CH4102-2018: End-Sem Exam: Time 3 hr. Marks$=7 \times 7 + 1 = 50$

Answer to the point and be precise. Clearly define all quantities.

1. Show that P_{12} commutes with the Hamiltonian for Li atom. Show that P_{12} and P_{23} do not commute with each other. Further show that P_{12} and P_{23} commute when they are applied to antisymmetric functions.

2. Consider the following ground- and excited-state configuration of C atom: $1s^2 2s^2 2p^2$ and $1s^2 2s^2 2p4p$. Find out the term symbols in each case. Write down the number of states in each case.

3. Give the possible spin multiplicities of the terms that arise from each of the following electron configurations: (i) f^1 (ii) f^2 (iii) f^3 (iv) f^7 (v) f^{12} (vi) f^{13}.

4. Give the levels that arise from each of the following terms, and give the degeneracy of each level: (i) ^1S (ii) ^2S (iii) ^3F (iv) ^4D.

5. Assuming χ_c, χ_r refer to occupied and unoccupied MOs, find expressions for ionization potential and electron affinity, within HF approximation. Use IP $= {}^{N-1}E_c - {}^N E_0$ and EA $= {}^N E_0 - {}^{N+1} E^r$.

6. Eigenfunctions α, β of Hermitian operator S_z form a complete, orthonormal set. Any one-electron spin function can be written as $C_1 \alpha + C_2 \beta$. For the representation that uses α, β as basis functions, derive the matrices that correspond to S_x, S_y, S_z, and S^2 operators. Find the eigenvalues and eigenvectors of S_x matrix. Use the commutation and anti-commutation relations of spin operators to prove the followings:

$$S_x \cdot S_y\, S_z\, S_y\, S_z\, S_x = -\frac{\hbar^6}{64}$$

$$S_x\, S_y\, S_x\, S_y\, S_z\, S_x = -\frac{i\hbar^5}{32} S_y$$

[Hint: You may use relations: $S_+ |s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s+1)}\ |s, m_s + 1\rangle$, $S_- |s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s-1)}\ |s, m_s - 1\rangle$]

7. Find out the MO energy eigenvalues for cyclobutadiene within HMO approxima- tion. Write down the electron distribution in the respective MOs for its ground state. Compare its stability with that of two isolated ethylene molecules.

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8. (a) Write down the expressions for Fock operators for α and β spins in UHF. Explain the significance of each term.

(b) Write down the electronic energy of following determinant $|\bar{\psi}_1 \psi_2 \bar{\psi}_2 \bar{\psi}_3\rangle$, in terms of h, J, K energies.

(c) Write down energies for Li wave functions, $|\Psi_{RHF}\rangle = |\psi_{1s} \bar{\psi}_{1s} \psi_{2s}\rangle$ and $|\Psi_{UHF}\rangle = |\psi_{1s}^\alpha \bar{\psi}_{1s}^\beta \psi_{2s}^\alpha\rangle$.

(d) Write down the Hückel determinantal equation for Benzene in terms of x ($x = \frac{\alpha - E}{\beta}$).

9. (a) By means of equations, show that Hartree-Fock energy for a general molecule is not equal to the sum of Hartree-Fock orbital energies.

(b) Show that the number of single and double excitations for a CI calculation of N_2 using a basis set consisting of 100 basis functions is over a million.

(c) Write down the Hamiltonian operator for electrons in the water molecule. Use summation signs with explicit index ranges. Use atomic units.

(d) Write down Slater determinantal wave function for a many-electron system. Explain how this satisfies Pauli exclusion principle and antisymmetry requirement.