

CHEMISTRY



Geometry and Shapes of Molecules

VSEPR Theory

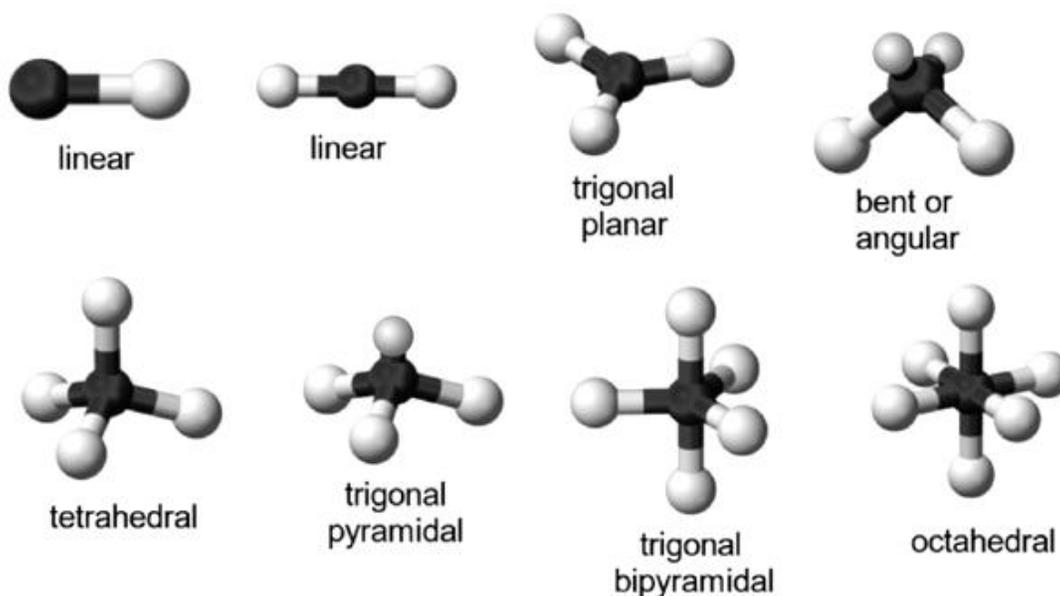
The Lewis concept is unable to explain the shapes of molecules. Sidgwick and Powell (1940) provided a useful idea for predicting shapes and geometries of molecules. The theory was based on the repulsions between electron pairs, known as **valence shell electron pair repulsion (VSEPR) theory**.

Postulates of this theory:

- In polyatomic molecules which contain three or more atoms, one of the atoms is called the central atom to which the other atoms are linked.
- The geometry of a molecule is dependent on the total number of valence shell electron pairs (bonded or not bonded) present around the central atom and their repulsion because of relative sizes and shapes.
- If the central atom is surrounded by bond pairs only, then it gives a symmetrical shape to the molecule.
- If the central atom is surrounded by a lone pair (lp) and bond pair (bp), then the molecule has a distorted geometry.
- The relative order of repulsion between electron pairs is $lp-lp > lp-bp > bp-bp$.
- A lone pair is concentrated around the central atom, while a bond pair is pulled out between two bonded atoms. As such repulsion becomes greater when a lone pair is involved.

e ⁻ Pairs	Notation	Name of VSEPR shape	Examples	Reason for the acquired shape
2	AX ₂	Linear	HgCl ₂ , ZnI ₂ , CS ₂ , CO ₂	
3	AX ₃	Trigonal planar	BF ₃ , GaI ₃	
	AX ₂ E	Non-linear	SO ₂ , SnCl ₂	Theoretically, the shape should have been triangular planar, but actually it is bent or v-shaped. The reason being the lone pair–bond pair repulsion is much more as compared to the bond pair–bond pair repulsion. So, the angle is reduced to 119.5° from 120°.
4	AX ₄	Tetrahedral	CCl ₄ , CH ₄ , BF ₄ ⁻	
	AX ₃ E	Trigonal pyramidal	NH ₃ , OH ₃ ⁻	Had there been a bp instead of a lp, the shape would have been tetrahedral; but one lone pair is present, and because of the repulsion between lp–bp (which is more than bp–bp repulsion), the angle between the bond pairs is reduced to 107° from 109.5°.

	AX_2E_2	Non-linear	H_2O , $SeCl_2$	The shape should have been tetrahedral if there were all bp, but two lp are present, so the shape is distorted tetrahedral or angular. This is because lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5° .
5	AX_5	Trigonal bipyramidal	PCl_5 , PF_5	
	AX_4E	Distorted tetrahedral	$TeCl_4$, SF_4	The lp is in an equatorial position, and there are two lp-bp repulsions. Hence, it is more stable.
	AX_3E_2	T-shaped	ClF_3 , BrF_3	The lp is at an equatorial position, so there are less lp-bp repulsions as compared to others in which the lp is at the axial position. So, a T-shaped structure is the most stable.
	AX_2E_3	Linear	I_3^- , ICl_2^-	
6	AX_6	Octahedral	SF_6 , PF_6^-	
	AX_5E	Square pyramidal	IF_5 , BrF_5	
	AX_4E_2	Square planar	ICl_4^- , BrF_4^-	



Valence Bond Theory

Valence bond theory (VBT) is a straightforward extension of Lewis structures. VBT was introduced by Heitler and London (1927) and developed further by Pauling and others. Valence bond theory says that electrons in a covalent bond reside in a region which is at the overlap of individual atomic orbitals.

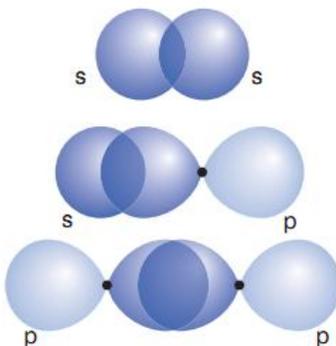
Postulates of valence bond theory:

- To form a covalent bond, two atoms must come close to each other so that the orbitals of one overlap with the other. When the two atoms are at a large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.
- Orbitals having unpaired electrons of anti-spin overlaps with each other. Greater the overlap, stronger is the bond formed between two atoms. Therefore, according to the orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell with opposite spins.
- After overlapping, a new localised bond orbital is formed which has maximum probability of finding electrons.
- A covalent bond is formed because of electrostatic attraction between radii and the accumulated electrons cloud and by attraction between spins of anti-spin electrons.
- Greater is the overlapping, lesser will be the bond length, more will be the attraction and more will be the bond energy and the stability of the bond will also be high.
- The extent of overlapping depends on the nature of orbitals involved in overlapping and the nature of overlapping.
- Closer the valence shells to the nucleus, more will be the overlapping and the bond energy will also be high.
- Between two subshells of the same energy level, the subshell more directionally concentrated shows more overlapping. Bond energy: $2s-2s < 2s-2p < 2p-2p$
- s-Orbitals are spherically symmetrical and thus show only head-on overlapping. On the other hand, p-orbitals are directionally concentrated and thus show either head-on overlapping or lateral overlapping. Overlapping of different types gives sigma (σ) and π (p) bonds.

Types of overlap

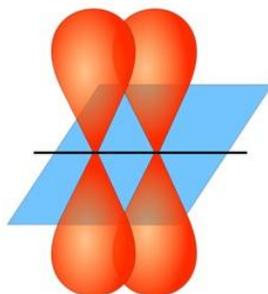
- **Sigma (σ) bond:**

The covalent bond formed because of overlapping of atomic orbitals along the internuclear axis is called the σ -bond. It is a stronger bond and cylindrically symmetrical. All sigma bonds have axial symmetry. A sigma bond is formed by s-s, s- p_z and p_z - p_z overlap.



- Pi (π) bond:**

The covalent bond formed by sidewise overlapping of atomic orbitals is called π -bond. In this bond, the electron density is present above and below the internuclear axis. It is relatively a weaker bond because the electrons are not strongly attracted by the nuclei of bonding atoms. If the Z axis is assumed to be the molecular axis, then the π -bond is given by p_x-p_x and p_y-p_y .



Differences between sigma and pi bonds

Sigma (σ) bond	Pi (π) bond
It results from the end-to-end overlapping of two s-orbitals or two p-orbitals or one s and one p-orbital.	It results from the sidewise (lateral) overlapping of two p-orbitals.
It is strong.	Less strong compared to the sigma bond.
It is stable.	Less stable compared to the sigma bond.
It is less reactive.	More reactive compared to the sigma bond.
The electron cloud is symmetrical about the internuclear axis.	The electron cloud is above and below the plane of the internuclear axis.