Atomic Modeling in the Early 20th Century: 1904 – 1913

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Introduction

The early years of the 20th century was a time when great strides were made in understanding the nature of atoms, which had long been thought of as indivisible components of matter, with no internal structure. According to Thomas Kuhn, such progress is typical when science is in a state of *crisis*, when what he calls *normal science* is unable to account for a growing number of experimentally observed phenomena. (Kuhn, 1962) Among the many mysteries to physicists of that time were: the stability of atoms, the discrete character of atomic spectra, the origin of atomic radiation, and the large-angle scattering of radiation by matter. Even though new proposals for the structure of matter were clearly required, it was generally taken for granted that the laws of classical physics should be universally valid, even at the atomic level. Since Maxwell's equations predict that accelerating charges will radiate energy continuously in the form of electromagnetic waves, any classical model involving discrete charges in motion within an atom would be faced with two immediate problems: a continuous spectrum of electromagnetic radiation would not account for the observed discreteness of atomic spectra; and most of the elements were known to be stable, yet such an atom would continue to radiate until its energy were completely exhausted. Such difficulties could not be overcome until the assumption of the universal applicability of the known physical laws was abandoned.

The Cavendish Laboratory in Cambridge was the scene for much of the early experimental and theoretical work on electron beams and atomic radiation, and it is no coincidence that the major figures in atomic modeling of the day, J. J. Thomson, Ernest Rutherford, and Niels Bohr, were all associated with Cambridge at one time or other. When Thomson, then director of the Cavendish, announced in 1897 that cathode rays were composed of negatively charged particles, his experiments had already led him to believe that these particles were a basic constituent of matter; he was later among the first to propose an atomic model containing electrons. As a research fellow at the same laboratory in 1898, Rutherford discovered two distinct types of radiation: α -rays and β -rays; his continuing interest in radioactivity led to a series of experiments on the scattering of α -particles by matter. These experiments, conducted by Hans Geiger and

Ernest Marsden at the University of Manchester, where Rutherford had taken up a professorship in 1907, provided Rutherford with the evidence he needed to infer the existence of the atomic nucleus. Bohr spent the better part of a year of post-doctoral studies in Cambridge under Thomson until Rutherford invited him to Manchester, where he spent the last of his months in England. The pioneering experimental and theoretical work on radioactivity by physicists at the University of Manchester planted the seeds in Bohr's mind that grew into his revolutionary proposal of a quantum model of hydrogen. (Pais, 1991)

The scope of this paper is to discuss the major works that appeared in the period of 1904 to 1913: atomic models proposed by Thomson and Hantaro Nagaoka (1904), Rutherford (1911), and Bohr (1913), and the experimental work that motivated them. It will be seen that, although all of the models discussed here were later shown to be incorrect or incomplete, each one represented an essential step towards an understanding of the nature of matter, a view of the physical world often taken for granted a century down the road.

J. J. Thomson (1904-1906)

The Center for History of Physics (a division of the American Institute of Physics) reports in a website¹ commemorating the discovery of the electron that "Thomson proposed a model, sometimes called the 'plum pudding' or 'raisin cake' model, in which thousands of tiny, negatively charged corpuscles swarm inside a sort of cloud of massless positive charge." In actuality, the model proposed by Thomson in his famous paper of 1904 was concerned specifically with the motion of a number, **n**, of

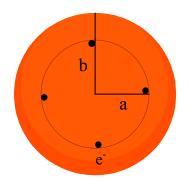


Figure 1 – Thomson's atomic model (1904) - b is on the order of a few Angstroms; a/b = 0.62 for an electrically neutral atom with a ring of four electrons in static equilibrium.

negatively charged particles arranged at equal-angular intervals around the circumference of a circle (of radius **a**), contained inside a sphere of uniform positive charge (with radius **b**, of atomic dimension; see Figure 1). Thomson did not speculate on whether any

¹ <u>http://www.aip.org/history/electron/jjelectr.htm</u>

amount of mass should be attributed to the sphere of positive charge, the question of which was anyways irrelevant to his analysis of the motions of the charges within his atom. And although it is true that Thomson had earlier proposed that electrons might be the sole constituents of matter (which in the days before relativity, *would* have implied the presence of many thousands of electrons, given the mass of an atom), the number of electrons considered in the model he put forth in 1904 was never more than on the order of 100; the majority of the first half of his paper is devoted to the problem of rings containing less than six charges.

Indeed, after briefly addressing the equilibrium conditions required for both a static and rotating ring of equally spaced charges in an electrically neutral atom, Thomson proceeded to consider the forces upon any single charge when slightly displaced from its equilibrium position. He found that, in order for a ring distorted from its circular shape to remain stable, the individual charges in the ring must oscillate about their equilibrium positions with specific frequencies, \mathbf{q} , given by the roots to a set of \mathbf{n} equations

(1)
$$\left(\frac{3}{4}\frac{e^2}{a^3}S_k + L_k - L_0 - mq^2\right) (N_0 - N_k - mq^2) = (M_k - 2m\omega q)^2$$
 $\mathbf{k} = 0, 1 \dots (\mathbf{n}-1)$

where S, L, N, and M are previously derived quantities (see Appendix A) and ω is the angular velocity of the ring. The roots of these equations must be real in order to produce an oscillatory solution. Through a series of calculations, Thomson showed that all the roots of these equations were real for $\mathbf{n} < 6$, provided that ω exceeded some minimum value; however, in the case of $\mathbf{n} = 6$, the $\mathbf{k} = 3$ frequency equation from (1) reads as

(2)
$$\left(-\frac{(14-8\sqrt{3})}{8}\frac{e^2}{a^3}-mq^2\right)\left(58\frac{e^2}{8a^3}-mq^2\right)=4m^2\omega^2q^2$$

so that one of the roots for \mathbf{q}^2 will be negative, making \mathbf{q} imaginary. A ring with 6 electrons would therefore be unstable, no matter the value of $\boldsymbol{\omega}$, *unless* an additional charge were placed at the center of the sphere – with 6 electrons in a ring and a single charge at the center, the roots of the suitably modified frequency equations are all positive in \mathbf{q}^2 , allowing for a stable configuration. Larger values of \mathbf{n} would require an increasing number of interior charges, \mathbf{p} , for mechanical stability (see Table 1).

n	5	6	7	8	9	10	15	20	30	40
р	0	1	1	1	2	3	15	39	101	232

Table 1 – (From Thomson 1904, p. 254) - n is the number of charges in an outer ring, p the minimum number of interior charges required for the mechanical stability of the atom.

Thomson hypothesized that these multiple interior charges would, due to their mutual electrostatic repulsion, be arranged in their own closed, stable orbits. He thereby deduced that many-electron atoms would be formed by a series of concentric shells, the number of charges varying from ring to ring, with a greater number of charges in the outer rings and fewer charges occupying the inner rings (see **Table 2**).

Ν	3	11	15	20	24	30	35	40	45	50	55	60
	3	3	5	1	3	5	1	3	4	1	1	3
		8	10	7	8	10	6	8	10	5	7	8
				12	13	15	12	13	14	11	12	13
							16	16	17	15	16	16
										18	19	20

Table 2 – (Adapted from Thomson 1904, p. 257) – N = n + p, the total number of charges in the atom; inner rings contain fewer charges than the surrounding outer rings. The N = 3, 11, 24, 40, and 60 atoms would form a single vertical column in the Periodic Table, each member of the group derived from the previous by the addition of a single ring.

Noting, for example, that the charge configuration for an atom of 60 electrons is identical to that containing 40, except for an additional surrounding ring of 20 charges, he hypothesized that groups of such atoms (each one derived from the previous by the addition of a single ring, as with N = 3, 11, 24, 40, and 60) would have similar chemical and spectral properties, and should therefore fall into the same vertical column in the Periodic Table. In a similar vein, the family of atoms with N = 59 - 67 each have 20 charges in their outer rings (see **Table 3**) and could therefore all be grouped in a single horizontal row. The greater the number of interior electrons, the more stable the outer ring, and so the outer ring for N = 59 would be the least stable, making it the most electropositive atom in the family; the outer ring for N = 67 would be the most stable,

Ν	59	60	61	62	63	64	65	66	67
	2	3	3	3	3	4	4	5	5
	8	8	9	9	10	10	10	10	10
	13	13	13	13	13	13	14	14	15
	16	16	16	17	17	17	17	17	17
	20	20	20	20	20	20	20	20	20

making it chemically inert. Thomson thus provided a plausible physical argument for the observed periodicity of the elements in their chemical and spectral properties.

Table 3 – (Adapted from Thomson, p. 258) - N = n + p is the total number of charges in the atom, arranged in the configuration shown, from inner (top) to outer (bottom) rings. The atoms N = 59-67 all have 20 electrons in their outer ring, and were hypothesized to belong to a single row in the Periodic Table.

Thomson also noted that, as a consequence of this structure, there would be two sets of vibrations associated with the motions of the charges: one set corresponding to the angular rotation of the rings, and another arising from the oscillatory motion of the charges about their equilibrium positions. Although more than half of his 1904 paper is devoted to calculating exactly what those allowed frequencies would be, he did not attempt to make a quantitative comparison of those frequencies with any known atomic spectra – there were no constraints on the angular velocity of each ring (other than that it must exceed a minimum value), the spacing of sequential frequency lines did not exhibit the same general characteristics of any known spectra, and he had no way of determining the actual number of electrons present in a given element.² Because he did not address the question of atomic mass, it is unclear if Thomson had completely abandoned his view of atoms as consisting of "many thousands of electrons," though he certainly had done so by 1906. In a paper published that year, while continuing to assume the existence of a

² Although it was known at the time that hydrogen could only be singly ionized, considering the lack of knowledge about the actual composition of atoms, this would have at best suggested that hydrogen had only a single electron that could be stripped from the atom, and not that hydrogen contained only a single electron. It was not until 1913 that there was sufficient reason to believe that hydrogen consisted of a single electron and proton (Pais, p. 128; Bohr 1913a, p. 30); in that same year, Henry Moseley discovered a method for measuring the atomic number of a given element, *Z*, but not until after the discovery of the neutron in 1932 was the significance of *Z* understood. (Whitaker, p. 71)

positive sphere of uniform charge, he made theoretical arguments for the determination of the number of electrons in an atom based on the current experimental data concerning three different phenomena (the dispersion of light, the scattering of X-rays, and the absorption of β -rays by various gases), all of which led him to the same general conclusion: the number of electrons in an atom is on the same order as its atomic mass number. He was aware that the evidence for such a conclusion was indirect, and the data not very numerous; he did state, however, that "...although no one of the methods can, I think, be regarded as quite conclusive by itself, the evidence becomes very strong when we find that such different methods lead to practically identical results." (Thomson 1906, p. 769)

It was not until the last page of his 1904 paper that Thomson finally addressed the problem of radiative instability. In considering a ring of charges initially moving with sufficient angular velocity, he imagined that,

"... in consequence of the radiation from the moving corpuscles, their velocities will slowly - very slowly - diminish; when, after a long interval, the velocity reaches the critical velocity, there will be what is equivalent to an explosion of the corpuscles [...] The kinetic energy gained in this way might be sufficient to carry the system out of the atom, and we should have, as in the case of radium, a part of the atom shot off." (Thomson 1904, p. 265, emphasis added)

He did not justify his claim that the dissipation of energy by electromagnetic radiation would be a "slow" process, except to mention that this would be consistent with the observation that the lifetimes of most atoms are very long. While his model did provide a semi-plausible explanation for the emanation of electrons from radioactive elements, such a view on the origin of atomic radioactivity would imply that every element would be ultimately unstable, and therefore radioactive, which was clearly not the case.

Hantaro Nagaoka (1904)

Just a few months after the appearance of Thomson's 1904 paper in the literature, another atomic model was proposed by Hantaro Nagaoka, a professor of physics at the Imperial University in Japan. His model was in direct analogy to a proposal by James Clerk Maxwell in his discussion of Saturn's rings (which Maxwell assumed to be composed of positive charges), but with negatively charged electrons orbiting about a massive central positive charge. As motivation for his proposal for atomic structure, he mentioned:



Figure 2 – A Japanese stamp commemorating Nagaoka's Saturnian Model of the atom

"The investigations on cathode rays and radioactivity have shown that such a system is conceivable as an ideal atom. In his lectures on electrons, Sir Oliver Lodge calls attention to a Saturnian system which probably will be of the same arrangement as that above spoken of. The objection to such a system of electrons is that the system must ultimately come to rest, in consequence of the exhaustion of energy by radiation..." (Nagaoka, p. 446)

So, Nagaoka acknowledged the problem of radiative instability straight away, though he imagined, like Thomson, that his model would "serve to illustrate a dynamical analogy of radioactivity..." (Nagaoka, p. 445) In fact, despite the differences in their models, their strategies for analysis have many similarities. Nagaoka's model differed from Thomson's in that the positive atomic charge was assumed to be at the center of the atom instead of spread out over a sphere of atomic dimensions, but he too considered the electrons to be arranged at equal angular intervals in a circle, repelling each other with electrostatic forces. Also like Thomson, he considered the conditions necessary for both a static and rotating ring, and then derived equations of motion for charges disturbed from their equilibrium position. Nagaoka, however, employed Lagrange's equations in his more elegant derivation, whereas Thomson had framed his analysis in terms of forces. Nagaoka imagined in his paper that "disturbance waves" would propagate around the

orbital ring, with certain allowed frequencies that vary with respect to a polynomial with integer dependence. He deduced from this integer dependence of the frequencies a qualitative picture of the regularity in spectral lines, showing that successive lines would be more closely bunched together at either end of the spectrum. He readily acknowledged that his model did not match well with experimental data;

"An important difference between the present result and the empirical formulae must not be forgotten. When [the integer values are] very great, the difference between successive lines begins to diverge, but in the empirical formulae given by various investigators in this field of research, the frequency ultimately tends to a limiting value. It seems doubtful if very large values will ever be observed." (Nagaoka, p.451)

His model did, however, provide some means of understanding the existence for line doublets, because both positive and negative roots existed as solutions to the equations of motions. Nagaoka also showed that for certain resonant frequencies, the ring structure would be mechanically unstable and, again, like Thomson, proposed that the destruction of unstable rings would account for the production of atomic radiation. In making further connections with known phenomena, he supposed that forced oscillations from incident electromagnetic waves could explain the effect of selenium having less resistance when exposed to light, and might also account for the phenomena of fluorescence and phosphorescence. Above all, he was conscious of the crudeness of his model, but anticipated its potential in applications to various fields of study:

"There are various problems which will possibly be capable of being attacked on the hypothesis of a Saturnian system, such as chemical affinity and valency, electrolysis and many other subjects connected with atoms and molecules. The rough calculation and rather unpolished exposition of various phenomena above sketched may serve as a hint to a more complete solution of atomic structure. (Nagaoka, p. 455)

Ernest Rutherford, Hans Geiger and Ernest Marsden (1906-1911)

The fact that α -particles are deflected when passing through matter was well-known to Rutherford long before his seminal paper of 1911. He had already reported as much in a 1906 paper concerned with the slowing of α particles as they passed through a series of layers of aluminum foil:

"From measurements of the width of the band [recorded on photographic plates] due to the scattered α -rays, it is easy to show that some ...

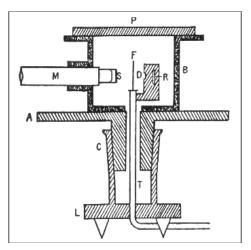


Figure 3 – Schematic diagram of the apparatus used by Geiger and Marsden

have been deflected from their course by an angle of about 2° . It is possible that some were deflected through a considerably greater angle; but, if so, their photographic action was too weak to detect on the plate. [A scattering angle of 2°] would require over that distance an average transverse field of about 100 million volts per cm. Such a result brings out clearly the fact that the atoms of matter must be the seat of very intense electrical forces..." (Rutherford 1906, p. 144-5, emphasis added)

At Rutherford's suggestion, Hans Geiger explored the matter further using an experimental setup (see **Figure 3**) where α -particles were detected by observing scintillations on a phosphorescent screen (made of zinc-sulphide) with a microscope, instead of by the previously employed method using photographic plates. The crux of a paper authored by Geiger in 1908 was to unambiguously show that the scattering of α -particles by matter was a real phenomenon, and not an artifact of previous experimental methods. He did so by demonstrating that the effect was almost negligible for α -particles passing through an evacuated tube, but was clearly present when aluminum and gold foils were placed in front of the source. (Geiger 1908, p. 176)

It was also well-known in 1908 that directing β -rays at a metal plate would result in radiation being produced on the same side of the plate as the incident particles. Though it

had been assumed by many that this was a secondary effect, recent experiments had shown that the observed radiation was actually comprised of primary particles having been scattered to such an extent that they had been reflected backwards. (Geiger and Marsden 1909, p. 495) This was likely the motivation for Rutherford to suggest that Geiger, together with Ernest Marsden, should attempt to see if α -particles would be reflected in a similar manner, which he did in early 1909. In Marsden's own words:

"One day Rutherford came into the room where [Geiger and I] were counting α -particles ... turned to me and said, 'See if you can get some effect of α -particles directly reflected from a metal surface." ... I do not think he expected any such result ... To my surprise, I was able to observe the effect looked for ... I remember well reporting the result to Rutherford a week after, when I met him on the stairs." (Quoted in Pais, p. 123)

Having further refined their scintillation method for detecting α -particles, Geiger and Marsden were able to make quantitative measurements with unprecedented accuracy. In a 1909 paper, they reported their investigation of the phenomenon by studying the relative amount of reflection of α -particles from different metals with varying thicknesses and varying angles of incidence, and were able to estimate that approximately 1 in 8000 α -particles were reflected at angles greater than 90°, an effect they referred to as "diffuse reflection". Such an estimate was now possible since Geiger and Rutherford had recently made a determination of the rate of α -particles produced by various sources. (Geiger and Marsden 1909, p. 499)

Geiger eventually decided that the α -particle source used in his previous experiments, a glass tube filled with radium and sealed at one end with a thin sheet of mica, had not been adequate for truly accurate measurements. Geiger's experiments had shown that the degree of α -ray deflection was dependent on the particles' velocities, and the "radium emanation" he had used had not been pure, resulting in α -rays of varying velocities, which also in turn suffered some absorption, or slowing, by the gas within the tube. After partially purifying a sample of radium through a process developed by Rutherford, Geiger was able to chemically deposit an amount of bismuth 214 (radium C) on the

interior of an evacuated glass tube, and thus created a homogeneous source of α -particle radiation. (Geiger 1910, p. 492-3) He was then able to determine that the most probable scattering angle increased at a rate proportional to the square root of the thickness of the scattering medium (or, equivalently, proportional to the square root of the number of atoms traversed by the radiation). Geiger took the diameter of a gold atom to be about two Angstroms, so that the number of atoms traversed in a gold foil of thickness 8.6×10^{-8} m would be "about 160 (sic)." The most probable angle of deflection for a single atom of gold would then be on the order of 1/200th of a degree (i.e., the most probable angle of deflection by a gold foil of the above stated thickness would be about 1°). He thereby concluded that, since the most probable angle of deflection through a foil was small compared to 90°, the probability of an α -particle being scattered through a large angle as a result of compound scattering was exceedingly small, and on a different order of magnitude than what his experiments suggested. He concluded by explicitly stating: "It does not appear profitable at present to discuss the assumption which might be made to account for this difference." (Geiger 1910, p. 500) The necessary assumption, of course, was that the mass associated with the positive charge inside an atom was very large compared to the mass of an α -particle, and concentrated within a very small radius at the center of the atom. Armed with the experimental data available to him from his own previous work and the experiments of Geiger and Marsden, Rutherford was finally ready in 1911 to present his own atomic model to the world.

Rutherford proposed in his 1911 paper to discuss an atom of "simple structure" that would be capable of producing a large deflection of an α -particle, and then to compare the theory with experimental data. His atom consisted of a charge of +Ne at its center (where e is the fundamental unit of charge³ and N some integer; his main deductions were independent of the sign of the central charge), and a negative charge of the same magnitude uniformly distributed over a sphere of atomic dimensions (with radius R). Rutherford sidestepped the pitfall encountered by atomic modelers who had preceded him: "The question of the stability of the atom proposed need not be considered at this

³ Rutherford used $e = 4.65 \times 10^{-10}$ in electrostatic units (compare with the current value of 4.80×10^{-10}).

stage, for this will obviously depend upon the minute structure of the atom, and on the motion of the constituent parts." (Rutherford 1911, p. 671)

In relating the potential energy of a particle due to such a charge distribution (with $N \sim 100$) to the kinetic energy of an α -particle with a typical velocity $v \sim 2x10^7$ m/s, he found that:

(3)
$$\frac{1}{2}m_{\alpha}v^2 = 2kNe^2\left(\frac{1}{b} - \frac{3}{2R} + \frac{b^2}{2R^3}\right)$$
 so that $b \approx \frac{2kNe^2}{\frac{1}{2}m_{\alpha}v^2} \sim 3x10^{-14}$ meters, for $\frac{b}{R} \ll 1$

where **b** is now the distance of closest approach for an α -particle directly incident on the nucleus. Rutherford took this distance as an upper-limit on the size of the nucleus, and with **b** being very small compared to **R**, he also concluded that the influence of a uniform distribution of negative charge could be ignored without significant error.

The main point of Rutherford's 1911 paper was to demonstrate that the scattering distribution of particles due to encounters with atoms could not be explained alone by compound scattering off of the type of atom proposed by Thomson, but could be explained by single encounters with atoms possessing a massive central charge, where the amount of charge would be approximately equal to a multiple of the atomic mass number of the scatterer. As evidence for this conclusion he calculated that the probability for single scattering through some angle off an atom with a central charge would always be greater (and often much greater) than the probability for compound scattering through the same angle off of atoms with a distributed positive charge. (Rutherford 1911, p. 679)

Although Rutherford believed the data from Geiger and Marsden's earlier experiments to be not quite suitable for quantitative comparisons with theoretical calculations, he did state (without proof) that it could be shown that the observed fraction of diffusely reflected particles (1/8000) would be about what would be expected from his theory, with the assumption that elements such as platinum or gold have a central charge of about 100e. His theory also allowed him to derive (see **Appendix B**) the dependence of the scattering angle θ on the impact parameter **p**, the perpendicular distance of the incident trajectory from the center:

$$(4) \quad \cot\left(\frac{\theta}{2}\right) = \frac{2p}{b}$$

with the result that **y**, the number of α -particles scattered into unit area through an angle θ is given by:

(5)
$$y = \frac{ntb^2 Q}{16r^2 \sin^4(\theta/2)}$$

where **Q** is the total number of incident particles, **r** the distance from the scatterer to the detecting screen, **n** the number of scattering atoms per unit volume, and **t** the thickness of the scatterer. Since **b** is proportional to the central charge (which was assumed to be proportional to the atomic mass number **A**), and since it had already been shown by others⁴ that the effective cross-sectional area for a single atom is proportional to $A^{-1/2}$, the quantity $y^*A^{-3/2}$ should be independent of the scatterer. The data he presented from Geiger and Marsden as corroboration of the theory is reproduced in **Table 4**, along with the data published by Geiger and Marsden in 1913,⁵ and the results they *would have* obtained had they known the actual atomic number **Z** of the elements tested. Although he made no statistical analysis of the data (as was normal for the times; the *coefficient of variation*⁶ for the data set turns out to be 5.6%), Rutherford felt that, "[c]onsidering the difficulty of the experiments, the agreement between theory and experiment is reasonably good." (Rutherford 1911, p. 681)

In his concluding thoughts, because he felt the quality of available data was not the best, Rutherford was conscious that his model lacked full corroboration:

"Considering the evidence as a whole, *it seems simplest* to suppose that the atom contains a central charge distributed through a very small volume, and that the large single deflexions are due to the central charge as a whole, and not to its constituents. At the same time, the experimental evidence is not precise enough to negative the possibility

 $^{^4}$ Both Rutherford and Geiger refer without specific citation to the work of William H. Bragg (who was a doctoral student of J. J. Thomson) on the scattering of β -rays.

⁵ Geiger and Marsden 1913, p. 617. In the subsequent two years, they had systematized their method to the extent that they were also able to corroborate the angular dependence of eq. (5).

⁶ The *coefficient of variation* is defined as the standard deviation divided by the mean and multiplied by 100%. According to Allan Franklin, it was not yet common at the time for physicist to make statistical analyses of their data, since the mathematical tools for statistical analysis had only been recently developed.

that a small fraction of the positive charge may be carried by satellites extending some distance from the centre." (Rutherford 1911, p. 687, emphasis added)

He had also not yet found a means of determining the sign of the central charge, and he further commented on the need to correct for the motion of the scatterer for the lighter elements. Although Rutherford was agnostic (at least in this article) on how the electrons in an atom were arranged, it is interesting that he makes reference in his last page to the "Saturnian" model proposed by Hantaro Nagaoka in 1904, but only to note that Nagaoka had found conditions for the mechanical stability of such an atom, and that Rutherford's conclusions were essentially independent of whether the atom was viewed as a sphere or a disk. (Rutherford 1911, p. 688)

Substance	Atomic	Atomic	1911 ^a	1911 ^a	1911*	1913 ^b	1913 ^b	1913*
	Weight	Number		NA ^{-3/2}				
	A ^a	Z	Ν	$(x10^{-4})$	$NA^{1/2}Z^{-2}$	Ν	NA ^{-3/2}	$NA^{1/2}Z^{-2}$
Aluminum	27.1	13	3.4	243	0.10	34.6	0.24	1.07
Iron	56	26	10.2	250	0.11	-	-	-
Copper	63.6	29	14.5	225	0.14	115	0.23	1.09
Silver	107.9	47	27	241	0.13	198	0.18	0.93
Tin	119	50	34	226	0.15	270	0.21	1.18
Platinum	195	78	63	232	0.14	-	-	-
Gold	197	79	67	242	0.15	581	0.21	1.31
Lead	207	82	62	208	0.13	-	-	-
Mean				233	0.13		0.21	1.11
Standard				13	0.015		0.02	0.13
Deviation				15	0.015		0.02	0.15
Coefficient				5.6%	13.0%		9.5%	11.7%
of Variation				5.070	13.070		9.570	11.//0

Table 4 – Data presented by Rutherford from Geiger and Marsden as support for his theory.

a – Data from Rutherford 1911, p. 681

b – Data from Geiger and Marsden 1913, p. 617

* - Calculated from current known values of Z for the given elements

Niels Bohr in England and Copenhagen (1911-1913)

Following the successful defense of his doctoral thesis on the electron theory of metals in May 1911, a 26 year-old Dane by the name of Niels Bohr received a stipend from the Carlsberg Foundation to study abroad for one year. Considering the topic of his dissertation, it seems natural that Bohr would be attracted to the Cavendish Laboratory under the direction of J. J. Thomson, the discoverer of the electron. Indeed, when asked later why he chose the Cavendish Laboratory for his post-doctoral studies, Bohr

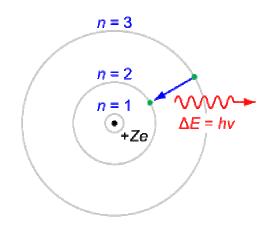


Figure 4 – A depiction of the Bohr model (1913) – the radius of each orbit is given by n^2a_0 .

stated that he considered Cambridge at the time to be the center of physics and expressed great admiration for Thomson and his work. (Pais, p. 119) His first encounter with Thomson, however, did not go as well as he might have hoped. Their meeting has been recounted by many, and essentially amounts to Bohr entering Thomson's office with a copy of one of Thomson's books on atomic structure, opening the book to a certain page and politely stating: "This is wrong." Apparently, Thomson did not respond well – Bohr's wife, Margarethe, remembered: "Thomson was always very nice... but he just was not so great as my husband because he didn't like criticism." (Pais, p. 120)

Bohr's overall experience at the Cavendish during his stay there was a disappointment to him. Frustrated with the tedious aspects of laboratory work, such as having to blow his own glass, Bohr resolved to spend the spring term away from the laboratory, and instead follow some lectures and "read, read, read (and perhaps calculate a little and think)." (Quoted in Pais, p. 121) Still, even if his stay in Cambridge was not all that he might have hoped for, it was his association with the Cavendish that led him to meet Rutherford for the first time in November 1911, just a few months after the publication of Rutherford's nuclear model. Bohr was visiting a friend of his late father's in England, who had also invited Rutherford to join them.

"[B]ut we didn't talk about Rutherford's own discovery [of the nucleus] ... I told Rutherford that I would like to come up and work and also get to know something about radioactivity. And he said I should be welcome, but I had to settle with Thomson. So I said I would when I came back to Cambridge." (Quoted in Pais, p. 124)

Released from his obligations in Cambridge, Bohr arrived in Manchester in March 1912, where, after attending a short course on experimental techniques, Rutherford set him to work on studying the absorption of α -particles in aluminum. Again, Bohr found that he had little enthusiasm for experimental work, and decided to concentrate instead on theoretical problems. Ironically, although Bohr and Rutherford got on quite well together, it was not Rutherford himself who would be of greatest influence on him during his stay there:

"At that time, the Rutherford model was not taken seriously. We cannot understand it today, but it was not taken seriously at all. There was no mention of it in any place. [...] You see, there was not so much to talk about. I knew how Rutherford looked at the atom, you see, and there was really not very much to talk about." (Quoted in Pais, p. 125-6)

Instead, it was the work of Charles Galton Darwin (grandson of Charles Robert Darwin) that was a source of inspiration to him. Darwin, who held a degree in applied mathematics from Cambridge, had been set by Rutherford on the theoretical problem of the loss of energy of α -particles when traversing matter. In his work, Darwin had assumed that the loss of energy was almost entirely due to interactions with inter-atomic electrons, which he treated as free particles. His results depended on only two parameters: the charge of the nucleus and the atomic radius **r**. In comparing his results with the available data, he found that

"...in the case of hydrogen it seems possible that the formula for \mathbf{r} does not hold on account of there being only few electrons in the atom. If it is regarded as holding then [their number equals] one exactly.⁷ Thus, as late as the spring of 1911 [when Darwin's

⁷ Darwin 1912, p. 919-20.

paper appeared] it was not yet absolutely clear that the hydrogen atom contains one and only one electron!" (Pais, p. 128)

Bohr decided that the discrepancy between Darwin's results and experimental observation might be due to his treatment of the atomic electrons as free particles. He started work on his own analysis of the problem while still in Manchester, in which he instead treated the electrons as harmonic oscillators bound to the nucleus. His paper, on which he continued to work after returning to Denmark in July 1912, and which was not published until January 1913, is significant not only because it marks the beginnings of his quest to understand the structure of atoms, but also because he subjected his "atomic vibrators" to quantum constraints:

"According to Planck's theory of radiation we further have that the smallest quantity of energy which can be radiated out from an atomic vibrator is equal to v.k, where v is the number of vibrations per second and $k = 6.55.10^{-27}$. This quantity must be expected to be equal to, or at least of the same order of magnitude as, the kinetic energy of an electron of velocity just sufficient to excite the radiation..." (Bohr 1913a, p. 26-7)

Furthermore, in his conclusions at the end of the paper, because of the excellent agreement of his results with experimental data, Bohr states:

"[I]t seems that it can be concluded with great certainty ... that a hydrogen atom contains only 1 electron outside the positively charged nucleus, and that a helium atom only contains 2 electrons outside the nucleus [...] These questions and some further information about the constitution of atoms which may be got from experiments on the absorption of α -rays will be discussed in more detail in a later paper." (Bohr 1913a, p. 31)

That "later paper" promised by Bohr was not his seminal paper of 1913. In the months following his return to Denmark, Bohr had been in the process of writing up his many ideas on the structure of atoms, and via post had repeatedly turned to Rutherford for guidance and approval. Their correspondence ultimately led to Bohr producing a paper

for Rutherford's consideration, which later became known as "The Rutherford Memorandum", but went unpublished until after Bohr's death. (Pais, p. 136) In that memorandum (summarized in Pais, p. 135-9), the key theme was stability. Bohr was troubled by both the mechanical and radiative instability inherent to all previous atomic models. He proposed to resolve these problems by introducing a "...hypothesis for which there will be given no attempt at a mechanical foundation (as it seems hopeless) [...] This seems to be nothing else than what was to be expected as it seems rigorously proved that the mechanics cannot explain the facts in problems dealing with single atoms." (Quoted in Pais, p. 137) The hypothesis to which he was referring was not the quantization of the angular momentum of the electron in its orbit, which was actually not an entirely novel idea: "It was in the air to try to use Planck's ideas in connection with such things," Bohr later said of that time. (Quoted in Pais, p. 144) Indeed, Bohr makes reference in his famous paper of 1913 to the prior work of J. W. Nicholson, who (in Bohr's words) had "obtained a relation to Planck's theory showing that the ratios between the wave-length of different sets of lines of the coronal spectrum can be accounted for with great accuracy by assuming that the ratio between the energy of the system and the frequency of rotation of the ring [of charges] is equal to an entire multiple of Planck's constant." (Bohr 1913b, p. 6) Still, Bohr argued that this could not account for the stability of atoms, and could not actually account for line-spectra, in that such a system, as modeled by Nicholson, where the frequency is a function of the energy "cannot emit a finite amount of a homogenous radiation; for, as soon as the emission of radiation is started, the energy and also the frequency of the system are altered." (Bohr 1913b, p. 7)

It was in response to such problems that Bohr posited two assumptions as the basis of his theory. First, he assumed that electrons in atoms would occupy discrete orbits of constant energy, and that "the dynamical equilibrium of the systems in the stationary states can be discussed by help of the ordinary mechanics, *while the passing of the systems between different stationary states cannot be treated on that basis.* [...] *[T]he ordinary mechanics cannot have an absolute validity*, but will only hold in calculations of certain mean values of the motion of the electrons." (Bohr 1913b, p. 7, emphasis added) He further assumed

that, in making a transition between stationary states, an electron would radiate a single photon,⁸ where the relationship between the frequency of the photon and its energy would be given by $\mathbf{E} = \mathbf{h}\mathbf{v}$, à la Planck and Einstein. Transitions between stationary states would be the only way in which an atom could emit or absorb radiation. In marked contrast to his predecessors, Bohr did not assume that atomic spectra were due to the motions of the electrons within the atom.

These assumptions were all in contradiction to the ideas of classical physics, but Bohr felt them to be necessary in order to account for experimental facts, such as the spectrum of hydrogen, and the empirical formula from Balmer that describes it, but which theretofore had no theoretical explanation.

"On a number of occasions Bohr has told others ... that he had not been aware of the Balmer formula until shortly before his own work on the hydrogen atom and that everything fell into place for him as soon as he heard about it. [...] Bohr recalled: 'I think I discussed [the paper] with someone ... that was Professor Hansen ... I just told him what I had, and he said "But how does it do with the spectral formulae?" And I said I would look it up, and so on. That is probably the way it went. I didn't know anything about the spectral formulae. Then I looked it up in the book of Stark ... other people knew about it but I discovered it for myself." (Pais, p. 144)

With the use of "ordinary mechanics", Bohr was able to calculate quantities that agreed in order of magnitude with the accepted values of the linear dimensions of an atom, its optical frequencies, and the ionization potential of hydrogen; but this had been accomplished by others before him using similar considerations.⁹ It was in deriving the Rydberg constant

(6)
$$R_Z = \frac{2\pi^2 m_e Z^2 e^4}{h^3}$$

and then, by way of his two principle assumptions, deriving the Balmer formula,

⁸ In the first (abandoned) version of his paper, Bohr had entertained the possibility that multiple photons might be produced in a transition. (Pais, p. 147)

⁹ Bohr 1913b, p. 6. Bohr refers in his paper to the works of A. E. Haas (1910), A. Schidlof (1911), E. Wertheimer (1911), F. A. Lindemann (1911), and F. Haber (1911).

(7)
$$v_{ab} = R_1 \left(\frac{1}{b^2} - \frac{1}{a^2} \right)$$
 a, b = positive integers, **b** < **a**,

for the spectrum of hydrogen, that Bohr had succeeded where all others had failed: predictions for spectral frequencies in agreement with observation. Yet, the success of his model did not end there. In applying it later that year to singly-ionized helium, he was able to produce a formula that could accurately describe what were then known as Pickering lines, which had been observed in starlight and had been erroneously attributed to hydrogen, but did not fit with the Balmer formula. This time taking the finite mass of the nucleus into account, Bohr calculated the ratio

(8)
$$\frac{R_2}{R_1} = 4.00163$$
.

"Up to that time no one had ever produced anything like it in the realm of spectroscopy, agreement between theory and experiment to five significant figures." (Pais, p. 149)

Conclusion

It should be emphasized that, during the period considered here, there were few scientists who had the inclination or the courage to propose atomic models:

"It is perhaps not unfair to say that for the average physicists of the time, speculations about atomic structure were like speculations about life on Mars – very interesting for those who like that sort of thing, but without much hope of support from convincing scientific evidence and without much bearing on scientific thought and development." (Pais, p. 118)

Without a means of experimental verification, the strengths of the early models were in their qualitative correspondence with some known phenomenon, either the periodicity of the elements (Thomson) or general features of the line spectra (Nagaoka). Rutherford's theory was incomplete as an atomic model; it might rather be thought of as a model for the scattering of α -particles. He had (with justification) completely ignored the role of atomic electrons in the scattering process. At the same time, Darwin had (also with justification) ignored the role of the nucleus in his treatment of α -particle absorption.

And so, up until that time the nucleus and atomic electrons had been treated separately, leaving it up to Bohr to tie it all together. The problem of radiative instability had plagued every previous attempt to model the atom, and it was clear to Bohr that no progress could be made if it was thought that the "ordinary mechanics" was universally applicable. Note that Bohr did not imply that the laws of "ordinary mechanics" were wrong (indeed, he used them to calculate the electron orbits and their energy levels, given the notion that the angular momentum of the electron was quantized); he merely states that they cannot be thought to apply universally, and in particular, not at the atomic level. It was known to him that atoms were stable, and so he simply *declared* the ground state to be stable. Yet, by doing so, and asserting that transitions between orbits would result in the production of a single photon of specific energy, he was able to produce a formula for the spectrum of hydrogen, which had been well-known for decades prior – a classic example from the history of science regarding the novel prediction of phenomena, rather than the prediction of novel phenomena.

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Appendix A – Quantities Appearing in Thomson's Spectral Formulae

Let
$$S_n = \csc ec \frac{\pi}{n} + \csc ec \frac{2\pi}{n} + \dots + \csc ec \frac{(n-1)\pi}{n}$$

Then the radial repulsion experienced by one particle due to the other (n-1) is equal to $\frac{e^2}{4a^2}S_n$.

$$L_{k} = \frac{e^{2}}{8a^{3}} \left(\cos \frac{2k\pi}{n} \left(\frac{1}{\sin \frac{\pi}{n}} + \frac{1}{\sin^{3} \frac{\pi}{n}} \right) + \cos \frac{4k\pi}{n} \left(\frac{1}{\sin \frac{2\pi}{n}} + \frac{1}{\sin^{3} \frac{2\pi}{n}} \right) + \cos \frac{6k\pi}{n} \left(\frac{1}{\sin \frac{3\pi}{n}} + \frac{1}{\sin^{3} \frac{3\pi}{n}} \right) + \dots \right) \right)$$

$$N_{k} = \frac{e^{2}}{4a^{3}} \left(\cos \frac{2k\pi}{n} \frac{\cos \frac{\pi}{n}}{\sin^{2} \frac{\pi}{n}} \left(\cot \frac{\pi}{n} + \frac{1}{2} \tan \frac{\pi}{n} \right) + \cos \frac{4k\pi}{n} \frac{\cos \frac{2\pi}{n}}{\sin^{2} \frac{2\pi}{n}} \left(\cot \frac{2\pi}{n} + \frac{1}{2} \tan \frac{2\pi}{n} \right) + \dots \right) \right)$$

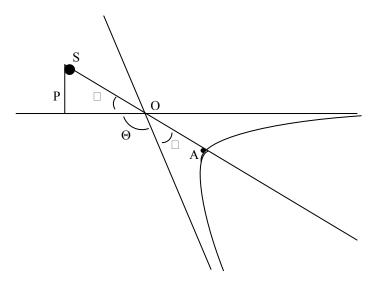
$$M_{k} = \frac{ne^{2}}{8a^{3}} \left(\sin \frac{2k\pi}{n} \frac{\cos \frac{\pi}{n}}{\sin^{2} \frac{\pi}{n}} + \sin \frac{4k\pi}{n} \frac{\cos \frac{2\pi}{\sin^{2} \frac{2\pi}{n}}}{\sin^{2} \frac{2\pi}{n}} + \sin \frac{6k\pi}{n} \frac{\cos \frac{3\pi}{\sin^{2} \frac{3\pi}{n}}}{\sin^{2} \frac{3\pi}{n}} + \dots \right) \quad \text{where } k=0, 1, \dots, (n-1)$$

Thomson used these expressions to write his frequency equations in a compact form:

$$\left(\frac{3}{4}\frac{e^2}{a^3}S_k + L_k - L_0 - mq^2\right)\left(N_0 - N_k - mq^2\right) = (M_k - 2m\omega q)^2$$

 ω must be such that the roots for q² are positive, so that the q's are all real, allowing for a stable charge configuration.

Appendix B – Derivation of Rutherford's Scattering Formula



Let SA be the distance of closest approach to the nucleus, with V the particle's initial speed, v its speed at A, and p the impact parameter (the perpendicular distance of the incident trajectory from the center).

By conservation of angular momentum,

$$(B1) \qquad p * V = \overline{SA} * v$$

and by conservation of energy,

$$(B2) \quad \frac{1}{2}m_{\alpha}V^{2} = \frac{1}{2}m_{\alpha}v^{2} + \frac{2kZe^{2}}{\overline{SA}}.$$

$$\Rightarrow \frac{1}{2}m_{\alpha}v^{2} = \frac{1}{2}m_{\alpha}V^{2}\left(1 - \left(\frac{2kZe^{2}}{\frac{1}{2}m_{\alpha}V^{2}}\right)\frac{1}{\overline{SA}}\right) = \frac{1}{2}m_{\alpha}V^{2}\left(1 - \frac{b}{\overline{SA}}\right)$$

where **b** is defined as in (3). Then, by (B1) and the above result,

(B3)
$$\frac{v^2}{V^2} = \frac{p^2}{\overline{SA}^2} = \left(1 - \frac{b}{\overline{SA}}\right).$$

Since
$$\overline{SA} = \overline{SO} + \overline{OA} = \frac{p}{\sin(\phi)} + \frac{p}{\tan(\phi)} = \frac{p}{\sin(\phi)} (1 + \cos(\phi)) = \frac{p}{2\sin\left(\frac{\phi}{2}\right)\cos\left(\frac{\phi}{2}\right)} 2\cos^2\left(\frac{\phi}{2}\right),$$

(B4)
$$\overline{SA} = p \cot\left(\frac{\phi}{2}\right),$$

so that, together with (B3),

$$p^{2} = \overline{SA}(\overline{SA} - b) = p \cot\left(\frac{\phi}{2}\right) \left(p \cot\left(\frac{\phi}{2}\right) - b\right)$$

and

$$b = \frac{p^2 \left(\cot^2\left(\frac{\phi}{2}\right) - 1\right)}{p \cot\left(\frac{\phi}{2}\right)} = p \left(\cot\left(\frac{\phi}{2}\right) - \tan\left(\frac{\phi}{2}\right)\right) = 2p \cot(\phi)$$

But since the scattering angle θ is related to ϕ by $\theta + 2\phi = \pi$,

$$\left|\cos\left(\frac{\pi}{2} - \frac{\theta}{2}\right)\right| = \sin\left(\frac{\theta}{2}\right), \text{ and } \left|\sin\left(\frac{\pi}{2} - \frac{\theta}{2}\right)\right| = \cos\left(\frac{\theta}{2}\right), \text{ then}$$

(B5) $\frac{2p}{b} = \cot\left(\frac{\theta}{2}\right)$

Now, let **P** be the probability for a particle to encounter an atom with an impact parameter of **p**, then

$$(\mathbf{B6}) \quad P = \pi p^2 nt$$

(where **n** is the number of scattering atoms per unit volume, and **t** the thickness of the scatterer), and

$$(B7) \qquad dP = 2\pi pnt * dp$$

is the probability of striking an annulus with radii **p** and **p+dp**.

From the previous result **(B5)**,
$$p = \frac{b}{2} \cot\left(\frac{\theta}{2}\right)$$
 and $dp = \frac{b}{4} \csc^2\left(\frac{\theta}{2}\right)^* d\theta$, so that

(B8)
$$dP = (2\pi nt)\frac{b}{2}\cot\left(\frac{\theta}{2}\right)\frac{b}{4}\csc^{2}\left(\frac{\theta}{2}\right)*d\theta = \frac{\pi ntb^{2}}{4}\cot\left(\frac{\theta}{2}\right)\csc^{2}\left(\frac{\theta}{2}\right)*d\theta$$

Let y be the number of particles falling on unit area and deflected through an angle θ , and Q the total number of incident particles; then

(B9)
$$y^*(2\pi r^2 \sin(\theta)d\theta) = Q^*dP$$
,

(where **r** is the distance from the scatterer to the point of observation), and

(B10)
$$y = \frac{QdP}{2\pi r^2 \sin(\theta)d\theta} = \frac{\pi ntb^2 Q}{(4)(2\pi r^2)} \frac{\cos\left(\frac{\theta}{2}\right)}{\sin(\theta)\sin^3\left(\frac{\theta}{2}\right)} \frac{d\theta}{d\theta}$$
 and using $\sin(\theta) = 2\sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right)$

so that the final result for \mathbf{y} is given by:

(B11)
$$y = \frac{Qntb^2}{16r^2 \sin^4\left(\frac{\theta}{2}\right)}.$$