# *The structure of the atom before Bohr*

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The second Solvay conference, held in the autumn of 1913, was devoted to "The Structure of the Atom". During those days at the Hotel Metropole, in Brussels, the most influencing physicists of the time discussed about the internal composition of atoms, with, mainly, two pictures in competition: the recently proposed model of Bohr, which included the quantum principle in a radically new form, and the nth remaking of Thomson's model, this time also including a mechanism to account for Einstein's formula for the photoeffect.[1] The previous year, 1912, had seen the first big conference dedicated specifically to atomic constitution.[2]

The internal structure of the atom was not, in the first decade of the 20th century, a catalyst for direct scientific research but, rather, a topic left, to a great extent, to speculation in footnotes, appendixes, and popular lectures. The emergence on the scientific stage of the new phenomena and entities of radioactivity, X-rays, and the corpuscle-electron, gave scientists unexpected new elements on which to work before they could seriously address the question about the structure of the atom. Information gathered from these new researches was seen as a window into the interior of the atom, but it was too premature to build a consistent picture with the scattered, and often contradictory, data that was available.

Certainly, the atom was one of the main characters in the 19th century *physical sciences*: its very existence, behaviour, experimental evidence, and theoretical utility were under constant discussion by chemists and physicists alike. As is well known, there was a broad spectrum of stances on this discussion, ranging from those denying the existence

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[1] La Structure de la Matiere (Solvay, 1913)
[2] Les idees modernes sur la constitution de la matiere (Curie, Langevin, Perrin, Poincare, Weiss).

of atoms to those who speculated on the possibility of sub-atomic components. In this context, it is not surprising to find people suggesting models for the internal structure of the atom, models that could account for their macroscopic—statistical—behaviour. But for most, the atom was the unit of matter, the basis for the explanation of phenomena as diverse as the composition of molecules, the periodic table, thermodynamic variables (via statistical mechanics), or spectra. Moving inside the atom, when its existence and properties were still under scrutiny, was going a step too far.

This general reluctance to speculate about the sub-atomic world is partly responsible for the complexities in the story of the "discovery" of the electron. And also, when the corpuscle-electron was generally accepted as a sub-atomic particle, there was more work done in studying its properties and behaviour than in using it as the building block of matter. With a few exceptions, the atom was not yet seriously modelled in terms of its components before these were properly understood. Joseph John Thomson appears as the main exception to this trend, inaugurating a research program that would eventually end in Bohr's model of the atom.[3]

***Pre-corpuscle models***

Nineteenth century developments of atomic theories in physics and chemistry generally led to "eliminate both the Lucretian (hard, impenetrable mass) and the Boscovichean (point-centre plus force fields) models of the atom".[4] Spectroscopy, kinetic theory, and chemical combination seemed to indicate that atoms behaved as if hey had some internal dynamism, some degrees of freedom, or even some inner structure. But as to how to model the atom, there was no one major trend. Informing many of these theories, however, we find what Kragh calls the Proutean tradition: in 1815, W. Prout had suggested that the mass of the components of all chemical elements was a multiple

[3] Heilbron's picture sees Bohr's model as being in continuity and dependence of what he calls Thomson's program.
[4] MacKinnon, p. 102

of a fundamental unit, and that this corresponded to the mass of hydrogen.[5] Since then, there was a lot of speculation on the unity of all matter.

One popular theory among mid-Victorian physicists was the vortex-ring atom, which had its origin in 1867, when William Thomson suggested an atomic model in which atoms could be represented as vortex rings in the ether. Hermann von Helmholtz had shown, in a previous paper, that vortex filaments in a perfect fluid would not be destroyed or dissipated. The ether was mainly understood as a fluid, and these results served to account for the indestructibility of atoms, and, at the same time, to treat them as special manifestations of the ether. The impact of this conception was considerable among scientists, and in the 70s and 80s "British physicists became increasingly attracted to this simple picture of atomic matter involving a concentration of ether spinning like a smoke ring in air".[6]

William Thomson, as the father of the vortex atom model, felt that the theory was consistent with two of his key philosophical prejudices: his enthusiasm for dynamical models and his profound dislike for atomism, or, as he said, "the monstrous assumption of infinitely strong and infinitely rigid pieces of matter".[7] In the years up to 1880, Thomson worked at this hypothesis and tried to explain many physical phenomena, including gravitation, the kinetic theory of gases, the dissipation of energy and the wave motions in solids and liquids.[8]

The young J.J. Thomson worked on this theory for almost a decade since 1882. That year, he won the prestigious Adams Prize with a long and mathematically intricate essay "On Vortex Rings". Besides being a typical example of Cambridge mathematical work, the last section of the essay reveals that all these calculations "would enable us to work out a complete dynamical theory of gases".[9] Atoms could thus be represented in terms of these vortex rings in a fluid ether, and he concluded that there could be stable

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[5] Kragh, in Histories of the Electron.
[6] Topper 1980, p. 41. See also Klein (1973) and Kragh (2002).
[7] (Thomson 1867, 15)
[8] Smith and Wise (1989), chap. 12.
[9] J.J. (1883a, 51)

combinations of up to six such rings. This was in agreement with the possible valences of most elements, and he was led to speculate as follows: "The atoms of the different chemical elements are made up of vortex rings all of the same strength, but some of these elements consist of only one of these rings, others of two of the rings linked together, others of three, and so on", which meant that "each vortex ring in the atom would correspond to a unit of affinity in the chemical theory of quantivalence".[10] In this model, the mass of the atoms ceases to be their fundamental characteristic and their chemical affinity assumes such a role. Furthermore, it was not one vortex ring, but several, that accounted for one atom. This shows that Thomson was very much interested in chemical combinations of elements and substances as a way to better understand the foundations and the constitution of matter.

The vortex ring theory was essentially dynamical. It diluted the atom and its structure into the properties of an ether that was understood as a fluid. Other models in the late 19th century were more mechanical in character, emphasising such things as the size of the atom, the number of sub-corpuscles, or the intra-atomic forces to keep the atom together. The nascent statistical mechanics was the field in which many of these speculations took place, since it was hypotheses on such properties that were at the very basis of any kinetic theory. But seldom were these assumptions taken realistically.[11]

Last but not least, the fast-developing field of experimental spectroscopy provided with a new setting for speculating on the nature of chemical elements. Spectral analysis was soon seen not only as a tool for chemical analysis, but also as a new way to understand the structure, and even the evolution, of atoms.[12] In particular, Norman Lockyer, brought forward the suggestion that, in the same way molecules dissociate into their component atoms with an increase in temperature, one can think of atoms also splitting with a further increase in temperature. The hypothesis materialised around 1873 as a possible explanation of the fact that there were coincidental lines in the spectra of

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[10] J.J. (1883a, 54)
[11] MacKinnon, p. 101-102.
[12] In the evolutionary Zeitgeist of late 19th century... The hottest stars had a major proportion of light elements than the colder ones, and that was interpreted as evidence of the evolution of atoms and elements.

simple different elements.[13] In analogy to what had happened with the vortex-ring theory, Lockyer's hypothesis was motivated, not only by experimental results, but also by the assumption of the continuity in Nature. In the preface to his *Chemistry of the Sun*, of 1887, he stated that "The question, then, it will be seen, is an appeal to the law of continuity, nothing more and nothing less. Is a temperature higher than any yet applied to act in the same way as each higher temperature which has hitherto been applied has done? Or is there to be some unexplained break in the uniformity of nature's process?"[14]

This metaphysical continuity, together with the huge data obtained from both laboratory and solar spectra, was the main argument with which Lockyer defended himself from the accusation that such dissociation of atoms was tantamount to opening the door to old alchemical dreams of transmutation of elements. Talk of intra-atomic components was, for many, synonymous of attempting to turn lead into gold.

### *The discovery of the electron*

According to a plaque on the façade of the old Cavendish laboratory, in Cambridge, "Here in 1897 … J.J. Thomson discovered the electron subsequently recognised as the first fundamental particle of physics, and the basis of chemical bonding, electronics, and computing". A more historiographically elaborated position may want to extend the process of the discovery of the electron "stretching from Faraday's investigation of electrolysis to Millikan's oil-drop experiments",[15] or even to Davison and Germer's and G.P. Thomson's evidence for electron diffraction in 1927.[16] Of course, part of the problem resides in determining what an electron is—or, better, what it was—and what were the uses given to it by the different scientists involved in the story.

[13] Meadows, Science and Controversy, chap 6.
[14] Lockyer, Chemsitry of the Sun, p. xi.
[15] Arabatzis, T., "Electrons", in Greenberger and Hentschel… p. 195
[16] Laszlo Tiszla, quoted in Arabatzis' Representing Electrons, p. 61.

The first theoretical "electrons", or "monads", or "ions" were intended as an explanation for the origin of electromagnetic phenomena. While in Maxwell's approach the electric charge was an epiphenomenon in the ether, H.A. Lorentz and J. Larmor's theories introduced charged particles, or singularities in the ether, as sources of the field. The extent to which these were considered real entities or simple theoretical devices is a matter of much discussion, and more strongly linked to a history of relativity than a history of quantum physics. From an experimental perspective, some people have argued that P. Zeeman's observations of the broadening of some spectral lines due to a magnetic field was the first evidence for the real existence of electrons.

In this chapter, however, our interest lies in the electron *qua* building block of matter. From this point of view, the electron first appeared as the particle of which cathode rays were composed. In mid-1897, both J.J. Thomson, in Cambridge, and W. Kaufmann, in Berlin, measured the ratio e/m (charge to mass) for cathode rays. While the latter thought this result to be evidence that the corpuscular explanation for cathode rays might be inadequate, the former dared to suggest that the large value for this ratio was an indicator for the existence of a subatomic particle. In his lecture of April 30 at the Royal Institution, Thomson suggested that "the size of the carriers must be small compared with the dimensions of ordinary atoms or molecules", and he later called this particles 'corpuscles'.

This move was not obvious and, as Thomson himself recalled in his memoirs, his announcement was met with a great deal of scepticism.[17] The problem was not so much the corpuscular nature of cathode rays, but Thomson's explicit advocacy for a substructure of the atom. On his view, "we have in the cathode rays matter in a new state, a state in which the subdivision of matter is carried very much further than in the ordinary gaseous state: a state in which all matter--that is, matter derived from different sources such as hydrogen, oxygen, &c.--is of one and the same kind; this matter being the substance from which all the chemical elements are built up".[18] In wanting to gain

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[17] Thomson, Recollections, p. 341.
[18] Thomson, Philosophical Magazine, 44, 293 (1897), p.....

legitimacy for his position, Thomson could rely, not on the tradition of physicists, but on that of some chemists:

> "The explanation which seems to me to account in the most simple and straightforward manner for the facts is founded on a view of the constitution of the chemical elements which has been favourably entertained by many chemists: this view is that the atoms of the different chemical elements are different aggregations of atoms of the same kind. In the form in which this hypothesis was enunciated by Prout, the atoms of the different elements were hydrogen atoms; in this precise form the hypothesis is not tenable, but if we substitute for hydrogen some unknown primordial substance X, there is nothing known which is inconsistent with this hypothesis, which is one that has been recently supported by Sir Norman Lockyer for reasons derived from the study of the stellar spectra".[19]

This search for support from the chemists was quite natural to his life-long interests.[20] Since the early 1880s, after graduating as second wrangler in the Cambridge Mathematical Tripos, Thomson had already shown a strong interest in chemical issues, especially in the constitution of matter and chemical bonding. His essay on Vortex Rings, his first book of 1888, *Applications of Dynamics to Physics and Chemistry*, and his research on electrical discharges in tubes filled with gases, all witness to a serious interest in chemical questions, since he regarded chemistry as part of the unified *Physical Sciences*.[21] And it was this all-encompassing interest that partly explains why Thomson soon tried something that almost no other physicist or chemist of his time did: to attempt a model of the atom based on the new—and only—elementary particle, the corpuscle-electron.

### ***Thomson's models***

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[19] Thomson, Philosophical Magazine, 44, 293 (1897), p.....
[20] Chayut
[21] Navarro (2006)

As he introduced the new sub-atomic particle, Thomson immediately started to speculate on the role of his corpuscles in the constitution and internal structure of atoms:

> "If we regard the chemical atom as an aggregation of a number of primordial atoms, the problem of finding the configurations of stable equilibrium for a number of equal particles acting on each other according to some law of force … is of great interest in connexion with the relation between the properties of an element and its atomic weight. Unfortunately the equations which determine the stability of such a collection of particles increase so rapidly in complexity with the number of particles that a general mathematical investigation is scarcely possible. We can, however, obtain a good deal of insight into the general laws which govern such configurations by the use of models, the simplest of which is the floating magnets of Professor Mayer. In this model the magnets arrange themselves in equilibrium under the mutual repulsions and a central attraction caused by the pole of a large magnet placed above the floating magnets".

The above fragment is quite characteristic of J.J. Thomson's style. In the absence of exact mathematical solutions, he was happy with visual models that could provide with an approximate picture of the reality under discussion. In his first proto-model, Thomson referred to the stable configurations of magnets in a fluid under the action of an external magnetic field that American physicist A.M. Mayer had found in 1878. For J.J., and similar to what had happened with his vortex-ring model of the atom, "a study of the forms taken by these magnets seems to me to be suggestive in relation to the periodic law", since these were concentric configurations that followed a periodic pattern analogous to the one in the periodic table.

In 1899, Thomson moved a step forward and faced, for the first time, the problem of the neutral charge of the atom. From his point of view, "though individual corpuscles behave like negative ions, yet when they are assembled in a neutral atom their negative effect is balanced by something which causes the sphere through which the corpuscles are spread to act as if it had a charge of positive electricity equal in amount to the sum of the negative charges on the corpuscles".[22] The nature of positive charge was, in this statement, very obscure, as was in all his models until about 1906. As mentioned above, J.J. Thomson was keen on monistic interpretations of matter, and a one-particle model was the best possibility. Furthermore, his corpuscles were precisely that, corpuscles, and not some singularity in the ether, like in Lorentz or Larmor's theory. That means that, for him, the essential characteristic of his corpuscles was the fact that they were mass particles that happened to be electrically charged. And in this framework, the existence of positively charged particles similar to the corpuscles was not needed.

If the atom was composed only of corpuscles, their number had to be high (in the order of the thousands) in order to account for all the mass of the atom. That was, in principle, supported by the complexity of atomic spectra, and it also helped the stability of the atom. It must be emphasised that atomic models with thousands of corpuscles as components could be dynamically and electromagnetically stable.[23] Instabilities in the dynamic equilibrium of the corpuscles could also be the source of radioactive emission, against those who, like D. Mendeleev or J. Perrin, thought of radioactivity as a phenomenon induced from outside the atom.

Around 1906, Thomson's own work brought a severe blow to his model. With three independent methods (the scattering of X-rays, the scattering of beta particles, and the refractive index for monoatomic gases) he concluded that the number of electrons in the atom had to be of the order of magnitude of the atomic number. This involved two problems: first, that the mass of the atom was mainly due to the positive electrification, and, second, that there was radiative instability in the atom. That the positive electrification was massive, did not involve, for Thomson, that there were necessarily positive corpuscles. In his 1907 book on *The Corpuscular Theory of Matter*, Thomson acknowledged that "The form in which this positive electricity occurs in the atom is at present a matter about which we have very little information… In default of exact knowledge of the nature of the way in which positive electricity occurs in the atom, we shall consider a case in which the positive electricity is distributed in the was most

[22] JJ, BAAS meeting 1899
[23] Using Larmor's 1897 theorem of radiation, Thomson proved that the radiation of corpuscles was negligible if their number was high.

amenable to mathematical calculation, i.e., when it occurs as a sphere of uniform density, throughout which the corpuscles are distributed".[24] This uncertainty on the nature of positive electricity led him to start an experimental research program on positive or canal rays.

As for the radiation instability, he did not address the problem directly, hoping for some mechanism that would explain the stability of the corpuscles in the atom. Such mechanism never came, and was only solved—or dismissed—by Bohr's model of the atom, to come in 1913. A model that Thomson never accepted due to its obvious violation of the most basic mechanical principles.

***Other models***

Where Thomson had, at first, tried to explain the atom in terms of negative corpuscles only, people like Oliver Lodge or James Jeans soon included in the atom hypothetical positive corpuscles. The arrangements and rearrangements of corpuscles with opposite charge could be imagined as providing with atomic instabilities that would explain radioactivity. Incidentally, we should here emphasise that, in the early years of the 20th century, the origin of radioactivity was totally unknown: opinions were divided between those who considered it to be an intra-atomic phenomenon, and those who advocated for external triggering. Among the latter, Jean Perrin would, as late as 1923, still defend that radioactivity was triggered by some sort of external radiation of either terrestrial or cosmic origin.[25]

Astronomical models were also relatively common. Jean Perrin was the first to consider that the atom might be like a solar system, in which "one or several masses very strongly charged with positive electricity, in the manner of positive suns whose charge will be very superior to that of a corpuscle" around which one could find "a multitude

[24] JJ *The Corpuscular Theory of Matter*, p. 103.
[25] Kragh, 1997, AHES

of corpuscles, in the manner of small negative planets".[26] Another attempt was the comparison between the formation of atoms and that of nebulae brought forward by Filippo Re, also in Paris.[27] The longer lasting analogy from astronomy was, however, Hantaro Nagaoka's "Saturnian" model, which closely followed Maxwell's 1856 calculations on the stability of Saturn's rings. Nagaoka supposed that atoms were composed of a core positive nucleus around which the negative corpuscles would organise in concentric rings. The model was not only qualitative, but also tried to give quantitative descriptions of some spectra as well as a mechanism for radioactivity. Needless to say that this particular model soon proved to be mechanically unstable: while Maxwell's analysis involved only attractive forces, Nagaoka's model included repulsive forces and this was responsible for the atom's instability.

The last astronomical model worth mentioning is that of Cambridge astronomer John William Nicholson, who was the first to introduce Planck's quantum in the structure of the atom. Interested in explaining both stellar spectra and chemical elements in terms of the internal composition of the atom, Nicholson suggested, in 1911, a model in which "positive electricity exists in units very small in radius compared even with the electrons, and is the source of nearly the whole mass of the atom. The revolving system is therefore a planetary one". Here, Nicholson could already refer to Rutherford's experimental evidence "that the planetary system is the most probable".[28] Nicholson's model is surprising in that he suggests that all atoms of chemical elements are composed of what he calls the four "protyles", and for which he thinks to have experimental evidence from the spectrum of the solar corona: Coronium, composed of two electrons and the corresponding positive nucleus, Hydrogen with three, Nebulium with four, and Protofluorine with five. Just to give an example, an atom of Helium would be the combination of one Nebulium and one Protofluorine. Nicholson shows that this hypothesis is consistent with the known atomic weights of the atoms. In this schema, there was no room for one-electron atoms, which were totally unstable due to the obvious problem of radiation, while the four basic protyles could subsist: "This can be seen intuitively, in fact; for if $n$ electrons are rotating at equal distances round the

[26] Perrin, in Kragh, 1997, p. 342
[27] See Kragh, 1997, p. 342.
[28] Nicholson, Phil Mag, 1911, p. 865-6.

same circle, they each have an acceleration of the same amount towards the centre, and the vector sum of this accelerations is zero. This is Larmor's condition for the absence of radiation".[29]

While atomic weights seemed to agree with his model, Nicholson found, at first, serious difficulties to predict the spectrum of the solar corona in terms of internal vibrations of Coronium, Nebulium, and Protofluorine. The solution came in the early months of 1912, when he realised that the vibrations of a ring of electrons perpendicular to the plane of motion could be stable and, in the case of his basic protyles, the total angular momentum of the atoms was always a multiple of Planck's constant. With this, Nicholson found himself serving the "double purpose of confirming the suggested origin of the spectra of astrophysics, and of giving to Planck's theory and atomic foundation: a foundation of the kind which is now generally believed to be necessary, giving a concrete picture of the possible nature of a resonator".[30] In other words, Nicholson's atomic could, in a first approximation, explain the solar spectrum while, at the same time, was rendering the theory of quanta "more intelligibility, for it is not difficult to obtain fair mechanical models of atoms the angular momentum of which can only have a discrete set of values".[31]

Nicholson' model, although influential in Bohr's development of his atom, is essentially different from the latter, and bears witness to the continuity between late-nineteenth century notions of intelligibility and early-twentieth century attempts to explain the theory of quanta, especially in the British Isles. For Nicholson kept relating the spectral lines of an element to the angular momentum of electrons in the atom, and not, as Bohr did, to the transition between quantum states.[32] The quantum was, in Nicholson's model, an *explanandum* rather than an *explanans*.

[29] Nicholson, Phil Mag, 1911, p. 868.
[30] Nicholson, Montly Notices, 1912, p. 676-7
[31] Nicholson, Nature, 1912, p. 199.
[32] See McCormach, 1965.