How Spectroscopy Experiments Changed Atomic Structure Forever

Probing matter with light was crucial to understanding the building blocks of our universe and propelled us into the world of quantum physics

Utter the phrase 'quantum physics' in the presence of a budding undergraduate and they will shudder and wince. Mention the topic to a non-physicist and they might give you a puzzled look or vague reference to a half-dead, half-alive confined feline. Because of its deeply unintuitive nature, quantum physics has forever commanded an aura of mystique and paradox. And yet, despite its mind-bending suggestions, it is arguably the most successful scientific theory ever dreamt up.

Once, when delivering a talk on quantum electrodynamics, the esteemed Richard Feynman attempted to put its stunning predictive power into perspective with an analogy. He stated that the predictions of quantum theory match experimental data with the same margin of error as if you measured the distance from New York to Los Angeles and were correct to within the width of a human hair [1].

To create such an incredibly accurate theory is a huge achievement, especially when considering how challenging its assumptions are to our intuition. The emergence of quantum physics was closely connected to the development of new theories of atomic structure. Hence, to appreciate quantum physics, one must first understand the search for a coherent theory of atomic structure during the early 20th century. Formulating our modern conception of the atom was challenging and incremental. It was an international collaboration of many different scientists, all aiming to interpret key experimental results. In particular, spectroscopy experiments (which investigate how light interacts with matter) were vital to the work of Bohr and Sommerfeld. Although physicists weren't aware of the precise reason at the time, the fact that light is quantised ensures it interacts with atoms in a direct manner, allowing it to probe the internal structure of matter precisely. This article will discuss how spectroscopy fuelled the crucial contributions of Bohr and Sommerfeld to atomic structure and to quantum physics.

A Crisis in Physics

At the start of the 20th century, classical physics was hitting a wall. Two significant experimental results had dealt body blows to the established theories, proving them insufficient. The first result was related to blackbody radiation - the radiation which a theoretically perfect absorber and emitter of light would radiate. Classical electromagnetic theory, devised by Maxwell in 1865, had led English physicist Lord Rayleigh to predict that the ultraviolet wavelengths a blackbody emits would have an infinite intensity [2], [3]. Known as the 'ultraviolet catastrophe', this suggestion clearly violates the law of energy conservation and indicates that classical theory had to be wrong.

Secondly, when ultraviolet light was shone onto a metal plate, classical theory suggested that any frequency of light could eventually give electrons enough energy to be emitted, and yet, once again, the classical theory failed. Experiments showed that there existed a minimum cutoff frequency of light below which, no matter how long you shone the light on the metal, no electrons would ever be emitted. This became known as the photoelectric effect [3].

To address these problems, physicists had to embark on a new journey of quantisation. Max Planck theorised that black bodies emitted radiation in discrete quanta whose energy was dependent on frequency. This assumption predicted the emission curve of a black body with excellent agreement with reality (as shown in Figure 1) and gave the first suggestion that classical, continuous conceptions of matter and light were wrong [4]. Correspondingly, Einstein extended Planck's idea even further. He proposed that all electromagnetic radiation was quantised in this way, and using this idea, managed to fully explain the photoelectric effect, earning the Nobel Prize in physics for it in 1921 [3].

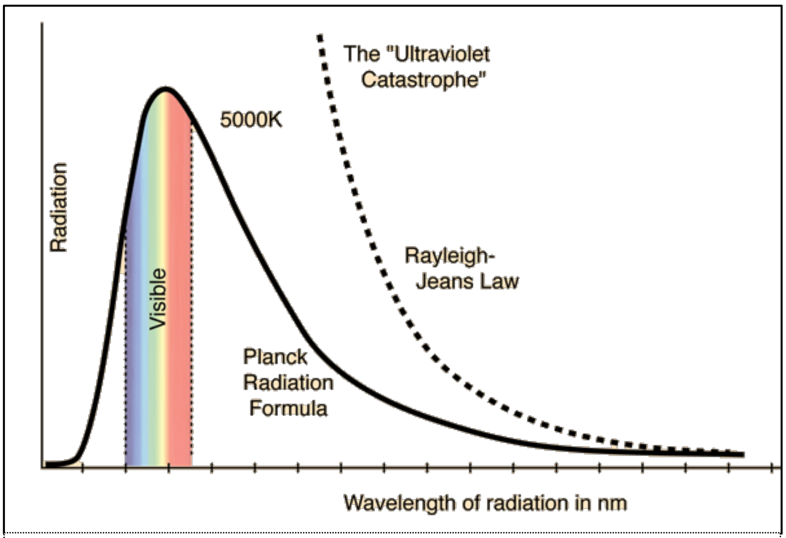

Figure 1 *- A graph of Rayleigh's predictions (the 'ultraviolet catastrophe') compared to Planck's formula, taken from [4].*

These two developments paved the way for Bohr to change our conceptions of something even more fundamental - the structure of matter itself.

Enter Bohr

At the beginning of the 20th century, prior to Bohr, the predominant theory of atomic structure was the nuclear model, proposed by Ernst Rutherford in 1911 following the results of his famous gold-foil experiment [5]. Rutherford's model was successful in that it correctly predicted the observed deflection angles of incident alpha particles and accurately described the position of positive and negative atomic charges relative to each other. However, it had key drawbacks. Classical electromagnetic theory suggested that any accelerating charge would emit radiation, and since electrons were proposed to be orbiting the nucleus, we would expect them to lose energy over time and spiral inwards. In fact, calculations suggested that they would spiral in and collapse the atom in approximately a trillionth of a second [3].

In addition, Rutherford's model was unable to explain key spectroscopic results. Spectral lines are the characteristic frequencies of light which a specific material will emit when excited or will absorb when they are incident on it [6]. For example, when white light is shone through a gas of hydrogen, photons of only very specific frequencies are absorbed. This is shown in Figure 2 [7]. Rutherford's model gave no indication as to how to calculate these frequencies, since his model permitted a continuous range of electron energies.

With the aim of addressing these two problems of instability and spectral line discreteness, Bohr took inspiration from Planck and Einstein and proposed his own radical quantisation. In his 1913 paper titled 'On the Constitution of Atoms and Molecules', Bohr hypothesised that electrons could only follow certain fixed orbits, namely those with an angular momentum of a multiple of the reduced Planck's constant, $\hbar$ [8]. Bohr used this assumption and the idea that the Coulomb force of attraction provided a centripetal force to an orbiting electron to derive an expression for the n-th energy level of a hydrogen atom electron. Bohr found that the difference in energy between energy levels with different n-values accurately corresponded to the spectral lines that hydrogen produced experimentally [8]. Finally, an atomic explanation had been found for the problem that spectroscopy had posed.

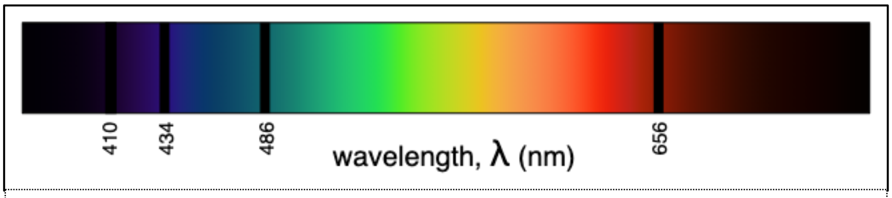

Figure 2 *– The absorption spectrum of hydrogen, adapted from [7].*

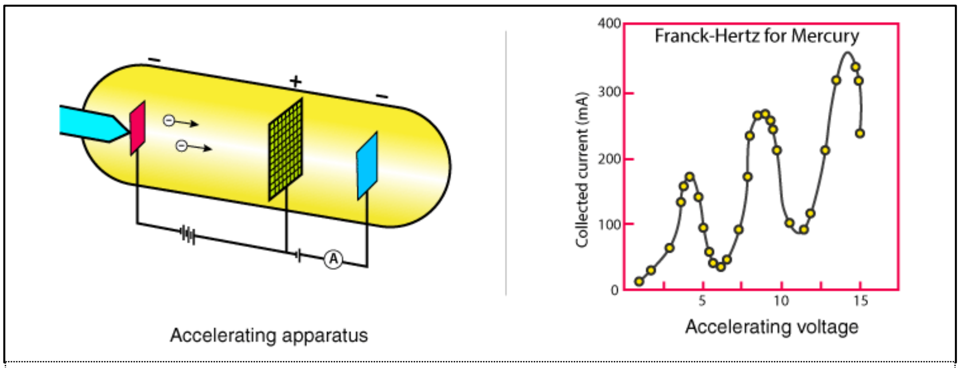

***Figure 3** – The setup and results of the Franck-Hertz experiment, adapted from [10].*

A Seal of Approval From the Mercurial Franck and Hertz

Shortly after its publication, Bohr's model received a strong boost from the results of an experiment of 1914 done by German physicists James Franck and Gustav Hertz [9]. The experimental set-up and results are shown in Figure 3 [10]. In the experiment, a glass tube is filled with mercury gas and a large voltage is supplied between a negative metal plate and a positive accelerating metal mesh grid. Behind the metal mesh grid lies a collector plate. The negative metal plate is heated, causing some electrons to be emitted. These electrons accelerate through the tube due to the electric field between the negative and positive plates. Many of these electrons collide with the collector plate, giving it an excess of electrons and thus causing a current to flow through the ammeter.

Franck and Hertz varied the accelerating voltage between the positive and negative plates and observed the effect on the collected current. For small voltage values, as the voltage increased, so did the current. This is as one would expect; a larger accelerating voltage provides a larger pull on the electrons. This ensures more of them collide with the collector plate and fewer of them miss it, thus causing a larger excess and thus current. However, when the accelerating voltage reached 4.9V, something extremely significant happened; the collected current dropped dramatically, almost to 0A. As Franck and Hertz increased the voltage beyond 5V, the current increased slowly again, until it dropped significantly once more at 9.8V.

The fact that there existed these specific points of dramatic significance suggested very strongly that some quantised behaviour was at play. If one tries to interpret the results through the lens of Bohr's model, one sees the findings fit excellently with what we would expect; it seems that the mercury atoms within the tube were only able to absorb very specific amounts of energy from the accelerating electrons - 4.9eV being the smallest example. When a mercury atom absorbed this energy, Bohr's model suggested that one of its electrons would be excited to an energy level precisely that much more energetic. In the range of 0 to 4.8V, this suggests that electrons were not accelerated enough to reach the level of kinetic energy that the mercury gas atoms could absorb. However, at 4.9V, electrons finally obtained this critical amount of energy, and hence when an electron and mercury gas atom collided, the mercury gas atoms could absorb virtually all of the electron's energy. Consequently, the electron's kinetic energy dropped to near 0, preventing it from reaching the collector plate and causing the measured current to drop dramatically. Above 4.9V, the electrons wouldn't lose all of their energy in a collision and so many of them would reach the collector plate. However, when 9.8V was reached, electrons would have enough energy for two collisions with mercury gas atoms to be possible, and hence they would lose all of their energy again, dropping the current significantly once more.

Thus, the findings directly supported the idea that energy levels within atoms are quantised, and only very specific changes in energy are permitted. Even more satisfyingly, Franck and Hertz analysed the light which the mercury atoms emitted following the collisions. They found that its wavelength corresponded to ultraviolet light of precisely 4.9eV, suggesting that mercury atom electrons were being excited to higher discrete energy levels during collision. When Einstein was presented with these results a few years later, he remarked that "It's so lovely, it makes you cry!" [11].

The Finer Details

Bohr's model was undoubtedly successful in reproducing the spectral lines of the hydrogen atom and in conceptually explaining the emission of light from the mercury gas of the Franck-Hertz experiment. However, there remained several problems which could not be ignored. For instance, Bohr was not able to explain why the angular momentum of electrons should be quantised in this way, nor could he provide any explanation of the mechanism by which electrons moved between these energy levels. Jim Al-Khalili captures this issue well in his book, 'Quantum: A Guide For the Perplexed': 'Bohr had introduced his formula in an ad hoc way. He hadn't derived it from deeper fundamental principles... Worst of all, his model only seemed to work for hydrogen, which contained just the one orbiting electron!' [3].

In addition to these concerns, there was a specific aspect of the spectral lines that Bohr's model could not explain. When one carried out high-resolution spectroscopy of a hydrogen atom, a surprising fact emerged; many spectral lines that were originally assumed to be singular were made of several lines, all very tightly spaced. A simple schematic of an example emission spectrum with a so-called 'fine structure' is shown in Figure 4 [12]. This is something Bohr had originally not been aware of but, by 1915, had accepted as a problem for his model [13]. In an attempt to explain this fine structure, the German physicist Arnold Sommerfeld proposed two important alterations to Bohr's model in 1915 and 1916.

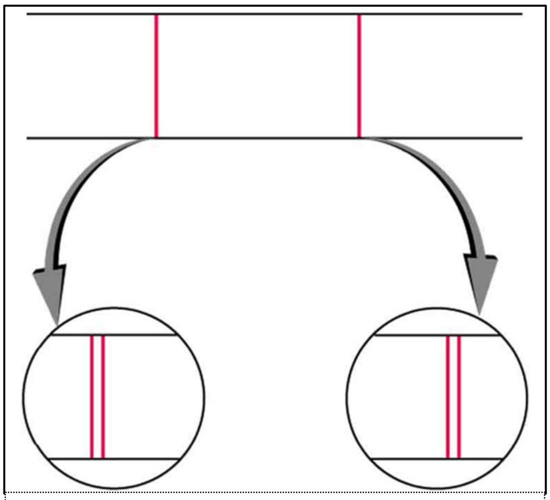

Figure 4 *– A simple schematic of an example emission spectrum with two lines amplified to show their fine structure, taken from [12].*

The first of Sommerfeld's contributions was to suggest that the discrete orbits electrons maintain around the nucleus need not be a perfect circle; instead, they might orbit in an ellipse with the nucleus situated at one of the foci [13]. He adapted Bohr's quantisation of angular momentum into two conditions, one on the radial component and one on the azimuthal component. This meant there were still only a fixed set of orbits allowed, but now some of them were ellipses of varying eccentricity. Sommerfeld described these orbits using an additional quantum number k, which ranged from 1 to n, (n being the principal quantum number and the only quantum number Bohr's model originally included). Figure 5 shows an illustration from Sommerfeld's 1921 book titled 'Atombau und Spektrallinien' (meaning 'Atomic Structure and Spectral Lines') of the different possible orbits of the hydrogen atom electron for n=1 on the left up to n=4 on the right [14].

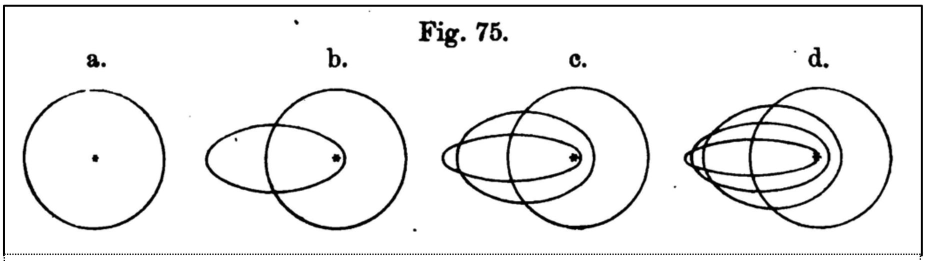

Figure 5 *– A diagram from Sommerfeld's book 'Atombau und Spektrallinien' showing various allowed elliptical orbits [14].*

In addition to the introduction of elliptical orbits, Sommerfeld also had the idea of including relativistic corrections into the calculations of spectral lines [13]. Relativistic corrections become important when an object moves at a significant fraction of the speed of light. Bohr calculated that a hydrogen atom electron in its ground state would have a speed 1/137th of the speed of light, so for hydrogen it isn't a significant correction. However, for larger elements this speed can be more than 50% the speed of light, so this correction is important to consider [15].

Incorporating both of these corrections, Sommerfeld was able to calculate estimates for the fine structure of different spectral lines. In 1916, German physicist Louis Paschen precisely measured the spectral lines of a positive helium ion and subsequently wrote to Bohr, telling him that his 'measurements are now finished and they agree everywhere most beautifully with your fine structures.' [13]. This was a huge vindication of Sommerfeld's proposals and once again showed the monumental power that spectroscopy had in revealing secrets of the atomic structure.

Unfinished Business

This isn't to say the so-called Bohr-Sommerfeld atom was the finished article. New experimental results continued to emerge and forced our conceptions of atomic structure to evolve. Just to take a few examples, the Bohr-Sommerfeld model was unable to deal with multi-electron atoms, made no mention of electron spin and could not account for other anomalous spectroscopic results such as the Zeeman effect. Clearly, our understanding still had a long way to go.

And yet despite the incompleteness of their work, Bohr and Sommerfeld were critical in the development of arguably the most successful scientific theory we have. Their pioneering work, supported by spectroscopy, laid the foundations for the flourishing field of quantum physics. From lasers and MRI scanners to solar panels and GPS, quantum physics supports a myriad of modern technologies we simply couldn't imagine life without [16]. As this article has demonstrated, none of these advancements would've been possible without the underrated technique of spectroscopy. Not only does this technique deserve our gratitude, but it also reminds us of how experimental physics can shape the future beyond our imagination.

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