M.Sc. Examination, 2018
Semester-III
Chemistry(Elective)
Course: CH-916
Optional (Physical Chemistry)

Time: Three Hours **Full Marks: 40**

Questions are of value as indicated in the margin.
Answer ***any four*** questions.

1. a) The relativistic effect is important only for heavier (high Z) atoms – Justify the statement. 2

   b) Show that $\left\langle \psi \left| \sum_i B(r_i) \right| \psi \right\rangle = \int \rho(r)B(r)dr$; where $\rho(r)$ is the electron density and $B(r_i)$ is an external potential. 2

   c) Prove that the electron density of two different systems whose Hamiltonians are differed by more than a constant can't have the same value. 4

   d) What is local density approximation? 2

2. a) What are the different approximations in Hückel molecular orbital theory? 2

   b) Consider cis-butadiene molecular and employ the Hückel approximation to write down the Hückel secular determinant for the molecule using $2p_Z$ orbitals of carbon atoms. Use the group theory to obtain symmetry adapted linear combination of atomic orbitals (SALC) for this molecule. Write down the Hückel determinant in terms of this SALC atomic orbitals. Hence offer your comments on the result. 1+4+2+1

   The character table for C_{2v} point symmetry group is

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	–1	–1
B_1	1	–1	1	–1
B_2	1	–1	–1	1

3. a) Construct the matrix form of the spin operator S_x in the basis function $|\alpha\rangle$ and $|\beta\rangle$. Hence calculate the eigen values and eigen function of S_x operator. 4

   b) Write down the possible spin orbitals for He atom in the first excited state ($1s^1$ $2s^1$) and identify them as singlet or triplets. 2

   c) What is Koopman's theorem? Justify the theorem in reference to Hartree equation and Hartree expression for total energy of a many body system. 4

4. a) Assuming the expression for radiation density $\rho(w)$ as $\rho(w) = \frac{A}{B}\frac{1}{\left(e^{\hbar w/k_B T} - 1\right)}$ (Symbols have their usual meaning). Show that the coefficient for spontaneous emission 'A' increases with the cube of the transition frequency. Discuss the importance of A and B with frequency. 3

   b) The first order time-dependent perturbation equation is $\dot{a}_k^{(1)}(t) = \frac{H'_{km}}{i\hbar}e^{-iw_{mk}t}$ (symbols have their usual meaning).

   Show that for time-independent perturbation, the transition probability is oscillatory and for short time it depends quadratically on time. 3

c) Calculate the approximate ground state energy of a system whose Hamiltonian is given by $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 + 0.3x^3 + 0.04x^4$. 4

5. a) Write down the expression for average energy of a closed shell atom having 2N number of electrons in the Hartree-Fock method. Hence explain the different terms in it (N, is the number of orbitals) 3

b) Write down the Hellmann-Feynman theorem and prove it for a time-independent Hamiltonian. Use the theorem to calculate $\langle x^2 \rangle$ for Harmonic oscillator. 4

c) The average value of any projection operator can have any value – Comment on the statement. 3

6. a) Comment on the applicability of the variation method to excited states. 2.5

b) With the help of a suitable example show that the Slater determinantal wave function satisfy the Pauli exclusion principle. 2.5

c) The ionization energy of H-atom in its ground state is approximately 13.6eV. What would be the value of approximate potential energy of He^+ in its ground state. 2.5

d) Derive the atomic unit of length. 2.5
