

1.4: Failures of Classical Physics

Imagine being a scientist in the year 1900. At the time, there was significant debate in society as to whether or not science was a valuable discipline for study. The argument was that Isaac Newton and others had already solved all of the important problems of physics and as such, there was nothing more to be learned. There were still a few problems remaining that didn't work perfectly according to Newtonian physics, but the prevailing thought was that it was a simple matter of finding the one small piece that people were missing and the entire package would be complete. As it turned out, they couldn't have been more incorrect!

Every new detail that was discovered on these pesky problems seemed to indicate something that was not commensurate with Newtonian physics at all. And the deeper investigators looked, the more perplexing the problems became – and the further from classical physics the solutions took them.

But the modeling of these problems formed the foundations of a new quantum theory. That theory, while completely counter-intuitive to scientists of the time, is now engrained in every aspect of how we think of the atomic and molecular nature of matter. As such, no study of chemistry is complete without exploring this bizarre world of quantum mechanics. So sit back, relax, and enjoy the story of the origins of the quantum theory.

Max Planck and Blackbody Radiation

One of the problems that perplexed scientists at the turn of the 20th century was that of the description of black-body radiation. The term “Black Body” was introduced by Gustav Kirchhoff in 1860. It refers to an object that absorbs all light that falls on it (i.e. it reflects no light.) The thermal radiation emitted by a black body is called **black body radiation**.

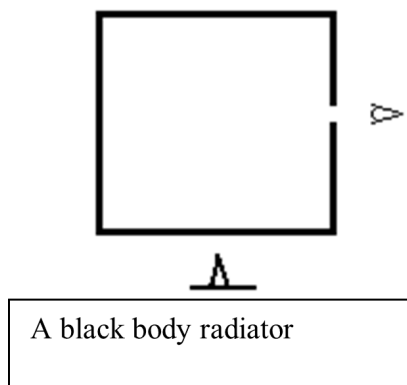


Figure 1.4.1

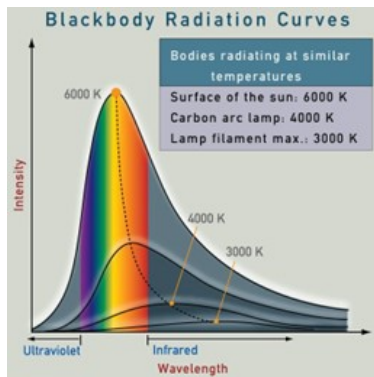


Figure 1.4.2

Black-body radiation is the light that is given off from a body that glows from being hot. Examples of blackbody radiators include incandescent light bulbs and the sun. In the laboratory, a black body radiator can be constructed by painting the inside of a metal box black (so that light is not reflected inside) and heating the box. The light given off by the box will be black body radiation.

The emission spectrum of a black-body radiator was well established and reproducible. The intensity increases at all wavelengths and the maximum intensity shifts to shorter wavelengths at higher temperatures. But while the experimental result was well

established and agreed upon, there was no theoretical model that predicted the result. Existing classical models could predict either the long-wavelength side of the spectrum or the short wavelength side, but not both.

Max Planck (1858-1947) produced the first theory that could predict both sides of the spectrum. He did this by making a ridiculous assumption about the nature of light. Despite the prevailing classical theories of the wave-nature of light and numerous experimental observations confirming these theories, Planck decided to model a light beam as a shower of energy packets (which he called Quanta) where the energy was proportional to the frequency of the light wave.

$$E = h\nu$$

In this model, E is the energy of a quantum, h is a constant of proportionality and ν is the frequency of the light wave.

This dual nature of light (having properties of both particles and waves) was revolutionary, and was thus met with great skepticism. Planck's model, published in 1901 [1], can be expressed by

$$I(\nu, T) = \frac{2h\nu^3}{c^2} \left(\frac{1}{e^{\frac{h\nu}{k_B T}} - 1} \right)$$

in which I is the intensity, T the temperature and c the speed of light, successfully described both sides of the black body radiation curve. It also provided a value of h , the constant of proportionality of

$$h = 6.36 \times 10^{-34} \text{ J} \cdot \text{s}$$

Planck was awarded the Nobel Prize in Physics in 1918 for this theory. But while interesting, Planck's theory only provided one possible explanation of the black body radiation problem. But without corroboration from other experiments involving other phenomena, Planck's theory of light quanta would not have gained any meaningful attention. That corroboration came in a paper published by Albert Einstein describing a quantum theory of the photoelectric effect.

Albert Einstein and the Photoelectric Effect

When Planck published his paper in 1901, Albert Einstein was working as a scientific expert in the Swiss patent office while working to secure a professorship in physics. He read Planck's paper. Through studying Planck's work, Einstein was able to apply a quantum theory of light to make sense out of another well-established, but as of then not understood experiment, the photoelectric effect.

The photoelectric effect involves shining light on the polished surface of metal under a vacuum. If the light has a wavelength shorter than a threshold value (characteristic of the individual metal), electrons are emitted from the surface.

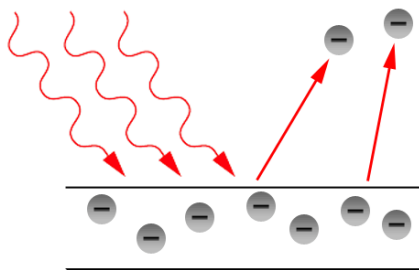


Figure 1.4.3

The challenge to understanding the result came from changing the intensity of the light. Classical physics tells us that the energy of a wave is determined by its amplitude, or in the case of light, the intensity. An increase in the intensity of incident light, therefore, should lead to an increase in the kinetic energy possessed by the emitted electrons. However, the kinetic energy of the electrons seemed to be a function not of the intensity of the light, but rather it's frequency. Einstein was able to explain [2] this using Planck's theory that light consisted of a shower of quant, each of which was a packet of energy the magnitude of which was proportional to the frequency of the light. ($E_{\text{photon}} = h\nu$)

In Einstein's model, the kinetic energy of the photoelectrons was determined as the difference between the photon energy and the "work function" or the energy necessary to rip an electron from the surface of the metal.

$$E_{kin} = h\nu - \epsilon$$

In this case, each quantum of light, or photon, can produce one photoelectron. If the energy of the photons are too small (less than ϵ), no photoelectrons are produced. But at frequencies that exceeded the threshold value, the kinetic energy was a linear function of the light frequency, with the slope of that line giving a value for Planck's constant of proportionality. Einstein's model provided a separate measurement for Planck's constant but yielded an identical result. At this point, the scientific community could no longer ignore this new quantum theory of light. Einstein was awarded the Nobel Prize in Physics in 1921 for explaining the photoelectric effect.

Johannes Balmer and the Emission Spectrum of Hydrogen

In 1885, J.J. Balmer [3](a high school teacher and amateur scientist) wrote about the series of lines in the visible emission spectrum of atomic hydrogen. The lines formed a pattern

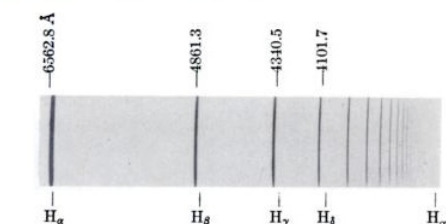


Figure 1.4.4

where the spacing decreased in decreasing wavelength and seemed to converge on a series limit. The wavelengths (λ) of lines in this spectrum fit the pattern:

$$\lambda = G \left(\frac{n^2}{n^2 - 4} \right)$$

where $G = 3647.053 \text{ Å}$, or the series limit, and $n = 3, 4, 5, \dots$

In modern terms, this expression is given as

$$\frac{1}{\lambda} = \tilde{\nu} = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

where R_H is known as the "Rydberg constant" for hydrogen, and has the value given by $R_H = 109677.581 \text{ cm}^{-1}$. Also, $n_l < n_u$ and either value must obey $n = 1, 2, 3, \dots$

In Balmer's paper, the expression is purely empirical (meaning it is based only on observation and not tied to any theoretical value.) While he was unable to provide any theory for the pattern he had derived from data, he did state that such a simple pattern could not be a coincidence.

The job of theoretical physics was to derive a theory of the H-atom that would yield energy levels, transitions between which would produce the observed spectrum and the simple pattern determined by Balmer. The first quantum theory of the hydrogen atom was proposed by Niel's Bohr (who was born in 1885 – the year that Balmer's paper was published!) Bohr's model is consistent with the wave nature of matter predicted by Louis de Broglie.

Louis de Broglie and wave nature of matter

Louis de Broglie (1892-1987) was intrigued by the notion that light, which every sensible physicist knew propagated as waves, could be described as though it was a stream of particles. Not to be outdone, he decided to examine the ramifications of doing something equally preposterous – treat something everyone knew was a particle, as a wave. de Broglie proposed that all particles would behave with a wave nature, and would have a wavelength determined by their momentum and Planck's constant.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Based on this theory, de Broglie predicted in his 1923 Ph.D. dissertation that interference patterns could be observed in electron beams diffracted by regular patterns, much in the same way that such results could be seen with light waves or water waves. This phenomenon was observed in electron beams diffracted off of nickel surfaces in 1927 [4]. de Broglie was awarded the Nobel Prize in physics in 1929 for the work in his dissertation – the first time the prize was awarded for a PhD thesis!

Niels Bohr and the Hydrogen Atom

Niels Bohr (1885-1962) was the first person to offer a quantum theory of the hydrogen atom that satisfactorily predicted the patterns seen in the emission spectra of atomic hydrogen. Basically, Bohr suggested that the electron in a hydrogen atom orbited the nucleus (a proton) in a circle, the circumference of which had to be an integral multiple of de Broglie wavelengths. (Bohr's model was actually published in 1913 [5] – 10 years before de Broglie's Nobel Prize winning thesis, but it is easily explained based on the de Broglie principle.)

Bohr suggested that the angular momentum of an orbiting electron had to be an integral multiple of Planck's constant divided by 2π .

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

This expression is easily rearranged to yield the de Broglie relationship:

$$mvr = \frac{nh}{2\pi}$$
$$2\pi r = \frac{nh}{mv} = n\lambda$$

Based on this relationship, and balancing the electrostatic attractive forces with the centripetal force acting on the orbiting electron, Bohr was able to derive the value of the Rydberg constant for hydrogen and predict the pattern seen in the emission spectrum of hydrogen.

While the theory does a remarkable job of describing the empirical model of Balmer, it has many shortcomings as well. For example, a charged electron orbiting a charged proton should eventually see its orbit decay and the electron will crash into the proton. Clearly this does not happen, contrary to the predictions of classical physics. Also, the Bohr theory is not applicable to atoms that have more than one electron, meaning it has not real application on most of the atoms in which chemists have interest. None the less, Bohr's foothold into the quantum world was important. And some important aspects of a quantum theory can be easily demonstrated using the model as well.

Heisenberg, Schrödinger and Dirac

While quantum mechanics is most often taught (and will be discussed in this text) in terms of the formalisms of Erwin Schrödinger (1887-1961), the first formal theory was derived by Werner Heisenberg (1901-1976) in 1925 (he was awarded the Nobel Prize in physics in 1932 for this theory) using a matrix formalism. Schrödinger's methodology uses integrals and eigenvalue-eigenfunction relationships and was first published in 1926. Schrödinger was awarded the Nobel Prize in Physics in 1933. Two years later, he proposed the famous "Schrödinger's Cat" thought experiment (after consulting with Albert Einstein, who never fully accepted quantum mechanics) aimed at disproving the very theory that had won Schrödinger the Nobel Prize. Schrödinger clearly lamented his contributions to the scientific foofaraw that quantum theory would become. In particular, he was dissatisfied by the notion of "quantum jumps" that were needed to describe electronic transitions in the hydrogen atom. In one heated debate with Niels Bohr, Schrödinger exasperated

If we are going to have to put up with these damn quantum jumps, I'm sorry that I ever had anything to do with quantum theory. [6]

Paul Dirac's (1902-1984) seminal textbook on quantum theory published in 1930 showed that the formalisms of Heisenberg and Schrödinger were mathematically identical. Dirac shared the 1933 Nobel Prize with Schrödinger. Among the many significant contributions that Dirac made, was a January 1928 paper in the *Proceedings of the Royal Society* that helped to explain the nature of electron spin. The consequences of his relativistic interpretation of the nature of an electron also predicted the existence of antimatter.

There is a lot more to the story of the development of quantum theory and a great many colorful characters involved. While this text will focus on the applications of quantum theory to understand molecular behavior rather than the history of its development, the history of the science is definitely something about which reading is extremely worthwhile.

Also, given the efforts towards a unified field theory in physics, there is no time that studying quantum mechanics could be more valuable. In the development of these theories, quantum mechanics and relativity often struggle against one another, but it is quantum mechanics that always seems to win these struggles. As such, quantum theory is bound to play an enormous role as modern physics continues to evolve. It is my sincerest hope that this introduction will not only provide a background required to make sense out of modern chemistry, but also whet the appetite for more knowledge and understanding on this fascinating subject.

[1] M. Planck, "On the Law of Distribution of Energy in the Normal Spectrum," *Annalen der Physik*, vol. 4, p. 553, 1901. W310W9405

[2] A. Einstein, "On a Heuristic Viewpoint Concerning the Production and Transformation of Light," *Annalen der Physik*, vol. 17, pp. 132-148, 1905. W310W9405

[3] J. J. Balmer, "Hinweis auf die Spektrallinien des Wasserstoffs," *Annalen der Physik und Chemie*, vol. 25, pp. 80-85, 1885. W310W9405

[4] C. Davisson and L. Germer, "Diffraction of Electrons by a Crystal of Nickel," *Physical Review*, vol. 30, pp. 705-740, 1927. W310W9405

[5] N. Bohr, "On the Constitution of Atoms and Molecules, Part I," *Philosophical Magazine*, vol. 26, pp. 1-24, 1913. W310W9405

[6] J. Baggot, *The Meaning of Quantum Theory*, New York: Oxford Science Publications, 1992, p. 28. W310W9405

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