Group Problems #34 - Solutions

Monday, November 21

Problem 1 *The radial wavefunction*

An electron in a hydrogen atom is in a $3d$ state.

(a) What are the principle quantum number and angular momentum quantum number for this electron?

For a $3d$ state, we have $n = 3$ and $\ell = 2$.

(b) What is the radial wavefunction for this electron? (Hint: $L_0^5 = 1$)

From the notes, we have:

$$R(r) = \left(\frac{2}{na_0}\right)^{3/2} \sqrt{\frac{(n-\ell-1)!}{2n[(n+\ell)!]}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{\ell} L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right), \tag{1}$$

where the last parentheses denote the argument of the associated Laguerre polynomials, $L_{n-\ell-1}^{2\ell+1}$. For the $3d$ state, we have $n = 3$ and $\ell = 2$, so the polynomial term is $L_0^5 = 1$. Evaluating the other constants gives:

$$\begin{aligned}
R_{3,2}(r) &= \left(\frac{2}{3a_0}\right)^{3/2} \sqrt{\frac{1}{6(5!)}} e^{-r/3a_0} \left(\frac{2r}{3a_0}\right)^2 L_0^5 && (2) \\
& && (3) \\
&= \frac{2\sqrt{2}}{(3a_0)^{3/2}} \frac{4}{9a_0^2} \frac{1}{12\sqrt{5}} r^2 e^{-r/3a_0} && (4) \\
& && (5) \\
&= \frac{1}{(3a_0)^{3/2}} \frac{2\sqrt{2}}{27\sqrt{5}\, a_0^2}\, r^2\, e^{-r/3a_0} && (6) \\
& && (7) \\
&= (A_{3,2})\, r^2\, e^{-r/3a_0}, && (8)
\end{aligned}$$

where $A_{3,2}$ is a constant.

(c) What is the most probable radius to find the electron?

The most probable radius for the electron can be found by taking the derivative of the probability density, $r^2 R^2(r)$ with respect to r and setting this to zero. In particular,

$$
\begin{aligned}
r^2 R_{3,2}^2(r) &= (A_{3,2})^2\, r^6\, e^{-2r/3a_0} && (9)\\
&&& (10)\\
\Longrightarrow \frac{d(r^2R^2)}{dr} &= (A_{3,2})^2 \left[6r^5 e^{-2r/3a_0} + r^6 \left(-\frac{2}{3a_0}\right) e^{-2r/3a_0}\right] && (11)\\
&&& (12)\\
&= (A_{3,2})^2\, r^5 e^{-2r/3a_0} \left[6 - \frac{2r}{3a_0}\right] = 0. && (13)
\end{aligned}
$$

Eqn. (13) is true at $r = 0$, $r = \infty$, and when the expression in square brackets is zero. The first two options are not interesting, thus we have:

$$6 = \frac{2r}{3a_0} \Longrightarrow r = 9a_0. \tag{14}$$

Problem 2 *High angular momentum orbitals in hydrogen*

Show that for those orbitals with the largest possible angular momentum, the most probable radius for the electron is quantized.

We follow a similar procedure as problem 1(c), starting with the general expression in Eqn. (1). The states with maximum possible angular momentum have $\ell = n - 1$, so the radial wavefunctions become:

$$R_n(r) = A_n\, e^{-r/na_0}\, r^{n-1} \Longrightarrow r^2\, R_n^2(r) = A_n^2\, r^{2n}\, e^{-2r/na_0}, \tag{15}$$

where the constant A_n has all the terms not containing r. As above, now we just need to take the derivative of r^2R^2 and set it to zero:

$$
\begin{aligned}
\frac{d(r^2R^2)}{dr} &= A_n^2 \left[2n\, r^{2n-1}\, e^{-2r/na_0} + r^{2n} \left(-\frac{2}{na_0}\right) e^{-2r/na_0}\right] && (16)\\
&&& (17)\\
&= A_n^2\, 2r^{2n-1}\, e^{-2r/na_0} \left[n - \frac{r}{na_0}\right] = 0 && (18)\\
\Longrightarrow r &= n^2 a_0. && (19)
\end{aligned}
$$