MCH-018

ASSIGNMENT BOOKLET

M.Sc. in Chemistry Programme
(MSCCHEM)

QUANTUM CHEMISTRY AND GROUP THEORY

Valid from 1st July, 2024 to 30th June, 2025

School of Sciences
Indira Gandhi National Open University
Maidan Garhi
New Delhi-110068
(2024)

Dear Student,

Please read the sec1on on assignments in the Programme Guide for M.Sc. in Chemistry that we sent you after your enrolment. A weightage of 30 per cent, as you are aware, has been earmarked for continuous evaluation, which would consist of one tutor-marked assignment for this course. The assignment is in this booklet, and covers all blocks of the course. The total marks of all the parts are 100, of which 40% are needed to pass it.

Instructions for Formatting Your Assignments

Before attempting the assignment please read the following instructions carefully:

1) On top of the first page of your answer sheet, please write the details exactly in the following format:

Enrolment NO.: ……

NAME: ……

ADDRESS: ……

……

……

COURSE CODE: …….

COURSE TITLE: …….

ASSIGNMENT NO.: ……

STUDY CENTRE: …….. DATE: ……..

PLEASE FOLLOW THE ABOVE FORMAT STRICTLY TO FACILITATE EVALUATION AND TO AVOID DELAY.

2) Use only foolscap size writing paper (but not of very thin variety) for writing your answers.

3) Leave 4 cm margin on the left, top and bottom of your answer sheet.

4) Your answers should be precise.

5) Submit the complete assignment answer sheets within the due date.

6) The assignment answer sheets are to be submitted to your Study Centre within the due date. Answer sheets received after the due date shall not be accepted.

We strongly suggest that you retain a copy of your answer sheets.

7) This assignment is valid from 1st July, 2024 to 30th June, 2025. If you have failed in this assignment or fail to submit it by June, 2025, then you need to get the assignment valid from 1st July, 2025, and submit it as per the instructions given in the Programme Guide.

8) You cannot fill the examination form for this course until you have submitted this assignment.

We wish you good luck.

ASSIGNMENT

Quantum Chemistry and Group Theory

Course Code: MCH-018

Assignment Code: MCH-018/TMA/2024

Maximum Marks: 100

Note: Attempt all questions. The marks for each question are indicated against it.

1. Answer **any five** of the following in brief. **(2x5)**

   (a) Give the significances of de Broglie's idea of matter waves and Heisenberg's uncertainty principle with reference to the description of behaviour of electron in an atom.

   (b) Why can't the ground state energy of a particle confined to a one-dimensional box be zero?

   (c) What is accidental degeneracy?

   (d) Calculate the number of possible orientations of the orbital angular momentum for an electron with $l = 3$.

   (e) Differentiate between probability density and probability of finding the electron in an atom.

   (f) Why do we need to transform the SWE for the relative motion of electron in hydrogen like ions to spherical polar coordinates?

   (g) Why does the expression for energy levels of a hydrogen-like atom get modified in multielectron atoms?

   (h) The average distance of the electron in the ground state of hydrogen atom is more than its most probable distance in the same state. Justify the statement qualitatively.

2. (a) Define blackbody and discuss how classical mechanics was inadequate in explaining the results of black body problem. **(5)**

   (b) i) What are the characteristics of a well behaved wavefunction?

   ii) Define Hermitian operators and show that they give real values of the observables. (**2+3)**

3. (a) i) Devise the Schrödinger wave equation for a particle of mass m confined in one dimensional box of length L.

   ii) Calculate the energy of the first excited state of an electron confined in a one-dimensional box of length $L = 2 \times 10^{-10}$ m. **(3+2)**

   (b) Define degeneracy and calculate the degeneracies of first five energy levels for a particle of mass m confined in a cubic box of edge length=L. **(5)**

4. (a) i) Derive the expression for the rotational energy levels of a rigid rotor.

   ii) Calculate the ground state energy of a diatomic molecule behaving as a quantum harmonic oscillator.

   (Given: Force constant, $k = 500$ N/m and reduced mass $\mu = 1.67 \times 10^{-27}$ kg.) **(3+2)**

   (b) Formulate the Schrödinger wave equation for the hydrogen atom. Discuss the strategy to solve it. You are expected to outline different stages involved in solving the SWE and not to solve it. **(5)**

5. (a) i) Calculate the most probable distance of the electron from the nucleus in the ground state of the hydrogen atom. You may use the normalised radial wavefunction for hydrogen atom from Table 7.1.

ii) Calculate the wavelength of light emitted when an electron in a helium ion (He^+) makes a transition from the n = 4 energy level to the n = 2 energy level. **(3+2)**

(b) Evaluate, $[L_y, L_z]$ and $[L^2, L_z]$ and outline the significance of the outcome. **(5)**

6. Answer **any five** of the following in brief. (**2 x 5)**

(a) What is the difference between a symmetry element and a symmetry operation?

(b) A symmetry operation can be expressed in terms of a transformation matrix. Give the transformation matrix for a C_2 rotation.

(c) State Born-Oppenheimer's approximation and outline its significance.

(d) What are Coulomb's and exchange integrals?

(e) What are the basic requirements of linear combination of atomic orbitals-molecular orbital (LCAO-MO) approach?

(f) What determines whether the 2s and 2p orbitals of the elements of period 2 would undergo mixing or not?

(g) VBT completely ignores the ionic terms in the trial wavefunction for hydrogen molecule whereas the MOT over emphasises them. Comment

(h) Give the assumptions of Hückel molecular orbital theory.

7. (a) Using the variational method, approximate the ground-state energy of a particle in a one-dimensional box with a trial wavefunction, $\psi(x) = Ax\,(L - x)$. Normalise the wavefunction and calculate the expectation value of the energy. (**5)**

(b) Formulate the Schrödinger wave equation for helium atom. Find the approximate ground state energy of helium atom by ignoring the electron-electron repulsion. **(2+3)**

8. (a) What is perturbation method? Formulate the expression for the energy of helium atom by considering the electron-electron repulsion as a first order perturbation. You need to just formulate the expression and not evaluate it. **(2+3)**

(b) i) Identify the symmetry elements and assign point group for water molecule

ii) Generate group multiplication table for water molecule **(2+3)**

9. (a) State Great Orthogonality theorem. Using the consequences of Great Orthogonality theorem derive the characters of irreducible representation of C_{3v} point group. **(2+3)**

(b) Illustrate LCAO-MO approach to chemical bonding by taking the example of hydrogen molecule ion. Give detailed solution to get the expressions for the wavefunctions. (**5)**

10.(a) Discuss the key differences in the Valence Bond and Molecular Orbital approach to chemical bonding by taking the example of bonding in hydrogen molecule. **(5)**

(b) Give the assumptions of Hückel molecular orbital (HMO) theory for conjugated molecules. Determine the expressions for the energy levels for ethylene molecule by using HMO. **(5)**