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CHAPTER-1 STRUCTURE AND QUANTUM CHEMISTRY

PRACTICE QUESTIONS

1. The ratio of $(E_2 - E_1)$ to $(E_4 - E_3)$ for He^+ ion is approximately equal to (Where E_n is the energy of n^{th} orbit)
(A) 10 (B) 15
(C) 17 (D) 12

2. The ionization energy of H atom is $21.79 \times 10^{-19} J$ then the value of binding energy of second excited state of Li^{2+} ion.
(A) $3^2 \times 21.7 \times 10^{-19}$ (B) 21.79×10^{-19}
(C) $\frac{1}{3} \times 21.79 \times 10^{-19}$ (D) $\frac{1}{3^2} \times 21.79 \times 10^{-19}$

3. Electron in hydrogen atom is in fourth stationary state. What is maximum number of spectral lines that can be observed as it de-excited
(A) 4 (B) 3
(C) 12 (D) 6

4. The de Broglie wavelength of an electron moving in a circular orbit is λ. The minimum radius orbit is
(A) $\frac{\lambda}{\pi}$ (B) $\frac{\lambda}{2\pi}$
(C) $\frac{\lambda}{4\pi}$ (D) $\frac{\lambda}{3\pi}$

5. Alveoli are the tiny sacs of air in the lungs whose average diameter is 50 pm. Consider an oxygen molecule Trapped within a sac. Calculate uncertainty in the velocity of oxygen molecule?
(A) $1.98 \times 10^{-2} ms^{-1}$ (B) $19.8\ ms^{-1}$
(C) $198 \times 10^{-4} ms^{-1}$ (D) $19.8 \times 10^{-6} ms^{-1}$

6. The energy required to break one mole of Cl-Cl bonds in Cl_2 242 kg mol^{-1}. The longest wavelength of light capable of breaking a single Cl-Cl bond is
(A) 594 m (B) 640 nm
(C) 700 nm (D) 494 nm

7. If Ψ_n, l, m denotes the eigen function of Hamiltonian for H-atom and
$\Psi_n, l, m = \frac{1}{5}[3\Psi_{211} + \Psi_{210} - \sqrt{15}\,\Psi_{21-1}]$
Calculate the expectation value of E
(A) $-\frac{3.4}{4} ev$ (B) $-\frac{13.6}{4} ev$
(C) $-\frac{13.6}{2} ev$ (D) $\frac{13.6}{4} ev$

8. The operation $\left[x, \left[x,\ \widehat{p_x}^2\right]\right]$ is identical with
(A) $[\widehat{p_x}.x,\ [x,\ \widehat{p_x}]]$ (B) $[x.\widehat{p_x}\ , [x,\ \widehat{p_x}]]$
(C) $-[\widehat{p_x}, [x^2,\ \widehat{p_x}]]$ (D) $[x, [x^2,\ \widehat{p_x}]]$

9. When the operator $-\hbar^2 \frac{d^2}{dx^2}$ operates on the function e^{-ikx} the result is
(A) $\hbar^2 k^2 e^{-ikx}$ (B) $-\hbar^2 k^2 e^{-ikx}$
(C) $k^2 e^{-ikx}$ (D) $\hbar^2 e^{ikx}$

10. e^{-3x^2} is an eigen function of the operator $(\frac{d^2}{dx^2} - 36\,x^2)$ *the eigan value is*
(A) -2 (B) -3
(C) -4 (D) -6

11. Suppose Ψ_1 and Ψ_2 are two hybrid orbitals:-
$\Psi_1 = 0.12\ \Psi_{3s} + 0.63\Psi_{3px} + 0.77\Psi_{3py}$
$\Psi_2 = 0.12\ \Psi_{3s} - 0.63\Psi_{3px} - 0.77\Psi_{3py}$
The angle (in degree) between them is
(A) 12 (B) 178
(C) 91 (D) 89

12. The set of eigen functions $\sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} (0 \le x \le a)\ n = 1,2,3, \ldots.)$ is
(A) orthogonal
(B) Normalised
(C) Both orthogonal and normalised
(D) un normalised

13. The wave function of a $1 - \mathrm{D}$ harmonic oscillator between $x = +\infty$ to $x = -\infty$ is given by $\Psi_{(x)} = N(2x^2 - 1)e^{-\frac{x^2}{2}}$. Find the value of N.
(A) $\frac{1}{\sqrt{2}\,\pi}$ (B) $\frac{1}{\pi\sqrt{2}}$
(C) $\sqrt{\frac{1}{2\sqrt{\pi}}}$ (D) $\frac{1}{2\sqrt{\pi}}$

SOLUTION

1. Solution:

$E_n = -13.6\,\frac{Z^2}{n^2}\,ev$

E_1 for He⁺ $= -13.6 \times \frac{2^2}{1} = -13.6 \times 4\,eV$

E_2 for He⁺ $-13.6 \times \frac{2^2}{2^2} = -13.6\,eV$

E_3 for He⁺ $-13.6 \times \frac{2^2}{3^2} = -13.6\,eV \times \frac{4}{9}eV$

E_4 for He⁺ $-13.6 \times \frac{2^2}{4^2} = -13.6\,eV \times \frac{4}{16}eV$

$\Rightarrow E_2 - E_1 = -13.6eV - (-13.6 \times 4\,eV)$

$E_2 - E_1 = +408eV \Rightarrow 40.8eV$

$(E_4 - E_3) = -13.6 \times 4/16\,eV - (-13.6 \times \frac{4}{9}eV)$

$\Rightarrow -3.4eV + 6.044 \Rightarrow 2.64eV$

$\frac{E_2 - E_1}{(E_4 - E_3} = \frac{40.8eV}{2.64eV} = 15$

Hence, option (B) is correct.

2. Solution:

Binding energy $= I.E. \times \frac{n^2}{z^2}$

$\Rightarrow \frac{21.79\times10^{-19}}{(3)^2}(3)^2$

$B.E. \Rightarrow 21.79 \times 10^{-19}$

Hence, option (B) is correct.

3. Solution:

Maximum number of spectral lines from n^{th} state

$= \frac{n(n-1)}{2} = n = 4$

$\frac{n(n-1)}{2} = \frac{4(4-1)}{2} = 6$

Hence, option (D) is correct.

4. Solution:

We know $2\pi r = n\lambda$

For minimum radius $n = 1$

$2\pi r_{min} = \lambda\,; r_{min} = \frac{\lambda}{2\pi}$

Hence, option (B) is correct.

5. Solution:

$\Delta x = 50\,pm$

So, $\Delta V = \frac{n}{4\pi.m\,\Delta x} = \frac{6.626\times10^{-34}\times6.02\times10^{23}}{4\times3.14\times32\times10^{-3}\times50\times10^{-12}}$

$0.0019853 \times 10^4 m/sec$

$\Rightarrow 19.853\,m/sec$

Hence option (B) is correct

6. Solution:

Energy required to break one mole $Cl - Cl$ bonds in Cl_2 is 242 kg mol $^{-1}$

For 1 molecule $\Rightarrow \frac{242\,kg\,mol^{-1}}{6.023\times10^{23}Mol^{-1}}$

Energy required to break $Cl - Cl$ bond is

$\Rightarrow 4.0179 \times 10^{-19} Joule$

Energy = $\frac{hC}{\lambda}$

$4.0179 \times 10^{-19} Joule = \frac{6.626\times10^{-34}\times3\times10^8 ms^{-1}}{\lambda}$

$\lambda = \frac{19.878\times10^{-26}}{4.0179\times10^{-19}}$ m

$\lambda = 4.947 \times 10^{-7} m$

$\lambda = 494 \times 10^{-9} m$

$\lambda = 494\,nm$

Hence, option (D) is correct.

7. Solution:

In general $\Psi_1 = C_1\phi_1 + C_2\phi_2 + C_3\phi_3$

$\Psi_{n,l,m} = \frac{3}{5}\Psi_{2,1,1} + \frac{1}{5}\Psi_{2,1,0} + \frac{-\sqrt{15}}{5}\Psi_{2,1-,1}$

$\langle o, b\rangle = P_1(ob)_1 + P_2(ob)_2 + P_3(ob)_3$

$\langle E\rangle = \left(\frac{3}{5}\right)^2 E_1 + \left(\frac{1}{5}\right)^2 E_2 + \left(\frac{-\sqrt{15}}{5}\right)^2 E_3$

$\Rightarrow \frac{9}{25}\left(-\frac{13.6}{n_1^2}\right) + \frac{1}{25}\left(-\frac{13.6}{n_2^2}\right) + \frac{15}{25}\left(-\frac{13.6}{n_3^2}\right)$

$\Rightarrow \frac{9}{25}\left(-\frac{13.6}{2^2}\right) + \frac{1}{25}\left(-\frac{13.6}{2^2}\right) + \frac{15}{25}\left(-\frac{13.6}{2^2}\right)$

$\Rightarrow -\frac{13.6}{4}\left[\frac{9}{25} + \frac{1}{25} + \frac{15}{25}\right]$

$\Rightarrow -\frac{13.6}{4}\left[\frac{9+1+15}{25}\right]$

$\Rightarrow \langle E\rangle = -\frac{13.6}{4}ev$

Hence, option (B) is correct.

8. Solution:

$[\hat{x}, [\hat{x}, \hat{p}x^2]$

$[\hat{x}, \hat{p}x^2] = 2\hat{p}x[\hat{x}, \hat{P}x] = 2\hat{P}x\,i\hbar$

$\#\,[\hat{x}\,, 2\hat{P}x\,i\hbar\,] = 2i\hbar[\hat{x}, \hat{P}x]$

$\Rightarrow\ 2\,i\hbar(i\hbar) = 2(i)^2\hbar^2$

$\Rightarrow -2\hbar^2$

(A) $\left[\widehat{P_x}.x\,, [x, P_x]\right] = \left[\hat{P}x.x, [\hat{x}, \hat{P}x]\right]$

$\Rightarrow \left[\hat{P}x\,.\hat{x}, i\hbar\right] \Rightarrow 0$

(B) $[x.px, [x, px]\} = [xpx, i\hbar] = 0$

(C) $-[Px, [x^2, Px]] = -[px, 2x\,i\hbar]$

$\Rightarrow\ -2i\hbar\,[\hat{P}x, x^2]$

$\Rightarrow\ -2i\hbar(-i\hbar) = 2(-1)\hbar^2$

$\Rightarrow\ -2\hbar^2$

(D) $[x, [x^2, Px]] = [x^2, px] = 2\hat{x}, [\hat{x}, \hat{P}x] = 2xih$

$\Rightarrow [\hat{x}, 2\hat{x}(i\hbar)] = 0$

Hence, option (C) is correct.

9. Solution:

$-\hbar^2\,\frac{d^2}{dx^2}\{e^{-ikx}\} = -\hbar^2\,\frac{d}{dx}.\frac{d}{dx}e^{ikx}$

$\Rightarrow\ --\,\hbar^2\,\frac{d}{dx}\,\{e^{-ikx}(-ik)\}$

$\Rightarrow i\hbar^2 k\,\frac{d}{dx}\,e^{-ikx} = i\hbar^2 k e^{-ikx}\,(-ik)$

$\Rightarrow -i^2\hbar^2 k \frac{d}{dx} e^{-ikx} = \hbar^2 k e^{-ikx}$

$\Rightarrow \hbar^2 k\ e^{-ikx}$

Hence, option (A) is correct.

10. Solution:

(operator $\left(\frac{d^2}{dx^2} - 36\,x^2\right) e^{-3x^2}$

$\frac{d^2}{dx^2} e^{-3x^2} - 36x^2 \times e^{-3x^2}$

$\frac{d}{dx}.\frac{d}{dx} e^{-3x^2} - -36x^2 e^{-3x^2}$

$\frac{d}{dx}\left(-6xe^{-3x^2}\right) - 36x^2 e^{-3x^2}$

$-6e^{-3x^2} - 6x \times (-6x)e^{-3x^2} - 36x^2 e^{-3x^2}$

$-6e^{-3x^2} + 36x^2 e^{-3x^2} - 36x^2 e^{-3x^2}$

$-6e^{-3x^2}$ (Eigen function)

Eigen value -6

Hence, option (D) is correct.

11. Solution:

$\cos\theta$

$= \frac{0.12 \times 0.12 + (0.63 \times -0.63) + (0.77 \times -0.77)}{\sqrt{0.12^2 + 0.63^2 + 0.77^2}\ \sqrt{0.12^2 + 0.63^2 + 0.77^2}}$

$\cos\theta = -0.9754$

$\theta = \cos^{-1}\ (-0.9754)$

$\theta = 178°$

Hence, option (B) is correct.

12. Solution:

Check Normalised

$\int_0^a \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} . \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}\ dx$

$\Rightarrow \frac{2}{a} \int_0^a\ sin^2 \frac{n\pi x}{a} dx$

$\Rightarrow \frac{2}{a} \int_0^a \left(\frac{1-\cos 2\frac{n\pi x}{a}}{2}\right) dx$

$\Rightarrow \frac{1}{a}\left[x - \frac{\sin 2\frac{n\pi x}{a}}{\frac{2\pi\pi}{a}}\right]_0^a$

$\rightarrow \frac{1}{a}[a - 0] = \frac{1}{a} \times a = 1$

So, $\Psi_1 = \sqrt{\frac{2}{a}} \sin\frac{\pi x}{a}$

$\Psi_2 = \sqrt{\frac{2}{a}} \sin\frac{2\pi x}{a}$

$\Rightarrow \int_{-\infty}^{\infty} \Psi_1\, \Psi_2 d\tau = 0$

A.T.Q

$\int_0^a \sqrt{\frac{2}{a}} \sin\frac{\pi x}{a} . \sqrt{\frac{2}{a}} \sin\frac{2\pi x}{a}\ dx$

$\Rightarrow \frac{2}{a} \int_0^a \frac{2}{2} (\sin\frac{\pi x}{a} . \sin\frac{2\pi x}{a})\ dx$

$\Rightarrow \frac{2}{2a} \int_0^a 2\sin\frac{\pi x}{a} . \sin\frac{2\pi x}{a}\ dx$

$2\sin A \sin B = \cos(A - B) - \cos(A + B)$

$\Rightarrow \frac{1}{a} \int_0^a [\cos\left(\frac{\pi x}{a} - \frac{2\pi x}{a}\right) - \cos\left(\frac{nx}{a} + \frac{2\pi x}{a}\right)]dx$

$\Rightarrow \frac{1}{a} \int_0^a [\cos\left(-\frac{nx}{a}\right) - \cos\left(\frac{3\pi x}{a}\right)]dx$

$\Rightarrow \frac{1}{a} [\int_0^a \cos\left(\frac{\pi x}{a}\right) dx - \int_0^a \cos\left(\frac{3\pi x}{2}\right) dx -$

$\Rightarrow \frac{1}{a} [\frac{\sin\frac{\pi x}{a}}{\frac{\pi}{a}} - \sin\frac{\frac{3\pi x}{a}}{\frac{3\pi}{a}}]_0^a$

$\Rightarrow \frac{1}{a} [\frac{a}{\pi} \sin\frac{\pi x}{a} - \frac{a}{3\pi} \sin\frac{3\pi x}{a}]_0^a$

$\Rightarrow \frac{1}{a} [\frac{a}{\pi} \sin\frac{\pi a}{a} - \frac{a}{3\pi} \sin\frac{3\pi a}{a} - \sin 0 - \sin 0]$

$\frac{1}{a}\left[\frac{a}{\pi} \times 0 - 0 - 0 - 0\right] = 0$ so orthogonal

Hence, option (C) is correct.

13. Solution:

$N = \sqrt{\frac{1}{\int_{-\infty}^{\infty} \Psi^*\Psi d\tau}}$

$\int_{-\infty}^{\infty} \mathrm{N}(2\mathrm{x}^2 - 1)\mathrm{e}^{-\mathrm{x}^2/2} . \mathrm{N}(2\mathrm{x}^2 - 1)\mathrm{e}^{-\mathrm{x}^2/2}\mathrm{dx} = 1$

$\Rightarrow N^2 \int_{-\infty}^{\infty} (2x^2 - 1)^2\, e^{-x^2/2 - x^2/2}\, dx = 1$

$\Rightarrow N^2 \int_{-\infty}^{\infty} (4x^4 + 1 - 4x^2)e^{-x^2} dx = 1$

$\Rightarrow N^2 \left[\frac{\frac{4\Gamma(4+1)}{2}}{(1)^{\frac{5}{2}}} + \frac{\frac{\Gamma(0+1)}{2}}{(1)^{\frac{1}{2}}} - \frac{\frac{4\Gamma(2+1)}{2}}{(1)^{\frac{3}{2}}}\right] = 1$

$\Rightarrow N^2 \left[4 \times \frac{3}{2} \times \frac{1}{2} \times \sqrt{\pi} + \sqrt{\pi} - 4 \times \frac{1}{2} \times \sqrt{\pi}\right] = 1$

$\Rightarrow N^2\left[3\sqrt{\pi} + \sqrt{\pi} - 2\sqrt{\pi}\right] = 1$

$\Rightarrow N^2 = \frac{1}{2\sqrt{\pi}}$

$\Rightarrow N = \frac{1}{2\sqrt{\pi}} = \frac{1}{\sqrt{2}\,\pi^{1/4}}$

$N = \frac{1}{\sqrt{2}\,\pi^{1/4}}$

Hence, option (C) is correct.

14. Solution:-

$E = (nx^2 + ny^2 + nz^2)\frac{h^2}{8ml^2}$

$E = 14\frac{h^2}{8ml^2}$

$(nx^2 + ny^2 + nz^2) = 14$

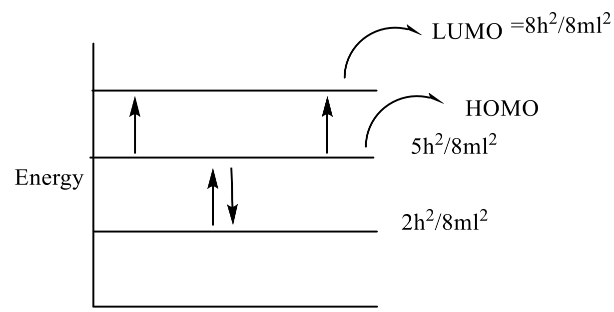
(3, 2, 1)

(3, 2, 1), (312), (213), (231), (123), (132)

So total degeneracy is 6

Hence, option (B) is correct.

15. Solution:



Energy Gap = $\frac{8h^2}{8ml^2} - \frac{5h^2}{8ml^2} = \frac{3h^2}{8ml^2}$