Limitations of the Octet Rule:

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table.

There are three types of exceptions to the octet rule.

- The incomplete octet of the central atom: In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3, BeF_2, BF_3, $AlCl_3$.

- Odd-electron molecules : In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide (NO_2), the octet rule is not satisfied for all the atoms. e.g. NO, ClO_2 , ClO_3

- The expanded octet : Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases. Some of the examples of such compounds are: PF_5, SF_6, PCl_5, HNO_3, SO_3, SO_2, H_2SO_4 and a number of coordination compounds.

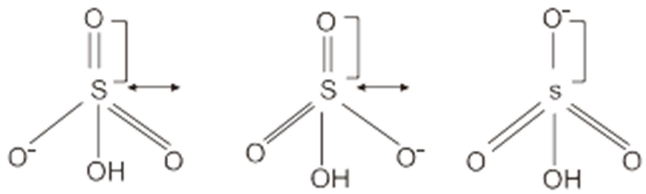
Other drawbacks of the octet theory:

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

Bond Order Calculation:

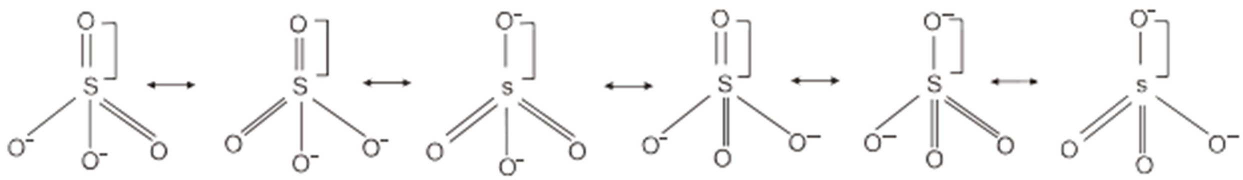
Bond order in oxoanions and corresponding acids :

Let's starts with example of HSO_4^-



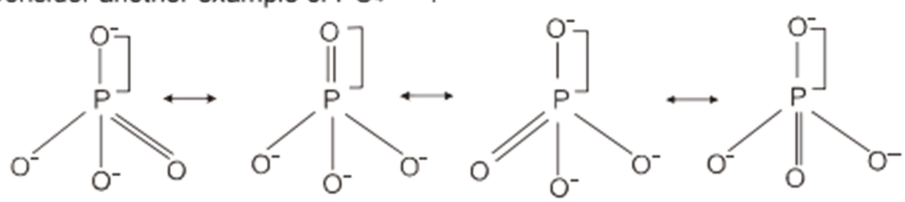
- Bond order = $\frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{2+2+1}{3} = 5/3$

Consider another example of SO_4^{--} :



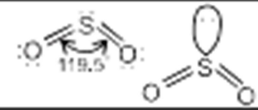
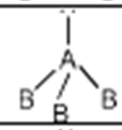
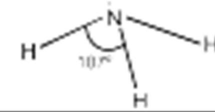
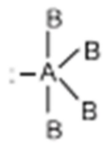
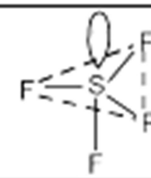
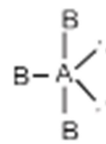
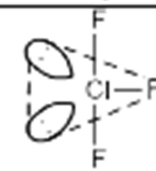
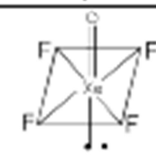
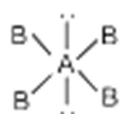
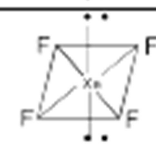
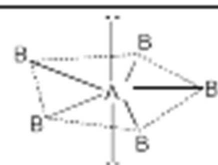
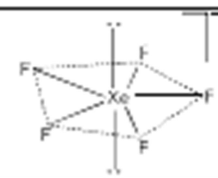
- Bondorder= $\frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{2+2+1+2+1+1}{6} = 1.5$

Consider another example of PO_4^{---} :

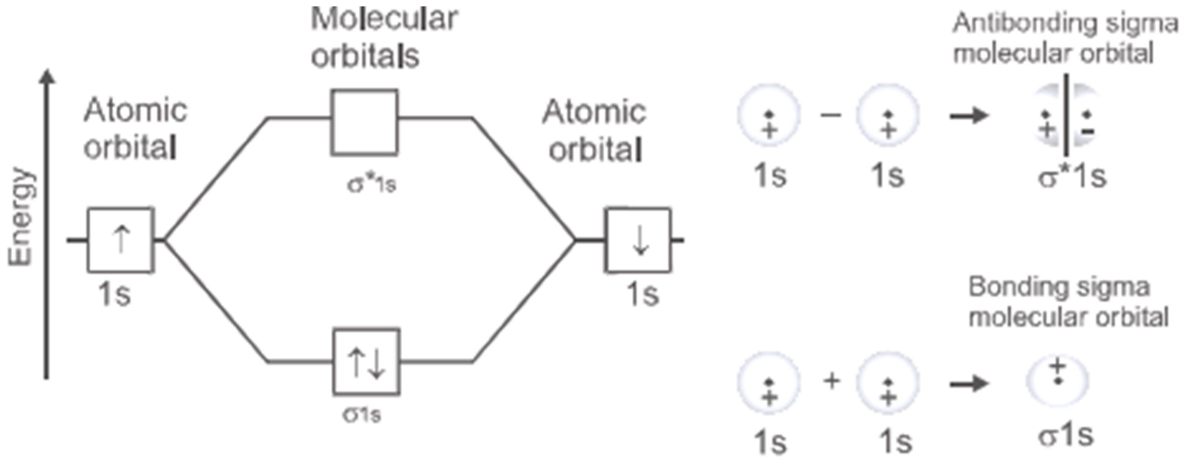


- Bond order = $\frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{1+2+1+1}{4} = 5/4$

Steric number	Types of Hybridisation	Geometry	Involving orbitals
2	sp	Linear	ns, np_x / p_z / p_y
3	sp^2	Trigonal planar	ns, np_x, p_z / p_y, p_z/p_x . p_y
4	sp^3	Tetrahedral	ns, np_x, p_z , p_y
5	sp^3d	Trigonal bipyramidal	ns, np_x, p_z, p_y, d_{z^2}
6	sp^3d^2	Octahedral	ns, np_x, p_z, p_y, $d_{z^2} d_{x^2-y^2}$
7	sp^3d^3	Pentagonal bipyramidal	ns, np_x, p_z, p_y, $d_{z^2} d_{x^2-y^2}$, d_{xy}

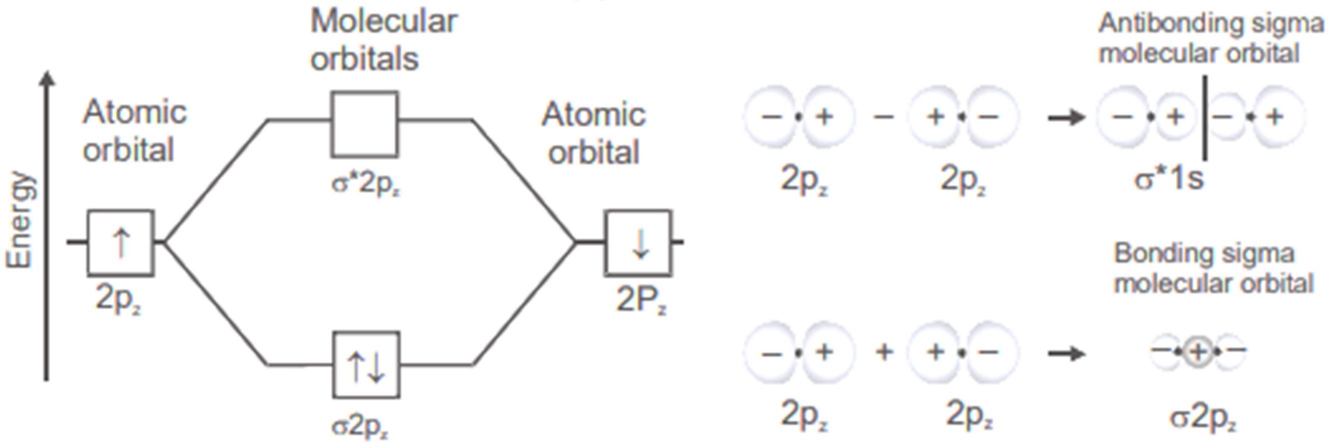
General formula type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples	
AB_2E	2	1		Bent	SO_2, O_3	
AB_3E	3	1		Trigonal Pyramidal	NH_3	
AB_2E_2	2	2		Bent	H_2O	
AB_4E	4	1		See saw	SF_4	
AB_3E_2	3	2		T–shape	ClF_3	
AB_5E	5	1		Square Pyramidal	$XeOF_4$	
AB_4E_2	4	2		Square Planar	XeF_4	
AB_5E_2	5	2		Pentagonal Planar	XeF_5^-	

Shapes of Molecules containing Bond Pair and Lone Pair



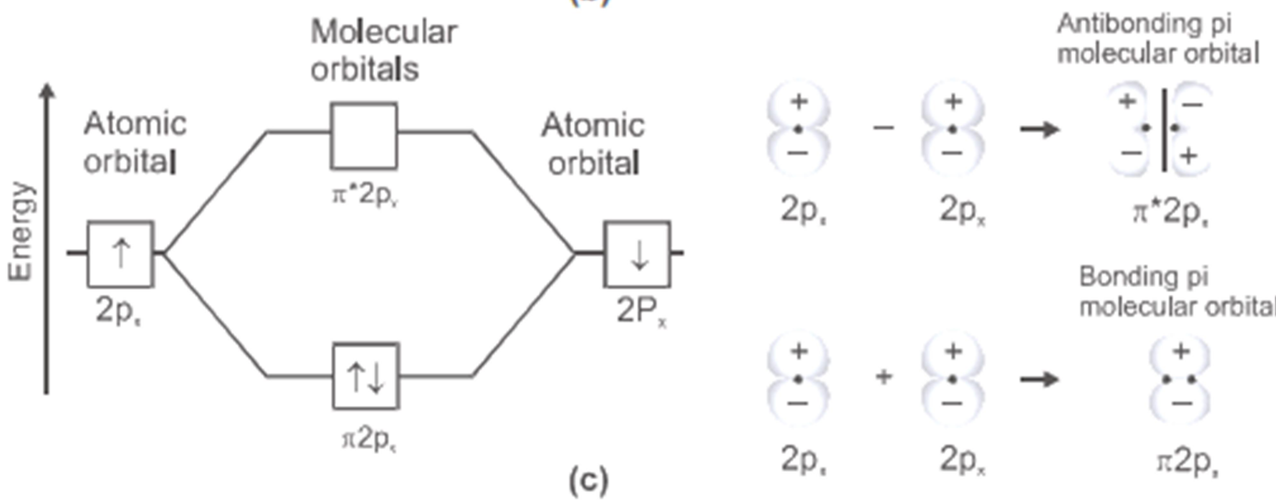
Molecular orbitals
Energy
Atomic orbital
Atomic orbital
σ*1s
σ1s
1s
1s
Antibonding sigma molecular orbital
1s
1s
σ*1s
Bonding sigma molecular orbital
1s
1s
σ1s

(a)



Molecular orbitals
Energy
Atomic orbital
Atomic orbital
σ*2pz
σ2pz
2pz
2Pz
Antibonding sigma molecular orbital
2pz
2pz
σ*1s
Bonding sigma molecular orbital
2pz
2pz
σ2pz

(b)



Molecular orbitals
Energy
Atomic orbital
Atomic orbital
π*2px
π2px
2px
2Px
Antibonding pi molecular orbital
2px
2px
π*2px
Bonding pi molecular orbital
2px
2px
π2px

(c)