



INTERNATIONAL COLLEGE
OF PHARMACEUTICAL
INNOVATION

国际创新药学院

Fundamentals of Medicinal and Pharmaceutical Chemistry

FUNCHEM.12 Biocoordination Chemistry II

Professor Dan Wu

DATE: 1st November 2024

Learning outcomes

At the end of this lecture, the learner will be able to

- Recall the shapes of the metal ion d orbitals.
- Explain crystal field theory.
- Recall d orbital splitting in an octahedral complex.
- Define 'd orbital splitting energy'.
- Explain high spin and low spin complexes.
- Explain paramagnetic and diamagnetic.

Recommended reading

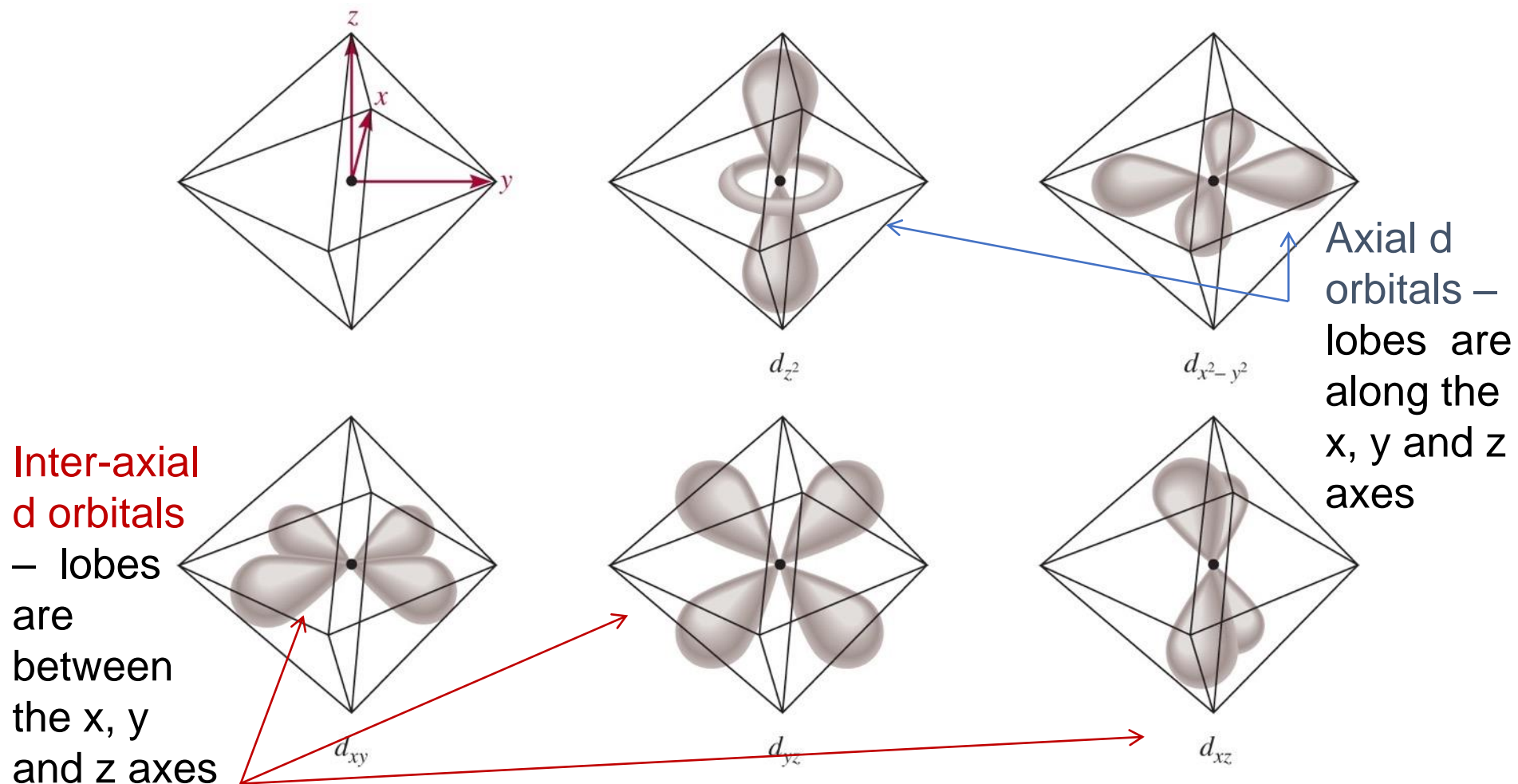
- General Chemistry - The Essential Concepts by Chang and Goldsby 7e
 - Chapter 20
 - Chapter 10, Section 10.1 on molecular geometry

Crystal Field Theory – a theory that describes bonding in transition metal complexes

Basic assumption:

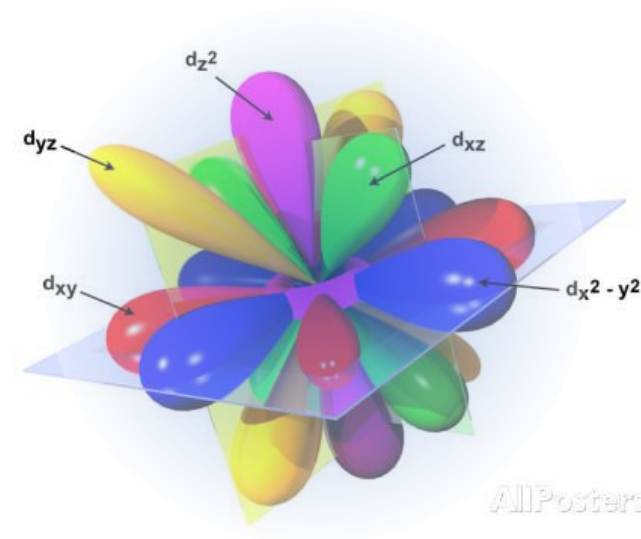
- Electrostatic (+/-) interaction between ligand (-) and metal (+)
– *provides stability*
- The ligands are regarded as point negative charges
- The lone pair of electrons on ligands are repulsed by electrons in metal d orbitals

Crystal Field Theory – Take a closer look at the d-orbitals

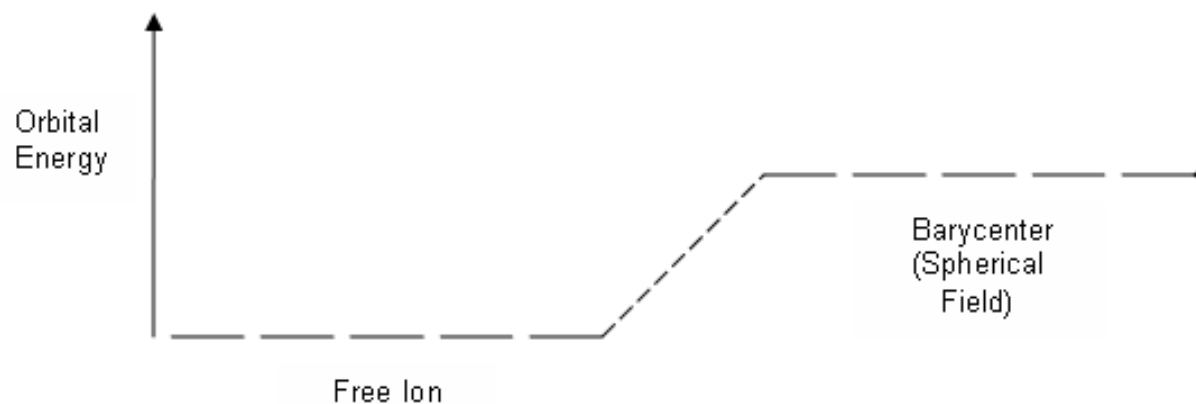


d orbitals are of equal energy – we say they are degenerate

Imagine ligands approaching the
metal d orbitals in a symmetrical field
+/- attraction
-/- repulsion



This -/- repulsion will raise the energy of the
d orbitals but to the same extent



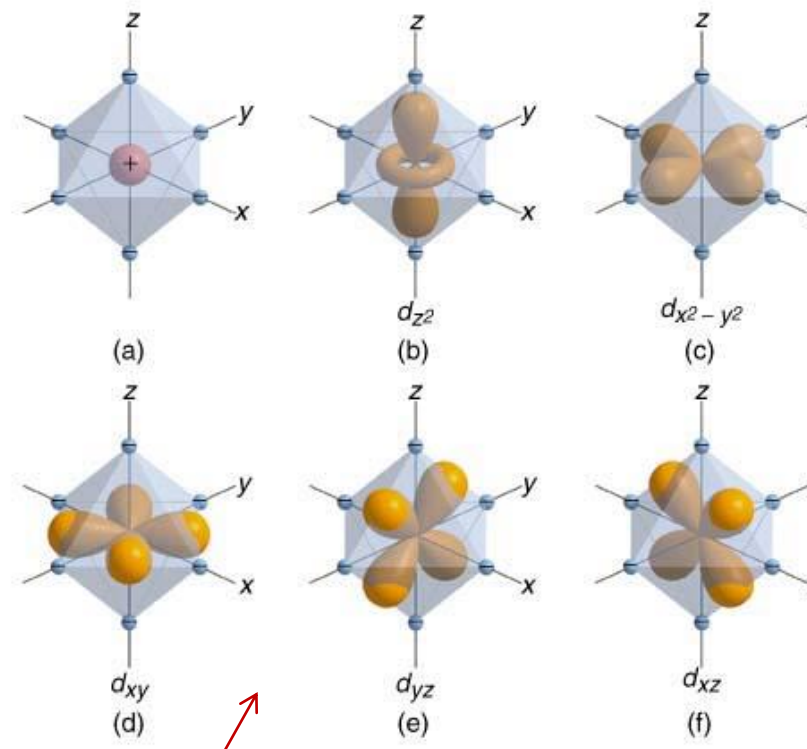
Spherical field is
equal distance
from all d orbitals

Imagine the ligands approaching the metal

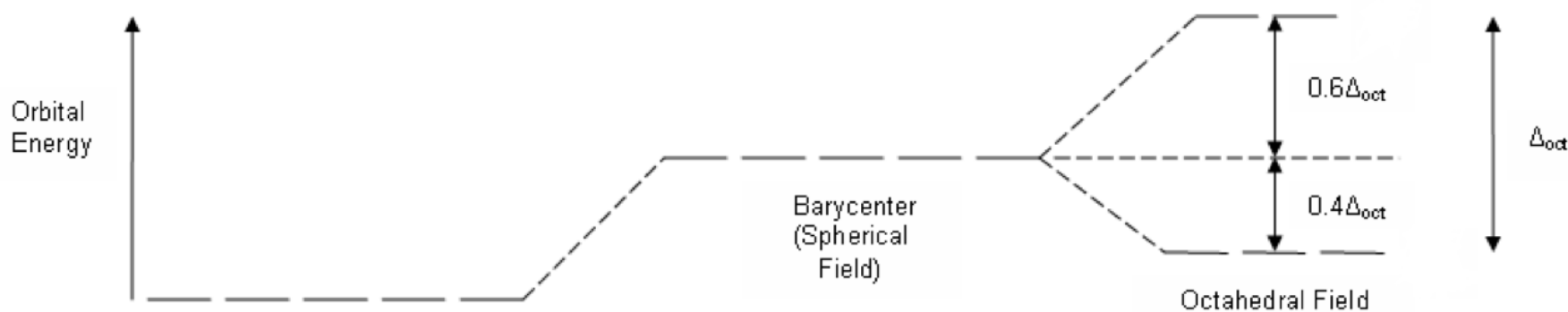
d orbitals in an **octahedral** field

- +/- attraction
- -/- repulsion

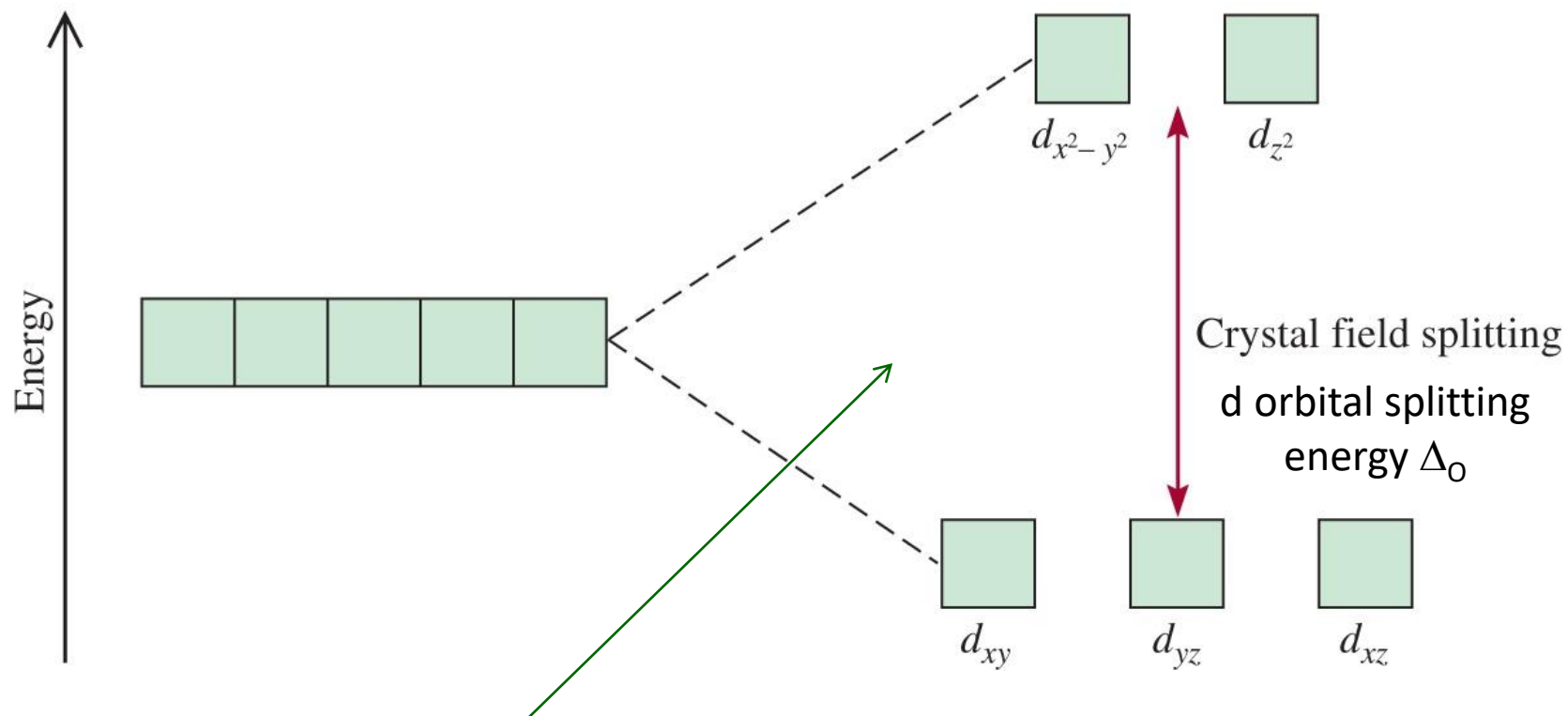
This -/- repulsion will be greater between the ligand electrons and electrons in **axial d orbitals** as compared to repulsion between the ligand electrons and those in the d **inter-axial** orbitals



6 points of electron density approaching the d orbitals

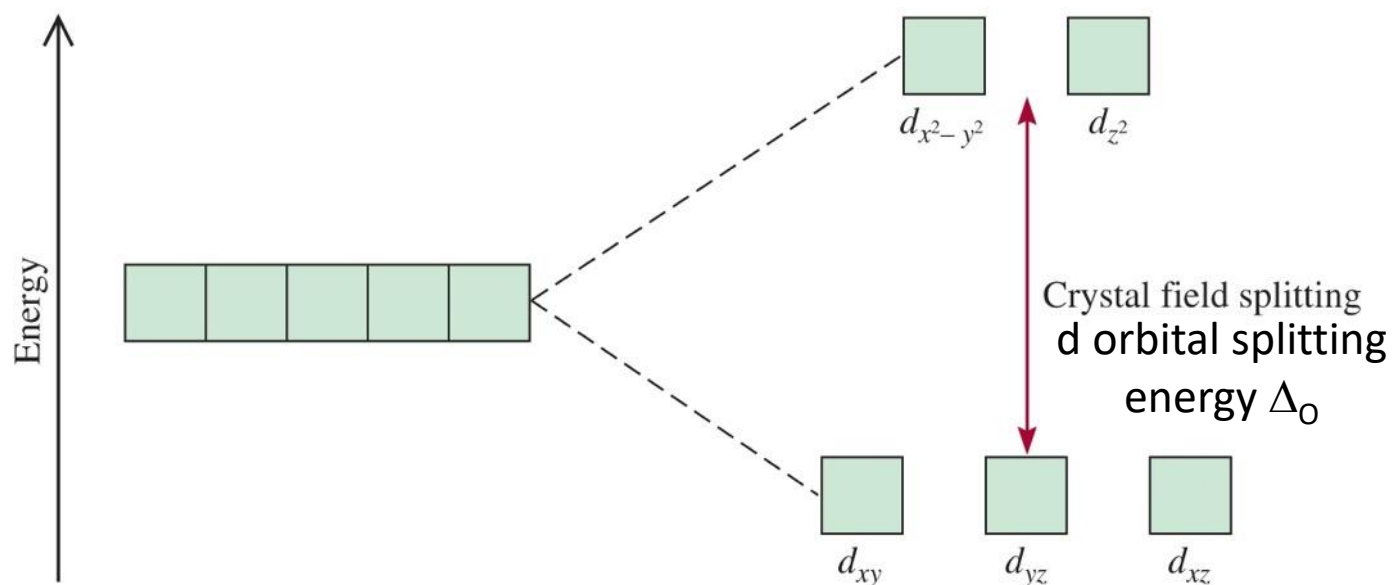


d orbital splitting diagram in an octahedral complex



The extent of d orbital splitting depends on the metal ion, the charge on the metal ion and the ligands coordinated

Factors affecting size of splitting energy

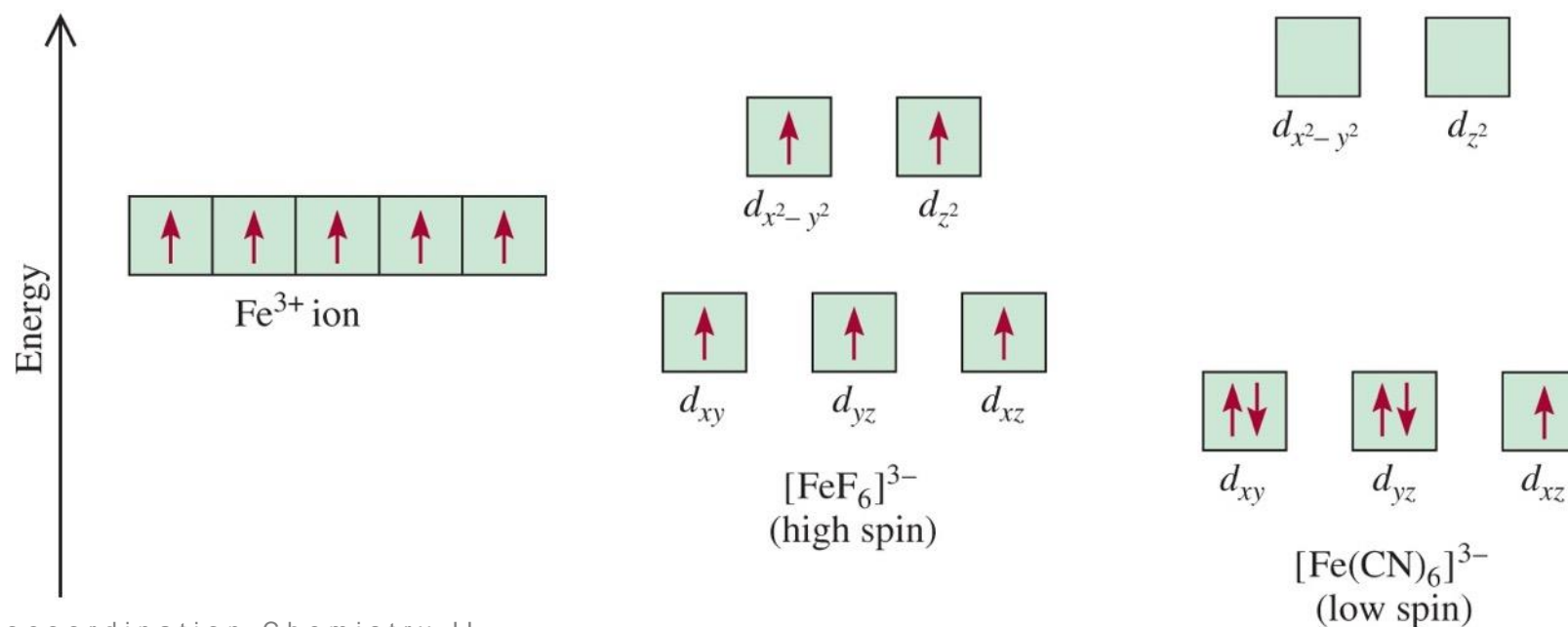


- Metal: Larger metal \rightarrow larger splitting
- Higher Oxidation State \rightarrow larger splitting
- Ligand: Spectrochemical series
 $\text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- < (\text{N-bonded}) < \text{CN}^- < \text{CO}$
- **Weak Field Ligand:** Low electrostatic interaction: small splitting
- **High Field Ligand:** High electrostatic interaction: large splitting

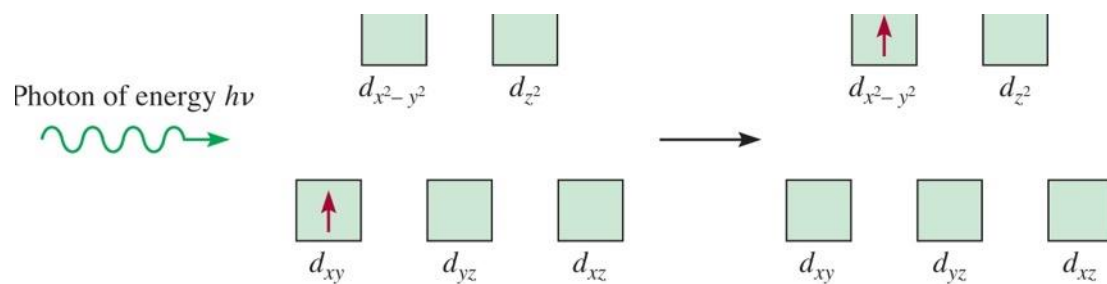
Spectrochemical series



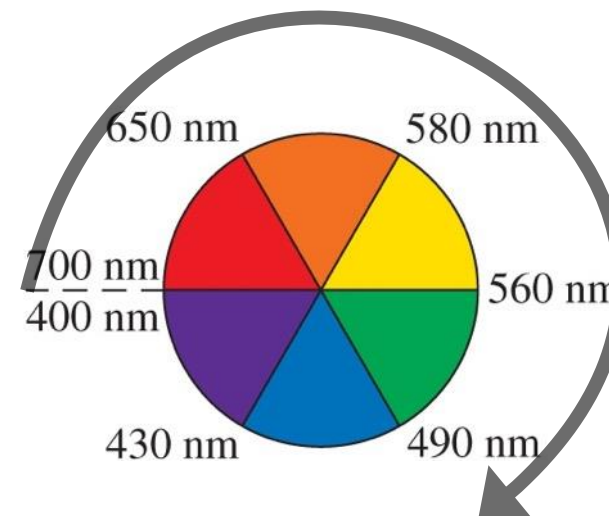
Typically, CN^- produces very large values of Δ , while F^- produces very small values



Colour of metal complexes explained by splitting energy



- Photons with the appropriate energy can cause electrons to be promoted from lower energy to high energy d orbitals.
- If the splitting energy for a metal complex has the same energy as red light (e.g. 680 nm) then red light will be absorbed and the complex will appear green, which is the complimentary colour of red.

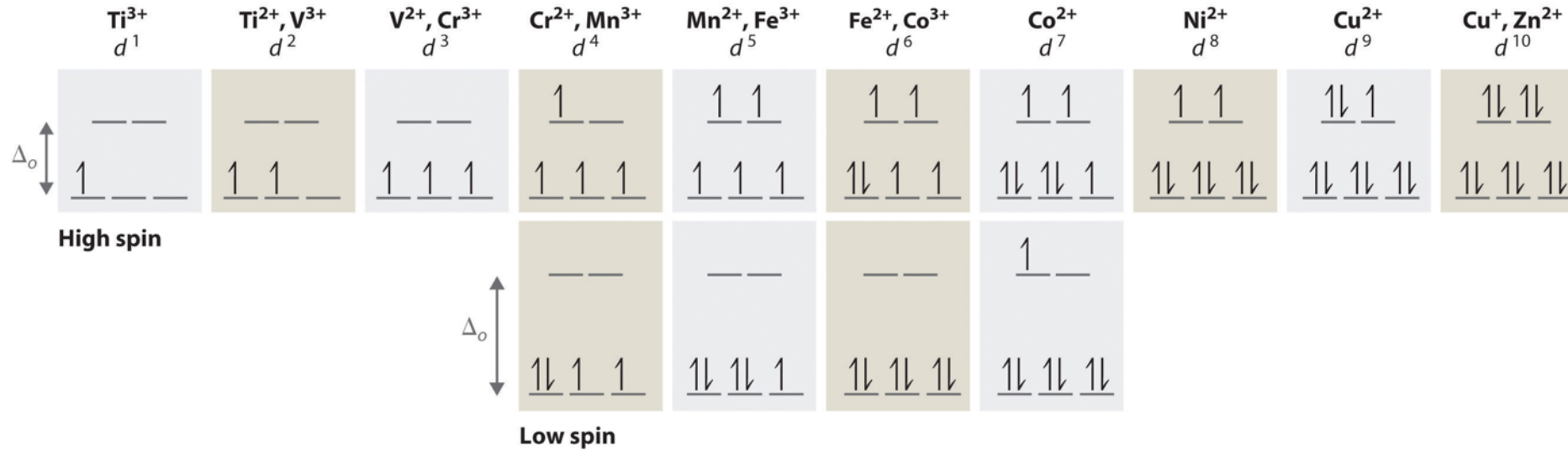


Increasing energy of photons
in light 700 nm to 400 nm



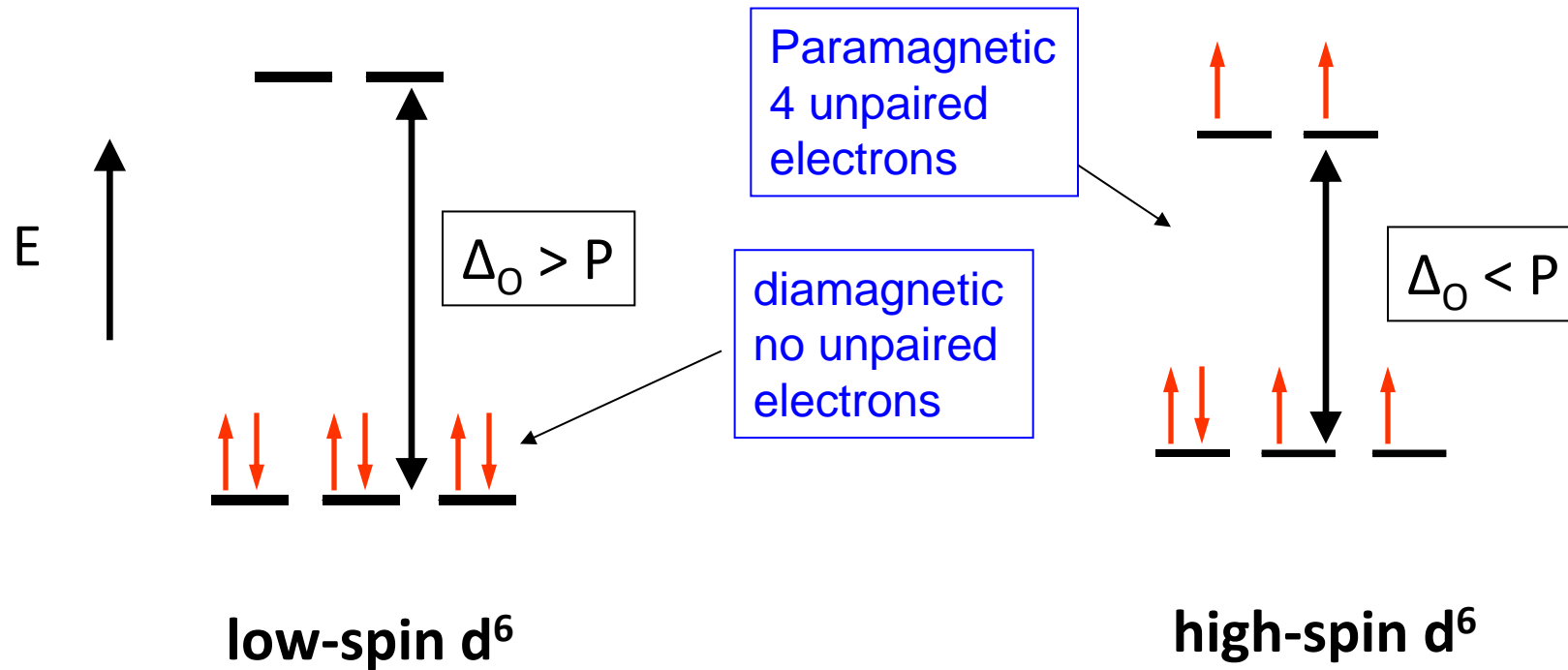
Watch the animation titled 'Absorption of light in metal complexes'

High Spin Versus Low Spin Complexes (d^1 to d^{10})



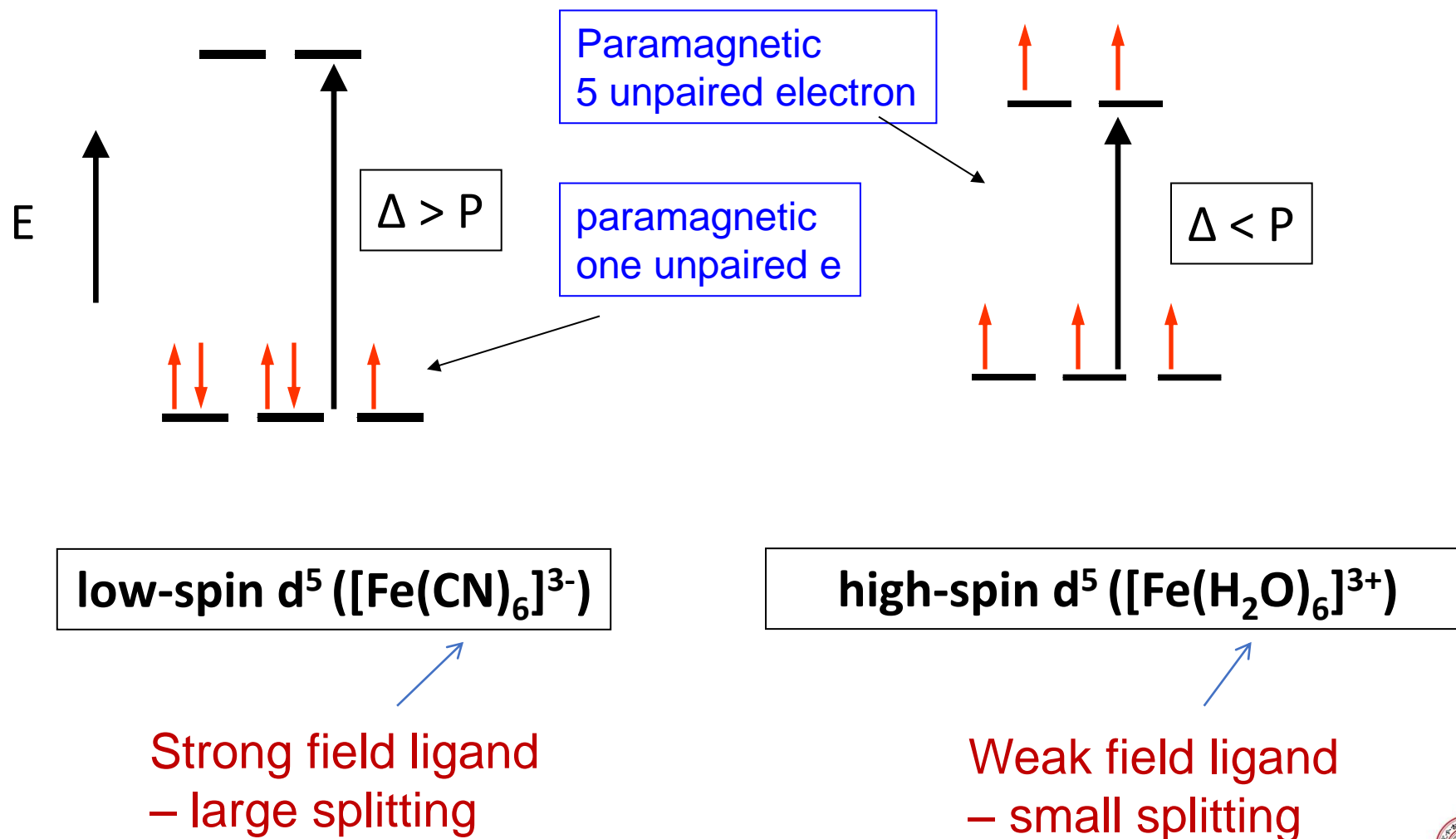
- Electrons fill lowest energy orbitals first i.e. the inter-axial d orbitals
- However for the d^4 through d^7 cases, depending on the d orbital splitting:
 - If low splitting, then electrons can fill inter-axial and axial orbitals singly before pairing – **high spin complexes**
 - If large splitting, then electrons will completely fill inter-axial orbitals first – **low spin complexes**

High Spin Versus Low Spin Complexes (d^4 to d^7)



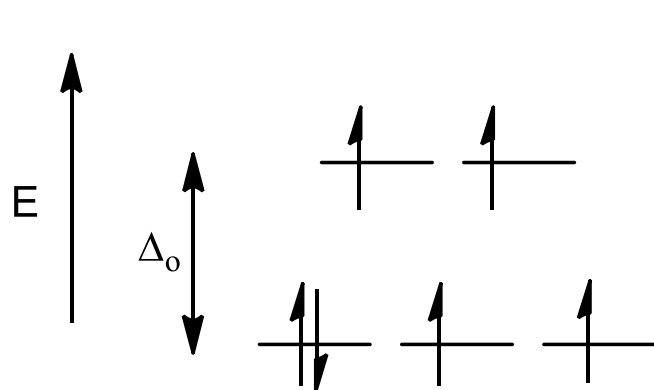
P = Electron Pair Repulsion Energy

High Spin Versus Low Spin Complexes

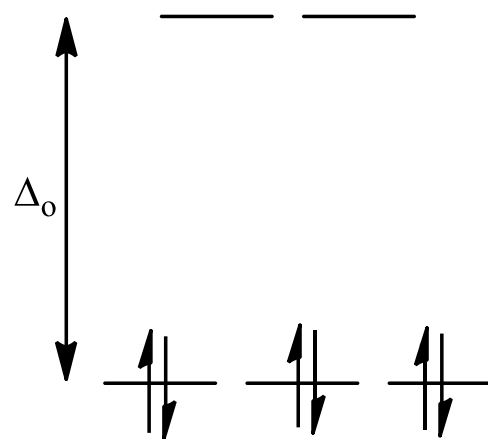


Consider a d^6 ion - like Fe^{II} which is present in haemoglobin or myoglobin

- Two possible configurations.
 - High spin, paramagnetic.
 - Low spin, diamagnetic.



High spin (paramagnetic)



Low spin (diamagnetic)

Learning Objectives

- Recall the shapes of the metal ion d orbitals.
- Explain crystal field theory.
- Recall d orbital splitting in an octahedral complex.
- Define 'd orbital splitting energy'.
- Explain high spin and low spin complexes.
- Explain paramagnetic and diamagnetic.

Thank you

FOR MORE INFORMATION PLEASE CONTACT

Professor Dan Wu

EMAIL: danwu@suda.edu.cn



INTERNATIONAL COLLEGE
OF PHARMACEUTICAL
INNOVATION
国际创新药学院



INTERNATIONAL COLLEGE
OF PHARMACEUTICAL
INNOVATION
国际创新药学院