INDEX

TIFR - CHEMISTRY PYQ

SECTION-I:

PHYSICAL CHEMISTRY

SECTION-II:

ORGANIC CHEMISTRY

SECTION-III:

INORGANIC CHEMISTRY

-------------------END---------------

SECTION-I

PHYSICAL CHEMISTRY

TIFR CHEMISTRY: NUMBER OF QUESTIONS ASKED IN TIFR EXAM (2010 to 2024)

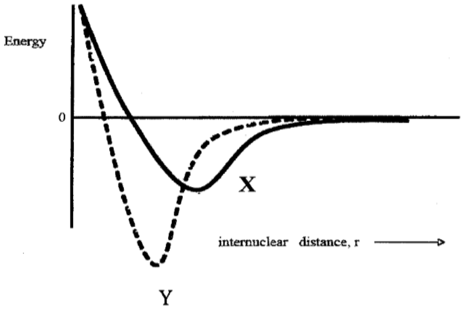
TOPIC		2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
1	STRUCTURE & QUANTUM CHEMISTRY	2	1	5	5	3	5	3	5	5	4	3	4	3	10	5
2	GROUP THEORY	-	1	-	2	-	2	1	-	1	1	1	-	-	-	1
3	MOLECULAR SPECTROSCOPY	3	-	2	-	4	1	1	-	3	3	1	-	2	-	-
4	EQUILIBRIUM	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	UNIT 4.1: CHEMICAL THERMODYNAMICS	1	2	3	4	3	2	5	4	2	5	3	3	3	2	3
	UNIT 4.2: CHEMICAL EQUILIBRIUM	1	-	-	2	-	-	-	1	-	-	-	1	3	-	-
	UNIT 4.3: ELECTROCHEMISTRY	3	3	3	-	4	2	1	2	2	1	-	1	1	2	3
	UNIT 4.4: PHASE EQUILIBRIUM	-	1	1	-	-	1	2	-	1	1	-	-	2	-	1
	UNIT 4.5: STASTICAL THERMODYNAMICS	-	-	-	-	1	1	-	-	-	-	-	1	-	2	1
5	KINETICS	3	4	3	2	2	5	2	1	3	3	3	3	1	1	2
6	SURFACE & INTERFACES	2	3	1	3	3	2	2	1	1	1	-	-	-	1	2
7	MATHEMATICS	3	6	3	1	3	2	3	3	3	1	1	2	2	6	3

CHAPTER-1 STRUCTURE AND QUANTUM CHEMISTRY

PREVIOUS YEAR EXAM QUESTIONS

(TIFR 2010)

1. Consider the two diatomic molecules CN and CN^-, and the potential energy diagram shown below.



Which of the following is the correct statement?

(a) Bond order of CN is 2.5 and the curve Y corresponds to CN.

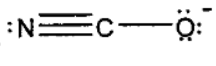
(b) Bond order of CN is 3 and the curve X corresponds to CN.

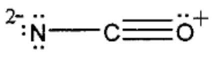
(c) Bond order of CN^- is 3 and the curve Y corresponds to CN^-.

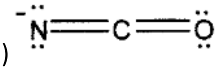
(d) Bond order of CN^- is 2.5 and the curve X corresponds to CN^-.

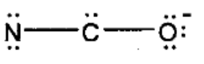
(TIFR 2010)

2. In valence-bond calculations, contributions of various resonance structures are used to calculate the total energy of a molecule. Given below are four resonance structures of the cyanate ion. Which one contributes least to the total energy?

(a) 

(b) 

(c) 

(d) 

(TIFR 2011)

3. An electronic state of a hydrogen atom is prepared to be a superposition energy of the eigenstates of the hydrogen atom, and for which the normalized wave function is written as:

$\phi = \frac{1}{\sqrt{2}}|1s\rangle + \frac{1}{\sqrt{4}}|2s\rangle + C_{3s}|3s\rangle$

Here $|1s\rangle, |2s\rangle$ and $|3s\rangle$ are the exact energy eigenstates of the hydrogen atom, and C_{3s}, is a constant. What would be the average value of energy, associated with this wavefunction ϕ, in a.u.?

(a) $-0.2951\ a.u.$ (b) $-0.4161\ a.u.$

(c) $-0.2269\ a.u.$ (d) $-0.3929\ a.u.$

(TIFR 2012)

4. The transition probability for spontaneous emission from state m to state n is given by an expression

$A_{m\to n} = \left(\frac{64\pi^4 v_{mn}^3}{3hc^3}\right)\cdot\left(|\langle m|\hat{d}|n\rangle|^2\right)$

Where, V_{mn} is the frequency of transition, and the term in the parenthesis is the transition dipole. Assuming that the magnitude of the transition dipole is same for all types of transitions, arrange the average lifetimes for the electronic, vibrational, and rotational transitions in the proper order.

(a) vibrational < rotational < electronic

(b) electronic < vibrational < rotational

(c) rotational < vibrational < electronic

(d) electronic < rotational = vibrational

(TIFR 2012)

5. In a spherical polar coordinate system, a point A at (x, y, z) in the Cartesian coordinate system can be described by (r, θ, ϕ) where r, θ, and ϕ have their usual meaning. Expression for the volume of an infinitesimally small cube confined by dx, dy, and dz in terms of the spherical coordinate system is given by

(a) $dr d\theta d\phi$ (b) $r sin\theta dr d\theta d\phi$

(c) $r^2 \sin^2\theta\, dr d\theta d\phi$ (d) $r^2 \sin\theta\, dr d\theta d\phi$

(TIFR 2012)

6. The degeneracy of the energy level $12h^2/8ma^2$ of a particle in a three dimensional cube of length "a" is

(a) 1 (b) 3

(c) 6 (d) 12

(TIFR 2012)

7. For the above, if the states were non-degenerate and with energy eigenvalues E and -E respectively, then what would be the expectation value of the energy?

(a) 3E (b) 5E

(c) E (d) None of the above

(TIFR 2012)

8. A quantum mechanical state Q is a superposition of two normalized energy eigenstates A and B in an amplitude ratio 2:1. If the two states are degenerate with a common eigenvalue E, what is the energy of the state Q?

(a) 0 (b) E

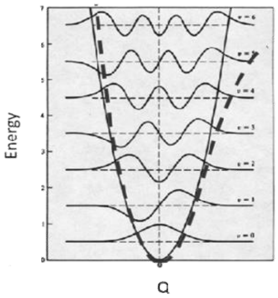
(c) 5E (d) 3E

(TIFR 2013)

9. Given three systems, A, B, and C, what could be they if the spacing between the neighbouring energy levels in A decreases with increasing energy, while that for B is constant, and that for C increases with increasing energy?
   (a) A = particle in a one-dimensional box, B = harmonic oscillator, C = electron in hydrogen atom
   (b) A = electron in hydrogen atom, B = harmonic oscillator, C = particle in a one-dimensional box
   (c) A = particle in a one-dimensional box, B = electron in hydrogen atom, C = harmonic oscillator
   (d) A = electron in hydrogen atom, B = particle in a one-dimensional box, C = harmonic oscillator

(TIFR 2013)

10. Shown below in solid-line is the harmonic potential of a quantum oscillator for a diatomic molecule. If the harmonic potential is suddenly transformed into Morse potential shown in dashed-line how would the zero point energy and shape of wave functions change?



   (a) Zero-point energy remains the same and wave functions do not change.
   (b) Zero-point energy remains the same but wave function reflects a change on the high Q side.
   (c) Zero-point energy changes and wave function reflects a change on the high Q side.
   (d) Potentials never reflect any change in the shape of the wave function

(TIFR 2013)

11. Consider a classical harmonic oscillator with a mass m and a force constant k oscillating with a frequency v. Which of the following statements is NOT true for this system?
   (a) v increases ifm decreases.
   (b) The oscillator is most likely to be found at its equilibrium position.
   (c) The acceleration is maximum at its turning points.
   (d) v does not depend on how large the amplitude of the oscillation is.

(TIFR 2013)

12. What is the degeneracy of the energy level with n-6 (n being the principal quantum number) in a hydro genic atom or ion?
   (a) 16 (b) 9
   (c) 36 (d) 25

(TIFR 2013)

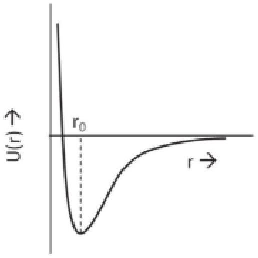
13. Which of the following experimental observations best demonstrates the wavelike character of electrons?
   (a) The photoelectric effect
   (b) The flow of electrons in a metal wire
   (c) The diffraction pattern of electrons scattered from a crystalline solid
   (d) The deflection of an electron beam by electrical plates

(TIFR 2014)

14. The potential energy of a diatomic molecule, as a function of the inter nuclear separation r, is approximated as

   $U(r) = \frac{A}{r^a} - \frac{B}{r^b}$

   Where A and B are positive constants and $a > b$



   As shown in the above figure, r_0 is the equilibrium bond length. What is the energy necessary to break the bond from its equilibrium position?
   (a) $\frac{A}{r_0^a} - \frac{B}{r_0^b}$
   (b) $\frac{B}{r_0^b} - \frac{A}{r_0^a}$
   (c) $\frac{A}{r_0^a}\left(\frac{a}{b} - 1\right)$
   (d) both B and C

(TIFR 2014)

15. Transition states in chemical reactions are generally not directly observed in experiments because
   (a) their structures are different from reactants and products
   (b) they have the highest kinetic energy and hence difficult to capture
   (c) they have the highest potential energy and their lifetimes are short
   (d) all of the above

(TIFR 2023)

56. If $A = \begin{pmatrix} 1 & -2 \\ 1 & 4 \end{pmatrix}$, find the smallest eigenvalue of A^{10}
    (a) 10 (b) 59049
    (c) 1024 (d) 0.999

(TIFR 2023)

57. Which of the following is NOT a linear operator?
    (a) $\frac{d}{dx}$ (b) $\int dx$
    (c) $(\ )^2$ (d) $\frac{d^2}{dx^2}$

(TIFR 2023)

58. Which of the following operators is Hermitian?
    (a) $-\frac{d}{dx}$ (b) $e^{-\frac{i\pi}{2}}\frac{d}{dx}$
    (c) $\frac{d}{dx}$ (d) $x + \frac{d}{dx}$

(TIFR 2023)

59. If A and B are two operators that do not commute, which amongst the following is the correct statement (here $[A, B] = AB - BA$ is the commutator and $\{A, B\} = AB + BA$ is the anticommutator):
    (a) A and B can be measured simultaneously with zero error.
    (b) $\exp(A)\exp(B) = \exp(A + B)$
    (c) $\exp(A)\exp(B) = \exp\left(A + B + \frac{1}{2}[A, B] + \frac{1}{12}[A, [A, B]] - \frac{1}{12}[B, [A, B]] + \cdots\right)$
    (d) $\exp(A)\exp(B) = \exp\left(A + B + \frac{1}{2}\{A, B\} + \frac{1}{12}\{A, \{A, B\}\} - \frac{1}{12}\{B, \{A, B\}\} + \cdots\right)$

(TIFR 2024)

60. Consider a proton confined inside a nucleus. Assuming a simplified model such as the proton is confined to a rectangular well with the nucleus of radius 0.5 x 10^{-15} m, calculate the first excitation energy.
    (a) 0.6 GeV (b) 13.6 eV
    (c) 0.5 MeV (d) 10.6 GeV

(TIFR 2024)

61. The state of a spin-1 system is given by $|\psi >= 2|1 > +i|0 >- 1\rangle$, where $|1\rangle$, $|0\rangle$, and $| - 1\rangle$ are the eigenstates of the | - 1 $>$ *are the* eigenstates of the $\hat{S}_z$ operator. When the z -component of the spin is measured, what is the probability that the system will be found in eigenstate $| - 1\rangle$?
    (a) –i (b) –i/3
    (c) 1⁄3 (d) 1/6

(TIFR 2024)

62. Which quantum mechanical phenomenon is primarily responsible for the tunable emission properties of quantum dots?
    (a) Quantum entanglement
    (b) Quantum tunneling
    (c) Quantum confinement
    (d) Quantum superposition

(TIFR 2024)

63. The wave function of a particle is given by $\psi(x) = e^{-|x-2|}$. What is the probability that the particle is found in the region 1 < x < 3?
    (a) −2 (b) −0.7689
    (c) 0.8647 (d) 0.7689

(TIFR 2024)

64. A particle in its ground state, given by the wavefunction ψ_g (x, y,z) is excited to a new ψ_e (x, y,z) state if r represents the position vector of the particle, the displacement in the particle`s position upon excitation is given by
    (a) $\int \psi_e^*$ r $\psi_e$dxdydz - $\int\int \psi_e^*$ r $\psi_g$dxdydz
    (b) $\int \psi_e^*$ r $\psi_g$dxdydz - $\int\int \psi_g^*$ r $\psi_e$dxdydz
    (c) $\int \psi_g^*$ r $\psi_e$dxdydz
    (d) $\int \psi_e^*$ r $\psi_e$dxdydz

Answer Key									
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
(a)	(b)	(a)	(b)	(d)	(a)	(d)	(b)	(b)	(d)
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
(b)	(c)	(c)	(d)	(c)	(a)	(b)	(b)	(d)	(c)
21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
(a)	(c)	(c)	(a)	(d)	(b)	(c)	(b)	(d)	(b)
31	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
(d)	(c)	(b)	(b)	(c)	(d)	(d)	(d)	(d)	(c)
41	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**
(a)	(d)	(c)	(d)	(a)	(b)	(c)	(b)	(d)	(b)
51	**52**	**53**	**54**	**55**	**56**	**57**	**58**	**59**	**60**
(c)	(c)	(a)	(b)	(b)	(c)	(c)	(b)	(c)	(a)
61	**62**	**63**	**64**						
(d)	(c)	(c)	(a)						

SOLUTIONS

1. **Correct Answer is (a)**
   Bond order of CN is 2.5
   Bond order and inter nuclear distance inverse relation. Lower bond order, higher inter nuclear distance.

2. **Correct Answer is (b)**
   More electronegative element has negative charge. More stable compound has less energy and unstable compound has more energy.

3. **Correct Answer is (a)**

normalized wavefunction; $C_1^2 + C_2^2 + C_3^2 = 1$

$\left(\frac{1}{\sqrt{2}}\right)^2 + \left(\frac{1}{\sqrt{4}}\right)^2 + C_3^2 = 1$

$C_3^2 = \frac{1}{4}$

Energy of hydrogen atom in a.u is

$E = -0.5\left(\frac{z^2}{n^2}\right)$

Average energy;

$< E > = C_1^2E_1 + C_2^2E_2 + C_3^2E_3$

$= \left(\frac{1}{\sqrt{2}}\right)^2\left(-\frac{0.5}{1^2}\right) + \left(\frac{1}{\sqrt{4}}\right)^2\left(-\frac{0.5}{2^2}\right) + \left(\frac{1}{4}\right)\left(-\frac{0.5}{3^2}\right)$

$= -0.2951 a.u$

4. **Correct Answer is (b)**

Assuming the magnitude of the transition dipole moment (|dmn|) is the same for all transitions, the transition probability is directly proportional to the cube of the transition frequency (vmn3).

- Electronic transitions: ~$10^{15} Hz$
- Vibrational transitions**:** ~$10^{13} Hz$
- Rotational transitions: ~$10^{11} Hz$

Since the transition probability is proportional to the cube of the frequency, the order of the average lifetimes (which are inversely proportional to the transition probability) is:

electronic < vibrational < rotational

5. **Correct Answer is (d)**

In spherical coordinates, an infinitesimally small volume element is not a cube, but rather a wedge-shaped region. However, the concept of a small volume element still applies, and we can express it as:

$dV = r^2 sin\theta dr d\theta d\phi$

6. **Correct Answer is (a)**

Energy of a particle in 3 dimensional is ;

$E = \left(n_x^2 + n_y^2 + n_z^2\right)\frac{h^2}{8ma^2}$

$= \left(n_x^2 + n_y^2 + n_z^2\right)\frac{h^2}{8ma^2} = \frac{12h^2}{8ma^2}$

$n_x^2 + n_y^2 + n_z^2 = 12$

$2^2 + 2^2 + 2^2 = 12$

If $n_x = n_y = n_z$ then degeneracy is 1

7. **Correct Answer is (d)**

it's impossible to determine the expectation value of the energy.

8. **Correct Answer is (b)**

$Q = \frac{2}{\sqrt{5}}\left|A > + \frac{1}{\sqrt{5}}\right|B >$

The energy operator H^ acting on a state |A⟩ gives the energy eigenvalue E, and similarly, acting on state |B⟩ also gives E. Therefore, the expectation value of the energy operator H^ for the state |Q⟩ is:

$< Q|H|Q > = \left(\frac{2}{\sqrt{5}}\right)^2 E + \left(\frac{1}{\sqrt{5}}\right)^2 E$

$= \frac{4}{5}E + \frac{1}{5}E = E$

9. **Correct Answer is (b)**

The energy of a hydrogen atom and its neighbouring distance have an inverse relationship. This means:

Lower energy: Corresponds to a larger neighbouring distance between the electron and the nucleus.

Higher energy: Corresponds to a smaller neighbouring distance between the electron and the nucleus.

In harmonic oscillator neighbouring distance constant. In one dimension with increasing energy neighbouring distance increases.

10. **Correct Answer is (d)**

The potential never reflect any change in the shape of the wavefunction.

11. **Correct Answer is (b)**

The probability of finding the oscillator at different positions depends on its energy state. At higher energy states, the oscillator is equally likely to be found anywhere within its range of motion.

12. **Correct Answer is (c)**

In a hydrogenic atom degeneracy $= n^2$

$= 6^2 = 36$

13. **Correct Answer is (c)**

Electron diffraction is the key to demonstrating the wave nature of electrons.

14. **Correct Answer is (d)**

At equilibrium bond length r_0 the potential energy is minimum, meaning the molecule is stable. Therefore, the potential energy at r_0 is;

$U(r_0) = \frac{A}{r_0^a} - \frac{B}{r_0^b}$

To break the bond, we need to consider the dissociation limit where the molecule completely dissociates into two separated atoms. In this case, the potential energy approaches zero, as the atoms are infinitely far apart. So, at the dissociation limit, the potential energy is;

$U(\infty) = 0$

Energy to break the bond $U(\infty) - U(r_0) = 0 - \left(\frac{A}{r_0^a} - \frac{B}{r_0^b}\right)$

$= \frac{B}{r_0^b} - \frac{A}{r_0^a}$

15. Correct Answer is (c)

They exist only for a brief period during the reaction, making it challenging to capture them using standard experimental techniques.

16. Correct Answer is (a)

Partition function;

$Z = e^{-E_0/k_BT} + e^{-E_1/k_BT} + e^{-E_2/k_BT}$

$P_0 = e^{-\frac{E_0}{k_BT}}$

$= e^{-\frac{0}{1.38} \times 10^{-23}}$

$P_0 = 0.919$

$P_1 = e^{-\frac{E_1}{k_BT}}$

$= e^{-1 \times \frac{10^{-20}}{1.38} \times 10^{-23} \times 298}$

$P_1 = 0.081$

$P_2 = e^{-E_2/k_BT}$

$= e^{-3\times10^{-20}/1.38\times10^{-23}\times298}$

$P_2 = 0.001$

17. Correct Answer is (b)

The time-dependent Schrodinger equation governs the evolution of wave functions in quantum mechanics and is given by;

$i\hbar \frac{\partial}{\partial t}\, \varphi(x,t) = H\varphi(x,t)$

H is the Hamiltonian operator.

When $\varphi(x,t)$ can be separated into f(t) and g(x). it implies that the wavefunction is in a state of definite energy. It is an eigenstate of the hamoltonian operator. This is the time independent Schrodinger equation.

Therefore, the probability of finding the particle between x and x+dx for such a system is independent of time.

18. Correct Answer is (b)

For a harmonic oscillator, the energy levels are equally spaced at low quantum numbers. Morse potential is a more realistic model than the harmonic oscillator and can be used to describe the **vibrations of molecules** as it accounts for anharmonicity and bond dissociation behavior.

19. Correct Answer is (d)

The Heisenberg uncertainty principle states that the position (x) and momentum (p) operators cannot be known simultaneously with perfect accuracy. Mathematically, this translates to the non-commuting property: [x, p] ≠ 0. However, the statement asks about **commuting**, which means their commutator is **zero**: [x, p] = 0. This is indeed true, signifying the inherent uncertainty principle in quantum mechanics.

20. Correct Answer is (c)

The particle's **total energy remains constant** throughout the tunneling process. It cannot gain or lose energy simply by passing through the barrier.

21. Correct Answer is (a)

Condition for acceptable wave function;

1) function must be continuous

2) finite area

3) single valued

$\psi = \exp(-x)$

$x = 0$; $\varphi = 1$; Single valued acceptable wavefunction.

22. Correct Answer is (c)

Consider the linear combination vector $X = \sum_k N\, C_k X_k$ where C_k are non-zero scalar coefficients.

To determine whether X is an eigenvector of A we need to check if $AX = \lambda X$ for some scalar λ.

$AX = A(\sum_{k=1}^{N} C_k X_k) = \sum_{k=1}^{N} C_k A X_k$

Using the eigen value equation;

$AX_k = \lambda_k X_k$

$AX = \sum_{k=1}^{N} C_k \lambda_k X_k$

Now, X will be the eigenvector of A if we can express AX in the form λX

$AX = A(\sum_{k=1}^{N} C_k \lambda_k X_k) = \lambda \sum_{k=1}^{N} C_k X_k$

For this equation to hold it must be the case that

$\lambda = \sum_{k=1}^{N} C_k\, \lambda_k$

It states that X is an eigenvector of A only if the λk's are all equal.

23. Correct Answer is (c)

Energy of Hydrogen atom is; $E = -13.6 \times \frac{Z^2}{n^2}$

Energy of photon ; $E_P = E_i - E_f$

$4.25 = E_i - E_f$

$4.25 = (-13.6) \times \frac{Z^2}{n_i^2} - (-13.6) \times \frac{Z^2}{n_f^2}$