# M.Sc. Examination 2019

**Semester - II**

**Chemistry**

**Course: CH-809**

**( Physical Chemistry )**

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

Questions are of value as indicated in the margin.
Notations and symbols have their usual meanings.
Attempt ***any four*** questions.

1. a) The radial Schrödinger equation for H-like atoms is given by

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

using suitable mathematical transformation reduce above equation to the following form:

$$\frac{d^2R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{d\rho}+\left[-\frac{1}{4}+\frac{n}{\rho}-\frac{\ell(\ell+1)}{\rho^2}\right]R(\rho)=0.$$

From above equation find an expression of energy for H-like atoms. 3+2

b) Show that above reduced equation can be further cast into the following form:

$$\rho\frac{d^2u}{d\rho^2}+(2\ell-\rho+2)\frac{du}{d\rho}+(n-\ell-1)u=0, \text{ where } R(\rho)=\rho^{\ell}e^{-\rho/2}u(\rho).$$

Compare above equation with associated Laguerre differential equation and obtain the complete radial solution for H-like atoms in unnormalized form. 3+2

2. a) Show that a two-particle system interacting under potential energy function V(r) that depends only on the relative coordinates of the particles can be separated into two independent one-particle problem. In this context briefly discuss how concept of reduced mass arises. 4+1

b) The unnormalized radial wave function of H-like atoms is given by

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

Normalize the above wave function. Given standard integral:

$$\int_0^{\infty}e^{-x}x^{\beta+1}\left\{L_{\alpha}^{\beta}(x)\right\}^2dx=\frac{(\alpha!)^3}{(\alpha-\beta)!}(2\alpha-\beta+1).$$ 5

3. a) The ladder operator $\hat{L}_+$ in polar coordinate is given by $\hat{L}_+=\hbar e^{i\phi}\left(\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right)$.

Using the fact that $\hat{L}_+Y_{max}=0,$ obtain an expression of normalized $S_{\ell,\ell}(\theta)$ function.

Given, standard integral: $\int_0^{\pi}\sin^{(2\ell+1)}\theta\,d\theta=\frac{2(2^{\ell}\ell!)^2}{(2\ell+1)!}$. 5

**P.T.O.**

b) Show that (i) $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$ and (ii) $\left[\hat{L}^2, \hat{L}_x\right] = 0.$ 3+2

4. a) Show that there can be only one group of order 3. Show that the group is abelian. 3
   b) If A is conjugate to B and C separately then show that B and C are conjugate to each other. 2
   c) An object has a four-fold rotation axis, a two-fold rotation axis perpendicular to it and a $\sigma_h$ plane. What are the possible symmetry operations that constitute the point group of the object? What is the point group of the object? 2
   d) Show that if $RS = T$ then $D(R)\cdot D(S) = D(T)$ where R, S and T are symmetry operations. 3

5. a) If two symmetry operations P and Q are connected through a similarity transformation show that the characters of the corresponding matrices for P and Q are same. 3
   b) Using the character table of given $T_d$ point symmetry group show that 3

$$\sum_{i=1}^{k} n_i \chi^{T_1}(c_i)\chi^{E}(c_i) = 0 \quad \text{and} \quad \sum_{i=1}^{k} n_i \chi^{T_2}(c_i)\chi^{T_2}(c_i) = 24.$$

The character table for $T_d$ point symmetry group:

| $T_d$ | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | |
|---|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 1 | $x^2+y^2+z^2$ |
| $A_2$ | 1 | 1 | 1 | –1 | –1 | |
| E | 2 | –1 | 2 | 0 | 0 | $2z^2-x^2-y^2,\ x^2-y^2$ |
| $T_1$ | 3 | 0 | –1 | 1 | –1 | $(R_x, R_y, R_z)$ |
| $T_2$ | 3 | 0 | –1 | –1 | 1 | $(x, y, z), (xy, xz, yz)$ |

   c) Consider the 1S atomic orbital of N and three H-atoms of $NH_3$ molecule. Employ projection operator technique to obtain the symmetry adapted linear combination of atomic orbitals for $NH_3$ molecule. The character table for $C_{3v}$ point group is given below: 4

| $C_{3V}$ | E | $2C_3$ | $3\sigma_V$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | –1 |
| E | 2 | –1 | 0 |

6. a) How to ascertain that there is one total symmetric irreducible representation for each point symmetry group? 2
   b) Consider the character table of $T_d$ point symmetry group given above. Using the table determine the irreducible representation to which the normal modes of vibration of $CH_4$ molecule belong. Identify which of these modes are IR and Raman active. 4+2+2

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