



B.Sc.III_Inorganic Chemistry

Code: B-306

Dr. Sachin Kumar

**Assistant Professor
Chemistry Department**

**Sanjay Gandhi (P.G.)
College Sarurpur
Khurd Meerut**

SYLLABUS IS COVERED IN FOUR UNITS

SUBTOPICS OF EACH UNITS ARE WRITTEN BELOW

Unit I

- Metal Ligand Bonding in transition Metal Complexes
- Thermodynamics and Kinetics Aspects of metal Complexes

Unit II

- Magnetic Properties of Transition Metal Complexes
- Electronic Spectra of Transition Metal Complexes

Unit III

- Organometallic Chemistry
- Silicones and Phosphazenes

Unit IV

- Hard and Soft Acids and Bases (HSAB)
- Bioinorganic Chemistry

**Maximum
marks**

75

**Objective
pattern**

UNIT I

METAL LIGAND BONDING IN TRANSITION METAL COMPLEXES

FULL SUBTOPIC

Limitation of valence bond theory, an elementary idea of crystal field theory, crystal field splitting in octahedral, tetrahedral and square planar complexes, factors affecting the crystal-field parameters.

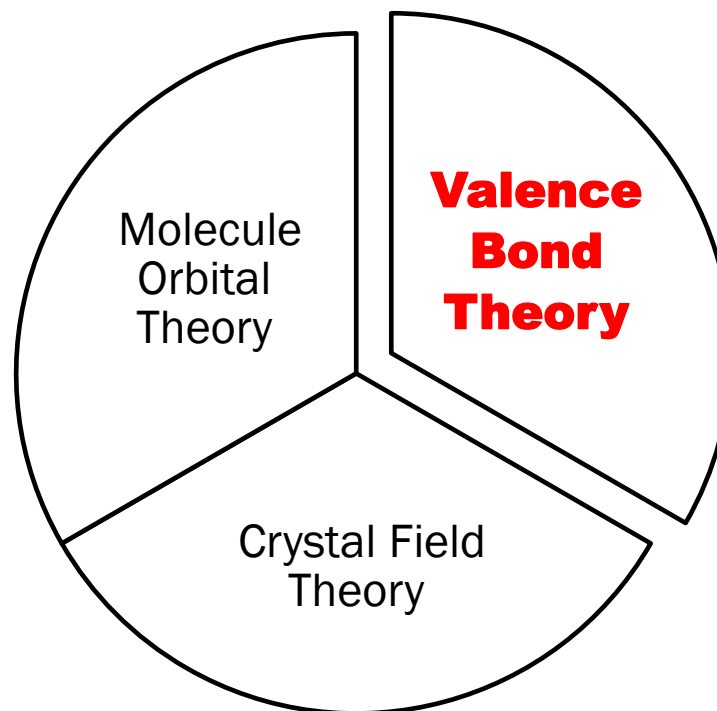
In this presentation we will discuss the limitations of valence bond theory only

BOOKS CONSULTED & RECOMMENDED

- | | | |
|--------------------------------------|--|----------------------------------|
| 1. Principles of Inorganic Chemistry | Puri, Sharma , Kalia | Milestone Publishers |
| 2. Concise Inorganic Chemistry | J. D. Lee | Blackwell Science |
| 3. Inorganic Chemistry | James E. Huheey, E. A. Keiter, R. L. Keiter | Harper Collins College |
| 4. Inorganic Chemistry | Shriver & Atkins | W. H. Freeman & Company New York |
| 5. Inorganic Chemistry | Malik, Tuli, Madan | S. Chand |
| 6. Inorganic Chemistry | Catherine E. Housecroft & Alan G. Sharpe | Pearson prentice Hall |

MODERN THEORIES OF METAL-LIGAND BOND

Mainly, three modern theories have been developed for the basic understanding of metal ligand bonds and their properties.



The VBT developed by Linus Pauling, has two key concepts, Hybridization of orbitals and resonance. Linus Pauling takes advantages from the previously established Lewis theory and Heitler-London theories, and put forward a quiet remarkable theory of metal ligand bonding, in order to explain how atoms come together and form molecules.

Knowing the magnetic property or the types of hybridisation, the VBT was able to account for some stereochemical and magnetic properties of coordination compounds.

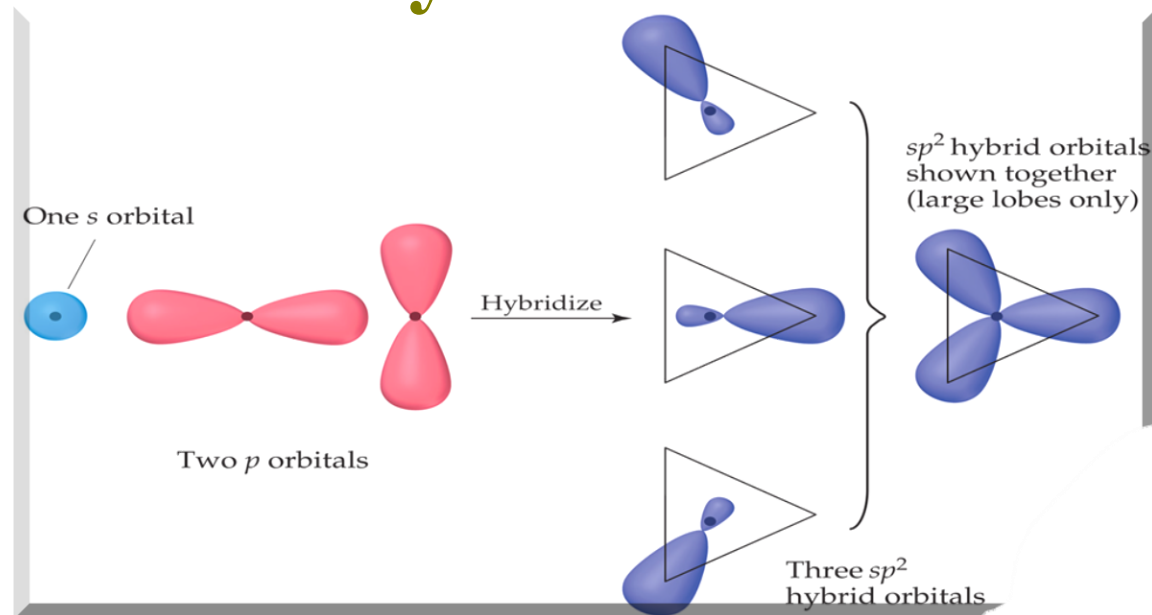
VALENCE BOND THEORY

The main points of the theory may be summed up as follows:

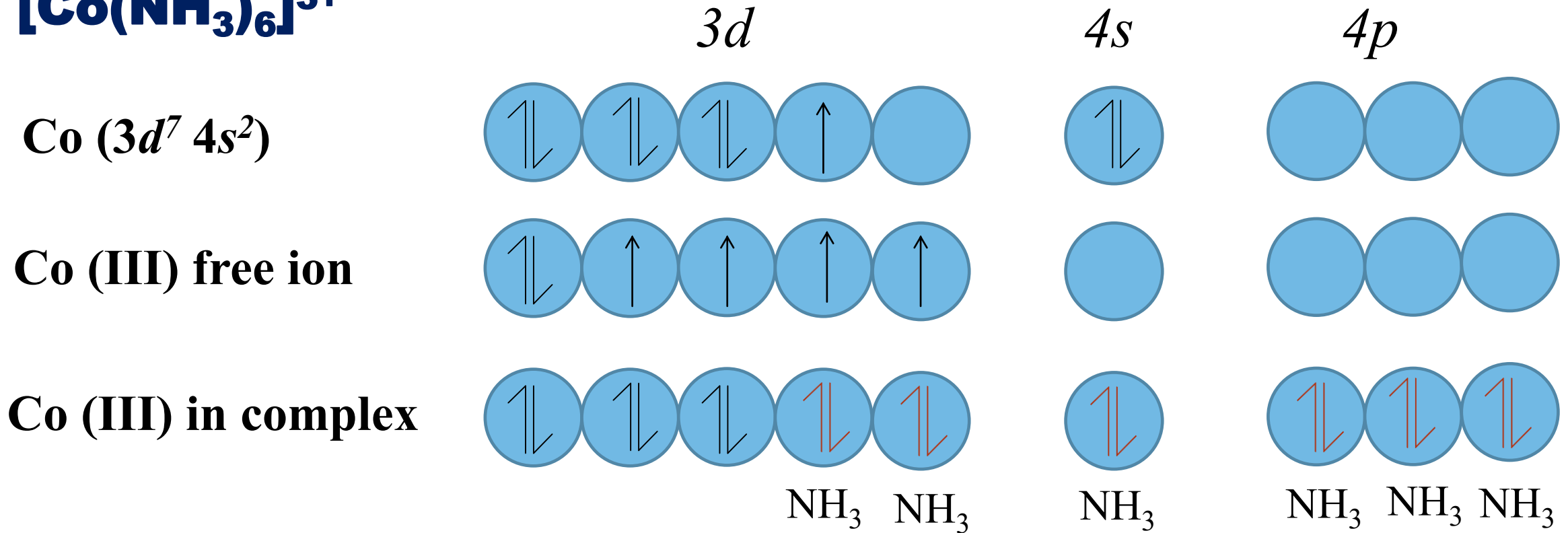
1. Central metal ion in the complex makes available an adequate number of empty orbitals for the formation of coordinate bonds with suitable ligands.
2. The number of empty orbitals made available for the purpose is equal to the coordination number of the central ion.
3. Each Ligands has at least one orbital containing a lone pair of electrons.
4. The appropriate atomic orbitals (s , p and d) of the metal hybridise to give an equal number of equivalent energy hybrid orbitals.
5. The hybrid orbitals are directed towards the ligand positions according to the geometry of the complex.
6. The empty hybrid orbitals of metal ions overlap with fully filled orbitals of the ligand to produce a new combined orbital containing two electrons of opposite spin.

7. This overlapping of hybrid orbitals results in a decrease in the energy of the atoms forming the bond and the shared electron pair is most likely to be found in the space between the two nuclei of the atoms.
8. The d -orbital in the hybridisation may be inner (low spin) or outer orbitals (high spin).
9. Diamagnetic and paramagnetic properties of the compound can be predicted qualitatively.
10. The geometry and magnetic properties are interrelated in this theory.

Hybridization



VBT Example



d²sp³ hybridisation

Information Revealed:

1. Inner orbital complex, (outer 4d orbital not used)
2. Pairing of electron of cobalt occurs, low spin complex
3. Diamagnetic behaviour
4. Octahedral geometry



SHORTCOMINGS OF VALENCE BOND THEORY

Although VBT establishes a good correlation between hybridisation, geometry and magnetic properties in many coordination compounds, however like most of the theories, it has some flaws.

Some of them are discussed below.

1. Although this theory gives a beautiful pictorial representation of bonding, it does not have a theoretical and qualitative nature about the electronic excited states and energies associated with them. As a result,

this theory failed to predict the number, positions and the intensities of the band observed in the electronic spectrum of the coordination complexes.

2. According to VBT, the magnetic moment of a complex originates from the magnetic field generated by the spins of the electrons in the metal ion (μ_{spin}) only. It does not give any credit to the orbital magnetic moments (μ_{orbit}). We know that,

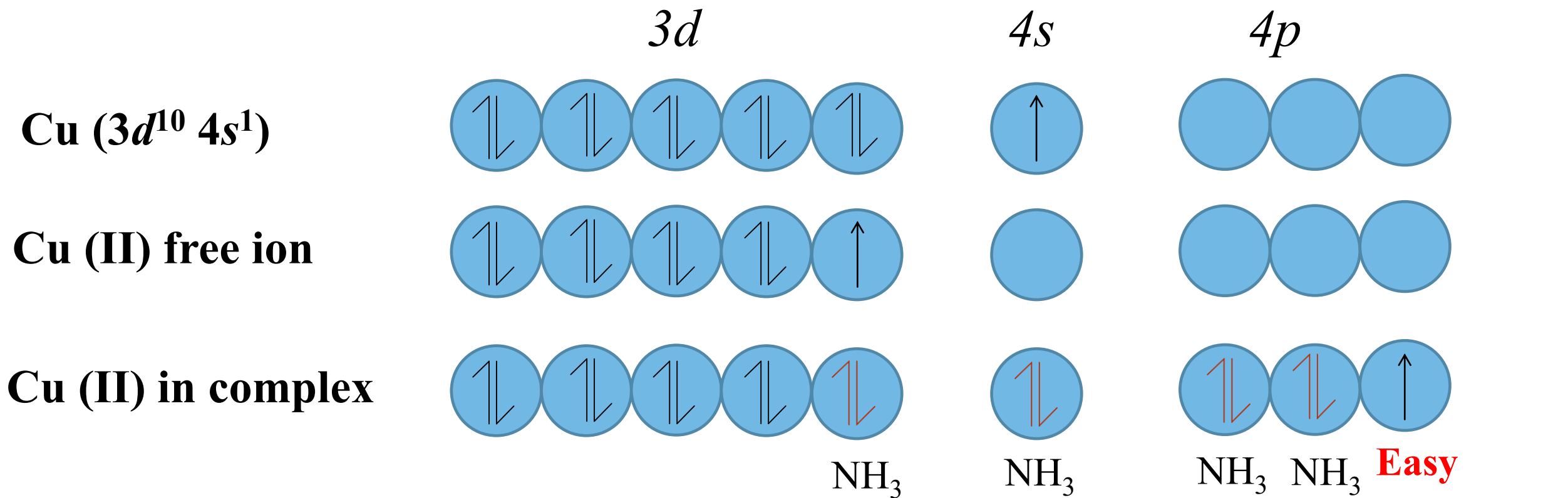
$$(\mu_{\text{total}}) = (\mu_{\text{spin}}) + (\mu_{\text{orbit}}), \text{ So,}$$

Experimental values of magnetic moments in these complexes generally differ from the calculated values.

3. It does not consider the **splitting of 'd' orbitals**. In some cases, it also fails to predict the geometry if more than one geometries are possible for a particular coordination number.

[Cu(NH₃)₄]²⁺

4. According to VBT, it is easier to oxidize Cu (II) in square planar ammonia copper complex to Cu (III).



dsp² hybridisation

Square Planar

Easy to Oxidize Outermost Electron??

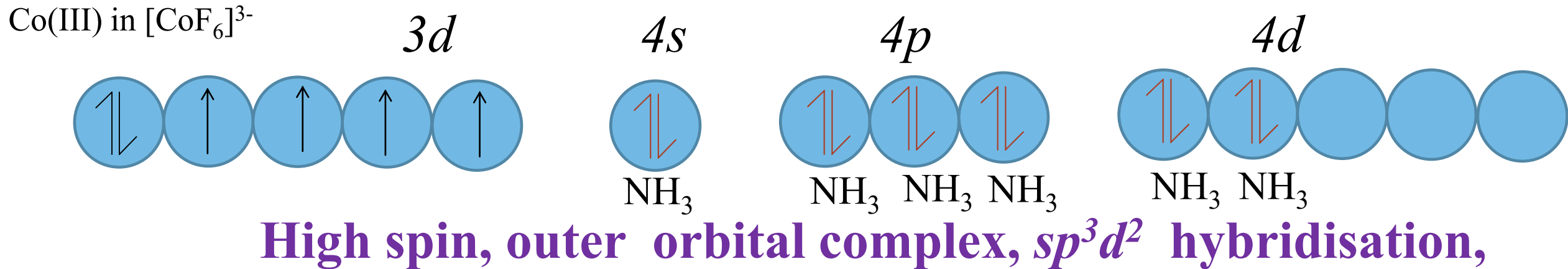
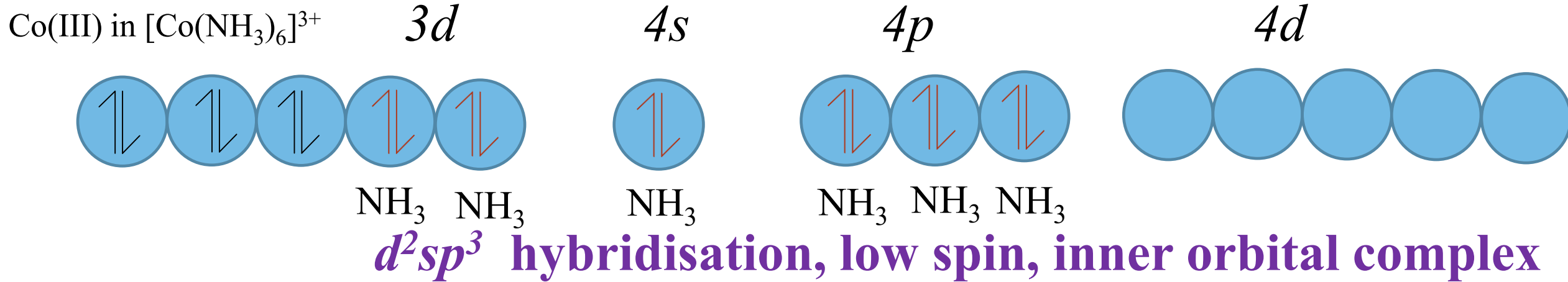
Two Problems:

- ESR study confirmed that single electron does not stay in outermost orbital (4p_z) all the time as shown in VBT.
- Why electron jump from 3d to 4p, no explanation is given by VBT (quite high energy is needed for jump).

Cu (III) not form at all

5. The VBT does not clarify enough that why metal in same oxidation state behave differently,
 For example: **[Co(NH₃)₆]³⁺** is a low spin diamagnetic compound while **[CoF₆]³⁻** is high spin paramagnetic compound.

Where cobalt is in +3 oxidation state in both the two case.

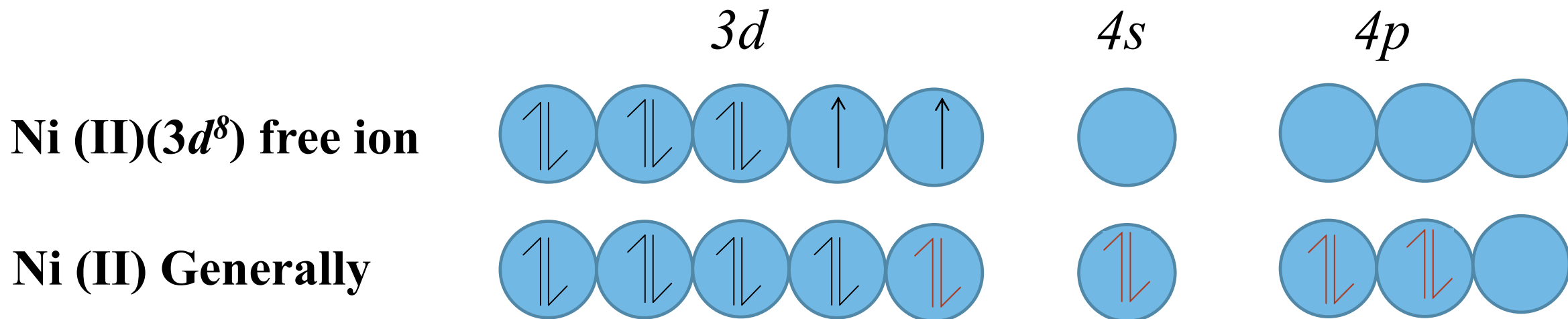


VBT fails to explain why inner orbital complex (low spin) is formed in one case and outer orbital complex (high spin) is formed in other case.

6. Sometimes the relation between the geometry of a complex and its magnetic behavior is quite deceptive.

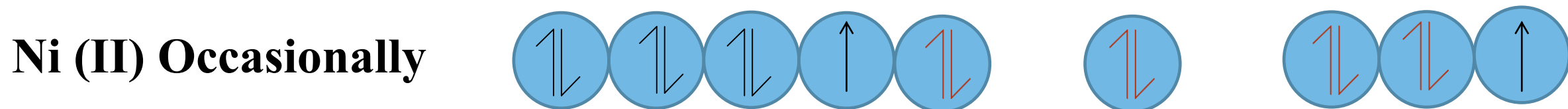
For example,

According to VBT, all square planar complexes of Ni(II) should be diamagnetic in nature, however in some case square planar complexes of Ni(II) have been found paramagnetic in nature.




No unpaired electron, diamagnetic

Both the complexes having, dsp^2 hybridisation, square planar



Two unpaired electron, paramagnetic

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7. It does not give any information regarding **thermodynamic and kinetic stabilities** as well as **reactivities** of these complexes.
 8. It does not give any information about **optical properties like, origin of colour**, in these complexes.
 9. According to VBT, **oxygen molecule should be diamagnetic in nature** but experimentally oxygen molecule is found to be **paramagnetic** in nature.
 10. This theory also does not come into picture for **radical complexes as well as electron-deficient molecules** like, diborane.
 11. It also fails to explain the **distortion in coordination compounds** (“Jahn-Teller Distortion”).
 12. **Relative ligands strength** and their effect on pairing in coordination complexes is not considered.

■ Thank you

If any queries/doubt are present, feel free to write an email to sachin2282@gmail.com or write down in your note book and contact me in college.



Crystal Field Theory