**Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031**

**1st Semester, 2017-2018**

# CHEM F213: Physical Chemistry-II

**Date: October 09, 2017** **Time: 90 minutes**

**Mid-semester Test (Closed Book)** **Max. Total Marks 60**

**General Instructions:**

*1. Write your name, ID no., Course No., Course Title, Date and Day legibly, correctly and completely on the main answer-sheet as well as on the supplement(s) (if any) used.* ***Incomplete or wrong information will result in deduction of up to 5 marks.***

*2. All the questions are compulsory. You may solve the questions in any order. However, solve all the sub-questions of a question before going to new question.*

*3. Only scientific and non-programmable calculators may be used for numerical calculations. Use of calculators with operating systems is strictly prohibited. Use of mobile phones, iPhones, pagers, are strictly prohibited.*

**Q. 1.** Consider a particle confined in a rectangular box such that U(x,y)=0 for $0 \le x \le a$; $0 \le y \le 2a$ and $U(x,y) = \infty$ otherwise.

**(a)** Write expression for normalized wavefunction in terms of the quantum numbers $n_x$ and $n_y$. **[2]**

**(b)** Identify the lowest four energy states (write the quantum numbers only) and calculate the separation between the first and the fourth energy states in terms of $h^2/8ma^2$. **[5]**

**(c)** Calculate the probability that the particle in the state corresponding to $n_x=n_y=2$ is found in the region: $0\le x\le a$, $0\le y \le a/2$. **[3]**

**Q. 2.** Consider a particle moving with uniform circular motion in an orbit with a fixed radius. The stationary states of the system are described by Hamiltonian eigenfunctions:

$\Phi_m(\phi)=\frac{1}{\sqrt{\pi}}e^{-\Im[\phi-(m\hbar t/2\mu\rho^2)]}; m=0,\pm1,\pm2,\ldots$ where, μ is the mass of the particle and, ρ its distance from the centre of the orbit. In 2D-polar coordinate system, the operator ∇ takes the form:

$$\nabla=\frac{1}{\rho}\left(\frac{\partial}{\partial\rho}\rho+\frac{\partial}{\partial\phi}\right)$$

.

**(a)** Obtain the expression for probability current. **[7]**

**(b)** Calculate the probability current corresponding to m=0,+1,−1 ; respectively. **[3]**

**Q. 3.** The electron-spin functions, α and β are degenerate eigenfunctions of spin-angular momentum squared operator $\boldsymbol{\sigma}^2$ with eigen value $0.75\hbar^2$. These functions also obey eigenvalue equation of the operator $\boldsymbol{\sigma}_z$ (z-component of spin-angular momentum) and the corresponding eigenvalues are $0.5\hbar$ and $-0.5\hbar$, respectively.

**(a)** Define the ladder operators, $\boldsymbol{\sigma}_\pm$. **[2]**

**(b)** Using known concepts about spin angular momentum of electron, guess the effect of action of the raising and the lowering operators on these eigenfunctions **[4]**

**(c)** Check whether the following functions: $(\boldsymbol{\sigma}_+\beta \pm i\boldsymbol{\sigma}_-\alpha)$ are eigenfunction sof (i) $\boldsymbol{\sigma}_z$; and (ii) $\boldsymbol{\sigma}^2$. **[4]**

**Q .4** Given F={$f_1$, $f_2$, $f_3$, $f_4$} is a complete orthonormal set of eigen-functions of hermitian operator, **A** with eigen-values $a_1$ =5, $a_2$=$a_3$=7, $a_4$=9. Another complete orthonormal set G={$g_1$, $g_2$, $g_3$, $g_4$} is related to the set F as follows: $g_1 = 0.7071(f_1 + f_4)$; $g_2=0.7071(f_2 + f_3)$; $g_3=0.7071(f_2 - f_3)$; $g_4=0.7071(f_1 - f_4)$; The functions in G happen to be eigen-functions of another hermitian operator **B**, with eigen-values $b_1$=6; $b_2$=$b_3$=8, $b_4$=10. The sets F and G form two distinct complete sets of degenerate eigenfunctions of yet another hermitian operator **D** with eigenvalue d=25.

**(a)** Write the commutation relationships between these operators. **[2]**

**(b)** If measurement is made with operator A and value 9 is found, what is the state of the system immediately after the measurement? **[2]**

**(c)** Immediately after the measurement in (b), if measurement with operator B is done, what is the probability of getting the value 6? **[2]**

**(d)** If measurement with operator A is done and value 7 is found, measurement with operator B is done immediately after that, what is the probability that value 8 will be found? **[2]**

**(e)** If the system is prepared to be in the normalized state: $\psi = 3^{-1/2}f_1 + 0.5(f_2 + f_3) + c_4f_4$; (I) Find the value of the positive constant $c_4$. (II) What will be the average value of operator **D** in this state? **[2]**

**Q. 5. (a)** Consider the following orbital of a hydrogen atom:
$\Psi(r,\theta,\varphi) = (3/\pi a_0^3)^{1/2}\,(r^3/187500a_0^3)\,(20 - r/a_0)\; e^{-r/5a0}\sin(\theta)\sin(2\theta)\cos(2\varphi)$
(i) Identify the number of radial node(s) and locate the same. **[1]**
(ii) Identify the number of angular nodes. **[1]**
(iii) Identify the orbital. **[2]**
(iv) Is it an eigenfunction of $L_z$ operator? If yes, what is the eigenvalue? If no, what is $|m_l|$? **[2]**
**(b)** Hermite polynomials defined by $H_n(y) = (-1)^n e^{y^2} d^n (e^{-y^2})/dy^n$, obey the Hermite's differential equation:
$H''(y) - 2yH'(y) + (\lambda - 1)H(y) = 0$. Prove that $yH_n(y) = (½)H_{n+1}(y) + nH_{n-1}(y)$ **[4]**

***** END *****