M.Sc. Examination, 2017

Semester-II

Chemistry

Course: CH-809

(Physical Chemistry)

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

Questions are of value as indicated in the margin.

Answer ***any four*** questions.

1. a) The radial equation of hydrogen-like atoms is given by

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2\mu}{\hbar^2}\left[E-V(r)-\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right]R=0.$$

Analyze the nature of the bound state solutions for $r\to\infty$ and $r\to 0$ mathematically. 3+4

b) Let us propose a relation $\hat{L}_{-}Y_{\ell,\,m}=NY_{\ell,\,m-1}$ where N is a constant. Justify the proposal. (Terms have usual significances). 3

2. a) Starting from the radial equation of hydrogen-like atoms (see question No. 1.a), arrive at the energy expression after suitable mathematical transformation. 4

b) Using ladder operator technique determine the eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ operators. 6

3. a) The radial wave function of hydrogen-like atoms is given by

$$R(r)=L_{n+\ell}^{2\ell+1}\left(\frac{2zr}{na_0}\right)\cdot\left(\frac{2zr}{na_0}\right)^{\ell}e^{-zr/na_0}.$$

Normalize the wave function using the following standard integral:

$$\int_0^{\infty}e^{-x}x^{\beta+1}\left\{L_{\alpha}^{\beta}(x)\right\}^2dx=\frac{\alpha!^3}{(\alpha-\beta)!}(2\alpha-\beta+1).$$ 4

b) From the expression of hydrogen-like radial wave function analyze the appearance of nodes for s-orbitals and other orbitals. In this context also mention what happens as ℓ assumes its maximum value. 3+1

c) Briefly discuss the characteristics of effective potential energy in hydrogen-like atoms. 2

4. a) Mention the point symmetry group of the following molecules. List the symmetry operations they possess and arrange them according to classes: 1.5+1.5

i) *trans*-1,2-difluoroethylene

ii) free nitrate ion

b) What is cyclic group? Give one example of such a group. 1

c) Prove that "no two classes of a group can share a common element". 1.5

d) Using four 's' orbitals of N and H-atoms in NH_3 molecule construct the matrix representation of rotation operations the molecule possesses. 1+1

e) Show that if RS = T, then D(R) D(S) = D(T); where R, S, T form a group and D(R) etc. are the matrix representations of the symmetry operations. 2.5

5. a) Write down the Great Orthogonality Theorem and hence obtain the orthogonality theorem in terms of character. Show that $\sum_R\left[\chi^{\mu}(R)\right]^2=g$ (symbols have their usual meaning). 3

b) Prove the following relation:

$$a_{\mu}=\frac{1}{g}\sum_R\chi^{red}(R)\chi^{\mu}(R)$$ (Symbols have their usual meaning). 2.5

P.T.O.

c) Show that the character of a matrix remains invariant under a similarity transformation. 2

d) The T_d point group has 24 elements and 5 classes. Given that it has two 3-dimensional irreducible representations (IRs). What will be the number of 1-d IRs for T_d point group? 1.5

e) What is Mulliken symbol for the following irreducible representation? 1

E	c_n	nc_2	i	σ_n
1	1	–1	–1	–1

6. a) The molecule pyridine belongs to C_{2v} point group. Determine the irreducible representation to which the normal modes of vibration of CH_2Cl_2 molecule belong. Also examine the IR and Raman activity of these normal modes of vibration. 3+1.5+1.5

b) Prove that in a 2-dimensional vector space there cannot be more than two orthogonal vectors. 3

c) Write down the expression of projection operator in group theory. The character table of C_{2v} point group is given below: 1

C_{2v}	E	C_2	σ_{v_1}	σ_{v_2}	
A_1	1	1	1	1	z, x^2, y^2, z
A_2	1	1	–1	–1	R_z, xy
B_1	1	–1	1	–1	x, R_y, xz
B_2	1	–1	–1	1	y, R_x, yz