

- 1 (a) g_1, g_2, \dots, g_n are the eigen functions of an operator \hat{O} with corresponding eigenvalue o_1, o_2, \dots, o_n , respectively. Particular state of a system is described by a normalized wavefunction, Ψ given by: $\Psi = \frac{1}{2} g_1 - \left(\frac{3}{8}\right)^{1/2} g_2 + \left(\frac{3}{8}i\right)^{1/2} g_3$. What would be the outcome of measuring the observable corresponds to the operator \hat{O} ? [6]
- (b) An unperturbed system is having a doubly degenerate energy level. The perturbation integrals are having the values $H'_{11} = 4b, H'_{12} = 2b, H'_{22} = 6b$, where b is a positive constant, $H'_{jk} = \langle \psi_j^{(0)} | \hat{H}' | \psi_k^{(0)} \rangle$, and $\delta_{jk} = \langle \psi_j^{(0)} | \psi_k^{(0)} \rangle$. (i) Express the form of the secular equation and determine the values of $E^{(1)}$ in terms of b . (ii) Find the normalized correct zeroth-order wave functions. [4+10]
- 2 (a) Suppose you are measuring Z-component of spin angular momentum (\hat{S}_Z) using a Stern-Gerlach type of instrument. Outcome of the measurement for an electron is $\frac{1}{2}\hbar$. Then you direct the electron to enter into a second Stern-Gerlach type of instrument to measure the X-component of spin angular momentum (\hat{S}_X). What would be the probability of each possible outcome? Explain your answer. [5]
- (b) Consider the following determinantal wave function: [2+2]
- $$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{211}\alpha(1) & \psi_{21-1}\beta(1) \\ \psi_{211}\alpha(2) & \psi_{21-1}\beta(2) \end{vmatrix}$$
- where $\psi_{21\pm 1}$ is a hydrogen atom wave function. Determine whether Ψ is an eigen function of $\hat{L}_{Z,\text{total}}$ and $\hat{S}_{Z,\text{total}}$.
- (c) (i) Prove that the Hartree-Fock orbital energies ϵ_i can be expressed as $\epsilon_i = E - E^+$, [8+3] where E and E^+ are the energies of the neutral atom and ion, respectively.
(ii) Use this concept to determine $(E - E^+)$ for Be and Be^+ system.
- 3 (a) Use Heitler-London valence-bond treatment of H_2 starting with $\Psi = c_1\Psi_1 + c_2\Psi_2$, where $\Psi_1 = \begin{vmatrix} 1s_A\alpha(1) & 1s_B\beta(1) \\ 1s_A\alpha(2) & 1s_B\beta(2) \end{vmatrix}$, $\Psi_2 = \begin{vmatrix} 1s_A\beta(1) & 1s_B\alpha(1) \\ 1s_A\beta(2) & 1s_B\alpha(2) \end{vmatrix}$.
- (i) Determine the values of H_{ii} and H_{ij} . [3]
- (ii) Determine the values of S_{ii} and S_{ij} . [4]
- (iii) Write down the expression for Secular determinant using the results obtained in part (i) and part (ii). [2]
- (b) Predict the electronic configuration and π -electron binding energy in case of [3+3]
(i) butadiene anion and (ii) butadiene cation.
- (c) The infrared absorption spectrum of $^1\text{H}^{35}\text{Cl}$ has its strongest band at 8.65×10^{13} Hz. [5]
For this molecule D_0 is 4.43 eV. Find D_e for $^1\text{H}^{35}\text{Cl}$.

4 (a) For an electronic transition the transition moment integral is having the form: $M = \int \psi^* \hat{\mu} \psi d\tau$, where ψ^* represents the wave function for electronic excited state, ψ represents the wave function for electronic ground state, and $\hat{\mu}$ is the dipole moment operator. Derive the expression for (i) Franck-Condon factor, (ii) basis of orbital selection rule, and (iii) basis of spin selection rule. [8]

(b) In pure rotational Raman spectroscopy, selection rule is $\Delta J = 0$ or ± 2 only. [2]

(i) What would be the frequency for $\Delta J = 0$ transition.

(ii) What would be the frequency of Stoke's and Anti-Stoke's lines for $\Delta J = \pm 2$ transitions. Derive an expression for each type. [6]

(c) Consider the following vibrational mode of benzene (6a). Assume, ν_1 , ν_2 , and ν_3 are the frequency of 6a vibrational mode in electronic ground state (S_0), electronic excited state (S_1), and ionized state, respectively. Arrange these frequencies in ascending order with explanation. [4]



***** End *****