Roll No. 1651505 -

C–1354

C. B. S. (Fifth (Semester)
EXAMINATION, Jan.-Feb., 2019
QUANTUM CHEMISTRY
(C–501)

Time : Three Hours] [*Maximum Marks : 40*

Note : Attempt all Sections as directed.

Section—A

$\frac{1}{2}$ each

(Objective/Multiple Choice Questions)

Note : Attempt all questions.

Choose the correct answer :

1. The de-Broglie wavelength of a particle having kinetic energy E_k is given by :

   (a) $\lambda = \frac{h}{\sqrt{E_k}}$

   (b) $\lambda = \frac{h}{\sqrt{2E_k}}$

   (c) $\lambda = \frac{h}{\sqrt{mE_k}}$

   (d) $\lambda = \frac{h}{\sqrt{3E_k}}$

2. Classical mechanics does not provide satisfactory explanation for the following :
   (a) Black body radiation
   (b) Photoelectric effect
   (c) Heat capacity of solids
   (d) All of the above

3. According to Schrödinger, a particle is equivalent to a :
   (a) Wave packet
   (b) Single wave
   (c) Light wave
   (d) None of these

4. The time independent Schrödinger's equation of a system represents the conservation of the :
   (a) Total binding energy of the system
   (b) Total potential energy of the system
   (c) Total kinetic energy of the system
   (d) Total energy of the system

5. The quantum mechanical operator for the momentum of a particle moving in one-dimensional is given by :
   (a) $i\hbar\frac{d}{dx}$
   (b) $-i\hbar\frac{d}{dx}$
   (c) $i\hbar\frac{d}{dt}$
   (d) $\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$

6. The eigen function of a rigid rotor are :
   (a) Hermite polynomials
   (b) Legendre polynomials
   (c) Spherical polynomials
   (d) Tchebyshev polynomials

7. The operation of the commutator $\left[x, \frac{d}{dx}\right]$ on a function $f(x)$ is equal to :
   (a) 0
   (b) $f(x)$
   (c) $-f(x)$
   (d) $x\frac{df}{dx}$

8. An electron of mass 'm' is confined to a 1D-Box of length 'b'. If it makes a radiative transition from second excited state to the ground state. The frequency of the photon emitted as :
   (a) $\frac{9h^2}{8ma^2}$
   (b) $\frac{3h}{8mb^2}$
   (c) $\frac{h}{mb^2}$
   (d) $\frac{2h}{ma^2}$

9. If ϕ is any normalized function, then :

(a) $\int \phi^* H \phi \, d\Gamma \geq E_0$

(b) $\int \phi^* H \phi \, d\Gamma \leq E_0$

(c) $\int \phi^* H \phi \, d\Gamma \geq E_0^2$

(d) $\int \phi^* H \phi \, d\Gamma \leq E_0^2$

10. A certain 2 level system has stationery state energy E_1 and E_2 $(E_1 < E_2)$ with the normalization wave function ψ_1 and ψ_2 respectively in the presence of a perturbation (V), the 2nd order correction to the energy for the 1st state ψ_1 will be :

(a) $\dfrac{\langle \psi_1 | \Delta H | \psi_2 \rangle}{E_1 - E_2}$

(b) $\dfrac{\langle \psi_1 | V | \psi_2 \rangle}{E_2 - E_1}$

(c) $\dfrac{\langle \psi_1 | \Delta H | \psi_2 \rangle^2}{E_1 - E_2}$

(d) $\dfrac{\langle \psi_1 | \Delta H | \psi_2 \rangle^2}{(E - E_2)^2}$

11. For non-degenerated perturbation theory for ground state, with $E_0^{(0)}$ as zeroth order energy $E_0^{(1)}$ as the first order perturbation correction and E_0 as the exact energy, which of the following is true ?

(a) $\left(E_0^{(0)} + E_0^{(1)}\right)$ is always equal to E_0

(b) $\left(E_0^{(0)} + E_0^{(1)}\right) \leq E_0$

(c) $\left(E_0^{(0)} + E_0^{(1)}\right) \geq E_0$

(d) $\left(E_0^{(0)} \leq E_0^{(0)} + E_0^{(1)}\right)$

12. The following are the statement about perturbation theory :

(A) Second order perturbation correction to the ground state energy is always negative.

(B) Sum of the zeroth order and the first order corrections to the ground state energy is always greater than the exact ground state energy.

(C) Sum of the zeroth order and the first order corrections to the ground state energy is less than the exact energy.

From the following which one is correct ?

(a) Only (A) is true

(b) Both (A) and (B) are true

(c) Only (C) is true

(d) Both (B) and (C) are true

13. The number of radial nodes a $3s$ and $2p$ orbitals are respectively :

(a) 2, 0

(b) 0, 2

(c) 1, 2

(d) 2, 1

14. According to the LCAO-MO model which one of the following second period diatomic molecules has double bond in the ground electronic state ?

(a) Li_2

(b) Be_2

(c) B_2

(d) C_2

15. Using Huckel molecular orbital approximation, the two roots of secular equation of ethylene are :

(a) $(\alpha - \sqrt{2\beta}), (\alpha + \sqrt{2\beta})$

(b) $(\alpha + \beta), \alpha$

(c) $(\alpha - \beta), (\alpha + \beta)$

(d) $(\alpha - 2\beta), (\alpha + 2\beta)$

16. The energy for a single electron excitation in cyclopropenium cation according to Huckel theory is :

(a) β

(b) 3β

(c) 2β

(d) 4β

17. The term symbol for $\left[Fe(H_2O)_6\right]^{2+}$ is :

(a) $^6S_{5/2}$

(b) $^5D_4$

(c) $^3F_2$

(d) $^5D_0$

18. The symbol for He_2^+ is :

(a) $^0\Lambda$

(b) $^3\Sigma$

(c) $^2\pi$

(d) $^2\Sigma$

19. The microstate for $^4F_{3/2}$:

(a) 1

(b) 2

(c) 3

(d) 4

20. The allowed transition among the following is :

(a) $^1\Sigma_g \leftrightarrow {}^3\Sigma_g$

(b) $^1\Delta_g \leftrightarrow {}^2\Delta_g$

(c) $^3\phi_g \leftrightarrow {}^3\Delta_u$

(d) $^2\pi_u \leftrightarrow {}^4\Sigma_g$

Section—B

(Very Short Answer Type Questions) 0.75 each

Note : Attempt all questions.

1. What is the de-Broglie wavelength of a body of mass 1 mg moving with velocity of 10 m/s ?

2. Give the time independent Schrödinger wave equation.
3. Identify the following operators whether they are Hermitian or anti-Hermitian :

   (i) $A^{\dagger}A$

   (ii) $\left[\frac{d}{dx}\right]^{\dagger}$

   (iii) $\left[A + A^{\dagger}\right]$

4. Write Schrödinger wave equation for particle in three-dimensional box.
5. Write the name of approximation methods used in quantum chemistry.
6. What is Slater determinant ?
7. What is the delocalization energy of benzene ?
8. What is ab-initio method for the calculation of molecular orbitals ?
9. Calculate term symbol for d^1.
10. Find the multiplicity for $\left[V(H_2O)_6\right]^{3+}$.

1.25 each

Section—C

(Short Answer Type Questions)

Note : Attempt all questions.

1. What is photoelectric effect ?
2. Write a short note on Blackbody radiation.
3. Explain concept of tunneling.

4. What is eigen function and eigen value ? Explain with examples.
5. Write a note on Slater type orbitals.
6. Write about variational principle.
7. Explain LCAO method.
8. The energy levels for cyclobutadiene are $\alpha + 2\beta, \alpha$ and $\alpha - 2\beta$. Calculate the delocalization energy of this molecule.
9. Determine wave function for BH_3 molecule.
10. Explain Russell-Saunders coupling (LS-coupling).

2 each

Section—D

(Long Answer Type Questions)

Note : Attempt all questions.

1. An electron has a mass of 9.11×10^{-31} kg and a charge of 1.602×10^{-19} C. Calculate the de-Broglie wavelength of a electron that has been accelerated by a potential of 100 V.

   Or

   What is uncertainty principle ? Prove it by one slit experiment.

2. Setup the Schrödinger wave equation for a simple harmonic oscillator and solve it for the energy eigen values.

   Or

   Derive an expression for the energy of a rigid rotor using the Schrödinger wave equation.

3. Explain Hartree-Fock self-consistent field theory in detail.

   Or

   Discuss the time-independent perturbation theory.

4. Explain Huckel molecular orbital theory for H_2 molecule.

Or

Discuss about Born-Oppenheimer approximation method in detail.

5. Write a note on selection rule for the transitition in diatomics.

Or

What is hybridization ? Determine wave function for sp^3 hybridization.

B – 1353

C.B.S. (Fifth Semester)

Semester Examination Dec.- 2017 1533321

Quantum Chemistry

(C-501)

Time : Three Hours] [Maximum Marks : 40

PART-A

(Multiple choice question) (0.5 marks each)

1. The value of Planck's constant is-
   a. $6.626X10^{-34}$ Js b. $6.023X10^{23}$ Js
   c. $6.26X10^{-27}$ Js d. $6.266X10^{-24}$ Js
2. Which of the following series of line in atomic spectrum of hydrogen appear in the visible region?
   a. Lyman b. Paschen c. Brackett d. Balmer
3. Which of the following is discrete in Bohr's theory?
   a. Potential energy b. Kinetic energy
   c. Velocity d. Angular momentum
4. The dual nature of radiations was proposed by-
   a. Max-Planck b. de-Broglie c. Einstein d. Schrodinger
5. If the uncertainity in the position of an electron is zero, the uncertainity in its momentum would be -
   a. zero b. greater than $\hbar/4\pi$ c. less than $\hbar/4\pi$ d. ∞
6. The wave-mechanical model of atom is based upon -
   a. de-Broglie concept of dual character of matter
   b. Heisenberg's uncertainity principle
   c. Schrodinger wave equation
   d. All of the three above
7. According to photoelectric effect, the kinetic energy of the ejected electrons is directly proportional to -
   a. Wave length of light b. intensity of light
   c. Frequency of light d. Velocity of incident radiation
8. Bohr's model of atom is in conflict with
   a. Pauli's exclusion principle b. Heisenberg's uncertainity principle
   c. Max planck's quantum theory d. All above three
9. If wave length of photon is 2.2×10^{-11} m, n + 6.6×10^{-34} Js the momentum of photon is -
   a. 3×10^{-23} kg/s b. 3.3×10^{22} kg/s
   c. 1.452×10^{-44} kg/s d. 6.89×10^{-43} kg/s
10. A perfect Black body -
    a. Absorbs all the incident radiation
    b. Allow all the incident radiation to pass through it
    c. Reflects all the incident radiation
    d. None of the above
11. Schrodinger equation is a -
    a. Partial differential equation b. differential equation
    c. Integral equation d. None of the above
12. The complete term symbol has general formula -
    a. $^{25+1}L_J$ b. $^{2L+1}S_J$ c. $^{2J+1}L_S$ d. $^{25+1}L_o$
13. Zeeman effect in an atom is result of
    a. Only atom's magnetic moment
    b. External magnetic field
    c. Interaction of atom's magnetic moment and external magnetic field
    d. None of the above
14. The value of n_1, for Balmer series in the given formula is -

$$\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

    a. 1 b. 2 c. 3 d. 4
15. The possible J values for ^3D term symbol are -
    a. 2 b. 3 c. 4 d. 5
16. According to spin selection rule the allowed transition is-
    a. $^3T_{1g} \rightarrow {}^1T_{2g}$ b. $3P \rightarrow 1P$ c. $^3T_{1g} \rightarrow {}^3T_{2g}$ d. $3P \rightarrow 1S$
17. The number of microstates for d^6 electronic configuration is -
    a. 110 b. 35 c. 210 d. 42
18. The term symbol in $[Sc(H_2o)_6]^{3t}$ is
    a. $^2D_{1/2}$ b. $^1S_0$ c. $^4F_{3/2}$ d. $^6S_{5/2}$
19. The forbidden transition among the following is -
    a. $^3\pi_g \leftrightarrow {}^3\pi_4$ b. $^3\phi_g \leftrightarrow {}^3\Delta_g$ c. $^1\Sigma^+_g \leftrightarrow {}^3\Sigma_{ut}$ d. $^3\Sigma_g \leftrightarrow {}^3\pi_4$

20. The term symbol in $[Fe\ Cl_4]^{2-}$ is
    a. $^6D_{3/2}$ b. $^2I_{3/2}$ c. $^5D_0$ d. $^5D_4$

PART-B

Very short answer type question - (0.75 marks each)

1. What is the laplacian operator?
2. Explain Azimuthal quantum number.
3. What is photoelectric effect?
4. Give Heisenberg's principle of uncertainity.
5. Write limitations of Bohr's model.
6. Explain Blackbody radiation.
7. Write the value of Rydberg's constant.
8. Explain spin-spin interaction.
9. How to calculate J value, explain with example.
10. Calculate the microstate in d^4 electronic configuration.

PART-C

Short answer type question - (1.25marks each)

1. What is eigen function, Explain it.
2. Calculate the wave length of the second line in the paschen series and show that this line lies in the near infrared region.
3. Prove that $y(x) = A\ Cos\ x + B\ sin\ x$ (where A and B are constants), is a solution to the differential equation
$$\frac{d^2y}{dx^2} + y(x) = 0$$
4. What is Born-Oppenheimer Approximation? Explain it.
5. Explain the concept of tunneling in detail.
6. Explain operator concept in quantum chemistry.
7. Explain LCAO method.
8. Determine wave function for $BeCl_2$ molecule.
9. Explain Russell Saunders coupling.
10. Calculate the term symbol and possible j values in $[Co(H_2O)_6]^{2t}$

PART-D

Long answer type question - (2 marks each)

1. What is Schrodinger wave equation? Derive it and give its application too. Also give the significance of Ψ.

OR

Explain time-dependent perturbation theory in detail.

2. Derive all forms of de-Broglie equation. Write its application too.

OR

Explain following –
    a. Slater Determinant b. Slater type orbital's.

3. What is angular momentum? Explain rigid rotator for diatomic molecules. Also derive equation

OR

Explain Hartree-Fock self consistent field theory in detail.

4. Explain spectroscopic term symbol for N_2 molecule. Write the selection rule for the transion in diatoms.

OR

Explain microstate. Give spectroscopic term symbol for F_2 molecule.

5. Explain Hybridization with example. Determine wave function for SP^3 hybridization.

OR

Write conditions for calculating the coefficients of Atomic orbital's used in hybridization. Determine wave function for SP^2 hybridization.

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