

Birla Institute of Technology & Science, Pilani, Rajasthan 333031

Second Semester 2022-2023

Comprehensive Examination

Course Name: Electron Correlation in Atoms and Molecules

Course Code: CHEM F413

Date: 15-05-2023, Time: 1 Hrs 45 minutes; Max. Marks: 25

(CLOSED BOOK)

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

1. (a) A system in a particular state is represented by the wave function  $|\Psi_1\Psi_2\rangle$  and in another state represented by the wave function  $|\psi_1\bar{\psi}_2\rangle$ . The corresponding energies of the two states are represented by  $E(\uparrow\uparrow)$  and  $E(\uparrow\downarrow)$ , respectively. Prove which one is lower. What does it signify? [1.5+1.5+1=4]
- (b) One of the diagonal elements in the full CI matrix of minimal basis  $H_2$  model is given as  $\langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle$  (in spin orbital form and physicist's notation). Derive the corresponding spatial orbital form in chemist's notation. Here, the notation convention is,  $1 \equiv \chi_1(\mathbf{x}) \equiv \psi_1(\mathbf{r})\alpha(\mathbf{w})$ ,  $2 \equiv \chi_2(\mathbf{x}) \equiv \psi_1(\mathbf{r})\beta(\mathbf{w})$ ,  $3 \equiv \chi_3(\mathbf{x}) \equiv \psi_2(\mathbf{r})\alpha(\mathbf{w})$  and  $4 \equiv \chi_4(\mathbf{x}) \equiv \psi_2(\mathbf{r})\beta(\mathbf{w})$  [7]
- (c) Prove that the Coulomb operator is invariant to Unitary transformation. [2]
2. (a) If the net dipole moment ( $\bar{\mu}$ ) of a molecule is represented by  $\bar{\mu} = \sum_i q_i \vec{r}_i + \sum_A Z_A R_A$  (where the symbols have their usual meaning) then what are the two terms in the right hand side of the above equation represent here? Write the expression of the dipole moment in density matrix form explaining all the terms. [0.5+1.5=2]
- (b) Draw the pictorial form of the Slater determinant of an unrestricted open-shell system. How do you express  $\rho_{\mu\nu}^\alpha$  (i.e. the  $\mu\nu^{\text{th}}$  element of the charge-density bond-order matrix corresponding to  $\alpha$ -electron) and  $\rho_{\mu\nu}^\beta$  (i.e. the  $\mu\nu^{\text{th}}$  element of the charge-density bond-order matrix corresponding to  $\beta$ -electron) [1+1+1=3]
3. (a) Starting from the intermediate normalized form of CI wave function show that,
- $$E_{corr} = \sum_{\substack{c \leftarrow d \\ t \leftarrow u}}^N C_{cd}^{tu} \langle \Psi_0 | H | \Psi_{cd}^{tu} \rangle$$
- where the symbols have their usual meaning. [4]
- (b) Comment on the variational and size consistency properties of Configuration Interaction (CI) and Möller - Plesset perturbation theory (MPPT) based methods. [3]

END

Birla Institute of Technology & Science, Pilani, Rajasthan 333031

Second Semester 2022-2023

Comprehensive Examination

Course Name: Electron Correlation in Atoms and Molecules

Course Code: CHEM F413

Date: 15-05-2023, Time: 1 Hrs 15 minutes; Max. Marks: 15

(OPEN BOOK)

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

1. (a) If for H<sub>2</sub>O molecule  $\sum_{\mu \in H_1} (PS)_{\mu\mu} = 0.76442$  (where  $\mu$ 's are the basis functions,  $P$  is

the 'charge-density bond-order' matrix,  $S$  is the overlap matrix), then what will be the values of  $\sum_{\mu \in H_2} (PS)_{\mu\mu}$  and  $\sum_{\mu \in O} (PS)_{\mu\mu}$ ? Here,  $H_1$ ,  $H_2$  and  $O$  represent the two

hydrogen atoms and the oxygen atom respectively. [2]

(b) If the net dipole moment ( $\vec{\mu}$ ) of a molecule is represented by  $\vec{\mu} = \sum_i q_i \vec{r}_i + \sum_A Z_A R_A$

(where the first and second terms are the electronic and nuclear contributions, respectively, and the symbols have usual meaning) then what will be the dipole moment of CO<sub>2</sub> molecule? Explain (in not more than five sentences). [1+2=3]

(c) The total energy ( $E_{Tot}$ ) of a chemical system is represented by

$E_{Tot} = E_0 + \sum_A \sum_{B > A} \frac{Z_A Z_B}{R_{AB}}$ , where  $E_0$  is the 'electronic energy' and

$\sum_A \sum_{B > A} \frac{Z_A Z_B}{R_{AB}}$  is the nucleus-nucleus repulsion energy. Which of the following

statement is correct and why (answer within five sentences)?

(i)  $E_{Tot} > E_0$  (ii)  $E_{Tot} < E_0$  [1+2=3]

(d) What will be the total number of basis functions and primitive Gaussians for C<sub>2</sub>H<sub>5</sub>OH molecule in 6-31G\*\* basis set? [2+2=4]

(e) Showing relative position of energy values of neutral, cationic and anionic systems explain why Koopmans' IP a somewhat acceptable approximation of actual IP whereas Koopmans' EA is not. [3]

END