SOLUTIONS

PROBLEM SET 6

CHM 3411, Dr. Chatfield

1. $\psi = N(6 - 6\rho + \rho^2)e^{-\rho/2}$

In general, $\psi = N\rho^l L^{2l-1}_{n-l-1}(\rho)e^{-\rho/2} Y_{l,m_l}(\theta,\phi)$

Comparing: $\rho^l = 1$ $\quad L^{2l-1}_{n-l-1} = 6 - 6\rho + \rho^2$ $\quad Y_{l m_l} = \text{const.}$

(a) 2 radial nodes [L^{2l-1}_{n-l-1} is <u>quadratic</u>]

(b) $l = 0$ [$\rho^l = 1$]

(c) 3s [# angular nodes/nodal planes $= l = 0$
Total # nodes $= 2$
" " $= n-1 \Rightarrow n = 3$
$l = 0 \Rightarrow s$]

(d) H atom $\Rightarrow Z = 1$

$$E_n = \frac{-\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2} \cdot \frac{Z^2}{n^2} \approx -\frac{1}{n^2} \cdot hcR_\infty = 2.41 \times 10^{-19}\ \text{J}$$
$$3^2 = 9$$

(e) – next page –

(e) $\int \psi_{1s}^* \psi_{3s}\, d\tau = \int N_{1s} e^{-\rho_{1s}/2} N_{3s}(6-6\rho_{3s}+\rho_{3s}^2) e^{-\rho_{3s}/2}\, d\tau$

$$\rho_{1s} = \frac{2Zr}{na} \approx \frac{2r}{a_0} \qquad \rho_{3s} \approx \frac{2r}{3a_0}$$

Define $\rho = \rho_{3s}$. Then $\rho_{1s} = 3\rho$ $\quad -\frac{\rho}{2} - \frac{3\rho}{2}$

$$\int \psi_{1s}^* \psi_{3s}\, d\tau = N_{1s} N_{3s} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} (6-6\rho+\rho^2) e^{-2\rho} r^2 \sin\theta\, dr\, d\theta\, d\phi$$

$r = \frac{3a_0}{2}\rho \quad dr = \frac{3a_0}{2} d\rho \quad$ Integrals over θ & ϕ give 4π

$$\int \psi_{1s}^* \psi_{3s}\, d\tau = \underbrace{N_{1s} N_{3s} \left(\frac{3a_0}{2}\right)^3 \cdot 4\pi}_{A} \int_0^{\infty} (6-6\rho+\rho^2)\rho^2 e^{-2\rho}\, d\rho$$

$\infty \leftarrow r=\infty \rightarrow \rho=\infty$; $\quad r=0 \Rightarrow \rho=0$

$$= A\left[6\int_0^{\infty} \rho^2 e^{-2\rho} d\rho - 6\int_0^{\infty} \rho^3 e^{-2\rho} d\rho + \int_0^{\infty} \rho^4 e^{-2\rho} d\rho\right]$$

$\left\{ \text{Note: } \int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad \text{Here, } x=\rho \quad a=2 \right\}$

$$= A\Big[\underbrace{6\cdot\frac{2!}{2^3} - 6\cdot\frac{3!}{2^4} + \frac{4!}{2^5}}_{\frac{3}{2} - \frac{9}{4} + \frac{3}{4} = 0}\Big]$$

$\int \psi_{1s}^* \psi_{3s}\, d\tau = 0$ <u>orthogonal</u>

From Table: $\left(\frac{1}{4\pi}\right)^{1/2}$

2. $\psi_{2s} = R_{2,0}(\rho)\, Y_{0,0}(\theta,\phi)$

From Table: $\frac{1}{\sqrt{8}}\left(\frac{3}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$ $\qquad \rho = \frac{2 \cdot \overset{Z}{3} r}{2\underset{a \approx a_0}{a_0}} = \frac{3r}{a_0}$

$$\psi_{2s} = N(2-\rho)e^{-\rho/2} \quad \text{with} \quad N = \frac{1}{\sqrt{32\pi}}\left(\frac{3}{a_0}\right)^{3/2}$$

Ave. potential energy $= \langle V \rangle$

$$\hat{V} = \frac{-\overset{3}{Z}e^2}{4\pi\varepsilon_0 r} = \frac{-3e^2}{4\pi\varepsilon_0 r}$$

$$\langle V \rangle = \int \psi_{2s}^* \hat{V} \psi_{2s}\, d\tau = \frac{-3e^2}{4\pi\varepsilon_0}\int \psi_{2s}^* \frac{1}{r}\psi_{2s}\, \overset{r^2 \sin\theta\, dr\, d\theta\, d\phi}{d\tau}$$

$$= \underbrace{\frac{-3e^2}{4\pi\varepsilon_0}\cdot\frac{1}{32\pi}\cdot\left(\frac{3}{a_0}\right)^3\cdot 4\pi}_{A} \underbrace{\int_0^\infty r(2-\rho)^2 e^{-\rho}\, dr}_{B}$$

Result of integrating over θ & ϕ

Evaluate B: $r\,dr = \left(\frac{a_0}{3}\right)^2 \rho^2\, d\rho$

$$B = \left(\frac{a_0}{3}\right)^2 \int_0^\infty \rho(2-\rho)^2 e^{-\rho}\, d\rho \quad \left\{\begin{array}{l}\text{Note: } r=0 \Rightarrow \rho = 0 \\ \qquad\quad r = \infty \Rightarrow \rho = \infty\end{array}\right\}$$

$$= \left(\frac{a_0}{3}\right)^2\left[4\underbrace{\int_0^\infty \rho e^{-\rho}\, d\rho}_{1!} - 4\underbrace{\int_0^\infty \rho^2 e^{-\rho}\, d\rho}_{2!} + \underbrace{\int_0^\infty \rho^3 e^{-\rho}\, d\rho}_{3!}\right]$$

$$= 2\left(\frac{a_0}{3}\right)^2$$

$$\langle V \rangle = AB = \frac{-9e^2}{16\pi a_0 \varepsilon_0} = -9.81 \times 10^{-18}\,\text{J}$$

$$\text{Total energy} = \underset{2\nearrow}{E_n} \approx \frac{-m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \cdot \frac{\overset{3^2=9}{Z^2}}{\underset{2^2=4}{n^2}} = -hcR_\infty \cdot \frac{9}{4}$$

$$= -4.90 \times 10^{-18}\,\text{J}$$

$$\overset{\text{total}}{E} = \langle V \rangle + \langle E_K \rangle$$

$$\langle E_K \rangle = E - \langle V \rangle = +4.92 \times 10^{-18}\,\text{J}$$

We get $\langle E_K \rangle$ for almost no work!

Note: $|\langle V \rangle| = |\langle E_K \rangle|$ (the difference is probably roundoff error)

3. At classical turning radius, $V = E$

$$V = \frac{-e^2}{4\pi\varepsilon_0 r} \qquad E \simeq \frac{-m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

Solve for r:

$$r = \frac{8\pi\varepsilon_0\hbar^2}{m_e e^2} = 1.06\times10^{-10}\,m \approx 0.106\,nm$$

4. Radial distribution function $= P(r) = r^2 R^2(r)$

From Table, $R_{3,1}(\rho) = N(4-\rho)\rho e^{-\rho/2}$ where $N = \frac{1}{486^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}$

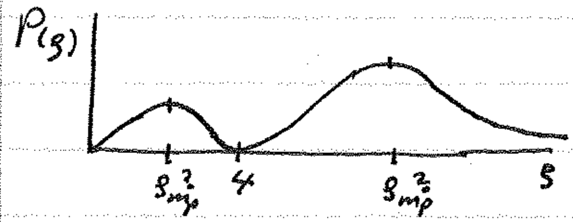
$3p \Rightarrow n=3,\ \ell=1$

$$P(r) = N^2 r^2 (4-\rho)^2 \rho^2 e^{-\rho} \qquad \rho = \frac{2\cdot \overset{Z}{2} r}{\underset{n}{3}\cdot a_0} = \frac{4r}{3a_0}$$

$a = a_0$

Convert everything to ρ for simplicity!

$$P(\rho) = \underbrace{N^2\left(\frac{3a_0}{4}\right)^2}_{A} \rho^4 (4-\rho)^2 e^{-\rho}$$



We do not know in advance which maximum is "higher"

To determine ρ_{mp} (most probable ρ), set $\frac{dP}{d\rho} = 0$

$$\frac{dP}{d\rho} = 0 = A\left[4\rho^3(4-\rho) - 2\rho^4 - \rho^4(4-\rho)\right](4-\rho)e^{-\rho}$$

$$= A\left[4(4-\rho) - 2\rho - \rho(4-\rho)\right]\rho^3(4-\rho)e^{-\rho}$$

$$= A\left[\rho^2 - 10\rho + 16\right]\rho^3(4-\rho)e^{-\rho}$$

$$= A(\rho-2)(\rho-8)(4-\rho)\rho^3 e^{-\rho}$$

$\Rightarrow \quad \rho = 0, 2, 4, 8$

$\rho = 0$ & 4 are minima

Test $\rho = 2$ & 8 to see which give larger $P(\rho)$:

$$P(\rho=2) = A\, 2^4 (4-2)^2 e^{-2} = 64A \cdot e^{-2} = 8.7A$$

$$P(\rho=8) = A\, 8^4 (4-8)^2 e^{-8} = 21.0A$$

$\therefore \rho_{mp} = 8$

$$r_{mp} = \frac{3a_0}{4}\rho_{mp} = 6a_0 = 3.18 \times 10^{-10}\,m = 0.318\,nm$$

5. The point here is that $^4He^+$ and $^3He^+$ have slightly different reduced masses, and consequently different energies, which leads to different spectral frequencies.

$E_n = -\frac{hc Z^2 \tilde{R}_N}{n^2}$ where $\tilde{R}_N$ is the Rydberg constant for the species in question

$$\Delta E(n=3 \to 2) = -hc \underbrace{Z^2}_{Z=2\,(He)} \tilde{R}_N \overbrace{\left(\frac{1}{2^2} - \frac{1}{3^2}\right)}^{5/36}$$

$\Delta E + E_{photon} = 0$ (conservation of energy)

$$h\nu = hc\tilde{\nu} \Rightarrow \tilde{\nu} = 4\tilde{R}_N\left(\frac{5}{36}\right) = \frac{5}{9}\tilde{R}_N$$

$$\Delta E(N=2 \to 1) = -hcZ^2\tilde{R}_N \overbrace{\left(\frac{1}{1^2} - \frac{1}{2^2}\right)}^{3/4} \Rightarrow \tilde{\nu} = 3\tilde{R}_N$$

$$\tilde{R}_N = \frac{\mu_N}{m_e}\tilde{R}_\infty \qquad \tilde{R}_\infty = 1.097373157 \times 10^5\ cm^{-1}$$

$^4He^+$ is composed of 2 protons, 2 neutrons and 1 electron. The binding energy will reduce the mass slightly, but we approximate as the sum of the masses of the individual particles

$$m(^4He^+) = [2(1.672621777) + 2(1.674927351)] \times 10^{-27}\ kg + 9.10938291 \times 10^{-31}\ kg = 6.696009194 \times 10^{-27}\ kg$$

$$m(^3He^+) = 5.021081843 \times 10^{-27}\ kg$$

$$\mu(^4He^+) = \frac{m(^4He^+)\, m_e}{m(^4He^+) + m_e} = 9.108143820 \times 10^{-31}\ kg$$

$$\mu(^3He^+) = \quad \cdots \quad = 9.107730561 \times 10^{-31}\ kg$$

$$\tilde{R}(^4He^+) = \frac{\mu(^4He^+)}{m_e}\tilde{R}_\infty = 1.097223888\times10^5\ \text{cm}^{-1}$$
$$\tilde{R}(^3He^+) = \quad \cdots \quad = 1.097174105\times10^5\ \text{cm}^{-1}$$

For $^4He^+$,
$$\tilde{\nu}(n=3\to2) = 6.095\boxed{6}88269\times10^4\ \text{cm}^{-1}$$
$$\tilde{\nu}(n=2\to1) = 3.291\boxed{6}71665\times10^5\ \text{cm}^{-1}$$

For $^3He^+$,
$$\tilde{\nu}(n=3\to2) = 6.095\boxed{4}11693\times10^4\ \text{cm}^{-1}$$
$$\tilde{\nu}(n=2\to1) = 3.291\boxed{5}22314\times10^5\ \text{cm}^{-1}$$

Notice that the $^4He^+$ and $^3He^+$ frequencies differ in the 5th significant figure. This is well within the accuracy of modern spectrometers.