

Consider an excited state of hydrogen atom with electron in the 2p orbital with  $m_l = -1$ . Answer the following questions. You don't need to provide fully numerical answers – they can be expressed via a combination of numerical factors and physical constants, like  $e$ ,  $\hbar$ ,  $\epsilon_0$ ,  $a_0$ , etc

**A.** Write the expression for the probability density to find the electron at a given point  $(r, \theta, \phi)$  in the 3D space. (You may leave the numerical factors as they are: no need to reduce or calculate them.)

$$P = |\Psi_{2,1,-1}|^2 = (R_{2,1}(r))^2 |Y_{1,-1}(\theta, \phi)|^2 = \left(\frac{1}{8\sqrt{\pi}}\right)^2 (1/a_0)^3 \left(\frac{r}{a_0}\right)^2 e^{-r/a_0} \sin^2 \theta$$

**B.** In which point(s) in the 3D space within the atom you are least likely to find the electron?

We need to find points in space where the probability density  $P = |\Psi_{2,1,-1}|^2 = 0$ . The wave function (and hence the probability) equals zero when either its radial or angular part or both are zero. The radial part  $P_{\text{rad}}$  is zero only at  $r = 0$  (i.e. at the nucleus), whereas the angular part  $P_{\text{ang}}$  is zero when  $\sin \theta = 0$ , i.e.  $\theta = 0^\circ$  and  $\theta = 180^\circ$  (independent of the angle  $\phi$ ). This defines the z axis (which is now the nodal axis, and, naturally, it contains the origin,  $r = 0$ ) as the points in the 3D space where the electron cannot be found.

**C.** At what distance from the nucleus you are most likely to find the electron?

Since the question is about *distance* not just point(s) in the 3D space, we need to use the radial probability distribution function that gives the probability to find the electron at a *distance*  $r$  from

the nucleus,  $W_{2p}(r) = (R_{2,1}(r))^2 r^2 = \frac{1}{(2\sqrt{6})^2} \frac{r^4}{a_0^5} e^{-r/a_0} \propto u^4 e^{-u}$  where for convenience of

subsequent handling this expression I defined a new variable:  $u = \frac{r}{a_0}$ . The most likely distance

corresponds to the maximum of  $W_{2p}(r)$ , so we need to solve the equation:  $\frac{d}{dr} W_{2p}(r) = 0$ .

$\frac{d}{du} W_{2p} \Rightarrow \frac{d}{du} [u^4 e^{-u}] = e^{-u} u^3 (4 - u) = 0$ . Of the solutions to this equation only  $u = 4$

corresponds to maximum of  $W_{2p}$ . So, recalling that  $u = \frac{r}{a_0}$ , the distance  $r$  at which we are most

likely to find the electron equals  $4a_0$ .

**D.** Calculate the mean value of the distance ( $\langle r \rangle$ ) of the electron from the nucleus and compare it with the  $\langle r \rangle$  value for 1s electron (you will need to calculate this one, too). Provide an explanation for why the  $\langle r \rangle$  value for one of the electrons is larger than for the other electron.

You can simply plug  $r$  into the expectation value equation from the 4<sup>th</sup> postulate and evaluate the corresponding integrals. Because  $r$  does not depend on the angles, the integrals over the angular parts of the wave function in the numerator and denominator cancel each other, and so do the numerical factors.

$$\langle r \rangle_{2p} = \frac{\int \Psi_{2,1,-1}^* r \Psi_{2,1,-1} dv}{\int \Psi_{2,1,-1}^* \Psi_{2,1,-1} dv} = \frac{\int_0^\infty [R_{2,1}(r)]^2 r^3 dr}{\int_0^\infty [R_{2,1}(r)]^2 r^2 dr} = \frac{\int_0^\infty r^5 e^{-r/a_0} dr}{\int_0^\infty r^4 e^{-r/a_0} dr} = \frac{5! a^5}{4! a^6} = \frac{5}{a} = 5a_0. \text{ Here I used the table}$$

integral  $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$  where  $n=5$  in the numerator and  $n=4$  in the denominator, and  $a=1/a_0$ .

An alternative way to get the answer is to use the expression for the radial distribution function  $W(r)$  (which gives the probability to find the electron at a given distance  $r$  from the nucleus) and calculate the average distance as the following integral (make sure you use the correct normalization factor):

$$\langle r \rangle_{2p} = \int_0^\infty r W_{2p}(r) dr = \int_0^\infty r [R_{2,1}(r)]^2 r^2 dr = \frac{1}{24} \frac{1}{a_0^5} \int_0^\infty r^5 e^{-r/a_0} dr = \frac{1}{24 a_0^5} \left[ \frac{5!}{(1/a_0)^6} \right] = 5 a_0$$

To answer the second question let's calculate  $\langle r \rangle$  for 1s electron (I will use the radial distribution function here):

$$\langle r \rangle_{1s} = \int_0^\infty r W_{1s}(r) dr = \int_0^\infty r [R_{1,0}(r)]^2 r^2 dr = 4 \frac{1}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr = \frac{4}{a_0^3} \left[ \frac{3!}{(2/a_0)^4} \right] = 1.5 a_0.$$

We find that the mean distance from the nucleus for 2p electron is greater than for 1s electron.

There are several explanations for this. Qualitatively, since the energy is negative, a higher energy of the 2p electron implies a weaker absolute value of the Coulomb interaction (remember that this interaction is negative), hence generally longer distance from the nucleus, because  $V_C \propto 1/r$ . In specific terms, if you compare the radial parts of the wave function for 2p and 1s electrons: the exponential  $e^{-r/2a_0}$  falls off with  $r$  slower than  $e^{-r/a_0}$ , resulting in the wave function of 2p stretching farther from the nucleus than for 1s electron. Furthermore, the wave function of 1s electron is nonzero at the nucleus (and has no radial nodes) whereas for 2p electron the wave function has a zero value at the nucleus, reflecting the centrifugal force acting on the 2p electron due to its nonzero angular momentum. As a result, the electron "crowd" for 2p electron is shifted farther away from the nucleus than for 1s electron, resulting in the larger average value of  $r$ .

**F.** Calculate the average potential energy of the electron in this orbital and compare it with the total energy in this state. Does the relationship ( $\langle V \rangle = 2E$ ) we derived in class for the 1s orbital still hold?

You can simply plug  $\hat{V} = -\frac{e^2}{4\pi\epsilon_0 r}$  into the expectation value equation from the 4<sup>th</sup> postulate and

evaluate the corresponding integrals, as we did in class for the 1s electron. Let's first put the

numerical factor  $-\frac{e^2}{4\pi\epsilon_0}$  aside and calculate the average value of  $\frac{1}{r}$ . Because  $\frac{1}{r}$  does not depend

on the angles, the integrals over the angular parts of the wave function in the numerator and denominator cancel each other, and so do the numerical factors (the normalization coefficient and  $a_0$ ) in the wave function.

$$\left\langle \frac{1}{r} \right\rangle = \frac{\int \Psi^* \frac{1}{r} \Psi dv}{\int \Psi^* \Psi dv} = \frac{\int_0^\infty [R_{2,1}(r)]^2 r dr}{\int_0^\infty [R_{2,1}(r)]^2 r^2 dr} = \frac{\int_0^\infty r \left(\frac{r}{a_0}\right)^2 e^{-r/a_0} dr}{\int_0^\infty r^2 \left(\frac{r}{a_0}\right)^2 e^{-r/a_0} dr} = \frac{1}{a_0} \frac{\int_0^\infty u^3 e^{-u} du}{\int_0^\infty u^4 e^{-u} du} = \frac{1}{a_0} \frac{\frac{3!}{(1)^4}}{\frac{4!}{(1)^5}} = \frac{1}{4a_0}$$

Here, as in Q.C, I introduced a new variable,  $u = \frac{r}{a_0}$ , and used the table integral

$$\int_0^\infty x^m e^{-ax} dx = \frac{m!}{a^{m+1}} \text{ where } a=1 \text{ and we have different values of } m. \text{ Now all we need it to bring back}$$

the numerical factor  $-\frac{e^2}{4\pi\epsilon_0}$  to get:  $\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{4a_0}$  and convert this expression

into a form that can be compared with the expression for the total energy of the electron in this state. From the definition of  $a_0$ ,  $a_0 = \frac{\hbar^2}{m_e} \frac{4\pi\epsilon_0}{e^2}$ , we get  $\frac{e^2}{4\pi\epsilon_0} = \frac{\hbar^2}{m_e} \frac{1}{a_0}$ , and substituting it into the equation for the average potential energy, we finally obtain:

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{\hbar^2}{m_e a_0^2} \frac{1}{4} = 2E_{n=2}. \text{ Therefore we conclude that the relationship } (\langle V \rangle = 2E)$$

we derived in class for the 1s orbital holds also for 2p electron.

A similar relationship holds for other states of electron, see for example, Example Problem 9.2 in the textbook.

As in Q.D, a somewhat simpler, alternative way to get the answer is to use the expression for the

radial distribution function,  $W(r) = (R_{2,1}(r))^2 r^2 = \frac{1}{24} \frac{r^2}{a_0^3} \left(\frac{r}{a_0}\right)^2 e^{-r/a_0}$  (which gives the

probability to find the electron at a given distance  $r$  from the nucleus) and calculate the average value of  $1/r$  as the following integral:

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty \frac{1}{r} W(r) dr = \int_0^\infty \frac{1}{r} [R_{2,1}(r)]^2 r^2 dr = \frac{1}{24} \frac{1}{a_0^3} \int_0^\infty \frac{r^2}{a_0^2} \frac{r^2}{r} e^{-r/a_0} dr = \frac{1}{24} \frac{1}{a_0} \int_0^\infty u^3 e^{-u} du = \frac{1}{24} \frac{1}{a_0} \frac{3!}{1^4} = \frac{6}{24} \frac{1}{a_0} = \frac{1}{4a_0}$$

The following table integral could be useful for some calculations:  $\int_0^\infty x^m e^{-ax} dx = \frac{m!}{a^{m+1}}$