Chemical Bonding

Draw the structure of following molecule

16. H_2O_2

17. C_2H_6

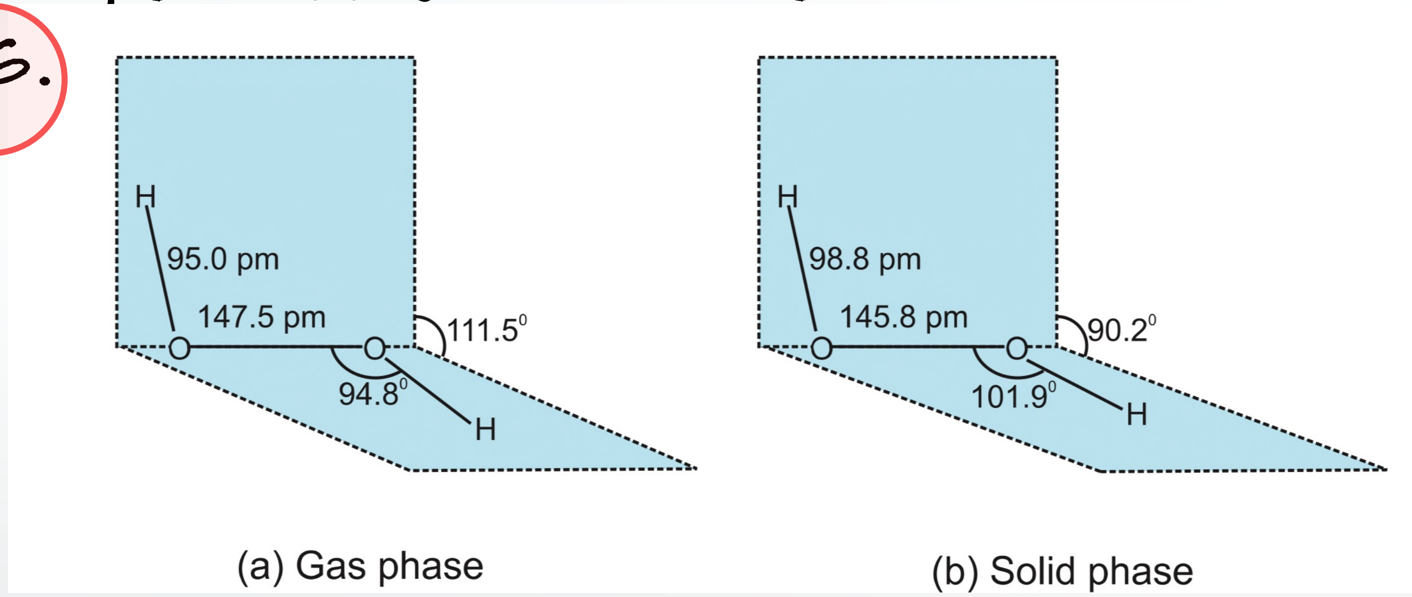
18. C_2H_4

19. C_2H_2

20. CO_3^{2-}

Open book structure

16.



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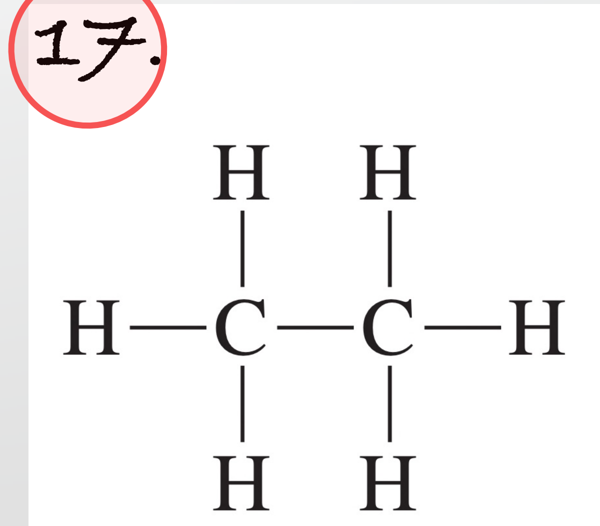

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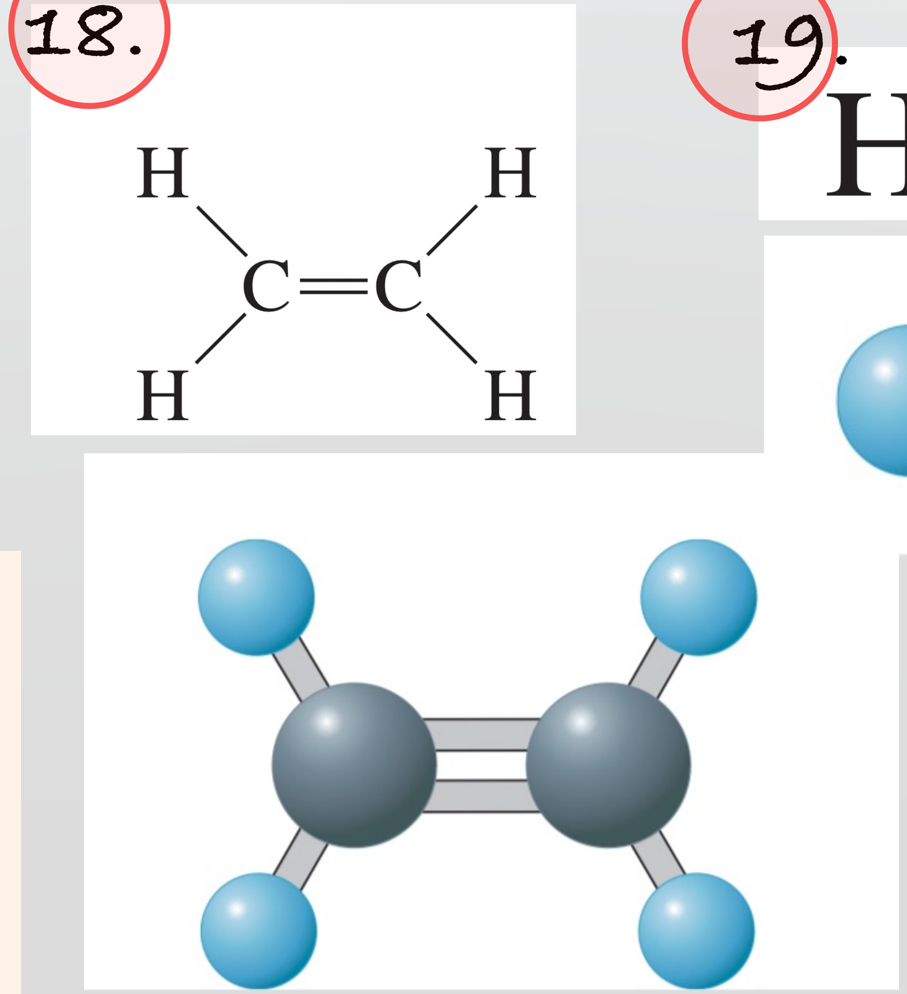

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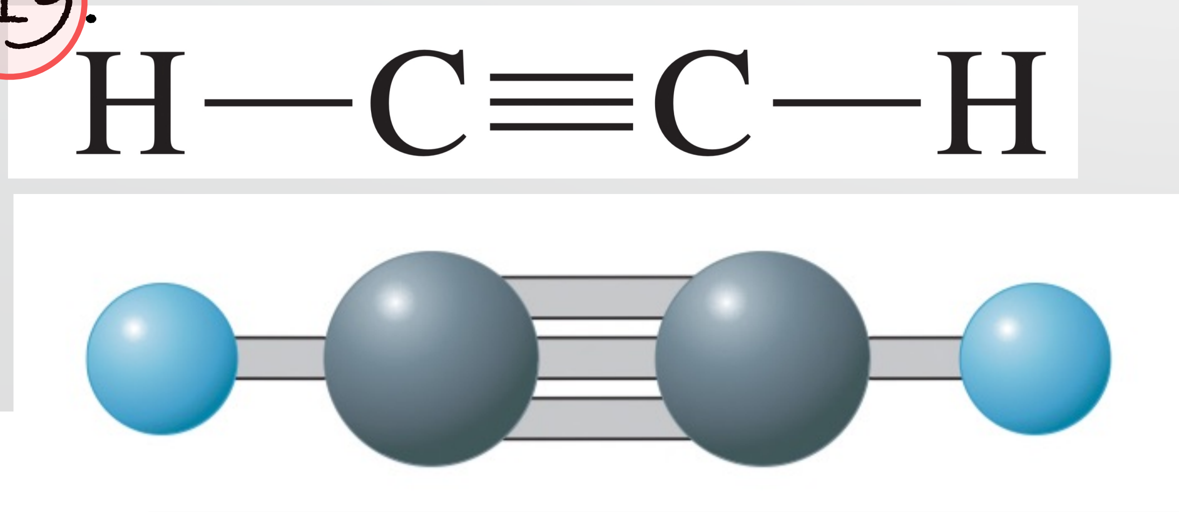

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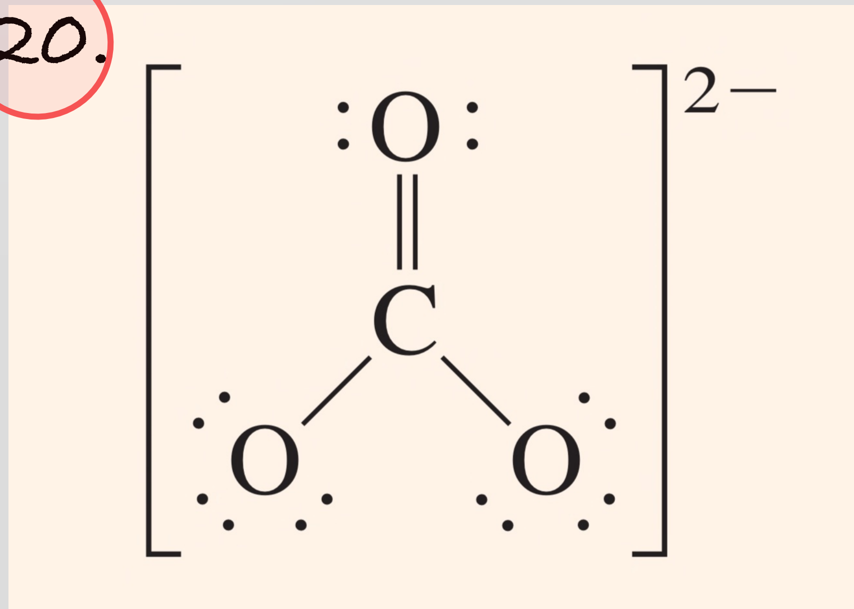


21.monothiocarbonate ion

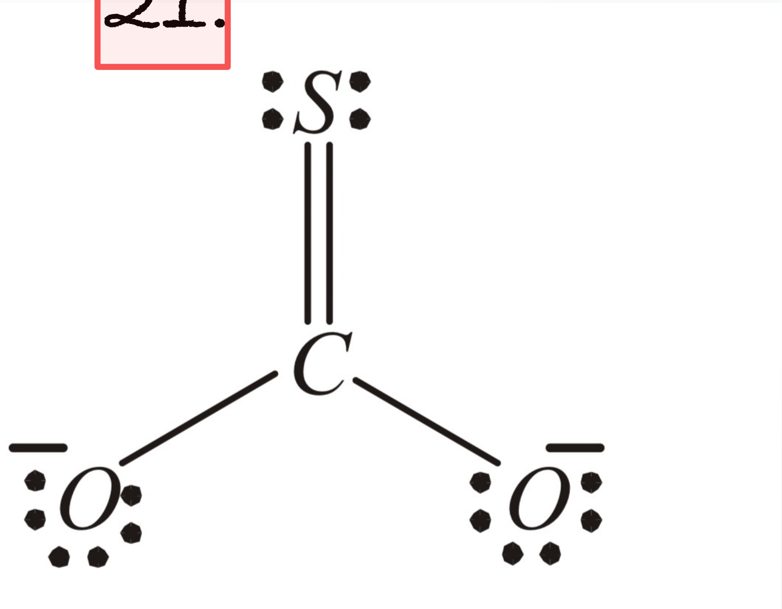
22.N2O3

23.N2O4

24.N2O5

25. POCl 3

21.



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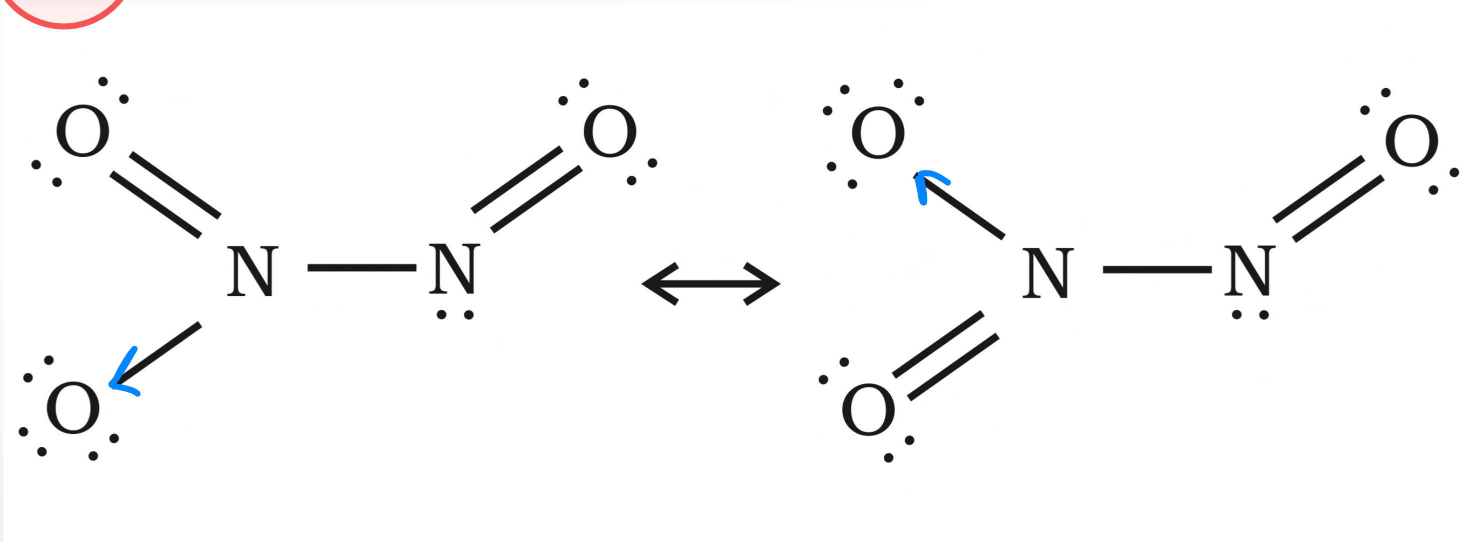

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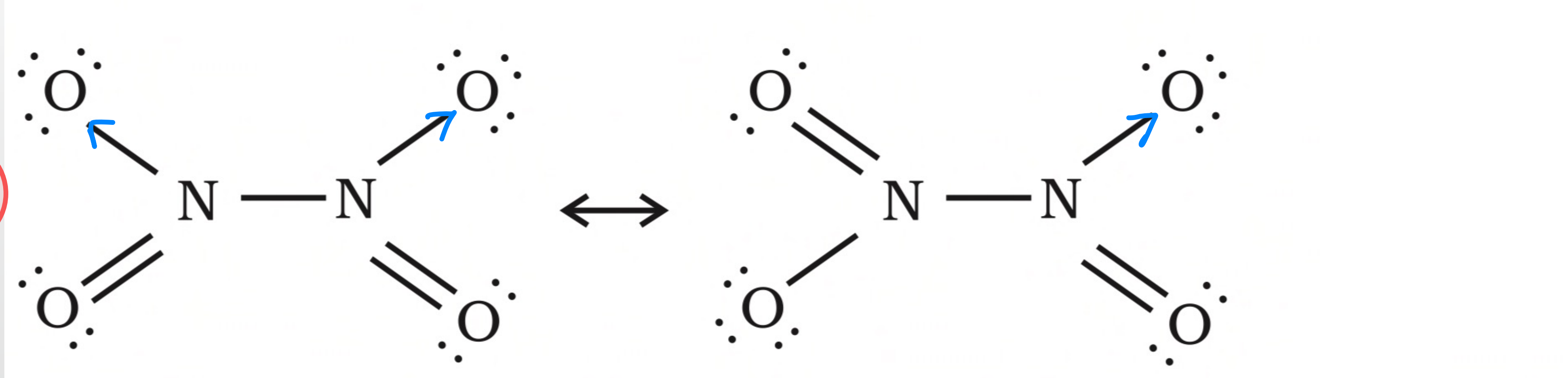

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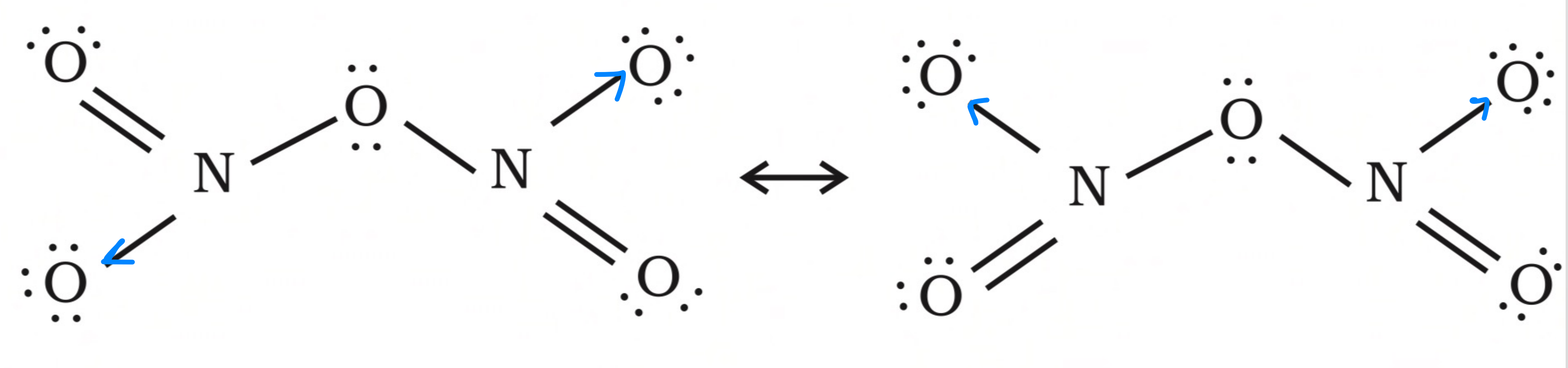

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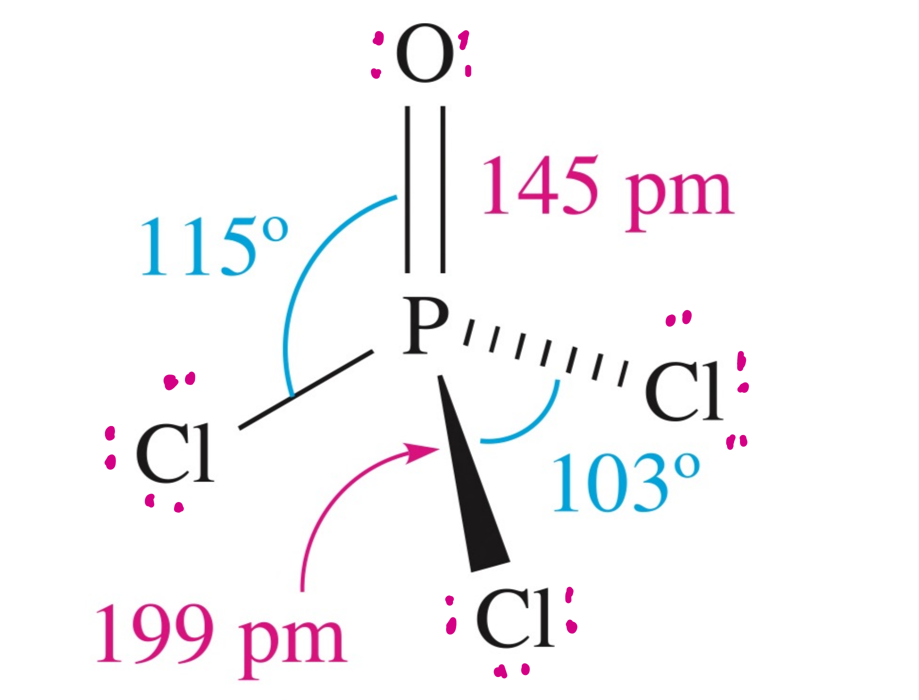

Chemical Bonding

(Q) find the order of thermal stability.

(A) HClO. (B) $HClO_2$. (C) $HClO_3$. (d) $HClO_4$

Number of bond increases energy required increases thermal stability increases

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Covalency /variable valency in covalent bonds

* number of bonds formed by element in ground state or excited state

(i) Variable valencies are shown by those elements which have empty orbitals in outermost shell.

(ii) Lone pair electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.

(iii) The energy required for excitation of electrons is called promotion energy.

(iv) Promotion rule – Excitation of electrons in the same orbit.

Ex.

(a) Phosphorus → Ground state

3s	3p			Covalency
↿⇂	↿	↿	↿	Covalency 3 (PCl_3)

Phosphorus → Excited state

3s	3p			3d					Covalency
↿	↿	↿	↿	↿					Covalency – 5 (PCl_5)

Covalency.	Ground state.	FES
Phosphorus.	3.	5

Sulphur $\rightarrow$ Ground state.

3s	3p			3d				
↑↓	↑↓	↑	↑					

Covalency - 2 (SF_2)

Sulphur $\rightarrow$ Excited state

I[st] excited state

3s	3p			3d				
↑↓	↑	↑	↑	↑				

Covalency - 4 (SF_4)

(SO_2)

2[nd] excited state

3s	3p			3d				
↑	↑	↑	↑	↑	↑			

Covalency - 6 (SF_6)

So variable covalency of S is 2, 4, & 6.

Covalency.	GS.	FES.	SES
Sulphur.	2.	4.	6

(Q) SO_3 → which excited state ?

2nd. excited state ✓

Iodine has three lone pair of electrons

(Ground state)

5s	5p			5d				
↑↓	↑↓	↑↓	↑					

So it shows three excited states – Maximum number of unpaired electrons = 7

Variable Valencies are 1, 3, 5, 7

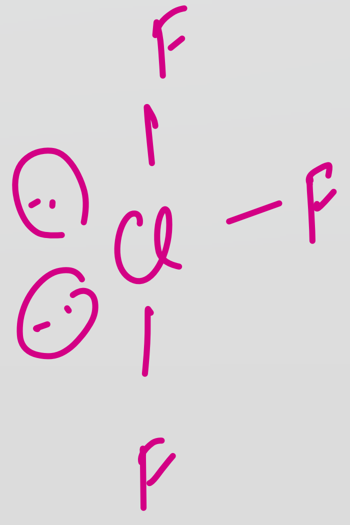
Covalency.	GS.	FES.	SES.	TES
(CL/Br/I).	1.	3.	5.	7

H.W

Draw orbital diagram of all excited state

(19) In ClF_3 ? Excited state of Cl ?

* I^{st} excited state.



	5s	5p			5d					
Xe :- (G.S.)	↑↓	↑↓	↑↓	↑↓						
(I[st] E.S.) :-	↑↓	↑↓	↑↓	↑	↑					(Covalency is 2) E.g. : XeF_2 etc.
(2[nd] E.S.) :-	↑↓	↑↓	↑	↑	↑	↑				(Covalency is 4) E.g. : XeF_4 etc.
(3[rd] E.S.) :-	↑↓	↑	↑	↑	↑	↑	↑			(Covalency is 6) E.g. : XeF_6 etc.
(4th E.S)	↑	↑	↑	↑	↑	↑	↑	↑		(Covalency is 8) E.g. : XeO_4 et

So variable covalency of Xe is 2,4,6,8.

(Q) what is the excited state of Xe in XeO_2F_2 ?

3^{rd} excited state

Chemical Bonding

For second period element

$_7N$: $1s^2$ $2s^2$ $2p^3$

$1s^2$	$2s^2$	$2p^3$		
↑↓	↑↓	↑	↑	↑

*absence of 2d orbital

Covalency (3/4)

Note : Exicatiton is not possible from one shell to another shell because very high amount of energy will be required which could be even higher than bond energy

So jump to 3S not favourable

(Q) which of the following exist?

✓ NCl_3. ✗ NCl_5

✓ PCl_3. ✗ PCl_4. ✓ PCl_5

✓ OF_2. ✗ OF_4. ✗ OF_6

✓ SF_2. ✓ SF_4.

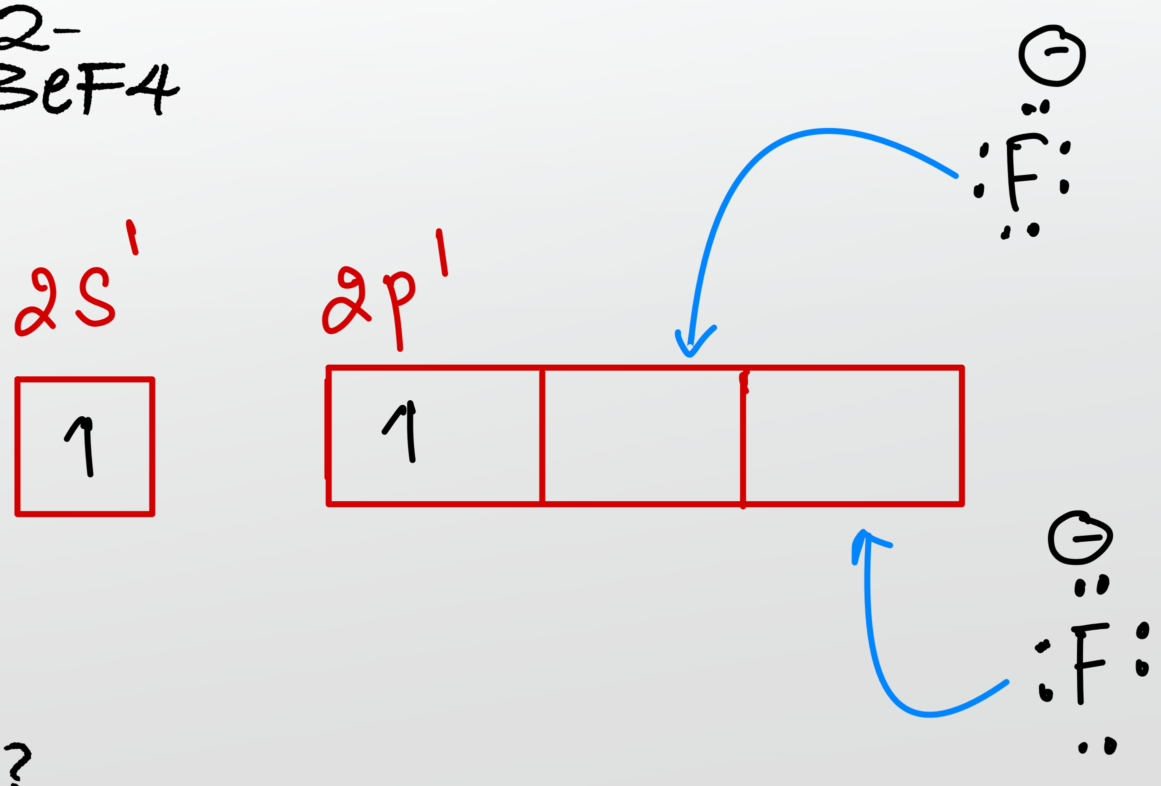
Chemical Bonding

Sidgwick Rule

*Atom which has vacant orbital in outermost shell can extend their valency.

1. $BeF_2 + 2F^{\ominus} \rightarrow BeF_4^{2-}$

Be*. [He] $2s^1$ $2p^1$



Be

G.S [He] $2s^2$ $2p$

Be* F.E.S [He] $2s^1$ $2p^1$

Is BeF_5^{3-} possible ?

* not possible.

Chemical Bonding

2. $BF_3 + F^- \longrightarrow BF_4^-$

B^* [He] $2s^1$ $2p^2$

$\boxed{\uparrow}$ $\boxed{\uparrow \mid \uparrow \mid \ \ }$

$\ddot{F}^{\ominus}$

(Q) will BF_6^{3-} Exist? does not exist.

(Q) will. CF_6^{2-} Exist? does not exist

$CF_4 + 2F^{\ominus}$

$_6C$ [He] $2s^2$ $2p^2$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow \mid \uparrow \mid \ \ }$

$_6C^*$ [He] $2s^1$ $2p^3$

$\boxed{\uparrow}$ $\boxed{\uparrow \mid \uparrow \mid \uparrow}$

Covalent bond (introduction to VBT)

* covalent bond formation is explained by valence bond theory (VBT) which also explained by orbital overlap concept.

* valence Bond theory (VBT)

It was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals and the hybridization of atomic orbitals.

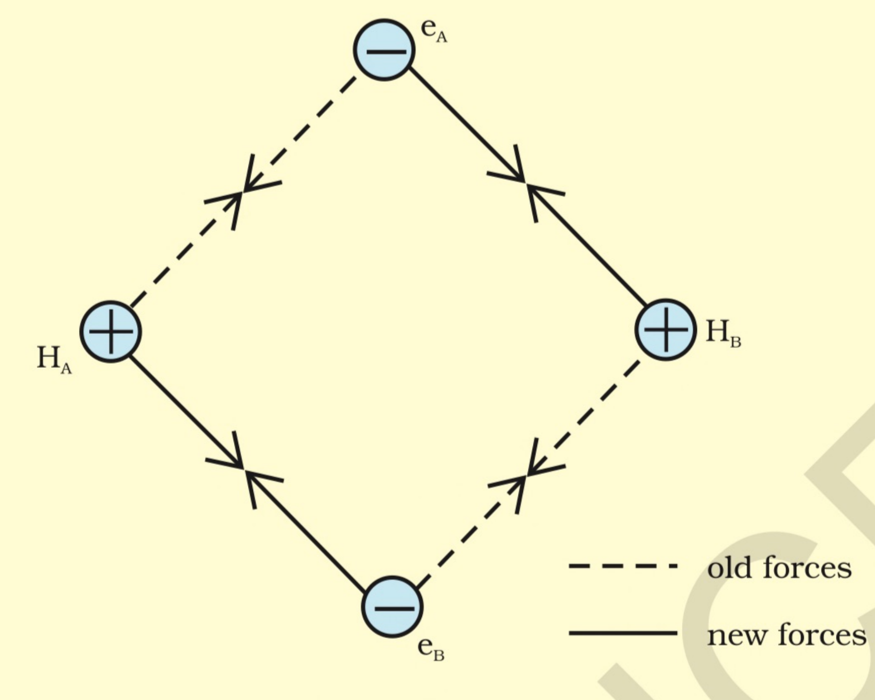
Formation of H_2 molecule :

When two 'H'-atoms approaches towards each other for the formation of H_2 molecule. The following interactions takes place.

(i) e-e repulsion

(ii) e-p attraction

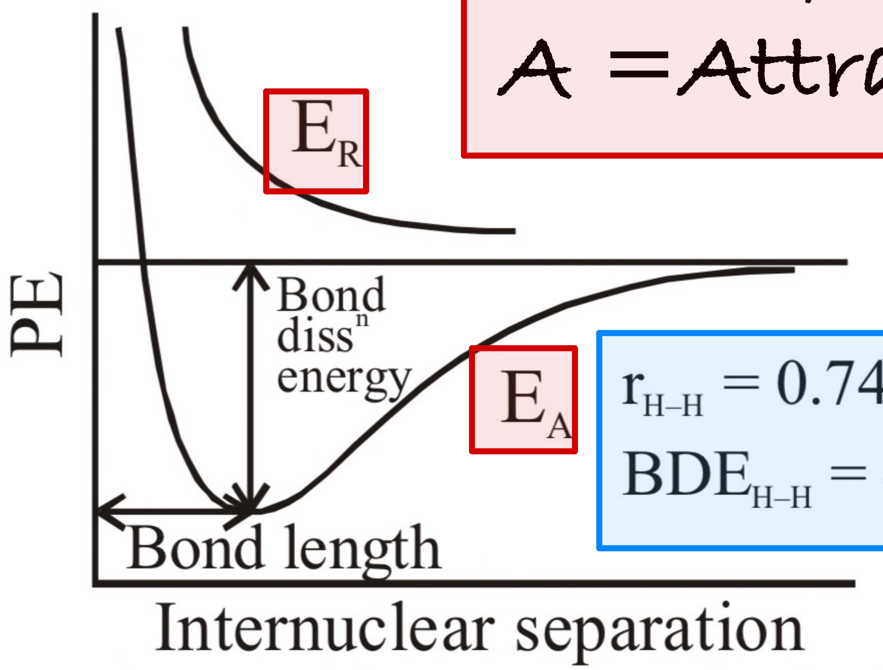
(iii) p-p repulsion



Attractive Forces

R = Repulsion.

A = Attraction



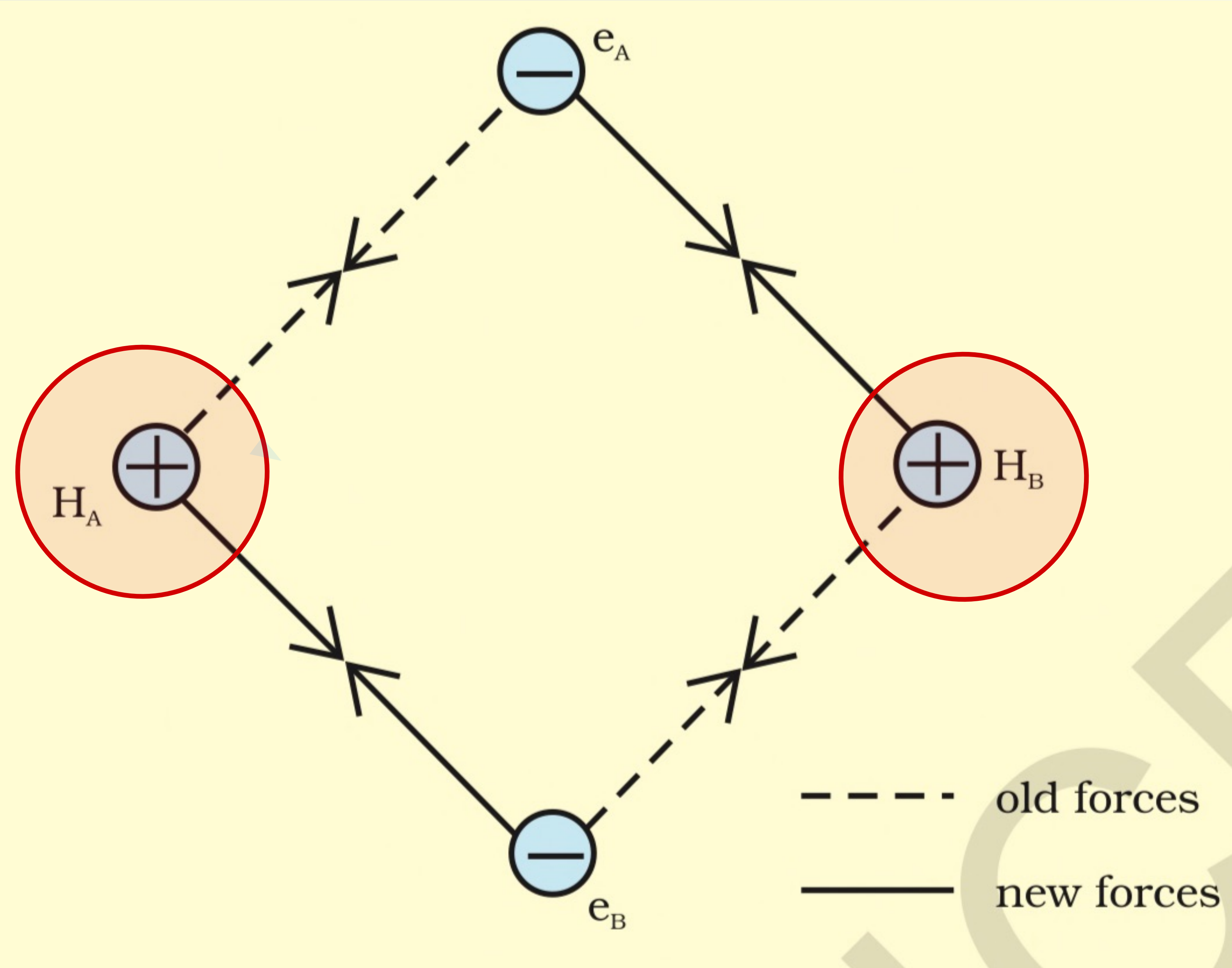
$r_{H-H} = 0.74Å$

$BDE_{H-H} = 434.2$ kJ/mol

The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.

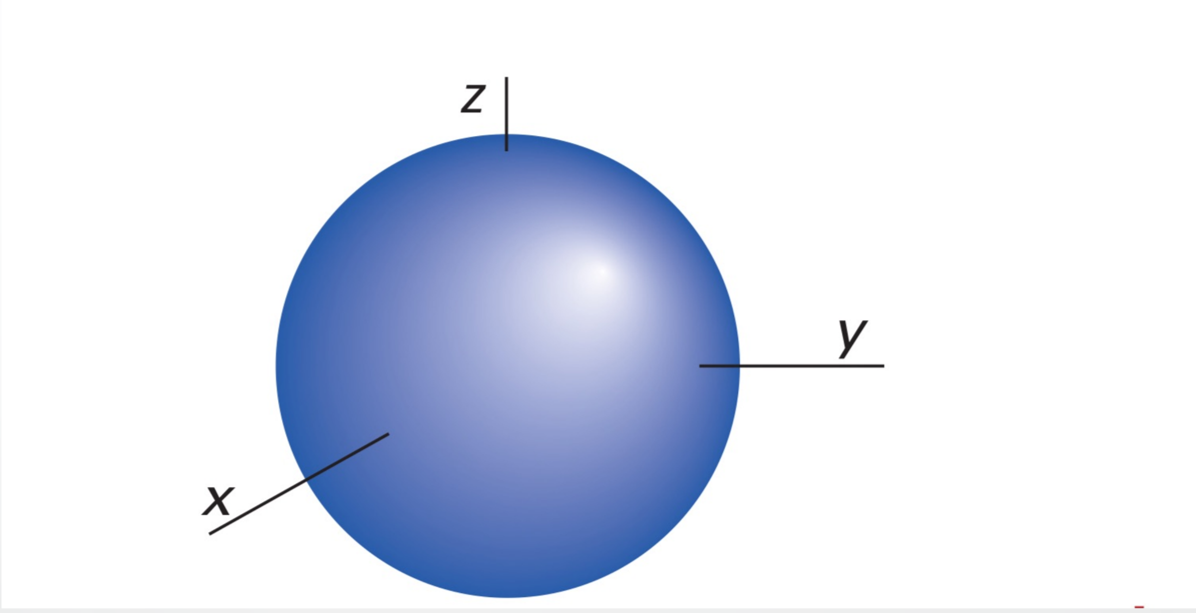
Chemical Bonding

Experimentally, it has been found that the magnitude of attractive forces is more than the repulsive forces. As a result, when two atoms approach each other then potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy.

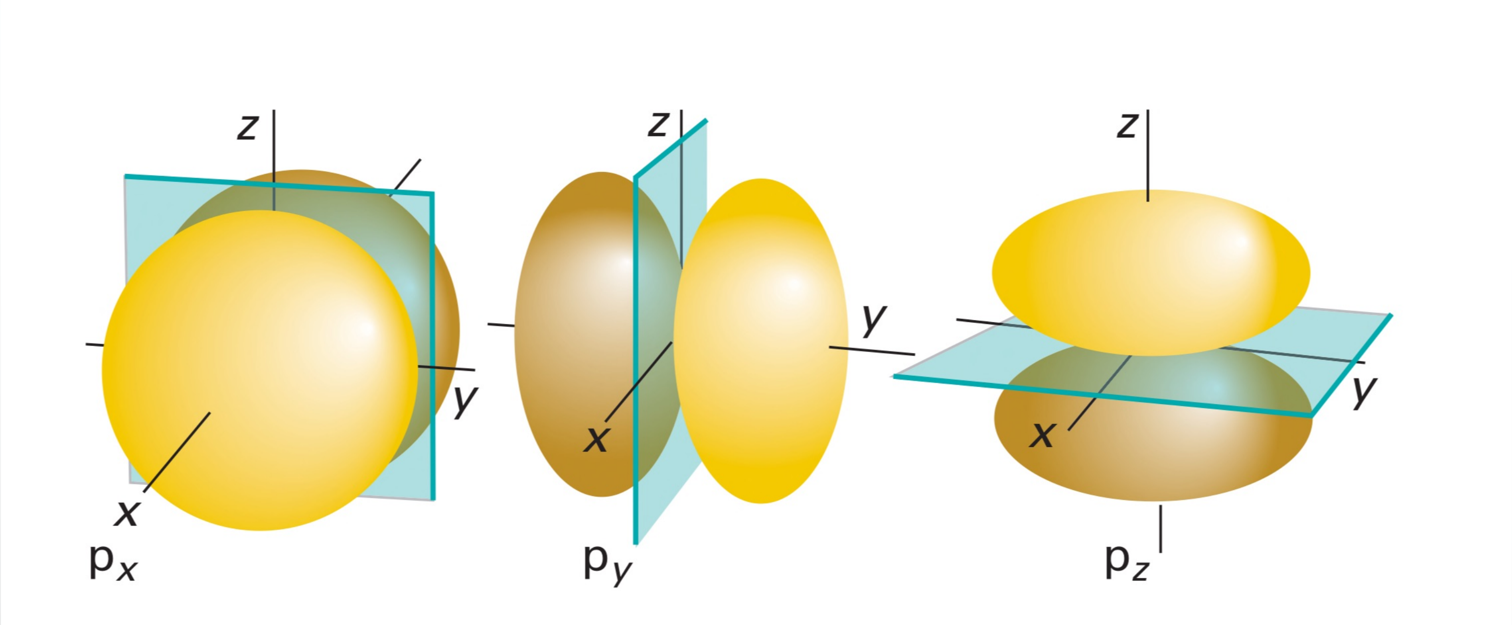


Attractive Forces

Shapes of orbital (revision)

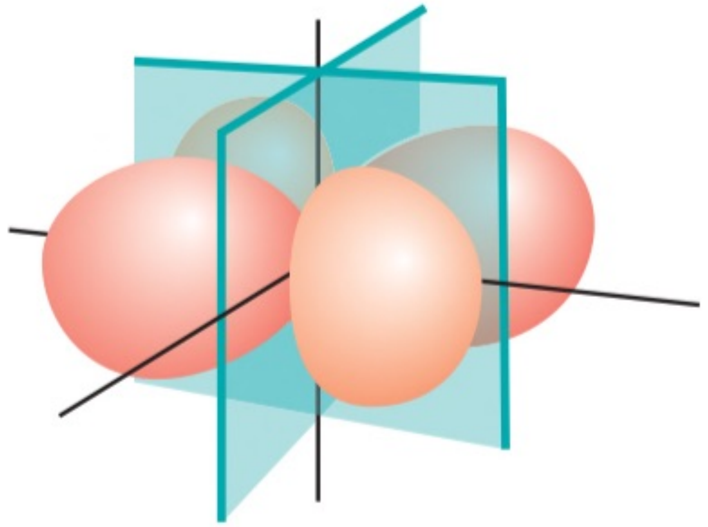


S orbital

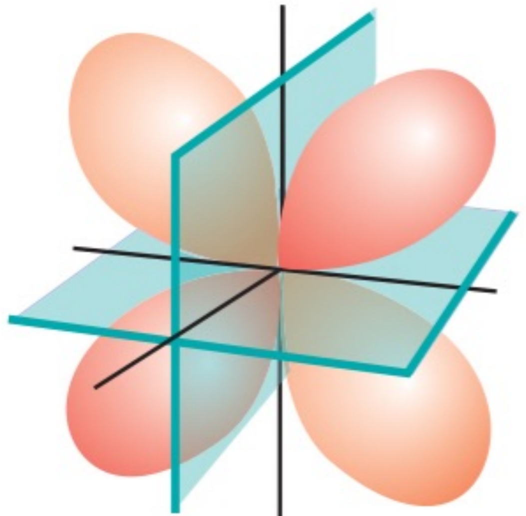


P orbital

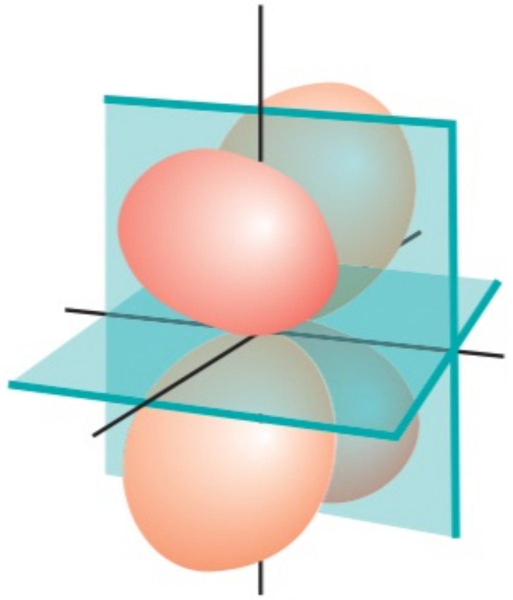
d orbital



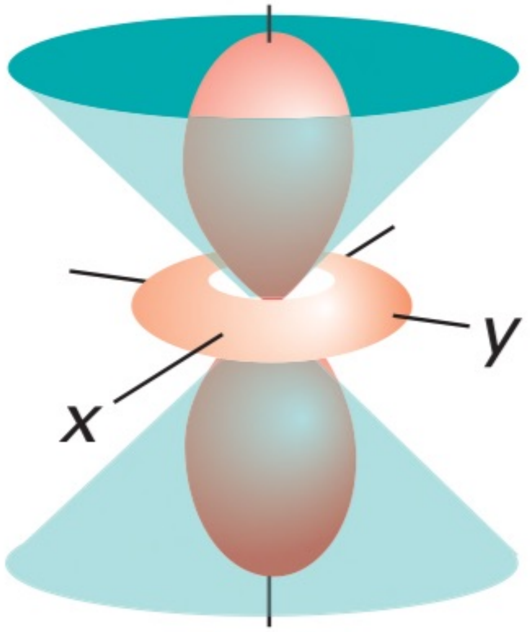
d_{xy}



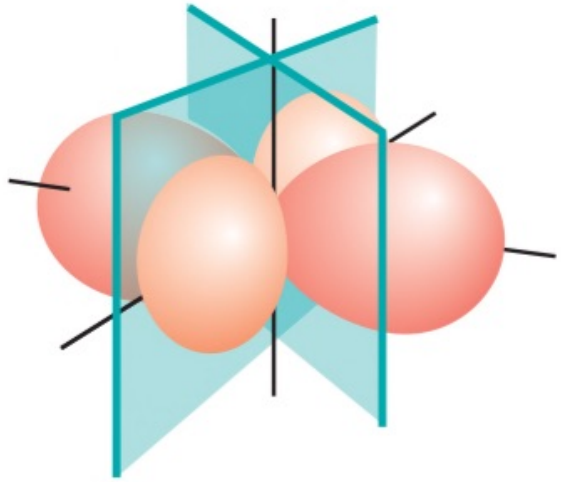
d_{yz}



d_{zx}



d_{z^2}

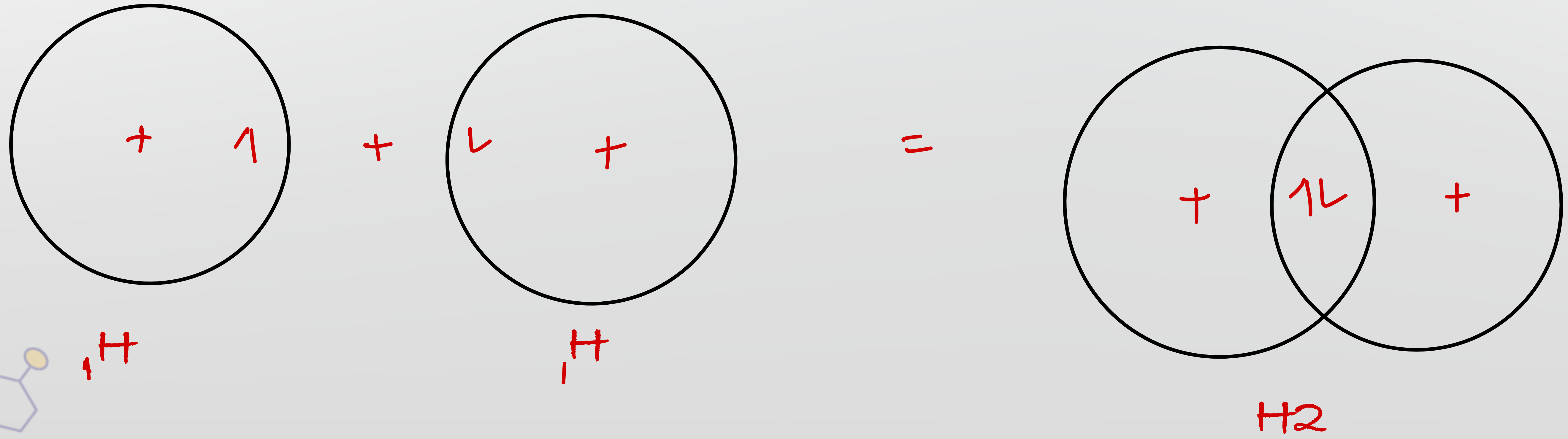


$d_{x^2-y^2}$

Chemical Bonding

Orbital overlapping concept

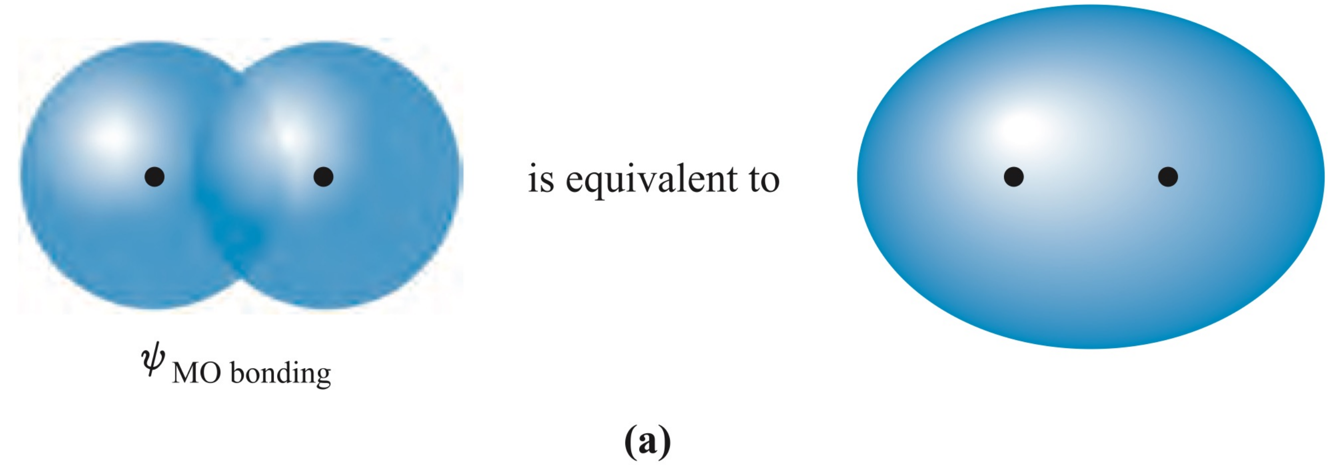
In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing or merging of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons, present in the valence shell having opposite spins.

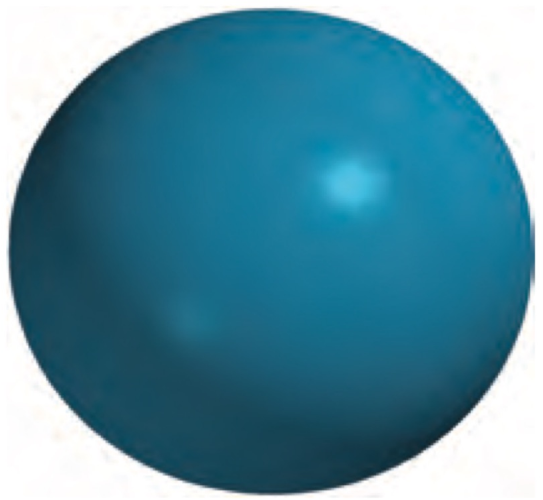


s orbital s orbital. s-s overlapping

Chemical Bonding

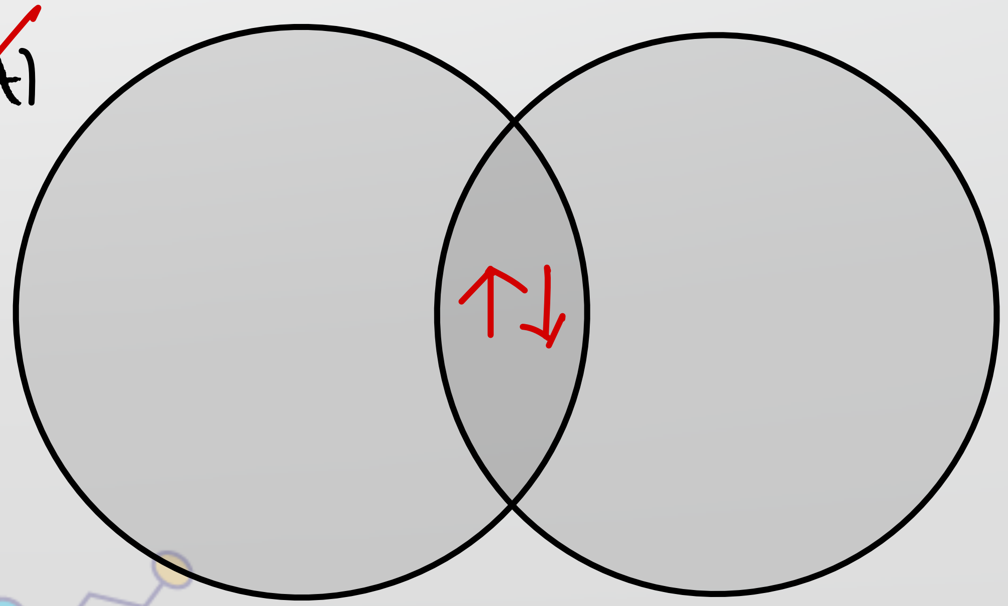
s orbital s orbital.   s- s overlapping



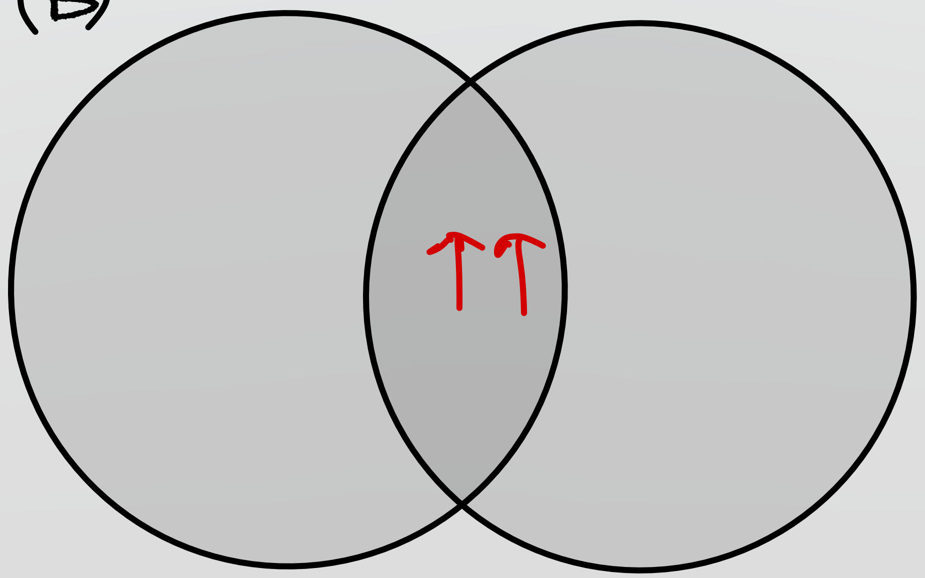


Q) which of the following overlapping is correct?

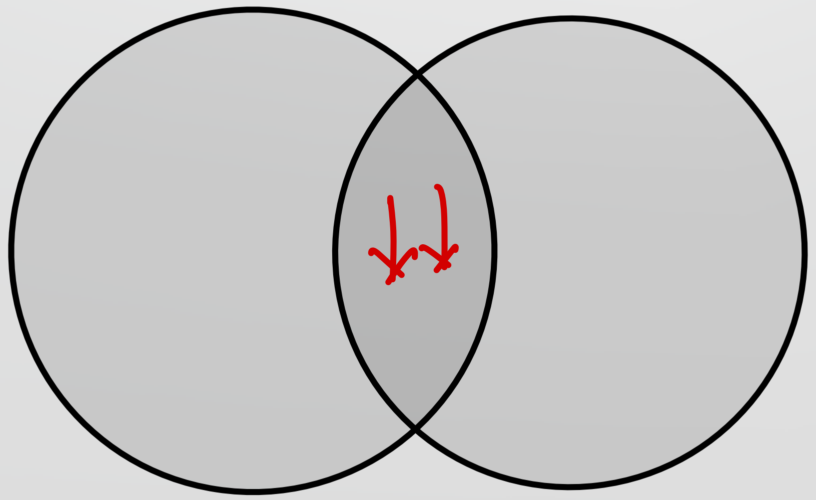
(A)



(B)



(C)



Chemical Bonding

Types of overlapping

Analogy

(i) Head on / co-axial overlapping :

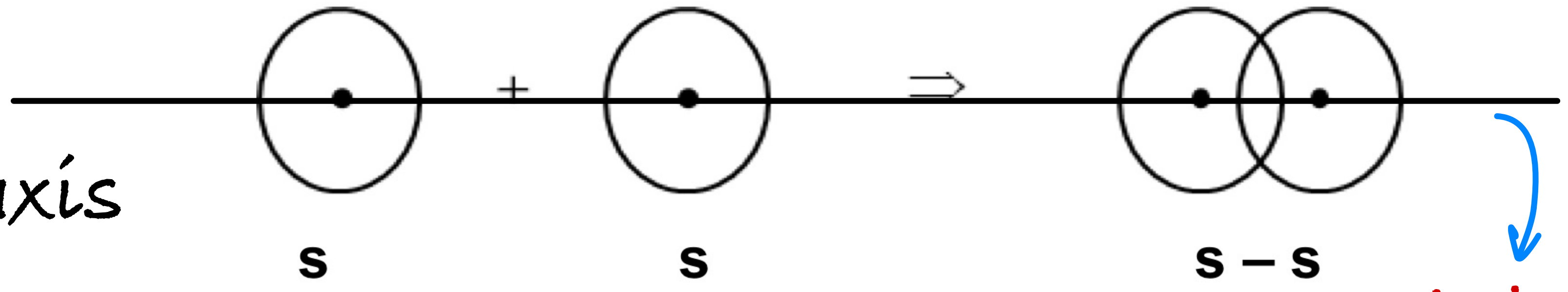
- Atomic orbitals overlap head to head along the internuclear axis.
- Sigma (σ) bond is formed.

Let z-axis is internuclear axis.

(A) s—s overlapping :-

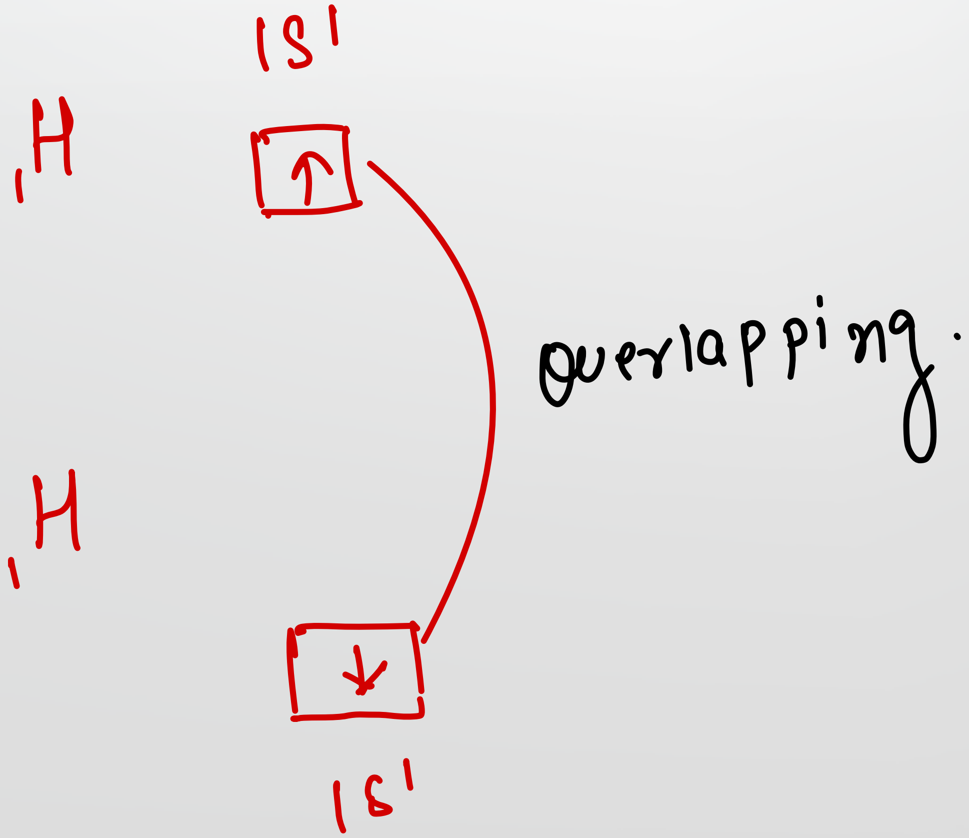
Axis connecting the nucleus of two orbital

Zaxis

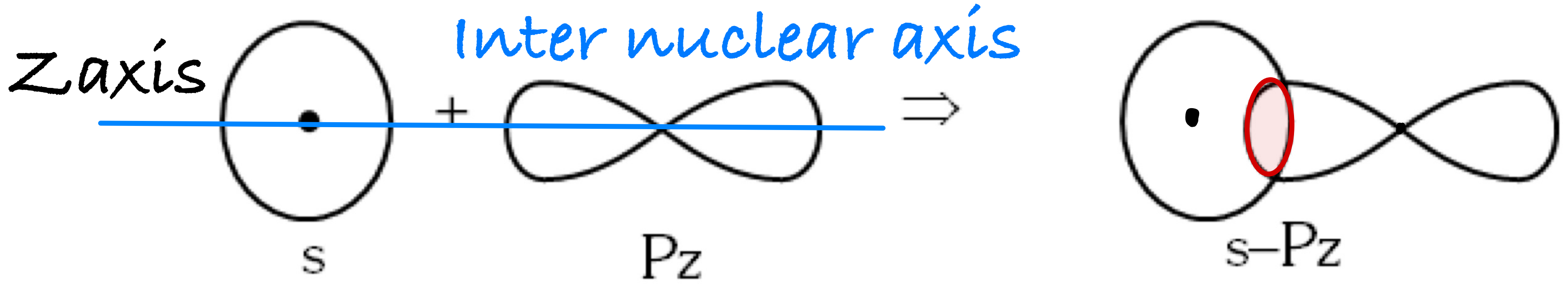


e.g. $H \overset{\sigma}{—} H$

Inter nuclear axis



(B) s—p overlapping :-

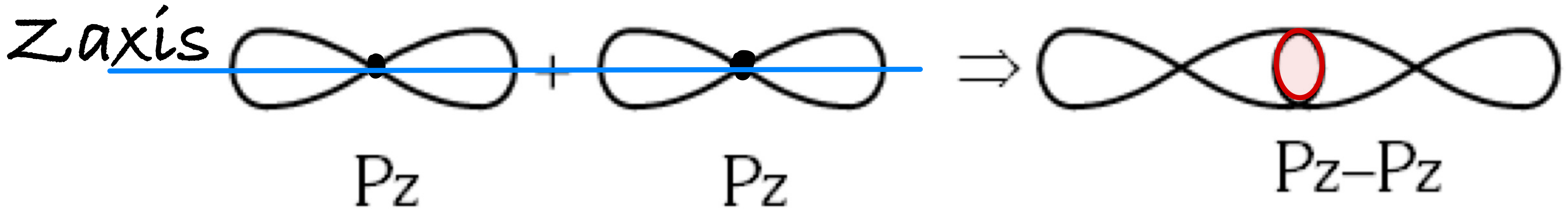


e.g. $H \overset{\sigma}{-} F$

$H \overset{\sigma}{-} Cl$

Analogy

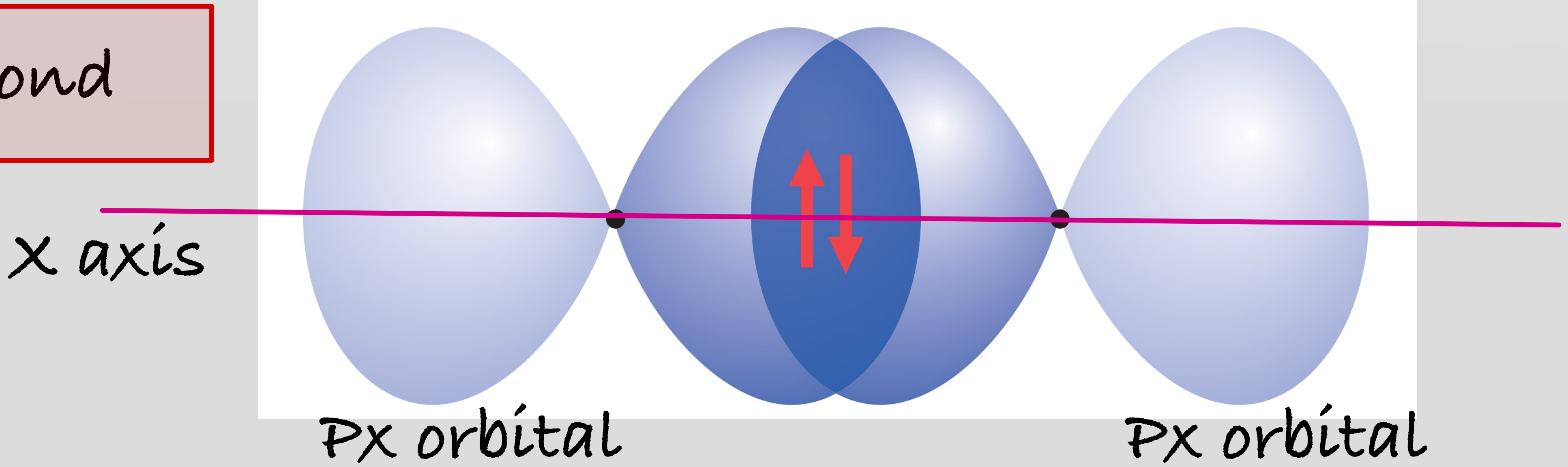
(C) p—p overlapping :-



e.g. $F \overset{\sigma}{-} F$

$Cl \overset{\sigma}{-} Cl$

Note: S orbital do not form pie bond



Chemical Bonding

example : 1 $_1H$ $1s^1$ $\boxed{\uparrow}$

$_9F$ [He] $2s^2$ $2p^5$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow \mid \uparrow\downarrow \mid \downarrow}$

H — F

1s — 2p (Head on overlapping)

2 H — Cl

1s — 3p (overlapping)

3 H — Br (overlapping)

1s — 4p

4 F_2 (2p – 2p) overlapping.

$_9F$ [He] $2s^2$ $2p^5$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow \mid \uparrow\downarrow \mid \uparrow}$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow \mid \uparrow\downarrow \mid \downarrow}$

$_9F$ [He] $2s^2$ $2p^5$

Explain Bonding in (a) HF, HCl, HBr, HI (b) F_2, Cl_2, Br_2, I_2

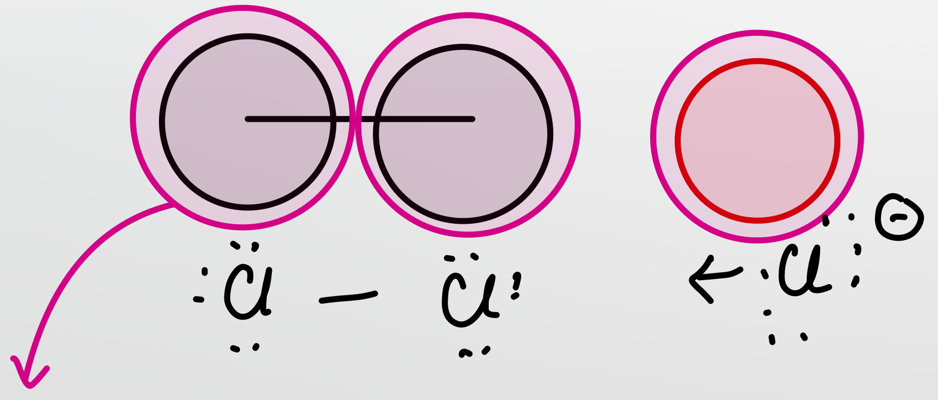
HW

Chemical Bonding

1. $F_2 + F^{-} \longrightarrow F_3^{-}$. Not possible absence of 2d orbital

$\times$ 2d.

2. $Cl_2 + Cl^{-} \longrightarrow Cl_3^{-}$. Don't exist to high electron repulsion due to high charge density on Cl_2



Charge density

3. $Br_2 + Br^{-} \longrightarrow Br_3^{-}$. Exist

4. $I_2 + I^{-} \longrightarrow I_3^{-}$. Exist

Exist with large cation $Cs^{+} + I_3^{-} \longrightarrow CsI_3$

$Tl^{+} + I_3^{-} \longrightarrow TlI_3$

The correct statement for the molecule, CsI_3 is

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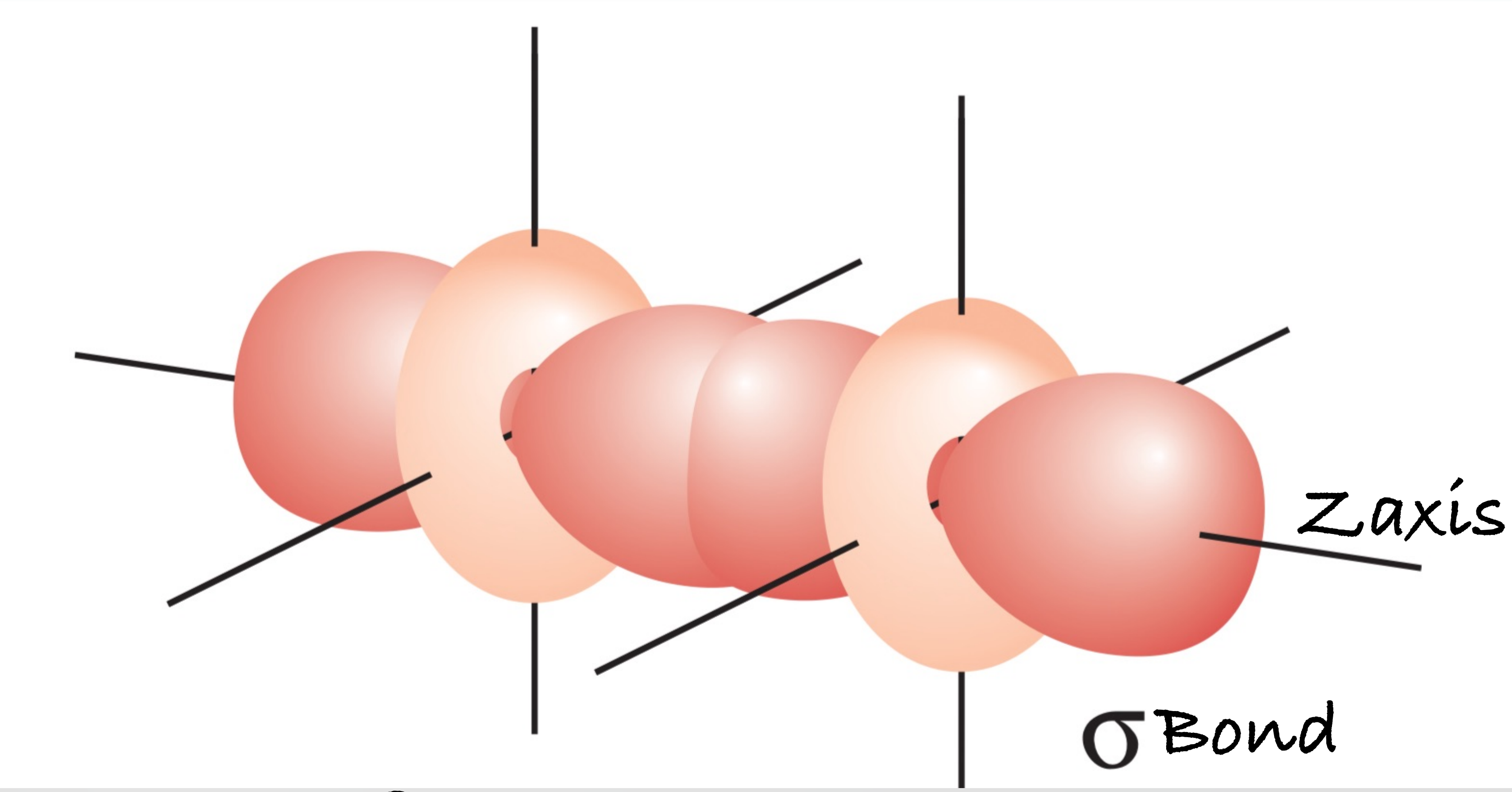
(a) it is a covalent molecule
(b) it contains Cs^+ and I_3^- ions
(c) it contains Cs^{3+} and I^- ions
(d) it contains Cs^+, I^- and lattice I_2 molecule

(d) d - d overlapping



dz^2 dz^2

Chemical Bonding

Bond strength of sigma bond $\propto$ Extent of overlapping

1. Bond strength $\propto \frac{1}{\text{Size}}$

** (dominant)

2. When size is constant (n = constant)

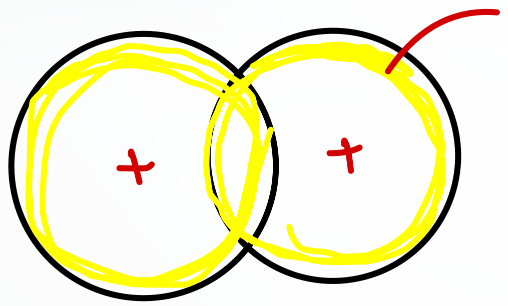
Bond strength. $\propto$ directional-nature

S orbital - non directional

P orbital - directional nature

Chemical Bonding

Example : 1S - 1S > 1S -2S. > 2S -2S (by n)

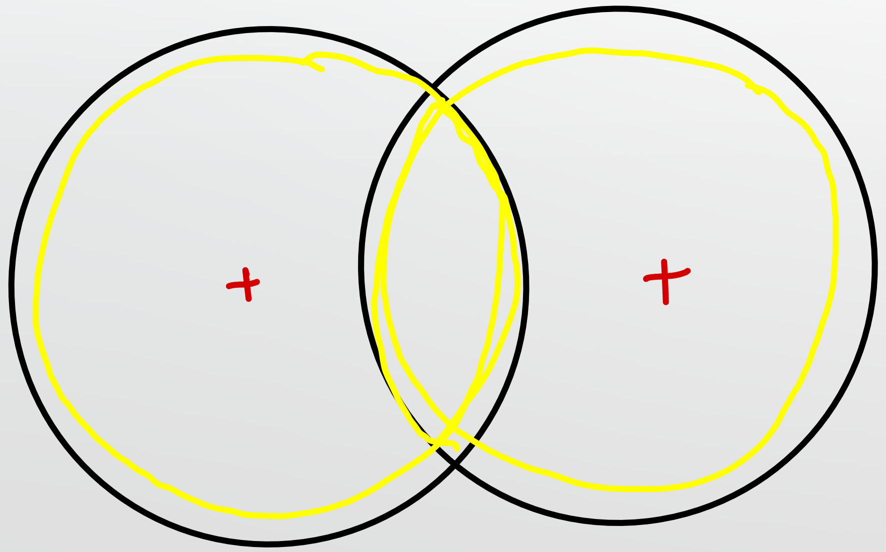


Explanation :

1.Probability of finding e

2. Distance from nucleus increases attractin decreases bond strength decreases.

Analogy : finding a person in small space or large space



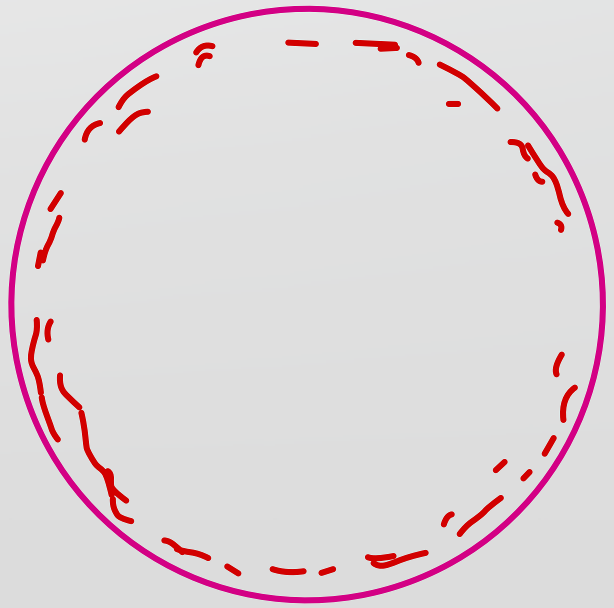
2S - 2S. < 2S- 2P. < 2P-2P

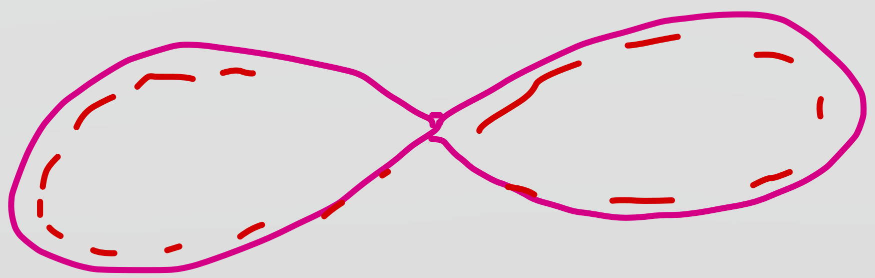
é density 1/3. 1/3. 1/3. 1/2. 1/2 - 1/2

More is the extent of overlapping between the two atomic orbital, stronger will be bond.

s – s < s – p < p – p [Principal Quantum no. same, n = 2]

(σ) (σ) (σ)





(Q) compare extent of overlapping

$\underbrace{1S\text{-}1S > 1S}_{\text{Size}}\text{-}\underbrace{2P > 1S}_{\text{directional character}}\text{-}2S$

Extent of overlapping

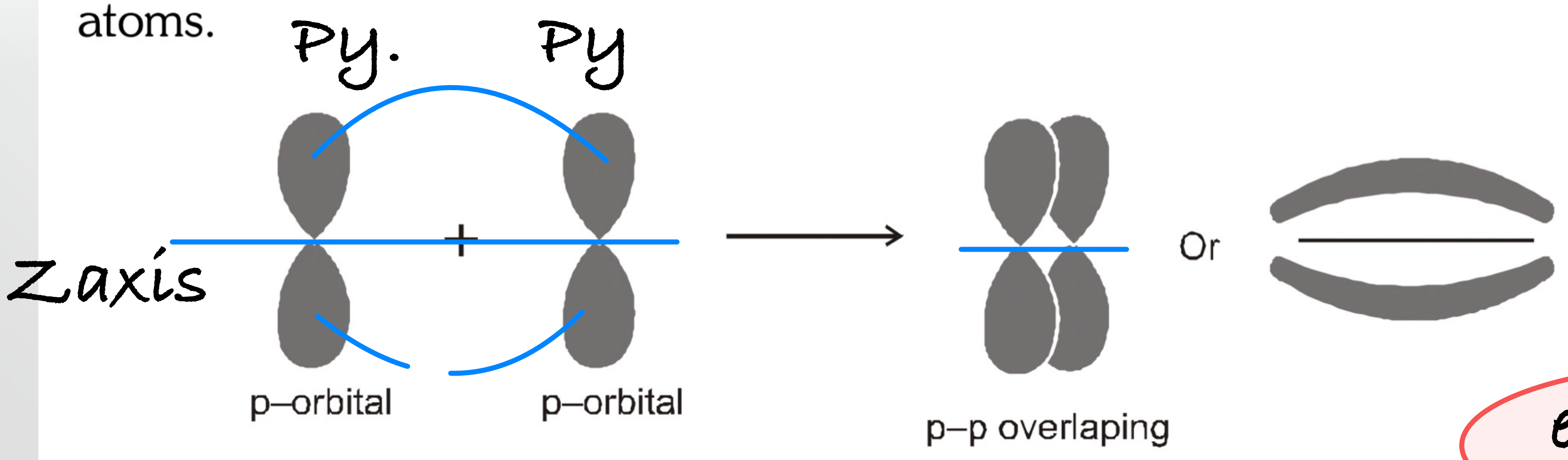
1S-1S. > 1S-2P. > 1S-2S. > 2P-2P. > 2S-2P. > 2S-2S. > 2S-3P
2S-3S. > 3P-3P. > 3S-3P. > 3S-3S

(ii) Sidewise overlapping :

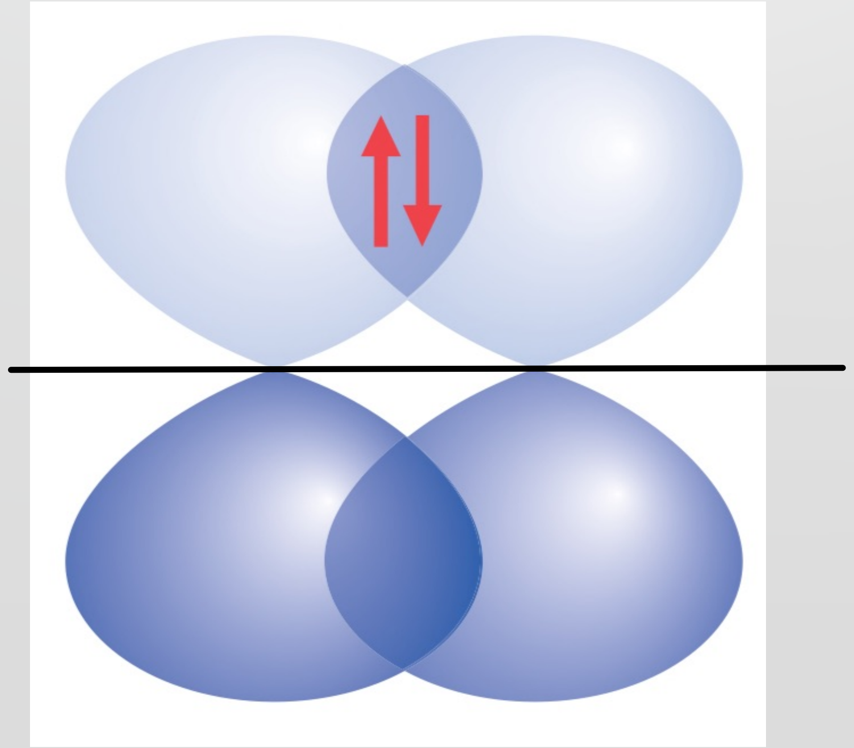
- Atomic orbitals overlap side by side along the internuclear axis.
- Pi(π)bond is formed.

Overlapping perpendicular to axis

pi(π) bond : In the formation of π bond the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

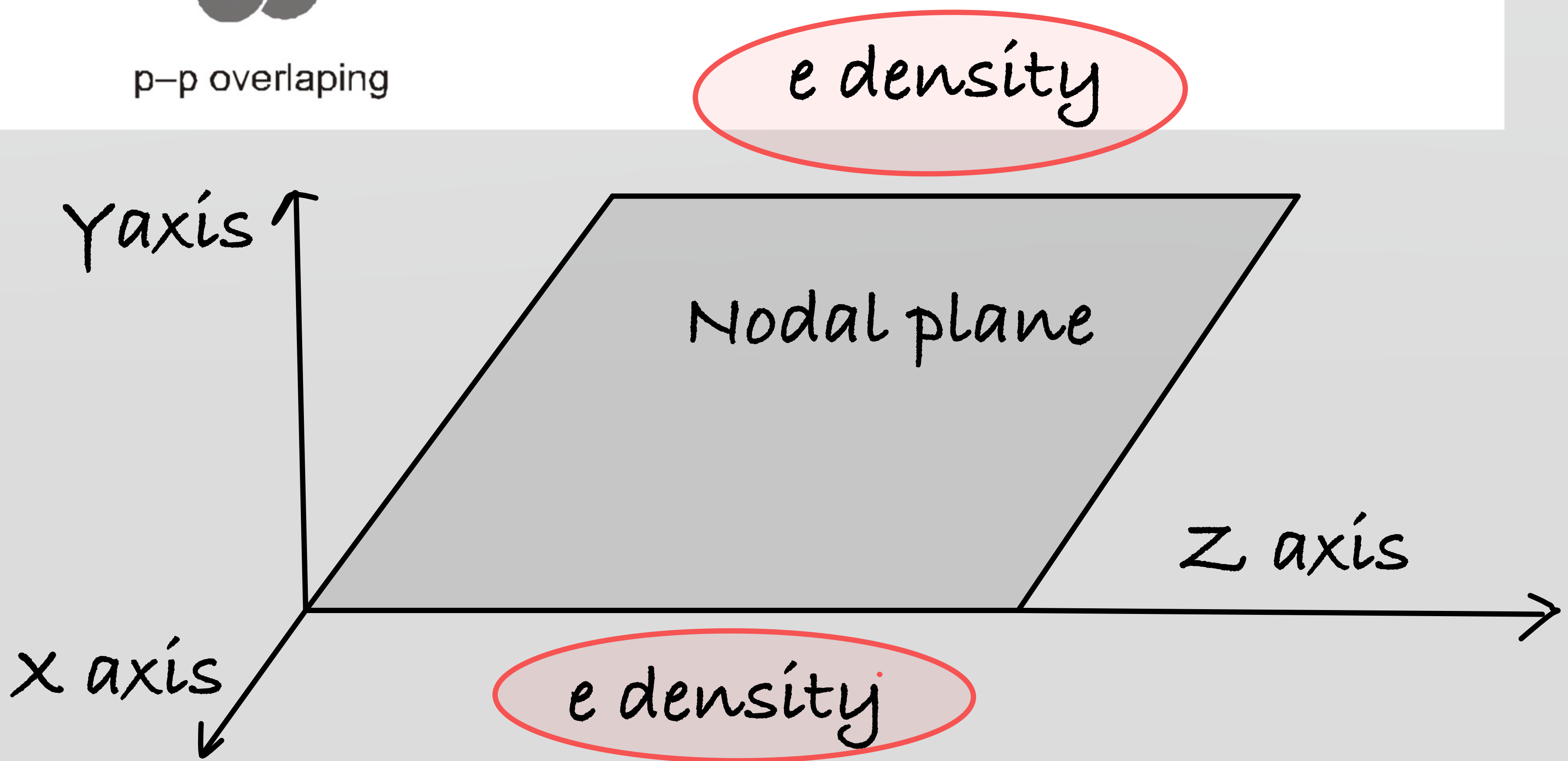


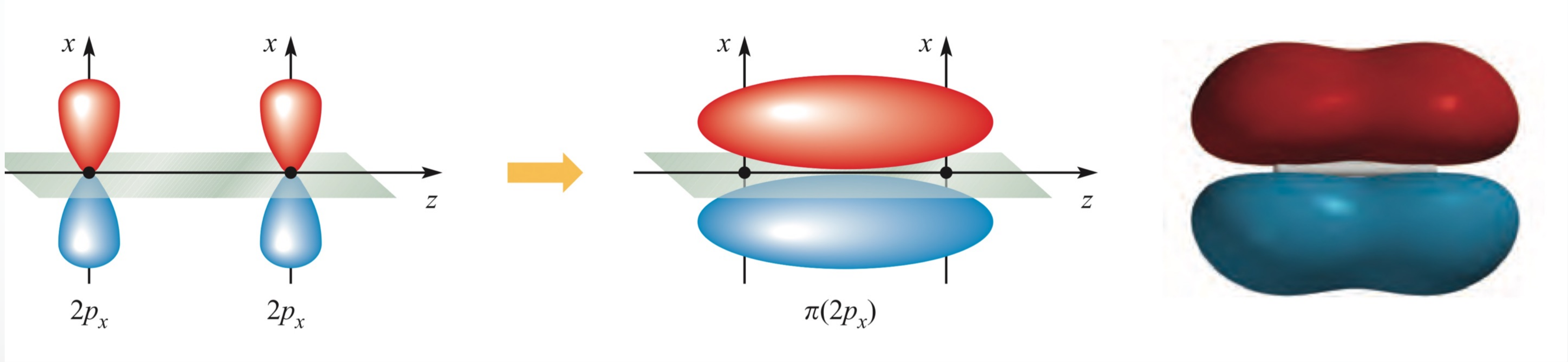
Analogy :Namaste



The formation of a π bond.

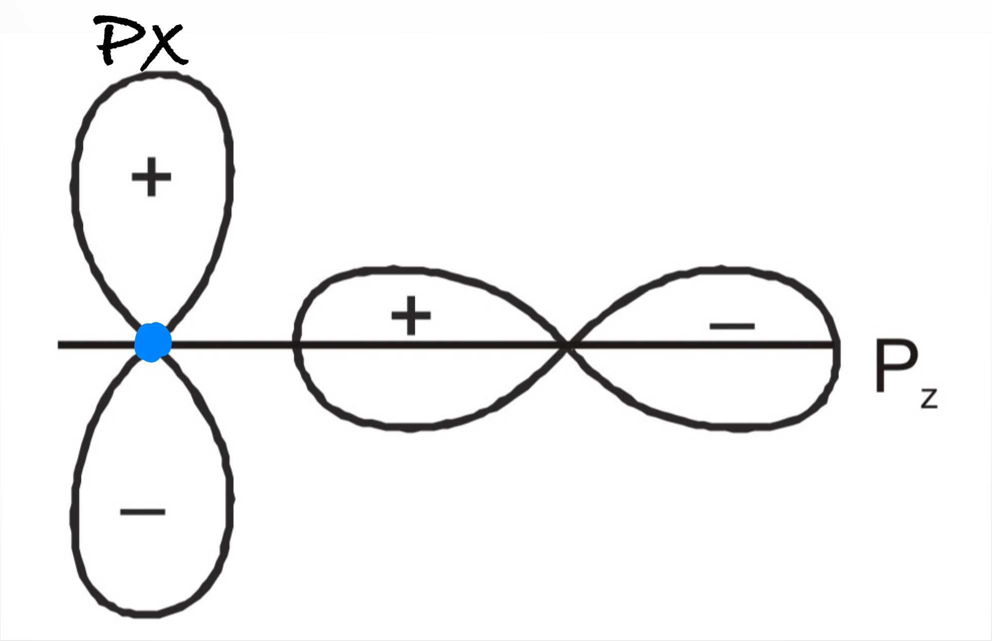
Two lobe interactions

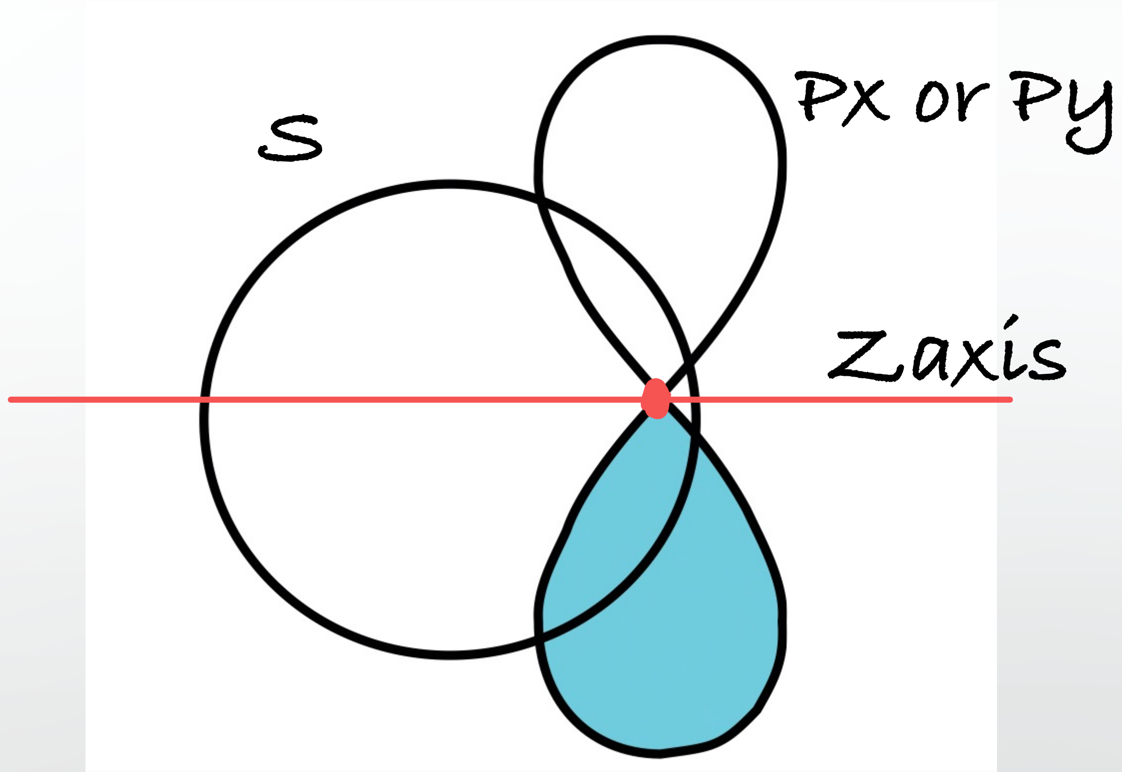



x
x
z
2p_x
2p_x
x
x
z
π(2p_x)

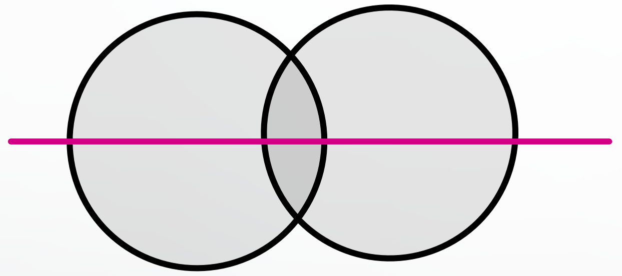
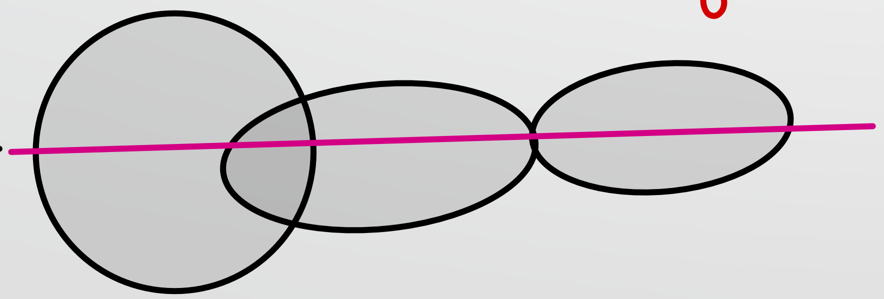
Chemical Bonding

Zero over lapping

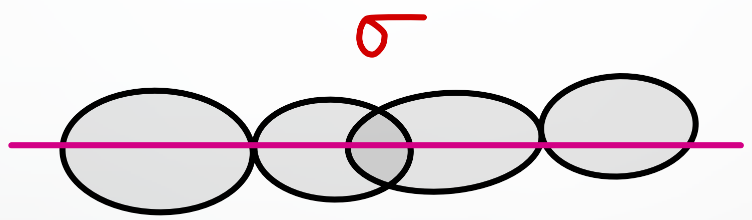
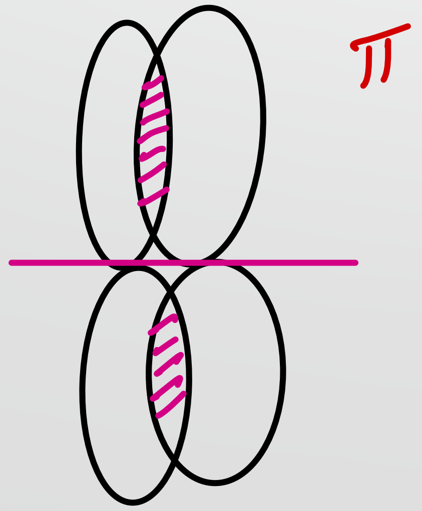




Note : If not specified then Z axis is assumed to be inter nuclear axis

	Overlapping	Internuclear axis	Type of bond	Example
1.	S - S	X axis	Sigma	 σ
		Y axis		
		Z axis		
2.	S+Px	X axis	Sigma	 σ
	S+Py	Y axis	Sigma	
	S+Pz	Z axis	Sigma	

Any other S - P over lapping not possible

	Overlapping	Inter nuclear axis	Type of bond	Example
3.	Px + Px	X	Sigma	
	Py + Py	Y	Sigma	
	Pz + Pz	Z	Sigma	
4.	Px-Px	Y or z	Pie	
	Py-Py	X or z	Pie	
	Pz-Pz	X or y	Pie	

Any other P-P overlapping not possible

(Q) which of the following overlapping is not possible if x is inter nuclear axis. Also write the type of bond from whether sigma or pie .

(a) P_x-P_x

(b) P_x -P_y

(c) P_y-P_y

(d) P_z - P_z

(e) P_x-P_z

(f) P_y-P_z

(g) $s+P_x$

(h) $s+P_y$

H.W

(Q) which of the following overlapping is not possible . Also write the type of bond from whether sigma or pie .

(a) Px-Px

(b) Px -Py

(C) Py-Py

(d) Pz - Pz

(e) Px-Pz

(f) Py-Pz

(g) S+Px

(h) S+Py