Quantum Physics 1 - Homework 6

Due on Monday (Oct 17) at 11:59 AM

1. A photon with a wavelength of 102.56 nm excites a hydrogen atom from the ground state.

(a) [1pt.] Ignoring spin, what are the possible quantum numbers (n, l, and m) of the excited electron?

The energy levels of hydrogen are given by:

$$E_n = \frac{-13.6\,\mathrm{eV}}{n^2}. \tag{1}$$

When a photon is absorbed by an electron, the photon energy corresponds to a difference between two energy levels. For the energy of a photon we know that

$$E = hf = \frac{hc}{\lambda}, \tag{2}$$

which in this case gives

$$E = \frac{6.626 \cdot 10^{-34}\,\mathrm{m^2\,kg\,s^{-1}} \cdot 3 \cdot 10^{8}\,\mathrm{m\,s^{-1}}}{102.56 \cdot 10^{-9}\,\mathrm{m}} = 1.934 \cdot 10^{-18}\,\mathrm{J} = 12.09\,\mathrm{eV}, \tag{3}$$

The photon is excited from the ground state at which $E_1 = -13.6\,\mathrm{eV}$, and absorbs 12.09eV. Thus, thee energy of the excited state is $E_n = -1.51\,\mathrm{eV}$, which corresponds to

$$n = \sqrt{\frac{-13.6\,\mathrm{eV}}{E_n}} = \sqrt{\frac{-13.6}{-1.51}} = 3. \tag{4}$$

Since l ranges from 0 to $n-1$, the allowed values for l are $0, 1, 2$. For each of these, we have that m ranges from $-l$ to l, giving the following allowed states:

$$\begin{aligned}(n, l, m) =&(3,0,0),\\ &(3,1,-1),(3,1,0),(3,1,1),\\ &(3,2,-2),(3,2,-1),(3,2,0),(3,2,1),(3,2,2).\end{aligned}$$

(b) [1pt.] What is the degeneracy of this level, i.e. how many values can the quantum numbers take that all share this same energy? Is this equal or different to the degeneracy of the 3D infinite square well? Provide a brief explanation for your finding.

The degeneracy is n^2 for the hydrogen atom, so in this case 9. This differs from the infinite square well which has degeneracy $2l + 1$.

(c) [2pt.] Consider the states within the energy level of (a) (if you didn't find an answer, take e.g. $n = 4$). If we only look at the radial part of the wavefunction, we see that there is a *most probable* radius for each state. For which allowed value of l is the most probable radius the largest? Write down the values of the radii in terms of the Bohr radius a. (You may plot the graphs to support your answer.)

The wavefunction ψ of the hydrogen atom can be separated into a radial and an angular part:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi). \tag{5}$$

We only consider the radial part of the wavefunction, which depends on n and l. Expressions for these are given in the book.

To compute the most probable radius, we find the maximum value of $|R_{nl}(r)|^2 \cdot r^2$. Since $R_{nl}(r)$ is a real function, looking for a maximum in $|R_{nl}(r)| \cdot r$ suffices.

$$\begin{align}
R_{30}r &= \frac{2}{3\sqrt{3}} a^{-3/2} \left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right) e^{-r/3a} \cdot r, \tag{6}\\
&= \frac{2}{3\sqrt{3}} a^{-3/2} \left(r - \frac{2}{3}\frac{r^2}{a} + \frac{2}{27}\frac{r^3}{a^2}\right) e^{-r/3a}. \tag{7}\\
& \tag{8}
\end{align}$$

$$\begin{align}
\frac{dR_{30}r}{dr} &= \frac{2}{3\sqrt{3}} a^{-3/2} \left[\frac{d}{dr}\left(r - \frac{2}{3}\frac{r^2}{a} + \frac{2}{27}\frac{r^3}{a^2}\right) e^{-r/3a} + \left(r - \frac{2}{3}\frac{r^2}{a} + \frac{2}{27}\frac{r^3}{a^2}\right)\frac{d}{dr} e^{-r/3a}\right], \tag{9}\\
&= \frac{2}{3\sqrt{3}} a^{-3/2} \left[\left(1 - \frac{4r}{3a} + \frac{6r^2}{27a^2}\right) e^{-r/3a} + \left(r - \frac{2}{3}\frac{r^2}{a} + \frac{2}{27}\frac{r^3}{a^2}\right) e^{-r/3a} \cdot -\frac{1}{3a}\right], \tag{10}\\
&= \frac{2}{3\sqrt{3}} a^{-3/2} \left[1 - \frac{5r}{3a} + \frac{12r^2}{27a^2} - \frac{2r^3}{81a^3}\right] e^{-r/3a}, \tag{11}\\
&= \frac{2}{3\sqrt{3}} a^{-3/2} \cdot \frac{1}{81a^3}\left[81a^3 - 135a^2 r + 36ar^2 - 2r^3\right] e^{-r/3a}. \tag{12}
\end{align}$$

Solving $\frac{dR_{30}r}{dr} = 0$ gives $81a^3 - 135a^2r + 36ar^2 - 2r^3 = 0$. Using Wolfram, we find the radii $r \approx 0.740a$, $r \approx 4.186a$ and $r \approx 13.09a$. From the graph we can see that the largest of the three radii corresponds to the maximum value of $|R_{30}|r$, and hence $r_{max} \approx 13.09a$.

$$\begin{align}
R_{31}r &= \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right) e^{-r/3a} \cdot r, \tag{13}\\
&= \frac{8}{27\sqrt{6}} a^{-3/2} \left(\frac{r^2}{a} - \frac{1}{6}\frac{r^3}{a^2}\right) e^{-r/3a}. \tag{14}
\end{align}$$

$$\frac{dR_{31}r}{dr} = \frac{8}{27\sqrt{6}}a^{-3/2}\left[\frac{d}{dr}\left(\frac{r^2}{a} - \frac{1}{6}\frac{r^3}{a^2}\right)e^{-r/3a} + \left(\frac{r^2}{a} - \frac{1}{6}\frac{r^3}{a^2}\right)\frac{d}{dr}e^{-r/3a}\right], \tag{15}$$

$$= \frac{8}{27\sqrt{6}}a^{-3/2}\left[\left(\frac{2r}{a} - \frac{3r^2}{6a^2}\right)e^{-r/3a} + \left(\frac{r^2}{a} - \frac{1}{6}\frac{r^3}{a^2}\right)e^{-r/3a}\cdot -\frac{1}{3a}\right], \tag{16}$$

$$= \frac{8}{27\sqrt{6}}a^{-3/2}\left[\left(\frac{2r}{a} - \frac{5r^2}{6a^2} + \frac{r^3}{18a^3}\right)\right]e^{-r/3a}, \tag{17}$$

$$= \frac{8}{27\sqrt{6}}a^{-3/2}\cdot\frac{1}{18a^3}\left[\left(36a^2r - 15ar^2 + r^3\right)\right]e^{-r/3a}. \tag{18}$$

Solving $\frac{dR_{31}r}{dr} = 0$ gives $36a^2r - 15ar^2 + r^3 = 0$. We get the radii $r = 0$, $r = 3a$ and $r = 12a$. From the graph we can see that the largest of the two radii corresponds to the maximum value of $|R_{31}|r$, and hence $r_{max} = 12a$.

$$R_{32}r = \frac{4}{81\sqrt{30}}a^{-3/2}\left(\frac{r}{a}\right)^2 e^{-r/3a}\cdot r, \tag{19}$$

$$= \frac{4}{81\sqrt{30}}a^{-3/2}\frac{r^3}{a^2}e^{-r/3a}. \tag{20}$$

$$\frac{dR_{32}}{dr} = \frac{4}{81\sqrt{30}}a^{-3/2}\left[\frac{d}{dr}\left(\frac{r^3}{a^2}\right)e^{-r/3a} + \frac{r^3}{a^2}\frac{d}{dr}e^{-r/3a}\right], \tag{21}$$

$$= \frac{4}{81\sqrt{30}}a^{-3/2}\left[\frac{3r^2}{a^2}e^{-r/3a} + \frac{r^3}{a^2}e^{-r/3a}\cdot -\frac{1}{3a}\right], \tag{22}$$

$$= \frac{4}{81\sqrt{30}}a^{-3/2}\left[\left(\frac{3r^2}{a^2} - \frac{r^3}{3a^3}\right)\right]e^{-r/3a}, \tag{23}$$

$$= \frac{4}{81\sqrt{30}}a^{-3/2}\cdot\frac{1}{3a^3}\left[\left(9ar - r^2\right)e^{-r/3a}\right]. \tag{24}$$

Solving $\frac{dR_{32}r}{dr} = 0$ gives $9ar - r^2 = 0$. We get the radii $r = 0$ and $r = 9a$. From the graph we can see that the largest of the two radii corresponds to the maximum value of $|R_{32}|r$, and hence $r_{max} = 9a$.

The most probable radius is largest for $l = 0$.

(d) [1pt.] Interpret your answer for exercise (c). How does this result make sense intuitively?

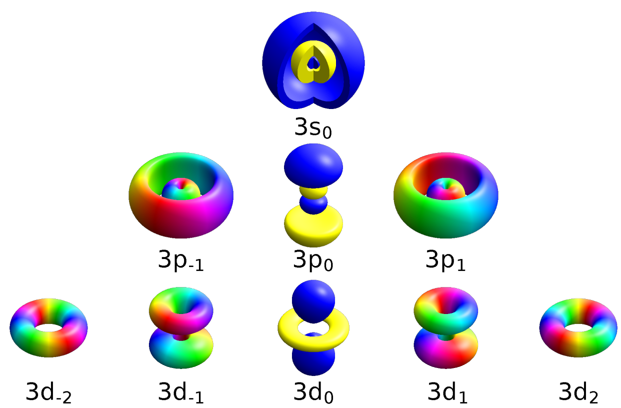
Since the potential well is much steeper for small r than for large r, the electron spends more time at large r than small r. If we increase the value of l, the width of the potential well decreases. This means that the radius where the electron spends most time, and hence where it is most likely to be found, decreases as well.

Another way of looking at this more intuitively: The value of l corresponds to the angular momentum of the electron in a hydrogen atom. If we restrict ourselves to a single value of n, we are considering states with the same energy. Clasically, kinetic energy is proportional to L^2, and

inversely proportional to I^2 where I is the moment of inertia. Thus, kinetic energy is proportional to $(L/r)^2$. If L is increased while the kinetic energy is kept constant, r has to decrease.
The most important difference between results in classical mechanics and quantum mechanics is that in QM, the angular momentum takes on discrete values, whereas classically L would be continuous.

(e) [2pt.] Draw/plot the different density plots that are possible for this excited hydrogen atom from all sides (looking along the x, y, and z axis. You may use Wolfram or other software to help you here. Duplicate drawings can of course be skipped.)

The density plots for the different states are shown below. Here, l is indicated by a letter ($l = 0, 1, 2$ correspond to s, p, d respectively) and the subscript corresponds to the value of m.
For all of the density plots, looking along the x or y axis does not change the image. All plots with negative m are the same as the plots with corresponding positive m, so the left side of the figure can be ignored.



(f) [2pt.] What possible decay paths to the ground state does the electron have? Give the wavelengths of the photons released in the different paths.

The electron can decay from the $n = 3$ energy level in two different paths: it either decays to the ground state directly (path A), or it decays to $n = 2$ and $n = 1$ successively (path B).

- For path A, the released energy is the same as the energy the electron absorbed initially. Hence, the wavelength of the photon will be 102.56 nm.
- For path B, we calculate the wavelengths as follows: since all the emitted energy goes to the photon, we note that

$$\Delta E = \frac{hc}{\lambda}, \tag{25}$$

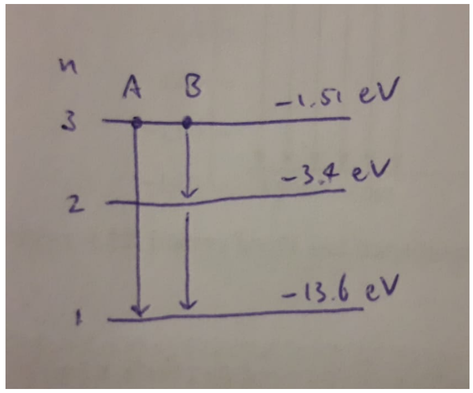
$$\implies \lambda = \frac{hc}{\Delta E}. \tag{26}$$

The energy of the $n = 2$ energy level is $E_2 = \frac{-13.6\,\mathrm{eV}}{2^2} = -3.4\,\mathrm{eV}$.
With this, we find that $\Delta E_{1,2} = 10.2\,\mathrm{eV} = 1.63 \cdot 10^{-18}\,\mathrm{J}$ and $\Delta E_{2,3} = 1.89\,\mathrm{eV} = 3.02 \cdot 10^{-19}\,\mathrm{J}$.
Hence, the photon emitted when the electron decays from $n = 3$ to $n = 2$ has a wavelength of

$$\lambda = \frac{hc}{E_3 - E_2} = \frac{6.626 \cdot 10^{-34}\,\mathrm{m^2\,kg\,s^{-1}} \cdot 3 \cdot 10^8\,\mathrm{m\,s^{-1}}}{3.02 \cdot 10^{-19}\,\mathrm{J}} = 658\,\mathrm{nm}, \tag{27}$$

and the photon emitted when the electron decays from $n = 2$ to $n = 1$ has a wavelength of

$$\lambda = \frac{hc}{E_2 - E_1} = \frac{6.626 \cdot 10^{-34}\,\mathrm{m^2\,kg\,s^{-1}} \cdot 3 \cdot 10^{8}\,\mathrm{m\,s^{-1}}}{1.63 \cdot 10^{-18}\,\mathrm{J}} = 122\,\mathrm{nm}, \tag{28}$$



(g) [1pt.] Suppose the already excited electron absorbs another photon of the same wavelength. What happens to the electron and the hydrogen atom?

The photon energy is equal to 12.09 eV, as found in exercise (a). The electron starts out with an energy of -13.6 eV and reaches the second excited state after absorbing the photon. If it absorbs another photon of the same energy, the final energy of the electron will be $-13.6\,\mathrm{eV} + 2 \cdot 12.09\,\mathrm{eV} = 10.58\,\mathrm{eV}$. However, the hydrogen atom only supports bound states up to an energy of 0 eV. Hence, the electron will go to a scattering state and leave the atom, and as a result the hydrogen atom will be ionized.

Grade $\in \{1, 4, 7, 10\}$.