REV-01
MSC/03/05

2023/08

SET A

M.Sc. CHEMISTRY
SECOND SEMESTER
QUANTUM CHEMISTRY & MOLECULAR SPECTROSCOPY II
MSC – 204 [SPECIAL REPEAT]

USE OMR FOR OBJECTIVE PART]

Duration: 3 hrs. **Full Marks: 70**

(Objective)

Time: 30 min. **Marks: 20**

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

1. Potential energy of a rigid rotator is
   a. Positive b. Negative
   c. Either positive or negative d. Zero

2. What is the most probable value of r in 1s orbital? [a_0 is Bohr radius]
   a. a_0 b. ½ a_0
   c. 3/2 a_0 d. 2/3 a_0

3. Normalization constant for the wavefunction e^imφ is equal to (φ = 0 to 2π)
   a. $1/\sqrt{2\pi}$ b. 2π
   c. $1/2\pi$ d. $\sqrt{2\pi}$

4. The microwave spectrum of HCl consists of a series of equally spaced lines separated by 6.26 X 10^{11} Hz. Calculate the bond length of HCl if reduced mass is 1.61 X 10^{-27} kg.
   a. 1.28 Å b. 1.29 Å
   c. 1.30 Å d. 1.31 Å

5. According to variational principle
   a. $E_\phi \leq E_0$ b. $E_\phi \geq E_0$
   c. $E_\phi \sim E_0$ d. $E_\phi = E_0$

6. Let E is the ground state energy of the harmonic oscillator. If cos ax is used as a trial function for solving harmonic oscillator variationally then what will be the energy?
   a. 0.14E b. 2.14E
   c. 3.14E d. 1.14E

7. 1Eh unit of energy is equal to
   a. 2625.5 kJ/mol b. 27.211eV
   c. Both a & b d. None

8. Which of the following is antisymmetric orbital?
   a. ψ(1,2) + ψ(2,1) b. ψ(2,1) – ψ(1,2)
   c. Both a & b d. None

9. For hydrogen atom term symbol which of the following is a value of j for l = 3?
   a. 1/2 b. 3/2
   c. 7/2 d. 0

10. By Huckle molecular orbital theory which of the following integral have non-zero value for butadiene.
   a. H24 b. S13
   c. H13 d. S11

11. The allowed transition is
   a. $^3\Sigma g^- \leftrightarrow {}^3\Sigma u^-$ b. $^3\Sigma g^- \leftrightarrow {}^1\Sigma g^+$
   c. $^3\Sigma g^- \leftrightarrow {}^3\Sigma u^+$ d. $^3\Sigma g^- \leftrightarrow {}^3\Delta u$

12. The equilibrium dissociation energy of a molecule (De) is approximately equal to
   a. $\omega e/4\chi e$ b. $\omega e\chi e/4$
   c. $4\chi e/5\omega e$ d. $¾\ \omega e/\chi e$

13. In Helium-Neon Laser, laser transition takes place from (Neon atom)
   a. 5s → 3s b. 5s → 3p
   c. 3P → 3s d. 3p → 2p

14. The electron which contributes to isomer shift in Mossbaeur spectra is
   a. p-electron b. s-electron
   c. d-electron d. f-electron

15. The selection rule for transition among energy levels due to quadrupole splitting is
   a. $\Delta mI = 0$ b. $\Delta mI = -1$
   c. $\Delta mI = 0, \pm 1$ d. $\Delta mI = 1$

16. Band head occurs in the P branch of the rotational spectra line when
   a. $re' = re''$ b. $re' > re''$
   c. $re' < re''$ d. $re' >> re''$

17. The number of ESR spectral lines of benzene radical anion is
   a. one b. three
   c. six d. seven

18. Larmor frequency (in Hertz) is given by
   [μ = Dipole moment; I= Nuclear spin; $h = h/2\pi$; Bz = Magnetic moment along z direction]
   a. $IBz/2\pi\mu$ b. $IBz/2\pi h$
   c. $hBz/2\pi I$ d. $\mu Bz/2\pi I$

19. The intensities of hyperfine lines of CH3. Radical is in the ratio
   a. 1:3:3:1 b. 1:3:1:3
   c. 1:4:5:1 d. 3:1:1:3

20. The nucleus which don't exhibit NMR spectra is
   a. ^{18}O b. ^{11}B
   c. ^{19}F d. ^{31}P

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Descriptive

Time : 2 hrs. 30 mins. Marks : 50

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

1. a. State the selection rule on the basis of symmetry properties of electronic states. 2

   b. What are the different types of intensity distribution of the vibrational bands in electronic transitions? State the principle behind it. Apply the principle to explain the intensity distribution of oxygen molecule. 3+2+3 =8

2. a. Explain the basic principle of ESR spectroscopy and find the condition of resonance. Why ESR spectrum is represented in derivative mode? 3+2+2 =7

   b. What do you mean by hyperfine interaction in ESR spectra? Give the expression for 'g' value and calculate the g value of a free electron. 1+1+1 =3

3. a. Show that in order to have nuclear resonance absorption the line width must be equal or greater than the loss of gamma (γ) ray energy due to recoil of the nucleus. Why the source and sample are put in the crystal to have a Mossbauer spectrum? 4+2=6

   b. Explain what do you mean by stimulated emission of radiation. Why four level laser is superior to three level laser? 1+2+1 =4

4. a. Define chemical shift and explain cause of chemical shift in NMR spectroscopy. Why TMS is used as a reference in proton NMR spectroscopy? Draw high resolution NMR spectra of dry C2H5OH. 3+3+2 =8

   b. What are the different types of relaxation in NMR transition? Explain briefly. 2

5. a. Why lines of pure rotational spectrum are not equally spaced? Explain with the help of figure. 3+3+4 =10

   b. To a good approximation, the microwave spectrum of $H^{35}Cl$ consists of a series of equally spaced lines, separated by 6.26 x

10^{11} Hz. Calculate the bond length of $H^{35}Cl$.

c. Show that the hydrogen-like atomic wave function ψ_{210} is nonnalized and that it is orthogonal to ψ_{200}.

6. a. Draw the probability density curves associated with 1s, 2s, 2p, 3s, 3p, 3d orbitals of hydrogen atom. 4+3+3 =10

b. Using a Gaussian type trial function, $\varphi(r) = e^{-\alpha r^2}$ find the ground state energy of a hydrogen atom variationally.

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

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma_3 x^3 + \frac{1}{24}\gamma_4 x^4$$

7. a. Explain Born—Oppenheimer approximation using hydrogen molecule as an example. 3+3+4 =10

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

c. 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?

8. a. Derive Hartree-Fock equation for Helium atom. Explain how it is solved by Self Consistent Field (SCF) method. 4+2+4 =10

b. Write the determinantal wave functions of Lithium and Beryllium atoms.

c. Normalize $\psi_2(1,2)$ wave function given by the following equation considering 1s is normalized.

$\psi_2(1,2) = \psi(1,2) - \psi(2,1) = 1s\alpha(1)\beta(2) - 1s\alpha(2)\beta(1)$

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