Birla Institute of Technology & Science, Pilani, Rajasthan 333031
Second Semester 2022-2023
Mid-Semester Examination
Course Name: Electron Correlation in Atoms and Molecules Course Code: CHEM F413

Date: 16-03-2023, Time: 1 Hrs 30 minutes; Max. Marks: 30

(CLOSSED BOOK)

- **Answer all questions.**
- **Answers should be brief relevant and to the point:**

---

1. (a) Prove that total electronic energy of a system is equal to the sum of the orbital energies when HP wave-function and the corresponding total electronic Hamiltonian is used. **[3M]**

(b) What is the deficiency of Hartree-product (HP) wave-function and how it can be solved? **[2+2=4M]**

(c) If the ground state wave function of a N-electron system is represented by $\left|K\right\rangle = |\cdots\cdots mn\cdots\cdots\rangle$ and an excited state wave function is represented by $\left|L\right\rangle = |\cdots\cdots pn\cdots\cdots\rangle$ then write the expression of $\left\langle K\middle|O_2\middle|L\right\rangle$ where O_2 represents the two-electron operator. **[2M]**

2. (a) Write the explicit form of coulomb and exchange integrals in Fock operator. Why the exchange part in Fock operator is called a 'non-local' operator (answer within 4-5 sentences)? **[1+1+2=4M]**

(b) How can you convert Hartree-Fock equation from 'non-canonical' eigenvalue form to 'canonical' eigenvalue form? What is the physical justification behind this transformation? [**2+2=4M**]

(c) After linear expansion of spatial molecular orbitals in terms of basis functions derive Roothaan Equations from spatial Hartree-Fock equation. **[1+3=4M]**

3. (a) If each individual occupied molecular orbital ψ_a (containing two electrons) of a system (having total N electrons) are represented by $\psi_a = \sum_{\nu=1}^{k} C_{\nu a}\phi_\nu$, $a = 1, 2, 3, \text{-------} k$, then show that $\rho(r) = \sum_{\mu\nu}^{k} P_{\mu\nu}\phi_\mu(r)\phi_\nu^*(r)$, where $P_{\mu\nu}$ is the charge-density bond - order matrix. **[3M]**

(b) For the above system also show that $\int dr\rho(r) = N$ **[2M]**

(c) If for any spin orbital χ_m, the eigenvalue equation (i.e. the Hartree-Fock equation) is written as $f\left|\chi_m\right\rangle = \varepsilon_m\left|\chi_m\right\rangle$ (here 'f' is the Fock operator), then derive the spin-orbital energy expression (i.e. ε_m).. Also write down the corresponding energy expression in the spatial orbital form **[2+2=4M]**

END