Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
Mid-Semester Test, First Semester, AY: 2017-2018
CHEM G553: Advanced Physical Chemistry

Time: 90 minutes **Max. Marks: 90**

There are six questions. Attempt all the questions. Pencil should not be used. Don't scribble on the question paper.
Useful date: h = 6.63 X 10^{-34} J s; Velocity of light = 2.998 X 10^{8} ms^{-1}; Mass of the electron = 9.1 × 10^{-31} kg,
1 amu = 1.66054 × 10^{-27} kg

1 (a) Show that a function x^k is an eigen function of the operator, $\widehat{\boldsymbol{O}}$ = [a + bx $(\frac{d}{dx})$], where k, a, and b are constants. What is the eigen value? Is the function f(x) = x^3 + 3x an eigen function of the given operator? **[6]**

(b) In an X-ray photoelectron experiment, a photon of wavelength 150 pm ejects an electron from the inner shell of an atom and it emerges with a speed of 21.4 × 10^6 m/s. Calculate the binding energy of the electron in Joule. **[5]**

(c) Which of the following expressions are acceptable wave functions? Briefly justify **[4]**
(i) Ψ = x^2 + 1, where x can have any value
(ii) Ψ = 1/(4-x); 0 ≤ x ≤ 3

2 (a) A particle of mass m is confined to move in two dimension. The potential energy V = 0 for 0 ≤ x ≤ L_1, 0 ≤ y ≤ L_2 and V = ∝ elsewhere. Answer the following questions:

(i) Write down the form of the normalized wave function for the particle. **[3]**

(ii) Write down the expression for energy of the particle. **[3]**

(iii) Consider, L_1 = L and L_2 = 2L. Show that there is a degeneracy between the states |1,4⟩ and |2,2⟩. **[6]**

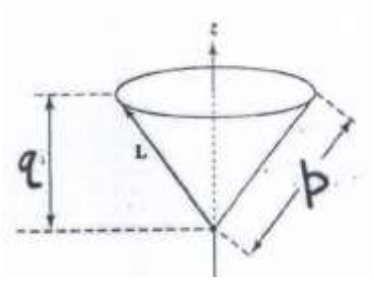
(b) What is the magnitude of the momentum of a free particle having momentum eigen function, ψ = e^{i4x}? **[3]**

3 (a) Determine the normalization constant, N, for the wave function Ψ(ϕ) for particle of mass m on a ring which is having the form, Ψ(ϕ)= $Ne^{im\phi}$. **[6]**

(b) Evaluate the magnitude of angular momentum associated with the particle of mass m as described in the previous question. Wave function of the particle is Ψ(ϕ)= $Ne^{im\phi}$. **[3]**

(c) Consider a diatomic molecule, $^1H^{35}Cl$. The force constant of the bond is k_f=516.3 N m^{-1}. Determine the frequency of the oscillation for $^1H^{35}Cl$. Determine the energy separation between the v = 0 and v = 1 states. **[6]**

4 (a)



Orbital angular momentum quantum number of a rigid rotor, represented in the Figure, is '***l***'. Answer the following

[1]

[1]

(i) Magnitude of slant height, ***p***, of the total angular momentum vector '**L**'. **[1]**

(ii) Magnitude of the altitude, ***q***. **[2]**

(iii) How many values are possible for ***q***.

(iv) Why the vector **L** lie on the surface of a cone? Explain in one or two sentences.

(b) Consider an electron in the $3p_x$ orbital of H-atom. Answer the following questions:

(i) What would be outcome(s) of the $\widehat{L_Z}$ operator? Do mention the probability of each outcome(s). **[3]**

(ii) What would be the value(s) of spin magnetic quantum number of the electron? **[2]**

(c) Fluorescence emission spectra of molecules in the solution are in general independent of the excitation wavelength. Explain briefly. **[2]**

(d) The molar absorption coefficient of solute at 540 nm is 286 dm^3 mol^{-1} cm^{-1}. When light of that wavelength passes through a 6.5 mm cell containing a solution of the solute, 46.5 percent of light absorbed. What is the concentration of the solution? **[3]**

5 (a) Normalize the molecular orbital, $\varphi = \psi_A + \lambda\psi_B$ in terms of the parameter λ and the overlap integral S. **[4]**

(b) Arrange the species O_2^+, O_2, O_2^-, and O_2^{2-} in order of increasing bond order. Do mention the bond order of each species. What is the spin state of ground state O2 molecule? **[6]**

(c) The lowest observed microwave absorption frequency of $^{12}C^{16}O$ [Reduced mass, μ = 1.13850 $\times$ 10^{-26} kg] is 115271 MHz. Compute (a) bond distance in $^{12}C^{16}O$ and (b) predict the next two lowest microwave absorption frequencies of $^{12}C^{16}O$. **[5]**

6 (a) Symmetric stretch vibration of CO_2 is IR-inactive. Explain briefly. **[2]**

Can you measure the frequency of the same mode using any spectroscopic method? Explain you answer. **[2]**

(b) A transition is observed at 3185 cm^{-1} while recording vibrational spectrum of water. Other transitions, appeared at 3760 cm^{-1} (anti-symmetric stretch), 3650 cm^{-1} (symmetric stretch), and 1600 cm^{-1} (bending). Answer the following questions:

(i) Determine the zero-point vibration energy of water. **[3]**

(ii) Assign the transition observed at 3185 cm^{-1}. **[2]**

(c) Calculate resonance frequency for proton in a 12.0 T magnetic field. γ_N is 2.6752 $\times$ 108 T^{-1} s^{-1}. **[3]**

(d) Consider a nucleus with δ=1.00 in a 500 MHz NMR spectrometer. Calculate the shift of the nucleus relative to the reference. What would be the shift in 100 MHz instrument? **[3]**

**********End**********