IISER Kolkata – Mid-Semester Examinations

CH4210- Advanced Quantum Chemistry

Total marks = 40 Duration: 1and ½ hours

1. (a)Which of the following is an eigenfunction of the operator P_r =−i(h/2π)r−1 (∂/∂r) r

   (A) exp(ikr) (B) sin(kr) (C) r−1 exp(ikr) (D) r exp(ikr) (E) exp(−kr2) (4)

   (b) The corresponding eigenvalue equals (A) 0 (B) (h/2π)k (C) i (h/2π) (D) $(h/2\pi)^2k^2$ (2)

2. Prove that for any arbitrary function $\tilde{\Psi}$, which is normalized to unity, $\langle\tilde{\Psi}|H|\tilde{\Psi}\rangle \geq E_0$, where E_0 is exact ground state. (5)

3.. $[\tilde{E}_i]^{[m]}$ and $[\tilde{E}_i]^{[m+1]}$ are the variationally optimized energies for a linear variation using [3] and [4] basis functions. Identify all the completely correct statement by a tick. (More than one option may be correct).

$a.\ [\widetilde{E_1}]^{[3]} \leq [\widetilde{E_1}]^{[4]} \leq [\widetilde{E_2}]^{[3]}$
$b.\ [\widetilde{E_2}]^{[4]} \geq [\widetilde{E_1}]^{[3]}$
$c.\ [\widetilde{E_1}]^{[4]} \leq [\widetilde{E_1}]^{[3]} \leq [\widetilde{E_2}]^{[4]} \leq [\widetilde{E_3}]^{[3]}$ (4)
$d.\ [\widetilde{E_3}]^{[4]} \leq [\widetilde{E_3}]^{[3]} \leq [\widetilde{E_4}]^{[4]}$

4. The Fock operator is $f(1) = h(1) + \sum \int \chi_b^*(2) \frac{1}{r_{12}} (1 - P_{12}) \chi_b(2)\, d\tau_2$. Show that the above Fock operator is hermitian. (4)

5. Write the canonical form of spin-integrated one-particle Hartree-Fock equation for closed shells and using basis expansion, derive the Hartree-Fock- Roothaan equation. (4+5)

6. (a) Show that the determinant of a hermitian matrix is real. (3)

   (b) A unitary matrix, U is defined by $U^{+}U = I$. Show that the determinant of U is a phase factor $e^{i\theta}$. (Hint: det(AB)=det(A)det(B)) (3)

P.T.O.

7. The coulomb integral J_{ab} and K_{ab} are defined by $J_{ab} = \langle \Psi_a \Psi_b | \Psi_a \Psi_b \rangle$ and $K_{ab} = \langle \Psi_a \Psi_b | \Psi_b \Psi_a \rangle$ where Ψ_a and Ψ_b are space orbitals. (5)

Show that:

(a) $J_{aa} = K_{aa}$

(b) $J^*_{ab} = J_{ab}$ and $K^*_{ab} = K_{ab}$

(c) $J_{ab} = J_{ba}$ and $K_{ab} = K_{ba}$

8. Show that in the above expression of K_{ab} in problem 3, if Ψ_a and Ψ_b are real spatial orbitals,

$K_{ab} = \langle \Psi_a \Psi_a | \Psi_b \Psi_b \rangle = \langle \Psi_b \Psi_b | \Psi_a \Psi_a \rangle$. (3)