- **Instructor:**

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- **Course information:**

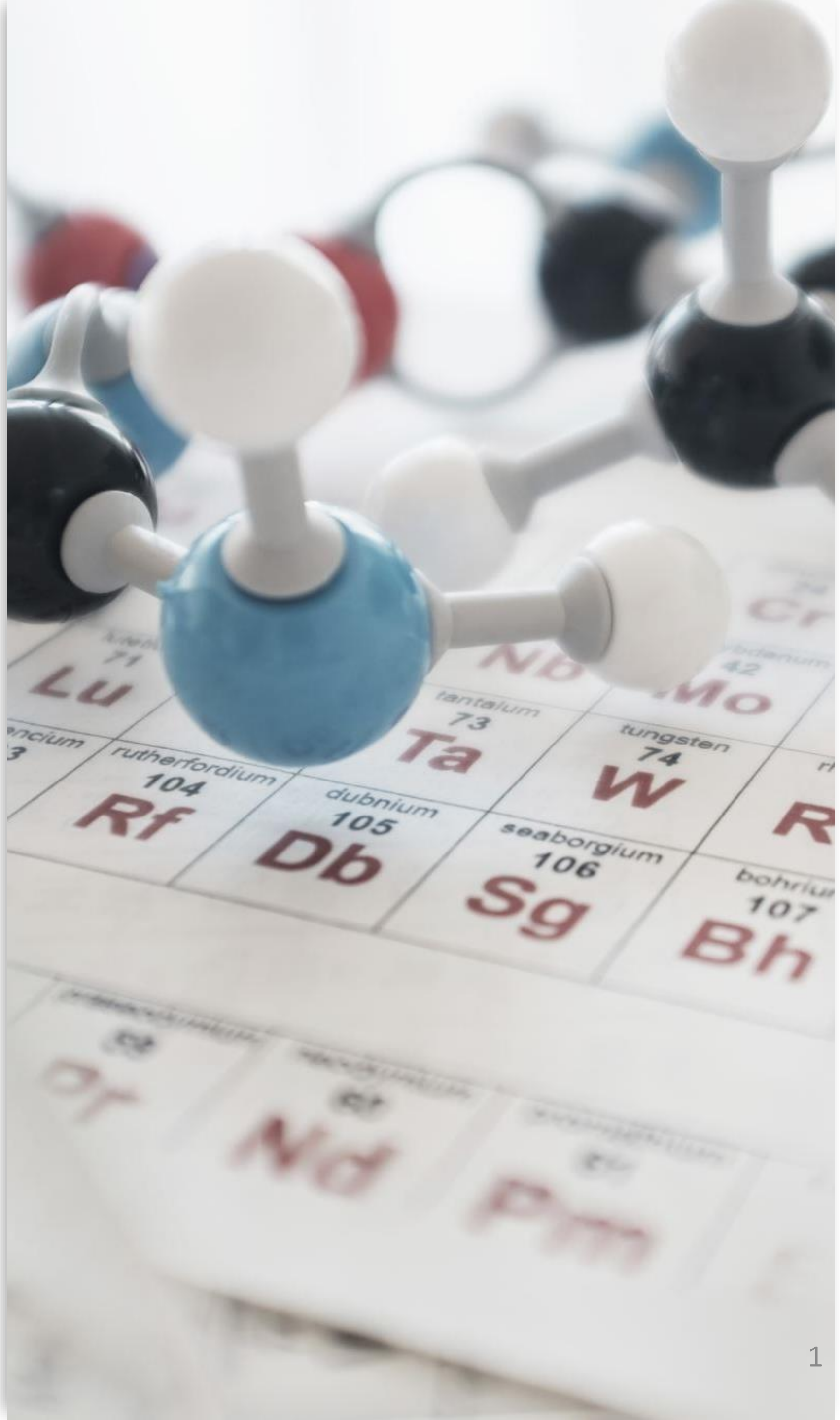
- Physical Methods in Inorganic Chemistry
- 523 Chem
- 2 credit hours

- Resources:

- Textbook: Shriver & Atkins' Inorganic Chemistry
- Textbook: Atkins' Physical Chemistry
- Textbook: Raymond Chang, Chemistry for GenChem

- Office hours:

- Everyday at noon 12-1 or after lecture time
- *(an appointment should be scheduled prior to office hours by email)*



Course Main Objectives:

- After completing this course, the student will be able to understand the key features of spectroscopy of inorganic compounds, including:
- Electronic spectroscopy of transition metal complexes, selection rules, The Russell Saunders Coupling Scheme, Term symbols, Microstate and ground state, Spectroscopic Term Symbols
- Vibrational spectroscopy, selection rules, Interpretation of IR Spectra of ligands and metal complexes.
- Rotational spectroscopy, selection rules, Interpretation of IR Spectra of ligands and metal complexes.
- ESR spectroscopy: selection rules, Characteristics of g, Factors Affecting the Magnitudes of g-Values, Application of ESR.
- NMR spectroscopy: principal of NMR, chemical shift, splitting of signals, integration of signals, Coupling Constant, Application of NMR in Inorganic Compounds.
- Mossbauer spectroscopy
- X- ray single crystal analysis

GRADING SYSTEM FOR THE COURSE

This course will be graded as follows:

No	Performance	Marks
1	3-4 Quizs	15%
2	Assignments	15%
3	1 Mid term exam	30 %
4	Final term exam	40 %
Total		**100%**

Limitations of Simple Electron Configurations

The Problem: A configuration like d^2 tells us there are two electrons in the d-orbitals , but it ignores the interelectronic repulsion.

The Concept: Electrons are negatively charged; their mutual repulsion leads to different energy levels even within the same configuration.

The Goal: We need a way to describe the state of the entire atom rather than individual electrons. These states are called **Terms**.

The Concept of Microstates

- **Definition:** A microstate represents a specific electronic configuration of a system, defined by a unique set of magnetic m_l and spin m_s quantum numbers for each electron.
- **Quantum Constraints:** The total number of microstates is constrained by the Pauli Exclusion Principle, which dictates that no two electrons in an atom can possess an identical set of quantum numbers.
- **Statistical Analysis:** For a d^2 configuration, we consider the available **degenerate states** (5 orbitals × 2 spin orientations = 10 available spin-orbitals). The microstates represent the distinct permutations of distributing r (electrons) among n available (spin-orbitals).

$$N = \frac{n!}{r!(n-r)!}$$

- **Conclusion:** These 45 microstates represent the total degeneracy of the d2 configuration, which is subsequently lifted by interelectronic repulsions to form distinct energy levels **(Terms).**

Russell-Saunders (L-S) Coupling Scheme

- **Mechanism:** In lighter elements (first-row transition metals), the electrostatic repulsions are dominant over spin-orbit coupling.
- **Coupling:** *

  - Individual orbital angular momenta (l_i) couple to form a total orbital angular momentum, L.

  - Individual spin angular momenta (s_i) couple to form a total spin angular momentum, S.
- **Significance:** The resulting **Term Symbols** provide a concise description of the energy levels (states) arising from these interactions.

Determination of Total Orbital Angular Momentum (L)

- **Calculation:** L is determined by the vector sum of the magnetic quantum numbers: $L = \sum m_l$.

- **Permissible Values:** L can take values $|l_1+l_2|, \ldots, |l_1-l_2|$

- Alphabetic Notation:

L= 0= S

L= 1= P

L= 2= D

L= 3= F

Spin Multiplicity and Total Spin (S)

- **Calculation:** S is the vector sum of the spin quantum numbers: $S = \sum m_s$.

- **Spin Multiplicity:** Defined by the expression $2S + 1$.
- **Nomenclature:**
- $2S+1 = 1$: Singlet
- $2S+1 = 2$: Doublet
- $2S+1 = 3$: Triplet

Spectroscopic Term Symbol $^{2S+1}L_J$

- $2S+1$→ **Spin multiplicity**

It comes from the **total spin** S of all electrons.

L→ **Total orbital angular momentum**

J→ **Total angular momentum**

From the coupling of $L$and S: $J = L + S,\ L + S - 1, \ldots, | L - S |$

Illustrative Example (1) – The d^1 Configuration

For a single electron in a d-orbital ($l = 2$):

L: The only possible value is 2, resulting in a **D** term.

S: The spin is 1/2, leading to a multiplicity of $2(1/2) + 1 = 2$.

Resulting Term Symbol: ^2D.

Physical Meaning:

In the absence of an external field or ligands, the 10 microstates of d^1 are grouped into a single, 10-fold degenerate ^2D state.

So, The term symbol ^2D. tells you the **type of angular momentum** associated with that group of microstates.

Energy Level Distribution for d^1

- **The 45 microstates for a d^2system are grouped into five specific terms based on their L and S values:**
- $^3F,\quad ^3P,\quad ^1G,\quad ^1D,\quad ^1S$
- **Observation:** Terms with higher multiplicity (Triplets: $^3F,\quad ^3P$) generally lie lower in energy than Singlets ($^1G,\quad ^1D,\quad ^1S$) due to reduced electron–electron repulsion.
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Hund’s Rules for Term Stability

To determine the **Ground State Term** (the state with the lowest energy), we apply Hund’s empirical rules:

1. **Maximum Multiplicity**: The term with the highest value of 2S+1 is the most stable.
2. **Maximum L**: If multiplicities are equal, the term with the highest L value lies lowest in energy.

Hund’s First Rule – The Spin Effect

- **Principle:** The ground state is the term with the highest spin multiplicity.

- **Quantum Mechanical Basis:** Electrons with parallel spins are spatially further apart (due to the Pauli principle/exchange hole), which minimizes destabilizing Coulombic repulsion.

- So, Electrons prefer to align with **parallel spins** because it keeps them farther apart, reducing repulsion — so the state with the **highest spin multiplicity** is the **most stable** (lowest in energy).

Hund’s Second Rule (Orbital Effect) & Total Angular Momentum

- **Hund’s Second Rule – The Orbital Effect**
  Principle: For terms with identical multiplicity, the state with the highest total orbital angular momentum (L) is the ground state.
  Example: Comparing $^3F(L = 3)$ and $^3P(L = 1)$ for a d^2 ion:
  The ^3F term is the ground state.

- **Total Angular Momentum (J) and the "Half-Filled" Rule**
  The J Quantum Number: J ranges from $L + S$ to | $L - S$ |.
  Ground State J Value:
- Less than half-filled (e.g., d^1 to d^4): The state with the **minimum** J is most stable.
- More than half-filled (e.g., d^6 to d^9): The state with the **maximum** J is most stable.

Comprehensive Case Study: Cr^{3+}(d^3 ion)

- Step 1: Calculate Multiplicity $(S = 3/2 \rightarrow 2S + 1 = 4)$.
  Step 2: Calculate Max $L\left(m_l\text{values: } +2, +1{,}0 \rightarrow L = 3 \rightarrow \mathbf{F}\right)$.
  Step 3: Determine J(Less than half-filled $\rightarrow J =| 3 - 1.5 |= 3/2$).
- **Result:** The ground state term for $Cr^{3+}$is ${}^4F_{3/2}$.
- **Transition to Coordination Chemistry or From Atoms to Complexes**: While these Terms describe free ions, the presence of ligands in an octahedral or tetrahedral field will cause these Terms to split further.