

Lecture 32 CH101 A1 (MWF 9:05 am) Fall 2017 Copyright © 2017 Dan Dill dan@bu.edu

[TP] Which energy change has the smallest  $E_{\text{photon}}$ ?

25% 1. H:  $n = 1 \rightarrow 2$   
25% 2. H:  $n = 2 \rightarrow 6$   
25% 3. He<sup>+</sup>:  $n = 1 \rightarrow 2$   
25% 4. He<sup>+</sup>:  $n = 2 \rightarrow 3$

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Lecture 32 CH101 A1 (MWF 9:05 am)  
Wednesday, November 29, 2017

For today ...

- H atom energy diagrams: Beyond Balmer's formula
- H, He<sup>+</sup>, Li<sup>2+</sup>, etc., photon energies

Next lecture: Ionization (photoelectric effect); Review: Lewis structures, formal charge and oxidation number; Review: Electron clouds; More than one electron: Orbital (yikes!) approximation

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H atom photon energies: Beyond Balmer's formula

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H atom photon energies: Beyond Balmer

Sketch the H atom energy diagram and include the energy-change arrows corresponding to the red and violet lines of the emission spectrum.

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## H atom photon energies: Beyond Balmer

Balmer's formula always involves  $E_2 = -\frac{Ry}{2^2}$ .

What about extending the formula in terms of  $E_1 = -\frac{Ry}{1^2}$ , as

$$\Delta E_{\text{light}} = E_{\text{photon}} = \frac{hc}{\lambda} = \left| -\frac{Ry}{1^2} + \frac{Ry}{n^2} \right| = Ry \left( \frac{1}{1^2} - \frac{1}{n^2} \right), n = 2, 3, 4, 5, \dots, \infty ?$$

Where in the spectrum would absorption  $n = 1 \rightarrow 2$  be?

$\lambda = 121 \text{ nm}$ , so in the UV.

It turns out this "line" is there!



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## H atom photon energies: Beyond Balmer

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Where in the spectrum would absorptions  $n = 1 \rightarrow 3, 4$ , etc., be?

$\lambda < 121 \text{ nm}$ , so also in the UV.

It turns out the "lines" are there!



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## H atom photon energies: Beyond Balmer

What about extending the formula in terms of  $E_3 = -\frac{Ry}{3^2}$ , as

$$\Delta E_{\text{light}} = E_{\text{photon}} = \frac{hc}{\lambda} = \left| -\frac{Ry}{3^2} + \frac{Ry}{n^2} \right| = Ry \left( \frac{1}{3^2} - \frac{1}{n^2} \right), n = 4, 5, 6, 7, \dots, \infty ?$$

Where in the spectrum would lines given by this formula occur?

In the IR.

It turns out the lines are there!



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## H atom photon energies: Beyond Balmer

In a similar way, H atom electron cloud motion occurs for all combinations

$$n \rightarrow n + 1, n + 2, \dots$$

$$\Delta E_{\text{light}} = E_{\text{photon}} = \frac{hc}{\lambda} = \left| -\frac{Ry}{n^2} + \frac{Ry}{n'^2} \right| = Ry \left( \frac{1}{n^2} - \frac{1}{n'^2} \right), n' = n + 1, n + 2, \dots$$

For example, the series of lines for combinations  $n = 4 \rightarrow 5, 6, 7, \dots$ , occurs in the **microwave region** of the spectrum.

Etc.



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H, He<sup>+</sup>, Li<sup>2+</sup>, etc., photon energies

The H atom expressions for  $E_{\text{photon}}$  also work for all **one-electron ions**, when multiplied by the **square of the nuclear charge** of the ion.

For He<sup>+</sup>,  $Z = 2$ ; for Li<sup>2+</sup>,  $Z = 3$ ; etc.

$$E_{\text{photon}} = \frac{hc}{\lambda} = \text{Ry } Z^2 \left( \frac{1}{1^2} - \frac{1}{n^2} \right), n = 2, 3, 4, \dots$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \text{Ry } Z^2 \left( \frac{1}{2^2} - \frac{1}{n^2} \right), n = 3, 4, 5, \dots$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \text{Ry } Z^2 \left( \frac{1}{3^2} - \frac{1}{n^2} \right), n = 4, 5, 6, \dots$$

etc.



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H, He<sup>+</sup>, Li<sup>2+</sup>, etc., photon energies

**Practice:** What is  $E_{\text{photon}}$  and the corresponding **wavelength** and **spectral region** for He<sup>+</sup>  $n = 3 \rightarrow 5$  absorption?

$$E_{\text{photon}} = \text{Ry } 4 \left( \frac{1}{9} - \frac{1}{25} \right) = \text{Ry} \times 0.284$$

$$\lambda_{\text{photon}} = \frac{hc}{E_{\text{photon}}} = \frac{hc}{\text{Ry } 0.284} = 321 \text{ nm}$$

**UV region**



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H:  $n = 1 \rightarrow 2, \lambda = 121 \text{ nm}$

H:  $n = 2 \rightarrow 6, \lambda = 410 \text{ nm (violet)}$

He<sup>+</sup>:  $n = 1 \rightarrow 2, \lambda = 30.3 \text{ nm}$

He<sup>+</sup>:  $n = 2 \rightarrow 3, \lambda = 164 \text{ nm (1/4 of H: } n = 2 \rightarrow 3, 656 \text{ nm)}$



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