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14 (CHM-I) CH 104

2017

CHEMISTRY

Paper : CH 104

(Quantum Chemistry)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1 Answer ***any four*** of the following :

5×4=20

(a) Define a linear operator and an eigenfunction. Prove that eigenfunction of a linear operator belonging to different eigenvalues are linearly independent.

1+1+3

Contd.

- (b) The wave function for a particle in a box is

$$\Psi(x) = A \sin \frac{n\pi}{a} x$$

Normalize the function.

Write down the normalized wave functions ψ_1 and ψ_2 for $n=1$ and $n=2$ respectively. Prove that wave functions ψ_1 and ψ_2 are orthogonal. $2\frac{1}{2}+2\frac{1}{2}$

- (c) Define a hermitian operator. Show that the product of two hermitian operators is hermitian if and only if they commute. $1+4$

- (d) Explain the technique of Schmidt's orthogonalization. 5

- (e) (a) For the general angular momentum operator J , prove that

$$[J^2, J_z] = 0 \quad 3$$

- (b) Derive the expression of orbital angular momentum operator from the theories of classical mechanics. 2

- (f) What do you understand by the term "space quantization" of orbital angular momentum? Discuss the space quantization of an orbital angular momentum of magnitude $\sqrt{6}\hbar$. $1+3+1$

Define spin operators.

2. Explain the axiom of completeness of an eigenfunction. 4

3. Answer **any two** of the following: $5 \times 2 = 10$

- (a) Derive the expression for the eigenfunction of a linear harmonic oscillator in its first excited state.

- (b) For ground state of the one dimensional harmonic oscillator, find the average value of kinetic energy and potential energy and verify that $\langle T \rangle = \langle V \rangle$

- (c) Two particles of masses m_1 and m_2 are constrained to move in one dimension and their interaction is given by the potential function.

$$V = \frac{1}{2} K (x_1 - x_2)^2$$

Show that this problem is equivalent to the following *two* independent problems:

- (i) A free particle of mass $M = m_1 + m_2$ moving in one dimension
(ii) A particle of mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

executing simple harmonic motion.

4. Answer **any one** of the following: 5

- (a) What are the assumptions of Rayleigh-Schrödinger perturbation theory? Derive the first and second-order energy correction of the time-independent perturbation theory for non-degenerate case. 1+4

- (b) What is the significance of Rabi formula? Derive the explicit expression of the coefficient of a state which was initially unoccupied with the help of variation of constants for many levels system. 1+4

5. Answer **any one** of the following: 6

- (a) Consider a H -atom in an electric field of strength e . The Hamiltonian operator for this system is 1+5

$$\hat{H} = \frac{-\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + e\epsilon r \cos\theta$$

Identify $H^{(0)}$ and $H^{(1)}$ terms.

Calculate the first-order correction to the ground state energy and the total ground state energy of an anharmonic oscillator whose potential energy is

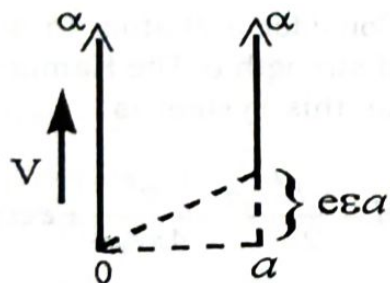
$$U(x) = \frac{1}{2} kx^2 + \frac{1}{6} \gamma x^3 + \frac{1}{24} bx^4$$

Given

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/2} \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\int_{-\infty}^{\infty} x^{2n} \exp(-\alpha x^2) dx = \frac{1 \cdot 3 \cdot 5 \dots (2n-1)}{2^{n+1} \alpha^n} \left(\frac{\pi}{\alpha}\right)^{1/2}$$

- (b) Consider an electron in a potential box having length a . When an electric field is turned on in the X -direction, the electron experiences a force equal to $-e\epsilon$ and the potential function has added to it the term $-e\epsilon X$. The potential has the form as shown below: 1+5



What is the lowest allowed energy (in a first order approximation) for the electron?

6. What is the significance of variation theorem? Derive the secular equation for a linearly varied trial function that depends on certain parameters. 1+4
7. Why Hartree product is not acceptable in quantum mechanics? What do you mean by an STO? Show that an STO satisfies the antisymmetry principle. What is the degeneracy of a ^2D term? 1+1+2+1

8. Answer **any one** of the following: 5

- (a) What is Stark effect? Find the optimum form of a trial function of the form $\exp(-\alpha r)$ and the upperbound to the ground state energy of a hydrogenic atom. 1+4
- (b) Define normal and anomalous Zeeman effect. Account for the form of the Zeeman effect and analysis the spectra when a magnetic field is applied to the following transitions:

(a) $^1D \rightarrow ^1P$

(b) $^3D_2 \rightarrow ^3P_1$

How large are the splittings in units of $\mu_B B$? 1+4