

PHY 251 Fall 2009: homework problem set 8, due in the PHY 251 drop box in room A-129 by noon on Friday, Nov. 13.

1. Serway 8.7

*Answer:* This problem is separable, in that one can solve the Schrödinger equation for each dimension separately. Let's assume

$$\psi(x, y, z) = A \sin(n_1\pi \frac{x}{L_1}) \sin(n_2\pi \frac{y}{L_2}) \sin(n_3\pi \frac{z}{L_3})$$

and integrate to normalize:

$$1 = A^2 \left[ \int_{x=0}^{L_1} \sin^2(n_1\pi \frac{x}{L_1}) dx \right] \left[ \int_{y=0}^{L_2} \sin^2(n_2\pi \frac{y}{L_2}) dy \right] \left[ \int_{z=0}^{L_3} \sin^2(n_3\pi \frac{z}{L_3}) dz \right]$$

Now all three integrals have identical form. Let's solve for  $x$ , using  $a = n_1\pi/L_1$ :

$$\begin{aligned} \int_{x=0}^{L_1} \sin^2(ax) dx &= \left[ \frac{x}{2} - \frac{\sin(2ax)}{4a} \right] \Big|_{x=0}^{x=L_1} \\ &= \left[ \frac{L_1}{2} - \frac{\sin(2n_1\pi L_1/L_1)}{4n_1\pi/L_1} \right] - \left[ \frac{0}{2} - \frac{\sin(2n_1\pi 0/L_1)}{4n_1\pi/L_1} \right] \\ &= \left[ \frac{L_1}{2} - 0 \right] - [0 - 0] = \frac{L_1}{2} \end{aligned}$$

because  $\sin(2n_1\pi) = 0$  and  $\sin(0) = 0$ . We thus have

$$1 = A^2 \frac{L_1}{2} \frac{L_2}{2} \frac{L_3}{2}$$

or  $A = \sqrt{8/(L_1 L_2 L_3)}$ .

2. Write out the full wavefunction  $\psi$  for the  $2p$  state of hydrogen with  $L_z = -\hbar$ . What's the Bohr model energy for this state?

*Answer:* The  $2p$  state with  $L_z = -\hbar$  has  $n = 2$ ,  $\ell = 1$ , and  $m_\ell = -1$ , so the wavefunction is

$$\psi = R_{n=2,\ell=1}(r) Y_{\ell=1}^{m_\ell=-1}(\theta, \phi) = \left( \frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{\sqrt{3}a_0} e^{-Zr/2a_0} \frac{-1}{2} \sqrt{\frac{3}{2\pi}} \sin(\theta) e^{+i\phi}$$

where we have used Table 8.4 on p. 280 for  $R_{n\ell}(r)$  and Table 8.3 on p. 269 for  $Y_\ell^{m_\ell}(\theta, \phi)$ .

3. Calculate numerical values for the net angular momentum, and for all possible  $\hat{z}$  axis angular momenta, for the  $2p$  and  $4d$  states of hydrogen.

*Answer:* The  $2p$  state has  $n = 2$  and  $\ell = 1$ , with  $m_\ell = -1, 0, +1$ . Numerical values are

$$|L| = \hbar \sqrt{\ell(\ell+1)} = (1.055 \times 10^{-34} \text{ J} \cdot \text{s}) \sqrt{1(1+1)} = 1.492 \times 10^{-34} \text{ J} \cdot \text{s}$$

and  $L_z = \{-1, 0, 1\} \cdot 1.055 \times 10^{-34} \text{ J} \cdot \text{s}$ . The  $4d$  state has  $n = 4$  and  $\ell = 2$  with  $m_\ell = -2, -1, 0, 1, 2$ , so

$$|L| = \hbar \sqrt{\ell(\ell+1)} = (1.055 \times 10^{-34} \text{ J} \cdot \text{s}) \sqrt{2(2+1)} = 2.584 \times 10^{-34} \text{ J} \cdot \text{s}$$

and  $L_z = \{-2, -1, 0, 1, 2\} \cdot (1.055 \times 10^{-34} \text{ J} \cdot \text{s})$ .

4. Serway 8.19

Answer: I “unassigned” this problem!

5. Calculate  $\langle r \rangle$ ,  $\langle r^2 \rangle$ , and  $\sigma_r$  for the  $2s$  state of hydrogen.

Answer: The  $2s$  state of hydrogen has  $n = 2$ ,  $\ell = 0$ , and  $m_\ell = 0$ , so the wavefunction is

$$\psi = R_{20}(r) Y_1^0(\theta, \phi) = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0} \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos(\theta).$$

Now since  $\psi = R(r)Y(\theta, \phi)$  is separable, we can separately integrate out the  $(\theta, \phi)$  dependencies; in fact, since the spherical harmonics are already normalized, their integral gives 1. The volume element of integration in spherical coordinates is  $r^2 dr$ , so we have

$$\begin{aligned} \langle r^n \rangle &= \int_{r=0}^{\infty} r^n R_{n\ell}^2(r) r^2 dr \\ &= \int_{r=0}^{\infty} r^{2+n} \left(\frac{Z}{2a_0}\right)^3 \left(2 - \frac{Zr}{a_0}\right)^2 e^{-Zr/a_0} dr. \end{aligned}$$

Now let  $x \equiv (Z/a_0)r$  so  $r = (a_0/Z)x$  and  $dr = (a_0/Z)dx$ . We also then have

$$\left(2 - \frac{Zr}{a_0}\right)^2 = (2 - x)^2 = (4 - 4x + x^2).$$

The integral then becomes

$$\begin{aligned} \langle r^n \rangle &= \left(\frac{Z}{2a_0}\right)^3 \left(\frac{a_0}{Z}\right)^{2+n} \frac{a_0}{Z} \int_{x=0}^{\infty} x^{2+n} (4 - 4x + x^2) e^{-x} dx \\ &= \frac{1}{8} \left(\frac{a_0}{Z}\right)^n \left[4 \int_{x=0}^{\infty} x^{2+n} e^{-x} dx - 4 \int_{x=0}^{\infty} x^{3+n} e^{-x} dx + \int_{x=0}^{\infty} x^{4+n} e^{-x} dx\right] \end{aligned}$$

with  $n = 1$  for  $\langle r \rangle$ , and  $n = 2$  for  $\langle r^2 \rangle$ . Now the definite integrals are of the form

$$\int_0^{\infty} x^{z-1} e^{-x} dx = \Gamma(z) \Rightarrow (z-1)! \text{ for positive integer } z$$

so we have

$$\begin{aligned} \langle r \rangle &= \frac{1}{8} \left(\frac{a_0}{Z}\right) \left[4 \int_0^{\infty} x^{4-1} e^{-x} dx - 4 \int_0^{\infty} x^{5-1} e^{-x} dx + \int_0^{\infty} x^{6-1} e^{-x} dx\right] \\ &= \frac{a_0}{8Z} [4(3!) - 4(4!) + (5!)] = \frac{a_0}{8Z} [24 - 96 + 120] = 6 \frac{a_0}{Z} \end{aligned}$$

and

$$\begin{aligned} \langle r^2 \rangle &= \frac{1}{8} \left(\frac{a_0}{Z}\right)^2 \left[4 \int_0^{\infty} x^{5-1} e^{-x} dx - 4 \int_0^{\infty} x^{6-1} e^{-x} dx + \int_0^{\infty} x^{7-1} e^{-x} dx\right] \\ &= \frac{a_0^2}{8Z^2} [4(4!) - 4(5!) + (6!)] = \frac{a_0^2}{8Z^2} [96 - 480 + 720] = 42 \frac{a_0^2}{Z^2}. \end{aligned}$$

Finally we have for  $Z = 1$  with hydrogen the result

$$\sigma_r = \sqrt{\langle r^2 \rangle - (\langle r \rangle)^2} = \sqrt{42a_0^2 - (6a_0)^2} = \sqrt{6}a_0 = 2.45a_0$$

so we have a very broad distribution with  $\langle r \rangle = 6a_0$  and  $\sigma_r = 2.45a_0$ .

6. Serway 8.23

*Answer:* In the problem, they use  $k$  for  $1/(4\pi\epsilon_0)$  in the Coulomb force law, so I'd rather do what we did in lecture 8 and write

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c}.$$

a. Numerical evaluation of the inverse (inputting all mks units) gives

$$\frac{1}{\alpha} = \frac{4\pi\epsilon_0 \hbar c}{e^2} = \frac{4\pi(8.854 \times 10^{-12})(1.055 \times 10^{-34}) \cdot (2.998 \times 10^8)}{(1.602 \times 10^{-19})^2} = 137.1.$$

b. The classical electron radius is

$$r_e = \frac{e^2}{4\pi\epsilon_0 m_e c^2} = \frac{e^2}{4\pi\epsilon_0 \hbar c} \frac{\hbar}{m_e c} = \alpha \frac{1}{2\pi} \lambda_C$$

where in the last step we have put in both the fine structure constant  $\alpha$  and the Compton wavelength  $\lambda_C = h/(m_e c)$ . Therefore we can write the ratio  $\lambda_C/r_e$  as

$$\frac{\lambda_C}{r_e} = \frac{\lambda_C}{\alpha \frac{1}{2\pi} \lambda_C} = \frac{2\pi}{\alpha} \simeq 2\pi \cdot 137.$$

c. The Bohr radius  $a_0$  is

$$a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = \frac{4\pi\epsilon_0 \hbar c}{e^2} \frac{\hbar}{m_e c} = \frac{1}{\alpha} \frac{1}{2\pi} \frac{h}{m_e c} = \frac{1}{\alpha} \frac{1}{2\pi} \lambda_C$$

so the ratio of the Bohr radius  $a_0$  to the Compton wavelength  $\lambda_C$  is given by

$$\frac{a_0}{\lambda_C} = \frac{\frac{1}{\alpha} \frac{1}{2\pi} \lambda_C}{\lambda_C} = \frac{1}{2\pi\alpha} \simeq \frac{137}{2\pi}.$$

d. The Rydberg wavelength  $1/R_\infty$  is defined by

$$\frac{1}{R_\infty} = \frac{hc}{E_0} \quad \text{with} \quad E_0 \equiv \frac{m_e e^4}{8h^2 \epsilon_0^2}$$

so we can write

$$\frac{1}{R_\infty} = \frac{hc}{m_e e^4} = \left( \frac{4\pi\epsilon_0 \hbar c}{e^2} \right)^2 \frac{h}{m_e c} = \frac{2}{\alpha^2} \lambda_C$$

and find that the ratio of the Rydberg wavelength to the Bohr radius is

$$\frac{1/R_\infty}{a_0} = \frac{\frac{2\lambda_C}{\alpha^2}}{\frac{1}{\alpha} \frac{1}{2\pi} \lambda_C} = \frac{4\pi}{\alpha} \simeq 4\pi \cdot 137.$$

So  $\alpha$  is a nice way to deal with some common constants.

7. Serway 8.26

*Answer:* Bohr radii are given by  $r_n = a_0 n^2 / Z^2$  or  $r_{n=2} = 4a_0$ . The probability  $P(r')$  of being within a given distance  $r'$  of  $r = 0$  is given by

$$P(r') = \int_0^{r'} [R_{n\ell}(r)]^2 r^2 dr$$

which with  $Z = 1$  for the  $2s$  wavefunction is

$$P_{2s}(4a_0) = \int_{r=0}^{4a_0} \left[ \left( \frac{1}{2a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \right]^2 r^2 dr.$$

Now use  $x \equiv r/a_0$  or  $r = a_0 x$  and  $dr = a_0 dx$  to write this as

$$\begin{aligned} P_{2s}(4a_0) &= \left( \frac{1}{2a_0} \right)^3 a_0^3 \int_{x=0}^4 x^2 (2-x)^2 e^{-x} dx \\ &= \frac{1}{8} \int_{x=0}^4 x^2 (2-x)^2 e^{-x} dx \end{aligned}$$

which we can solve with Maple as

`evalf((1/8)*int(x^2*(2-x)^2*exp(-x), x=0..4))`; =0.176. For the  $2p$  state we have (again using  $x \equiv r/a_0$ )

$$\begin{aligned} P_{2p}(4a_0) &= \int_{r=0}^{4a_0} \left[ \left( \frac{1}{2a_0} \right)^{3/2} \frac{r}{\sqrt{3}a_0} e^{-r/2a_0} \right]^2 r^2 dr \\ &= \left( \frac{1}{2a_0} \right)^3 \frac{1}{3} a_0^3 \int_{x=0}^4 x^4 e^{-x} dx = \frac{1}{24} \int_{x=0}^4 x^4 e^{-x} dx. \end{aligned}$$

which we can solve with Maple as `evalf((1/24)*int(x^4*exp(-x), x=0..4))`; =0.371.

We therefore see that the  $2s$  electron spends only 17.6% of its time inside the Bohr radius, while the higher excited  $2p$  state spends 37.1% of its time inside the Bohr radius.

8. Serway 9.4

*Answer:* An electron in the  $3d$  subshell has  $n = 3$  and  $\ell = 2$ . It can have  $m_\ell = \{-2, -1, 0, 1, 2\}$  and for each  $m_\ell$  it can have  $m_s = \{-1/2, +1/2\}$ . In the  $3p$  subshell we have  $n = 3$  and  $\ell = 1$ , so  $m_\ell = \{-1, 0, 1\}$  and for each  $m_\ell$  we can have  $m_s = \{-1/2, +1/2\}$ .

9. Serway 9.11

*Answer:* For a  $d$  electron, we have  $\ell = 2$  and  $m_\ell = \{-2, -1, 0, 1, 2\}$ . The values for  $j$  are  $j = \ell + m_s = \{2 + \frac{1}{2}, 2 - \frac{1}{2}\}$  or  $j = \{\frac{5}{2}, \frac{3}{2}\}$ .

10. Serway 9.12

*Answer:*

(a) For  $n = 7$ ,  $\ell = 4$ , and  $j = 9/2$  we have  $m_s = j - \ell = +1/2$ . This is a  $7g_{9/2}$  state.

(b) For  $n = 6$  and  $\ell = 5$ , we have  $m_s = \{-1/2, +1/2\}$  so we can either have a  $6h_{9/2}$  or a  $6h_{11/2}$  state.

11. Serway 9.21

*Answer:* For problems 9.21 and 9.22, it is helpful to look at Fig. 9.15 on p. 321. It shows how it is energetically more favorable for quantum states to get filled in a way in which unpaired “up” electron spins are loaded first. This is in essence what Hund’s rules dictate. Therefore our answer is as follows:

- a. Oxygen has 8 electrons in the configuration  $1s^2 2s^2 2p^4$
- b. Orbitals are filled in energy order. To find how orbitals with the same energy are filled, we need to follow Hund’s second and third rule (which have to be satisfied in numerical order):
  2. The lowest energy atomic state is the one which maximizes the total spin  $S = \sum m_s$ . This means shells of the same energy are filled with  $m_s = +\frac{1}{2}$  first.
  3. The lowest energy atomic state is the one which maximizes the total angular momentum  $L = \sum m_\ell$ . This means if several constellations with maximum total spin  $S$  are possible, the shells with highest magnetic quantum numbers  $m_\ell$  are filled first.

This leads to the following sets of quantum numbers:

$n$	1	1	2	2	2	2	2	2
$\ell$	0	0	0	0	1	1	1	1
$m_\ell$	0	0	0	0	+1	0	-1	+1
$m_s$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

12. Serway 9.22

*Answer:* The notation of [Ar] means the electronic configuration of argon. Consulting the periodic table in the back of Serway, which lists electron configurations, we see that Ar has its last electrons in the  $3p^6$  configuration which really means  $1s^2 2s^2 2p^6 3s^2 3p^6$  giving  $2+2+6+2+6=18$  electrons which of course makes sense for Ar with  $Z = 18$ . An electron configuration of [Ar] $3d^4 4s^2$  means that  $4+2=6$  electrons are added onto the 18 electrons of Ar, so for a neutral atom we must have  $Z = 24$  or Cr (chromium). Now in a  $d$  orbital we have  $\ell = 2$  and  $m_\ell = \{-2, -1, 0, 1, 2\}$  or five possible states which can be filled in with  $m_s = +1/2$ , and in a  $s$  orbital we have  $\ell = 0$  and  $m_\ell = 0$  or only one possible state which can be filled in with  $m_s = +1/2$ . Therefore [Ar] $3d^5 4s^1$  can be filled with all  $m_s = +1/2$  spin electrons, while [Ar] $3d^4 4s^2$  must be filled with both  $m_s = +1/2$  and  $m_s = -1/2$  electrons in the  $4s$  orbital. Since the  $3d$  and  $4s$  orbitals have similar energy (see the state ordering in energy on the bottom of Serway p. 321), it turns out to be more energetically favorable (lower energy) to have [Ar] $3d^5 4s^1$ .