

Instructions to candidates

Answer all questions.

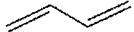
Duration: Two (02) hours

Number of questions: Four (04)

Point allocation: 400 points

1.
 - a. Write an expression for the **electronic** Hamiltonian for the nitrogen atom (use atomic units). (25 points)
 - b. Classify the various terms that are included in the above Hamiltonian as electronic kinetic energy, nuclear-electronic attraction, and electron repulsion. (10 points)
 - c. Which energy contributions are not included in the electronic Hamiltonian that are included in the full Hamiltonian? (10 points)
 - d. Explain what basis functions are, as used in electronic structure calculations. (15 points)
 - e. State the Gaussian product rule. (10 points)
 - f. Discuss the pros and cons in the usage of Slater-type orbitals (STOs) and Gaussian-type orbitals (GTOs). (15 points)
 - g. Explain the difference between STO-1G and STO-3G basis sets. (15 points)

2.
 - a. Explain what is meant by a potential energy surface (PES). (10 points)
 - b. State the Born-Oppenheimer (BO) approximation. (10 points)
 - c. Sketch the PES for H₂O assuming that the H-O distances are the same. (20 points)
 - d. Define "reaction coordinate" with respect to a PES. (10 points)
 - e. Give the mathematical definitions of a minimum and a transition state with respect to a PES. (10 points)
 - f. Explain the importance of normal mode analysis. (10 points)
 - g. Describe the steps involved in the normal mode analysis. (20 points)
 - h. Explain how a transition state gets a corresponding imaginary normal mode frequency. (10 points)

3.
 - a. Calculate the energies of the 4 energy levels of 1,3-butadiene () in terms of α and β . (75 points)
 - b. Calculate the delocalization energy of 1,3-butadiene in terms of α and β . (25 points)

4.
 - a. Explain the difference between molecular mechanics and molecular dynamics. (10 points)
 - b. Describe the following terms

- i. periodic boundary conditions (10 points)
 - ii. minimum image criterion (10 points)
- c. Write an equation for the general form of a force field (for total energy) and describe each term e.g. bond stretching, angle bending etc. (20 points)
- d. Describe the different stages in setting up an MD simulation. (25 points)
- e. Give two examples for each of the following
 - i. explicit water models (5 points)
 - ii. integration algorithms in molecular dynamics (5 points)
- f. Explain the importance of simulated annealing. (15 points)