Why did it take over 60 years for scientists to explain the atomic emission spectrum of Hydrogen? Why do we expect our students to understand the explanation in 30 minutes or less?

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How should the atomic emission spectrum of hydrogen fit into the larger story of the atom?

My plan:
• Brief overview of historical path to discovery with emphasis on work of Niels Bohr:
  • How is Bohr’s work treated (or mistreated) in textbooks?
  • An alternate approach to consider.
The Path to Discovery

Observation of discrete emission (line spectra) from gas discharge tubes ~1859

Balmer's equation 1885

Boltzmann's equation

Rydberg's equation 1888

Einstein accounts for the photoelectric effect in terms of light quanta: 

Plank accounts for black body radiation in terms of light quanta: 

Rutherford's nuclear model of the hydrogen atom with discrete energy levels.

Bohr's model of the hydrogen atom with discrete energy levels.

1901 1911 1913

1905

Wave equation derived and solved for the hydrogen atom. (Schrödinger)

1926

1911~1859 1885 1888 1901 1905 1911 1913 1926

Why are only specific wavelengths emitted in an observed pattern?

Balmer's equation:

Ryderberg Equation:

\[
\frac{1}{\lambda} = R_n \left( \frac{1}{n^2} - \frac{1}{m^2} \right)
\]

\[
\frac{1}{\lambda} = R_n \left( \frac{1}{m^2} - \frac{1}{n^2} \right)
\]

wavelength, \( \lambda \) (nm)

and more series ->

Difference between two terms

m, n = 1, 2, 3, 4... and \( n > m \)
What was missing?

According to classical physics the energy of light is related to the intensity (wave amplitude), and not the wavelength or frequency.

But this changed:

• Planck (1901), from his study of blackbody radiation, concluded the energy of the emitted light is quantized according to: $E = \tau h \nu'$, where $\nu'$ is a frequency of oscillation ('an atomic vibrator'), $h$ is a constant, and $\tau$ is a positive integer 1, 2, 3...

• Einstein (1905), from his study of the photoelectric effect, concluded that the energy of a single light particle is proportional to the frequency of the light according to: $E_{\text{photon}} = h \nu$
How is Bohr’s work treated (or mistreated)* in textbooks?

A. “Rigorous approach” (still used in P. Chem. & Physics texts)

\[ F_{es} = F_{ca} \]  
\[ mvr = \frac{\tau \hbar}{2\pi} \]  
\[ E_n = -\frac{e^4 m_e}{8\varepsilon^2 n^2 \hbar^2} \]  
\[ \text{where } n = 1, 2, 3... \]

B. “Modern approach”

- present a simplified equation without derivation
  \[ E_n = \frac{-2.18 \times 10^{-18} J}{n^2} \]
- relate observed emission lines to transitions between allowed states or orbits

The reconstructed derivation is problematic:
1. There is no apparent justification for the angular momentum assumption other than it leads to an expression that correctly predicts emission wavelengths.
2. It also ignores Bohr’s use of Planck’s work. Planck’s \( \tau \) is the source of Bohr’s quantum number!

In neither approach is the startling conclusion that the energy of the atom is restricted to specific allowed values (quantized) related to the earlier startling discovery of the particle nature of light.


Is there a more direct and compelling connection between atomic line spectra and the quantization of an atom’s energy?

For simplicity and improved rigor:

- Separate the two problems that Bohr was trying to solve:
  i. Where is the electron in the hydrogen atom and what is it doing?
  ii. Why do excited hydrogen atoms emit only specific wavelengths of light?

- First, demonstrate rigorously that the line spectrum of hydrogen requires that the energy of the atom be quantized, and derive an equation for the allowed energies.

- Then follow-up with the question of electron arrangement and behavior (Bohr & DeBroglie), and then the deeper question of why must the energy be restricted to discrete values (Schrödinger et al).

The implications of the hydrogen line spectrum – a more direct, yet rigorous, approach.

1. Starting point: Balmer/Rydberg empirical equation

\[ \frac{1}{\lambda} = R_e \left( \frac{1}{m^2} - \frac{1}{n^2} \right) \text{ where } m,n = 1,2,3,4... \text{ and } n > m \]

2. Use Einstein’s equation from his explanation of the photoelectric effect to rewrite the Rydberg equation in terms of photon energy:

\[
\frac{1}{\lambda} = R_e \left( \frac{1}{m^2} - \frac{1}{n^2} \right) \text{ where } R_e \text{ is } 1.097 \times 10^7 \text{ m}^{-1} \text{ and } m,n = 1,2,3,4... \text{ with } n > m
\]

becomes \[ E_{\text{ph}} = \frac{hc}{\lambda} = \frac{h c R_e}{m^2} \left( \frac{1}{m^2} - \frac{1}{n^2} \right) = \frac{hcR_e}{m^2} - \frac{hcR_e}{n^2} \]

The two terms have units of energy

Continued...

3. Apply energy conservation for emission: \[ E_{\text{photon}} = \Delta E_{\text{atom}} = E_{\text{initial}} - E_{\text{final}} \]

   • Assign the corresponding energy terms in the rewritten Rydberg equation to:

   \[
   E_{\text{initial}} = \frac{hcR_e}{m^2} \quad E_{\text{final}} = \frac{hcR_e}{n^2}
   \]

4. What type of energy are we talking about? What kind(s) of energy would be expected to exist in a hydrogen atom with a positive nucleus and an electron?

   • If electrostatic potential energy dominates, then energy terms must be negative.

   • What can be done to get a difference between two negative terms?

   \[
   E_{\text{ph}} = \frac{hcR_e}{m^2} - \frac{hcR_e}{n^2} \quad \text{or} \quad E_{\text{ph}} = \frac{-hcR_e}{n^2} - \frac{-hcR_e}{m^2}
   \]

   • Then with conservation of energy

5. Finally, generalize

\[
E_{n} = \frac{-hcR_e}{n^2} \text{ with } n = 1,2,3...\infty
\]
How should the atomic emission spectrum of hydrogen fit into the larger story of the atom?

- Line spectrum of hydrogen: \( \frac{1}{\lambda} = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right) \)
- Conservation of Energy: \( E_{\text{photon}} = \Delta E_{\text{atom}} = E_{\text{initial}} - E_{\text{final}} \)
- Einstein (photoelectric effect): \( E_{\text{photon}} = h \nu \)
- Energy of H atom restricted (quantized): \( E_n = -\frac{hcR}{n^2} \)
- \( E_{\text{atom}} \leq 0 \)

Why?
- Question of electron arrangement/behavior: credit Bohr (planetary model & energy states)
- DeBroglie (wave nature)
- Schrödinger (Quantum Theory)