

15P210

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Name.....

Reg. No.....

SECOND SEMESTER M.Sc. DEGREE EXAMINATION, JULY 2016

(CUCSS – PG)

(Chemistry)

CC 15P CH2 C05 - APPLICATIONS OF QUANTUM MECHANICS AND GROUP THEORY

(2015 Admission)

Time: Three Hours

Maximum: 36 Weightage

Section A

Answer *all* questions (1 weightage)

1. Write down the Hamiltonian operator for the lithium atom, in a.u.
2. What do you mean by first order perturbation method? Explain.
3. What is Born-Oppenheimer approximation?
4. Write down the Slater determinantal wave function for Li atom.
5. State and Explain variation theorem.
6. Differentiate between spin orbital and atomic orbital.
7. Explain non crossing rule in MO theory.
8. Write the molecular orbital configuration for NO. Find the bond order.
9. What are vanishing and non vanishing integrals?
10. Explain transition moment integral. How does it help in predicting spectroscopic transition?
11. Explain the term Inverse transformation.
12. Explain projection operators in group theory.

Section B

(Answer *any eight* questions) (2 weightage)

13. Illustrate perturbation treatment of particle in 1 D box with slanted bottom
14. Discuss the Frost -Hückel circle mnemonic device for cyclic polyenes.
15. Briefly discuss the Roothan's concept of basis functions.
16. Write a brief note of quantum mechanical treatment of sp³ hybridization.
17. Consider the He₂²⁺ molecular ion within a simple molecular orbital (MO) approximation.
(a) Write down the ground state MO configuration. (b) Write down the total wavefunction including spin. (c) What is the characteristic of the total wavefunction under exchange of electrons? (d) Compare this molecular ion with H₂⁺ and justify which one is more stable.
18. Write the four possible spin and orbital combinations of ground state of He atom. Which one will be true representation of the ground state?
- 19 (a) Write the total Hamiltonian for He-atom and H₂ molecule (include nuclear parts). How many variables do these wave functions depend on?

- (b) Specify the approximation under which solution of the electronic wave function become possible using Schrodinger equation for the He-atom.
- (c) Write the Hamiltonian under the Born-Oppenheimer approximation for the H₂ molecule.
20. Explain HMO treatment of ethylene, to find the π bond energy.
21. HCHO belongs to C_{2v} point group. Find the symmetry species of σ , π and non bonding orbitals of C=O group of HCHO.

C _{2v}	E	C ₂	σ_v	σ_v'
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	1	-1
B ₂	1	-1	-1	1

22. Using group theory rationalize rule of mutual exclusion principle.
23. How do you explain Laporte selection rule using group theory.
24. Using 2P_x orbital on Cis butadiene find out the reducible representation and reduce it to irreducible representation. Use the C_{2v} character table in question 21.

Section C

(Answer *any two* questions) (4 Weightage)

25. Using C₃ character table find out the MO's of Cyclopropenyl cation.

	E	C ₃	(C ₃) ²	linear, rotations	quadratic
A	1	1	1	z, R _z	x ² +y ² , z ²
E	1	e	e*	x+iy; R _x +iR _y x-iy; R _x -iR _y	(x ² -y ² , xy) (yz, xz)

$$e = \exp(2\pi i/3)$$

26. Find out the ground state energy and wave function of He atom using variation theorem (Hint $J = 5/8Z \int_0^\infty r \exp(-2Zr) dr = 1/2Z^2$).
27. Discuss briefly the self consistent field method of solving many electron atoms.
28. Discuss briefly the LCAO method of bonding applied to hydrogen molecule ion.
