

Understanding Atomic Structure: Is There a More Direct and Compelling Connection between Atomic Line Spectra and the Quantization of an Atom's Energy?

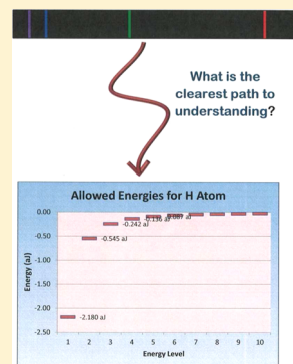
Robert C. Rittenhouse*

Department of Chemistry, Central Washington University, Ellensburg, Washington 98926, United States

S Supporting Information

ABSTRACT: The “atoms first” philosophy, adopted by a growing number of General Chemistry textbook authors, places greater emphasis on atomic structure as a key to a deeper understanding of the field of chemistry. A pivotal concept needed to understand the behavior of atoms is the restriction of an atom's energy to specific allowed values. However, the historical progression of discoveries and ideas that led to this understanding is often confusing to beginning chemistry students due to the number and nature of the concepts that must be logically connected to create a navigable path to understanding. The author suggests a more direct approach that relies on fewer concepts, yet is rigorous in forging the necessary logical and mathematical connections that lead from the hydrogen line spectrum to the inevitable conclusion that the energy of the atom is quantized. A critical thinking exercise that guides students through the derivation and application of the hydrogen atom energy equation has been tested, with encouraging results.

KEYWORDS: First-Year Undergraduate/General, Physical Chemistry, Curriculum, Textbooks/Reference Books, Misconceptions/Discrepant Events, Atomic Properties/Structure, Atomic Spectroscopy



One indication of an increased appreciation for the importance of atomic structure as a cornerstone of the chemical sciences is the growing number of General Chemistry textbooks adopting the “atoms first” approach.^{1–5} At least part of the expressed motivation for this trend is simple logic. If all the matter that surrounds us is constructed of atoms and the properties and behavior of matter can ultimately be explained in terms of the structure of the atom, then why not begin there and work forward to account for chemical bonding, molecular structure, reactivity, and far more? But what does it mean to understand the atom? The story of the atom is a vast and fascinating tale—fascinating only to those who are able to understand the story. What parts of this story do General Chemistry students need to comprehend as an essential foundation for topics to come later in their chemistry experience? Naturally, textbooks and instructors take a variety of perspectives that place more or less value on factual information, understanding of concepts, appreciation of the history and process of science, and so forth. Those of us for which conceptual understanding is a high priority find that many students struggle with this topic because (a) a large number of concepts must be integrated and logically connected and (b) many of the concepts are abstract and inconsistent with everyday experience.

Previous papers in this Journal^{6–8} have presented flowcharts of discoveries and ideas that led to our current understanding of the atom. These flowcharts portray the logical connections among a dozen or more key topics ranging from the discoveries of the subatomic particles through to the application of wave

mechanics. All together, this information presents something of a maze to the novice chemistry student and raises the issue of how much guidance is called for. How explicitly should the connections be demonstrated? A rapid progression through a list of discoveries and theoretical developments may seem, to the student, something akin to opening a gift box containing a new bicycle in the form of dozens of separate parts along with a small note that says “some assembly required”. Would it be possible to present the student with fewer parts and clearer instructions?

Certainly, one of the key milestones in the quest to understand the atom was the discovery that the energy contained in an atom is quantized, that is, restricted to specific values. Thus, energy cannot be lost or gained by atoms in arbitrary amounts as observed in the behavior of objects we work with in everyday life. When this concept is presented, it is difficult, if not impossible, for students to appreciate the importance of this discovery or imagine all of its implications and applications. The compelling evidence for discrete energy levels in atoms was the observation of atomic line spectra, specific frequencies of light emitted or absorbed by atoms of elements in the gaseous state.

THE HISTORICAL PATH TO DISCOVERY

Atomic line spectra, unique to each element, stood as an unsolved mystery for at least half a century. Even after Balmer⁹ and later Rydberg presented empirical expressions for the

pattern of line frequencies observed in the hydrogen emission spectrum, it was another 28 years before Niels Bohr accounted for the hydrogen line spectrum by deriving an equation for the allowed values of the atom's total energy, W

$$W_{\tau} = \frac{2\pi^2 m e^4}{\tau^2 h^2} \quad (1)$$

where m is the mass of the electron, e is the magnitude of the charge on the electron and the nucleus, h is Planck's constant, and τ is restricted to positive integer values.¹⁰

It may be helpful to ponder why it took it the great physicists of the time so long to solve this mystery. In hindsight, the implication of discrete emission and absorption frequencies in terms of discrete atomic energy states seems obvious to the trained chemist or physicist. We must remember, however, that prior to Planck's explanation of blackbody radiation in 1901, scientists were unaware of any link between the frequency and the energy of light.¹¹ The frequency of emitted light was thought to be somehow related to an oscillation or vibration occurring within the atom, for example, electron vibration.¹²

For students to better understand the importance of the discovery of discrete atomic energy states and its implications, students need to grasp the discovery itself. What is the simplest, most direct, yet rigorous, pathway that leads from the evidence to this important conclusion? If this pathway differs from the historical pathway, we are simply taking advantage of hindsight to promote clarity, as in many other instances. When choosing this route, it should be made clear to students that we're not recounting history. By comparing what seems in hindsight to be the clearest path to a discovery with the actual historical path to the discovery, students gain insight into the process of science and the individuality of famous scientists like Niels Bohr.

Nearly all General Chemistry textbooks give Bohr credit for the discovery of quantized atomic energy and for solving the long-standing mystery of atomic line spectra, but they vary greatly in their description of his contribution. As Blanca Haendler aptly pointed out,⁸ textbook authors have generally misrepresented Bohr's work, as described in his seminal paper,¹⁰ in order to simplify the story in the interest of student understanding. Bohr's model of the hydrogen atom was a planetary model based on the notion of stable orbits where electrostatic attraction is exactly balanced by centripetal acceleration, and the electron is necessarily exempted from radiating energy as any accelerating charged object is expected to behave according to the laws of classical electrodynamic theory. Because a stable orbit of this type is possible at any radius, the problematic portion of the story is how Bohr determined that only certain specific orbits with specific radii and energies were allowed.

In Bohr's paper,¹⁰ the allowed orbits were obtained by applying Planck's equation for the energy of light radiated from a blackbody oscillator of any specific frequency ν as $\tau h\nu$, where τ is a positive integer and h is the famous Planck's constant. Bohr equated the energy that would be lost by the hydrogen atom when the electron transitioned from "a great distance apart from the nucleus" to an orbit in the atom, with the energy of the emitted radiation, quantized as $\tau h\nu$. In doing this, he substituted the frequency of revolution for the electron in the orbit, ω , divided by two, for Planck's oscillator frequency. This substitution was justified as the average frequency of electron revolution because the initial ionized state was not an orbit and, therefore, had a revolution frequency, ω , of zero. The restriction of Planck's variable τ to positive integer values

resulted in the condition that the revolution frequency, ω , was also restricted to specific values, and only orbits meeting this condition could be "allowed".

On the basis of this application of Planck's work, Bohr derived an expression for the energies and radii of the allowed orbits, both containing Planck's original quantum number τ . Bohr used his energy expression to solve the mystery of hydrogen's atomic line spectrum by equating the photon energies of emitted frequencies of radiation to differences between energies of allowed orbits occupied by the electron before and after emission, and in so doing derived the Balmer-Rydberg equation. His predicted value for the Rydberg constant closely matched the best experimental number at the time.

Later in his paper, Bohr goes on to point out that a consequence of his derived expression for the allowed energies is that the angular momentum of the electron is confined to values allowed by

$$mvr = \frac{nh}{2\pi}$$

where m and v are the mass and velocity of the electron in a circular orbit of radius r , and n is the positive integer "quantum number".

Bohr's derivation of what turned out to be the correct equation for the allowed energy states of a hydrogen atom is somewhat problematic due the questionable nature of the substitution that is responsible for the quantization, that is, the average frequency of revolution of the orbiting electron being equivalent to Planck's oscillator frequency. It is interesting to note that Bohr's derivation was soon reconstructed by others to change the angular momentum restriction from a consequence into the assumption that leads to energy quantization.^{13,14} It has been suggested that Bohr's original derivation was the result of some "working backward" from the Balmer-Rydberg equation, which Bohr understood to imply quantized atomic energy states.^{8,15} Because the real source of the energy quantization was not discovered until a decade later, it is hard to fault Bohr for a little creative rationalization in efforts to justify his derivation. The reconstructed derivation is found in numerous chemistry and physics textbooks at various levels. The difficulty with presenting the reconstructed derivation to students is that the angular momentum "assumption" seems to have no justification whatever other than it leads to an equation for allowed energies of the atom that evidently works, in terms of predicting the line spectrum of hydrogen. Students are often less than impressed with this apparent avenue to discovery.

Rather than expose General Chemistry students to Bohr's original derivation or the reconstructed derivation, most recent textbooks provide a succinct description of the planetary model combined with a simplified form of the equation giving the allowed energy levels for the hydrogen atom, with little or no explanation of the logic by which it was obtained. Unfortunately, this approach misses the opportunity to draw together logically a few key discoveries and concepts to build a rigorous and compelling case for one of the most important characteristics of atoms; that energy is quantized.

■ A MORE DIRECT APPROACH

Suppose the historical path to discovery in this instance was unnecessarily complicated by circumstances. Might there be a much simpler, but rigorous, path to the conclusion that the energy contained in atoms is quantized? Bohr was really trying to solve two problems at the same time. He was working to

extend the recent Rutherford nuclear model of the atom to solve the question of electron arrangement and behavior in a way that could account for the stability of the atom. Well after he was committed to the concept of a planetary type of model, he was encouraged by a spectroscopist colleague, H. M. Hansen, to try to solve the long-standing mystery of the atomic line spectrum of hydrogen.^{8,15} Bohr correctly answered the energy question and solved the line spectrum mystery, but the planetary model of electron arrangement and behavior was ultimately found to be deficient.

In the spirit of splitting a very complex question into a sequence of two simpler questions, it is possible to consider the line spectrum mystery and its implications regarding allowed energy states in atoms quite apart from the question of electron arrangement and behavior. The following approach focuses first on the long-standing mystery of atomic line spectra, specifically that of hydrogen as the simplest case. The additional pieces of the cognitive puzzle that must be clearly defined and properly connected for the students are (1) based on Einstein's explanation of the photoelectric effect, the packets or photons of light emitted or absorbed by the atoms in line spectra experiments have energies given by $E_{\text{photon}} = h\nu$; (2) as a consequence of the Law of Conservation of Energy, any emission or absorption of energy in the form of light must be accompanied by a change in the energy of the atom that exactly matches the photon energy of the light; (3) due to electrostatic attraction between the negative electron and the positive nucleus, the potential energy of the atom has a negative value that increases (becomes less negative) as the distance between the electron and nucleus increases, approaching zero as the distance approaches infinity.

An expression for the allowed energies of the hydrogen atom can be obtained in just a few simple steps as follows:

1. Convert the Balmer–Rydberg equation for the hydrogen atomic emission lines from reciprocal wavelength into photon energy using Einstein's equation for the energy of a photon of light.

With

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where R_{∞} is $1.097 \times 10^7 \text{ m}^{-1}$ and $n_1, n_2 = 1, 2, 3, \dots, \infty$ with $n_2 > n_1$ becomes

$$E_{\text{photon}} = hcR_{\infty} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2)$$

Equation 2 simply provides the photon energies corresponding to the possible emission wavelengths in the atomic emission spectrum of hydrogen. Not every frequency generated by the Balmer–Rydberg equation was observed in experimental spectra, but every observed frequency is produced by the equation. If the parentheses are eliminated, as follows, the right-hand side is clearly the difference between two energy terms

$$E_{\text{photon}} = \frac{hcR_{\infty}}{n_1^2} - \frac{hcR_{\infty}}{n_2^2} \quad (3)$$

2. The form of eq 3 invites the application of the Law of Conservation of Energy, suggesting the energy of the photon emitted must correspond exactly to the difference in the energy of the atom before and after emission. On the basis of a comparison of the energy conservation equation below with eq 3, it is tempting to equate the first term on the right-hand side of eq 3 with the higher energy state of the atom before emission, and the second term with the lower energy state after emission

$$E_{\text{photon}} = \Delta E_{\text{atom}} = E_{\text{higher}} - E_{\text{lower}} \quad (4)$$

Does it follow that $E_{\text{higher}} = ((hcR_{\infty})/(n_1^2))$ and $E_{\text{lower}} = ((hcR_{\infty})/(n_2^2))$? The problem here is that both of these energy terms can have only positive values, because all of the constants and the integer variable are positive. This opens an important question: Should the energy of the hydrogen atom be positive or negative?

3. Without knowing anything about the behavior of the electron, for example, its trajectory or momentum, all that can be assumed about the energy of the atom is that it includes potential energy due to the electrostatic attraction between the electron and the nucleus. The Coulombic potential energy E_p for opposite charges must be negative, increasing (becoming less negative) toward zero as the distance between the charges approaches infinity

$$E_p = k \frac{Q_p Q_e}{r} \quad (5)$$

where Q represents the charges on the proton and electron, r is the distance between the charges, and k is a proportionality constant.

The possibility of kinetic energy due to motion of the particles should not be overlooked. However, it is safe to assume that the potential energy is the largest component of the total energy.¹⁶ Therefore, the right-hand side of eq 3 must be rearranged to give the difference between two negative values, rather than two positive values. This can be accomplished by first switching the order of the two terms as follows:

$$E_{\text{ph}} = \frac{hcR_{\infty}}{n_1^2} - \frac{hcR_{\infty}}{n_2^2} = \frac{-hcR_{\infty}}{n_2^2} + \frac{hcR_{\infty}}{n_1^2}$$

Then replacing the “+” with “− (−)” for the second term to obtain a difference between two terms that are restricted to negative values for any allowed value of n_1 and n_2 less than infinity

$$E_{\text{ph}} = \frac{-hcR_{\infty}}{n_2^2} - \frac{-hcR_{\infty}}{n_1^2} \quad (6)$$

Comparing the right-hand side of eq 6 with the energy conservation equation, eq 4, we obtain expressions for the higher initial and lower final energies of the atom before and after emission of a photon

$$E_{\text{higher}} = \frac{-hcR_{\infty}}{n_2^2} \quad \text{and} \quad E_{\text{lower}} = \frac{-hcR_{\infty}}{n_1^2} \quad (7)$$

with $n_1, n_2 = 1, 2, 3, \dots, \infty$ and $n_2 > n_1$

4. The conclusion that the energy of the hydrogen atom is quantized, that is, restricted to specific values, emerges

when we recognize that the two equations for the initial and final energies have identical forms with the only variable residing in the denominator and confined to positive integer values. It is logical to assume the two equations are really just two special cases of a general equation with the same form, where the integer in the denominator simply counts the allowed energy states beginning with the lowest allowed energy. The integers n_2 and n_1 could just as easily be designated n_i and n_f for higher and lower energy levels. The resulting general equation for the energy of a hydrogen atom shows that the energy is restricted to specific values satisfied by

$$E_n = \frac{-hcR_\infty}{n^2} \quad \text{with } n = 1, 2, 3, \dots, \infty \quad (8)$$

Although step 3 in the previous derivation is not absolutely mathematically rigorous (equality between two differences does not require equality between corresponding terms), it is logical and intuitive. The compelling evidence for the validity of eq 8 is that it correctly reproduces the hydrogen atomic line spectrum as well as the ionization energy. It should also be made clear that the energy, E , in eq 8 is the total energy of the atom and cannot be assumed to consist solely of potential energy arising from electrostatic attraction. The only assumption made is that potential energy is the largest component of the total energy and, consequently, the energy must have a negative value.

The above treatment leads directly from the long-standing mystery of the atomic emission spectrum of hydrogen to the inevitable conclusion that the energy of the hydrogen atom is quantized, a conclusion that shook the foundation of physics. The derivation uses no information that was not available at the time Bohr published his landmark paper. With hindsight, the connections seem quite obvious—perhaps sufficiently obvious to be understood by novices in introductory chemistry and physics courses. Historically, the relatively simple and direct pathway outlined above was apparently overlooked by Bohr and other parties at the time who were trying to solve the atom. As mentioned previously, Bohr was pursuing a different question, developing an explanation for the behavior of the electron that could account for the stability of Rutherford's nuclear model of the atom. His consideration of the hydrogen line spectrum was a most fortunate digression that arose from the suggestion of a colleague.

It is important to recognize that the energy quantization conclusion, reached by the means presented here, sheds no light whatever on the reason for the quantization and adds little insight into the question of the arrangement and behavior of the electron other than the notion that increasing potential energy should correspond to an increasing separation between the electron and the nucleus. In discussing the story of the atom with students, an important follow up question to the quantized energy conclusion is the “why” question: What is it about the structure of the hydrogen atom that leads to the restriction of energy to specific allowed values? This provides a natural lead into the unsuccessful planetary model, de Broglie's insight, and modern quantum theory.

Although eq 8 is presented in two current General Chemistry textbooks, it is not derived for the students.^{17,18} Equation 8 is derived in a much older textbook,¹⁹ but the derivation is less straightforward.

■ A CLASSROOM APPLICATION

To help General Chemistry students grasp the logical and mathematical progression leading from the hydrogen line spectrum to the conclusion that the energy of the atom is restricted to specific values, a critical thinking exercise has been developed. Part 1 of this exercise guides students through the steps in the derivation while providing insights and asking questions about the rationale for each step. In part 2 of the exercise, students use their derived equation for the allowed energy levels to calculate the first 10 energy levels and plot them as an energy level diagram using Excel. The students then use their energy values to predict the wavelengths of two lines in the Balmer series to check the validity of the derived equation. This exercise was tested in two General Chemistry class sections of about 70 students each at Central Washington University, then refined for clarity and tested again in two subsequent classes. Class time was taken to work through much of the first part of the exercise together, and then students completed the exercise on their own. Although it was not a controlled study, student performance on test questions related to certain concepts developed in the exercise showed improved understanding of the following concepts:

- The discrete, noncontinuous, nature of hydrogen's atomic emission spectrum arises from restrictions on the amounts of energy that can be contained in an atom.
- The photon energy corresponding to an emitted wavelength must match the difference between two allowed energy values.
- The allowed atomic energies are negative because the main source of energy is the potential energy due to the attractive electrostatic force between oppositely charged particles.

Students seem to be easily confused by the notion of negative energy values and how positive photon energies must arise from differences between two negative atomic energies. The exercise helped students understand the reason for the negative atomic energy values. Building an energy level diagram for hydrogen and using the energy values to predict wavelengths of emission lines helped students make connections that form the basis for many types of spectroscopy. A copy of the exercise is available as Supporting Information.

■ CONCLUSION

An essential concept needed to understand the behavior of atoms is the quantization of an atom's energy. However, the progression of discoveries and ideas that led to this understanding is often confusing to beginning chemistry students due to the number and nature of the concepts that must be logically connected to create a navigable path to understanding. An alternative, more focused, approach has been presented that employs only the essential concepts and connections needed to rigorously demonstrate that quantized atomic energy must be the cause responsible for the discrete nature of atomic emission spectra. This approach carefully ties together (1) the Balmer-Rydberg law for the atomic line spectrum of hydrogen, (2) the particle nature of light and the link between photon energy and frequency, (3) the law of conservation of energy, and (4) the sign of the potential energy of the hydrogen atom arising from electrostatic attraction between electron and nucleus to build a more understandable and compelling case for the restriction of atomic energy to specific allowed values and to derive an expression that generates those values. A critical thinking

exercise for General Chemistry students has been developed and tested as a possible avenue to incorporating the approach developed here into the classroom teaching of this topic.

The logical path pursued from line spectra to energy quantization demonstrated here is not the historical path to this crucial discovery credited to Niels Bohr. A brief review of the circumstances surrounding his discovery sheds light on why the more direct path was apparently overlooked.

■ ASSOCIATED CONTENT

§ Supporting Information

The student critical thinking exercise described in this paper. This material is available via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rittenhr@cwu.edu.

Notes

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