

### ❖ $d\pi-p\pi$ Bonds

This is a special type of bonding found in the molecular species having a central atom with  $d$  or  $p$  valence shell and surrounding groups with empty, partially or completely filled  $p$  or  $d$  orbitals. In addition to direct overlap resulting in the  $\sigma$ -bonding,  $d\pi-p\pi$  bonds are formed by the sidewise overlap. The exact nature of the orbitals from central atom participating in the formation of  $d\pi-p\pi$  bond can be obtained by resolving the irreducible components of the reducible representation based upon the vectors-set perpendicular to the  $\sigma$ -bonds for a particular geometry.

#### ➤ *Molecules with Central Atom Having $d$ -Valence Shell for Sidewise Overlap*

Some of the most well-documented cases in main-group chemistry are  $AB_4$  type molecules like  $SiO_4^{4-}$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $ClO_4^-$ ,  $SiF_4$ ; which are found to have A–O bond lengths too short for the single bond confirming a  $d\pi-p\pi$  overlap responsible for this anomaly.

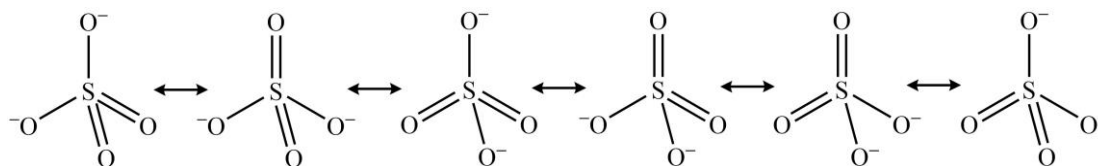


Figure 21. The  $d\pi-p\pi$  bonding in  $SO_4^{2-}$  ion.

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The character table for  $T_d$  point group is given below.

$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
$A_1$	1	1	1	1	1		$x^2 + y^2 + z^2$
$A_2$	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 + y^2, x^2 - y^2)$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$	
$T_2$	3	0	-1	-1	1	$(x, y, z)$	$(xy, xz, yz)$

The reducible representation based upon the  $s$ ,  $p$  and  $d$  orbitals of the central atom in tetrahedral geometry is:

Table 1. Reducible representation based on  $s$ ,  $p$  and  $d$  orbitals.

$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_\pi$	9	0	1	-1	3

Resolving the reducible into irreducible components, the symmetry designations of different orbitals of the central atom taking part in tetrahedral overlap are given below:

$s$	$a_1$
$p_x, p_y, p_z$	$t_2$
$d_{xy}, d_{xz}, d_{yz}$	$t_2$
$d_z^2, d_{x^2-y^2}$	$e$

The symmetry adapted linear combinations of atomic orbitals (SALCs) of surrounding groups for sidewise overlap can be obtained just by resolving the reducible representation based on the displacement vectors perpendicular to the axis of  $\sigma$  overlap.

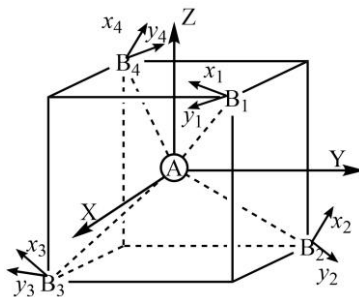


Figure 22. The  $\pi$ -basis set for ligand orbitals in tetrahedral molecules.

The symmetry adapted linear combinations of these fall into two triply and one doubly degenerate irreducible representations labeled as  $e$ ,  $t_1$  and  $t_2$ . The symmetry designations of different ligand orbitals taking part in sidewise overlap in tetrahedral molecules can be given as:

Table 2. Reducible representation based on perpendicular vectors in a tetrahedral geometry.

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Irreducible components
$\Gamma_\pi$	8	-1	0	0	0	$e + t_1 + t_2$

Two of these aforementioned sets are of  $e$  and  $t_2$  symmetry. The  $d_{x^2-y^2}$  and  $d_z^2$  orbitals set on the metal also have  $e$ -symmetry, and therefore the  $\pi$ -overlap between a central atom and four ligands is possible as far as the generation of molecular orbitals with  $e$ -symmetry is concerned. Moreover,  $p_x$ ,  $p_y$ ,  $p_z$  and  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  set are of  $t_2$  symmetry, and therefore, can take part in sidewise overlap. However, the  $p$ -subshell largely engaged in  $\sigma$ -bonding and therefore has little or no contribution. While the transition metals show a tendency to use their  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals for  $d\pi-p\pi$  interactions in octahedral complexes, the main group elements primarily use  $d_{x^2-y^2}$  and  $d_z^2$  as they generally form tetrahedral complexes. The primary reason for this selective behavior is that these two orbitals yield  $\sqrt{3}$  times higher  $d\pi-p\pi$  overlap than that of  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ . The general scheme for  $d\pi-p\pi$  overlap for main group compounds with tetrahedral geometry is shown in 'Figure 23'.

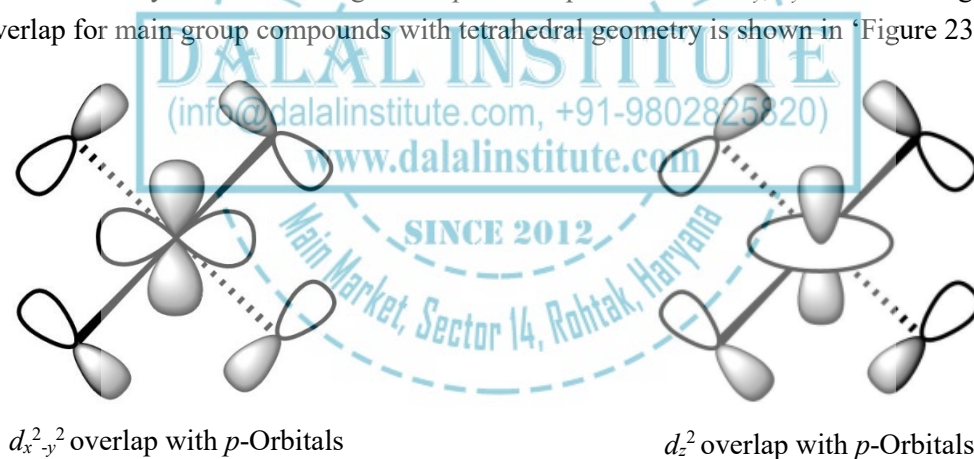


Figure 23. The overlap mechanism for the  $d\pi-p\pi$  interactions when the central atom has valence  $d$ -orbitals.

Apart from the tetrahedral molecules, some less symmetrical main group compounds are also found to have  $d\pi-p\pi$  interactions. Although the exact nature of these interactions is quite difficult to analyze as the lowering of symmetry makes the  $d$ -subshell of central atom susceptible to the surrounding groups to a different extent yet the inverse variation of bond length with bond order may be used to approximate the extent of  $d\pi-p\pi$  overlap. Quantum mechanical calculations have also shown that significant  $d\pi-p\pi$  interaction is present in molecules like  $SO_2F_2$ ,  $PF_3O$ ,  $ClO_3F$ ,  $ClO_2^-$ ,  $ClO_3^-$ .

➤ **Molecules with Central Atom Having  $p$ -Valence Shell for Sidewise Overlap**

Sometimes, the existence of  $d\pi-p\pi$  bonding can be viewed in terms of the molecular geometry. For example,  $\text{Si}_3\text{N}$  and  $\text{Ge}_3\text{N}$  skeleton is planar in  $(\text{H}_3\text{Si})_3\text{N}$ ,  $(\text{H}_3\text{Ge})_3\text{N}$  and  $\text{Si/Ge-N}$  bond length is somewhat shorter than what is expected for a single bond. This can be explained by assuming that the electron density from  $\text{N}(2p_z)$  is overlapping with the  $3d$  orbitals of surrounding Si and Ge.

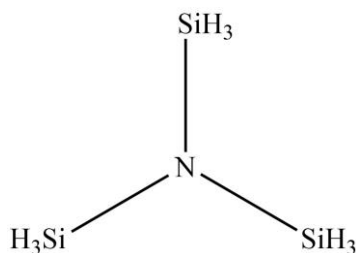


Figure 24. The  $d\pi-p\pi$  bonding in  $\text{N}(\text{SiH}_3)_3$  molecule.

The character table for the  $D_{3h}$  point group is given below.

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	1	1	1	1	1	1	$x^2 + y^2, z^2$
$A_2'$	1	1	-1	1	1	-1	$R_z$
$E'$	2	-1	0	2	-1	0	$(x, y)$
$A_1''$	1	1	1	-1	-1	-1	
$A_2''$	1	1	-1	-1	-1	1	$z$
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$

The reducible representation based on the  $s$ ,  $p$  and  $d$  orbitals of the central atom in trigonal planar geometry is:

Table 3. Reducible representation based on  $s$ ,  $p$  and  $d$  orbitals.

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$
$\Gamma_\pi$	9	0	1	3	0	3

Resolving the reducible into irreducible components, the symmetry designations of different orbitals of the central atom taking part in trigonal planar overlap are:

$s$	–	$a_1'$
$p_z$	–	$a_2''$

$p_x, p_y$	–	$e'$
$d_z^2$	–	$a_1'$
$d_{xy}, d_{x^2-y^2}$	–	$e'$
$d_{xz}, d_{yz}$	–	$e''$

The symmetry adapted linear combinations of atomic orbitals (SALCs) of surrounding groups for sidewise overlap can be obtained just by resolving the reducible representation based on the displacement vectors perpendicular to the axis of  $\sigma$ -overlap.

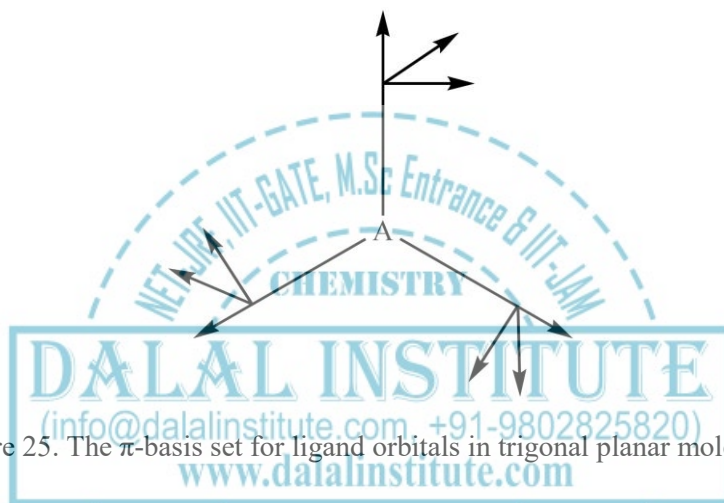


Figure 25. The  $\pi$ -basis set for ligand orbitals in trigonal planar molecules.

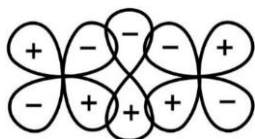
The symmetry adapted linear combinations of these fall into two singly and two doubly degenerate irreducible representations labeled as  $a_2'$ ,  $e'$ ,  $a_2''$  and  $e''$ . The symmetry designations of different ligand orbitals taking part in sidewise overlap in trigonal planar molecules are:

Table 4. Reducible representation based on perpendicular vectors in trigonal planar geometry.

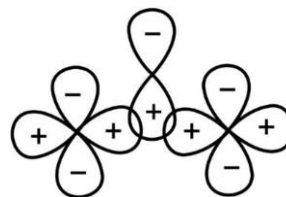
$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	Irreducible components
$\Gamma_\pi$	6	0	-2	0	0	0	$a_2' + e' + a_2'' + e''$

Three of these aforementioned sets are of  $a_2''$ ,  $e'$  and  $e''$  symmetry. The  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals set on the central atom also have  $e'$ -symmetry, while the  $d_{xz}$  and  $d_{yz}$  has  $e''$ -symmetry; therefore, the  $\pi$ -overlap between a central atom and the ligands is possible as far as the generation of molecular orbitals with  $e'$ - and  $e''$ -symmetry is concerned. Moreover,  $p_z$  orbital of the central atom is of  $a_2''$ -symmetry, and therefore, can also take part in sidewise overlap. Now though the symmetry allows the central atom to use  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  and  $p_z$ ; the overlap extent and energy criteria permits largely the  $p_z$  to do sidewise overlap.

However, the presence of partially filled  $p_z$  orbital of the central atom is prone to overlap with the empty  $d$ -subshell of surrounding groups yet it does not assure the sufficient  $d\pi-p\pi$  bonding leading to a planar structure in all cases. The Si–A–Si bond angles in  $\text{P}(\text{SiH}_3)_3$  and  $\text{As}(\text{SiH}_3)_3$  are  $96.5^\circ$  and  $93.8^\circ$  respectively and both of these compounds exist as pyramidal geometry like  $\text{P}(\text{GeH}_3)_3$  does. This is due to the fact that  $3p_z$  orbitals of P and As do not overlap with  $d$ -orbitals as efficiently as in the case of  $2p_z$  orbital of N atom. Furthermore,  $\text{S}(\text{SiH}_3)_2$  is bent with a Si–A–Si bond angle of  $98^\circ$  resembling its tri-coordinated pyramidal analogs in terms of  $d\pi-p\pi$  overlap. However,  $(\text{H}_3\text{Si})_2\text{O}$  is also bent in geometry with a bond angle of  $144^\circ$  but shows a small extent of  $d\pi-p\pi$  overlap which is also confirmed by the shortening of the Si–O bond length. The extent of  $d\pi-p\pi$  overlap is much larger in flat and linear geometries than that of bent ones.



$p_z$  overlap with  $d$ -Orbitals in linear molecules



$p_z$  overlap with  $d$ -Orbitals in bent molecules

Figure 26. The overlap mechanism for  $d\pi-p\pi$  interactions when the central atom has valence  $p$ -orbitals.

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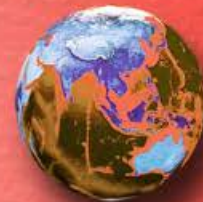
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# A TEXTBOOK OF INORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

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