

**B.Sc. Semester-IV
Core Course-VIII (CC-VIII)
Inorganic Chemistry**



I. Coordination Chemistry

3. Crystal Field Theory

(A. Energy of 3d-orbitals in Octahedral Field)



Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi

Coordination Chemistry: 20 Lectures

Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of $10 Dq$ (Δ_o), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of $10 Dq$ (Δ_o , Δ_t). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

Coverage:

- 1. Crystal Field Theory**
- 2. Arrangements of d -orbitals in Octahedral Field**
- 3. Splitting of Energy Levels of d -orbitals in Octahedral Field**

Crystal Field Theory

Crystal field theory considers the effect of different ligand environments (ligand fields) on the energies of the d -orbitals.

The energies of the d - orbitals in different environments determines the magnetic and electronic spectral properties of transition metal complexes.

Crystal field theory assumes an electrostatic model of metal-ligand interactions.

Relative Energies of metal-ion 3d electrons

- Because the $4s^2$ electrons are lost before the $3d$, the highest occupied molecular orbitals (HOMOs) in transition metal complexes will contain the $3d$ electrons.

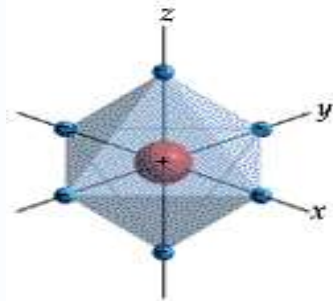
M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

- The distribution of the $3d$ electrons between the d -orbitals in any given complex will determine the magnetic properties of the complex (the number of unpaired electrons, the total spin (S) and the magnetic moment of the complex).
- Electronic transitions between the highest occupied d -orbitals will be responsible for the energies (λ_{\max}) and intensities (ϵ) of the $d-d$ bands in the electronic spectra of metal complexes.

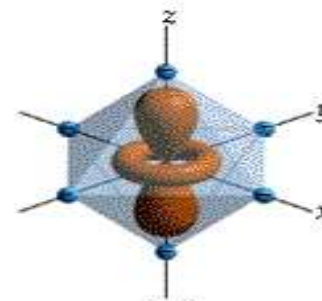
Crystal Field Theory



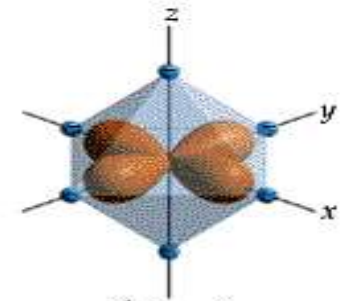
- The relationship between colors and complex metal ions



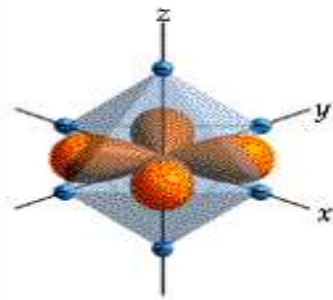
(a)



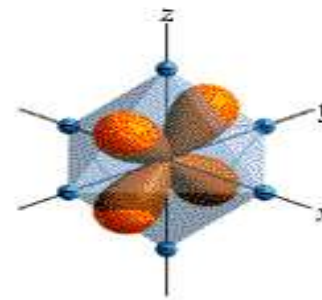
d_{z^2}
(b)



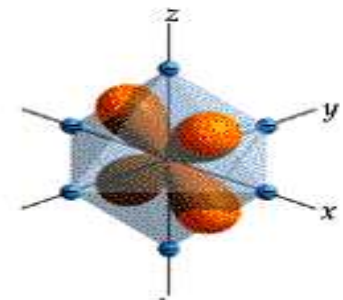
$d_{x^2-y^2}$
(c)



d_{xy}
(d)



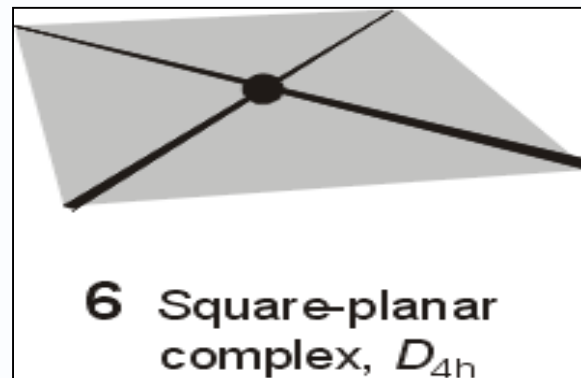
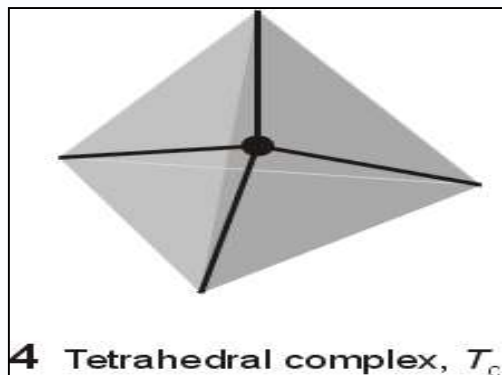
d_{yz}
(e)



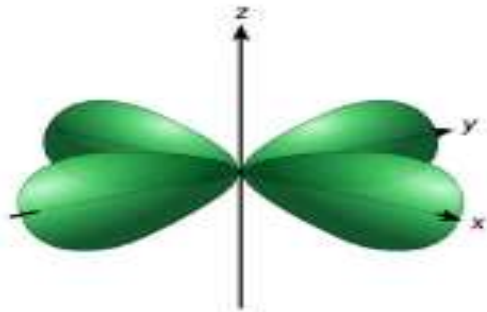
d_{xz}
(f)

Crystal Field Model

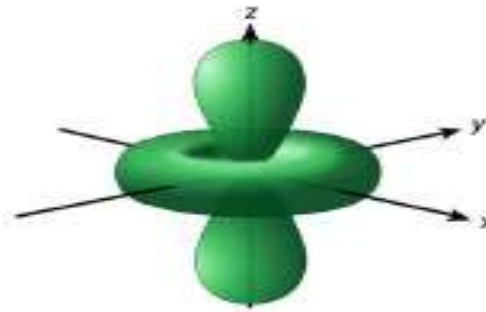
- A purely *ionic* model for transition metal complexes.
- Ligands are considered as point charge.
- Predicts the pattern of splitting of d-orbitals.
- Used to rationalize spectroscopic and magnetic properties.



d-orbitals: look attentively along the axis

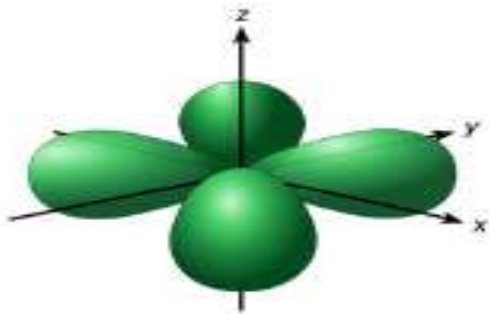


$d_{x^2-y^2}$

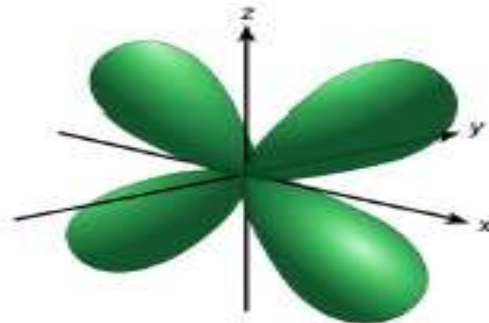


d_{z^2}

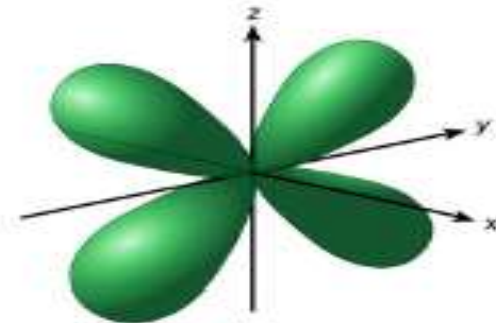
Linear combination of $d_z^2-d_x^2$ and $d_z^2-d_y^2$
 $d_{2z^2-x^2-y^2}$



d_{xy}

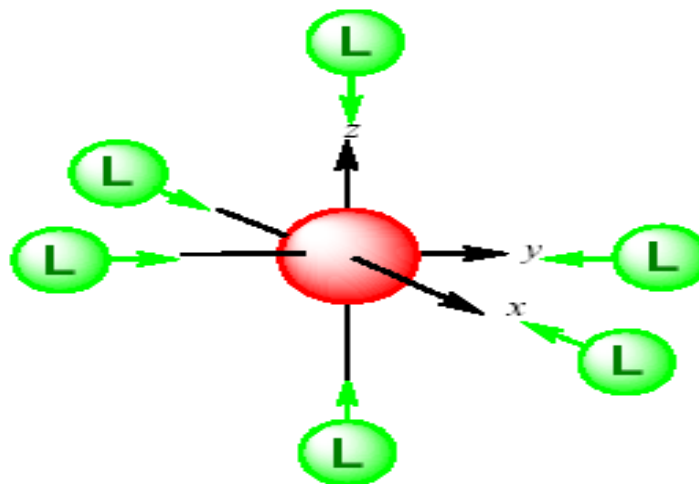


d_{xz}



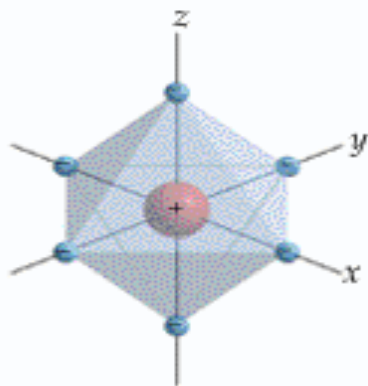
d_{yz}

Octahedral Field

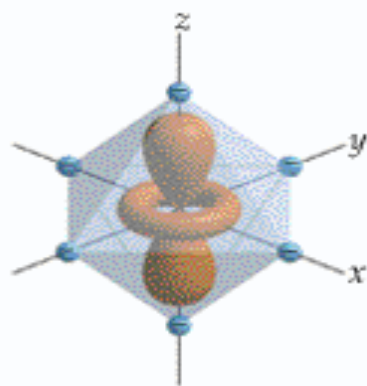


- We assume an octahedral array of negative charges placed around the metal ion (which is positive).
- The ligand and orbitals lie on the same axes as negative charges.
 - Therefore, there is a large, unfavorable interaction between ligand (-) and these orbitals.
 - These orbitals form the degenerate high energy pair of energy levels.
- The d_{xy} , d_{yz} and d_{xz} orbitals bisect the negative charges.
 - Therefore, there is a smaller repulsion between ligand and metal for these orbitals.
 - These orbitals form the degenerate low energy set of energy levels.

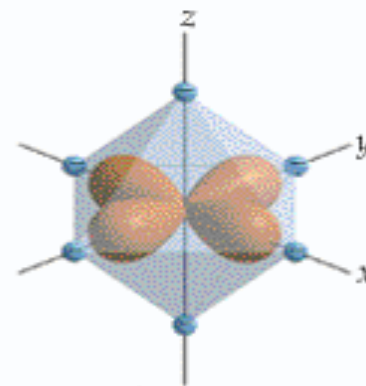
Arrangements of d -Orbitals in Octahedral Field



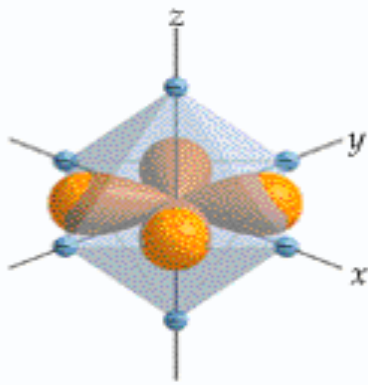
(a)



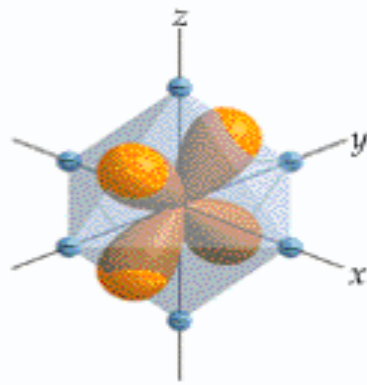
d_{z^2}
(b)



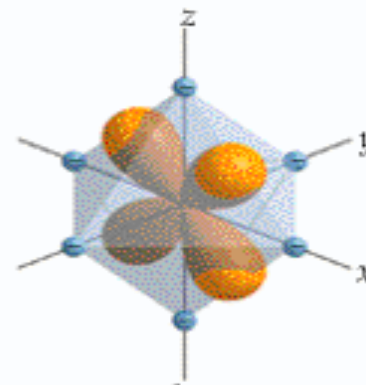
$d_{x^2-y^2}$
(c)



d_{xy}
(d)

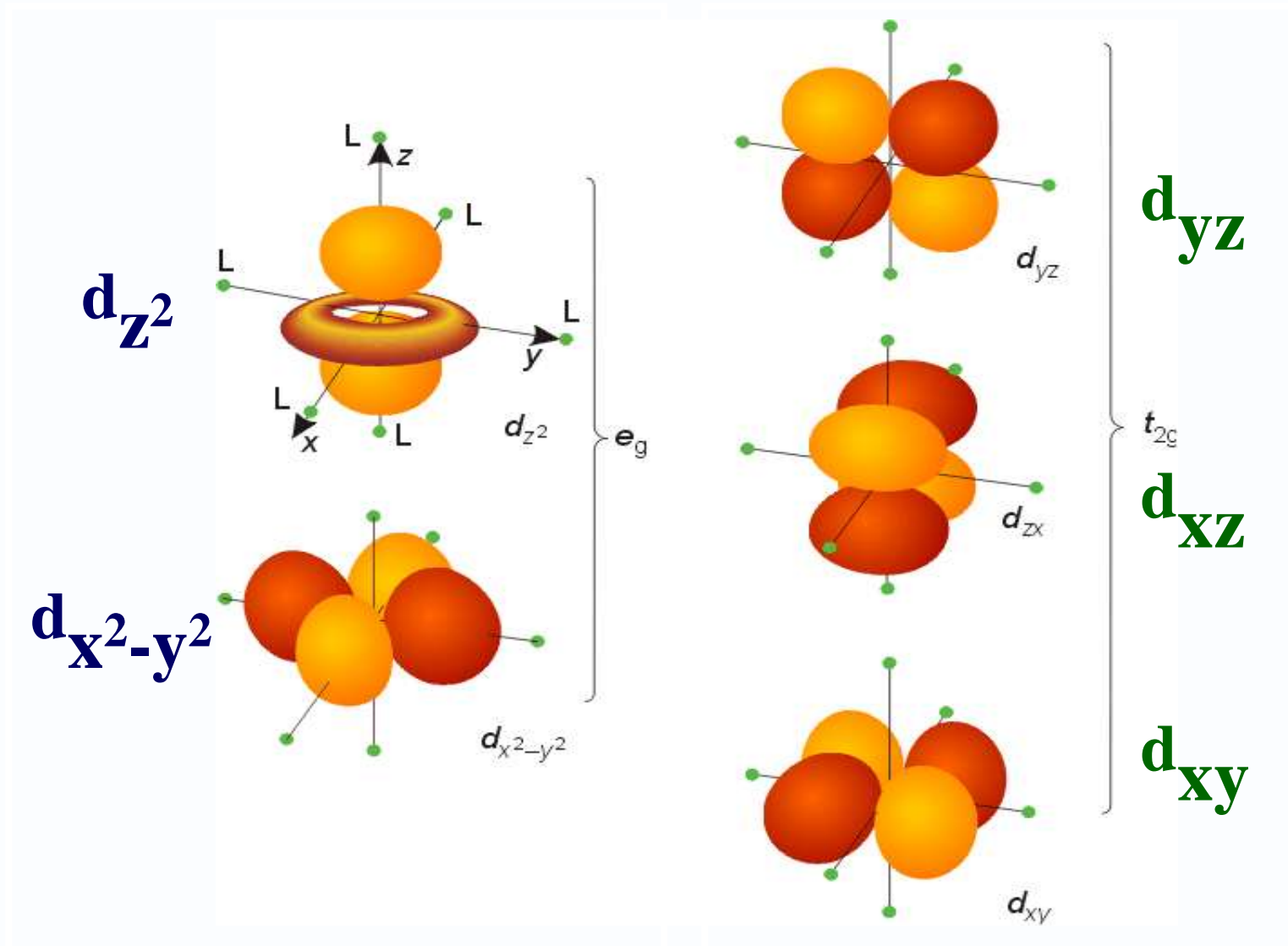


d_{yz}
(e)

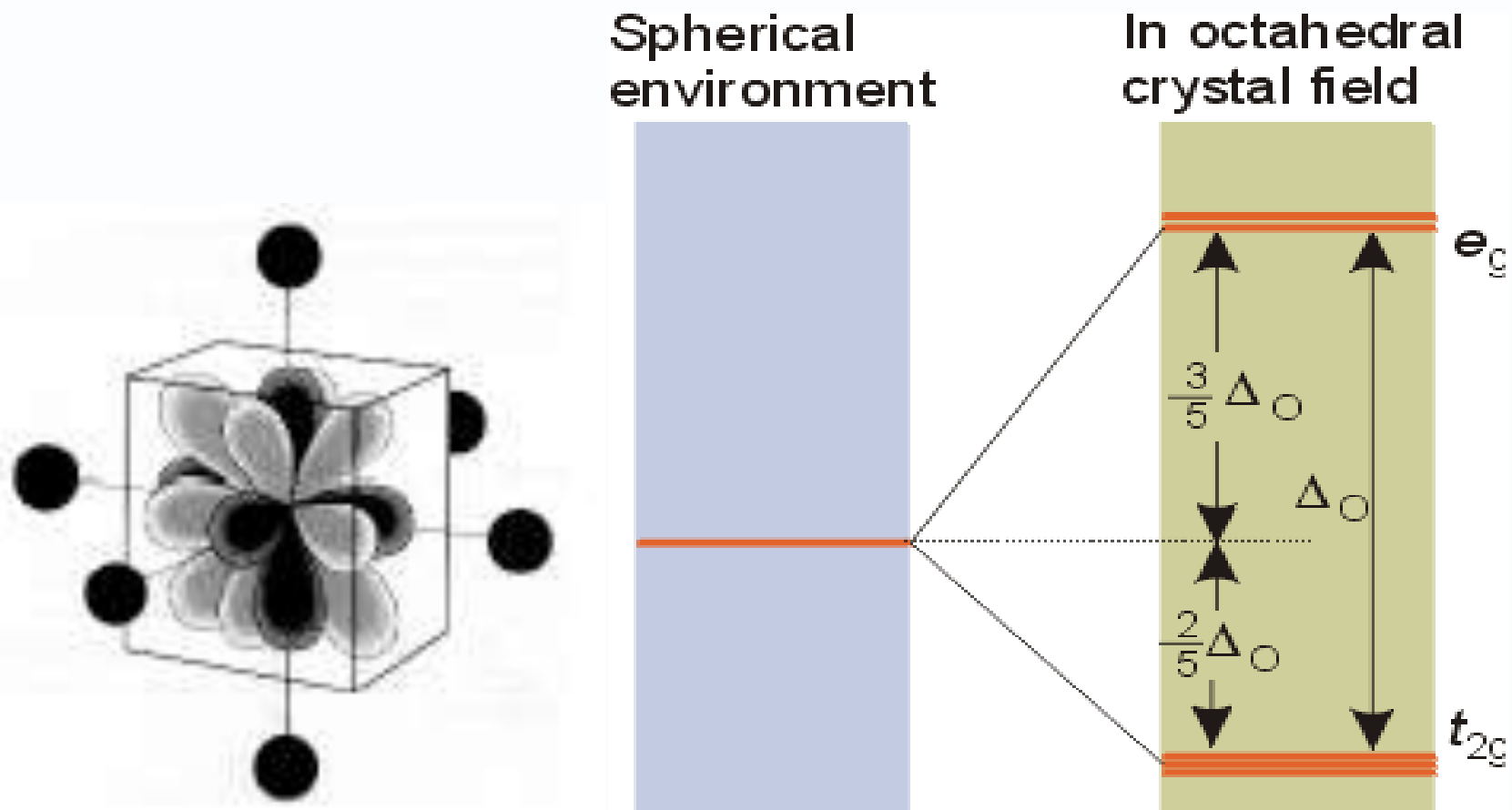


d_{xz}
(f)

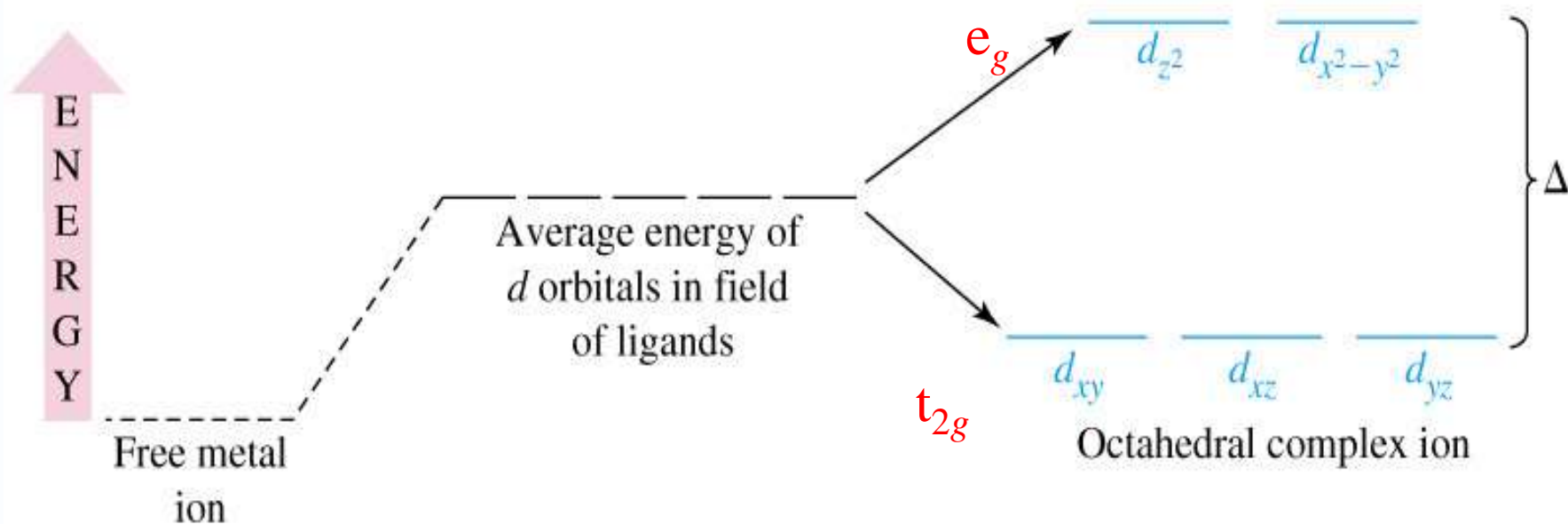
Arrangements of d -Orbitals in Octahedral Field



Splitting of Energy Levels of d -Orbitals in Octahedral Field



Energy of 3d orbitals in Octahedral field



Thank You



Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi