

## ❖ $d\pi-p\pi$ Bonds

This is a special type of bonding found in the molecular species having a central atom with a vacant  $d$  orbital in its valence shell and surrounding groups with empty, partially or completely filled  $p$  or  $d$  orbitals. In addition to the direct overlap resulting in the  $\sigma$ -bonding,  $d\pi-p\pi$  bonds are formed by the sidewise overlap. The energy levels of the orbitals from central atom participating in the formation of  $d\pi-p\pi$  bond can be obtained by reducing the irreducible components of the reducible representation based upon the vectors-set perpendicular to the bond axis 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  $\text{SiO}_4^{4-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{ClO}_4^-$ ,  $\text{SiF}_4$ ; 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.

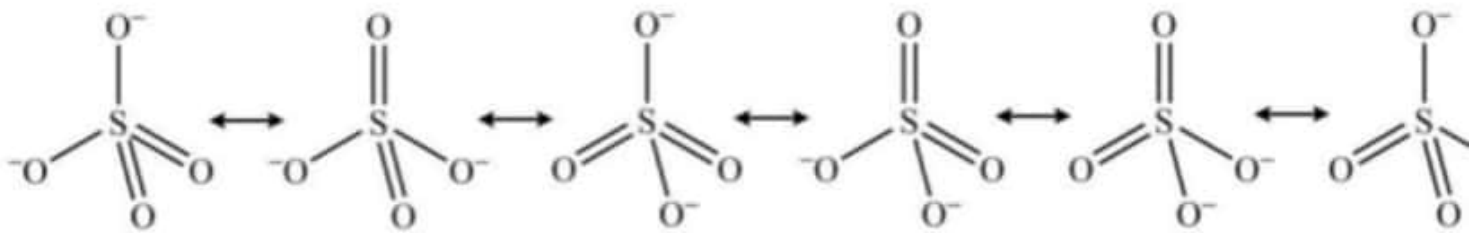
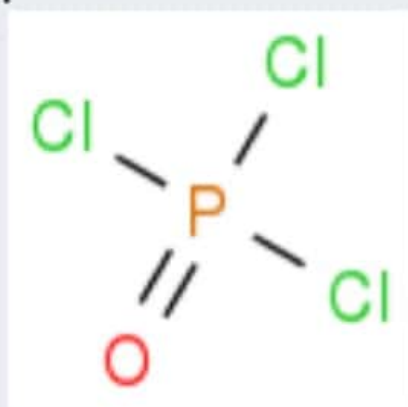


Figure 21. The  $d\pi-p\pi$  bonding in  $\text{SO}_4^{2-}$  ion.

Pi bonding refers to sidewise overlapping of orbitals . Therefore d-pi- p-pi refers to when one d orbital and p orbital of another atom overlap sidewise to form a pi bond .

Yes phosphorus shows  $d\pi - p\pi$  in  $\text{POCl}_3$  or similar

species .



$\text{POCl}_3$  is a  $sp^3$  hybridized , so 1 s and 3 p orbitals will be used for making sigma bonds . But there is still one pi bond between P and O , So d orbital of phosphorus will be used for sidewise overlapping with an p orbital of Oxygen .