BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, Pilani

SECOND SEMESTER 2020-2021
Course Handout (Part II)

Date: 18.01.2021

In addition to Part I (General Handout for all courses appended to the time table) this portion gives further specific details regarding this course.

Course No. **: CHEM F244**
Course Title **: Physical Chemistry III**
Instructor-in-charge **: RAM KINKAR ROY**

Scope and objective of the course: This course is designed in continuation to the Physical chemistry courses I and II, already offered to the students. Physical Chemistry III course is composed of two parts. In the first portion, students would be exposed to the molecular symmetry, principles of group theory, and its application in molecular spectroscopy. The second portion provides a comprehensive survey of various approximation methods in quantum chemistry.
Course Description: Symmetry - symmetry operations, point groups, reducible and irreducible representations, character tables, SALC, degeneracy, vibrational modes IR-Raman activity identification; stationary state perturbation theory; virial and Hellmann-Feynmann theorems; polyatomic molecules: SCF MO treatment, basis sets, population analysis, molecular electrostatic potentials, configuration interaction, Moller Plesset perturbation theory; Density Functional Theory: Hohenberg-Kohn theorems, Kohn-Sham self consistent field approach, exchange correlation functional; molecular mechanics.
Text Book (TB): TB-1: "Chemical Applications of Group Theory", F. Albert Cotton, Wiley Student Edition, Third Edition. **TB-2**: "Quantum Chemistry", Ira N. Levine, PHI Learning Private Limited, Sixth Edition, 2012.
Reference Books (RB): "Quantum Chemistry", Donald A McQuarrie, University Science Books (First Indian Edition 2003, Viva Books Private Limited)

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Course Plan:

Lecture No.	Lecture Session		Reference to Text	Learning Outcome
	Module 1: Molecular Symmetry and symmetry group			
1	Definitions and Theorems of Group Theory	Properties of a group, examples of groups, subgroups, classes	**TB-1** 2.1- 2.4	The symmetry elements and the corresponding mathematical operators will be learned. The recipe of determining symmetry group of given molecule will be learned. The effect of symmetry group on optical properties of molecules will be understood.
2-3	Symmetry elements and operations	Plane, center of inversion, proper axis, and improper axis, product of symmetry operations, point groups	**TB-1** 3.1 – 3.9	
4	Application of symmetry operations	Dipole moments, optical activity	**TB-1** 3.10	
5-6	Group Theory	Symmetry Point Group, Symmetry classification of molecules	**TB-1** 3.11 – 3.14	
	Module 2: Representation of Groups			
7-8	Equivalent and reducible representation	Unitary representation, reducible representation, transformation operators.	**TB-1** 4.2 – 4.5	Mathematical aspects of symmetry groups will be learned in more details. The great orthogonality theorem will be introduced along with its applications in quantum chemistry and molecular spectroscopy.
9-11	Irreducible representation	The "Great Orthogonality Theorem", characters, criterion for irreducibility, character tables and their construction	**TB-1** 4.2 – 4.5 Class notes	
12-13	Representation and quantum mechanics	Invariance of Hamiltonian operator under transformation, direct product representation, vanishing integrals	**TB-1** 5.1 – 5.3	
14-15	Symmetry adapted linear combination (SALC)	Projection operators, construction of SALCs using projection operators.	**TB-1** 6.1 – 6.3	
16-19	Molecular vibrations	Normal coordinates, vibrational levels, IR spectra, Raman spectra, selection rules.	**TB-1** 10.1 – 10.8	
	Module 3: Electronic structure of polyatomic molecules: (a) Theorems			
20-23	Theorems of molecular quantum mechanics	Virial theorem and Chemical Bonding, Hellmann-Feynman theorem, Electrostatic theorem	**TB-2** 14.1 – 14.7	Concepts of kinetic energy, potential energy and its components will be revisited in the light of the theorems in molecular quantum mechanics.
	Module 4: Electronic structure of polyatomic molecules: (b) Molecular Orbital treatment			
SELF STUDY	Approximation Theorem of Many Electron Atoms	The Hartree SCF Method and Hartree-Fock SCF Method for many electron atoms	**RB 1**	
24 - 29	Molecular electronic structure calculations	SCF-MO treatment, basis functions, population analysis, molecular electrostatic potential, localized MOs, SCF-MO treatment of H_2O	**TB-2** 13.15, 15.1 – 15.5, 15.6 – 15.9	Computational aspects of Hartree-Fock will be learned in detail. The basis sets and their features will be introduced.
30 - 32	Configuration Interaction	Configuration state functions, occupied and virtual molecular orbitals, excitation energy calculation.	**TB-2** 11.3, 16.1, class notes	Concepts of size-consistency and size-extensivity will be understood
33 - 34	Stationary state perturbation theory	Perturbation treatment of non-degenerate and degenerate states.	**TB-2** 9.1 – 9.7	Degenerate perturbation theory will be learned. Application of

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35 - 37	Møller– Plesset Perturbation theory	Many body perturbation theory, electron correlation effects, Møller– Plesset perturbation of 2nd, 3rd, and 4th order	**TB-2** 16.2	non-degenerate perturbation to Hartree-Fock wavefunction will be learned.
	Module 5: Electronic structure of polyatomic molecules: (c) Alternate approaches			
SELF STUDY	Valence-Bond approach	Coupling of electrons, bond eigenfunction, application of Valence-Bond treatment to different polyatomic molecules	**TB-2** 16.8	
38 - 42	Density Functional Theory	Hohenberg-Kohn Theorem, Kohn-Sham method, exchange correlation functional, hybrid functional	**TB-2** 16.4, class notes	Basic concepts of DFT will be understood.

Evaluation Scheme: (Total 200 Marks)

Component	Duration (minutes)	Weightage (%)	Date and Time
Continuous Evaluation$	10 (each)	30	To be announced in the class
Mid-semester	90	30	To be announced
Comprehensive Examination	120	40	07/5 FN

$ Assignment Tests, Quiz Tests, Computational assignments, etc.

Chamber Consultation Hours: To be announced in class.

Notices: Notices, if any, concerning the course will be displayed on nalanda.bits-pilani.ac.in.

Make up policy: Make up request would be considered only for **genuine cases.**

Instructor in charge

CHEM F244