

CHM 3411 – Problem Set 5

Due date: Wednesday, February 20<sup>th</sup>

Do all of the following problems. Show your work.

1) In discussing the TISE for the hydrogen atom we mentioned that to get the correct value for the Rydberg constant we need to substitute  $\mu$  for  $m_e$ , where

$$\mu = \frac{m_e m_N}{(m_e + m_N)} \quad (1.1)$$

where  $m_e$  = mass of electron       $m_N$  = mass of nucleus

We can look at the error involved in using  $m_e$  instead of  $\mu$  in the following way.

a) Starting with equation 1.1, divide every term in the numerator and denominator by  $m_N$ , the mass of the nucleus.

b) Use the power series expansion

$$\frac{1}{1+r} = 1 - r + \dots \quad (1.2)$$

to substitute into your result from part a.

c) If you have done the above correctly, the first term you obtain corresponds to making the approximation  $\mu = m_e$ , and the second term is the leading order correction term in that approximation. If  $m_N \gg m_e$ , that will be the only correction term you need. Based on that, find the error introduced by using  $m_e$  instead of  $\mu$  in the expression for the Rydberg constant. Find the value for the correction term for the case  $m_N = m_p$  (the nucleus for the normal isotope of hydrogen).

d) The theoretical value for the Rydberg constant for an infinitely heavy nucleus (corresponding to  $\mu = m_e$ ) is  $R_\infty = 109737. \text{ cm}^{-1}$ , while the experimental value for the Rydberg constant (corresponding to the value found for  $\mu$  for a  $^1\text{H}$  atom) is  $R_H = 109677. \text{ cm}^{-1}$ . Show that the difference between these two values for the Rydberg constant is consistent with your answer to part c of this problem.

2) Consider the following radial function

$$R(r) = N r \exp(-r/a_0) \quad (2.1)$$

where  $a_0$  is the Bohr radius, and  $N$  is a normalization constant.

a) Find the value for  $N$  that makes  $R(r)$  a normalized radial wavefunction.

b) Using your result from part a, find the value for  $\langle r \rangle$  and  $\langle 1/r \rangle$ , the average values for  $r$  and for  $1/r$ . As a check, note that if you do this problem correctly  $\langle 1/r \rangle \neq 1/\langle r \rangle$ .

c) Using your result from part a, find the value for  $r_{mp}$ , the most probable distance between the electron and the nucleus.

3) Expressions for the normalized radial wavefunctions for hydrogen are given in Table 9A.1 of Atkins.

a) Use the information in the table to write down the normalized radial wavefunction for the  $n = 3$ ,  $\ell = 1$  state of hydrogen. Give your wavefunction in terms of  $r$  and  $a_0$ .

b) How many radial nodes are there in the  $n = 3$ ,  $\ell = 1$  state of hydrogen? Where are they located?

4) The Rydberg constant for  $^1\text{H}$  is  $R_{\text{H}} = 109677. \text{ cm}^{-1}$ .

a) Using the value for the Rydberg constant for  $^1\text{H}$  and the expression for the energy levels of a hydrogen atom, find the wavelength (in nm) where the following transitions occur.

$$n = 3 \rightarrow n = 2$$

$$n = 4 \rightarrow n = 2$$

$$n = 5 \rightarrow n = 2$$

$$n = \infty \rightarrow n = 2$$

Note that the last of these transitions corresponds to the limiting (or shortest) wavelength for which transitions of this type will occur.

b) The above series of transitions are called the Balmer series, and were the first transitions observed in the  $^1\text{H}$  atom. Suggest a reason for this.

5) The wavefunction corresponding to a  $p_x$  orbital is

$$p_x = N \sin(\theta) \cos(\phi) \tag{5.1}$$

where  $N$  is a normalization constant.

- Find the value for  $N$  that makes 5.1 a normalized  $p_x$  orbital.
- For what value(s) of  $\phi$  does  $|p_x|$  have the largest magnitude? Explain why you would expect this result.
- Is  $p_x$  an eigenfunction of  $L_x$ , the operator for the x-component of the orbital angular momentum of an electron in a hydrogen atom? If your answer is YES, give the corresponding eigenvalue.
- Is  $p_x$  an eigenfunction of  $L_z$ , the operator for the z-component of the orbital angular momentum of an electron in a hydrogen atom? If your answer is YES, give the corresponding eigenvalue.

Solutions.

1) a) 
$$\mu = \frac{m_e m_N}{(m_e + m_N)}$$

If we divide the numerator and denominator by  $m_N$ , then we get

$$\mu = \frac{m_e}{[1 + (m_e/m_N)]}$$

b) Using the power series expansion  $\frac{1}{(1+x)} = 1 - x + \dots$

$$\mu \cong m_e [1 - (m_e/m_N)]$$

c) If we use  $m_e = 9.110 \times 10^{-31} \text{ kg}$   
 $m_p = 1.673 \times 10^{-27} \text{ kg}$

$$\text{then } m_e/m_N = [(9.110 \times 10^{-31}) / (1.673 \times 10^{-27})] = 5.445 \times 10^{-4}$$

d) If we look at the difference between  $R_\infty$  and  $R_H$

$$\frac{|R_\infty - R_H|}{R_\infty} = \left| \frac{109737 \text{ cm}^{-1} - 109677 \text{ cm}^{-1}}{109737 \text{ cm}^{-1}} \right| = 5.47 \times 10^{-4}$$

a difference that is the same (to within roundoff error) as we found using the power series expansion approach.

2) a) Normalization is the requirement

$$1 = \int_0^\infty r^2 [N r \exp(-r/a_0)]^2 dr$$
$$= N^2 \int_0^\infty r^4 \exp(-2r/a_0) dr$$

The general form for this integral is

$$\int_0^\infty x^n \exp(-ax) dx = \frac{n!}{a^{n+1}}$$

So  $1 = N^2 \frac{4!}{(2/a_0)^5} = N^2 \frac{3}{4} a_0^5$ , and so  $N = (4/3a_0^5)^{1/2}$ ,  $R(r) = (4/3a_0^5)^{1/2} r \exp(-r/a_0)$

b)  $\langle r \rangle = \int_0^\infty r^2 (4/3a_0^5)^{1/2} r \exp(-r/a_0) r (4/3a_0^5)^{1/2} r \exp(-r/a_0) dr$

$$= \frac{4}{3a_0^5} \int_0^\infty r^5 \exp(-2r/a_0) dr$$
$$= \frac{4}{3a_0^5} \frac{5!}{(2/a_0)^6} = (5/2) a_0$$

$$\begin{aligned}
\langle 1/r \rangle &= \int_0^\infty r^2 (4/3a_0^5)^{1/2} (1/r) \exp(-r/a_0) r (4/3a_0^5)^{1/2} r \exp(-r/a_0) dr \\
&= \frac{4}{3a_0^5} \int_0^\infty r^3 \exp(-2r/a_0) dr \\
&= \frac{4}{3a_0^5} \frac{3!}{(2/a_0)^4} = (1/2a_0)
\end{aligned}$$

c) For  $r_{mp}$ , we need to find  $dP(r)/dr = 0 = (d/dr) r^2 [ N r \exp(-r/a_0) ]^2$

$$\begin{aligned}
&= (d/dr) N^2 r^4 \exp(-2r/a_0) \\
&= N^2 \{ 4 r^3 \exp(-2r/a_0) - (2/a_0) r^4 \exp(-2r/a_0) \} = 0
\end{aligned}$$

If we multiply both sides of this equation by  $\frac{\exp(2r/a_0)}{N^2 r^3}$

then  $4 - (2r/a_0) = 0$  So  $r_{mp} = 2 a_0$

3) a) Using the information in Table 9A.1 of Atkins, and  $\rho = (2Z/na_0) r = 2r/3a_0$  (since  $Z = 1$  for hydrogen)

Then  $R(r) = (1/486)^{1/2} (1/a_0)^{3/2} [ 4 - (2r/3a_0) ] (2r/3a_0) \exp(-r/3a_0)$

b) The number of radial nodes is # nodes =  $(n - \ell) - 1 = 1$

Nodes will occur when the wavefunction is equal to zero (other than  $r = 0$  or  $r \rightarrow \infty$ ). If we inspect the wavefunction in a, it will be equal to zero when

$$[ 4 - (2r/3a_0) ] = 0 \quad \text{or} \quad r = 6a_0$$

4) a) The energies for these transitions will be  $E(\text{cm}^{-1}) = R_H \{ (1/2)^2 - (1/n)^2 \}$

n	$\Delta E(\text{cm}^{-1})$	$\lambda$ (nm)
3	15233.	656.5
4	20564.	486.3
5	23032.	434.2
$\infty$	27419.	364.7

b) The above transitions are (mostly) in the visible region of the spectrum, and so easy to observe. Transitions terminating with  $n = 1$  are in the UV region of the spectrum, and those terminating with  $n = 3, 4,$  and  $5$  are in the IR region of the spectrum. Because of this, these transitions are more difficult to observe.

5) a) Normalization means

$$\begin{aligned}
1 &= \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi [ N \sin\theta \cos\phi ]^2 d\phi \\
&= N^2 \int_0^\pi (\sin\theta)^3 d\theta \int_0^{2\pi} d\phi (\cos\phi)^2 d\phi
\end{aligned}$$

But  $\int_0^\pi (\sin\theta)^3 d\theta = [ (-1/3) \cos\theta (\sin^2\theta + 2) ]_0^\pi = 4/3$

$$\int_0^{2\pi} d\phi (\cos\phi)^2 d\phi = \{ (\phi/2) - (1/4) \sin 2\theta \}_0^{2\pi} = \pi$$

So  $1 = N^2 (4\pi/3)$  and so  $N = (3/4\pi)^{1/2}$

b)  $\cos\phi$  has its largest magnitude at  $\phi = 0$  and  $\phi = \pi$ . I would expect this as this is a  $p_x$  orbital, and so should lie along the x-axis.

c) To test this we use the eigenvalue equation

$$\begin{aligned} L_x p_x &= (\hbar) \left[ \sin\phi \frac{\partial}{\partial\theta} + (\cos\theta/\sin\theta) \cos\phi \frac{\partial}{\partial\phi} \right] [ N \sin\theta \cos\phi ] \\ &= (\hbar) \left\{ \sin\phi N \cos\theta \cos\phi - (\cos\theta/\sin\theta) \cos\phi N \sin\theta \sin\phi \right\} = 0 \end{aligned}$$

So an eigenfunction with eigenvalue = 0.

d) We can again test this using the eigenvalue equation

$$L_z p_x = (-\hbar) \frac{\partial}{\partial\phi} [ N \sin\theta \cos\phi ] = (-\hbar) [ -N \sin\theta \sin\phi ] \neq (\text{constant}) [ N \sin\theta \cos\phi ]$$

So  $p_x$  is not an eigenvalue of  $L_z$ .