KENYATTA UNIVERSITY

UNIVERSITY EXAMINATIONS 2011/2012

FIRST SEMESTER EXAMINATION FOR THE DEGREE OF BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION

SCH 408: QUANTUM CHEMISTRY

DATE: Thursday, 1st December, 2011 TIME: 2.00 p.m. – 4.00 p.m.

INSTRUCTIONS: Answer question **ONE** and any other **TWO** .

1 a) Define

i) A Hermitian operator (2 marks)

ii) Eigen value (2 marks)

iii) Eigen function (2 marks)

b) Starting from first principles, prove that eigenvalues of a Hermitian operator are real (4 marks)

c) Describe what is meant quantum mechanical tunneling (3 marks)

d) State and explain at least two basic postulates of quantum mechanics (6 marks)

Total **(19 marks)**

2 a) From the first principle, prove the variation principle, When ϕ is acceptable normalized wave function , E_0 is the lowest eigen value and H is the Hamiltonian operator for the system

$$\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_0$$

(8 marks)

a) Apply the variation function $\psi=Nx(L^2-x^2)$ to the particle in one dimensional box with infinite walls to calculate the energy, given that

$$H = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$$

(8 marks)

Total **(16 marks)**

3 For the hydrogen molecular ion, H_2^+ system, the trial LCAO-MO function is given by

$$\psi = a_1 1s_A + a_2 1s_B$$

b) By applying the variation method, show that the energy is given by

$$E_{\pm} = \frac{H_{AA} \pm H_{BB}}{1 \pm S_{AB}}$$

(8 marks)

c) Show that the normalized LCAO-MO wave functions are

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}[1s_A + 1s_{BA}]$$

$$\psi_- = \frac{1}{\sqrt{2(1+S)}}[1s_A - 1s_{BA}]$$

Respectively, such that

$1S_A$=1S orbital centered on hydrogen A

$1S_B$=1S orbital centered on hydrogen B (8 marks)

Total **(16 marks)**

4 a) Consider the allyl system, C_3H_5 (three π-electrons, open chain). Determine the energies and forms of the Hückel molecular orbitals that are generated by the set of p-π orbitals, (ϕ_1, ϕ_2, and ϕ_3), centered the carbon atoms. (12 marks)

b) Determine the π-bond orders and the distribution of positive charges amongst the carbon atoms of the system $C_3H_5^+$. (6 marks)

Total **(18 marks)**