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B.Sc. M.Sc. INTEGRATED PROGRAM
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SEMESTER-IV EXAMINATION-2019
PAPER CODE-BCH-CC12TH
PAPER TITLE: QUANTUM CHEMISTRY AND SPECTROSCOPY

Time: Three Hours **Max Marks: 75**

(Write your Roll No. on the top immediately on receipt of question paper.)
(Use of Scientific Calculator is permitted)

Attempt ALL questions.

Q1. Explain very briefly of the following (ANY FIFTEEN): **1 x 15 = 15**

a. Morse potential for anharmonic Oscillator?
b. Franck- Condon principal
c. Born-Oppenheimer approximation and Overtones
d. Spin-Spin Coupling Constant
e. Bohr frequency condition & Larmor precision
f. P, Q, R branches?
g. rotation vibration spectra of a rigid diatomic rotor
h. Chemical Shift
i. Molecular orbital Theory *vs* Valance Band theory?
j. Heisenberg Uncertainty principle
k. Bonding vs antibonding molecular orbital.
l. ESR Spectra
m. Predict the proton- NMR spectrum of ethanol and HD along with deuteron-NMR spectrum of HD
n. Schrodinger wave equation and its solution
o. Zero-point energy
p. Particle in one-dimension box
q. Heisenberg uncertainty principle
r. Show that the commutator [x, $\frac{\partial}{\partial x}$]= -1.
s. Show that (a) $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$ and (b) $[\hat{A}2, \hat{B}] = \hat{A}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{A}$
t. Show that the commutator $[\widehat{Xn}, \widehat{px}] = \frac{ih}{2} n x^{n-1}$ where n is a positive integer.
u. Discuss the Postulates of quantum mechanics?
v. If $\hat{A}$ and $\hat{B}$] cap are two operators such that $[\hat{A}, \hat{B}] = 1$, show that $[\hat{A}, \hat{B}2] = 2\hat{B}$.

Q2. Attempt ANY THREE of the following: **3 x 5 = 15**

I. The pure rotational (MW) spectra of spectra of gaseous HCl consist of a series of equally spaced lines separated by 20.80 cm^{-1}. Calculate the internuclear distance of the molecule. (Given the atomic masses ^{1}H= $1.673x10^{-27}$ Kg; ^{35}Cl= 58.06×10^{-27} Kg).

II. Different types of spectra given by a molecule and what is Stark effect in MW spectra? The fundamental vibration of HCl is 2890 cm^{-1}. Calculate the force constant of this molecule. (Given the atomic masses ^{1}H= $1.673x10^{-27}$ Kg; ^{35}Cl= $58.06x10^{-27}$ Kg).

III. A sample was excited by the 4359 Å line of mercury. A Raman line was observed at 4447 Å. Calculate the Raman shift in cm^{-1}. At what wavelength in Å would the anti-strokes line appear in the Raman spectrum of the sample? Why are the anti-stoke lines are less intense than the stoke line in the Raman spectrum?

IV. Discuss the factors affecting width and intensity of a spectral line? The fundamental vibrational frequencies of SO_2 are 1151.38, 517.69, and 1361.76 cm^{-1}. Account for the absorption bands at 1875.55, 2295.88 and 2499.5 cm^{-1}.

V. How MW spectroscopy used in investigation of internal rotation and inversion splitting of NH_3? Sketch the normal modes of vibration of CO_2 and H_2O and predict their IR activity with reason?

Q3. Attempt ANY THREE of the following: **3 x 5 = 15**

I. Calculate the nuclear spin angular momentum and the magnetic moment for a proton, given that I =1/2, g_N for proton is 5.585 and μ_N= 5.05x10-27 JT^{-1}. Calculate the magnetic field strength required to observe the NMR frequency for fluorine (^{19}F) at 60 MHz. Given g_N for ^{19}F = 5.257 and μ_N = 5.05x10-27 JT^{-1}.

II. The magnetic moment of ^{31}P is equal to 1.1305 nuclear magnetons, i.e. 1.1305 μ_N. Calculate its magnetogyric ratio and *g*-factor. Given $\mu_N = 5.05 \times 10^{-27}$ JT^{-1} and nuclear spin of ^{31}P is 1/2. Calculate the ESR frequency of an unpaired electron in a magnetic field of 0.33 T, given that for the free electron, g_e =2 and $u_B = 9.273 \times 10^{-24}$ JT^{-1}.

III. Which of the following nuclei do not show nuclear magnetic resonance: ^{1}H, ^{2}H, ^{12}C, ^{13}C, ^{14}N, ^{15}N, ^{16}O, ^{19}F, ^{31}P, and ^{32}S? Explain the Bathochromic, Hypsochromic, Hypochromic and Hyperchromic Shift

IV. In an ESR spectrometer, the ESR frequency of the free electron is 9.5 GHz. Calculate the magnetic field at which the spectrometer is operating, $g_e = 2$ and $u_B = 9.273 \times 10^{-24}$ J T^{-1}? Differentiate the proton- NMR spectrum of NH_3 from that of NH_4^+ ion?

V. How many kinds of proton are there in CH_3CH_3, $CH_3CH_2CH_3$, $(CH_3)_2CHCH_2CH_3$ and $C_6H_5CH_3$, $C_6H_5NO_2$, $CH_2=CH_2$, $CH_3CH=CH_2$? Which of the following molecule will show a spectrum and why?

Type of spectrum	Molecules
Pure rotational (MW)	H_2, HCl, CO, $CHCl_3$, H_2O, NH_3, and NH_4Cl
Vibrational (IR)	H_2, HCl, CO, $CHCl_3$, H_2O, NH_3, NH_4Cl, CH_3-CH_3, C_6H_6, CCl_4, and CO_2
Rotational Raman	H_2, HCl, CO, CH_4, $CHCl_3$, H_2O, NH_3, CH_3-CH_3, and SF_6
Vibrational Raman	H_2, HCl, CO, CH_4, $CHCl_3$, H_2O, NH_3, CH_3-CH_3, and SF_6

Q4. Attempt ANY THREE of the following: **3 x 5 = 15**

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I. Write the Hamiltonian operator for He_2^+ and K_2 molecule -ion?

II. Calculate the probability of finding the electron in a small volume element of 1 pm^3 located along the bonding axis in H_2^+ at r = 0.050 nm. Assume that the nuclei are separated at a distance of 0.1054 nm.

III. Assuming that the ionic character in H-Br bond is 11%, calculate the fraction of the contribution of ionic character to the valence bond wave function.

IV. Draw the molecular orbital diagram of Heteronuclear diatomic molecule (CO, NO, HF), HCl. Write the electronic configurations of H_2, H_2^+ and the hypothetical species H_2^- in terms of molecular orbital theory. Why does He^+ exist whereas He_2 does not?

V. Of the following species, which has the shortest bond length: NO, NO^+, NO_2^+, NO^-? Compare the bond energy, bond length & magnetic character of CN & CN^- spin with the help of MOT. Of the species O_2, O_2^+, O_2^-, and O_2^{2-}, which would have the maximum bond strength?

Q5. Attempt ANY THREE of the following: **3 x 5 = 15**

I. Find expression for the following operators:

(i) $\left(\frac{\partial}{\partial x} + x\right)^2$ (ii) $\left(\frac{\partial}{\partial x} + x\right)\left(\frac{\partial}{\partial x} - x\right)$ (iii) $\left(\frac{\partial}{\partial x} - x\right)\left(\frac{\partial}{\partial x} + x\right)$

II. Calculate the energies (in eV) of an electron constrained to move in a one-dimensional box of width 1 Å and exhibit them on an energy level diagram.

III. Explain if d^2/dx^2 and p_x for linear momentum is hermitian operator?

IV. Explain the postulates of quantum mechanics?

V. Indicate which of the following functions are acceptable as wave functions:

(i) $\psi = x$ (ii) $\psi = x^2$ (iii) $\psi = \sin x$ (iv) $\psi = e^x$

(v) $\psi = e^{-x}$ (vi) $\psi = e^{-x^2}$ (vii) $\psi = \tan x$

Terms have their usual meaning

Avogadro number: $N_A = 6 \times 10^{23}$/mol;

Universal gas constant: $R = 8.31 \times 10^7$ erg/mol/K;

Boltzmann Constant: $k_B = 1.38 \times 10^{-16}$ erg/K