## UNIVERSITY OF ALABAMA Department of Physics and Astronomy

PH 253 / LeClair

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## Problem Set 6 & 7, Question 1

The energies of the stationary states of hydrogen slightly depend on the orbital angular momentum quantum number l. An improved formula for the energy of the state of quantum numbers n and l for nonzero l is

$$\mathsf{E}_{n,l} = \frac{-\mathfrak{m}_{e}e^{4}}{2\left(4\pi\epsilon_{o}\right)^{2}\hbar^{2}n^{2}} \left[1 + \frac{e^{4}}{\left(4\pi\epsilon_{o}\right)^{2}\hbar^{2}c^{2}n}\left(\frac{1}{1+l+\frac{1}{2}\pm\frac{1}{2}} - \frac{3}{4n}\right)\right] \tag{1}$$

where the term  $\pm \frac{1}{2}$  corresponds to the spin parallel and antiparallel, respectively, to the orbital angular momentum.

(a) For the case of the first excited state, n = 2, l = 1 (2p), and the spin antiparallel to the orbital angular momentum, find the effective difference *in electron volts* between the energy calculated according to Bohr theory and the energy calculated according to the improved formula above.

Recall the energy for a level n according to the Bohr model:

$$\mathsf{E}_{\mathsf{n},\mathrm{Bohr}} = \frac{-\mathfrak{m}_{e}e^{4}}{2\left(4\pi\epsilon_{o}\right)^{2}\hbar^{2}\mathfrak{n}^{2}} = \frac{-13.6\,\mathrm{eV}}{\mathfrak{n}^{2}} = \frac{\mathsf{E}_{0,\mathrm{Bohr}}}{\mathfrak{n}^{2}} \tag{2}$$

With this, we can simplify our expression for  $E_{n,l}$  above:

$$\mathsf{E}_{n,l} = \frac{\mathsf{E}_{0,\text{Bohr}}}{n^2} \left[ 1 + \frac{e^4}{(4\pi\epsilon_0)^2 \hbar^2 c^2 n} \left( \frac{1}{1 + l + \frac{1}{2} \pm \frac{1}{2}} - \frac{3}{4n} \right) \right]$$
(3)

Next, we can factor out the Bohr energy out of the interior factor:

$$\frac{e^4}{(4\pi\epsilon_o)^2\hbar^2c^2n} = \frac{me^4}{2(4\pi\epsilon_o)^2\hbar^2}\frac{2}{nc^2}\frac{1}{n} = \frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|}{mc^2}\frac{1}{n} \approx \frac{2(13.6\,\mathrm{eV})}{511\,\mathrm{keV}}\frac{1}{n} \approx \frac{5.3\times10^{-5}}{n} \tag{4}$$

Thus, the overall energy for states of quantum number n and l can be written as a correction to the Bohr model, whose size depends on the ground state energy in the Bohr model ( $E_{0,Bohr}$ ) relative

to the electron's rest energy ( $mc^2 = 511 \text{ keV}$ ). The size of the correction is  $2E_{0,Bohr}/mc^2 \approx 10^{-5}$ , about 50 parts per million.

$$\mathsf{E}_{n,l} = \frac{\mathsf{E}_{0,\text{Bohr}}}{n^2} \left[ 1 + \frac{2|\mathsf{E}_{0,\text{Bohr}}|}{\mathsf{mc}^2} \frac{1}{\mathsf{n}} \left( \frac{1}{1+\mathsf{l}+\frac{1}{2}\pm\frac{1}{2}} - \frac{3}{4\mathsf{n}} \right) \right]$$
(5)

The difference between  $E_{n,l}$  and  $E_{n,Bohr}$  is now readily found:

$$|\mathsf{E}_{n,l} - \mathsf{E}_{n,\mathrm{Bohr}}| = \frac{\mathsf{E}_{0,\mathrm{Bohr}}}{n^2} \left[ 1 + \frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|}{\mathsf{mc}^2} \frac{1}{\mathsf{n}} \left( \frac{1}{1+\mathsf{l}+\frac{1}{2}\pm\frac{1}{2}} - \frac{3}{4\mathsf{n}} \right) \right] - \frac{\mathsf{E}_{0,\mathrm{Bohr}}}{\mathsf{n}^2} \tag{6}$$

$$=\frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|^2}{\mathsf{mc}^2}\frac{1}{\mathsf{n}^3}\left(\frac{1}{1+\mathsf{l}+\frac{1}{2}\pm\frac{1}{2}}-\frac{3}{4\mathsf{n}}\right) \tag{7}$$

The fractional difference depends only on the ratio of the ground-state Bohr energy to the electron rest mass and the quantum numbers n and l:

$$\frac{\mathsf{E}_{n,l} - \mathsf{E}_{n,\text{Bohr}}}{\mathsf{E}_{n,\text{Bohr}}} = \frac{2\mathsf{E}_{0,\text{Bohr}}}{\mathfrak{m}c^2} \frac{1}{\mathfrak{n}^3} \left( \frac{1}{1 + \mathfrak{l} + \frac{1}{2} \pm \frac{1}{2}} - \frac{3}{4\mathfrak{n}} \right)$$
(8)

For the particular case n=2, l=1, and antiparallel spin (thus taking the  $-\frac{1}{2}$  choice from  $\pm\frac{1}{2}$ ), we have

$$\mathsf{E}_{n,l} - \mathsf{E}_{n,\mathrm{Bohr}} = \frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|^2}{\mathsf{mc}^2} \frac{1}{2^3} \left( \frac{1}{1+1} - \frac{3}{4\cdot 2} \right) = \frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|^2}{\mathsf{mc}^2} \left( \frac{1}{64} \right) \tag{9}$$

(b) For n=2, l=1, find the difference in electron volts between the energies of spin parallel and antiparallel to the angular momentum calculated according to the improved formula above. Which of these states has the lowest energy?

First, we can write down the energies for the parallel and antiparallel states. Parallel corresponds taking the  $\frac{1}{2}$  choice from  $\pm \frac{1}{2}$ , and antiparallel means taking the  $-\frac{1}{2}$  choice. Thus,

$$\begin{split} \mathsf{E}_{\mathsf{n},\mathsf{l},\uparrow\uparrow} &= \frac{\mathsf{E}_{0,\mathrm{Bohr}}}{n^2} \left[ 1 + \frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|}{\mathsf{m}\mathsf{c}^2} \frac{1}{\mathsf{n}} \left( \frac{1}{2+\mathsf{l}} - \frac{3}{4\mathsf{n}} \right) \right] \\ \mathsf{E}_{\mathsf{n},\mathsf{l},\uparrow\downarrow} &= \frac{\mathsf{E}_{0,\mathrm{Bohr}}}{n^2} \left[ 1 + \frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|}{\mathsf{m}\mathsf{c}^2} \frac{1}{\mathsf{n}} \left( \frac{1}{1+\mathsf{l}} - \frac{3}{4\mathsf{n}} \right) \right] \end{split}$$
(10)

Their difference is also easily calculated:

$$\mathsf{E}_{n,l,\uparrow\uparrow} - \mathsf{E}_{n,l,\uparrow\downarrow} = \frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|^2}{\mathsf{mc}^2 \mathsf{n}^3} \left[ \frac{1}{2+l} - \frac{1}{1+l} \right] = \frac{2|\mathsf{E}_{0,\mathrm{Bohr}}|^2}{\mathsf{mc}^2 \mathsf{n}^3} \left[ \frac{-1}{(l+1)(l+2)} \right]$$
(11)

For the particular case n=2, l=1,

$$\mathsf{E}_{n,l,\uparrow\uparrow} - \mathsf{E}_{n,l,\uparrow\downarrow} = \frac{2 \,(13.6 \,\mathrm{eV})^2}{5.11 \times 10^5 \,\mathrm{eV} \,(2^3)} \left(\frac{-1}{6}\right) \tag{12}$$

Since the difference is negative, the antiparallel state has the lower energy.