M.Sc. CHEMISTRY
SECOND SEMESTER
QUANTUM CHEMISTRY & MOLECULAR SPECTROSCOPY II
MSC - 204
(Use Separate Answer Scripts for Objective & Descriptive)

Duration : 3 hrs.   Full Marks : 70

[PART-A: Objective]

Time : 20 min.   Marks : 20

Choose the correct answer from the following: *1X20=20*

1. For oxygen molecule (O_2)
   a. $r_e' = r_e''$
   b. $r_e' > r_e''$
   c. $r_e' < r_e''$
   d. $r_e' >> r_e''$

2. the vibrational quantum number (V_{max}) at which diatomic molecule dissociate is given by[x_e = anharmonicity constant]
   a. $1/2x_e + 1$
   b. $1/2x_e - 1$
   c. $2x_e + 1$
   d. $2x_e - 1$

3. The distance between the first spectral line of R branch and that of P branch of rotational fine structure in electronic transition is
   a. 10B
   b. 8B
   c. 4B
   d. 6B

4. The value of the chemical shift δ (ppm) is maximum in proton NMR spectroscopy for the molecule
   a. CH_4
   b. CH_3I
   c. CH_3Cl
   d. CH_3F

5. The number of ESR hyperfine spectral line of benzene radical anion is
   a. Seven
   b. Five
   c. Two
   d. One

6. The orange color of CrO_4^{2-} is due to
   a. MLCT
   b. LMCT
   c. Fluorescence
   d. d-d transition

7. The species which will not show ESR spectra is
   a. C_2H_5.
   b. Cu^{2+}
   c. N_2
   d. O_2

8. The intensities of hyperfine spectral lines of CH_3. radical is in the ratio
   a. 3:1:1:3
   b. 1:3:1:3
   c. 1:4:4:1
   d. 1:3:3:1

[1]

9. In He - Ne laser LASER transition takes place
   a. first in Helium, then in Neon
   b. First in Neon, then in Helium
   c. Neon only
   d. Helium only

10. mossbauer effect is prominent at lower temperature because it depend on
    a. Isomeric shift
    b. Doppler shift
    c. Electron density at the nucleus
    d. recoil free fraction of gamma ray emitting nucleus

11. Which one is the wrong atomic unit by symbol?
    a. Mass = m_e
    b. Length = a_0
    c. Angular momentum = h
    d. Permittivity = $4\pi\varepsilon_0$

12. The complete one-electron wave function is called
    a. Spherical harmonics
    b. Spin orbitals
    c. Radial functions
    d. None of them

13. If we don't include spin-orbit coupling the electronic energies of a hydrogen atom depend upon
    a. n; principle quantum number
    b. j; spin-orbit coupling
    c. n & j
    d. None of them

14. In case of spin-orbit coupling which of the following is conserved?
    a. L
    b. S
    c. J
    d. None of them

15. Associated Legendre function $P_J^{|m|} = 0$ if
    a. m=J
    b. m < J
    c. m > J
    d. All of them

16. The radial wave functions of hydrogen atom contain which of the following
    a. Legendre polynomial
    b. Hermite polynomial
    c. Associated Legendre function
    d. Associate Laguerre polynomial

17. The number of nodes in the radial wave function of hydrogen are
    a. n-1
    b. n-l-1
    c. n-l
    d. l-1

18. Which of the following system can be exactly solved?
    a. Helium atom
    b. Hydrogen molecule
    c. Hydrogen molecular ion
    d. All of them.

19. Which of the following is correct match for system and coordinate to solve it.
    a. Rigid rotator – cylindrical coordinates
    b. Hydrogen molecular ion – elliptical coordinates
    c. Both a & b
    d. None of them

20. The off-diagonal matrix elements of the effective Hamiltonian operator in the secular determinant are called
    a. Resonance integrals
    b. Exchange integrals
    c. Both a & b
    d. None of them

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Time : 2 hrs. 40 min.   Marks : 50

[Answer question no.1 & any four (4) from the rest]

1. a. Explain what happens when a magnetic field is applied on a bare electron.   4+3+3
       Show graphically the variation of energy in presence of continuously   =10
       varying magnetic field of an electron.

    b. Explain Born–Oppenheimer approximation using hydrogen molecule as
       an example.

    c. What is Huckel molecular orbital theory? Explain using ethene as an
       example.

2. a. What are different types of intensity distribution of vibrational bands in   7+3=10
       electronic transition. State the principle behind it and explain the intensity
       distribution with the type of it.

    b. Mention the selection rule on the basis of symmetry property of the
       electronic state.

3. a. What do you mean by dissociation and predissociation? Give an   4+4+2
       expression of equilibrium dissociation energy (D_e) in terms of equilibrium   =10
       oscillation frequency and anharmonicity constant.

    b. Show that the area under the curve $\Delta G_{v+\frac{1}{2}}$ versus v gives the dissociation
       energy of a molecule where $\Delta G_{v+\frac{1}{2}}$ is given by $G(v+1)- G(v)$.

    c. Write the properties of laser radiation.

4. a. What do you mean by spin-spin and spin-lattice relaxation ? Define   3+3+4
       relaxation time .   =10

    b. Write down the expression of g value of a paramagnetic electron in rare
       earth metal. Calculate the g value of Fe^{3+}.

    c. Derive Hartree–Fock equation for Helium atom. Explain how it is solved
       by Self Consistent Field (SCF) method.

5. a. Show that in order to have resonance absorption the line width must be   4+4+2
       equal or greater than the loss of gamma ray energy due to recoil. Why the   =10
       source and the sample are put in the crystal in Mossbauer spectroscopy?

    b. Why ESR spectrum is obtained in derivative mode ? Find the value of Bohr
       magneton if in a magnetic field of 0.339T, ESR frequency is found at 9.5
       GHz. (Given that ge = 2.0)

    c. Explain why four level laser is superior to three level laser.

6. a. Solve the following equation using $\qquad$ 5+3+2
=10

$$x = \cos\theta \text{ and } \Theta(\theta) = P(x)$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \beta\sin^2\theta = m^2$$

to obtain the Legendre equation

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[\beta - \frac{m^2}{1-x^2}\right]P(x) = 0$$

b. Explain with diagram why lines of pure rotational spectrum are not equally spaced.

c. What are P and R branches in rotation-vibration spectrum. Illustrate them with drawing.

7. a. Use the following trial function to calculate the ground state energy of a harmonic oscillator   4+4+2
=10
$\varphi = \cos\lambda x \quad -\pi/2\lambda < x < \pi/2\lambda$
where λ is the varriational parameter. Compare it with the exact ground state energy.

b. Calculate the first-order correction to ground state energy of an anharmonic oscillator whose potential is

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma_3x^3 + \frac{1}{24}\gamma_4x^4$$

c. Write Schrodinger equation of helium atom. Why is it not possible to solve.

8. a. What are Slater type orbitals. Write its equation and explain the terms. How is it different from hydrogen like orbitals.   4+6=10

b. Find the expression of π-electron energy levels of butadiene using Huckel molecular orbital theory. How much is the π-electron delocalization energy of butadiene?

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[4]