

Problem 1

Energy levels are $E_n = -\frac{E_0}{n^2}$, $E_0 = 13.6 \text{ eV}$

Transitions from the ground state to n : photon energy is

$$\frac{hc}{\lambda_{1n}} = E_0 \left(1 - \frac{1}{n^2}\right) \Rightarrow \lambda_n = \frac{hc}{E_0 \left(1 - \frac{1}{n^2}\right)}$$

$$\lambda_{1n} = \frac{1240}{13.6 \left(1 - \frac{1}{n^2}\right)} \text{ nm} = \frac{91.176}{\left(1 - \frac{1}{n^2}\right)}$$

$$\Rightarrow \lambda_{12} = 121.57 \text{ nm}, \lambda_{13} = 102.57 \text{ nm}, \lambda_{14} = 97.25 \text{ nm}$$

so incident radiation in range $100 \text{ nm} < \lambda < 200 \text{ nm}$ can excite electrons from ground state to $n=2$ and $n=3$ only.

Subsequent emissions will be:

$$n=2 \text{ to } n=1: \lambda_{12} = 121.57 \text{ nm}$$

$$n=3 \text{ to } n=1: \lambda_{13} = 102.57 \text{ nm}$$

$$n=3 \text{ to } n=2: \lambda_{23} = \frac{91.176}{\frac{1}{4} - \frac{1}{9}} = 656.47 \text{ nm}$$

Problem 2

$$L = m_e v r = n \hbar \quad . \quad \text{We have } r = a_0, \quad L = 3 \hbar \Rightarrow$$

$$m_e v a_0 = 3 \hbar \Rightarrow v = \frac{3 \hbar}{m_e a_0}$$

$$\frac{v}{c} = \frac{3 \hbar c}{m_e c^2 a_0} = \frac{3 \times 197.3 \text{ eV nm}}{511,000 \text{ eV} \times 0.0529 \text{ nm}} = 0.0219$$

$$\boxed{\frac{v}{c} = 0.0219} \quad (a)$$

(b) It's non-relativistic

$$K = \frac{1}{2} m_e v^2 = \frac{1}{2} m_e c^2 \left(\frac{v}{c}\right)^2 = \boxed{122.5 \text{ eV}}$$

(c) The total energy is $E = K + U \Rightarrow U = -K + E$

The state of the electron is $n=3$, since $L = n \hbar$

$$\text{The radius is } r_n = \frac{a_0 n^2}{Z} = a_0 \Rightarrow Z = n^2 = 9$$

$$\text{The energy is } E_n = -E_0 \frac{Z^2}{n^2} = -E_0 \cdot \frac{9^2}{3^2} = -9 E_0 = -122.4 \text{ eV}$$

There is some rounding error, since $E_n = -K_n$ for Bohr atom

$$U = -K + E = -122.5 \text{ eV} - 122.4 \text{ eV} = \boxed{-244.9 \text{ eV} = U}$$

Problem 3

$$L_{op}^2 = -\hbar^2 \left[\frac{\cos\theta}{\sin\theta} \frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]; [L_z]_{op} = \frac{\hbar}{i} \frac{\partial}{\partial\phi}$$

$$\Psi(r, \theta, \phi) = R(r) (3\cos^2\theta - 1) \equiv R(r) Y(\theta, \phi)$$

(a) z-component of angular momentum is

$$L_z = m_e \hbar$$

and $[L_z]_{op} Y = L_z Y = m_e \hbar Y$

with $Y(\theta, \phi) = 3\cos^2\theta - 1$

$$\text{since } \frac{\partial}{\partial\phi} Y = 0 \Rightarrow \boxed{m_e = 0} \Rightarrow \boxed{L_z = 0}$$

(b) $L_{op}^2 Y = \hbar^2 l(l+1) Y$

$$\frac{\partial}{\partial\theta} (3\cos^2\theta - 1) = -6\cos\theta \sin\theta$$

$$\frac{\partial^2}{\partial\theta^2} (3\cos^2\theta - 1) = -\frac{\partial}{\partial\theta} (6\cos\theta \sin\theta) = 6\sin^2\theta - 6\cos^2\theta$$

$$\Rightarrow L_{op}^2 Y = -\hbar^2 \left[\frac{\cos\theta}{\sin\theta} \cdot (-6\cos\theta \sin\theta) + 6\sin^2\theta - 6\cos^2\theta + 0 \right] =$$

$$= -\hbar^2 [-6\cos^2\theta + 6\sin^2\theta - 6\cos^2\theta] = -6\hbar^2 (\sin^2\theta - 2\cos^2\theta) =$$

$$\text{and } L_{op}^2 Y = -6\hbar^2 (1 - \cos^2\theta - 2\cos^2\theta) = 6\hbar^2 (3\cos^2\theta - 1)$$

$$\text{and } \hbar^2 l(l+1) Y = \hbar^2 l(l+1) (3\cos^2\theta - 1)$$

$$\Rightarrow l(l+1) = 6 \Rightarrow \boxed{l=2}$$

(c) Always true that $l \leq n-1 \Rightarrow n \geq l+1 \Rightarrow \boxed{n=3, 4, 5, \dots}$

Problem 4

$$R(r) = C r^3 e^{-r/2a_0}$$

$$P(r) = r^2 R(r)^2 = C^2 r^8 e^{-r/a_0}$$

(a) Most probable radius: r_m

$$P'(r_m) = 0 = 8 r_m^7 - \frac{r_m^8}{a_0} \Rightarrow \boxed{r_m = 8 a_0}$$

(b) $U(r) = -\frac{\hbar^2 z^2}{r}$; $\langle U(r) \rangle = -\hbar^2 z^2 \langle \frac{1}{r} \rangle$

$$\langle \frac{1}{r} \rangle = \frac{\int_0^\infty dr \frac{1}{r} P(r)}{\int_0^\infty dr P(r)} = \frac{\int_0^\infty dr r^7 e^{-r/a_0}}{\int_0^\infty dr r^8 e^{-r/a_0}} ; \text{ use } \int_0^\infty dr r^n e^{-\lambda r} = \frac{n!}{\lambda^{n+1}}$$

$$= \frac{7! (1/a_0)^8}{(1/a_0)^9 \cdot 8!} = \frac{1}{8 a_0}$$

$$\Rightarrow \langle U \rangle = -\frac{\hbar^2 z^2}{8 a_0} = -z \cdot \frac{1.44 \text{ eV nm}}{8 \times 0.0529 \text{ nm}}$$

$$\Rightarrow \boxed{\langle U \rangle = -3.40 z \text{ eV}}$$

(c) Assuming r_m is the Bohr radius for this orbit:

$$r_m = \frac{a_0}{z} n^2 = 8 a_0 \Rightarrow z = n^2 / 8$$

The exponential term in the radial wavefunction is e^{-zr/na_0}

$$\Rightarrow \frac{z}{n} = \frac{1}{2} \Rightarrow z = \frac{n}{2} = \frac{n^2}{8} \Rightarrow n = 4 \Rightarrow \boxed{z = 2}$$

Problem 5

electrons are initially in the $n=1, l=0$ state of hydrogen. $m_l=0$. Their spin quantum number is $m_s = \pm \frac{1}{2}$. In the absence of a magnetic field, they have the same energy, so there is just one energy value for that state, $E_1 = -E_0 = -13.5984 \text{ eV}$. That is the ionization energy.

When a magnetic field B is turned on, the states with $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ have different energy:

$$E_1(m_s) = E_1 - \vec{\mu}_s \cdot \vec{B} = E_1 + \frac{e}{2m_e} g S_z = E_1 + \frac{e\hbar}{2m_e} g \cdot m_s$$

$$\Rightarrow E_1(m_s) = E_1 \pm \frac{e\hbar}{2m_e} B = E_1 \pm \mu_B B, \text{ since } g=2, \mu_B = \frac{e\hbar}{2m_e}$$

The ionization energy is $I(m_s) = -E_1(m_s)$

The difference in ionization energies with and without B is 0.001 eV

$$\Rightarrow \mu_B B = 0.001 \text{ eV} \Rightarrow B = \frac{0.001}{5.79 \times 10^{-5}} \text{ T}$$

$$\Rightarrow \boxed{B = 17.27 \text{ T}}$$

The energy is lower for $m_s = -\frac{1}{2}$, higher for $m_s = +\frac{1}{2}$, with $\vec{B} = B \hat{z}$

~~So~~ The atoms with lower energy have higher ionization energy.

So the ionization energy is 13.5994 eV for the atoms with $m_s = -\frac{1}{2}$, and 13.5974 eV for the atoms with $m_s = +\frac{1}{2}$.

Because at room temperature $k_B T = \frac{300}{11,604} \text{ eV} = 0.026 \text{ eV} \gg 0.001 \text{ eV}$,

there will be about half of the atoms with $m_s = +1/2$, half with $m_s = -1/2$

$$\frac{N(m_s = +1/2)}{N(m_s = -1/2)} = e^{-\Delta E / k_B T} = e^{-0.002 / 0.026} = e^{-0.077} = 0.93$$