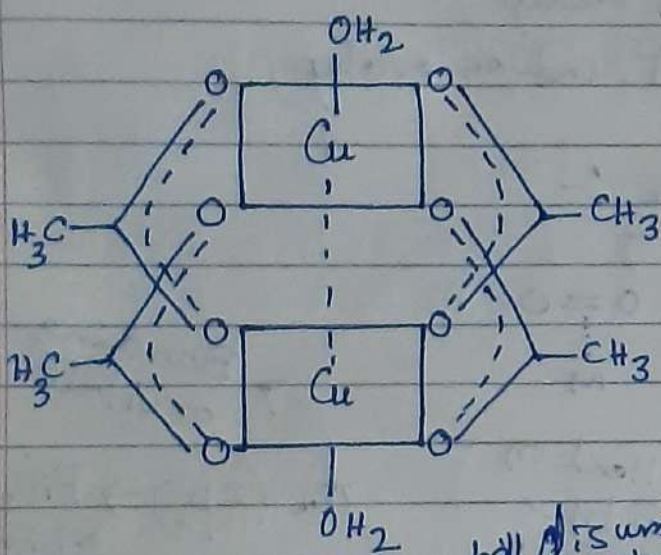


Thermodynamic & Kinetic aspect \Rightarrow
Activation of dioxygen through Complexes and orbital diagram for antiferromagnetic Coupling & Super exchange process

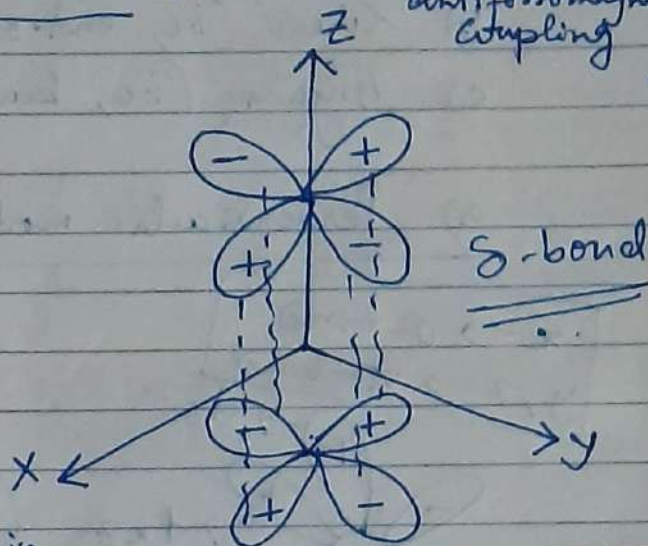
Some basic Concept of antiferromagnetic Coupling:-

- 1) Direct metal-metal interaction
- 11) Super exchange

1) Direct metal-metal interaction \Rightarrow



(mainly focusing on intramolecular antiferromagnetic coupling)

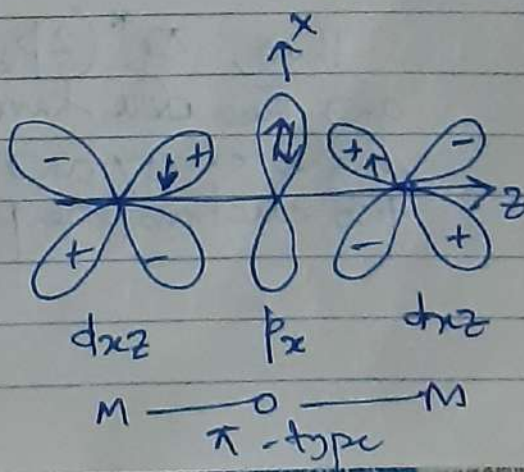
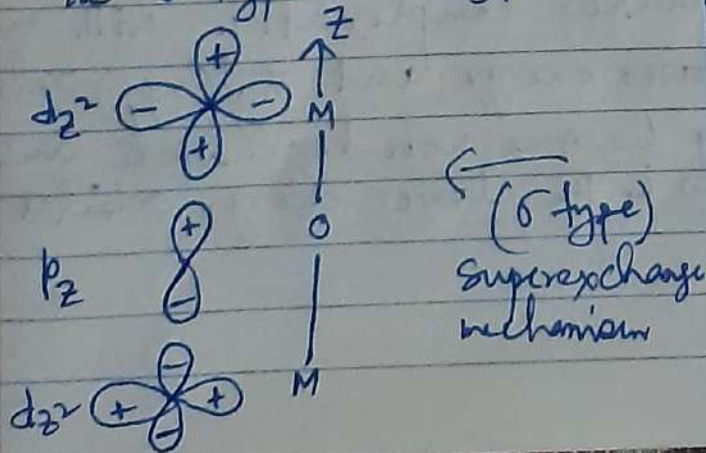


11) Superexchange \Rightarrow

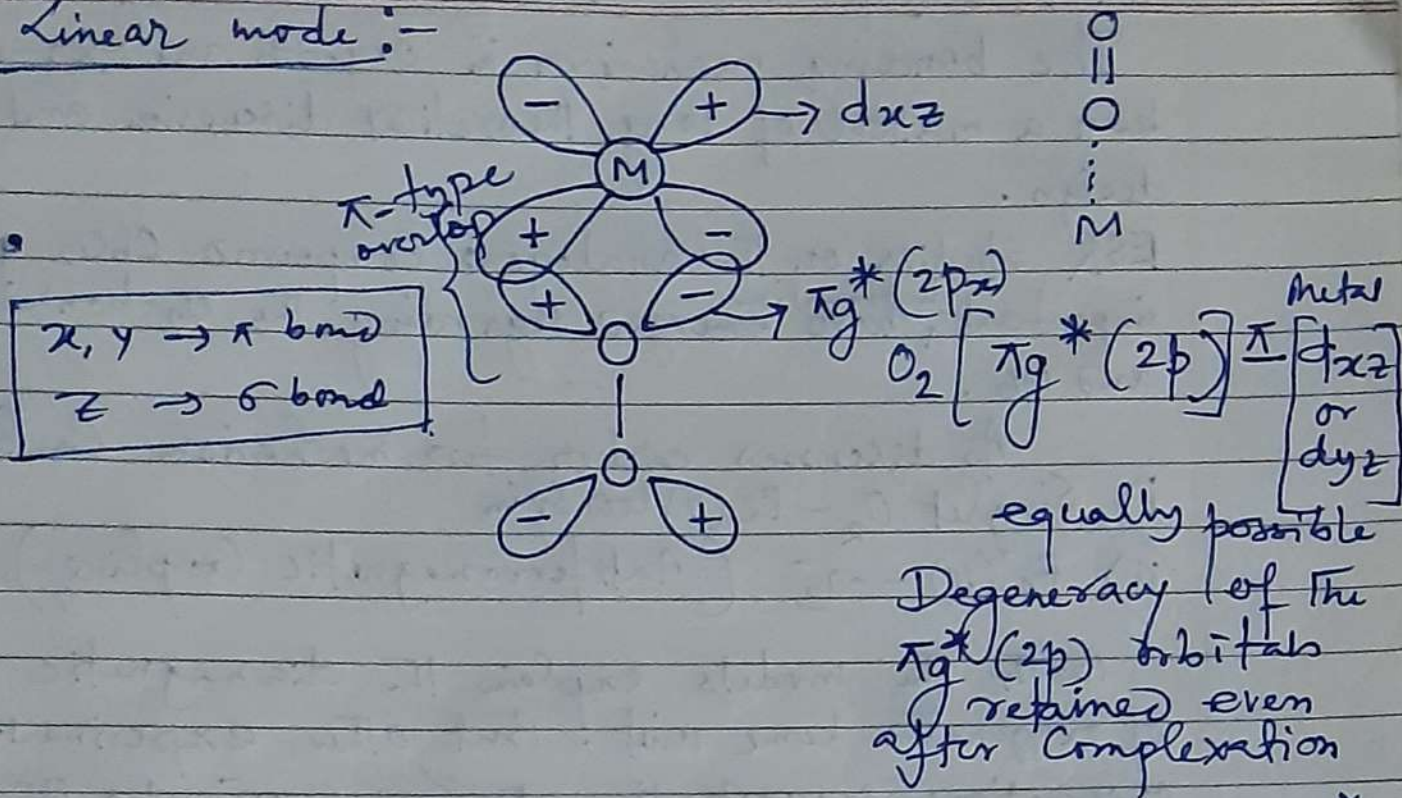
will discuss in details in next class

$d^3-d^3 \rightarrow 90^\circ$ Exchange Ferrromagnetic
 180° exchange Antiferromagnetic

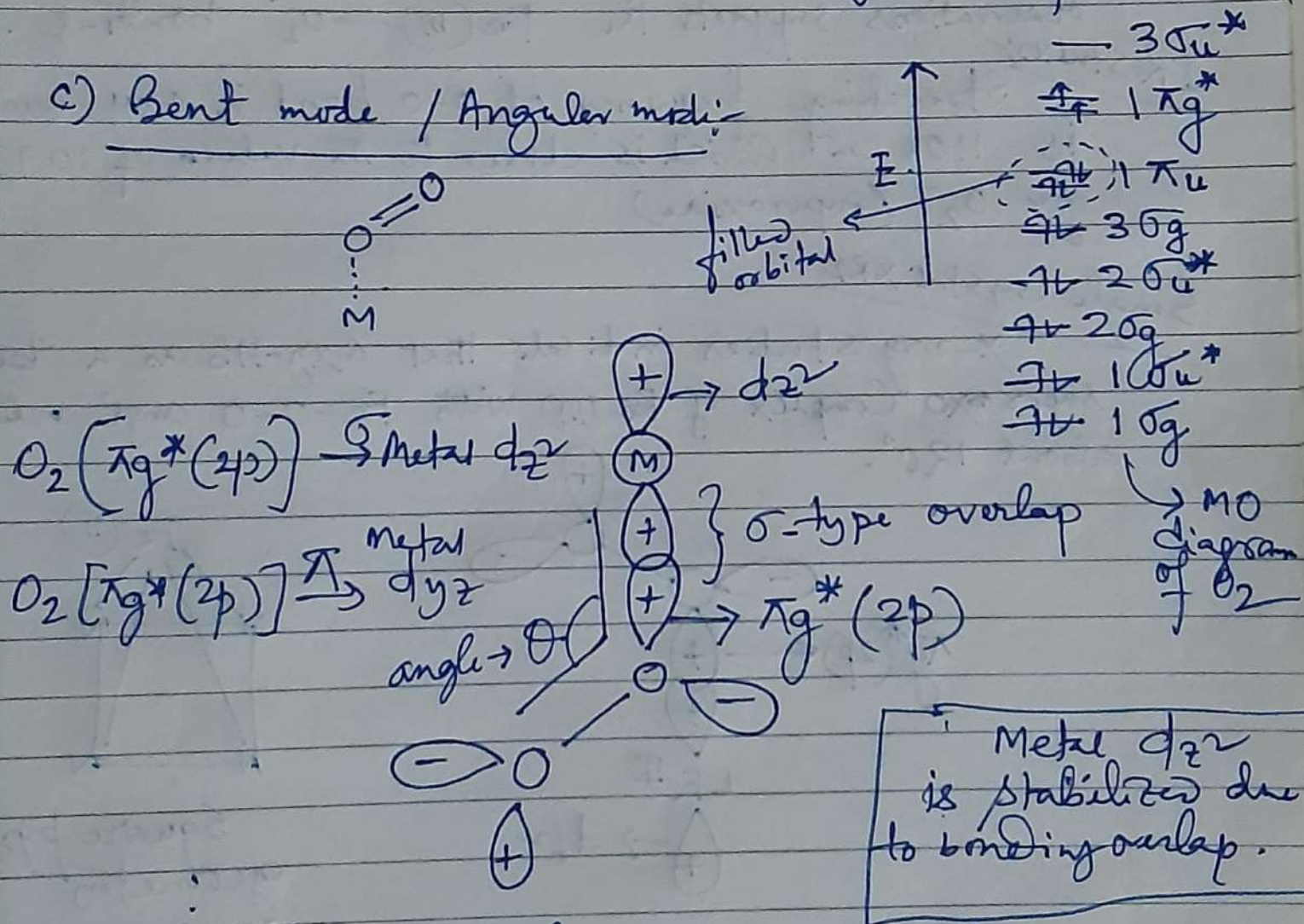
The indirect three atom exchange mechanism i.e., Superexchange, affords a suitable pathway for an antiferromagnetic interaction only when there is a joint overlap of suitable partially filled orbitals of two metal ions with a filled orbital of a ligand. The joint overlap may be of the σ type or π type.



b) Linear mode :-



c) Bent mode / Angular mode:-



This mode of overlap removes the degeneracy of $\pi^*(2p)$ orbitals of O_2 through Complexation.

Nature of Heme-Dioxygen bonding:-

The bonding mechanism in oxy-Hb and oxy-Mb has been a matter of long theoretical discussion and experimental design.

ESR studies on the analogous compound CVO_2 gives some important ^{information} have emerged regarding the O_2 -bonding to Hb and Mb.

As discussed earlier two mechanism can be possible.

- i) Singlet $\text{O}_2 - \text{Fe(II)}$ low spin
- ii) $\text{Fe(III)} - \text{O}_2^-$ (Antiferromagnetic Coupling)

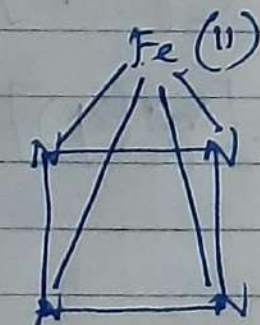
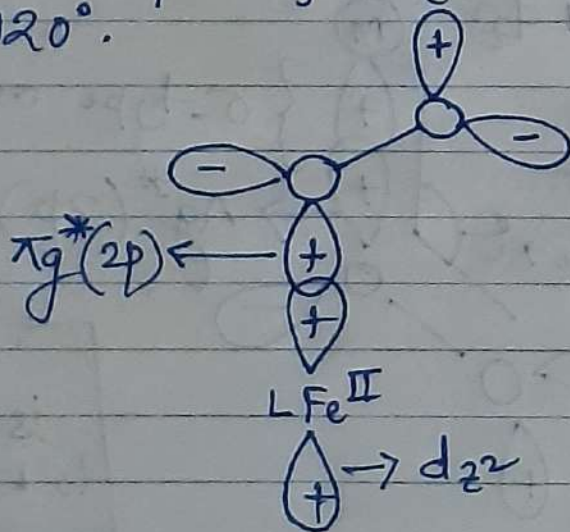
Both the models explain the diamagnetic character of oxygenated heme unit. But other experimental observations supports the $\text{Fe(III)} - \text{O}_2^-$ bonding.

IR Studies:-

Stretching frequency of O-O bond in oxy hemoglobin is 1106 cm^{-1} which is closer to the values of 1097 cm^{-1} for O_2^- (superoxide)

Single Crystal XRD:-

X-ray studies indicate that oxy-Hb as a bent superoxo complex of Fe(III) with Fe-O-O angle near about 120° .



Square pyramidal geometry

C_{4v} point group

When the degeneracy lost then the antibonding orbital electron configuration will be $\pi_g^{*2} \pi_g^{*0}$.

The MO of $LF\text{e}(O_2)$ adduct are enriched with π^* orbitals of O_2 .

Thus the flow of electrons from the metal center to the π^* orbital of O_2 .

Related topic :- (Next lecture) (2-3 lectures)

- Basic concept
- ① How $Fe(II)$ becomes low spin when $Fe(II)-O_2$ binds initially?
 - ② MO diagram of Heme- O_2 unit.
 - ③ Role of hemoglobin in pH balance & CO_2 transport
 - ④ Chemical & steric protection of Heme from irreversible oxidation — Role of Distal (E7) and Proximal (F8) histidine
 - ⑤ Chemistry of physiological buffers.
 - ⑥ Some interesting experimental proofs.
 - ⑦ Poisoning towards Hb & Mb.
- For exam preparation
- Basic concept
- Exam preparation

Next week onwards ~~exam~~ - Nitrogenase (4-5 lectures) Biological Nitrogen fixation
upto exam metals in medicine

- ① Introduction already discussed in class notes provided.

General Discussion (12th Standard)

classmate

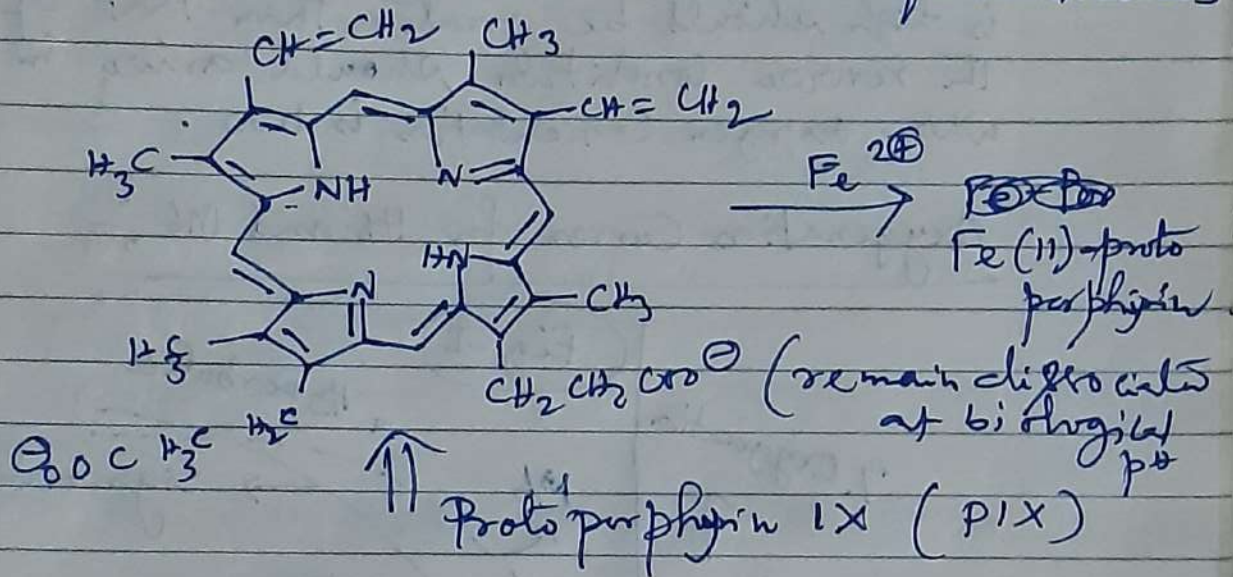
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Hemoglobin (Hb) and Myoglobin (Mb) in oxygen transport mechanism :-

⇒ Monomeric unit is myoglobin.

Hb & Mb use the Fe-protoporphyrin as the basic unit.

On oxygenation, the color changes as purple → red for Hb & Mb.
for vertebrates



Heme-b :-

