Name: **Solution**

Roll no.:

Section no.:

Information: $k_B = 1.38 \times 10^{-23}$ J K^{-1}; 1 $amu = 1.67 \times 10^{-27}$ kg; $R_H = 109677$ cm^{-1}; $\hbar = 1.06 \times 10^{-34}$ Js;

1 nm = 10^{-9} m; 1 pm = 10^{-12} m; c = 3×10^8 ms^{-1}; m_e = 9.1×10^{-31} kg; e = 1.6×10^{-19} C.

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RETURN THE QUESTION PAPER WITH YOUR ANSWER SCRIPTS.

(20 marks)

1. (a) Write the expression for the radial distribution function for the 2s and 2p$_z$ states of the H-atom.

Given: 2s state wavefunction of H-atom is given by $\psi_{2s} = constant.\left(2 - \dfrac{r}{a_0}\right)e^{-\left(\frac{r}{2a_0}\right)}$

and: $\psi_{2P_z} = C.r.e^{-r/2a_0}Y_{10}(\cos\theta)$ where C is a constant

In both cases, a_0 is the Bohr radius and is equal to 53 pm.

Solution: 4

Radial distribution function for the 2s state of H-atom is:

$$RDR = P(r) = r^2 R^2(r) = \left(const.\right)^2 r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}}$$

Radial distribution function for the 2p$_z$ state of H-atom is:

$$RDR = P(r) = r^2 R^2(r) = r^2 C^2 r^2 e^{-2r/2a_0} = C^2 r^4 e^{-r/a_0}$$

where C is a constant and a_0 is the Bohr radius = 53 pm = 53×10^{-12} m.

(b) Write the condition for calculating the distance r from the nucleus where the probability of finding the electron is maximum.

Solution: $\boxed{2}$

For calculating the distance r from the nucleus where the probability of finding the electron is maximum, we require to determine the locations (i.e., the values of r) of its maximum.

For the maximum locations: $\frac{dP(r)}{dr} = 0$ & $\frac{d^2P(r)}{dr^2} = -ve$

(c) Calculate the distance where the electron is most likely to be found in both the cases ($2s$ and $2p_z$ states). A final numerical value in pm is required.

Solution: $\boxed{10}$

Let us find $\frac{dP(r)}{dr} = 0$, locations:

For 2s :

$$2r\left(2-\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} + 2r^2\left(2-\frac{r}{a_0}\right)\left(-\frac{1}{a_0}\right)e^{-\frac{r}{a_0}} + r^2\left(2-\frac{r}{a_0}\right)^2\left(-\frac{1}{a_0}\right)e^{-\frac{r}{a_0}} = 0$$

For maxima, we also need: $\frac{d^2P(r)}{dr^2} = -ve$, which means that the maxima are at

$\left(3\pm\sqrt{5}\right)a_0$, i.e., at $0.765a_0 = 40.545\times10^{-12} = 40.545\,\text{pm}$ and $5.235a_0 = 277.455$ pm.

When $r = 40.5$ pm, we have:

$$RDR = P(r) = r^2R^2(r) = (const.)^2\, r^2\left(2-\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} = (const.)^2\,(40)^2\left(2-\frac{40}{53}\right)^2 e^{-\left(\frac{40}{53}\right)} = 1035.(const.)^2$$

And when $r = 277.455$ pm, we have:

$$RDR = P(r) = r^2R^2(r) = (const.)^2\, r^2\left(2-\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} = (const.)^2\,(277)^2\left(2-\frac{277}{53}\right)^2 e^{-\left(\frac{277}{53}\right)} = 4287.(const.)^2$$

So, the final numerical value of the distance where the electron is most likely to be found is 277 pm.

For $2p_z$:

$$\left(4C^2r^3e^{-r/a_0} - C^2\frac{r^4}{a_0}e^{-r/a_0}\right) = 0$$

For maxima, we also need: $\frac{d^2P(r)}{dr^2} = -ve$, which is only true for $r = 4a_0 = 4\times53$ pm = 212 pm

So, the final numerical value of the distance where the electron is most likely to be found is 212 pm.

(d) Are there any location of minima? If so, what do they signify.

Solution: 3

For minima, we have: $\frac{d^2 P(r)}{dr^2} = +ve$, at the locations of $\frac{dP(r)}{dr} = 0$.

For 2s: we find $\left(2 - \frac{r}{a_0} \right) = 0$; *i.e.*, $r = 2a_0 = 2 \times 53 \text{ pm} = 106 \text{ pm}$ as the minima location, which is a node. Thus, 2s wavefunction has one Radial Node.

For 2p$_z$: we find $r = \infty \; and \; r = 0$ as the minima location, which represent the edges of the Radial Distribution Function. As expected there are no Radial Nodes.

(e) Based on the results above, comment on the statement: "with increase in energy, the electron is most likely to be found farther from the nucleus".

Solution: 1

The GS of the H-atom: 1s has the probability maxima of locating the electron at Bohr radius (i.e., at 53 pm). For both 2s and 2p, the probability maxima of locating the electron much farther away from the nucleus (277 pm and 212 pm as per calculations here), which, for the comparison of probability maxima of locating the electron between the 1s and either of the 2s or 2p orbitals, justifies the statement: "with increase in energy, the electron is most likely to be found farther from the nucleus". However, as expected, there is hardly any difference in the probability maxima of locating electrons in 2s & 2p, since 2s & 2p are degenerate for the H-atom.

2. Four, noninteracting, electrons obeying Pauli exclusion principle are confined in a two-dimensional square box of length: L=100 pm.

(20 marks)

(a) Calculate the ground state energy of the system (in *Joules*).

Solution: 4

For particle in square box of side L :

$$E_{n_1 n_2} = \frac{\pi^2 \hbar^2}{2 m_e L^2} \left(n_1^2 + n_2^2 \right); \quad n_1 = 1, 2, ...$$

$$n_2 = 1, 2, ...$$

Ground state: particles 1 & 2 in $n_1 = 1$, $n_2 = 1$.

and particles 3 & 4 in $n_1 = 1, n_2 = 2$ $\quad \left(or, n_1 = 2, n_2 = 1 \right)$

$$\therefore \; E_{total, gs} = \frac{\pi^2 \hbar^2}{2 m_e L^2} \left(2 + 2 + 5 + 5 \right) = \frac{7 \pi^2 \hbar^2}{m_e L^2} = \frac{7}{4} \times \frac{h^2}{m_e L^2} \approx \frac{7 \times 10 \times 10^{-68}}{10^{-30} \times 10^{-20}} \approx 8.5 \times 10^{-17} \, J$$

(b) What is the longest wavelength transition (in *nm*)?

Solution: 4
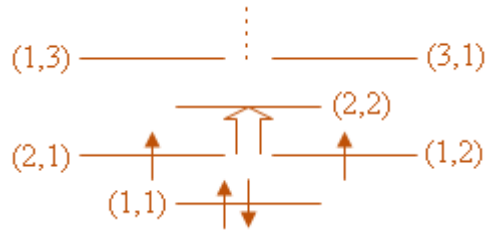
$$\lambda_{long} \Rightarrow (1,2) \rightarrow (2,2)$$

$$\Delta E = E_{22} - E_{21} = E_{22} - E_{12} = \frac{3\pi^2 \hbar^2}{2m_e L^2}$$

$$\approx \frac{3 \times 10 \times 10^{-68}}{2 \times 10^{-30} \times 10^{-20}} = 1.81 \times 10^{-17} J$$

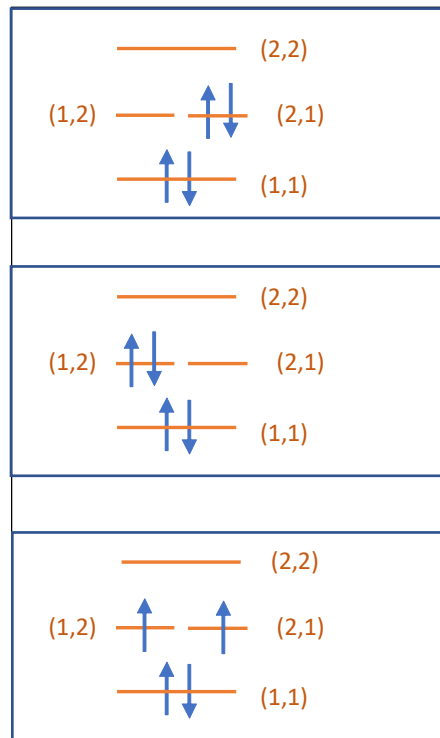$$\lambda_{long} = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{1.81 \times 10^{-17}} = 1.09 \times 10^{-8} m = 10.9 \text{ nm}$$

(c) Find the number of degenerate states in this system.

Solution: 4

Triplet degeneracy: possible configurations are:

(d) If the Pauli exclusion principle is ignored, determine the longest wavelength. Compare this result obtained with the one calculated in (b) part of this problem.

Solution: $\boxed{4}$

If the Pauli exclusion principle is ignored, all 4 electrons in (1,1) state.

Then, $\Delta E = E_{21} - E_{11} = \frac{3\pi^2\hbar^2}{2m_e L^2} = 10.9$ nm
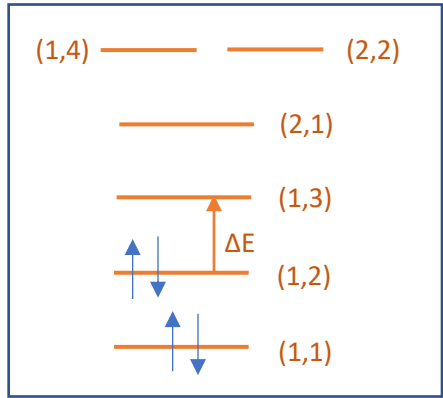
This is the same as seen in part (b) of the problem.

(e) How will the comparison in (d) change if the confinement is in a rectangular box where one side of the box is twice of the other ($L_1 = 100$ pm and $L_2 = 200$ pm)?

Solution: $\boxed{4}$

For particle in a rectangular box of side $L_1 \times L_2$:

$$E_{n_1 n_2} = \frac{\pi^2 \hbar^2 n_1^2}{2 m_e L_1^2} + \frac{\pi^2 \hbar^2 n_2^2}{2 m_e L_2^2}; \quad n_1 = 1, 2, ...; \quad n_2 = 1, 2, ...$$

$$\lambda_{long} = \frac{hc}{\Delta E}$$

$$\Delta E = E_{13} - E_{12} = \left(\frac{1^2 \pi^2 \hbar^2}{2m_e L_1^2} + \frac{3^2 \pi^2 \hbar^2}{2m_e L_2^2} \right) - \left(\frac{1^2 \pi^2 \hbar^2}{2m_e L_1^2} + \frac{2^2 \pi^2 \hbar^2}{2m_e L_2^2} \right) = \left(\frac{\pi^2 \hbar^2}{2m_e L_1^2} + \frac{9\pi^2 \hbar^2}{8m_e L_1^2} \right) - \left(\frac{\pi^2 \hbar^2}{2m_e L_1^2} + \frac{\pi^2 \hbar^2}{2m_e L_1^2} \right)$$

$$= \frac{9\pi^2 \hbar^2}{8m_e L_1^2} - \frac{4\pi^2 \hbar^2}{8m_e L_1^2} = \frac{5}{2} \frac{h^2}{m_e L_1^2} = 1.2 \times 10^{-17} J$$

$$\lambda_{long} = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{1.125 \times 10^{-17}} = 1.8 \times 10^{-8} m = 16 \ nm$$

However, in this case, if the Pauli exclusion principle is ignored, all 4 electrons in (1,1) state. Then,

$$\Delta E = E_{12} - E_{11} = \left(\frac{1^2 \pi^2 \hbar^2}{2m_e L_1^2} + \frac{2^2 \pi^2 \hbar^2}{2m_e L_2^2} \right) - \left(\frac{1^2 \pi^2 \hbar^2}{2m_e L_1^2} + \frac{1^2 \pi^2 \hbar^2}{2m_e L_2^2} \right) = \left(\frac{\pi^2 \hbar^2}{2m_e L_1^2} + \frac{\pi^2 \hbar^2}{2m_e L_2^2} \right) - \left(\frac{\pi^2 \hbar^2}{2m_e L_1^2} + \frac{\pi^2 \hbar^2}{8m_e L_1^2} \right)$$

$$= \frac{\pi^2 \hbar^2}{2m_e L_1^2} - \frac{\pi^2 \hbar^2}{8m_e L_1^2} = \frac{3}{2} \frac{h^2}{m_e L_1^2} = 0.375 \times 10^{-17} J$$

$$\lambda_{long} = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{0.375 \times 10^{-17}} = 5.31 \times 10^{-8} m = 45 \ nm$$

The two results are different by a factor of ~3: ignoring Pauli's principle gives a much less gap!

3. (a) Considering a harmonic oscillator model for $^1H_2$, $^1H^2D$ and $^2D_2$ and assuming the same force constants for all these molecules, show the comparative energy levels of their lowest energy states. (Numerically determine the relative lowest energy states of these molecules.)

(10 marks)

Solution:

For SHO model, we have: $E_v = \left(v + \frac{1}{2}\right)h\nu$

For lowest energy state, $v = 0$ & $E_0 = \frac{1}{2}h\nu \propto \sqrt{\frac{k}{\mu}}$

Since the force constant k is same for all the given cases of $^1H_2$, $^1H^2D$ and $^2D_2$, we can find their lowest energy states by finding the ratio of their respective reduced mass.

$$\mu_{D_2} = \frac{2 \times 2}{2+2} = 1; \; \mu_{HD} = \frac{1 \times 2}{1+2} = \frac{2}{3} = 0.67; \; \mu_{H_2} = \frac{1 \times 1}{1+1} = 0.5$$

i.e., $\mu_{D_2} : \mu_{HD} : \mu_{H_2} :: 1 : \frac{2}{3} : \frac{1}{2}$, and we get correspondingly: $E_{D_2} : E_{HD} : E_{H_2} :: 1 : \sqrt{\frac{3}{2}} : \sqrt{2}$

(b) Consider an excited state of He$^+$ ion having energy of -13.6 eV. If the z-component of orbital angular momentum of its electron in this state is $-\hbar$, logically identify the state.

(10 marks)

Solution

Energy expression for the He$^+$ ion is given as:

$$E_n = -\frac{Z^2}{n^2} 13.6 \text{ eV}$$

Since the given energy is -13.6 eV, we get:

$$-\frac{Z^2}{n^2} 13.6 \text{ eV} = -13.6 \text{ eV}$$

$\Rightarrow n^2 = Z^2 \Rightarrow n = Z = 2.$ Since Z = 2 for He.

The z-component of the angular momentum of electron is given by $L_z = m_l \hbar$

Now, given $L_z = -\hbar$, $\therefore m_l \hbar = -\hbar$, $\Rightarrow m_l = -1$.

Thus, the possible state is: n = 2, l = 1 and m_l = -1, which means it is 2p$_{-1}$ state.

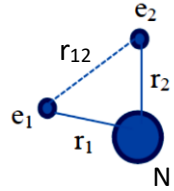4. (a) Write the total Hamiltonian for the He, He$^+$ atoms and H$_2$ molecule (include nuclear parts).
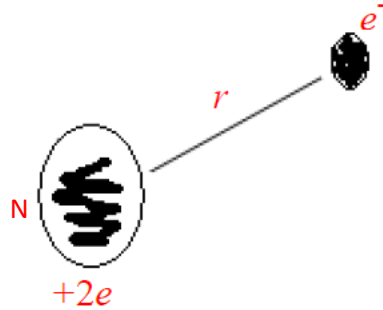
Solution: For He-atom (Z=2):

Total Hamiltonian = (KE)$_{nucleus}$ + (KE)$_{electron1}$ + (KE)$_{electron2}$ + (PE)$_{coulomb\ attraction1}$ + (PE)$_{coulomb\ attraction2}$ + (PE)$_{coulomb\ repulsion}$

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_{e_1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e_2}^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

where the subscript 'N' stands for nuclear, and e$_1$ and e$_2$ stands for the two electrons as seen in the adjacent model.
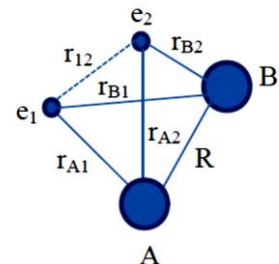
For He$^+$ ion (Z=2)

Total Hamiltonian = (KE)$_{nucleus}$ + (KE)$_{electron}$ + (PE)$_{coulomb\ attraction}$

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{2e^2}{4\pi\varepsilon_0 r}$$

For H$_2$-molecule (Z=1):

$$\hat{H} = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{\hbar^2}{2m_e}\nabla_{e_1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e_2}^2 - \frac{e^2}{4\pi\varepsilon_0 r_{A_1}} - \frac{e^2}{4\pi\varepsilon_0 r_{B_1}} - \frac{e^2}{4\pi\varepsilon_0 r_{A_2}}$$

$$- \frac{e^2}{4\pi\varepsilon_0 r_{B_2}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 R}$$

where the subscript 'A' and 'B' stand for the two nuclei, and '1' and '2' stands for the two electrons as seen in the adjacent model.

(b) How many variables does these wavefunctions depend on?

Solution: $\boxed{3}$

For the He-atom: 9-Dimensional

The Schrödinger wavefunction will depend on (3×3) = 9-variables (3-body problem)

Wavefunction depends on: $\psi\left(r_1, r_2, R \right)$

∴ 9 dimensional.   ⇑   ↑
when we consider both the electrons; Nuclear
all the possibilities   positions

For the He$^+$ ion: 6-Dimensional

Wavefunction depends on $\psi(r_e, R)$ which is 6 dimensional

when we consider both electron & nuclear positions and motions.

For the H$_2$ molecule: 12-Dimensional

The Schrödinger wavefunction will be depend on (4×3) =12-variables (4-body problem).

(c) Specify the approximation under which solution of the electronic wavefunction become possible using Schrodinger equation for the He-atom.

Solution: $\boxed{2}$

Exact solution for the Schrodinger equation is only possible for the He-atom case only under the following cases:
(i) Neglect the nuclear Kinetic Energy &
(ii) Neglect the electron-electron repulsion.

(d) From your knowledge of the H-atom problem: When can the electronic wavefunction solution become possible for He and He$^+$ using Schrodinger equation?

Solution: $\boxed{2}$

For the He-atom: For the electronic Hamiltonian, we consider Born-Oppenheimer Approximation where the motion of nuclei is negligible compared to that of the electrons due to their huge mass difference. Also, except the (PE)$_{\text{coulomb e-e repulsion}}$ term which represents the inter-electronic repulsion, all the other terms in the Hamiltonian is dependent on individual coordinates and so it could be decoupled. So, if the inter-electronic repulsion is neglected the Schrodinger equation would be soluble. ((c) reworded. Certainly, same Answer as (c) also accepted)

For He$^+$-ion: this is a two-body problem which can be reduced to an exactly solvable problem by separation of variables. This can be treated in an identical way to the H-atom problem. It is possible to solve the Schrodinger equation.

(e) Write the Hamiltonian under the Born-Oppenheimer approximation for the H$_2$ molecule.

Solution: 4

In Born-Oppenheimer Approximation, the inter-nuclear separation is kept constant. The H$_2$-molecule Hamiltonian under the Born-Oppenheimer approximation is written as:

$$\hat{H} = \left(-\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2\right) - \frac{\hbar^2}{2m_e}\nabla_{e_1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e_2}^2 - \frac{e^2}{4\pi\varepsilon_0 r_{A_1}} - \frac{e^2}{4\pi\varepsilon_0 r_{B_1}} - \frac{e^2}{4\pi\varepsilon_0 r_{A_2}}$$
$$- \frac{e^2}{4\pi\varepsilon_0 r_{B_2}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \underset{\text{constant}}{\frac{e^2}{4\pi\varepsilon_0 R}}$$

(f) Which spectroscopic technique(s): electronic, rotational and/or vibrational can distinguish between these three systems (He, He$^+$ and H$_2$) and why?

Solution: 4

Both atoms and molecules show 'Electronic Spectroscopy'. Since the energy levels are different for all these three cases (He, He$^+$ and H$_2$), these can be distinguished, in principle, by 'Electronic Spectroscopy'.
Please note, there would be no rotational and vibrational spectroscopy possible for atoms as these occur for molecules. Additionally, for rotational spectroscopy, permanent dipole moment is needed. Similarly, for vibrational spectroscopy, change in dipole moment is required. None of these are possible for homonuclear diatomic molecules, such as, H$_2$, which is our given molecule here.