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B Sc (Hons)/III

PHYSICS- Paper XXII(i) E

Modern Chemistry

Time : 3 Hours   Maximum Marks : 38

Attempt six questions in all.

Question No. 1 is compulsory.

Attempt at least one question from each section.

Use of calculators and log tables is allowed.

Values of some physical constants :

$h = 6.627 \times 10^{-34}$ Js

$m_e = 9.1091 \times 10^{-31}$ kg

$c = 3.0 \times 10^8$ ms^{-1}

1. Answer any *four*.
   (a) What do you understand by the term Linear Operator? Give an example.
   (b) What are the conditions under which a wave function is said to be a well-behaved wave function?
   (c) The transition corresponding to J=0 to J=1 is not necessarily the most intense line in microwave spectrum. Explain
   (d) What is the role of Trimethylsilane (TMS) in scanning the NMR spectrum of molecule?
   (e) Why do transitions take place when electromagnetic radiations interact with a molecule?   (2×4=8)

SECTION A

2. (a) Prove that the function Ae$^{(ikx)}$ is an eigen function of the angular momentum operator p$_x$. What is the eigen value?
   (b) Calculate the probability that a particle in a one dimensional box of length L is found to be between 0 and L/2.

(c) What inference can we draw if two quantum mechanical operators obey commutative law. Show mathematically.   (2×3=6)

3. (a) Draw the appropriate MO energy diagram for a homonuclear diatomic molecule and show that the bond energy decreases in going from N_2 to N_2^+ whereas it increases in going from O_2 to O_2^+.

(b) Using Hückel molecular orbital theory calculate the value of energy levels in terms of α and β for butadiene.   (2,4)

4. In the valence bond theory, the wave function for hydrogen molecule may be defind as

$$\Psi_t = \frac{1}{\sqrt{2}} [\Phi_A(1) \Phi_B(2) \pm \Phi_A(2) \Phi_B(1)]$$

where Φ_A and Φ_B are normalized wave functions for hydrogen atom.

(a) Show that the corresponding energy of these functions for H_2 molecule are

$$E_+ = 2E_H + Q + A$$
$$E_- = 2E_H + Q - A$$

where E_H is the ground state energy of the hydrogen atom,
Q and A are the coulomb and exchange integrals respectively.

(b) What is the physical significance of the integrals Q and A?

                                    (4,2)

5. (a) Draw the energy level diagram for the HF molecule and give its electronic configuration in the ground state .

(b) What are the characteristics of the atomic orbitals taking part in the formation of molecular orbitals ?

(c) Zero point energy is not zero. Comment.

                                    (2×3=6)

SECTION B

6. (a) What are symmetric and asymmetric stretching and bending modes? Illustrate these taking N_2O as an example.

(b) What is Raman effect? Explain the origin of stokes and anti-stokes lines?

                                    (3×2 = 6)

7. (a) Sketch the NMR spectrum of ethanol with respect to TMS under
(i) low resolution
(ii) high resolution

Indicate the relative positions of the peaks with respect to the TMS peak and also give the ratio of the peak areas observed in low resolution spectrum and the relative intensities of the split peaks obtained in high resolution spectrum.

(b) State and explain Frank-Condon principle.

(4,2)

8. (a) What do you understand by Larmour precession ? How does the precession frequency vary with the applied field strength?

(b) What is predissociation? Under what conditions it is observed?

(c) Sketch the hyperfine ESR spectrum of the CH_3 (Methyl radical)

(3×2=6)

9. Write short note on any *three* of the following

(a) Rule of Mutual Exclusion

(b) Spin-Spin coupling

(c) Variation Theorem

(d) Intersystem crossing and internal conversion.

(3×2=6)

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