Chemistry 691 Problem Set #2

1) $\rho = r a_0$ so $\frac{d}{dr} = \frac{d}{d\rho}\frac{d\rho}{dr}$ or $\frac{d}{d\rho} = \frac{d}{dr}\frac{dr}{d\rho} = \frac{1}{a_0}\frac{d}{dr}$

thus $\frac{d^2}{d\rho^2} = \left(\frac{1}{a_0}\right)^2 \frac{d^2}{dr^2}$ or $\frac{\hbar^2}{2m_e}\frac{d^2}{d\rho^2} = \frac{\hbar^2}{2m_e}\left(\frac{1}{a_0}\right)^2\frac{d^2}{dr^2}$

but $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ so $\frac{\hbar^2}{2m_e}\left(\frac{1}{a_0^2}\right) = \frac{\hbar^2}{2m_e}\frac{m_e^2 e^4}{(4\pi)^2\varepsilon_0^2\hbar^4}$

$= \frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2} = \frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2}$

2) $R(r) = G(r)/r$

$\frac{d}{dr}R(r) = \frac{dG/dr}{r} - \frac{1}{r^2}G(r)$ so that $r^2\frac{d}{dr}R(r) = r\frac{dG}{dr} - G(r)$

so $\frac{d}{dr}\left(r^2\frac{d}{dr}R(r)\right) = \cancel{\frac{dG}{dr}} + r\frac{d^2G}{dr^2} - \cancel{\frac{dG}{dr}}$ so $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{1}{r}\frac{d^2G}{dr^2}$

3 $1s = Ne^{-Zr}$ $\int_0^\infty 1s^2 r^2\,dr = 1$ so $N^2\int e^{-2Zr}r^2\,dr = 1$

now $\int e^{-\alpha r}r^n\,dr = n!/\alpha^{n+1}$ so $\int e^{-2rZ}r^2\,dr = \frac{2!}{(2Z)^3} = \frac{1}{4Z^3}$

thus $N_{1s} = \sqrt{4Z^3}$

for $2p$ $N^2\int e^{-Zr}r^4\,dr = 1$ or $N^2\frac{4!}{Z^5} = \frac{24}{Z^5}N^2$

or $N_{2p} = \sqrt{\frac{Z^5}{24}}$

now, $2s$ $R = N(1+Br)e^{-rZ/2}$

B is determined so that $\int 1s\,2s\,r^2\,dr = 0$ $\int N_{1s}N_{2s}(1+Br)e^{-3/2(rZ)}r^2$

or $N_{1s}N_{2p}\left[\int e^{-3/2\,rZ}r^2\,dr + B\int e^{-3/2\,rZ}r^3\,dr\right]$

$= N_{1s}N_{2s}\left[\frac{2!}{(3/2\,Z)^3} + B\frac{3!}{(3/2\,Z)^4}\right] = N_{1s}N_{2s}\left[1 + \frac{2B}{Z}\right]\frac{16}{27Z^3}$

so $[1 + 2B/Z] = 0$ or $B = -\frac{Z}{2}$ so $2s = N_{2s}\left(1 - \frac{Zr}{2}\right)e^{-Zr/2}$

then we need $\int R_{2s}^2 r^2\,dr = 1$

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or $N_{2s}^2 \int (1-\frac{Z}{2}r)^2 e^{-Zr} r^2 dr = N^2 \int (1-Zr+\frac{1}{4}Z^2r^2)e^{-rZ} r^2 dr$

$= N^2 \left[2! Z^{-3} - 3! Z^{-3} + 4! \frac{1}{4} Z^{-3}\right] = N^2 \left[2Z^{-3} - 6Z^{-3} + 6Z^{-3}\right] = N^2 2Z^{-3}$

so $N = \sqrt{\frac{Z^3}{2}}$

the node in the 2s wavefunction occurs when $1+Br=0$ or $\boxed{r=\frac{-1}{B}=2Z}$

finally

$\langle \frac{1}{r} \rangle = \int R(r) \frac{1}{r} R(r) r^2 dr = \int R^2(r) r\, dr$

$\langle r \rangle = \int R^2(r) r^3 dr$

so function $\langle 1/r \rangle$ $\langle r \rangle$

1s $N_{1s}^2 \int e^{-2Zr} r\, dr \; 4Z^3 \frac{1!}{(2Z)^2} = Z$ $\quad N_{1s}^2 \int e^{-2rZ} r^3 dr = \frac{Z^3}{4} \frac{3!}{(2Z)^4} = \frac{3}{2Z}$

2p $N_{2p}^2 \int e^{-rZ} r^3 dr = \frac{Z}{4}$ $\quad N_{2p}^2 \int e^{-rZ} r^5 dr = 5/Z$

2s $N_{2s}^2 \int e^{-rZ} \left[\frac{rZ}{2}-1\right]^2 r\, dr = \frac{Z}{4}$ $\quad N_{2s}^2 \int e^{-rZ} \left[\frac{rZ}{2}-1\right]^2 r^3 dr$

$\frac{1}{2Z^3} 12Z^4 = 6/Z$

Negative muon $= 1.884 \cdot 10^{-28}$ kg $= 0.1135$ amu

reduced mass $= \frac{0.1135 \times 1}{1.1135} = 0.1019$ amu $=$

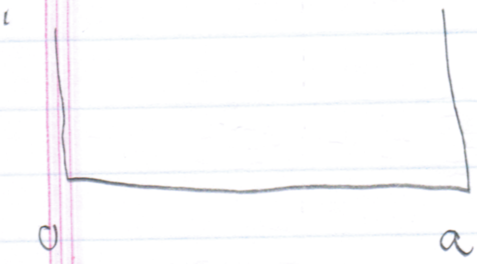
mass electron $= 5.49 \cdot 10^{-4}$ amu

so $\mu(\mu\text{-proton}) / \mu(e\text{-proton}) \simeq 187$

now, problem #1 $a_0 \sim \frac{1}{M_e}$

so for μ-proton $a_0 \sim \frac{a_0(\text{electron-proton})}{187}$

$$\boxed{\langle r \rangle = \frac{1}{187} a_0}$$



$$\left[-\frac{1}{2\mu}\frac{d^2}{dr^2}+\frac{J(J+1)}{2\mu r^2}\right]G(r)=\varepsilon G(r)$$

let $x=(2\mu\varepsilon)^{1/2}r$ $\quad r=x/\sqrt{2\mu\varepsilon}$

$$\frac{d}{dr}=\frac{d}{dx}\frac{dx}{dr}=\sqrt{2\mu\varepsilon}\frac{d}{dx}$$

so, SE in terms of x is

$$\frac{d^2}{dr^2}=2\mu\varepsilon\frac{d^2}{dx^2}$$

$$\left[-\frac{1}{2\mu}2\mu\varepsilon\frac{d^2}{dx^2}+\frac{J(J+1)2\mu\varepsilon}{2\mu x^2}\right]G(x)=\varepsilon G(x)$$

or $\left[-\frac{d^2}{dx^2}+\frac{J(J+1)}{x^2}-1\right]G(x)=0$ or $\left[\frac{d^2}{dx^2}-\frac{J(J+1)}{x^2}+1\right]G(x)=0$

or $\left[x^2\frac{d}{dx^2}-J(J+1)+x^2\right]G(x)=0$

solutions are

$w_0(x)=\sin x$ $\quad w_1(x)=\frac{1}{x}\sin x-\cos x$ $\quad w_2(x)=\left(\frac{3}{x^2}-1\right)\sin x-\frac{3\cos x}{x}$

solutions must vanish at $r=0$ or $x=\sqrt{2\mu\varepsilon}\,a$

now

$\sin(x)$ vanishes at $x=\pi, 2\pi$ when $x=n\pi$ $\quad\sqrt{2\mu\varepsilon}\,a=n\pi$

or $\varepsilon=\frac{n^2\pi^2}{2\mu a^2}$ [exactly like particle in a box! We expect this, since for $J=0$ the potential is like a particle-in-a-box

$\varepsilon=\frac{9.870}{2\mu a^2}\quad\frac{39.478}{2\mu a^2}$

now for $J=1$ look at vanishing of $w_1(x)$ $\quad x=4.484, 7.717$

or $\varepsilon=\frac{4.484^2}{2\mu a^2},\frac{7.717^2}{2\mu a^2}=\frac{20.114}{2\mu a^2},\frac{59.558}{2\mu a^2}$

$J=2$ look at vanishing of $w_2(x)$ $\quad x=5.7609$

$$\varepsilon=\frac{5.7609^2}{2\mu a^2}=\frac{33.188}{2\mu a^2}$$

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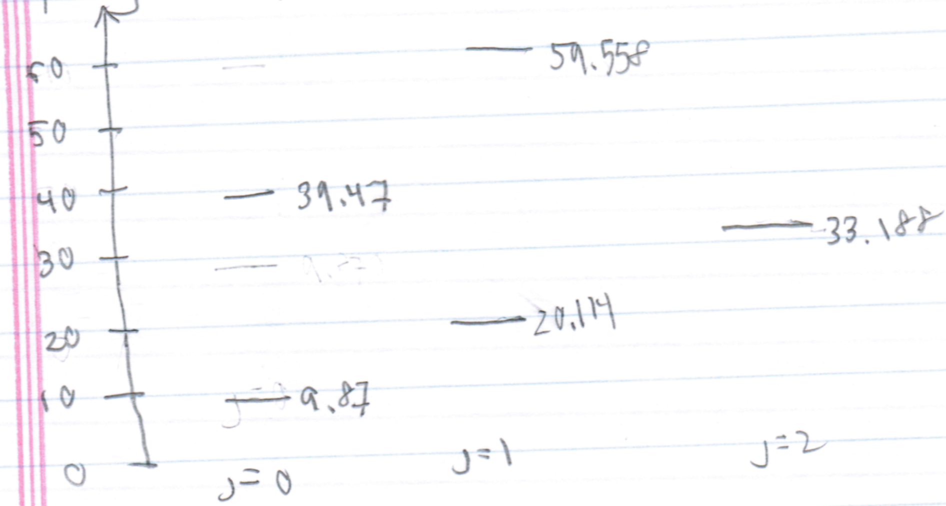
so, energies are (in units of $1/2\mu a^2$)

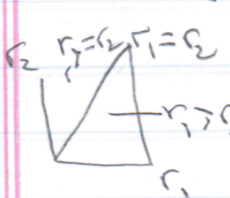


the $1s \rightarrow 2p$ transition $\quad 9.87 \rightarrow 20.114 = 10.244$

$\mu = 1$ (for electron) so $\Delta E = \dfrac{10.244}{2a^2} = -\dfrac{1}{2} \rightarrow -\dfrac{1}{8} = \dfrac{3}{8}$

so $\quad 2a^2\left(\frac{3}{8}\right) = 10.244 \quad a^2 = 13.659 \quad \boxed{a = 3.695\, a_0}$

c) $1s = \sqrt{4Z^3}\, e^{-Zr} \dfrac{1}{\sqrt{4\pi}} \qquad \dfrac{1}{r_{12}} = \dfrac{1}{r_>}$ this cancels when we integrate over angles θ and ϕ



$r_1 > r_2$ so $\dfrac{1}{r_>} = \dfrac{1}{r_1}$

$$\int_0^\infty 1s^2(2)\frac{1}{r_{12}} r_2^2\, dr_2 = \frac{1}{r_1}\int_0^{r_1} 4Z^3 e^{-2Zr_2} r_2^2\, dr_2 + \int_{r_1}^\infty 4Z^3 e^{-2Zr_2} r_2\, dr_2$$

$$= \frac{1}{r_1}\left[1 - 2Z^2 r_1^2 e^{-2Zr_1} - 2Zr_1 e^{-2Zr_1} - e^{-2Zr_1}\right] + Ze^{-2Zr_1}(2Zr_1 + 1)$$

$$= \frac{1}{r_1}\left[1 - e^{-2Zr_1}(1 + Zr_1)\right]$$

now $\int_0^\infty 1s^2(1) \int_0^\infty 1s^2(2) \frac{1}{r_{12}} dV_1 dV_2 = \int_0^\infty 4Z^3 e^{-2Zr_1} \left[1 - e^{-2Zr_1}(1+Zr_1)\right] \frac{r_1^2}{r_1} dr$

$= \frac{5Z}{8}$

7 $\langle 1s|h|1s\rangle = \overbrace{\int 1s \, -\frac{1}{2r^2} \frac{d}{dr} r^2 \frac{d}{dr} 1s}^{KE} \; \overbrace{- Z\int 1s \frac{1}{r} 1s}^{PE}$

again because of normalization, integral over angle cancels out

$1s = \sqrt{4Z^3}\, e^{-Zr}$ or $1s(\xi) = \sqrt{4\xi^3}\, e^{-\xi r}$

$\frac{d}{dr} 1s(\xi) = -\sqrt{4\xi^3}\, \xi e^{-\xi r}$

$r^2 \frac{d}{dr} 1s(\xi) = -\sqrt{4\xi^3}\, \xi r^2 e^{-\xi r}$

$\frac{d}{dr}\left(r^2 \frac{d}{dr} 1s(\xi)\right) = \sqrt{4\xi^3}\,(\xi^2 r^2 - 2\xi r) e^{-\xi r}$

$\frac{1}{r^2}\left(r^2 \frac{d}{dr} 1s(\xi)\right) = \sqrt{4\xi^3}\,\left(\xi^2 - \frac{2\xi}{r}\right) e^{-\xi r}$

so $KE = \frac{-1}{2} 4\xi^3 \int e^{-2\xi r}\left(-\frac{2\xi}{r} + \xi^2\right) r^2 dr = \frac{\xi^2}{2}$

potential energy is easier $-\int 1s(\xi) \frac{Z}{r} 1s(\xi) = -Z\, 4\xi^3 \int_0^\infty e^{-2\xi r} r\, dr = -Z\xi$

so the one-electron energy is $-Z\xi + \frac{\xi^2}{2}$, or, for 2 electrons $(-2Z\xi + \xi^2)$

8 Total energy is

$-2Z\xi + \xi^2 + \frac{5}{8}\xi = E \qquad \frac{\partial E}{\partial \xi} = -2Z + 2\xi + \frac{5}{8}$

for He, $Z=2$ $\quad \frac{\partial E}{\partial \xi} = -4 + 2\xi + \frac{5}{8}$ $\quad$ so, when $\frac{\partial E}{\partial \xi} = 0 \quad \xi = \; = 1.6875$

$E_{best} = -4\xi + \xi^2 + \frac{5}{8}\xi = (\xi = 1.6875) = -2.84765$