

## DISCIPLINE SPECIFIC ELECTIVE COURSE - 21 (DSE-21)

### Computational Chemistry

#### CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE

Course title & Code	Credits	Credit distribution of the course			Eligibility criteria	Pre-requisite of the course (if any)
		Lecture	Tutorial	Practical/ Practice		
Computational Chemistry (DSE-21)	04	02	--	02	Class 12 <sup>th</sup> with Physics, Chemistry	--

#### Course Objectives

The objectives of this course are as follows:

- To introduce the fundamental concepts and theoretical background of computational chemistry.
- To develop an understanding of quantum mechanical, semi-empirical and molecular mechanical methods used in molecular modeling and molecular dynamics.
- To enable learners to perform geometry optimization, energy calculations, and vibrational analysis using computational tools.
- To teach the interpretation of computational results in the context of chemical structure, and reactivity.
- To expose students to various software packages commonly used in computational chemistry
- To provide hands-on experience with setting up, running, and analyzing computational chemistry simulations.

#### Learning outcomes

By studying this course, the students will be able to:

- Demonstrate a solid understanding of key computational methods such as ab initio, semi-empirical, and molecular mechanical methods.
- Apply computational tools to predict and analyze molecular properties, geometries, and reaction mechanisms.
- Perform and interpret quantum chemical and molecular simulation calculations using standard software packages.
- Evaluate the accuracy and limitations of various computational approaches in relation to experimental data.
- Design and conduct computational experiments to solve problems in chemical research and development.

#### Unit 1: Fundamentals of Computational Chemistry

(6 Hours)

Conceptual background of computational chemistry and molecular modeling, Z-matrix of simple molecules, Born-Oppenheimer approximation and Potential Energy Surfaces (minima

and maxima), harmonic frequency calculations and intrinsic reaction coordinate. Charge analysis (Milliken, NBO, etc.). Cost and efficiency.

**Unit 2: Molecular Mechanics and Molecular Dynamics (12 Hours)**

Molecular Mechanics: Force Fields, Non-bonded interactions (van der Waals and electrostatic, hydrogen bonding), Parameterization. The applications of MM, the disadvantages, and the different variants of MM (MM1, MM2, MM3, MM4, AMBER, OPLS, etc.); Molecular Dynamics: Ensembles (microcanonical, canonical, isothermal – isobaric), Concept of periodic box, Ergodic hypothesis. Leapfrog and Verlet Algorithms (qualitative treatment), Typical MD simulations.

**Unit 3: Semi-empirical Methods (3 Hours)**

Brief idea of semi-empirical method; CNDO, INDO, MNDO, AM1, PM3.

**Unit 4: Quantum Mechanical Methods (9 Hours)**

Brief idea of quantum mechanical methods; HF, MP2, DFT, CC, and CI (conceptual and qualitative discussion only)

Conceptual ideas of Basis sets (STOs and GTOs), diffuse and polarization functions, Basis set superposition error (BSSE), Effective Core Potentials (ECP), and HOMO-LUMO. Awareness of available computational chemistry software.

**Practicals:**

**Credits: 02**

**(Laboratory periods:15 classes of 4 hours each)**

1. Find the Z-matrix of diatomic (i.e., H<sub>2</sub>, HCl), triatomic (i.e., H<sub>2</sub>O, HNO, HCN) and tetratomic (i.e., H<sub>2</sub>CO, HNO<sub>2</sub>, BH<sub>3</sub>, cis- and trans-diazene) molecules, etc.
2. Determine the optimized geometry of HF, HCl, and HBr molecules and compare the optimized geometrical parameters, formal charges, vibrational frequencies, and dipole moments using AM1, HF, and DFT (using at least three different basis sets).
3. Determine the optimized geometry of HF, HCl, and HBr molecules and compare the optimized geometrical parameters, formal charges, vibrational frequencies, and dipole moments by DFT method at least three different basis sets using any suitable method.
4. Determine the optimized geometry of H<sub>2</sub>O, H<sub>2</sub>S, and H<sub>2</sub>Se molecules and compare the optimized geometrical parameters, formal charges, vibrational frequencies, and dipole moments by HF, DFT and MP2 methods using at least three different basis sets.
5. Calculate and compare the C-C, C=C and C≡C bond dissociation energies of ethane, ethylene, and acetylene molecules, respectively, using any suitable method/basis set.
6. Calculate and compare the bond dissociation energies of HF, HCl, and HBr molecules using any suitable method/basis set.
7. Generate the potential energy surface diagram for the rotational profile of the ethane molecule around the C–C bond.
8. Generate the potential energy surface diagram for the rotational profile of the butane molecule around the C<sub>2</sub>–C<sub>3</sub> bond
9. Determination of Frontier Molecular orbitals of H<sub>2</sub>, CO, HF, H<sub>2</sub>O, H<sub>2</sub>CO and benzene molecules using any suitable method/basis set.

10. Determine the activation energy for the isomerization of cis-diazene to trans-diazene by computing the equilibrium geometries and the transition state structure using any suitable method/basis set.
11. Calculate the intrinsic reaction coordinate (IRC) for cis-diazene to trans-diazene transformation using any suitable method/basis set.
12. Using optimized geometries, calculate the reaction enthalpy at 298 K for the following industrially important reactions (Haber-Bosch process) based on the enthalpies of the involved species:  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$
13. Calculate formaldehyde/benzene's electronic UV/Visible absorption spectrum.
14. Based on the conceptual DFT, calculate the ionization potential (IP), electron affinity (EA), electronegativity, and electron chemical potential of a given set of molecules.
15. Study the mechanism of  $\text{S}_\text{N}2$  reaction between  $\text{Cl}^-$  and  $\text{CH}_3\text{Br}$  involving a Walden inversion computationally.
16. Compute the resonance energy of benzene by comparison of its enthalpy of hydrogenation with that of cyclohexene.
17. Predict the aromaticity of thiophene with respect to benzene by comparing their enthalpies of hydrogenation.
18. Arrange 1-hexene, 2-methyl-2-pentene, (E)-3-methyl-2-pentene, (Z)-3-methyl-2-pentene, and 2,3-dimethyl-2-butene in order of increasing stability.
19. Compare the basicity of the nitrogen atoms in ammonia, methylamine, dimethylamine, and trimethylamine by comparison of their charges and ESP maps.
20. Compare the HXH bond angles for the second-row hydrides ( $\text{BeH}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ) and compare with the results from qualitative MO theory (here, X = Be, C, N and O).
21. (a) Compare the shapes of the molecules: 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol. Note the dipole moment of each molecule. (b) Show how the shapes affect the trend in boiling points: (118 °C, 100 °C, 108 °C, 82 °C, respectively).

**Note:** Minimum 12 exercise to be performed. Any other practical may also be performed as directed by the instructor.

**NB:** Some suggested free open-source software tools include:

**(a)** For visualization and basic tasks: Avogadro, Jmol, RasMol, Molden, IQmol, PyMOL, VMD, MacMolPlt, ArgusLab, ChemCraft (for 150 days) or any other software may be used.

**(b)** For calculations and simulations: Avogadro, ArgusLab, Dalton, Ergo, GAMESS, ORCA, NW Chem, MPQC, Psi4, Quantum ESPRESSO, ABINIT, CP2K, TINKER or any other available software may be used.

### References:

1. C. J. Cramer, *Essentials of Computational Chemistry-Theories and Models*, John Wiley and Sons Ltd., 2nd Ed., 2004.
2. F. Jensen, *Introduction to Computational Chemistry*, John Wiley and Sons Ltd., 3<sup>rd</sup> Ed., 2017.

3. Free and open source software for computational chemistry education, S. Lehtola and A. J. Karttune, *Comput Mol Sci.* (2022); 12, e1610. doi: 10.1002/wcms.1610
4. Online manual of
  - a) *Gaussian 16*, [www.gaussian.com](http://www.gaussian.com)
  - b) *GAMESS*, [www.msg.ameslab.gov/games](http://www.msg.ameslab.gov/games)
  - c) *Q-Chem*, <https://manual.q-chem.com/latest/>
5. J. B. Foresman and Æ Frisch, *Exploring Chemistry with Electronic Structure Methods*, 3rd ed., Gaussian, Inc.: Wallingford, CT, 2015.

**Assessment Methods:** All examination and assessments methods shall be in line with the University of Delhi guidelines issued from time to time.