

Atomic and Molecular Physics

Homework #1

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The following table contains the Radial Wave Functions for hydrogen, for $n \in [3, 4]$ and $l \in [0, 1, 2]$:

l	3	4
0	$R_{30} = \frac{2}{3\sqrt{3}}a^{-\frac{3}{2}}(1 - \frac{2r}{3a} + \frac{2r^2}{27a^2})e^{-\frac{r}{3a}}$	$R_{40} = \frac{1}{4}a^{-\frac{3}{2}}(1 - \frac{3r}{4a} + \frac{r^2}{8a^2} - \frac{r^3}{192a^3})e^{-\frac{r}{4a}}$
1	$R_{31} = \frac{8}{27\sqrt{6}}a^{-\frac{3}{2}}(1 - \frac{r}{6a})(\frac{r}{a})e^{-\frac{r}{3a}}$	$R_{41} = \frac{5}{16\sqrt{15}}a^{-\frac{3}{2}}(1 - \frac{r}{4a} + \frac{r^2}{80a^2})(\frac{r}{a})e^{-\frac{r}{4a}}$
2	$R_{32} = \frac{4}{81\sqrt{30}}a^{-\frac{3}{2}}(\frac{r}{a})^2e^{-\frac{r}{3a}}$	$R_{42} = \frac{1}{64\sqrt{5}}a^{-\frac{3}{2}}(1 - \frac{r}{12a})(\frac{r}{a})^2e^{-\frac{r}{4a}}$

This will be useful to solve the exercise.

We shall also define the Radial Probability Density P_{nl} as:

$$P_{nl} = R_{nl}^2 r^2$$

Using the defined P_{nl} we can calculate the Radial Probability Densities for 3s, 3p and 3d:

$$P_{30} = R_{30}^2 r^2 = \frac{4}{27} \frac{r^2}{a^3} (1 - \frac{2r}{3a} + \frac{2r^2}{27a^2})^2 e^{-\frac{2r}{3a}}$$

$$P_{31} = R_{31}^2 r^2 = \frac{64}{4374} \frac{r^2}{a^3} (1 - \frac{r}{6a})(\frac{r}{a})^2 e^{-\frac{2r}{3a}}$$

$$P_{32} = R_{32}^2 r^2 = \frac{8}{98415} \frac{r^6}{a^7} e^{-\frac{2r}{3a}}$$

We should also solve for 4s, 4p, and 4d:

$$P_{40} = R_{40}^2 r^2 = \frac{1}{16} \frac{r^2}{a^3} (1 - \frac{3r}{4a} + \frac{r^2}{8a^2} - \frac{r^3}{192a^3})^2 e^{-\frac{r}{2a}}$$

$$P_{41} = R_{41}^2 r^2 = \frac{5}{768} \frac{r^4}{a^5} (1 - \frac{r}{4a} + \frac{r^2}{80a^2})^2 e^{-\frac{r}{2a}}$$

$$P_{42} = R_{42}^2 r^2 = \frac{1}{20480} \frac{r^6}{a^7} (1 - \frac{r}{12a})^2 e^{-\frac{r}{2a}}$$

1)

Plotting the Radial Probability Densities for 3s, 3p, and 3d:

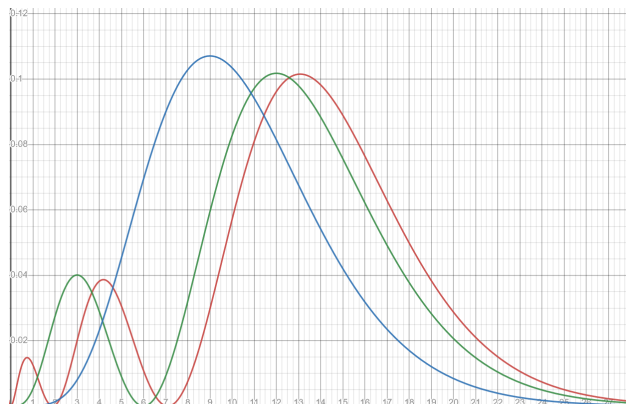


Figure 1: Graph of the Radial Probability Densities for 3s, 3p, and 3d

Using r as an a_o multiple we get a smooth graph from which we can confirm that 3s is the most penetrating since it has a much higher probability for smaller values of r , followed by 3p that has its Radial Probability Density slightly shifted to higher values of r , and finally by the 3d that has a single Radial Probability Density Peak around $r = 24.618a_o$, implying that 3d is the least penetrating.

2)

For this exercise we can, although we don't need to, create a simple function that gives a possible approximation of the real function that governs the physical principle.

$$Z(r) \approx -\frac{1}{r} - \frac{10}{r}e^{-r}$$

This simple function rapidly tends to $-\frac{1}{r}$ as $r \rightarrow \infty$ while also tending to $-\frac{11}{r}$ when $r \rightarrow 0^+$, (the positive sign on the zero is to show that this function is a bad approximation for negative values of r , but since we can't physically get a negative value for r this won't be a problem).

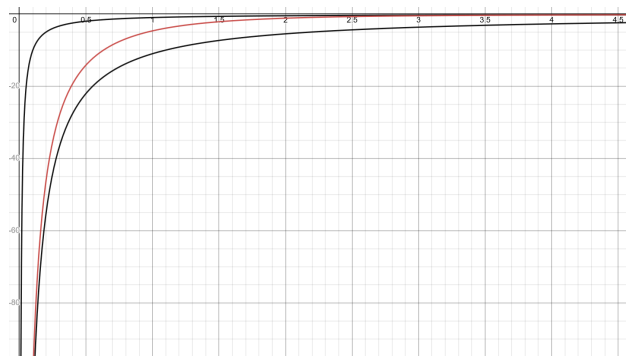


Figure 2: Plot of $-\frac{e^2}{r} - \frac{10e^2}{r}e^{-r}$ with the upper bound as $-\frac{e^2}{r}$, and lower bound as $-\frac{11e^2}{r}$, note however that the x-axis is shown in multiples of e^2 .

3)

As the r decreases the electron shielding effect becomes dimmer, and $Z(r)$ increases in absolute value, as a consequence the potential felt by an electron whose state is closer to the nucleus is far greater, so it is to be expected that the most penetrating states of the electron will be the most affected ones, whilst the least penetrating states will similarly be the least affected.

Since the most penetrating state is the 3s, this means that 3s will be the most affected, while 3d, the least penetrating state, will be the least affected.

4)

Since the most penetrating states have greater values of $Z(r)$ the potential felt is also greater in absolute value, then we should expect that the states of the electron that are more penetrating to have greater binding energies, therefore we can conclude that these results are in agreement with our penetration arguments.

5)

Using the expression :

$$E = \frac{z^2}{n^2} E_0$$

Where $E_0 = 13.6$ eV, we can solve for Z and get the expression:

$$Z = \sqrt{\frac{En^2}{E_0}}$$

Substituting $n = 3$, and using $E_{30} = 5.12$ eV , $E_{31} = 2.10$ eV and $E_{32} = 1.50$ eV.

State	Z
3s	1.84
3p	1.18
3d	0.99

From which we can conclude that the effective charge Z decreases as we go to less penetrating states, or in other words as we increase the angular quantum number, which agrees with all previous results.

6)

Now We shall be doing the same exercises using $n = 4$ and assuming $Z(r) = 1$ as $r \rightarrow \infty$ while also tending to $Z(r) = 19$ when $r \rightarrow 0$.

6.1)

Plotting the Radial Probability Densities for 4s, 4p, and 4d:

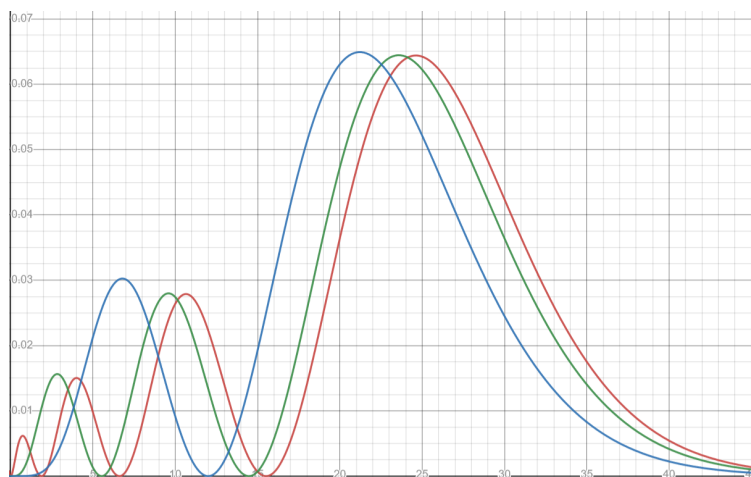


Figure 3: Graph of the Radial Probability Densities for 4s, 4p, and 4d

Again using r as an a_0 multiple we get to the same conclusions however for a different Energy Level, we conclude that 4s is the most penetrating state, followed by 4p and finally 4d.

We can also plot all of the Radial Probability Densities:

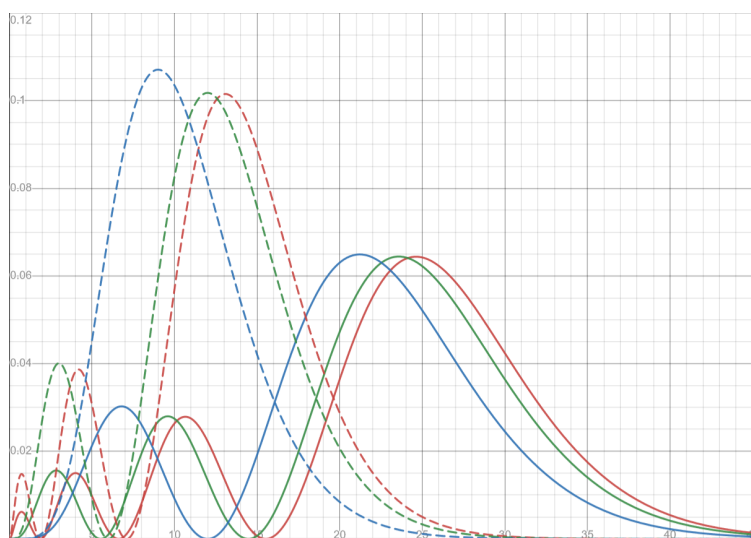


Figure 4: Graph of the Radial Probability Densities for s, p, and d, $n = 3$ is dashed.

From this plot we can observe that $n = 3$ is more penetrating than $n = 4$.

6.2)

Using a similar function to the one used in 2), we have:

$$Z(r) \approx -\frac{1}{r} - \frac{18}{r}e^{-r}$$

Which when plotted gives a very similar graph:

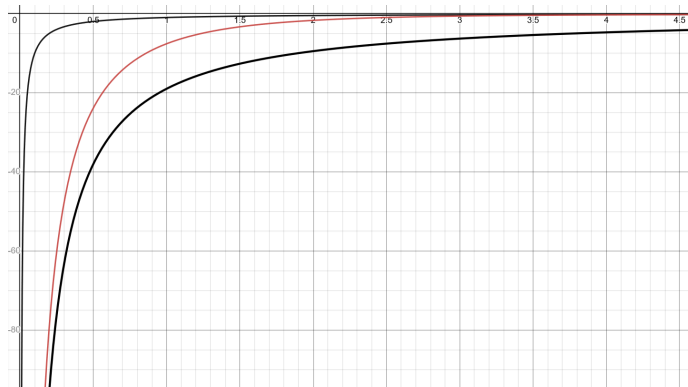
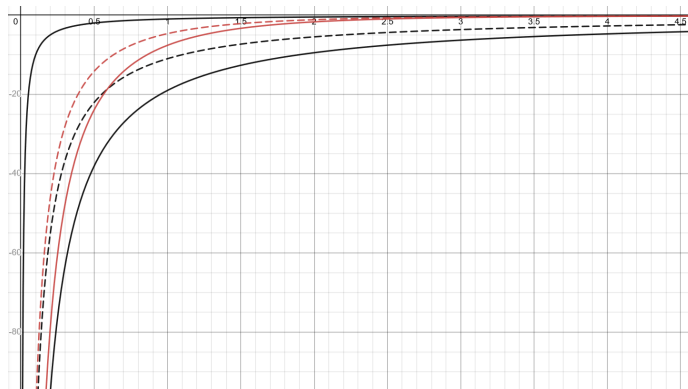


Figure 5: Plot of $-\frac{e^2}{r} - \frac{18e^2}{r}e^{-r}$ with the upper bound as $-\frac{e^2}{r}$, and lower bound as $-\frac{19e^2}{r}$, note however the x-axis is shown in multiples of e^2 .

We can still compare both of the functions and see they behave the same, as expected.



6.3)

Just as in 3) as we decrease the r , we decrease the electron shielding effect, as a consequence the $Z(r)$ increases, and since the 4s state has the highest probability for lower values of r , we conclude that 4s is the most penetrating state out of the 3, followed by 4p, and finally by the 4d.

6.4)

Again since the most penetrating states have greater values of $Z(r)$ the potential felt is also greater in absolute value, then it is to be expected that the states of the electron that are more penetrating will have greater binding energies, therefore we can conclude that these results are in agreement with our penetration arguments.

6.5)

The last thing we have to do is get values for E_{40} , E_{41} and E_{42} , and we can look these up on a table from Corliss and Sugar (1979)

From here we get that $E_{40} = 4.34$ eV , $E_{41} = 2.73$ eV and $E_{42} = 0.94$ eV.

Now following the same expression as before:

$$Z = \sqrt{\frac{En^2}{E_0}}$$

And lastly substituting $n = 4$, $E_{40} = 4.34$ eV , $E_{41} = 2.73$ eV and $E_{42} = 0.94$ eV we end up with:

State	Z
4s	2.26
4p	1.79
4d	1.05

Which again allows us to come to the conclusion that increasing the angular quantum number decreases the overall effective charge, since as shown by 1) and 6.1) , the Radial Probability Densities for lower angular quantum numbers have higher values for the same low values of r, and since being further away allows for electron shielding effects, the effective charge is reduced.

References

Corliss, C. and J. Sugar (1979). Energy levels of potassium, K I through K XIX. *Journal of Physical and Chemical Reference Data* 8.4, 1109–1146.