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## Workshop #9: The Atomic Spectrum of Hydrogen

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Emission and absorption spectra of hydrogen gave experimental evidence of quantized energy states for electrons within an atom. Niels Bohr tried to explain the observations with the first quantum theory in 1913.

Bohr's Quantum Theory: explains the emission and absorption spectra

1. An atom has discrete energy levels (orbits), where an electron may exist without emitting or absorbing electromagnetic radiation.
2. An electron may move from one orbit to another. By doing so, the electromagnetic radiation is absorbed or emitted.
3. An electron moves in circular orbits about the nucleus, and the energy of the electron is quantized.

Limitation: Bohr's theory works only for an atom or ion containing one electron.

According to this quantum theory, electrons within atoms can only exist in certain states, each of which has an associated fixed amount of energy. When an electron changes its state, it must absorb or emit an amount of energy equal to the difference between the energy of the initial and final states. This energy may be absorbed or emitted in the form of electromagnetic energy (i.e. infrared, visible, or ultraviolet light), in which case the relationship between the change in energy and the wavelength of the light which is associated with the transition is given by the equation:

$$|\Delta E| = \frac{hc}{\lambda} \quad (1)$$

where  $|\Delta E|$  is the absolute value of the change in energy in joules,  $h$  is Planck's constant,  $6.6262 \times 10^{-34}$  J·sec,  $c$  is the speed of light,  $3.00 \times 10^8$  m / sec, and  $\lambda$  is the wavelength. The change in energy,  $\Delta E$ , of the atom is positive if light is absorbed and negative if it is emitted.

Atomic and molecular spectra are the result of changes in energy which occur in atoms and molecules when they are excited. The emission spectrum of an atom gives us information about the spacing between the allowed energy levels of that atom. The different wavelengths present in the light can be used to establish the energy levels available to the atom. Conversely, given the set of energy levels for an atom, one can predict its atomic spectrum and determine which levels were involved in any observed line in the spectrum.

Ordinarily, an electron will occupy its lowest energy state, called the ground state. If the atom is excited, the electron which is now in a higher energy state will be unstable and will quickly make a transition back down to its ground state. In making the transition, the energy of the atom may be radiated as light.

The simplest atomic spectrum is that of the *hydrogen atom*. In 1886, Balmer showed that the lines in the spectrum of the hydrogen atom had wavelengths that could be expressed by a rather simple equation. In 1913, Bohr explained the spectrum on a theoretical basis with his famous model of the hydrogen atom. According to Bohr's theory, the energies  $E_n$  allowed to a hydrogen atom are all given by the following equation:

$$E_n = \frac{-B}{n^2} \quad (2)$$

where B is the constant,  $2.178 \times 10^{-18}$  J and n is an integer, 1, 2, 3, ..., called a quantum number. It has been found that all the lines in the atomic spectrum of hydrogen can be associated with differences between atomic energy levels which are predicted with great accuracy by Bohr's equation.

There are several ways in which one might analyze an atomic spectrum, given the energy levels of the atom, but a simple and powerful method is to calculate the wavelengths of some of the lines that are allowed and see if they match those which are observed. We shall use this method in our workshop.

### A. Energy Levels of Hydrogen

Given the expression for  $E_n$  in Equation 2, calculate the energy (in joules) for each of the levels of the H atom missing in the table below. Notice that the energies are all negative, so that the lowest energy will have the largest allowed negative value. Enter these values in the table of energy levels below:

Table One

Quantum Number	Energy, $E_n$ , in joules	Quantum Number	Energy, $E_n$ , in joules
1	$-2.178 \times 10^{-18}$ J	6	
2		7	
3		8	
4		10	$-2.178 \times 10^{-20}$ J
5		$\infty$	ZERO Joules

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**B. Calculation of Wavelengths in the Spectrum of the Hydrogen Atom**

The lines in the hydrogen spectrum all arise from jumps made by the atom from one energy level to another. The wavelengths in nanometers of these lines can be calculated by Equation 1, where  $|\Delta E|$  is the positive difference in energy between any two allowed levels. By rearranging Equation 1 it is possible to solve for wavelengths:

$$\lambda = \frac{hc}{|\Delta E|} \quad (3)$$

After putting in some constants we can solve for wavelength in nanometers.

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{sec})(3.00 \times 10^8 \text{ m / sec})}{|\Delta E|} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} \quad (4)$$

Calculate the  $|\Delta E|$  and wavelength for all the jumps indicated in the table below. Write  $|\Delta E|$ , the difference in energy in J between  $E_{n,hi}$  and  $E_{n,lo}$ , in the upper half of the box, and in the lower half of the box, write the  $\lambda$  (in nm) associated with that value. The box for the  $n_2 \rightarrow n_1$  transition is filled in for you.

Table Two

$n_{\text{higher}}$ $n_{\text{lower}}$	6	5	4	3	2	
1					$1.634 \times 10^{-18}$	$ \Delta E $ (J)
					121.6	$\lambda$ (nm)
2					$ \Delta E $ (J)	
					$\lambda$ (nm)	
3				$ \Delta E $ (J)		
				$\lambda$ (nm)		
4			$ \Delta E $ (J)			
			$\lambda$ (nm)			
5		$ \Delta E $ (J)				
		$\lambda$ (nm)				

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**C. Assignment of Wavelengths**

Compare the wavelengths you have calculated in Table Two with those listed in Table Three. You should notice that many wavelengths match within the error of your calculation. Fill in the quantum numbers of the upper and lower states for each line whose origin you can recognize by comparison of your calculated values with the observed values. Several wavelengths will not match at all; place those in Table Four and estimate the expected  $n_{hi} \rightarrow n_{lo}$  following the trends. Note that Table Two only covers transitions with  $n_{hi}$  less than or equal to six. Check your estimations by solving for  $\Delta E$  and wavelengths as you did on Table Two using  $n_{hi}$  numbers greater than six.

Table Three

Wavelength	$n_{hi} \rightarrow n_{lo}$	Wavelength	$n_{hi} \rightarrow n_{lo}$	Wavelength	$n_{hi} \rightarrow n_{lo}$
97.25		410.17		1,005.0	
102.57		434.05		1,093.8	
121.57	2 $\rightarrow$ 1	486.13		1,281.8	
388.91		656.28		1,875.1	
397.01		954.62		4,050.0	

Table Four: Wavelengths you cannot assign using Table Two data

Observed Wavelength (in nm)	Predicted transition $n_{hi} \rightarrow n_{lo}$	Calculated $\Delta E$ (in J)	Calculated Wavelength $\lambda$ (in nm)
388.91			

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**D. The Balmer Series**

When Balmer formulated his famous series for hydrogen in 1886, he was limited experimentally to wavelengths for the visible and near ultraviolet regions from 250 nm to 700 nm. All the lines in his series lie in this wavelength range. All transitions in the Balmer Series have  $n_{\text{final}} = 2$ .

1. What would be the longest POSSIBLE wavelength for a line in the Balmer Series?

\_\_\_\_\_ nm

2. What would be the shortest POSSIBLE wavelength for a line in the Balmer Series?

\_\_\_\_\_ nm

In a normal hydrogen atom, the electron is in the *lowest* energy state. The maximum energy of an electron in the hydrogen atom is 0 J, at which point the electron is in the  $n = \infty$  state, essentially removed from the atom. At this point, ionization has occurred.

3. How much energy in joules does it take to ionize the hydrogen atom?

\_\_\_\_\_ J

4. The ionization energy you have calculated is for one electron in a single hydrogen atom. Calculate the ionization energy for one mole of H atoms.

SHOW CALCULATIONS:

\_\_\_\_\_ kJ / mole

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**E. Energy Levels of Hydrogen Atom**

Show each of the first six lowest energy states in the chart below using the values from Table One. Draw horizontal lines for each level and identify them by writing its quantum number on the right side. Use vertical arrows to show the electron transitions calculated in Table Three.

**F. Hydrogen Line Spectra**

Draw the line spectra for hydrogen as it would appear in the visible region showing the lines calculated in Table Three within the Balmer Series.

