

P.G. Semester-IV Examination, 2023

CHEMISTRY

Course ID : 41451

Course Code : CHEM-401E

Course Title : Physical Chemistry Special

Time : 2 Hours

Full Marks : 40

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer any **five** of the following questions:

2×5=10

- Write down Hamiltonian (\hat{H}) of helium atom in terms of atomic units and identify the term corresponding to perturbation (\hat{H}').
- Show that energy of helium ion (He^+) in atomic unit is $-2E_h$, where E_h is the Hartree energy.
- What is Rabi oscillation frequency? Explain its significance.
- Find out ground state term symbol of Cr atom ($Z=24$).
- Classify each of these functions as symmetric,

antisymmetric, neither symmetric nor antisymmetric :

(i) $f(1)g(2)\alpha(1)\alpha(2)$;

(ii) $f(1)f(2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$;

(iii) $f(1)f(2)f(3)\beta(1)\beta(2)\beta(3)$;

(iv) $e^{-a(r_1-r_2)}$

- Write down Slater determinant of Li atom.
- Write down the Hückel secular determinant for benzene in terms of Coulomb integrals (α), exchange integrals (β) and energy (E).

2. Answer any **four** of the following questions:

5×4=20

- (i) State the variational theorem.
(ii) When the linear variation function $\phi = c_1f_1 + c_2f_2$ is applied to a certain problem, one finds that $\langle f_1|\hat{H}|f_1\rangle = 4a$, $\langle f_1|\hat{H}|f_2\rangle = a$, $\langle f_2|\hat{H}|f_2\rangle = 6a$, $\langle f_1|f_1\rangle = 2b$, $\langle f_2|f_2\rangle = 3b$, $\langle f_1|f_2\rangle = b$ where a and b are known positive constants. Use this ϕ to find (in terms of a and b) upper bounds to the lowest two energies.

2+3=5

b) (i) Show that if two degenerate states, Ψ_a and Ψ_b are eigen functions of \hat{H} with eigen-value E, then linear combination of Ψ_a and Ψ_b is also an eigen function of \hat{H} with same eigen value, E.

(ii) Application of variation function $\phi = e^{-cx^2}$ (where c is a variational parameter) to a problem with $V = af(x)$ where a is positive constant and $f(x)$ is certain function of x gives variational integral as $W = \frac{c\hbar^2}{2m} + \frac{15a}{64c^3}$. Show that minimum value of W for this variation function is, $0.7259 \frac{\hbar^{3/2} a^{1/4}}{m^{3/4}}$. 2+3=5

c) (i) The wave function of a two-level system in presence of a time-dependent perturbation is expressed as, $\Psi(t) = a_0(t)\Psi_0(t) + a_1(t)\Psi_1(t)$. Time dependence of the co-efficient associated to the state Ψ_1 is given by, $\frac{da_1}{dt} = \frac{1}{2}i\omega_R e^{-i\Delta t} a_0$, where ω_R is Rabi frequency and Δ is detuning frequency.

Starting from this equation show that transition probability, $P_{1\leftarrow 0}$, from the state ψ_0 to ψ_1 due to interaction with a weak monochromatic electromagnetic radiation is given by,

$$P_{1\leftarrow 0} = \frac{\omega_R^2}{\Delta^2} \sin^2\left(\frac{\Delta t}{2}\right)$$

(ii) Draw plots of transition probability vs time and transition probability vs angular frequency of electromagnetic radiation, and explain the nature of these two plots. 3+2=5

d) (i) Find out the eigen-values of permutation operator \hat{P}_{12} .

(ii) The antisymmetrization operator \hat{A} is defined as the operator that antisymmetrizes a product of n one-electron functions and multiples it $(n!)^{-1/2}$. For n = 2.

$$\hat{A}f(1)g(2) = \frac{1}{\sqrt{2}} \begin{vmatrix} f(1) & g(1) \\ f(2) & g(2) \end{vmatrix}$$

For n = 2, express \hat{A} in terms of permutation operator, \hat{P}_{12} . 2+3=5

e) (i) Given that $\hat{S}_x\alpha = \frac{1}{2}\hbar\beta$ and $\hat{S}_x\beta = \frac{1}{2}\hbar\alpha$. Use these two equations to construct two normalized eigenfunctions of \hat{S}_x with eigenvalues $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$.

(ii) Prove that, $[\hat{S}^2, \hat{S}_x] = 0$. 3+2=5

f) (i) The term symbols for an np^3 electron configuration are 2P , 2D and 4S . Calculate values of J associated with each of these term symbols. Which term symbol does represent the ground state?

(ii) How many states would belong to each of the following carbon configuration?

$$[\text{I}] 1s^2 2s^2 2p^2; \text{ and } [\text{II}] 1s^2 2s^2 2p^3 p. \quad 3+2=5$$

3. Answer any **one** of the following questions:

$$10 \times 1 = 10$$

a) i) For a non-degenerate system, write down 1st order perturbation correction to the energy in terms of unperturbed wave function $\psi^{(0)}$ and perturbation to the Hamiltonian, \hat{H}' . Provide an interpretation to the result.

ii) Consider one-particle, one-dimensional system with potential energy

$$V=V_0 \text{ for } \frac{1}{4}l \leq x \leq \frac{3}{4}l$$

$$= 0 \text{ for } 0 \leq x < \frac{1}{4}l$$

$$= 0 \text{ for } \frac{3}{4}l < x \leq l$$

$$= \infty \text{ elsewhere}$$

Treat this system as perturbed particle-in-a-

box. Find first-order correction to energy for the ground stationary state.

iii) If effective one electron Hamiltonian operator is defined as,

$$\hat{H}_1^{eff}(\vec{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(\vec{r}_1)$$

Then starting from Hartree-Fock equation obtain following expression of orbital energy, ϵ_1 of helium atom $\epsilon_1 = I_1 + J_{12}$

Total energy of a helium atom is given by, $E = I_1 + I_2 + J_{12}$. Noting that total energy of helium atom is not the sum of its orbital energies, arrive at Koopmans' theorem for calculation of ionization energy of an atom.

$$2+4+(3+1)=10$$

b) i) Consider time-dependent Hamiltonian $\hat{H} = \hat{H}^0 + V(t)$. For solving the Schrodinger equation $i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$, the wave function is expanded as

$$\psi(t) = \sum_i c_i(t) e^{-iE_i t/\hbar} \phi_i, \text{ where, } \hat{H}^0 \phi_i = E_i \phi_i.$$

Substitute this expansion into the Schrodinger equation and derive following set of coupled equations,

$$i\hbar \frac{d}{dt} c_j(t) = \sum_i c_i(t) \langle \phi_j | V(t) | \phi_i \rangle e^{i(E_j - E_i)t/\hbar}$$

Here, $\psi_i = e^{-iE_i t/\hbar} \phi_i$ are unperturbed orthonormal set of wave functions.

- ii) For the allyl carbonium ion, $CH_2 = CH - CH_2^+$, [I] Find out the energies of Hückel molecular orbitals, [II] the delocalization energy, and [III] the mobile bond orders. $4 + (2+2+2) = 10$
