## PHYSICAL CHEMISTRY

## ATOMIC STRUCTURE

1. For $\mathrm{He}^{+}$, a transition takes place from the orbit of radius 105.8 pm to the orbit of radius 26.45 pm .

The wavelength (in nm) of the emitted photon during the transition is $\qquad$ .
[JEE(Advanced) 2023]
[Use:
Bohr radius, $\mathrm{a}=52.9 \mathrm{pm}$
Rydberg constant, $\mathrm{R}_{\mathrm{H}}=2.2 \times 10^{-18} \mathrm{~J}$
Planck's constant, $\mathrm{h}=6.6 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
Speed of light, $\mathrm{c}=3 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$ ]
2. Consider a helium (He) atom that absorbs a photon of wavelength 330 nm . The change in the velocity (in $\mathrm{cm} \mathrm{s}^{-1}$ ) of He atom after the photon absorption is $\qquad$ .
(Assume: Momentum is conserved when photon is absorbed.
[Use: Planck constant $=6.6 \times 10^{-34} \mathrm{~J} \mathrm{~s}$, Avogadro number $=6 \times 10^{23} \mathrm{~mol}^{-1}$, Molar mass of $\mathrm{He}=4 \mathrm{~g} \mathrm{~mol}^{-1}$ ]
[JEE(Advanced) 2021]
3. The ground state energy of hydrogen atom is -13.6 eV . Consider an electronic state $\Psi$ of $\mathrm{He}^{+}$whose energy, azimuthal quantum number and magnetic quantum number are $-3.4 \mathrm{eV}, 2$ and 0 respectively. Which of the following statement(s) is(are) true for the state $\Psi$ ?
[JEE(Advanced) 2019]
(A) It has 2 angular nodes
(B) It has 3 radial nodes
(C) It is a 4 d state
(D) The nuclear charge experienced by the electron in this state is less than 2 e , where e is the magnitude of the electronic charge.
4. Answer the following by appropriately matching the lists based on the information given in the paragraph.
Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the $n^{\text {th }}$ orbit of the atom and List-II contains options showing how they depend on $n$.
[JEE(Advanced) 2019]

## List-I

(I) Radius of the $\mathrm{n}^{\text {th }}$ orbit
(II) Angular momentum of the electron in the $\mathrm{n}^{\text {th }}$ orbit
(III) Kinetic energy of the electron in the $\mathrm{n}^{\text {th }}$ orbit
(IV) Potential energy of the electron in the $\mathrm{n}^{\text {th }}$ orbit

## List-II

(P) $\propto \mathrm{n}^{-2}$
(Q) $\propto \mathrm{n}^{-1}$
(R) $\propto n^{0}$
(S) $\propto n^{1}$
(T) $\propto n^{2}$
(U) $\propto n^{1 / 2}$

Which of the following options has the correct combination considering List-I and List-II ?
(A) (II), (R)
(B) (I), (P)
(C) (I), (T)
(D) (II), (Q)
5. Answer the following by appropriately matching the lists based on the information given in the paragraph.
Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the $n^{\text {th }}$ orbit of the atom and List-II contains options showing how they depend on n .
[JEE(Advanced) 2019]

## List-I

(I) Radius of the $\mathrm{n}^{\text {th }}$ orbit
(II) Angular momentum of the electron in the $\mathrm{n}^{\text {th }}$ orbit
(III) Kinetic energy of the electron in the $\mathrm{n}^{\text {th }}$ orbit
(IV) Potential energy of the electron in the $\mathrm{n}^{\text {th }}$ orbit

## List-II

(P) $\propto \mathrm{n}^{-2}$
(Q) $\propto \mathrm{n}^{-1}$
(R) $\propto n^{0}$
(S) $\propto n^{1}$
(T) $\propto n^{2}$
(U) $\propto n^{1 / 2}$

Which of the following options has the correct combination considering List-I and List-II ?
(A) (III), (S)
(B) (IV), (Q)
(C) (IV), (U)
(D) (III), (P)

Answer Q.6, Q. 7 and $\mathbf{Q} .8$ by appropriately matching the information given in the three columns of the following table.
The wave function $\psi_{\mathrm{n}, l \mathrm{~m}_{1}}$ is a mathematical function whose value depends upon spherical polar coordinates ( $\mathrm{r}, \theta, \phi$ ) of the electron and characterized by the quantum numbers $\mathrm{n}, \mathrm{l}$ and $\mathrm{m}_{1}$. Here r is distance from nucleus, $\theta$ is colatitude and $\phi$ is azimuth. In the mathematical functions given in the Table, Z is atomic number $\mathrm{a}_{0}$ is Bohr radius.
[JEE(Advanced) 2017]

| Column-1 | Column-2 | Column-3 |
| :---: | :---: | :---: |
| (I) 1 s orbital | (i) $\psi_{\mathrm{n}, l, \mathrm{~m}_{1}} \propto\left(\frac{\mathrm{Z}}{\mathrm{a}_{0}}\right)^{\frac{3}{2}} \mathrm{e}^{-\left(\frac{\mathrm{Zr}}{\mathrm{a}_{\mathrm{e}}}\right)}$ | (P) |
| (II) 2 s orbital | (ii) One radial node | (Q Probability density at nucleus $\propto \frac{1}{\mathrm{a}_{0}^{3}}$ |
| (III) $2 \mathrm{p}_{\mathrm{z}}$ orbital | (iii) $\left.\psi_{\mathrm{n}, l, \mathrm{~m}_{1}} \propto\left(\frac{\mathrm{Z}}{\mathrm{a}_{0}}\right)^{\frac{5}{2}} \mathrm{re}-\frac{\mathrm{Zr}}{2 \mathrm{a}_{0}}\right) \cos \theta$ | (R) Probability density is maximum at nucleus |
| (IV) $3 \mathrm{~d}_{\mathrm{z}}{ }^{2}$ orbital | (iv) xy - plane is a nodal plane | (S) Energy needed to excite electron from $\mathrm{n}=2$ state to $\mathrm{n}=4$ state is $\frac{27}{32}$ times the energy needed to excite electron from $n=2$ state to $n=6$ state |

## ALLEN ${ }^{\text {® }}$

6. For the given orbital in column 1, the only CORRECT combination for any hydrogen - like species is :
(A) (IV) (iv) (R)
(B) (II) (ii) (P)
(C) (III) (iii) (P)
(D) (I) (ii) (S)
7. For $\mathrm{He}^{+}$ion, the only INCORRECT combination is
(A) (II) (ii) (Q)
(B) (I) (i) (S)
(C) (I) (i) (R)
(D) (I) (iii) (R)
8. For hydrogen atom, the only CORRECT combination is
(A) (I) (iv) (R)
(B) (I) (i) (P)
(C) (II) (i) (Q)
(D) (I) (i) (S)
9. $\quad \mathrm{P}$ is the probability of finding the 1 s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr, at a distance $r$ from the nucleus. The volume of this shell is $4 \pi r^{2} d r$. The qualitative sketch of the dependence of P on r is -
[JEE(Advanced) 2016]
(A)

(B)

(C)

(D)


## SOLUTIONS

1. Ans. (30)

Sol. For single electron system

$$
\mathrm{r}=52.9 \times \frac{\mathrm{n}^{2}}{\mathrm{Z}} \mathrm{pm}
$$

Given $\mathrm{Z}=2$ for $\mathrm{He}^{+}$

$$
\mathrm{r}_{2}=105.8 \mathrm{pm}
$$

So $105.8=52.9 \times \frac{\mathrm{n}_{2}^{2}}{2}$

$$
\mathrm{n}_{2}=2
$$

$$
r_{1}=26.45
$$

So $26.45=52.9 \times \frac{\mathrm{n}_{1}^{2}}{2}$

$$
\mathrm{n}_{1}=1
$$

So transition is from 2 to 1 .
Now $\frac{h c}{\lambda}=R_{H} Z^{2}\left(\frac{1}{n_{1}^{2}}-\frac{1}{n_{2}^{2}}\right)$
So $\lambda=30 \times 10^{-9} \mathrm{~m}=30$ nanometer.
Here ' $\mathrm{R}_{\mathrm{H}}$ ' is given in terms of energy value.
2. Ans. (30)

Sol. $\lambda=\frac{h}{p} \Rightarrow p=\frac{6.6 \times 10^{-34}}{330 \times 10^{-9}}=\frac{4 \times 10^{-3}}{6 \times 10^{23}} \times v(p=m \times v)$
$\mathrm{v}=0.3 \mathrm{~m} / \mathrm{s}=30 \mathrm{~cm} / \mathrm{s}$
3. Ans. (A, C)

Sol. $\#-3.4=\frac{-13.6 \times 4}{n^{2}} \Rightarrow n=4$
\# $\ell=2$
\# m = 0
Angular nodes $=\ell=2$
Radial nodes $=(\mathrm{n}-\ell-1)=1$
$\mathrm{n} \ell=4 \mathrm{~d}$ state
4. Ans. (C)
5. Ans. (D)

Solution for Q. No. 4 and Q. No. 5
$\begin{array}{lll}\text { Sol. } \mathrm{r}=0.529 \times \frac{\mathrm{n}^{2}}{\mathrm{z}} & \Rightarrow \mathrm{r} \propto \mathrm{n}^{2} & \Rightarrow(\mathrm{I})(\mathrm{T}) \\ \mathrm{mvr}=\frac{\mathrm{nh}}{2 \pi} & \Rightarrow(\mathrm{mvr}) \propto \mathrm{n} & \Rightarrow(\mathrm{II})(\mathrm{S}) \\ \mathrm{KE}=+13.6 \times \frac{\mathrm{z}^{2}}{\mathrm{n}^{2}} & \Rightarrow \mathrm{KE} \propto \mathrm{n}^{-2} & \Rightarrow(\mathrm{III})(\mathrm{P}) \\ \mathrm{PE}=-2 \times 13.6 \times \frac{\mathrm{z}^{2}}{\mathrm{n}^{2}} & \Rightarrow \mathrm{PE} \propto \mathrm{n}^{-2} & \Rightarrow(\mathrm{IV})(\mathrm{P})\end{array}$

## 6. Ans. (B)

Sol. (A) (IV) (iv) (R) $\Rightarrow$ incorrect, because, $\mathrm{d}_{\mathrm{Z}^{2}}$ has no nodal plane.
(B) (II) (ii) (P) $\Rightarrow$ correct, because 2 s orbtial has 1 radial node.

(C) (III) (iii) (P) $\Rightarrow$ incorrect, because probability density for 2 p at nucleus is zero.
(D) (I) (ii) (S) $\Rightarrow$ incorrect, because 1s orbital has no radial node.
7. Ans. (D)

Sol. The option (D) is incorrect because in the wave function of 1 s orbital , no angular function should be present.
8. Ans. (D)

Sol. We have to select only correct combination hence, the option (D) is correct.
For 1s orbital : $\Psi_{n, l, m} \alpha\left(\frac{Z}{a_{0}}\right)^{3 / 2} \mathrm{e}^{\frac{-z r}{a_{0}}}$
Energy needed to excite : from $\mathrm{n}=2$ to $\mathrm{n}=4$
$\Delta \mathrm{E}_{2-4}=13.6 \mathrm{Z}^{2} \times \frac{3}{16} \mathrm{eV}$
Energy needed to excite from : $\mathrm{n}=2$ to $\mathrm{n}=6$
$\Delta \mathrm{E}_{2-6}=13.6 \mathrm{Z}^{2} \times \frac{8}{36}$
$\Delta \mathrm{E}_{2-4}=\frac{27}{32} \mathrm{E}_{2-6}$ (hence, true)
9. Ans. (B)

Sol. For 1 s , radial part of wave function is
$\Psi_{(r)}=2\left(\frac{1}{a_{0}}\right)^{\frac{3}{2}} e^{-\frac{r}{a_{0}}}$
probability of finding an $\mathrm{e}^{-}$in a spherical shell of thickness, 'dr' at distance 'r' from nucleus,
$\mathrm{P}=\psi^{2}(\mathrm{r}) \cdot 4 \pi \mathrm{r}^{2} \mathrm{dr}=16 \pi \mathrm{r}^{2}\left(\frac{1}{\mathrm{a}_{0}}\right)^{3} \mathrm{e}^{\frac{-2 \mathrm{r}}{\mathrm{a}_{0}}} d r$
So P is zero at $\mathrm{r}=0$ and $\mathrm{r}=\infty$.

