The Richard Stockton College of New Jersey

Chemistry Program, School of Natural Sciences and Mathematics

PO Box 195, Pomoma, NJ

CHEM 3420: Physical Chemistry II — Spring 2009

Homework 5 — Solutions

1. The $2s$ and $2p$ orbitals have the same number of nodes (1 radial for $2s$ and 1 angular for $2p$) so that is not a reason for the difference in energy. If you take a look at the radial distribution function for each orbital (from the notes or text) you see that the $2s$ orbital has a finite probability of finding the electrons in a region close to the nucleus. It is for this reason that the $2s$ orbital has a slightly lower energy than the $2p$ orbital in boron.

2. To determine the symmetry of the complete wave function it is useful to consider the spatial and spin parts separately. If by exchanging the position of electron 1 and 2 the function switches sign it is antisymmetric. If after exchange the function is unchanged it is symmetric. If it results in a completely different wave function we say it is not symmetric.

   (a) $[\psi_{1s}(1)\psi_{2s}(2)+\psi_{2s}(1)\psi_{1s}(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)] = $ -1 $*[\psi_{1s}(2)\psi_{2s}(1)+\psi_{2s}(2)\psi_{1s}(1)][\alpha(2)\beta(1)-\beta(2)\alpha(1)]$ and is antisymmetric.

   (b) $[\psi_{1s}(1)\psi_{2s}(2)+\psi_{2s}(1)\psi_{1s}(2)]\alpha(1)\alpha(2) = [\psi_{1s}(2)\psi_{2s}(1)+\psi_{2s}(2)\psi_{1s}(1)]\alpha(2)\alpha(1)$ and is symmetric

   (c) $[\psi_{1s}(1)\psi_{2s}(2)+\psi_{2s}(1)\psi_{1s}(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)] = [\psi_{1s}(2)\psi_{2s}(1)+\psi_{2s}(2)\psi_{1s}(1)][\alpha(2)\beta(1)+\beta(2)\alpha(1)]$ and is symmetric

   (d) $[\psi_{1s}(1)\psi_{2s}(2)-\psi_{2s}(1)\psi_{1s}(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)] = [\psi_{1s}(2)\psi_{2s}(1)-\psi_{2s}(2)\psi_{1s}(1)][\alpha(2)\beta(1)-\beta(2)\alpha(1)]$ Since both terms flip sign, the overall wave function remains the same on exchange and thus is symmetric

3. For this problem, it was necessary to calculate the reduced mass for the hydrogen and tritium atom and use it in the given formula. This improves on the calculations we performed in class by using the true mass of the "two-body problem" (the nucleus and the electron)

$$\mu_H = \frac{9.1094\times10^{-31}\ kg)(1.6726\times10^{-27}\ kg)}{9.1094\times10^{-31}\ kg + 1.6726\times10^{-27}\ kg} = 9.10444\times10^{-31}\ kg$$

$$\mu_T = \frac{9.1094\times10^{-31}\ kg)(5.0074\times10^{-27}\ kg)}{9.1094\times10^{-31}\ kg + 5.0074\times10^{-27}\ kg} = 9.10774\times10^{-31}\ kg$$

So you can immediately see that our approximation ($\mu \approx m_e$) is okay, but not perfect.

For the energies of the hydrogen atom ($Z = 1$):

$$E_H(n) = \frac{\mu e^4}{32\pi^2\epsilon_o^2\hbar^2n^2} = \frac{(9.10444\times10^{-31}\ kg)(1.6021773\times10^{-19}\ C)^4}{32\pi^2(8.8541878\times10^{-12}\ C^2/Jm)^2(1.0544573\times10^{-34}\ Js)^2n^2}$$

$$E_H(n) = \frac{2.17869\times10^{-18}\ J}{n^2}$$

Similarly, using the reduced mass of tritium the following expression is obtained:

$$E_T(n) = \frac{2.17948\times10^{-18}\ J}{n^2}$$

The energy of a transition is related to a frequency of emitted light through Plank's relationship:

$$\Delta E = h\nu$$

So for each atom:

$$\nu_H = \frac{\Delta E}{h} = \frac{2.17869 \times 10^{-18}\ J}{6.6260755 \times 10^{-34}\ Js} \left(\frac{1}{1^2} - \frac{1}{4^2} \right) = 3.08255 \times 10^{15}\ s^{-1}$$

$$\nu_T = \frac{\Delta E}{h} = \frac{2.17948 \times 10^{-18}\ J}{6.6260755 \times 10^{-34}\ Js} \left(\frac{1}{1^2} - \frac{1}{4^2} \right) = 3.08367 \times 10^{15}\ s^{-1}$$

This amounts to a small frequency difference, but it is an observable one.

The transition can only be from $1s \rightarrow 4p$ since it is the only one of the three transitions listed that satisfy the selection rule of $\Delta l = \pm 1$.