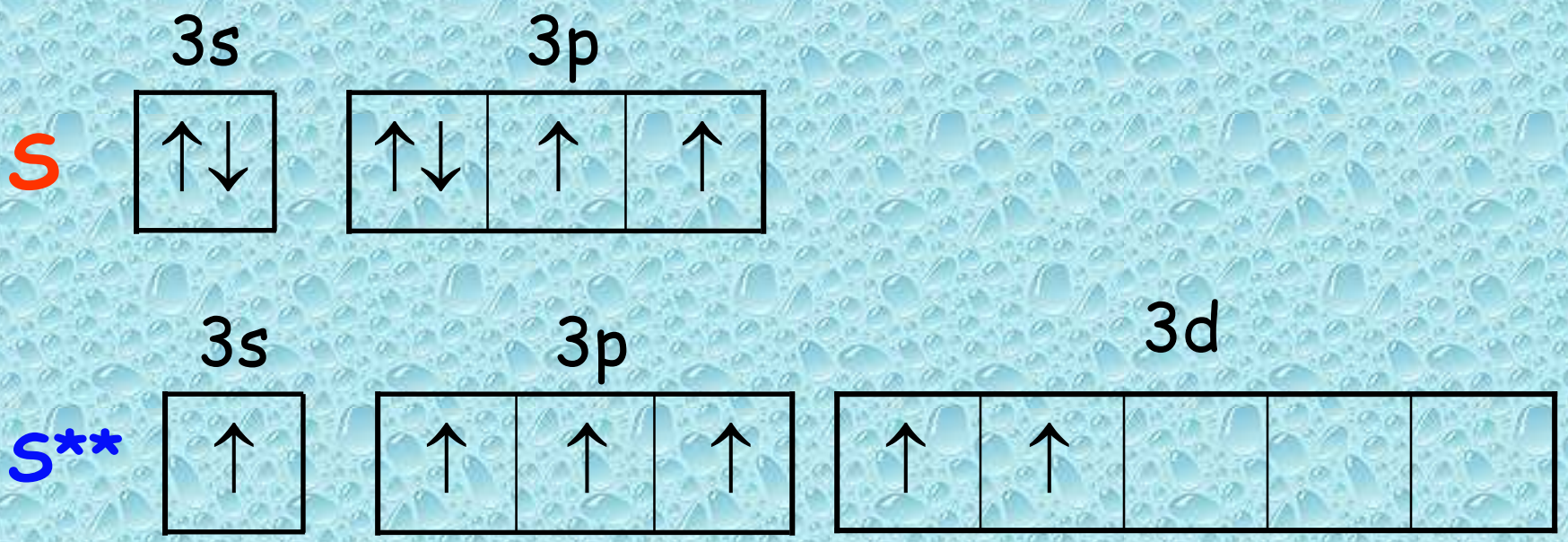


By VB Theory,

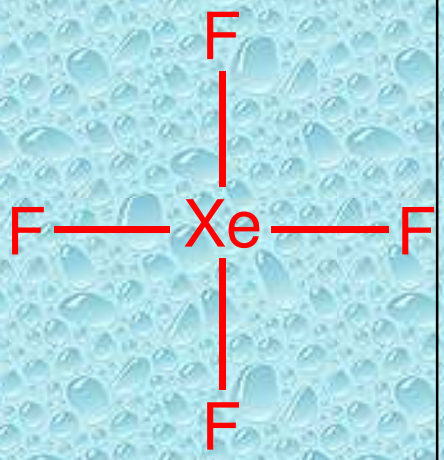
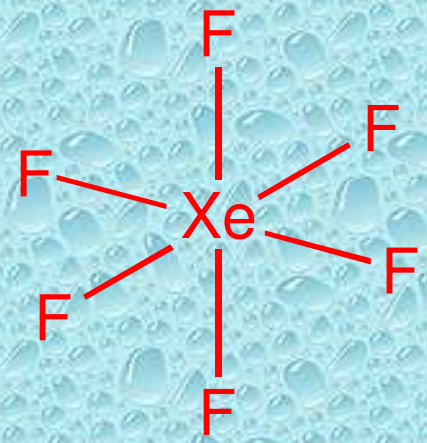
To form six S-F single bonds in SF_6, a 3s electron in S* has to be promoted to a 3d orbital.



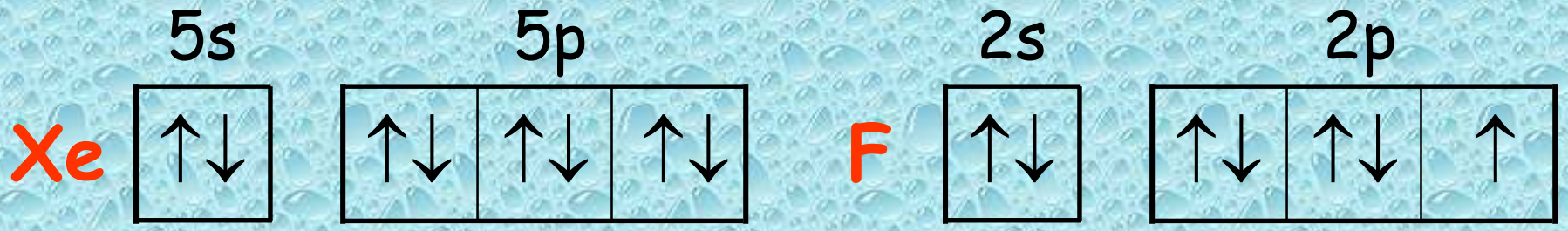
By VB Theory,



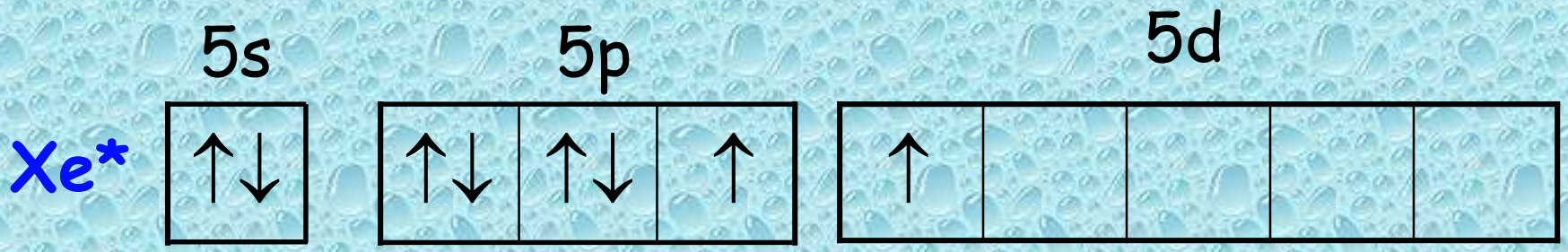
The energy released by forming more single bonds **outweighs** the energy required for promoting 3s and 3p electrons to 3d orbitals.

Molecule	XeF_2	XeF_4	XeF_6
Most stable Lewis Structure	F-Xe-F		

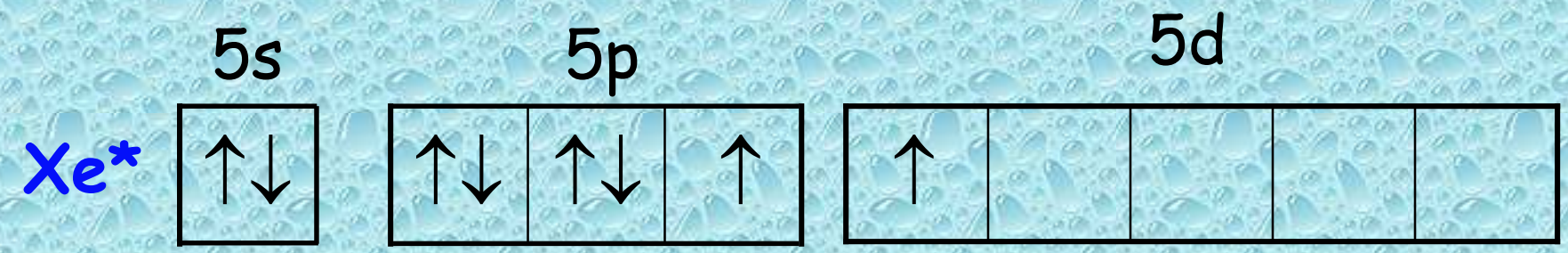
By VB Theory,



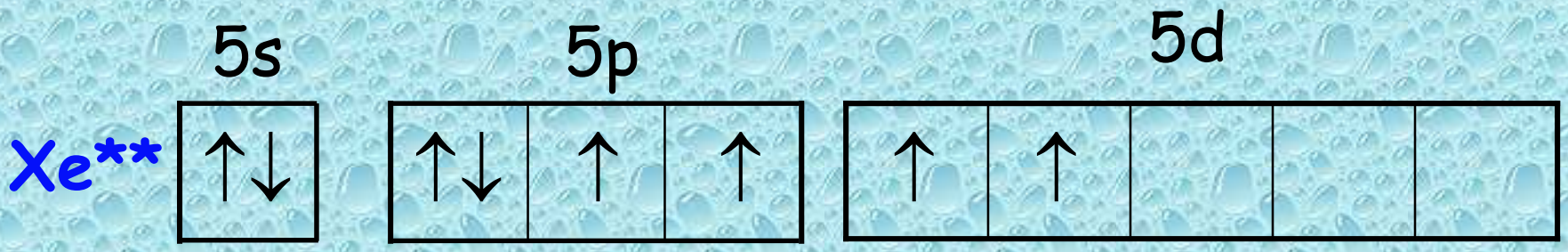
To form two Xe-F bonds in XeF_2, a 5p electron in Xe has to be promoted to a 5d orbital.



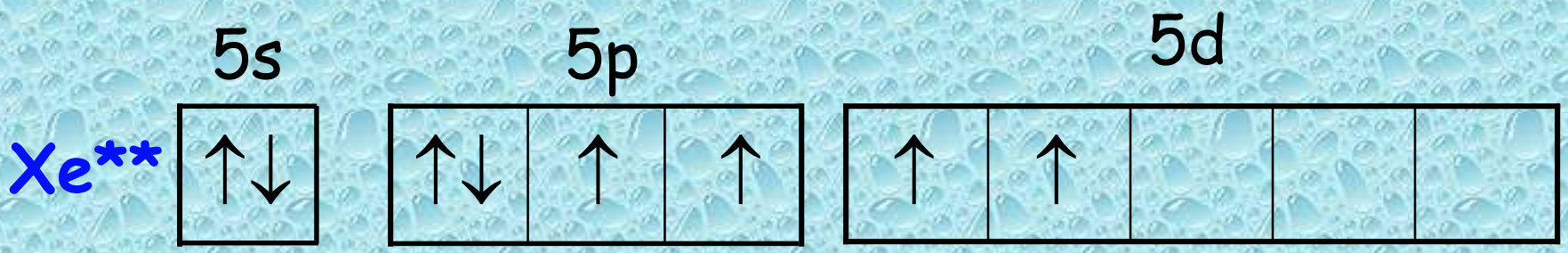
By VB Theory,



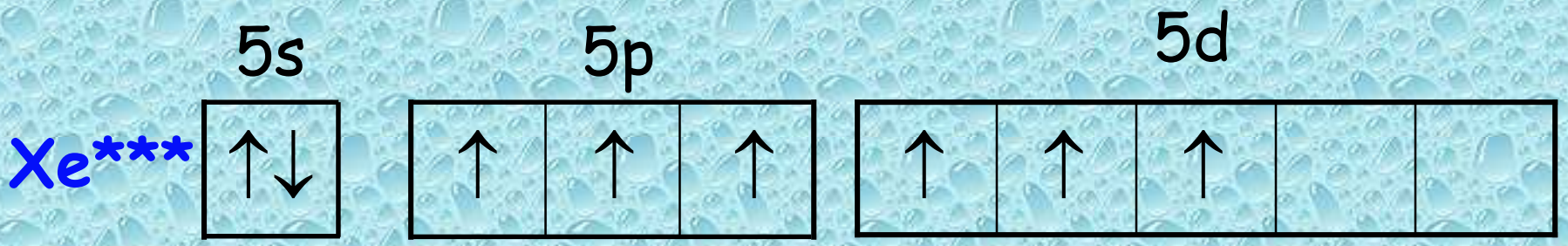
To form four Xe-F bonds in XeF_4, a 5p electron in Xe* has to be promoted to a 5d orbital.



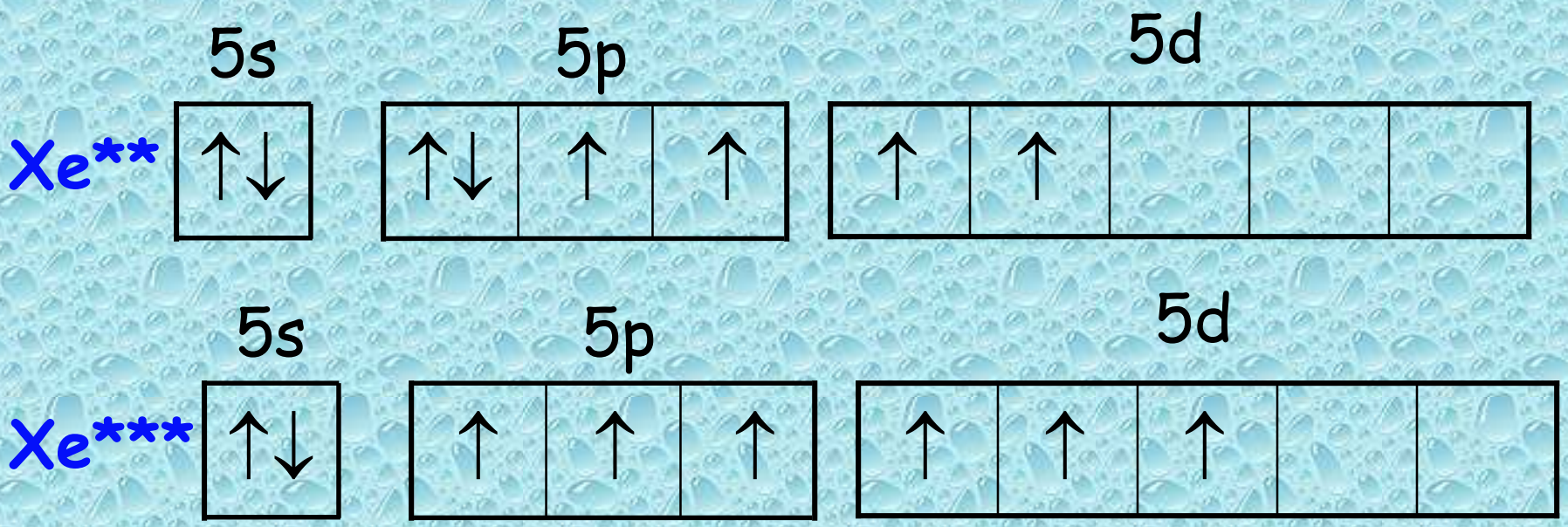
By VB Theory,



To form six Xe-F bonds in XeF_6, a 5p electron in Xe** has to be promoted to a 5d orbital.



By VB Theory,



The energy released by forming more single bonds outweighs the energy required for promoting 5p electrons to 5d orbitals.

Maximizing Bond Formation

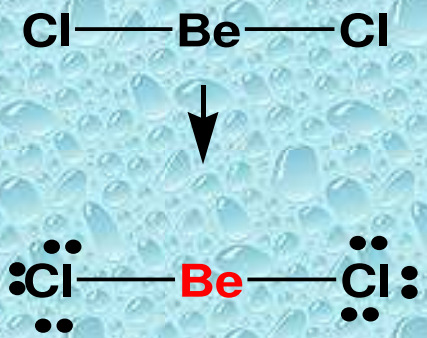
In order for "best overlap" to occur, valence electrons need to be re-oriented and electron clouds reshaped to allow optimum contact.

To form as many bonds as possible from the available valence electrons, sometimes separation of electron pairs must also occur.

We describe the transformation process as "orbital hybridization" and we focus on the central atom in the species...

"sp" Hybridization: all 2 Region Species

$BeCl_2$



Be 2
2Cl 14

16 e's/2= 8 prs

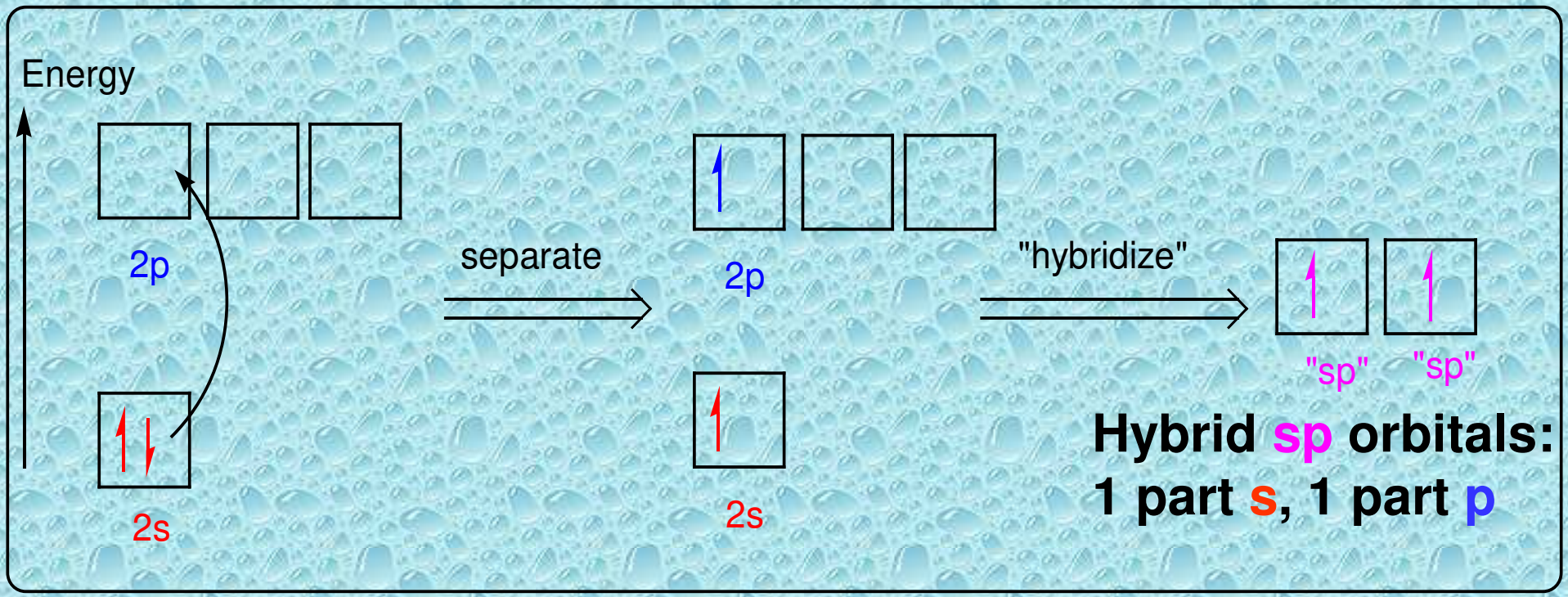
Number of regions around CENTRAL ATOM: 2

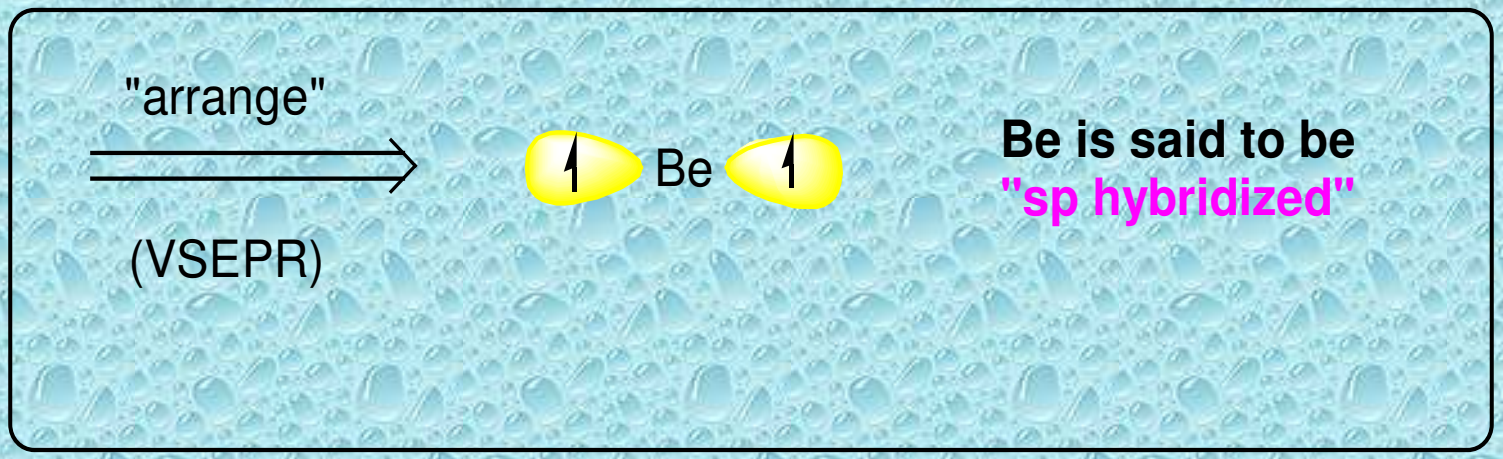
shape : LINEAR
bond angles: 180°

Hybridization of Be in $BeCl_2$

Valence e's

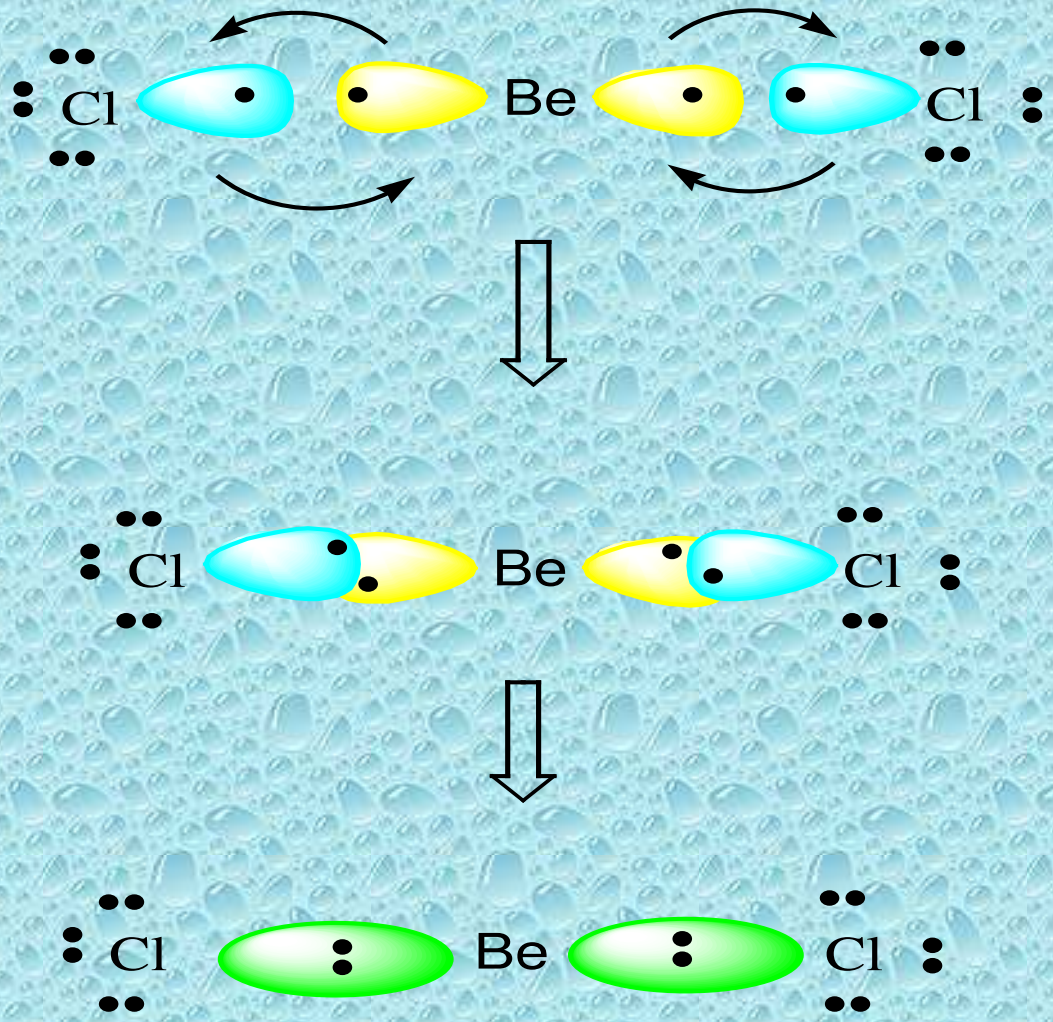
Atomic Be: $1s^2$ $2s^2$





FORMATION OF $BeCl_2$:

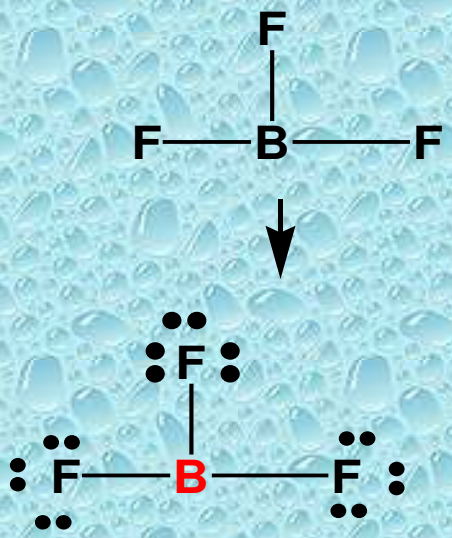
Each Chlorine atom, $1s^2 2s^2 2p^6 3s^2 3p^5$, has one unshared electron in a p orbital. The half filled p orbital overlaps head-on with a half full hybrid sp orbital of the beryllium to form a sigma bond.



sp hybridized, linear, 180° bond angles

"sp^2" Hybridization: All 3 Region Species

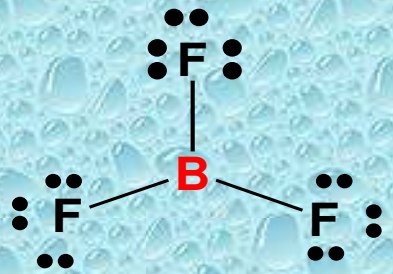
BF_3



B 3
3F 21

24 e's/2= 12 prs

Number of regions around CENTRAL ATOM: 3

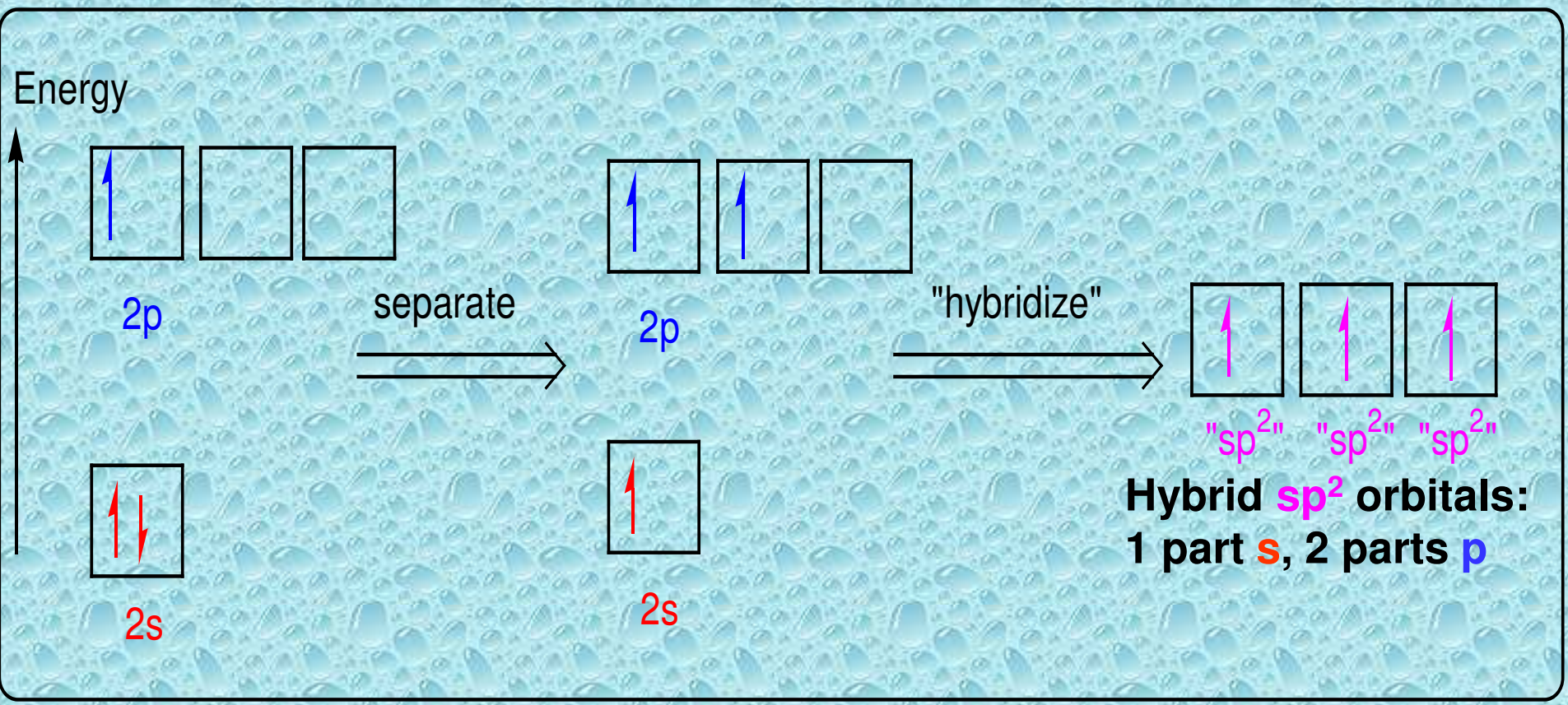


shape : TRIGONAL PLANAR
bond angles: 120°

Hybridization of B in BF_3

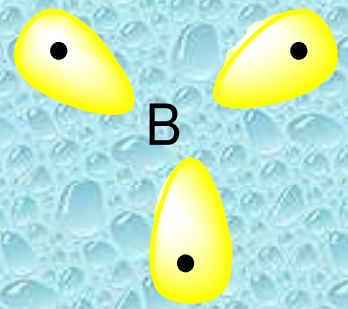
Valence e's

Atomic B : $1s^2\ 2s^2\ 2p^1$



"arrange"

(VSEPR)

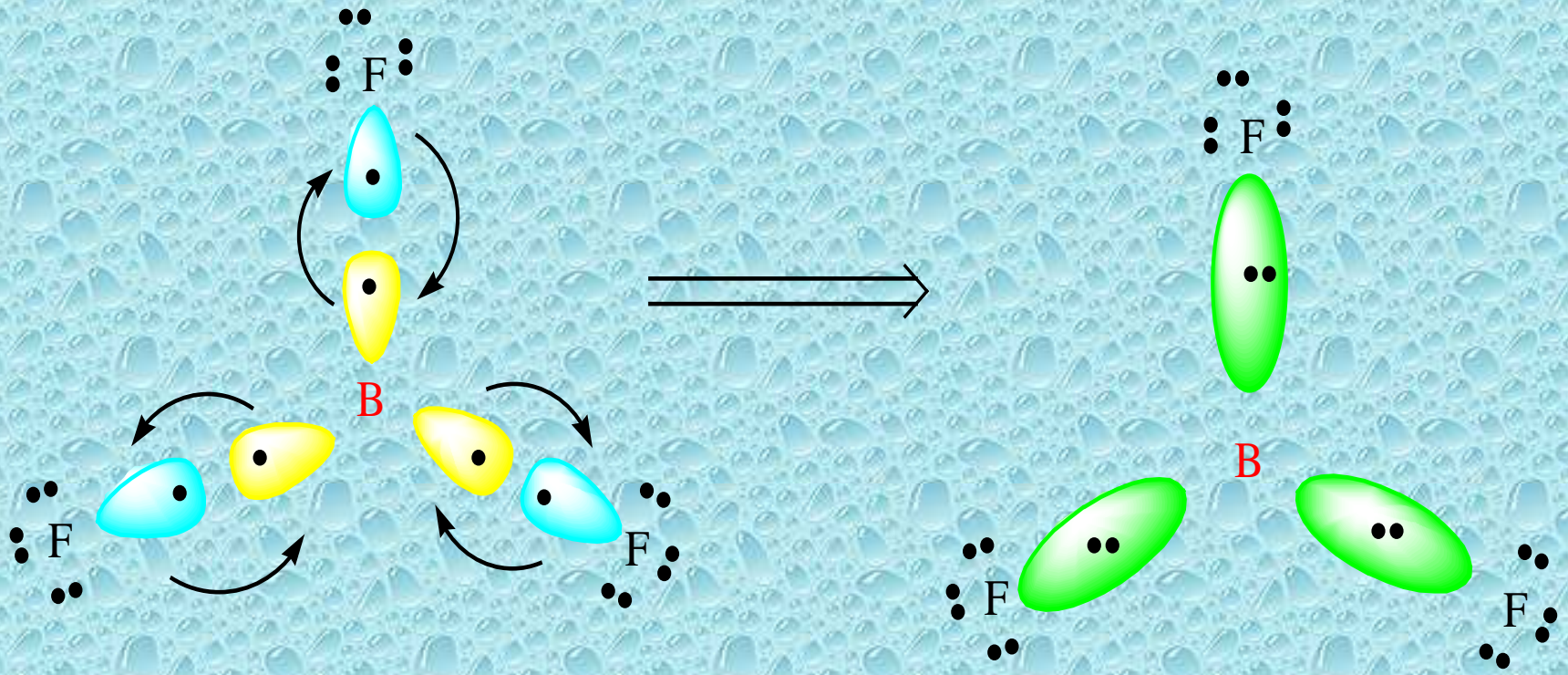


B is said to be "sp^2 hybridized"

FORMATION OF BF_3:

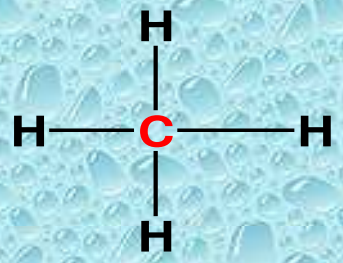
Each fluorine atom, $1s^2 2s^2 2p^5$, has one unshared electron in a p orbital. The half filled p orbital overlaps head-on with a half full hybrid sp^2 orbital of the boron to form a sigma bond.

sp^2 hybridized, TRIGONAL PLANAR,
120° bond angles



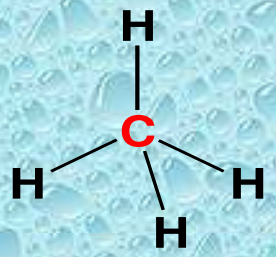
"sp^3" Hybridization: All 4 Region Species

CH_4



C 4
4H 4
8
8 e's /2 = 4 pr

Number of regions around CENTRAL ATOM: 4

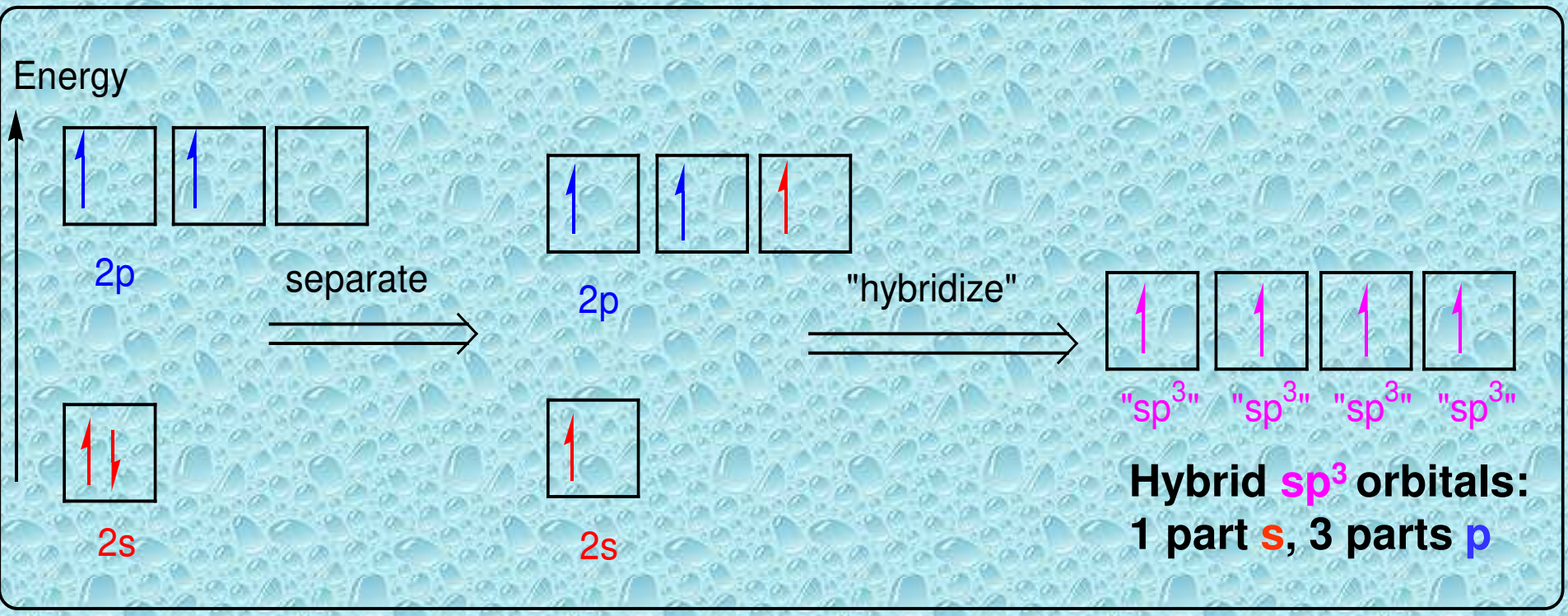


shape : TETRAHEDRAL
bond angles: 109.5°

Hybridization of C in CH_4

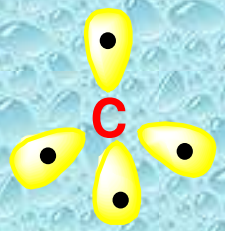
Valence e's

Atomic C : $1s^2\ 2s^2\ 2p^2$



"arrange"

(VSEPR)

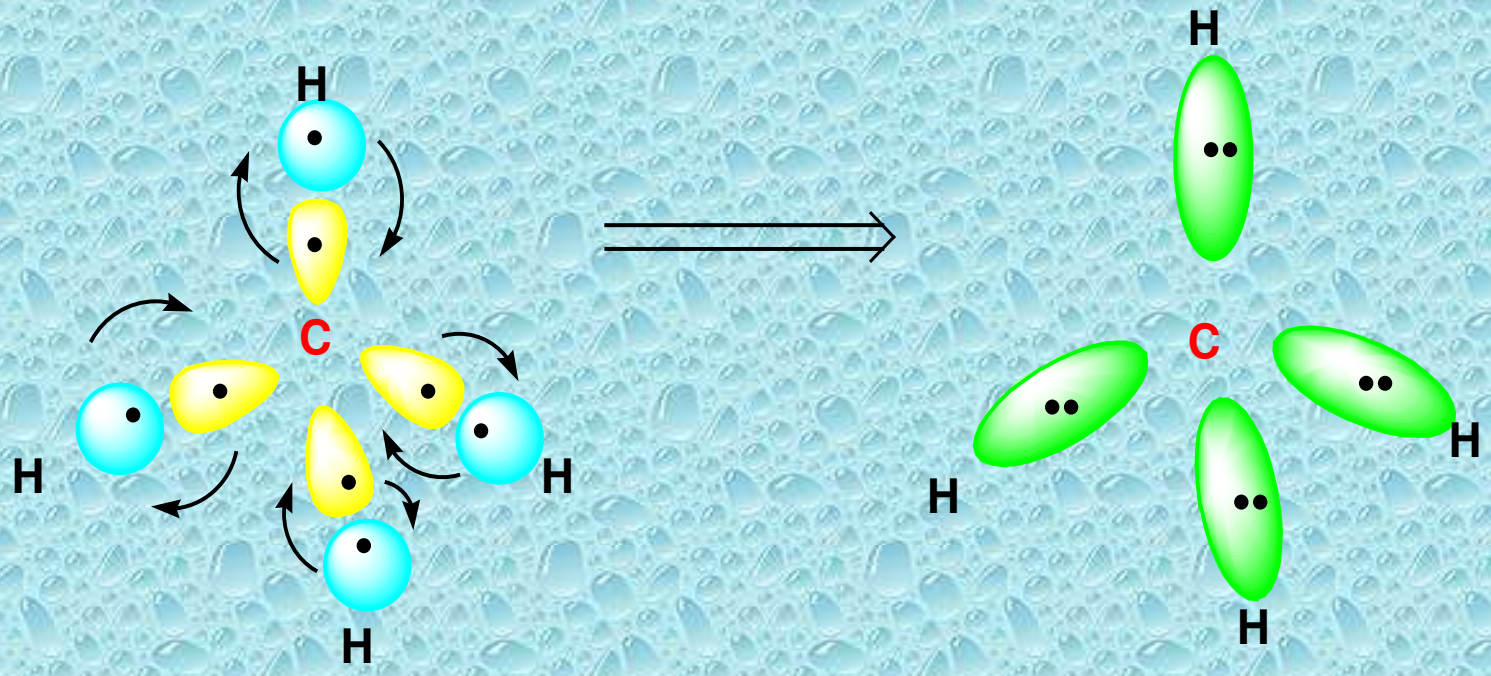


C is said to be "sp^3 hybridized"

FORMATION OF CH_4:

Each hydrogen atom, $1s^1$, has one unshared electron in an s orbital. The half filled s orbital overlaps head-on with a half full hybrid sp^3 orbital of the carbon to form a sigma bond.

sp^3 hybridized, TETRAHEDRAL,
109.5° bond angles

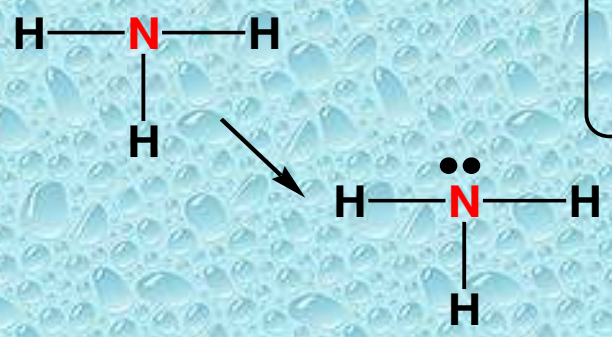


Unshared Pairs, Double or Triple Bonds

Unshared pairs occupy a hybridized orbital the same as bonded pairs: See the example of NH_3 that follows.

Double and triple bonds are formed from electrons left behind and unused in p orbitals. Since all multiple bonds are formed on top of sigma bonds, the **hybridization of the single (σ) bonds** determine the hybridization and shape of the molecule...

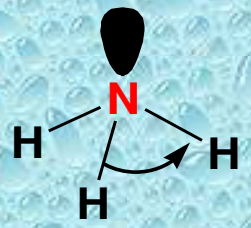
NH_3



N	5
3H	3

8e's/2=4 prs

Number of regions around CENTRAL ATOM: 4



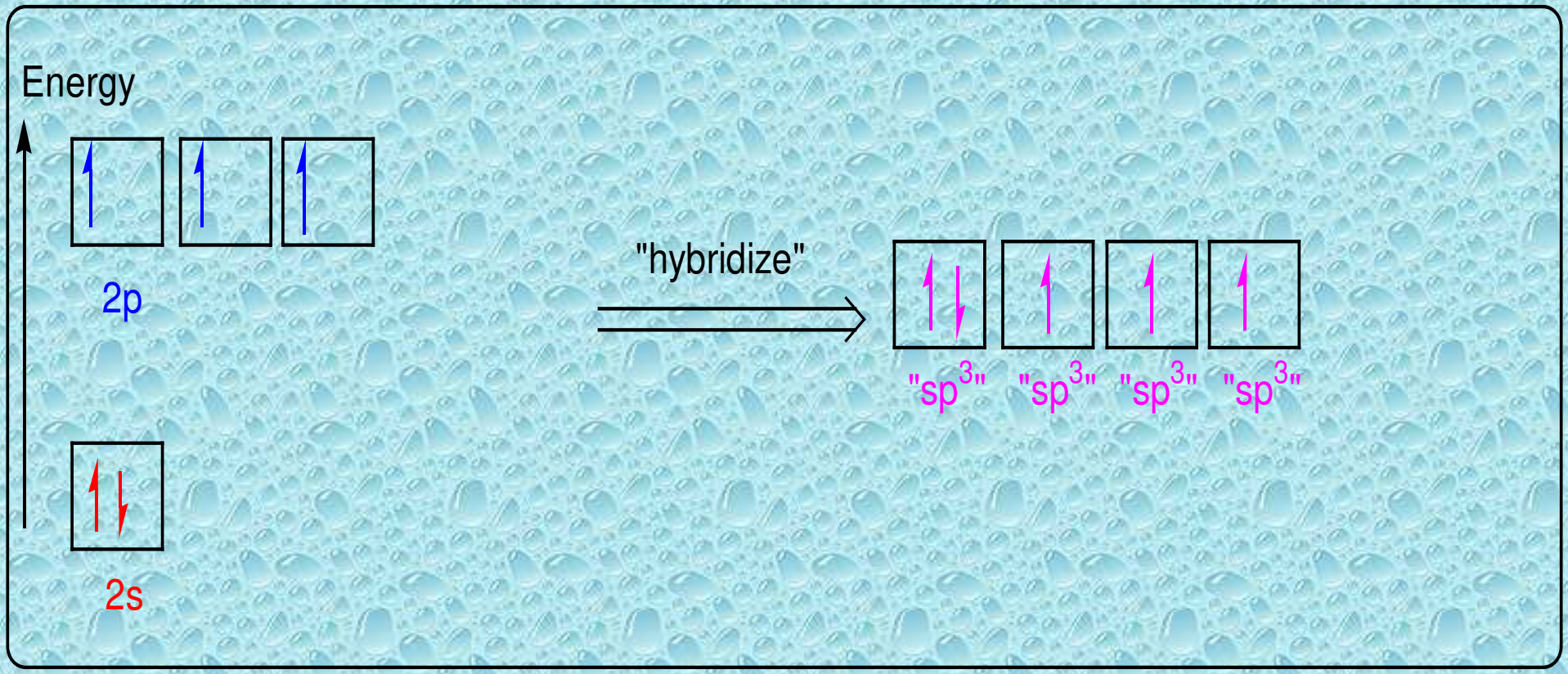
shape : TETRAHEDRAL

bond angles: < 109.5°

Hybridization of N in NH_3

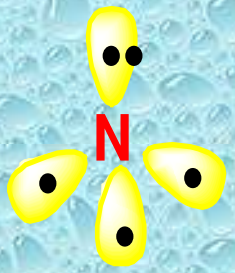
Valence e's

Atomic N: $1s^2$ $2s^2$ $2p^3$



"arrange"

(VSEPR)

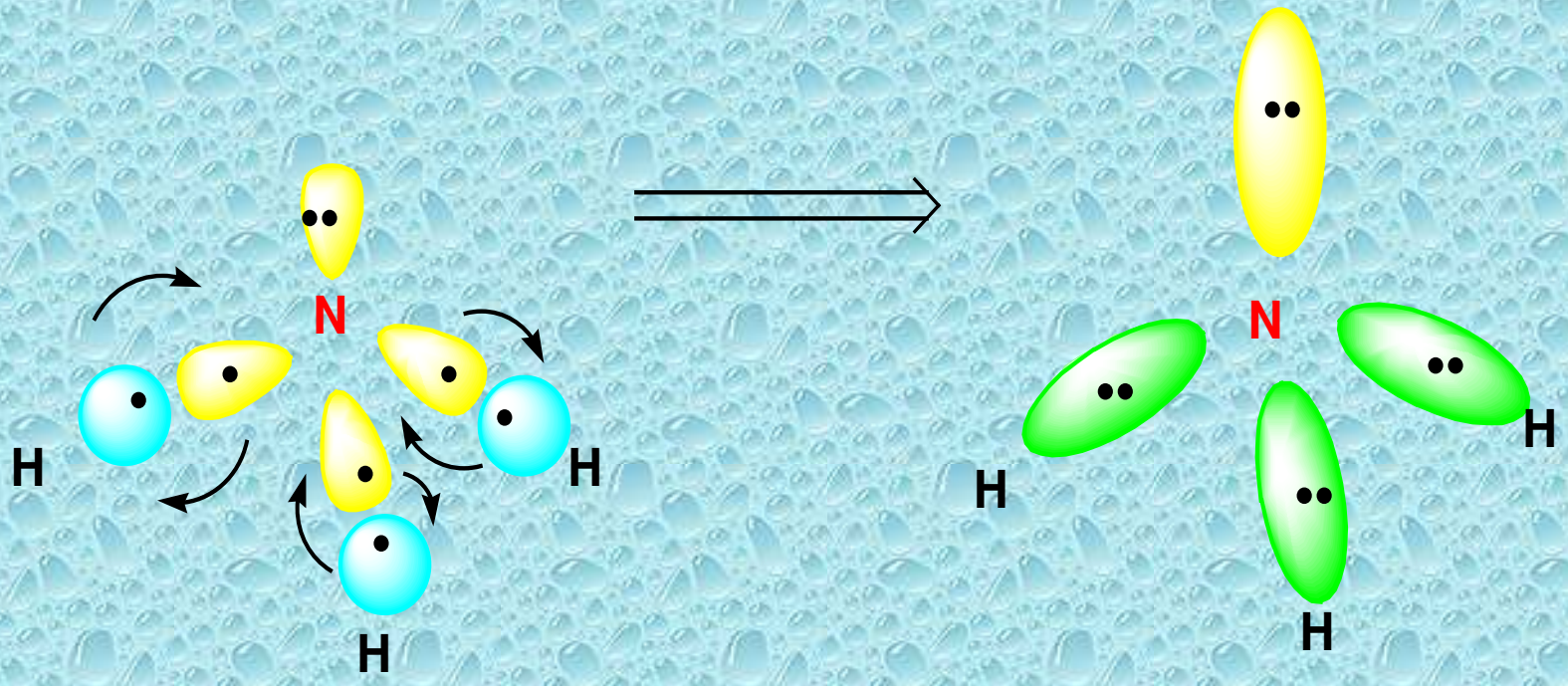


N is said to be "sp^3 hybridized"

FORMATION OF NH_3:

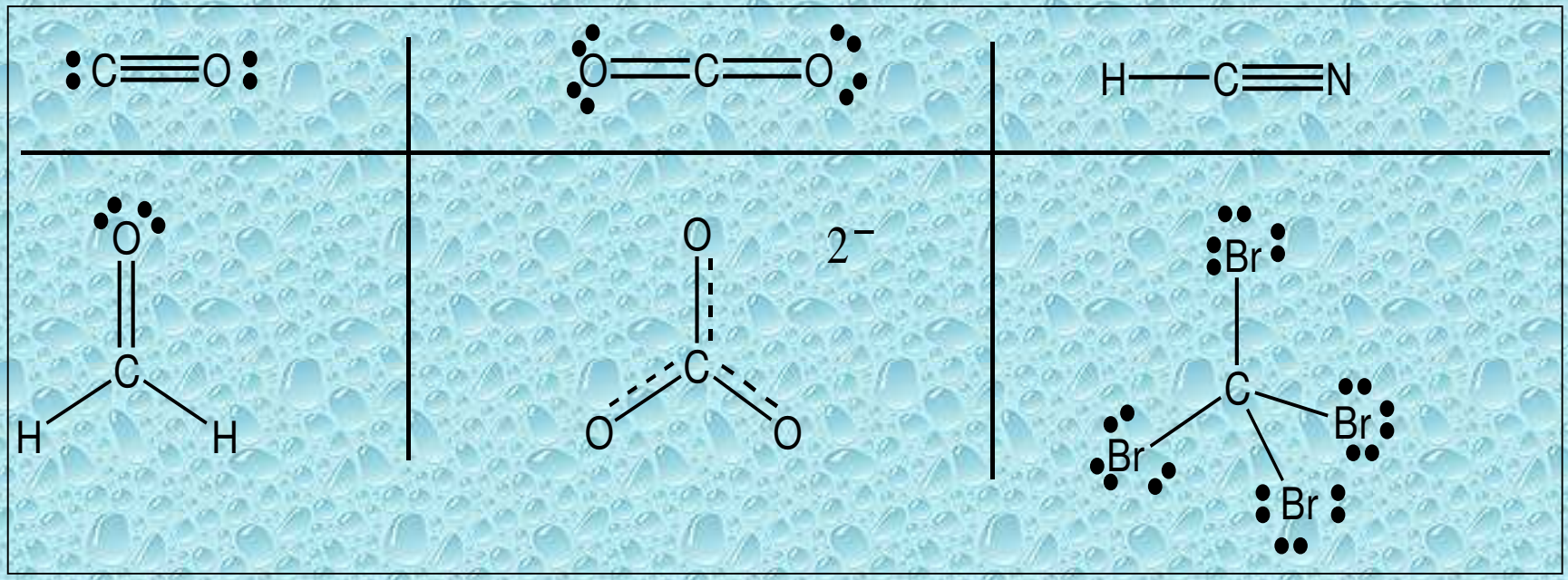
Each hydrogen atom, $1s^1$, has one unshared electron in an s orbital. The half filled s orbital overlaps head-on with a half full hybrid sp^3 orbital of the nitrogen to form a sigma bond.

sp^3hybridized, TETRAHEDRAL,
~107° bond angles

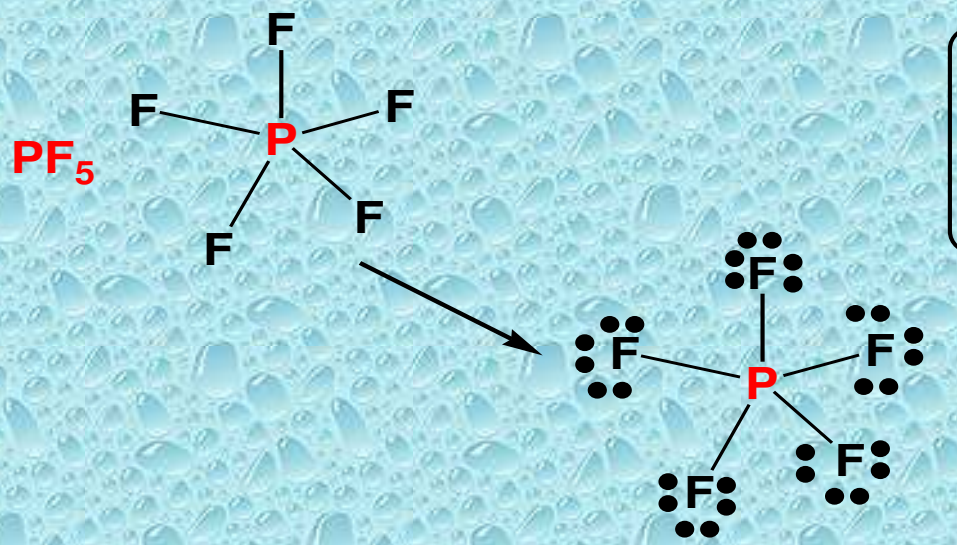


Describe Hybridization of C and shape of following species:

CO, CO_2, HCN, CH_2O, CO_3^{2-} , CBr_4

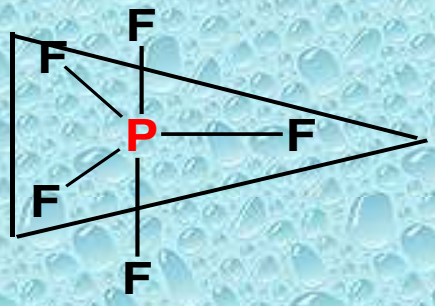


"sp^3d" Hybridization: All 5 Region Species



P 5
5F 35
40
40 e's /2 = 20 pr

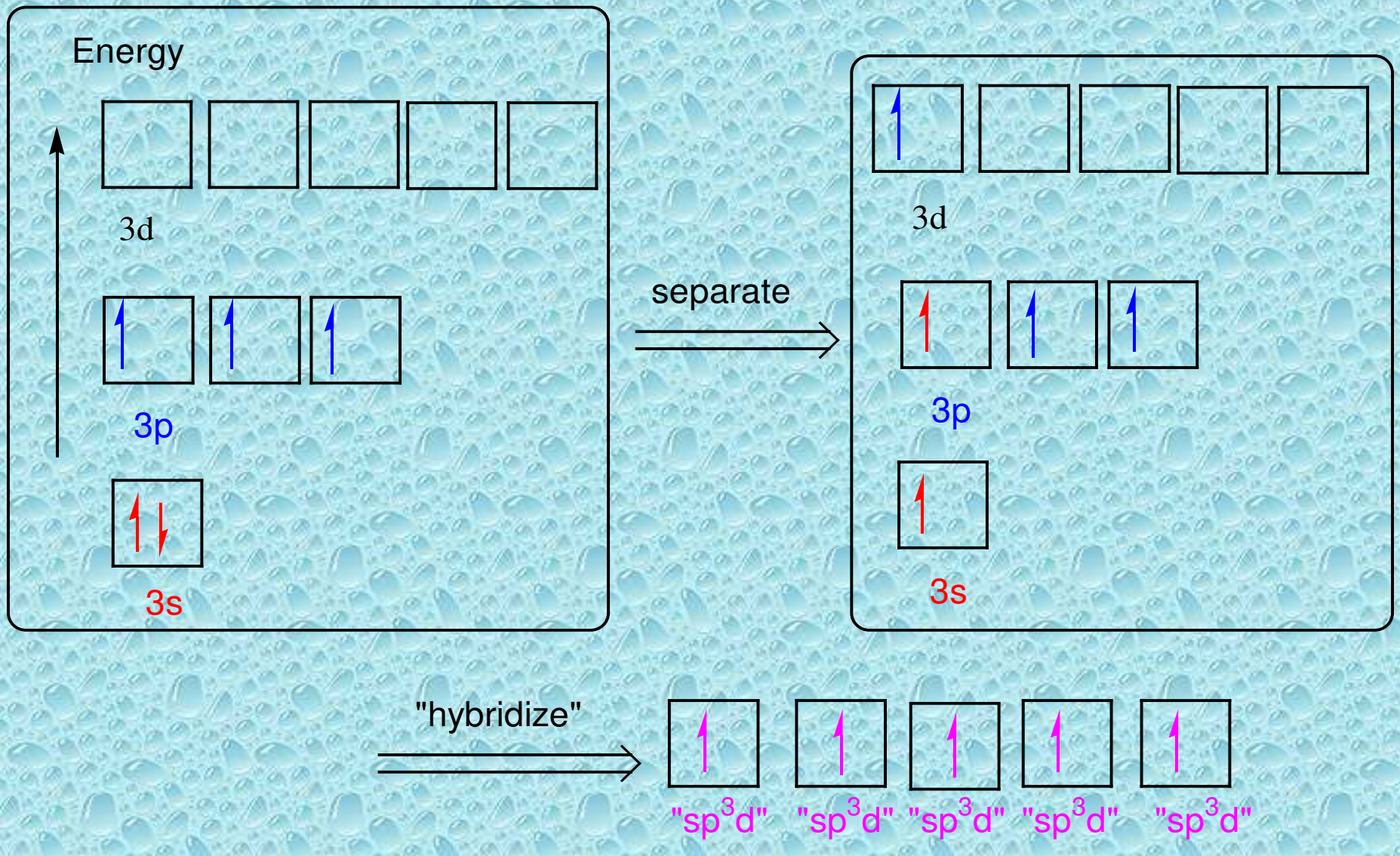
Number of regions around CENTRAL ATOM: 5



shape : TRIGONAL BIPYRAMIDAL
bond angles: 90, 120, 180°

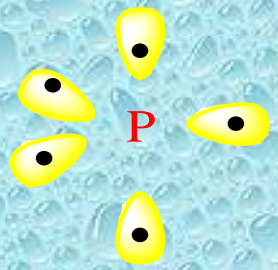
Hybridization of P in PF_5

P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$



"arrange"

(VSEPR)

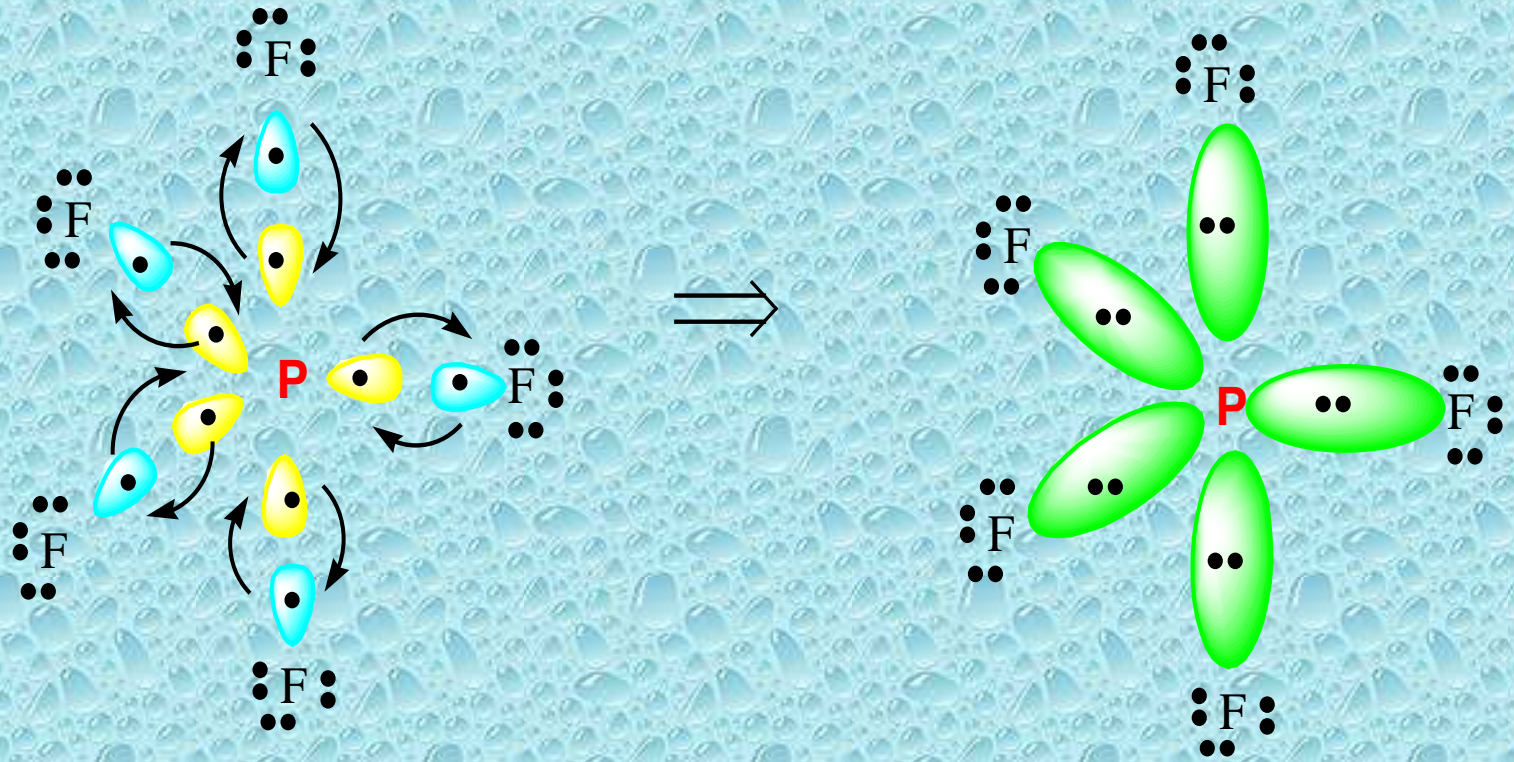


P is said to be "sp^3d hybridized"

FORMATION OF PF_5:

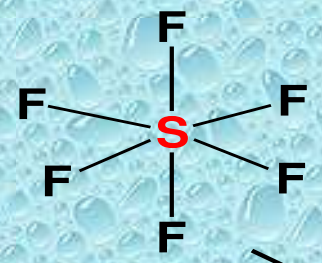
Each fluorine atom, $1s^2 2s^2 2p^5$, has one unshared electron in a p orbital. The half filled p orbital overlaps head-on with a half full hybrid sp^3d orbital of the phosphorus to form a sigma bond.

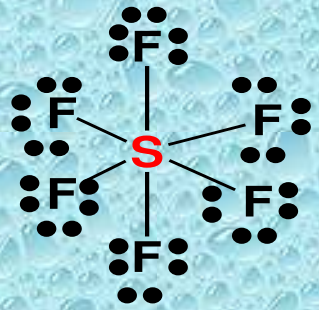
sp^3d hybridized, TRIGONAL BIPYRAMIDAL, 90, 120, 180^o bond angles



"sp^3d^2" Hybridization: All 6 Region Species

SF_6





S	6
6F	42
	48

48 e's /2 = 24 pr

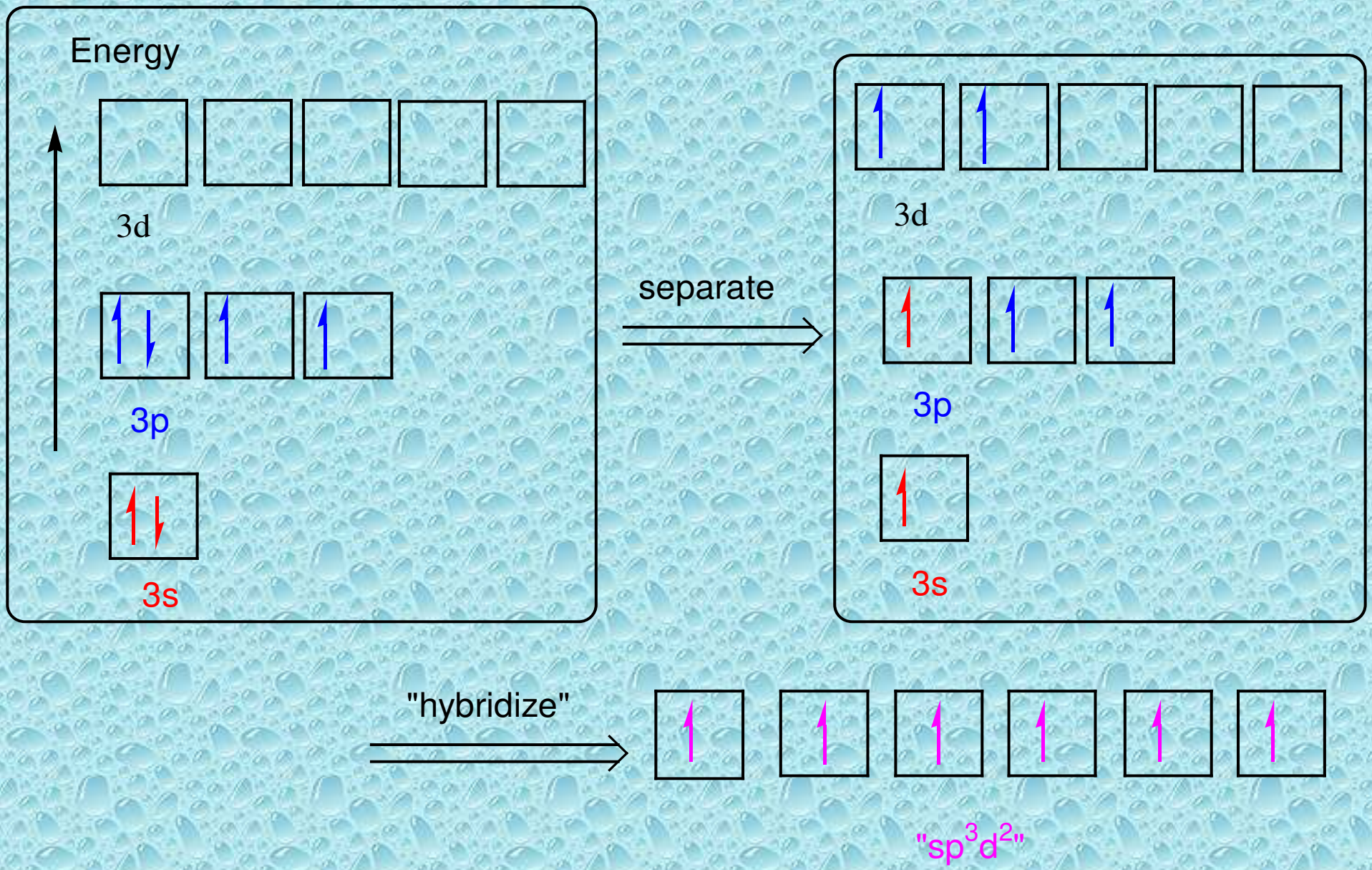
Number of regions around CENTRAL ATOM: 6

shape : OCTAHEDRAL

bond angles: 90, 180°

Hybridization of S in SF_6

S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$



"arrange"

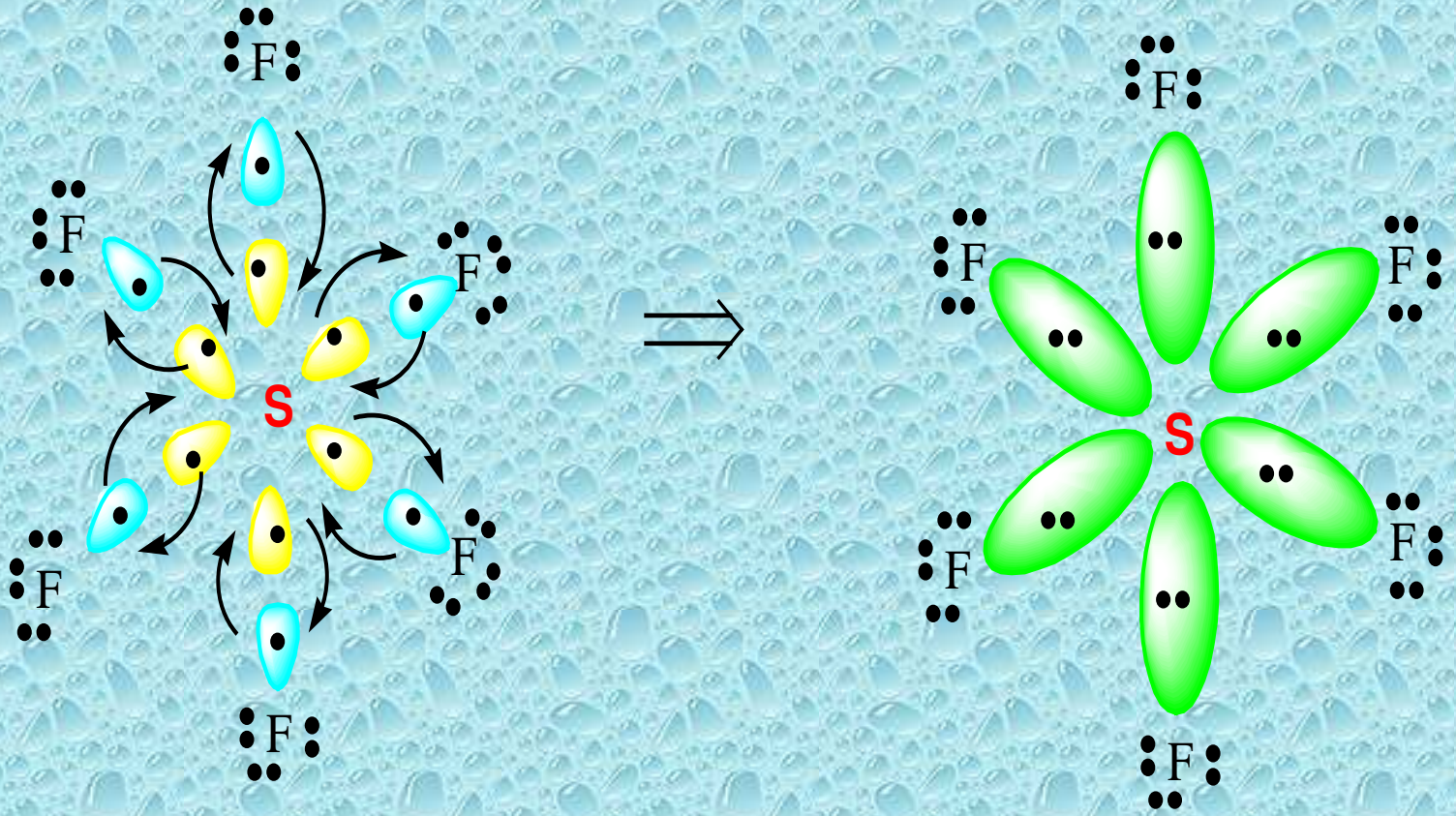
(VSEPR)

S is said to be "sp^3d^2 hybridized"

FORMATION OF SF_6:

Each fluorine atom, $1s^2 2s^2 2p^5$, has one unshared electron in a p orbital. The half filled p orbital overlaps head-on with a half full hybrid sp^3d^2 orbital of the phosphorus to form a sigma bond.

sp^3d^2 hybridization, OCTAHEDRAL, 90^o and 180^o bond angles



Summary: Regions, Shapes and Hybridization

Number of region	Shape	Hybridization
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^3d
6	Octahedral	sp^3d^2

IF you can draw a Lewis structure for a species,
and count electronic regions around central atom,
you can immediately determine:

- the shape of the species about the central atom
- the hybridization of the species based on the central atom

σ Bond	π bond
Formed by axial overlap of atomic orbitals	Formed by sidewise/lateral overlap of atomic orbitals
Can be formed by axial overlap of s-s, s-p, p-p, and d-d orbitals	Can be formed by sidewise overlap p-p, p-d and d-d orbitals
This is stronger as the extent of overlap is larger	This is weaker as the extent of overlap is smaller
The molecular orbital is symmetrical about the inter-nuclear axis and consists of a single charge cloud.	The molecular orbital is discontinuous and consists of two charge clouds above and below the plane of molecule
There can be free rotation about the bond	Free rotation is not allowed
Bond may be present between two molecules as the only bond	The bond is always associated with one σ bond
The shape of molecule is determined by the σ framework	π Bonds control the dimensions of the molecule

Molecular Orbitals

Molecular orbitals result from the combination of atomic orbitals. Since orbitals are wave functions, they can combine either constructively (forming a bonding molecular orbital), or destructively (forming an antibonding molecular orbital).

An approach to bonding in which orbitals encompass the entire molecule, rather than being localized between atoms.

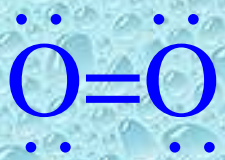
Molecular Orbitals

Molecular orbitals form when atomic orbitals with similar energies and appropriate symmetry can overlap.

Atomic orbitals with differing energies or the wrong spatial orientation (orthogonal) do not combine, and are called *non-bonding* orbitals.

Need for MO Theory

- Valence bond theory fails to explain the bonding in many simple molecules.
- The oxygen molecule has a bond length and strength consistent with a double bond, and it contains two unpaired electrons.
- Valence bond theory predicts the double bond, but not the paramagnetism of oxygen.



Need for MO Theory

- Resonance is another example of the limitations of valence bond theory.
- Bond lengths and strengths are intermediate between single, double or triple bonds.
- Molecular orbital theory is often a better approach to use with molecules that have extended π systems.

Molecular Orbital Theory

In order to simplify things, we'll consider the interaction of the orbitals containing valence electrons to create molecular orbitals.

The wave functions of hydrogen atom A and hydrogen atom B can interact either constructively or destructively.

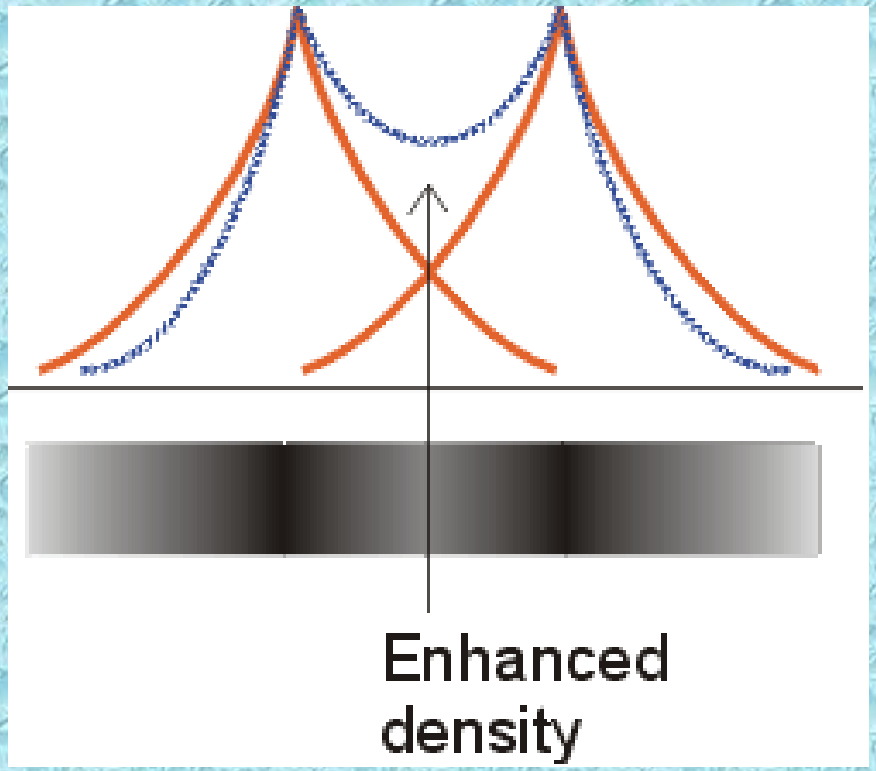
Constructively:

$$\Psi_{(\sigma)} \text{ or } \Psi_{+} = (1/\sqrt{2}\,)\,[\varphi_{(1sa)} + \varphi_{(1sb)}]$$

Destructively:

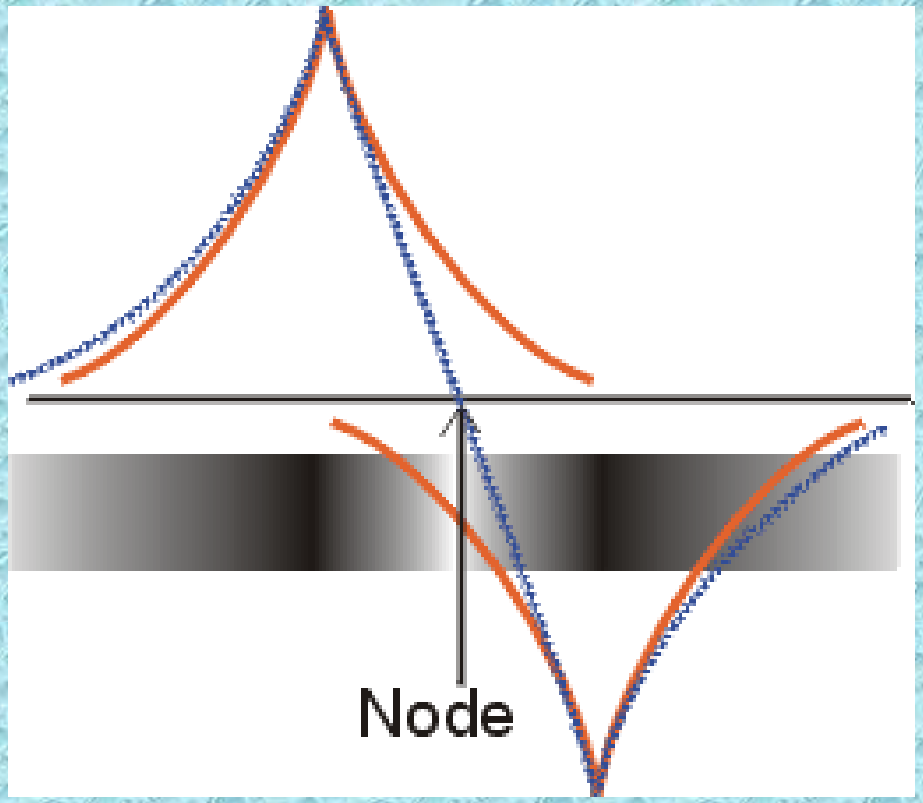
$$\Psi_{(\sigma^*)} \text{ or } \Psi_{-} = (1/\sqrt{2}\,)\,[\varphi_{(1sa)} - \varphi_{(1sb)}]$$

Molecular Orbital Theory



- The bonding orbital results in increased electron density between the two nuclei, and is of lower energy than the two separate atomic orbitals.

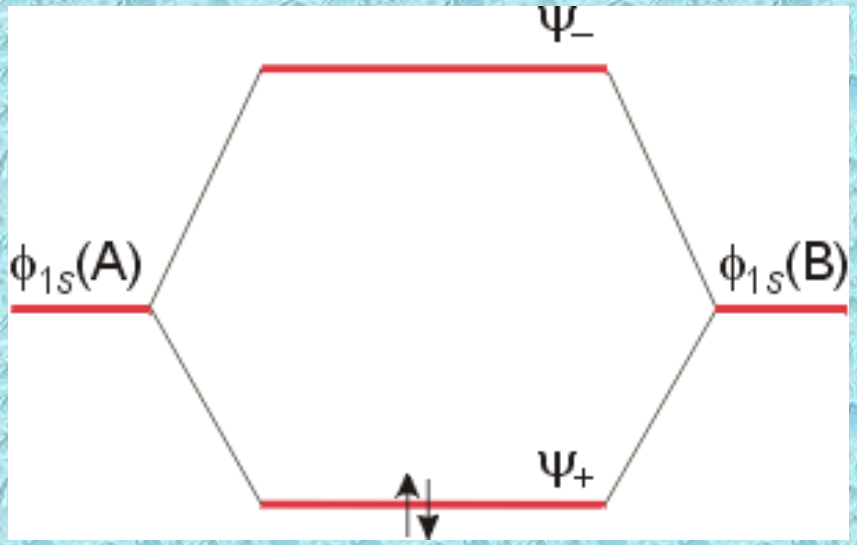
Molecular Orbital Theory



- The antibonding orbital results in a node between the two nuclei, and is of greater energy than the two separate atomic orbitals.

Molecular Orbital Theory

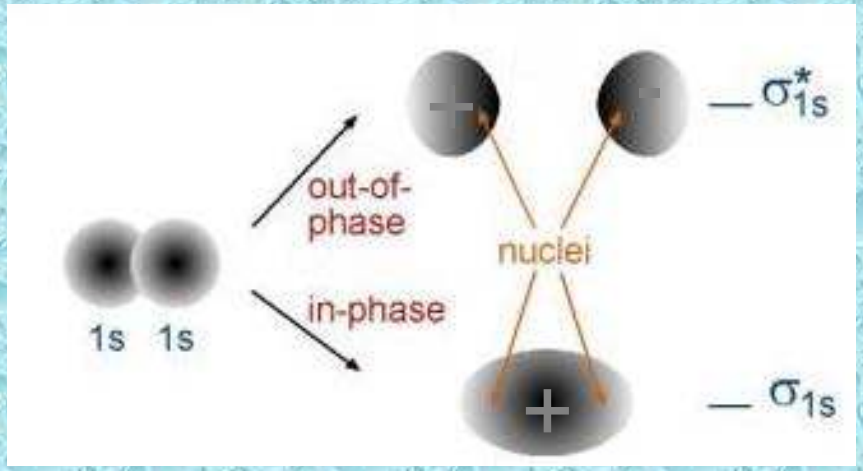
Anti bonding



Bonding

The result is an energy level diagram with the bonding orbital occupied by a pair of electrons. The filling of the lower molecular orbital indicates that the molecule is stable compared to the two individual atoms.

Molecular Orbital Theory



The bonding orbital is sometimes given the notation σ_g, where the ***g*** stands for ***gerade***, or symmetric with respect to a center of inversion.

The anti-bonding orbital is sometimes given the notation σ_u, where the ***u*** stands for ***ungerade***, or asymmetric with respect to a center of inversion.

The signs on the molecular orbitals indicate the sign of the wave function, not ionic charge.

Rules for Combining Atomic Orbitals

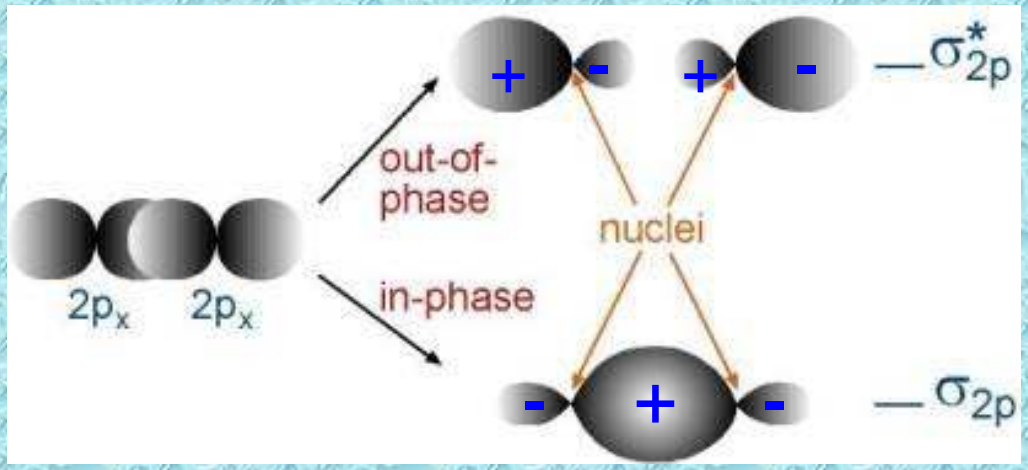
- The number of molecular orbitals formed = the number of atomic orbitals combined.
- The strength of the bond depends upon the degree of orbital overlap.
- Extent of overlap depends on symmetry and shape of orbitals
- Orbitals of similar (not necessarily identical) energy will overlap effectively.

Period 2 Diatomic Molecules

For the second period, assume that, due to a better energy match, *s* orbitals combine with *s* orbitals, and *p* orbitals combine with *p* orbitals.

The symmetry of *p* orbitals permits end-on-end overlap along the bond axis, or side-by-side overlap around, but not along, the internuclear axis.

MOs using *p* orbitals

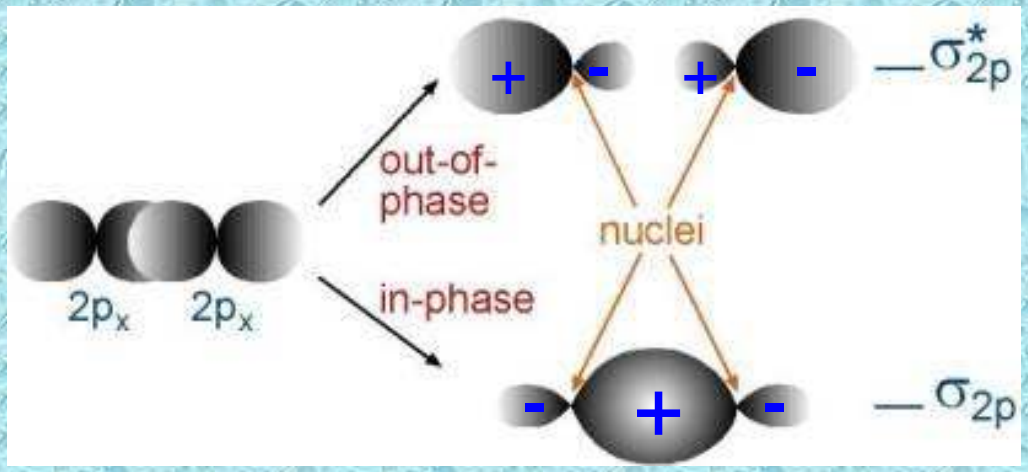


With the *x* axis as the bond axis, the p_x orbitals may combine constructively or destructively. The result is a σ bonding orbital and a σ anti-bonding orbital.

The designation σ indicates symmetric electron density around the internuclear (*x*) axis.

Some texts will use the symmetry designations of *g* (gerade) or *u* (ungerade) instead of indicating bonding or anti-bonding.

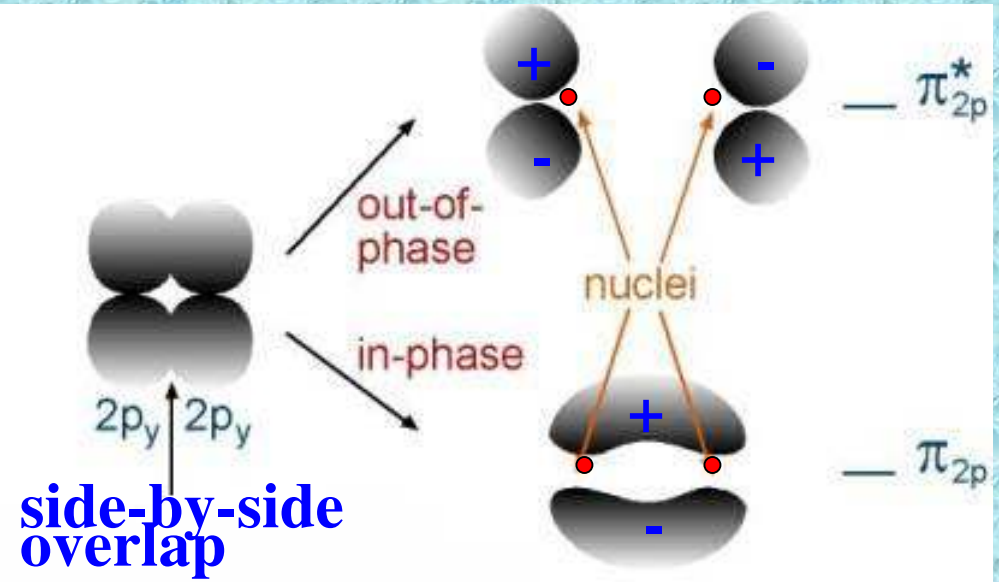
MOs using *p* orbitals



For these orbitals, the bonding orbital is *gerade*, or symmetric around the bond axis.

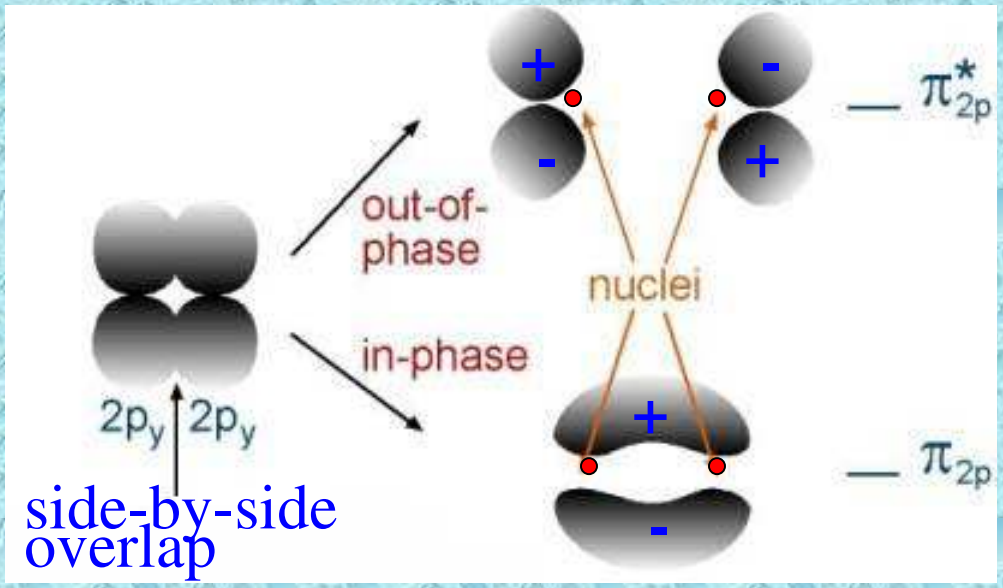
For these orbitals, the anti-bonding orbital is asymmetric about the bond axis, and is designated as σ_u. Note that the designations of *u* or *g* do not correlate with bonding or anti-bonding.

π Molecular Orbitals



- The orbital overlap side-by-side is less than that of overlap along the bond axis (end-on-end). As a result, the bonding orbital will be higher in energy than the previous example.
- π orbitals are asymmetric with respect to the bond axis. There is electron density surrounding the bond axis, with a node along the internuclear axis.

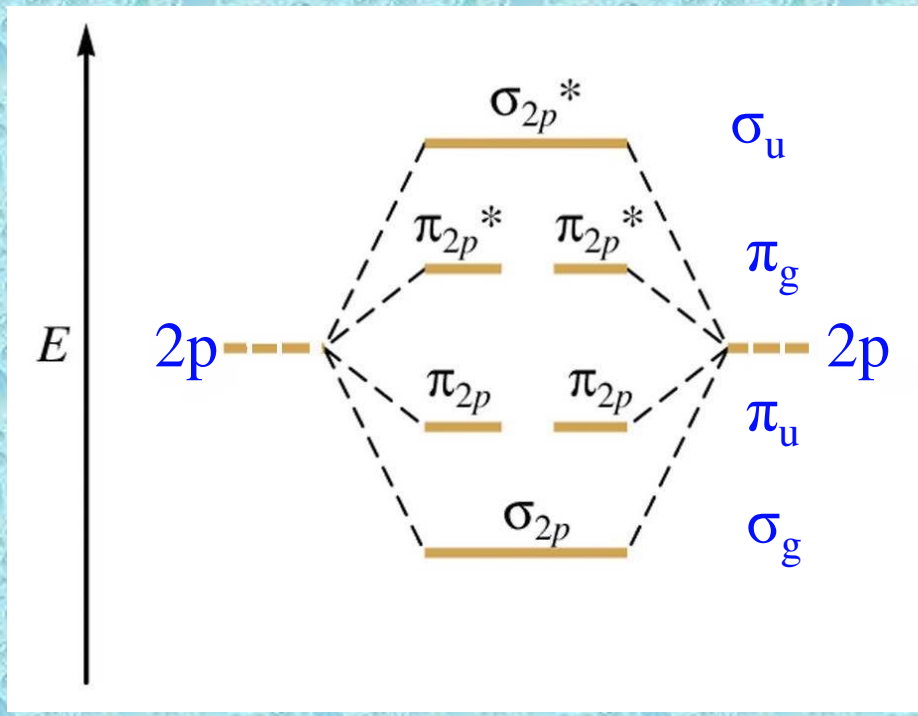
π Molecular Orbitals



- Some texts use the subscripts *g* and *u* instead of bonding and anti-bonding. In this example, the bonding orbital is ungerade, or asymmetric about a center of symmetry.
- The anti-bonding orbital is *gerade*, or symmetric about a center of symmetry.

Molecular Orbital Diagram

This is a molecular orbital energy level diagram for the *p* orbitals. Note that the σ bonding orbital is lowest in energy due to the greater overlap end-on-end.

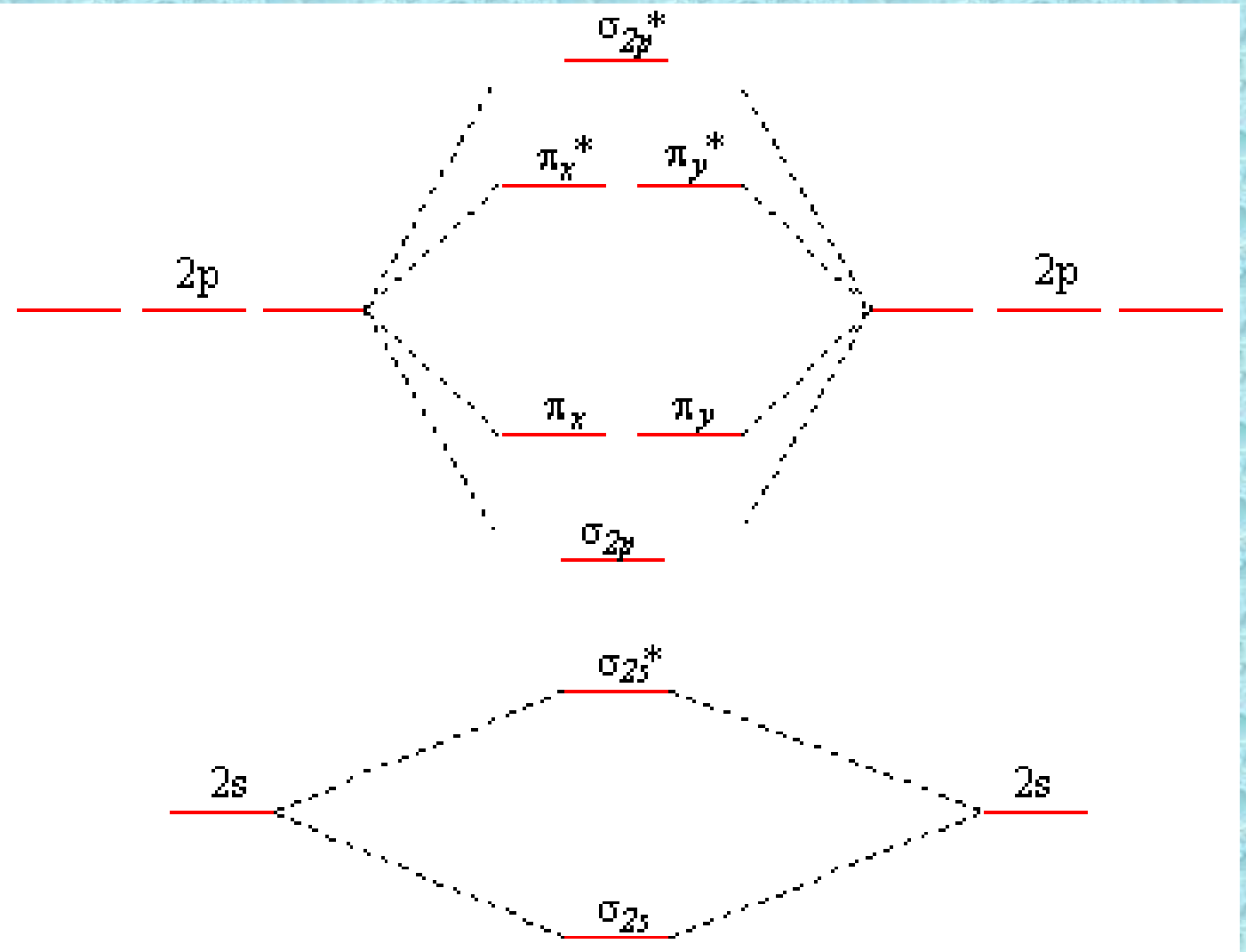


The alternate notation is provided on the right side of the energy level diagram.

Molecular Orbital Diagrams

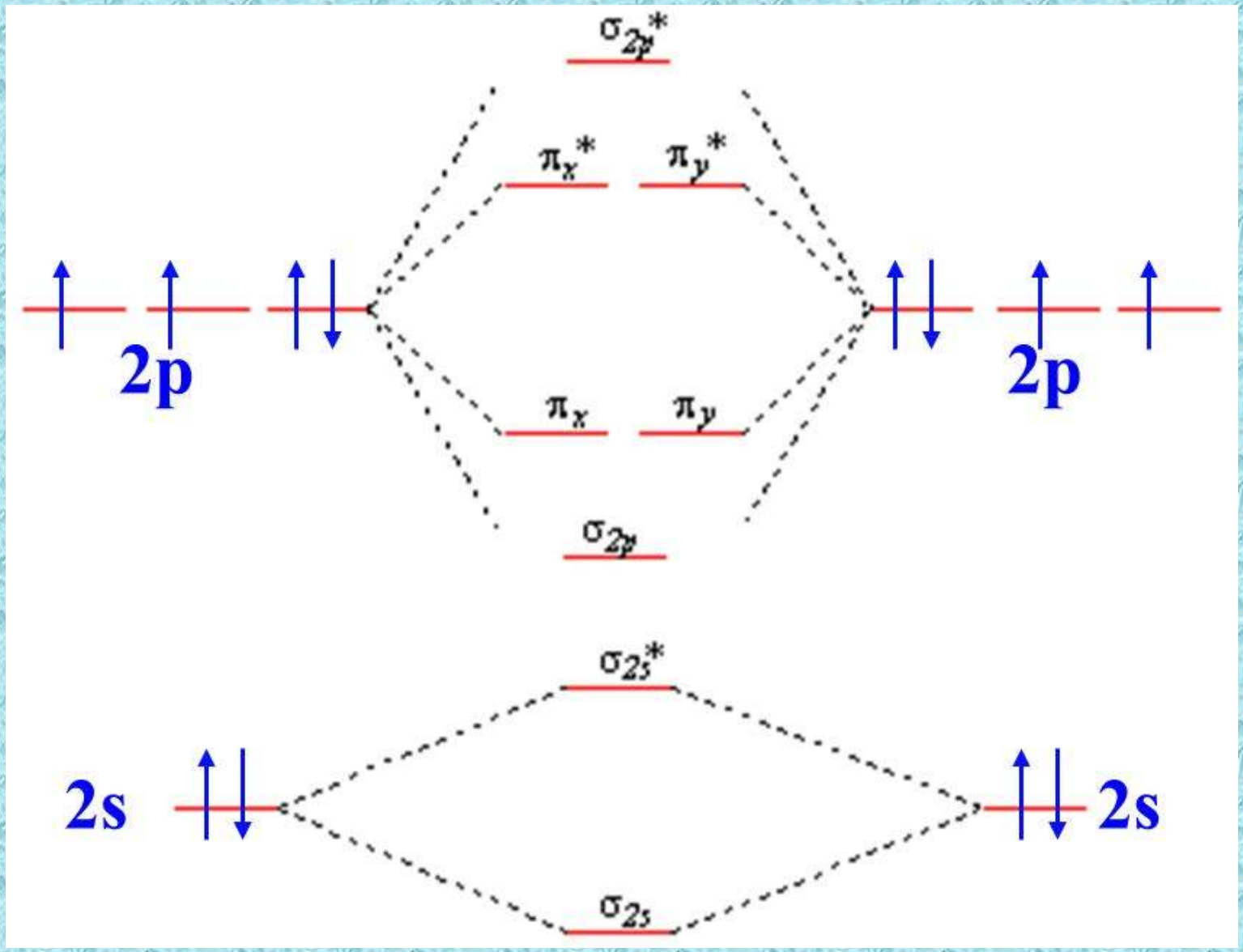
1. Electrons preferentially occupy molecular orbitals that are lower in energy.
2. Molecular orbitals may be empty, or contain one or two electrons.
3. If two electrons occupy the same molecular orbital, they must be spin paired.
4. When occupying degenerate molecular orbitals, electrons occupy separate orbitals with parallel spins before pairing.

Molecular Orbital Diagrams



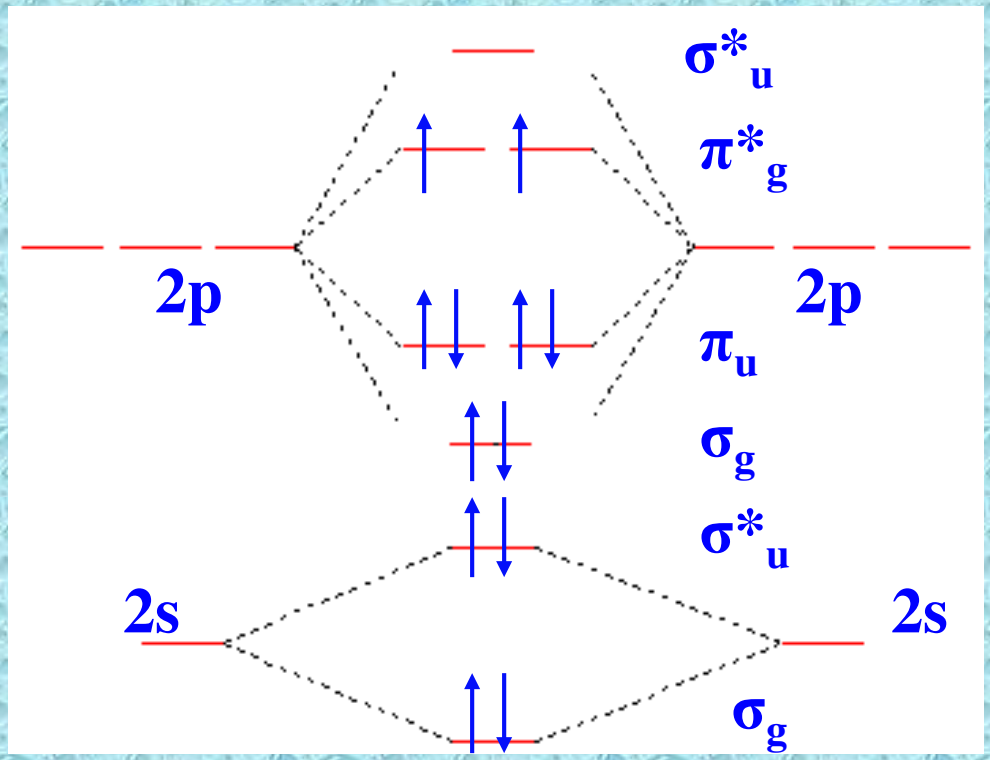
For O_2, there will be a total of 12 valence electrons that must be placed in the diagram.

Molecular Orbital Diagrams



For O_2, there will be a total of 12 valence electrons that must be placed in the diagram.

MO Diagram for O_2



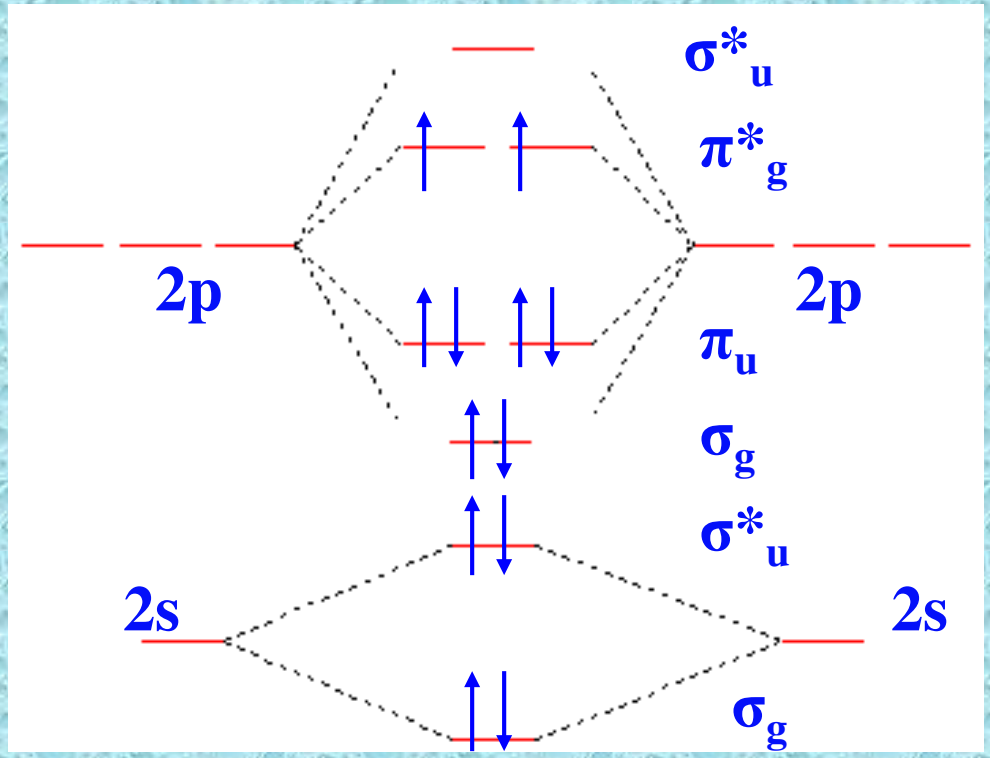
The molecular orbital diagram for oxygen shows two unpaired electrons, consistent with experimental data.

Bond Order: Bond order is an indicator of the bond strength and length. A bond order of 1 is equivalent to a single bond. Fractional bond orders are possible.

The bond order of the molecule =

$$\frac{(\#\ e^-\ \text{in bonding orbitls})}{2} - \frac{(\#\ e^-\ \text{in anti-bonding orbitls})}{2}$$

MO Diagram for O_2

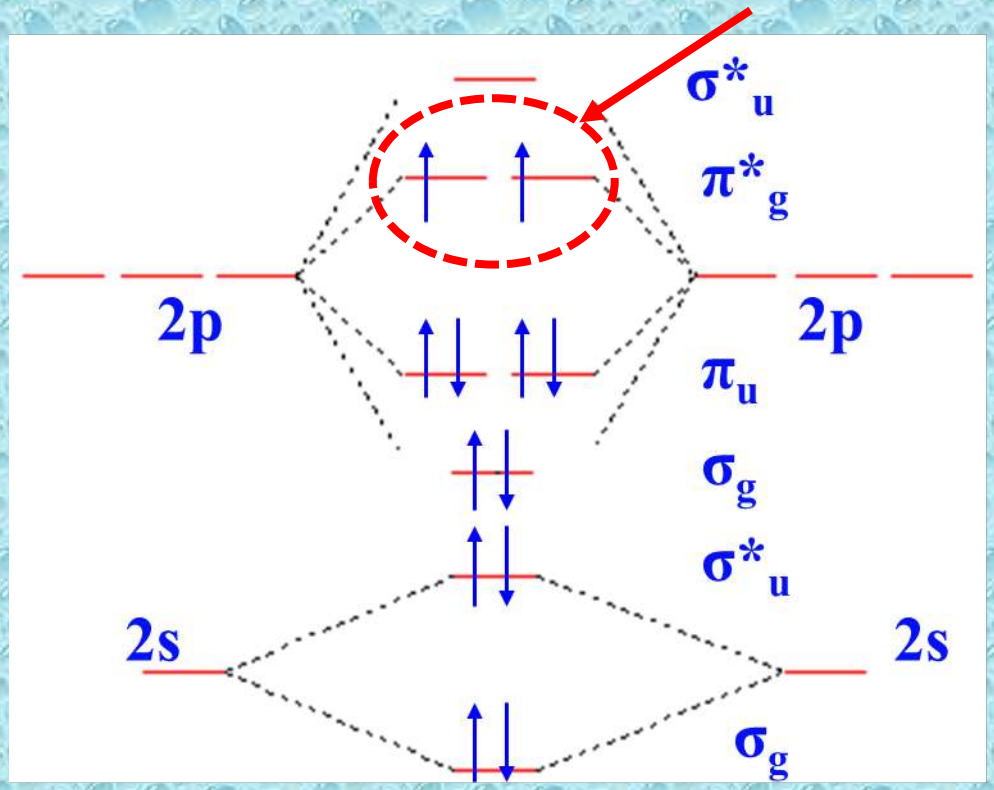


The bond order of O_2 is: $\frac{8-4}{2} = 2$

This is consistent with a double bond.

MO Diagram for O_2

Responsible for paramagnetic behavior of O_2

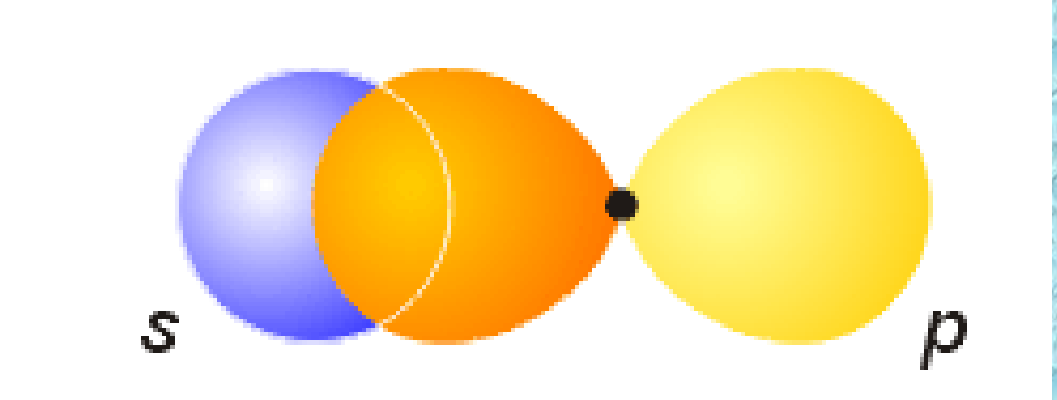


This energy level diagram works well for atoms in which the 2s and 2p levels are fairly far apart. These are the elements at the right of the table: O, F and Ne.

MO diagram for Li through N

Approach 1: The elements on the left side of period 2 have a fairly small energy gap between the 2s and 2p orbitals. As a result, interaction between s and p orbitals is possible. This can be viewed in different ways.

In some approaches, the s orbital on one atom interacts with the p orbital on another. The interaction can be constructive or destructive.

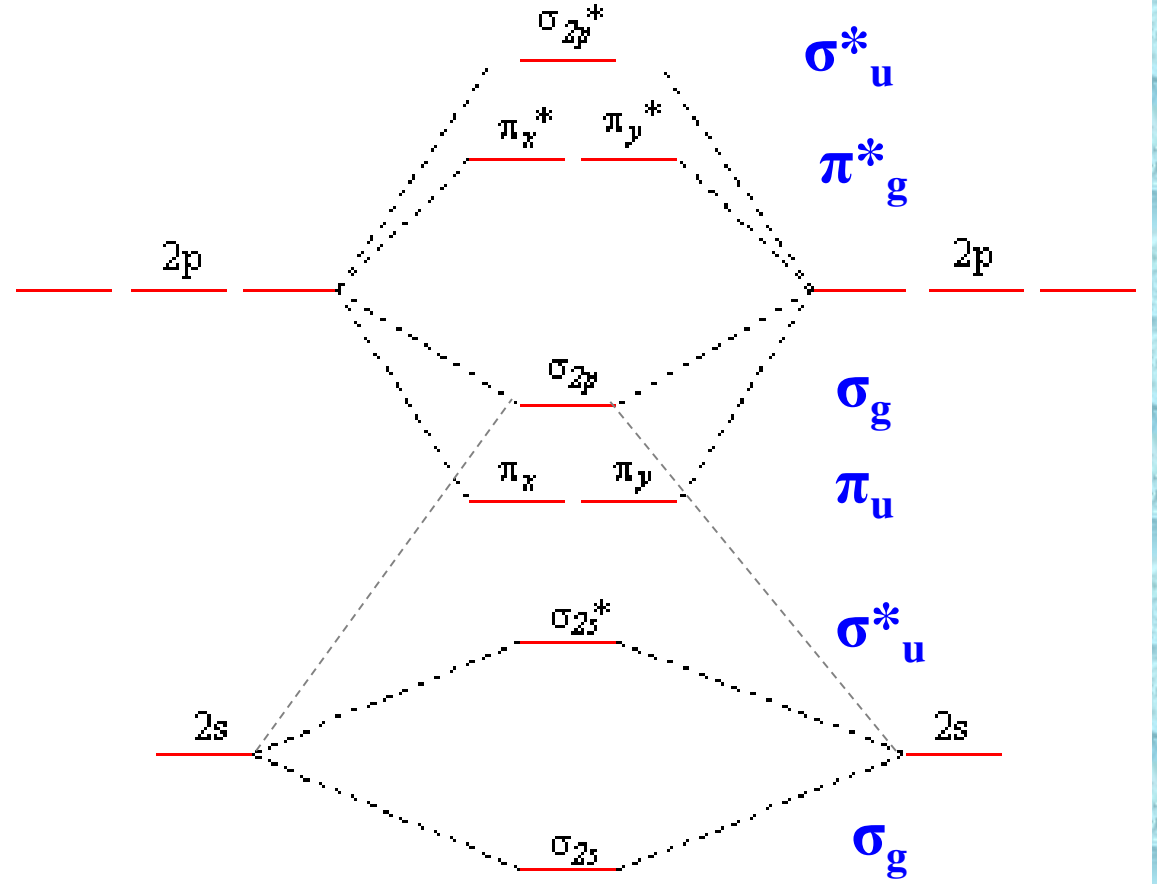


MO diagram for Li through N

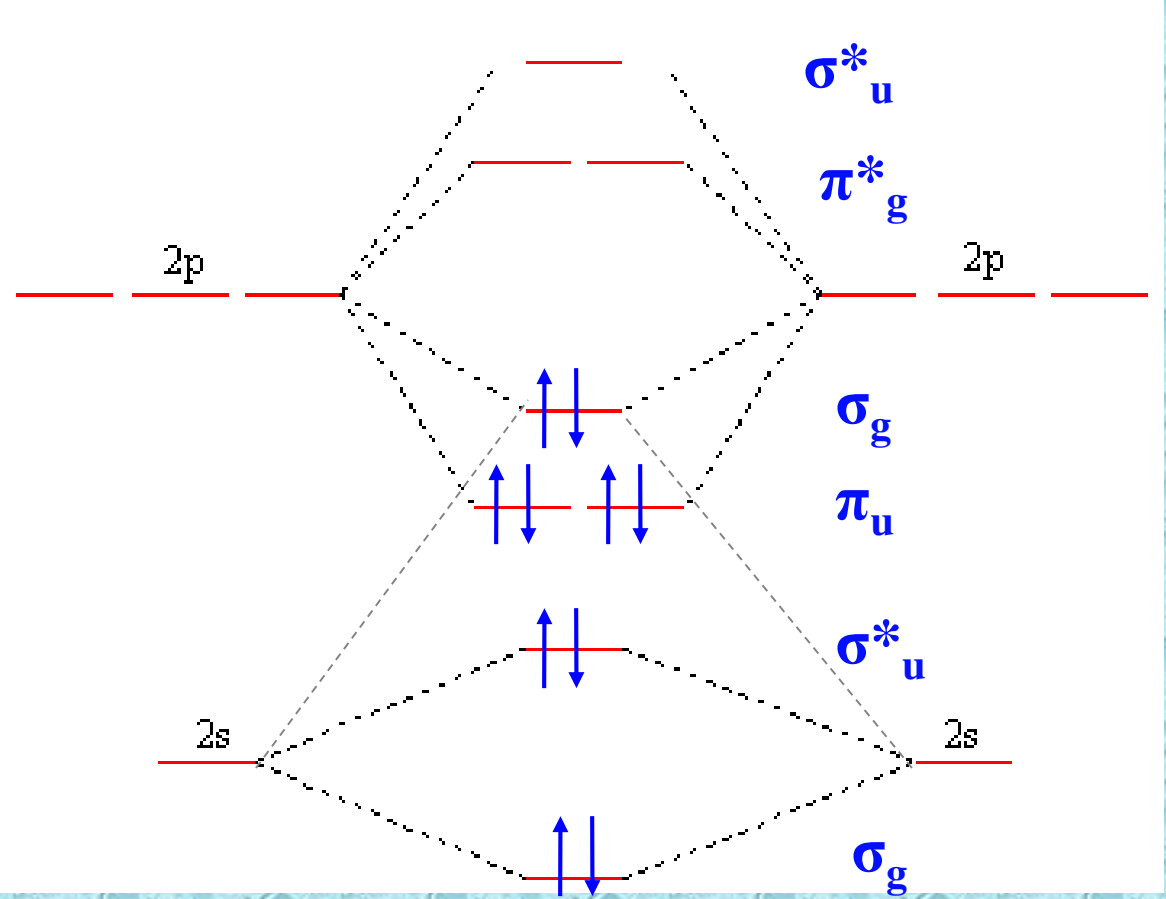
Approach 2: In another approach, the s and p orbitals on the same atom interact in what is called *orbital mixing*.

Either approach yields the same result. The σ bonding and anti-bonding orbitals are raised in energy due to the interaction with a *p* orbital.

MO diagram for Li through N



MO diagram for N_2



N_2 has 10 valence electrons.

Heteronuclear Diatomic Molecules

- The more electronegative atom will have orbitals of lower energy, and therefore contribute more to the **bonding orbitals**.
- The less electronegative atom has orbitals of higher energy, and contributes more to the **anti-bonding orbitals**.

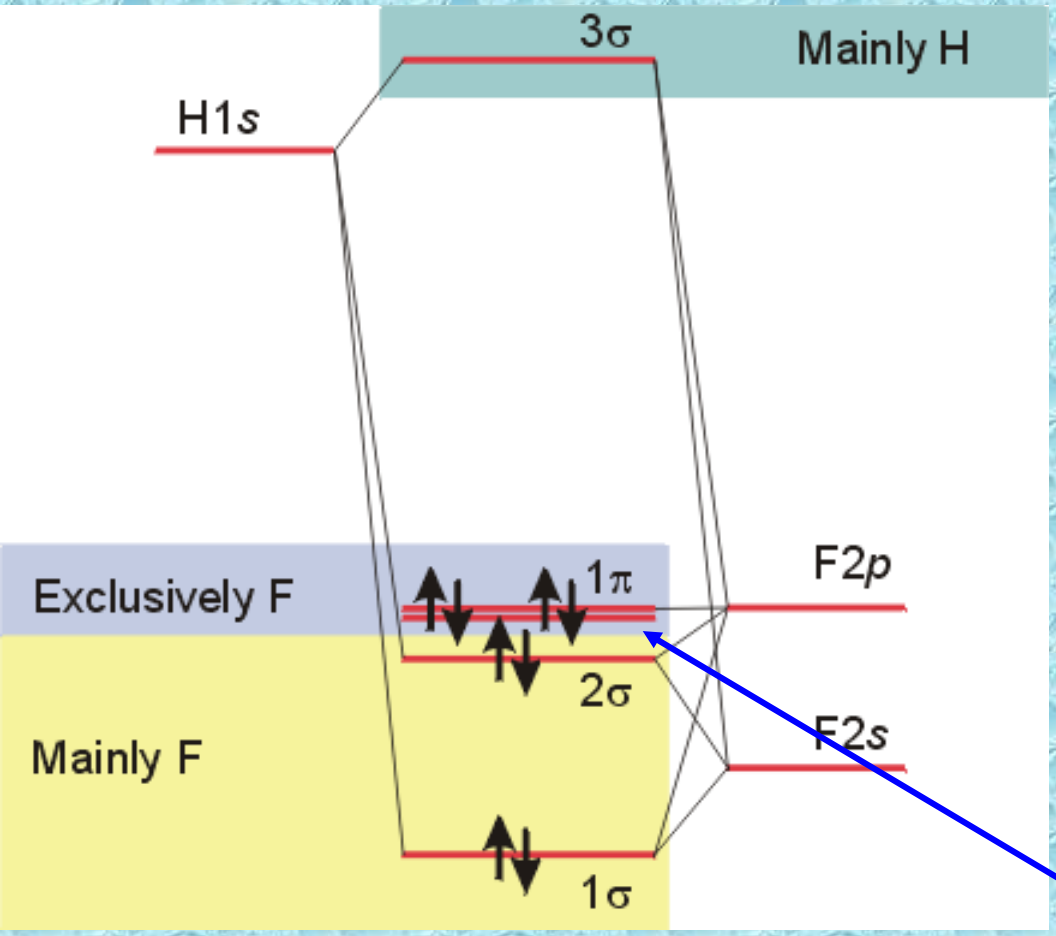
Rules for Combining Atomic Orbitals

For heteronuclear molecules:

1. **The bonding orbital(s) will reside predominantly on the atom of lower orbital energy (the more electronegative atom).**

2. **The anti-bonding orbital(s) will reside predominantly on the atom with greater orbital energy (the less electronegative atom).**

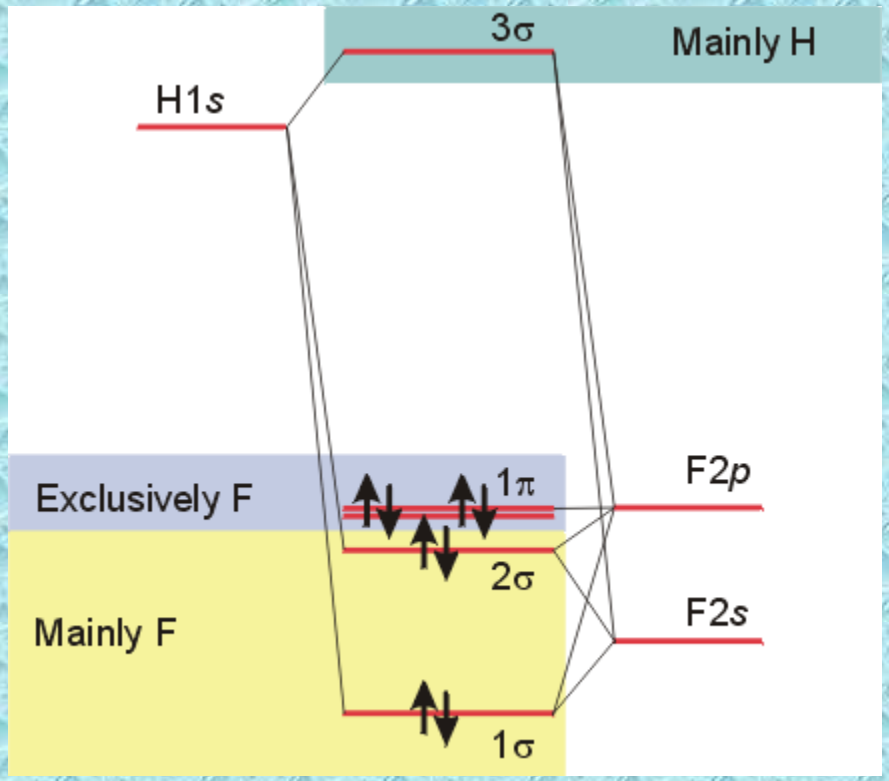
HF



The 2s and $2p_x$ orbitals on fluorine interact with the 1s orbital on hydrogen.

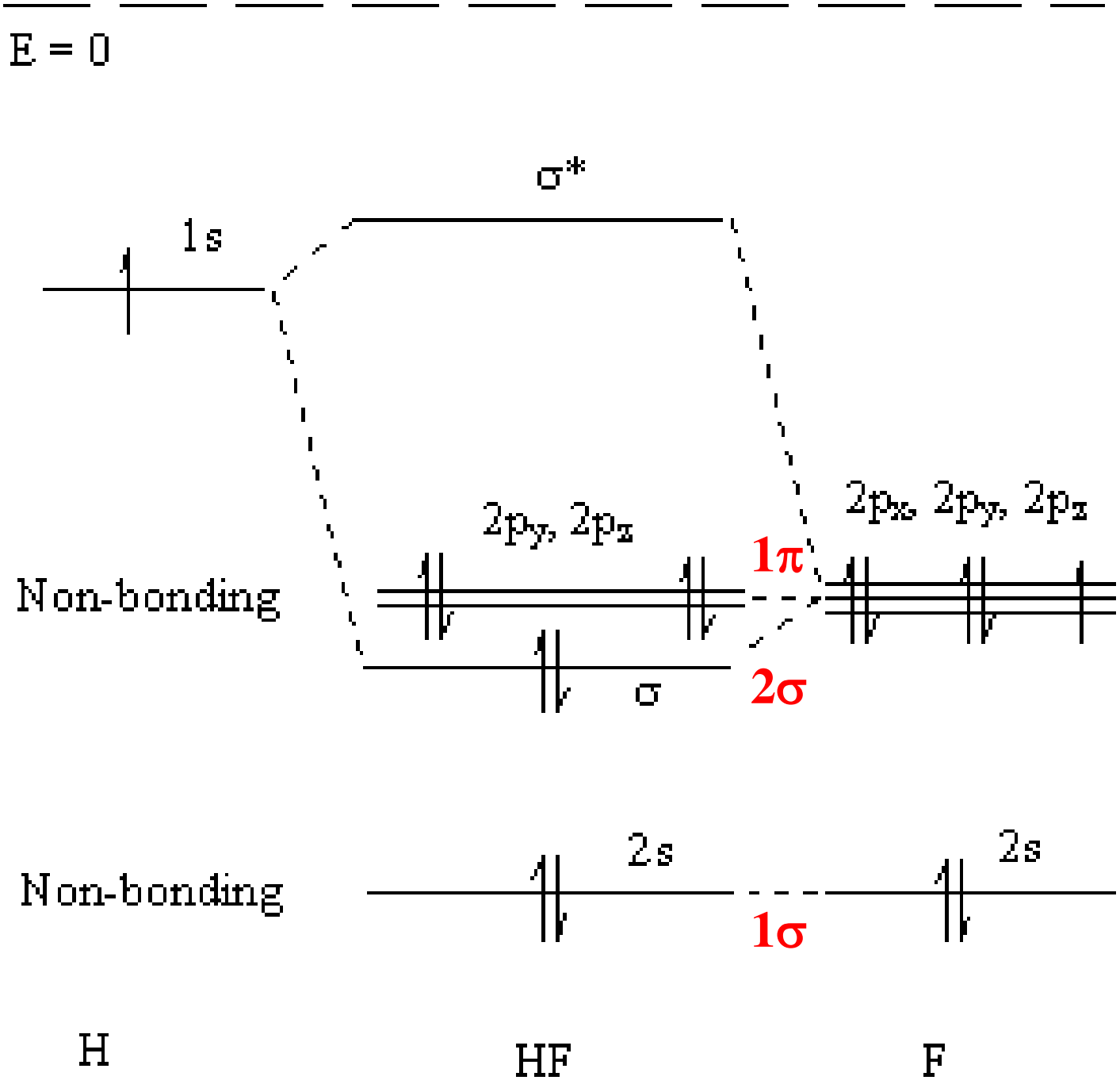
The p_y and p_z orbitals on fluorine lack proper symmetry to interact with hydrogen, and remain as non-bonding orbitals.

HF

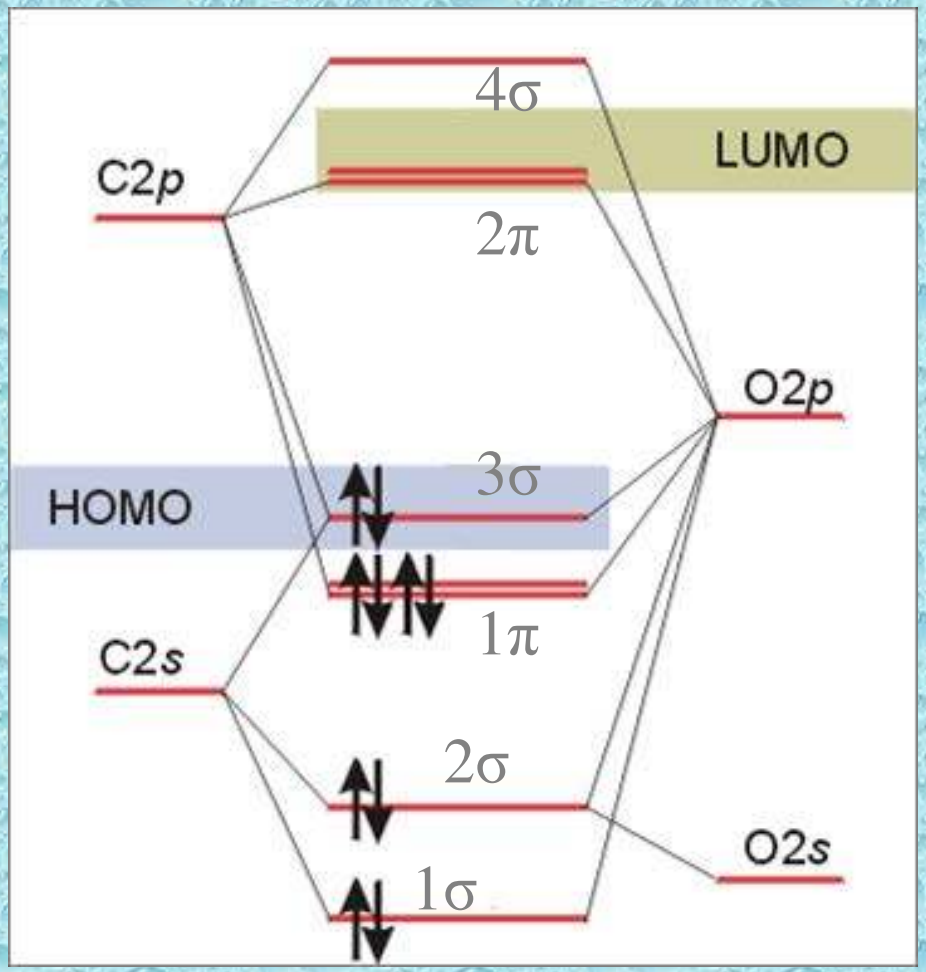


The anti-bonding orbital resides primarily on the less electronegative atom (H).

Note that the subscripts *g* and *u* are not used, as the molecule no longer has a center of symmetry.

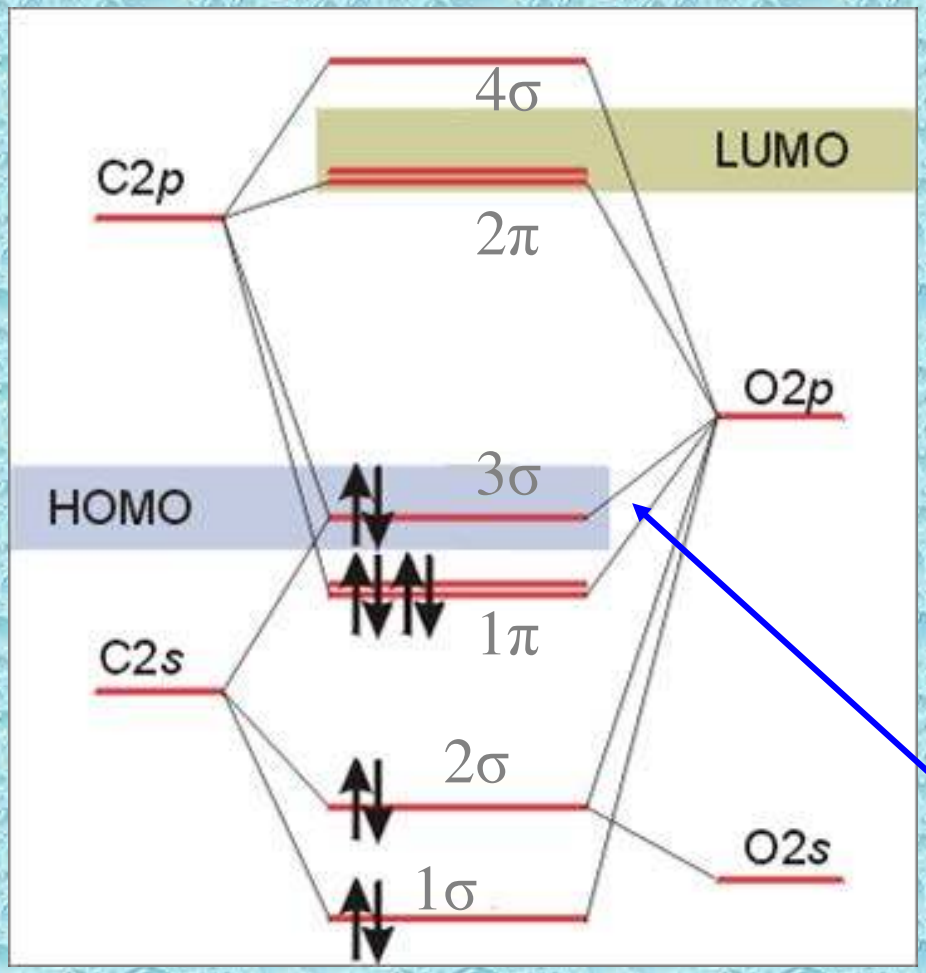

E = 0
σ*
1s
2p_y, 2p_z
2p_x, 2p_y, 2p_z
1π
Non-bonding
σ
2σ
2s
2s
Non-bonding
1σ
H
HF
F

Carbon monoxide



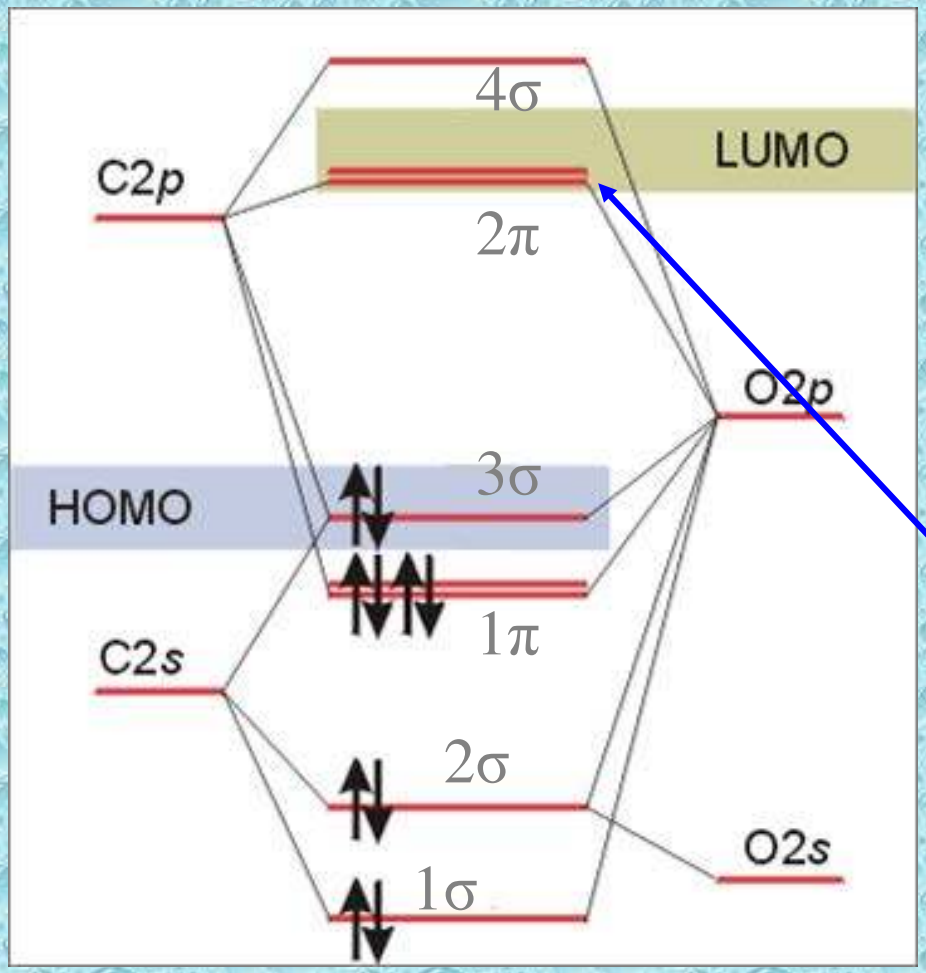
In carbon monoxide, HOMO reside more on the carbon atom, and the anti-bonding orbitals also reside more on the carbon atom. HOMO and LUMO both have more C character.

Carbon monoxide



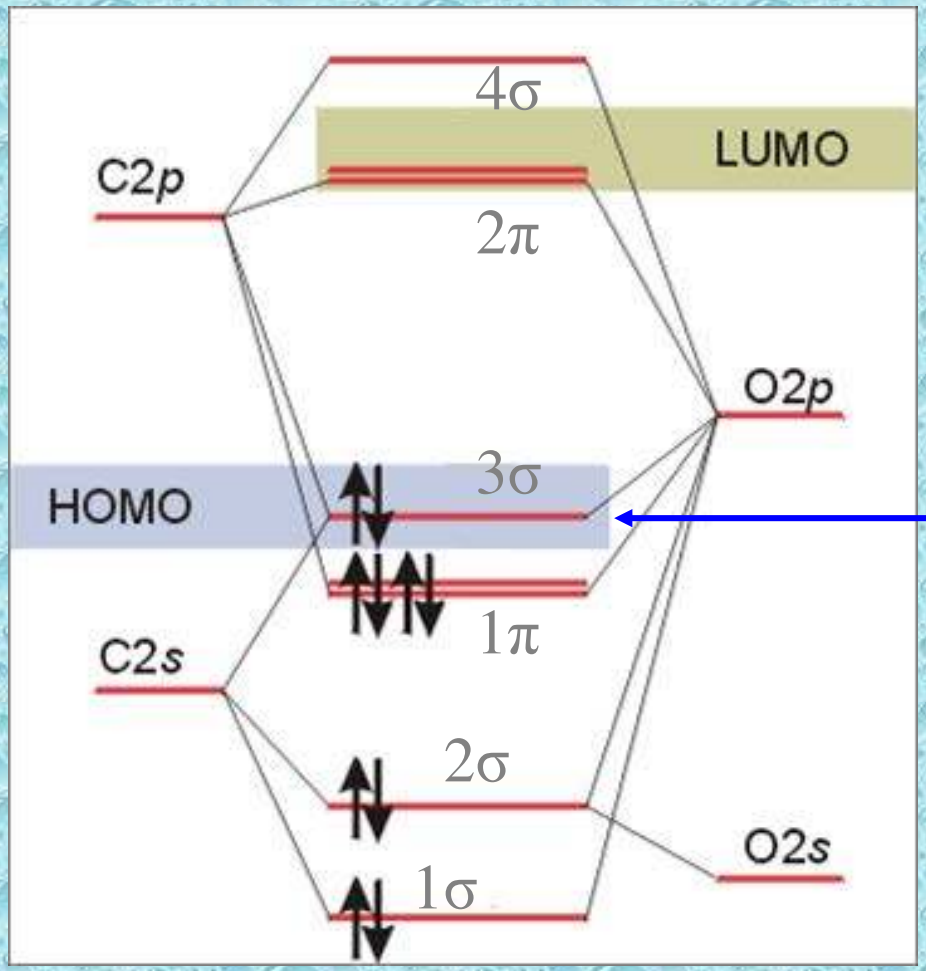
CO is a highly reactive molecule with transition metals. Reactivity typically arises from the highest occupied molecular orbital (HOMO), when donating electrons.

Carbon monoxide

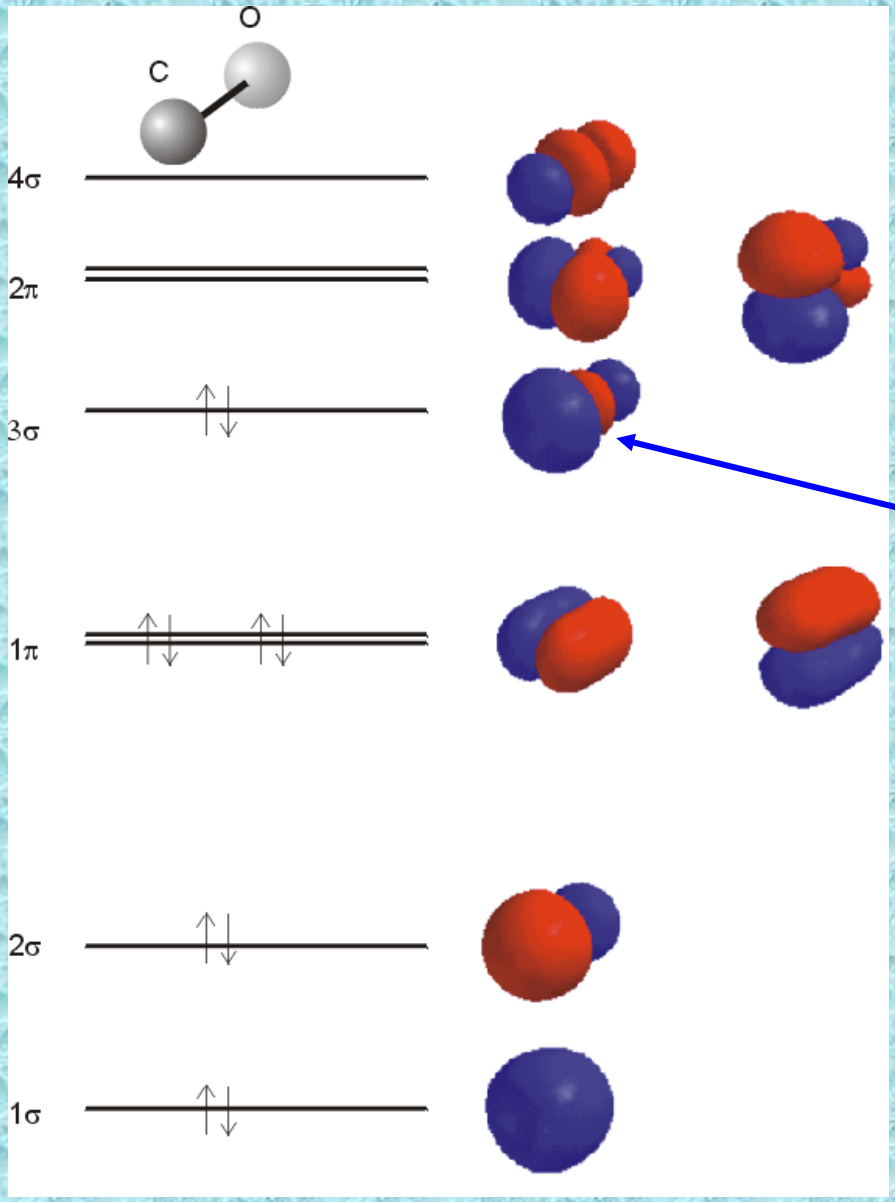


When acting as an electron pair acceptor, the lowest unoccupied molecular orbital (LUMO), is significant.

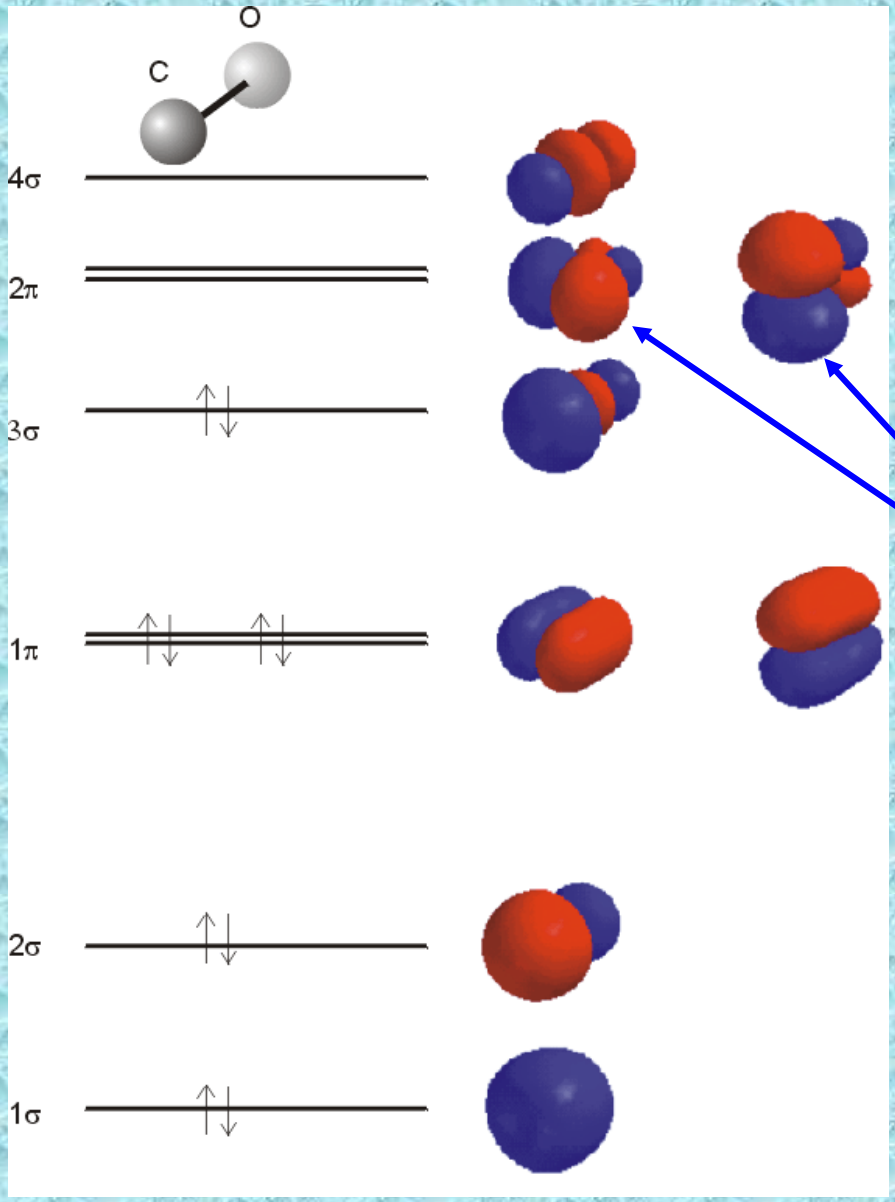
Carbon monoxide



When acting as an electron pair donor, the highest occupied molecular orbital (HOMO), is significant.



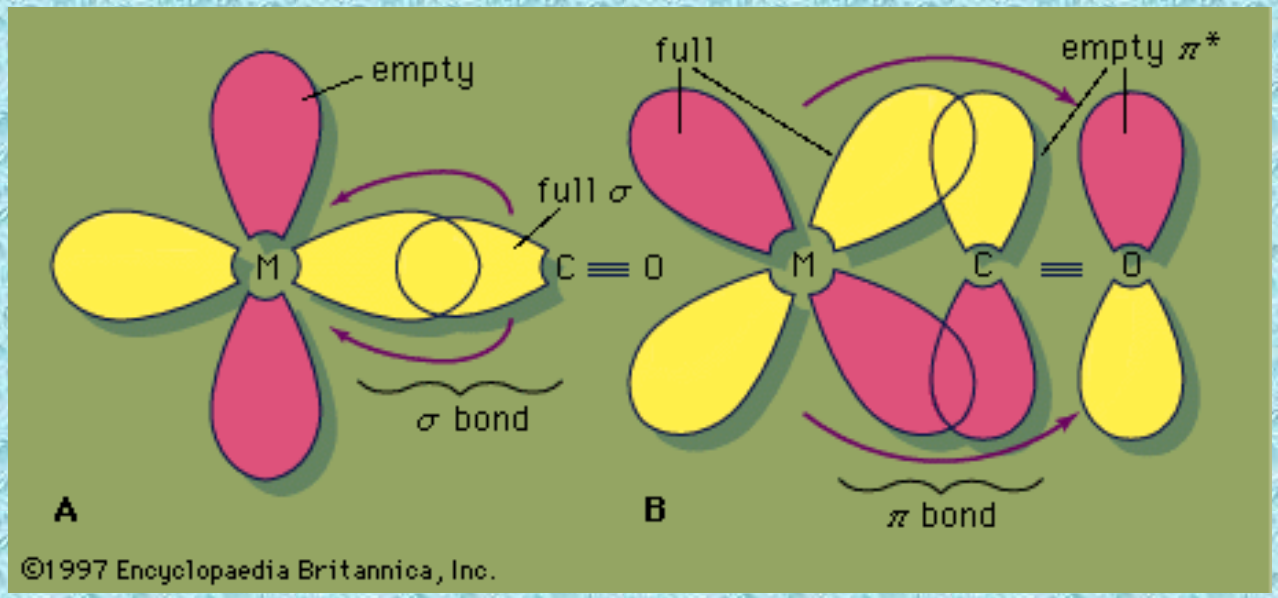
The highest occupied molecular orbital of CO is a molecular orbital which puts significant electron density on the carbon atom.



The lowest unoccupied molecular orbital of CO is the π* orbitals. The lobes of the LUMO are larger on the carbon atom than on the oxygen atom.

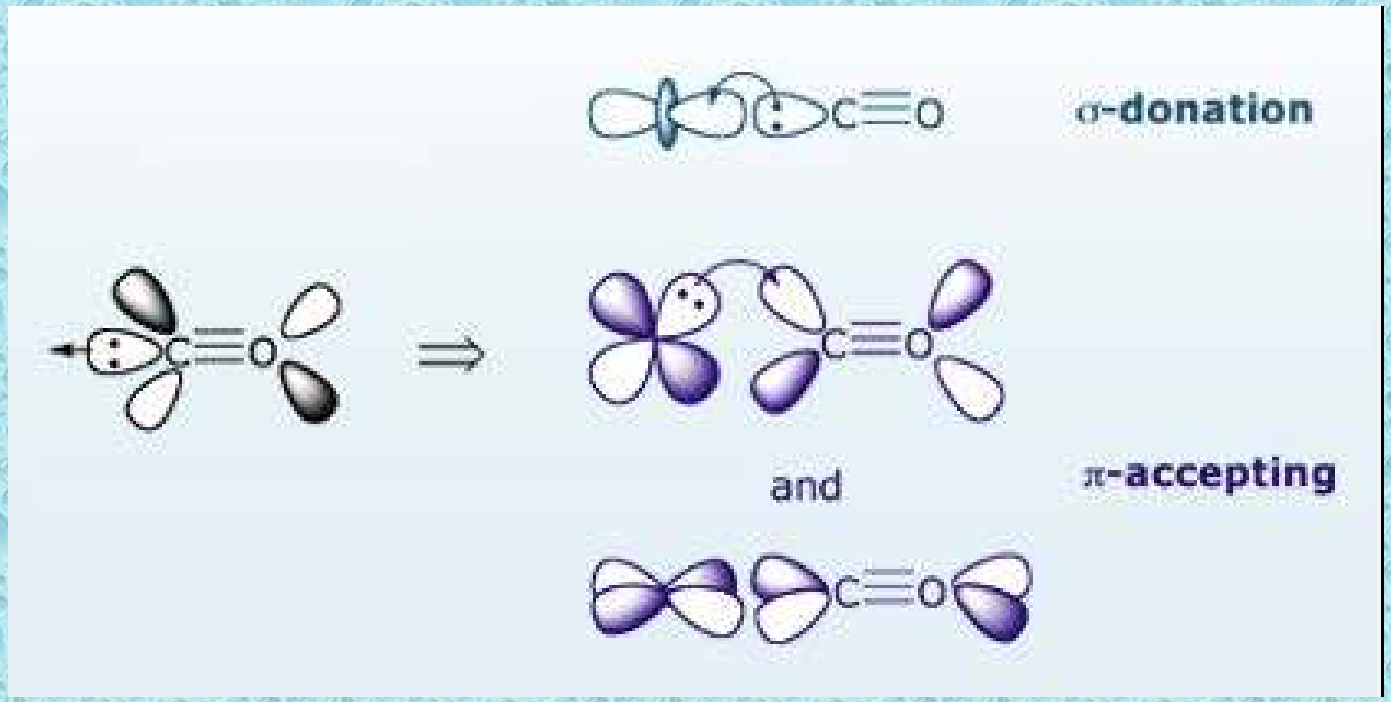
CO as a Ligand

Carbon monoxide is known as a σ donor and a π acceptor ligand. It donates electrons from its HOMO to form a sigma bond with the metal.



Carbon monoxide accepts electrons from filled *d* orbitals on the metal into its antibonding (LUMO) orbital.

CO as a Ligand



This phenomenon is called *back bonding*. The increased electron density in the antibonding orbitals of CO causes an increase in the C-O bond length and a decrease in its stretching frequency.

MOs for Larger Molecules

Group theory is usually used to develop molecular orbital diagrams and drawings of more complicated molecules. When a central atom is bonded to several atoms of the same element (H_2O, BF_3, or $PtCl_4^{2-}$], group theory can be used to analyze the symmetry of the orbitals of the non-central atoms, and then combine them with the appropriate orbitals of the central atom.