UNIVERSITY OF THE WEST INDIES
DEPARTMENT OF CHEMISTRY
C10J ATOMIC STRUCTURE (Tutorial #2 : Solutions) **Updated: (Sept. 2005)**

1. The Rydberg equation is of the form $\Delta E = hcR_H\left(\frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2}\right)$, where $n_{initial}$ corresponds to the energy level of origin, and n_{final}, to the destination energy level. The sign of ΔE (i.e. +ve or –ve) indicates whether energy is absorbed or emitted, respectively.

$\Delta E = hcR_H (1/1^2 - 1/2^2)$
$= (6.626 \times 10^{-34}$ J s) x $(2.998 \times 10^{10}$ cm s^{-1}) x (109,678 cm^{-1}) x (1 – ¼)
$= 2.179 \times 10^{-18}$ J x (¾)
= **1.635×10^{-18} J**

Note that the units are shown in the calculations. This is good practice, as the units an answer can indicate if you are on the right track. Also, the units of the different terms must be compatible: e.g. the speed of light is converted to **cm s^{-1}** since the Rydberg constant is expressed in **cm^{-1}**, **cm** and **cm^{-1}** will therefore cancel.
N.B. :(wavenumber, $\bar{\nu}$ has units of **cm^{-1}** whereas frequency**,** ν has units of **s^{-1})**

2. $E = hcR_H (1/n^2 - 1/m^2) = hcR_H(1/1^2 - 1/\infty^2) = 2.179 \times 10^{-18}$ J = **13.6 eV**.

The unit of the electronvolt (eV) is another convenient way of expressing energy. In fact, eV = the electronic charge, e multiplied by volts (V) = $(1.602 \times 10^{-19}$ C) x (V) = $(1.602 \times 10^{-19}$ **CV**), 1 CV is equivalent to 1 J. Therefore, 1 J is equivalent to 1.602×10^{-19} eV. Conversion of J to eV is brought about by dividing the energy quantity in Joules by the electronic charge e.

3. (a) $\lambda = h/p = h/mv = (6.626 \times 10^{-34}$ J s)/(9.109×10^{-31} kg x 0.5 x 2.998×10^{8} m s^{-1}) = **4.85×10^{-12} m**.

(b) $\lambda = h/p = h/mv = (6.626 \times 10^{-34}$ J s)/(60.0 kg x 10.0 m s^{-1}) = **1.10×10^{-36} m**

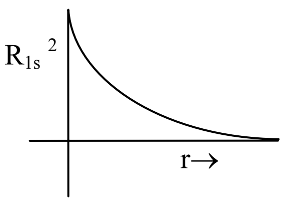
The diameter of the H-atom is ~ 1 Å ($=10^{-10}$ m) which makes the wavelength in (a) more meaningful. Wave properties of an object become important (significant) when the magnitude of the de Broglie wavelength that is associated with the object in question is comparable to the dimensions of the region of space in which the object is confined (bounded). The man's wavelength is ~ 10^{-36} m! Obviously the man cannot be confined in a space that is so small.

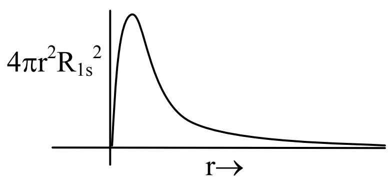
4&5. Ψ can be separated into two parts, an angular wavefunction Y, and a radial wavefunction R.

$$\Psi = R \cdot Y$$

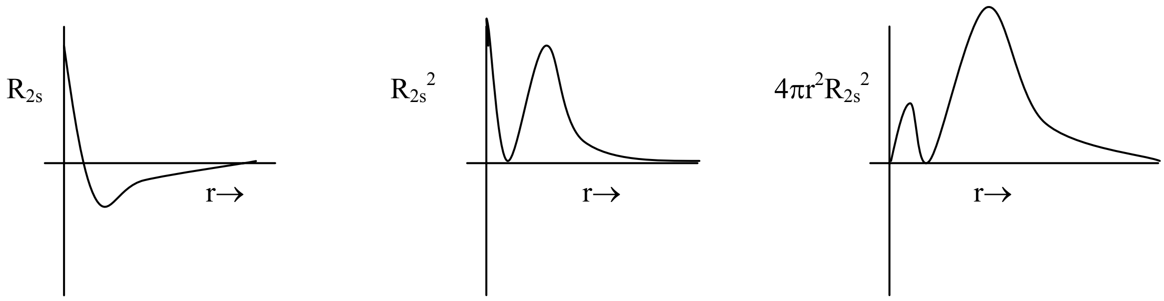
R^2 gives information about the variation (distribution) of electron density (in an orbital) with distance from the nucleus, and Y gives information about the region of space (shape) where this electron density is found.

For **1s**,

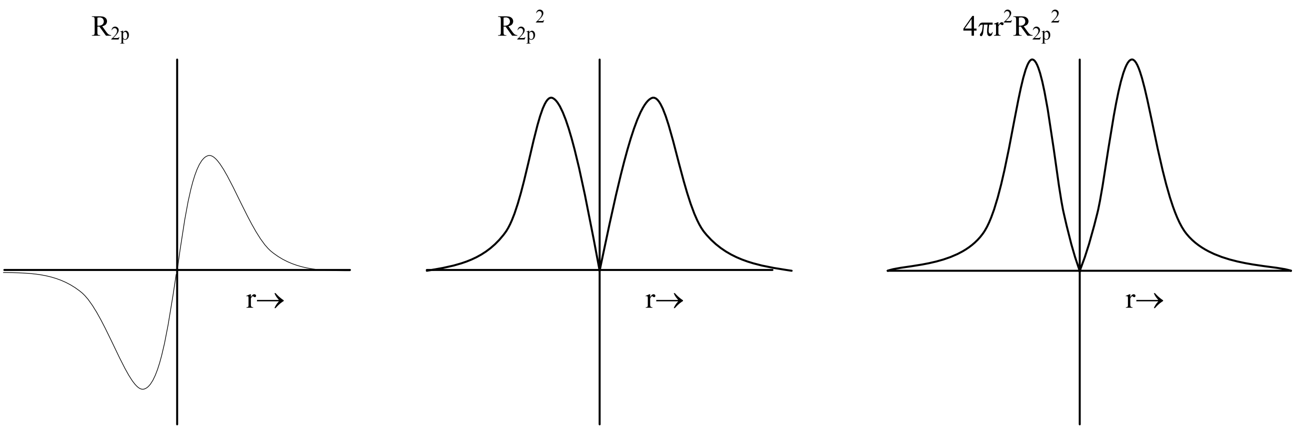




For **2s**



For **2p**,



The Radial Distribution Function (RDF), $4\pi r^2 R^2$, gives a more correct view of the average electron density distribution about the nucleus. $4\pi r^2$ is the area of a sphere of radius r. $4\pi r^2 R^2$ can be viewed as the total electron density on the surface of a sphere of radius r (i.e. this is an average taken in all directions around the nucleus at a fixed distance r). So, the RDF give s view of the variation of the electron density on the surface of a sphere

6. $\langle r \rangle = n^2\{1 + \frac{1}{2}[1 - l(l + 1)/n^2\}(a_o/Z)$

For the **3s** orbital n = 3, and l = 1. Z = 1 for hydrogen.

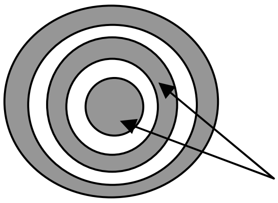
$\therefore \langle r \rangle_{3s} = 3^2\{1 + \frac{1}{2}(1 - 0)\}a_o = 9(3/2)\ a_o = (27/2)a_o$.

For the **3p** orbital n = 3 and l = 1.

$\therefore \langle r \rangle_{3p} = (25/2)a_o$.

Point out the effect of a higher nuclear charge. i.e. the stronger the attraction for the electrons the smaller the orbital size

The reason why the average radius for the 3s orbital is larger is due to the shielding of the outer portions of the 3s orbital by the inner core (of the same 3s orbital).



Inner core provides shielding of the outer core from full force of nucleus

7. The hydrogenic radial wave function for the **1s** orbital is

$$R_{1s} = 2(Z/a_o)^{3/2} e^{-(1/2)\rho}, \text{ where } \rho = 2Zr/na_o.$$

For the hydrogen 1s orbital, Z = 1 and n = 1. The pre-exponential term, $2(Z/a_o)^{3/2}$, is a constant and has a value of **5.20 x 10^15^** with a_o = 0.5292 Å = 5.292x 10^{-11} m. For the sake of plotting the graph we will ignore the 10^{15}.

The index of the exponential, $-\frac{1}{2}\rho = -\frac{1}{2}(2Zr/na_o) = -r/a_o$. So for the different values of r the following results were obtained:

r/a_o	0	0.2	0.4	0.6	0.8	1.0	1.2
R_{1s}	5.20	4.25	3.48	2.85	2.33	1.91	1.56

And the graph of R_{1s} against r is