IISER Kolkata – End-Semester Examinations

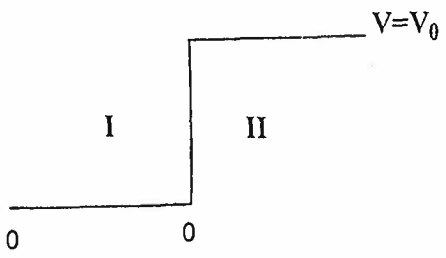
CH4210- Advanced Quantum Chemistry

Total marks = 100 Duration: 2and ½ hours

1. The energy of the ground state of hydrogen atom is approximately [6]
   - 13.6 eV. Find the following:
   (a) approximate energy of n=2 state of Li^{++}
   (b) approximate energy difference (absolute) between n=4 and n=3 state for He^{+}
   (c) The state (quantum number) of $Be^{3+}$with approximate energy of -13.6 eV.

2. Consider a particle travelling towards a finite step potential of height V_0 from left to right

$$V(x) = \begin{cases} 0, & x < 0 \\ V_0, & x \geq 0 \end{cases}$$



The general solution for the wave function in region I and II for $E > V_0$ are

$$\Psi_I(x) = Ae^{ik_1x} + Be^{-ik_1x}$$

$$\Psi_{II}(x) = Ce^{ik_2x}$$

where $k_1 = \sqrt{\frac{2mE}{\hbar}}$ and $k_2 = \sqrt{\frac{2m(E-V_0)}{\hbar}}$

(a) Apply the boundary conditions for continuity of the wave function and its first derivative at $x = 0$ and obtain the two conditions. [5]

(b) Show that: [5]

$$\left|\frac{B}{A}\right|^2 = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2$$

3. Let the exact solutions of a hermitian Hamiltonian H_0 (in 1-d) be [6]

$$H_0\phi_k^0 = E_k^0\phi_k^0 \qquad E_0^0 \leq E_1^0 \leq E_2^0 \ , \ k = 0,1,2, \ldots \ldots$$

show that $(E_k^0 - E_0^0)\langle\Phi_k^0|x|\Phi_0^0\rangle = -\frac{ih}{m}\langle\Phi_k^0|p_x|\Phi_0^0\rangle$

4. Let the Hamiltonian have a complete set of solutions,
   $H \mid n\rangle = E_n \mid n\rangle$

   Show that

   $\langle m \mid [A, [H,A]] \mid m\rangle = 2 \sum_n (E_n - E_m) \mid \langle m|A|n\rangle \mid^2$

For any Hermitian operator A. [Note this relation is the famous Thomas- Ritchie-Kuhn sum rule] [6]

5. For a Restricted Hartree-Fock wave function, Charge Density- Bond Order matrix, P, in the basis of atomic orbitals is defined as $P = 2\, C\, C^{+}$, where C is the matrix of coefficients of molecular orbitals in basis of Atomic orbitals. A column indicates coefficients of a molecular orbital. [4+6]

a) Show that $PSP = 2P$
b) $Tr(S^{1/2}\, P\, S^{1/2}) = N$

Where S is overlap matrix of atomic orbitals and N is the total number of electrons

6. Write normalized Slater determinant of a 4 electron closed shell system with a_1 and a_2 as spatial orbitals [4]
7. For H2O molecule RHF calculation using 6-311 G calculation, what is the total number of occupied and virtual spatial orbitals [6]
8. For the above problem as 7, if we perform CISD calculation, what will be the total number of Slater determinants? [6]
9. For minimal basis calculation, show that the energy of D-CI calculation for two noninteracting H_2 molecules is not the sum of a single H2 molecule by actually setting up D-CI matrix problem and solving. Show that it is approximately sqrt (2) times the energy of a single H2 molecule. [6+3]
10. If we start ground state perturbation theory with zeroeth order Hamiltonian as sum of one particle fock operators, show that the sum of zeroth and first order corrected energy is equal to the ground state Hartree Fock energy. [5]
11. Calculate the first order correction to the energy of the nth state of a harmonic oscillator whose centre of potential has been displaced from 0 to a distance l. [5]
12. Derive the anti-commutation $\{ a_i, a_j^{+} \} = \delta$ ij where a and a^{+} are annihilation and creation operators respectively. [7]
13. State and derive Hohenberg-Kohn Theorem [6]

14. Show also that $\partial \langle A \rangle / \partial t = 0$ for a function Ψ, which is a stationary state (i.e. eigen function of H), even if A does NOT commute with H, where A is an explicitly time-independent operator(You may prove by Ehrenfest Theorem or even from the property of stationary state) [4]

15. Using the above relation in 14, show by use of appropriate A that

$$\langle T \rangle = \tfrac{1}{2} \sum_k \langle xk \, \partial V / \partial xk \rangle, \qquad [5]$$

where xk is the position operator of the particle k, T is the kinetic energy operator and expectation values are evaluated with respect to a stationary state. (Statement of quantum Virial Theorem)

16. Answer the following multiple choice questions [5]

(a)Which of the following is NOT a solution of the differential equation $y''(x)+k^2y(x) = 0$?

(i) $\exp(-ikx)$ (ii) $\exp(-kx)$ (iii) $\sin kx$ (iv) $\cos kx$ (v) $\sin(kx-\alpha)$ (α = constant)

(b)Planck's constant has the same units as (i) angular momentum (ii) the Hamiltonian (iii) frequency (iv) quantum number (v) de Broglie wavelength

(c)The energy levels of the linear 1-dimensional harmonic oscillator are (i) all nondegenerate (ii) n-fold degenerate (iii) (n + 1)-fold degenerate (iv) (2n + 1)-fold degenerate (v) n^2-fold degenerate

(d)The ionization energy for hydrogen atom is 13.6 eV. The potential energy for the ground state of Li^{++} is approximately (i) -13.6 (ii) -27.2 (iii) -244.8 eV (iv) -54.4 (v) -122.4 eV

(e)For real atomic orbitals with quantum numbers n and l, the total number of nodal surfaces,(radial plus angular), equals (i) n (ii) n−1 (iii) n−l−1 (iv) n+l (v) 2l+1