PHYS 598 AQG HW1

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1. **Q1 Foot 2.4** *[1 pts]*

   Using the electronic wavefunction:

$$\psi(r) = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0} \tag{1}$$

   we calculate the probability of finding electron "inside" of a proton:

$$P_b = \int d^3r \, |\psi(r)|^2 = 4\pi \int_0^{r_b} dr \, \frac{r^2}{\pi a_0^3} e^{-2r/a_0} \simeq \frac{4}{a_0^3} \int_0^{r_b} dr \, r^2 (1 - \frac{2r}{a_0}) \tag{2}$$

$$P_b = \frac{4r_b^3}{3a_0^3} - \frac{2r_b^4}{a_0^4} + \mathcal{O}\Big[(\frac{r_b}{a_0})^5\Big] \tag{3}$$

   Using this probability and assuming it is uniformly distributed (to a good approximation it is), we calculate electronic charge density in a "proton region":

$$\rho_e = -\frac{eP}{V} = -\frac{e}{\pi a_0^3}(1 - \frac{2r_b}{a_0} + \mathcal{O}\Big[(\frac{r_b}{a_0})^2\Big]) \tag{4}$$

2. **Q2** *[3.5 pts]*

   (a) *[0.75 pts]*
   Naturally we choose $V(r \to \infty) = 0$. Then from Gauss' law:

$$E_r(r > r_p) = \frac{e}{4\pi\epsilon_0 r^2} = \frac{\rho_p r_p^3}{3\epsilon_0 r^2} \tag{5}$$

$$E_r(r < r_p) = \frac{e}{4\pi\epsilon_0 r} = \frac{\rho_p r}{3\epsilon_0} \tag{6}$$

   Thus the electrostatic potential $V(r) = -\int_\infty^{\vec{r}} \vec{E} \cdot d\vec{r} = -\int_\infty^r E_r dr$ is equal to:

$$V(r > r_p) = \frac{e}{4\pi\epsilon_0 r} = \frac{\rho_p r_p^3}{3\epsilon_0 r} \tag{7}$$

$$V(r < r_p) = V(r_p) - \int_{r_p}^r E_r dr = \frac{e}{8\pi\epsilon_0 r_p}\Big(3 - \frac{r^2}{r_p^2}\Big) = \frac{\rho_p r_p^2}{2\epsilon_0}\Big(1 - \frac{r^2}{3r_p^2}\Big) \tag{8}$$

(b) *[1.75 pts]*

$$H = H^0 + H' \tag{9}$$

where H^0 is the Hamiltonian for a point-like proton and H'-perturbation due to a finite size of the proton:

$$H'(r > r_p) = 0 \tag{10}$$

$$H'(r < r_p) = \frac{e\rho_p r_p^2}{2\epsilon_0}\Big(1 - \frac{r^2}{3r_p^2} - \frac{2r_p}{3r}\Big) \tag{11}$$

Using the first order perturbation theory we estimate the shift of the ground state to be:

$$\begin{aligned}\langle 1\mathrm{s}|H'|1\mathrm{s}\rangle = 4\pi\int_0^{r_p} dr\ r^2|\psi(r)|^2 H'(r) = \frac{2e\rho_p r_p^2}{a_0^3\epsilon_0}\int_0^{r_p} dr\ r^2 e^{-2r/a_0}\Big(1 - \frac{r^2}{3r_p^2} - \frac{2r_p}{3r}\Big) \simeq \\ \simeq \frac{2e\rho_p r_p^2}{a_0^3\epsilon_0}\int_0^{r_p} dr\ r^2\Big(1 - \frac{r^2}{3r_p^2} - \frac{2r_p}{3r}\Big)\end{aligned} \tag{12}$$

$$\langle 1s|H'|1s\rangle = \frac{2e\rho_p r_p^5}{15a_0^3\epsilon_0} = \frac{4r_p^2}{5a_0^2}hcR_\infty = 3.87\cdot 10^{-9}\mathrm{eV} \tag{13}$$

(c) *[1 pts]*

$$\begin{aligned}\langle 2\mathrm{s}|H'|2\mathrm{s}\rangle = \frac{e\rho_p r_p^2}{4a_0^3\epsilon_0}\int_0^{r_p} dr\ r^2 e^{-2r/a_0}\Big(1 - \frac{r}{a_0}\Big)^2\Big(1 - \frac{r^2}{3r_p^2} - \frac{2r_p}{3r}\Big) \simeq \\ \simeq \frac{e\rho_p r_p^2}{4a_0^3\epsilon_0}\int_0^{r_p} dr\ r^2\Big(1 - \frac{r}{a_0}\Big)^2\Big(1 - \frac{r^2}{3r_p^2} - \frac{2r_p}{3r}\Big)\end{aligned} \tag{14}$$

$$\langle 2\mathrm{s}|H'|2\mathrm{s}\rangle = \frac{r_p^2}{a_0^2}\Big(\frac{1}{10} - \frac{r_p}{12a_0} + \frac{3r_p^2}{140a_0^2}\Big)\mathrm{Ry} = 4.84\cdot 10^{-10}\mathrm{eV} \tag{15}$$

We note that both $\langle 1\mathrm{s}|H'|1\mathrm{s}\rangle$ and $\langle 2\mathrm{s}|H'|2\mathrm{s}\rangle$ scale with r_p quadratically (at least the dominant term does). Thus to detect the 1% change in proton radious in 2s→1s transition in H we would require a fractional accuracy of:

$$\begin{aligned}\frac{\Big(\langle 2\mathrm{s}|H'_{1.01\mathrm{F}}|2\mathrm{s}\rangle - \langle 1\mathrm{s}|H'_{1.01\mathrm{F}}|1\mathrm{s}\rangle\Big) - \Big(\langle 2\mathrm{s}|H'_{1.00\mathrm{F}}|2\mathrm{s}\rangle - \langle 1\mathrm{s}|H'_{1.00\mathrm{F}}|1\mathrm{s}\rangle\Big)}{E_{2\mathrm{s}\to 1\mathrm{s}}} = \\ = \frac{\big(1.01^2 - 1\big)\big(38.7 - 4.8\big)\cdot 10^{-10}\mathrm{eV}}{\frac{3}{4}\cdot 13.6\mathrm{eV}} = 6.68\cdot 10^{-12}\end{aligned} \tag{16}$$

which corresponds to the absolute shift of $6.814\cdot 10^{-11}$ eV or 16.48 kHz.

3. **Q3 Foot 3.5a** *[2.5 pts]*

   (a) *[1 pt]*

$$J_{1s^2} = 2 \cdot \frac{e^2}{4\pi\epsilon_0 a_0^6} \int_0^\infty \Big[\int_0^{r_2} 4Z^3 e^{-2Zr_1/a_0} r_1^2 dr_1 \Big] 4Z^3 e^{-2Zr_2/a_0} r_2 dr_2 \tag{17}$$

$$\alpha = \frac{2Z}{a_0} \tag{18}$$

$$\int_0^{r_2} r_1^2 e^{\alpha r_1} dr_1 = \frac{1}{\alpha^3}\Big(2 - e^{-\alpha r_2} - 2\alpha r_2 e^{-\alpha r_2} - \alpha^2 r_2^2 e^{-\alpha r_2}\Big) \tag{19}$$

$$\int_0^\infty r_2 \Big(2 - e^{-\alpha r_2} - 2\alpha r_2 e^{-\alpha r_2} - \alpha^2 r_2^2 e^{-\alpha r_2}\Big) dr_2 = \frac{5}{8\alpha^2} \tag{20}$$

$$J_{1s^2} = \frac{5Ze^2}{32\pi\epsilon_0 a_0} = \frac{5Z}{4}\text{Ry} = 34\text{eV} \tag{21}$$

   (b) *[1.5 pt]*
   Trial function: $\psi(r, Z) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}$. Evaluating the ground state energy as a function of Z without the el-el interaction:

$$\langle\psi(Z)|H_0|\psi(Z)\rangle = \frac{Z^3}{\pi a_0^3} \cdot 4\pi \int_0^\infty e^{-Zr/a_0}\Big(-\frac{\hbar^2 d^2}{2mdr^2} - \frac{e^2 Z}{4\pi\epsilon_0 r}\Big) e^{-Zr/a_0}\ dr = (Z^2 - 4Z)\ \text{Ry} \tag{22}$$

   Now taking into account the el-el interaction:

$$E_G(Z) = 2 \cdot \langle\psi(Z)|H_0|\psi(Z)\rangle + V_{el-el} = (2Z^2 - 8Z + \frac{5}{4}Z)\ \text{Ry} = (2Z^2 - \frac{27}{4}Z)\ \text{Ry} \tag{23}$$

   Minimizing $E_G(Z)$ with respect to Z, we obtain $E_{min} = -77.46$ eV with $Z_{min} = 1.688$.

4. **Q4 Foot 4.3** [1 pts]

$$E = \frac{\text{Ry}}{(n - \delta_l)^2} \tag{24}$$

Orbital	E (eV)	n^*	δ_l
3s	5.14	1.63	1.37
4s	1.92	2.66	1.34
5s	1.01	3.67	1.33
6s	0.63	4.64	1.36

   δ_l varies within 3%.

   The binding energy of the 8s orbital for Na:

$$E = \frac{13.6}{(8 - 1.35)^2} = 0.31\text{eV} \tag{25}$$

   while for H:

$$E = \frac{13.6}{8^2} = 0.21\text{eV} \tag{26}$$

5. **Q5 Foot 4.4** [1 pts]

Rb $\rightarrow$ [Kr]5s^1

$$E^{5\mathrm{s}} = \frac{13.6}{(5-\delta_l)^2} = 4.17(\mathrm{eV}) \tag{27}$$

$$\delta_l = 3.19 \tag{28}$$

$$E^{7\mathrm{s}} = \frac{13.6}{(7-3.19)^2} = 0.94(\mathrm{eV}) \tag{29}$$

$$\Delta E = 4.17 - 0.94(\mathrm{eV}) = 3.23(\mathrm{eV}) = 2h\nu = \frac{2hc}{\lambda} = 2 \cdot \frac{1240\mathrm{eV}\cdot\mathrm{nm}}{\lambda} \tag{30}$$

$$\lambda = 768\mathrm{nm} \tag{31}$$

6. **Q6 Foot 4.7** [1 pts]

$$\Delta E_{FS} = \frac{Z_i^2 Z_0^2}{(n^*)^3 l(l+1)}\ \alpha^2\ \mathrm{Ry} \tag{32}$$

For 3p configuration of Na^{10+}: $Z_i = Z_0 = 11$, $n^* = 3$, $\Delta E_{FS} = 0.2$ eV. This fine structure splitting is much larger than the fine structure splitting for the same orbital of a neutral Sodium and Hydrogen bc/ of the Z^4 scaling (to be compared with $(Z=11)^2$ scaling in Na or $(Z=1)^4$ in H).