GEORGE JOHNSTONE STONEY AND THE CONCEPTUAL DISCOVERY OF THE ELECTRON

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Summary

Against the commonly-held view that the electron was first 'discovered' in 1897 by Joseph John Thomson at Cambridge, it is argued in this essay that the conceptual and experimental discovery of the electron was a process that extended over a period of nearly seventy years from the first formulation of the laws of electrolysis by Michael Faraday, in 1833, until Thomson's establishment of the particulate nature of cathode rays and his conception of the famous corpuscle hypothesis. Thomson's discovery, which resulted from studies of discharge phenomena in gases and of cathode rays, had been made possible by advances over several decades in the fields of electrochemistry, kinetic theory, spectroscopy, and electromagnetic theory. Among several scientists who contributed to this process, the Irish physicist George Johnstone Stoney (1826-1911) deserves particular recognition. His role lay in the conceptual discovery and in preparing the way for the actual discovery.

Following an outline of Stoney's life and career, an attempt is made to assess his role in the conceptual discovery of electron. Then possible influences of Stoney's ideas in the actual discovery of the electron are considered. Furthermore, the reception of Stoney's work in modern scholarship, in particular the treatment of his contributions by historians of science, is examined. Finally, a reassessment and reevaluation of his role in the discovery is attempted.

Introduction

Stoney is a much-neglected figure in the history of science. A search through the international literature of the subject reveals three articles with Stoney's name in the title. One of these (Tsuneishi 1975) deals with Stoney's efforts towards a formalisation of the Abbe theory of microscopic vision of 1873. The other two articles are concerned with Stoney and the electron. One, by the author of this essay (O'Hara 1974-75), on "Stoney and the concept of the electron", represents a first outline that is expanded here into a more elaborate and comprehensive study. The third article, in Italian, on "Stoney's electron" (Robotti 1979), only partially fulfils this desideratum.

There is besides another category of literature which deals with Stoney's achievements. This consists of perhaps a dozen books, doctoral dissertations or articles on the discovery of the electron, nineteenth-century spectroscopy and related topics. It is in the context of these studies that we find the most extensive treatment of Stoney's role in the

events that culminated in the discovery of the electron (see Secondary Sources). The results of these considerations are summarised in this essay. None of the studies to date has made use of manuscript sources. No major body of manuscript letters and papers of Stoney is in fact extant. Apart from his correspondence with his nephew George Francis FitzGerald, consisting of 44 letters from the 1890s preserved at the Royal Dublin Society (hereafter abbreviated as RDS), only occasional items have survived.

Following a brief outline of his life and career, Stoney's achievements are treated in this essay under the following five headings: kinetic theory of gases; electrochemistry and electrolysis; spectroscopy; electrodynamics/electromagnetic theory; gas discharge phenomena and cathode rays. It was also along these five avenues that progress was made leading to the discovery of the electron.

Life and career

The best biographical information on Stoney is still that given in obituary notices written shortly after his death (see Obituaries). He was born on 15 February 1826 at Oakley Park, Clareen, about six miles from Birr in County Offaly, which was then King's County. The Stoney family came from Yorkshire and had settled in Ireland in the seventeenth century; his mother was from another Anglo-Irish family settled in County Clare. Having lost their property in the famine years, the family moved to Dublin to allow the children to pursue professional careers. George Johnstone graduated from Trinity College, obtaining a second senior moderatorship in mathematics and physics. Between 1848 and 1852 he spent two and-a half years as astronomical assistant to Lord Rosse at Parsonstown, Birr Castle, observatory. While there he read for the Trinity College fellowship, which would have opened up a scientific and academic career for him in Dublin. When he entered for the fellowship in 1852 he took second place and the Madden prize that had a value of about £300.

Through the influence of Lord Rosse he was appointed professor of natural philosophy at Queen's College, now University College, Galway where he remained for five years until he became Secretary or chief administrator to the Queen's University. The office of the Queen's University, with its constituent colleges in Belfast, Cork and Galway, was then situated in Dublin Castle. Stoney retained this post until the Queen's University was dissolved and replaced by the Royal University, a purely examining body, in 1882. Twenty five years later the Royal University was itself dissolved and replaced by the present National University of Ireland and Queen's University of Belfast. In his capacity of Secretary to the Queen's University and Superintendent of Civil Service Examinations in Ireland, Stoney devoted the greater part of his professional career to university policy and administration. At the same time, he was able to continue scientific and scholarly work through his close association with the RDS. From 1871 he was Honorary Secretary and from 1881 Vice President of the Society; much of his own research work was communicated to the Society and published in its scientific journals and, in 1899, he received the Society's first Boyle medal. In 1893, at the age of sixty seven, Stoney left Ireland and lived in retirement in London, intending to provide his children with better educational and career opportunities.

His life in London was largely devoted to the completion and publication of work begun in Ireland. His most important work (especially that on spectroscopy and the electron) was likewise accomplished in the course of his professional life in Dublin. John Joly (see Obituaries, xxxiiif.) relates that "in spite of heavy office work which afforded

none of the long-vacation leisure of university life, in spite of the absence of that stimulus which comes from a professional scientific life, Stoney published two or three papers each year. Through his middle years he rose at five o'clock in order to get in some scientific work before starting for his office...His Sundays were largely devoted to experiments or writing. His annual holiday was usually for the ten days of vigorous intellectual life of a British Association meeting". Stoney died in London at the age of 85 on 5 July, 1911. His body was cremated, and his ashes buried in a suburban graveyard at Dundrum, Dublin.

Kinetic theory of gases

The mean-free-path theory was developed in mathematical form in the middle decades of the nineteenth century, the most important contributions coming from Rudolf Clausius in Germany and James Clerk Maxwell in Britain. When, in about 1860, Stoney turned his attention to this theory, some important results were already available. Clausius had given an expression which allowed the determination of a mean velocity of gas molecules at a given temperature and pressure (Clausius 1857). Subsequently Clausius had found an expression for the mean free path of a molecule in terms of the mean molecular separation: where all the molecules of a hypothetical gas in a container move with the same velocity, the mean free path was found to be about 60 times the mean separation (Clausius 1859). Furthermore, Maxwell had developed a theory based on a distribution of velocities, which he then applied to the results of experiments on gaseous viscosity and diffusion in order to obtain real numerical values for the mean free path of molecules (Maxwell 1860).

In his first significant paper on gas theory, Stoney combined these results of Clausius and Maxwell to obtain a further important result (Stoney 1868). From an average of three values for the mean free path given by Maxwell, namely 7×10^{-8} m at atmospheric pressure and room temperature, he found the mean separation of gas molecules to be of the order of 10^{-9} m, or 10^{-6} mm, being about one sixtieth of the mean free path according to Clausius. Stoney could therefore deduce that the number of molecules in a cubic mm of gas at atmospheric pressure and room temperature was of the order of 10^{18}. This is of course a quantity closely related to Avogadro's constant. Stoney's calculation was first published in 1868, but he later claimed to have made a preliminary estimate following the publication of Maxwell's results in 1860 (Stoney 1906, xi). Stoney was thus one of the first to have obtained a numerical value for this important constant. Similar determinations were made by Joseph Loschmidt in 1865 and by William Thomson, the later Lord Kelvin, in 1870 (see O'Hara 1974-75).

The intention of Stoney's 1868 paper, as indeed its title "On the internal motions of gases compared with the motions of the waves of light" suggests, was to connect data about molecular magnitudes obtained from the kinetic theory with the known wavelengths and frequencies of light. An essential feature of this paper was the hypothesis that light waves arise from periodic motions within the atoms or molecules. Stoney's theory was more elaborate than some other theories current at the time. He suggested each molecule was a complex system, having two distinct forms of motion, namely translatory and internal motions and, elaborating on earlier considerations of Clausius, he maintained that the *vis viva*, expressed mathematically by the formula mv^2, of these internal motions constitutes a definite part of the total heat of the gas. Stoney described the internal motions as complex but regular orbital motions which affect the

surrounding ether, producing light of definite wavelengths. Using data from kinetic theory, he showed that the mean duration of molecular paths between collisions was more than 50,000 times the period of a double vibration or cycle of red light, and less than 100,000 times that of violet light. He therefore concluded that between 50,000 and 100,000 orbital motions were executed on average between molecular encounters.

These molecular encounters disturb the orbital motions, but such irregularities die away during the subsequent journey of the molecule. He believed that the internal motions could be resolved into a number of simple harmonic vibrations of definite periods; the amplitudes are independent of the molecular collisions, depending only on the *vis viva* or kinetic energy of the orbital motions. As early as 1868, therefore, we find the first intimation of Stoney's electron in the guise of molecular "orbital motions". It was, however, in the context of electrochemical studies that his concept of the electron matured.

Electrochemistry/electrolysis

The origins of the concept of the electron in the context of electrolytic theory can be traced back to the investigations of Michael Faraday (see Turpin 1980, 43-55). The work he undertook to reach his laws of electrolysis was carried out in January and June 1833 and was reported in the Third and Fifth Series of his celebrated *Experimental Researches in Electricity* (Faraday 1833a; 1833b; 1839-55). His establishment of a quantitative relationship between the amount of electrolyte decomposed and the electricity passed through it implied, in the context of his understanding of the nature of electricity, that a definite quantity of electricity was naturally associated with matter. Faraday held electricity and matter to be inseparable and electricity to be a "power" of matter, and not a fluid independent of it as had been commonly believed up to that time.

In the *Seventh Series* of his *Experimental Researches* Faraday contemplated the absolute quantity of electricity, associated with matter (Faraday 1834; 1839-55). He suggested that, although we are ignorant of the nature of both atoms and electricity, there was an abundance of facts which justify the belief "that the atoms of matter are in some way endowed or associated with electrical powers, to which they owe...their mutual chemical affinity" (*Ibid.*, par.852).

Faraday's laws — that a certain definite quantity of electricity is associated with matter, and that the same quantity of electricity decomposes the same number of chemical equivalents — do in fact imply that the equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity. In terms of the atomic theory, he interprets as follows: "if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalents to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them". To this he added a reservation however: "But I must confess I am jealous of the term *atom*; for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature" (Faraday 1834, par. 869).

The establishment by the 1840s of the validity of Faraday's laws did not rapidly lead to the acceptance of the notion of atomicity of charge, however. The laws were not even linked to atomic theory at this time. This association was only made in the 1860s when, following progress in kinetic theory, valency and the periodic table, the concept of the atom was transformed from the disembodied "equivalent" of Faraday's laws to a real physical entity. It was only then that Faraday's "definite quantity of electricity"

could be associated with an individual molecule or atom.

In 1873, James Clerk Maxwell, in his celebrated *Treatise on Electricity and Magnetism*, suggested that each individual molecule must be associated with a fixed amount or "unit" of electricity (Maxwell 1873, I par. 255). To Maxwell it appeared to be a fact of electrolysis that there was "a constant value of molecular charge" which he called "one molecule of electricity". However the concept was "gross.... and out of harmony" with the rest of the Treatise. Maxwell had in fact little faith in the actual physical reality of his "molecular charges". They were useful to explain the facts of electrolysis, but it was, he says, "extremely improbable that when we come to understand the true nature of electrolysis we shall retain in any form the theory of molecular charges" (*Ibid.* par. 260).

Therefore, as regards the existence of an atom or molecule of electricity, both Faraday and Maxwell were essentially agnostic. In the year following the publication of Maxwell's *Treatise*, Stoney openly opposed this interpretation of electrolysis in a paper presented in August 1874 at the Belfast meeting of the British Association for the Advancement of Science (hereafter abbreviated as BA). Only the title of the paper, "On the physical units of nature", was published in the Report of the meeting, and there is no account of either its content or reception (Stoney 1874). Nearly seven years later, on 16 February 1881, Stoney read a paper with the same title before the RDS, and it was published soon after in the *Philosophical Magazine* (Stoney 1881). In this paper Stoney discussed three systems of units, namely the BA Ohm Series, a metric Metre-Gramme-Second (MGS) system, and a system of natural units that he had devised himself. The first system had been developed by a committee of the Association first appointed in 1862 to establish a unit of electrical resistance. By 1874 the work of this committee, whose members included Maxwell, William Thomson and Stoney himself, had been extended, and a practical system of units for electrical measurements, known as the BA Ohm Series, had been established. Based on arbitrary units of length, mass and time (10^7 m, 10^{-11} g, and 1 s) a system of electrical units had been developed which included the ampère (unit of quantity), the ohm (resistance), the weber (current), the volt (emf) and farad (capacity).

Parallel to this system, Stoney discussed a second arbitrary Metre-Gramme-Second system. In connection with this system he introduced a special nomenclature, designating the fundamental and derived units as "lengthine", "massine", "timine", "forcine", "velocitine", etc. The unit of quantity of electricity or charge was then the "electrine". When compared with the BA Ohm Series, the "electrine" had a numerical value of 100 ampères. The third system of units proposed by Stoney was to be a natural system whose fundamental units were not arbitrary units of length, mass and time, but rather physical constants. The three units chosen were derived from electromagnetism, gravitation and electricity and designated V_1, G_1, and E_1, respectively. V_1 is the ratio connecting electrostatic and electromagnetic quantities in a medium of inductive capacity unity; it has the dimensions of a velocity and is numerically equal to the maximum velocity of electromagnetic radiation. G_1 is the coefficient of universal gravitation, and E_1 is the basic unit of quantity of electricity. The advantages of this natural system were that all electrostatic and electromagnetic units would be identical and all physical inverse square laws could be written without coefficients. Of no practical value were the derived units of length, mass and time in the natural system: 10^{-37} m, 10^{-7} g and $1/3 \times 10^{-45}$ s. Stoney later proposed the names "Maxwell" and "Newton" for V_1 and G_1, respectively (Stoney 1894), and "electron" for the third unit E_1 (Stoney 1891).

The magnitudes of V_1 and G_1 were well-known; the values given by Stoney in 1881

were 3×10^8 m/s and 10^{-13}, respectively. As regards the third fundamental unit E_1 he wrote: "And, finally, Nature presents us, in the phenomenon of electrolysis, with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear I shall express 'Faraday's Law' in the following terms, which, as I shall show will give it precision, viz.:- *for each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases.* This definite quantity of electricity I shall call E_1. If we make this our unit quantity of electricity we shall probably have made a very important step in our study of molecular phenomena" (Stoney 1881, 385)..."Now the whole of the quantitative facts of electrolysis may be summed up in the statement that a DEFINITE QUANTITY OF ELECTRICITY TRAVERSES THE SOLUTION FOR EACH CHEMICAL BOND THAT IS SEPARATED" (*Ibid*. 387).

The term "bond", used here in place of Faraday's "combining power", had been introduced in 1866 by the chemist Edward Frankland. It has been suggested that in using Frankland's valency theory to calculate Faraday's "definite quantity of electricity", Stoney converted what was basically an empirical law into a new theory of the nature of electricity (see Turpin 1980, 59f.). Stoney, however, went further and determined for the first time the mass and charge of the electrolytic hydrogen ion in the following way. The mass of a litre of hydrogen he knew to be about 0.1 g, and (from his 1868 result) the number of molecules in this quantity would be about 10^{24}; the mass of the hydrogen molecule must therefore be about 10^{-25} g. The mass of the chemical atom would only be half that of the molecule, but he decided to ignore this considering the approximate nature of his other data. From experiments on the electrolysis of water, the BA committee had established that every "ampère" of electricity effects the decomposition of 92×10^{-6} g of water, yielding about 10^{-5} g of hydrogen. His "electrine", i.e. 100 "ampère", would thus liberate about 1 mg of hydrogen. This quantity would contain about 10^{22} atoms or molecules, which represents the number of bonds broken by the passage of an "electrine" in the MGS system. The quantity of electricity (E_1) corresponding to each bond ruptured is therefore found by dividing the value of the "electrine" (100 "ampère") by 10^{22} which gives a value of 10^{-20} "ampère". This was about one-sixteenth of the correct value for the charge of the electron i.e. 1.6×10^{-19} coulomb or 4.8×10^{-10} CGS e.s.u.

Stoney's nomenclature also deserves comment from an etymological viewpoint. The Greek origin of the term "electron" is of course evident; nevertheless a number of authors suggest that in coining the term in 1891 Stoney was inspired by his "electrine" of 1881. Be this as it may, it is important to bear in mind that the two terms represent very different physical entities. As regards the formation of the term "electrine", it has been suggested that Stoney fashioned the fundamental units of his MGS system by adding the Irish diminutive ín, in an anglicised form ene, to the Greek etymon (see O'Hara 1974-75, 276; Keller 1983, 35). However such suggestions are purely speculative.

Stoney's proposal of this natural system of physical units also deserves comparison with a similar suggestion for a "natural system of coinage" that he made in 1871 when the coinage of the German empire was being remodelled (Stoney 1871). In "an appeal to the intelligence of Germany" he made a plea for the adoption of a system of decimal coinage, i.e. one "brought into the most intimate association that is possible both with numbers & with weights, and is on this account entitled to be regarded as the NATURAL SYSTEM OF COINAGE". The system was to be based on the fundamental unit "monad", representing the value of each gramme of pure coined gold. Stoney's proposal met with no response and German coinage came to be based on the silver mark; it is however histori-

cally interesting as evidence of his thinking in terms of natural systems of units as early as 1871.

Seven weeks after Stoney read his paper at the RDS in 1881, and a month before it was published in the *Philosophical Magazine*, a much more famous contemporary, Hermann von Helmholtz, also advocated the acceptance of the atom of electricity. Helmholtz, the patriarch of German science, had been invited to deliver a memorial lecture, commemorating the beginning of Faraday's investigations half a century earlier, to the fellows of the Chemical Society at the Royal Institution on 5 April 1881. On this occasion Helmholtz discussed the nature of electricity, saying that both positive and negative electricity were composed of elementary portions or atoms and he interpreted Faraday's laws in the following words: "Now, the most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite portions, which behave like atoms of electricity" (Helmholtz 1881, 290). Although he did not determine the magnitude of this atom of electricity, Helmholtz's lecture attracted much attention and provided a much more favourable climate for the reception of such ideas.

Thus the modern concept of the electron is indebted in large measure to the corpuscular interpretation of Faraday's laws of electrolysis given by Stoney and Helmholtz. There is however another tradition in nineteenth-century electrical theory within which the concept also developed (see Kragh 1989). In the middle decades two main trends in electrical theory emerged viz. British field theory, as developed by Faraday and Maxwell, and continental action-at-a-distance theory. The latter approach, which can be traced back to Ampère, operated with positive and negative elementary charges in instantaneous interaction, and tended to conceive the hypothetical electrical particles as fundamental constituents of matter or aether. The most celebrated of these mid-nineteenth-century electron theories was that developed by Wilhelm Weber from 1846 until his death in 1891. He considered the neutral aether to consist of positive and negative particles orbiting around each other and (partly in unpublished notes from his later years) developed a planetary atomic model out of these particles. Independently of Weber, others, including the Englishman Richard Laming, the German mathematician Hermann Grassmann and his brother Robert, suggested in the middle decades of the century nuclear atomic models with concentric electronic shells. Their ideas with regard to the constitution of matter and ether were of course purely speculative and lacked any empirical foundation. Helmholtz's and Stoney's conception, on the other hand, did have a sound empirical foundation in Faraday's laws.

Spectroscopy

It was in the context of the search for exact numerical relationships, that would lead to mathematical laws for the distribution of spectral lines and for a corresponding atomic model, that Stoney's work on spectroscopy was carried out. Already in his 1868 paper he had suggested that the periodic motions within atoms or molecules could be the source of spectral lines. However, it was in a paper of 1870 "On the cause of the interrupted spectra of gases" that he first began to grapple with the fundamental problem of how to explain the structure, often complex, of line spectra (Stoney 1870-71). If each line corresponded to a specific movement of the emitting molecule, how could this vibrate in so many different ways? Stoney adopted an analogy with acoustics, namely of a funda-

mental note and the harmonics produced by a vibrating string, which was to provide the context for all research in this area for the next twenty years. He considered that a complex undulation would be impressed on the ether by one of the periodic motions of a gaseous atom. In mathematical terms, this waveform could be represented by the Fourier Theorem, after some simplification, in the following form:

$$y\text{-}A_0 = C_1 sin(x + \alpha_1) + C_2 sin(2x + \alpha_2) + ...C_n sin(nx + \alpha_n).$$

The left-hand side of the expression represents the initial displacement from the position of rest, the first term on the right-hand side a simple harmonic motion of a certain period, and the remaining terms harmonics of this vibration, that is with periods 1/2, 1/3, etc. of the fundamental. The intensity of each vibration is C^2, being proportional to its *vis viva* or kinetic energy. As long as the undulation travels through vacuum it retains its complex form but, on entering a dispersing medium, the constituents separate, each travelling at a speed proportional to its period. If the dispersing medium be shaped as a prism, the constituents emerge in different directions and each appears as a line in the spectrum. Thus a single molecular vibration could give rise to a series of lines in a spectrum. Terms of the series would vanish if their coefficients were zero, and the corresponding lines in the spectrum would be missing; this was analogous to the suppression of harmonics in music. The existence of a number of fundamental motions in a molecule would account for the scattered appearance of lines observed in spectra, but the absence of most of the harmonics made the situation confused and hindered the task of identifying the various harmonic series.

Stoney applied his theory to the visible hydrogen spectrum, which had four known lines (H α, β, γ, δ) corresponding to the four lines of the solar spectrum C, F, a line near G, and h. Of these, he was able to ascribe the first, second and fourth to a single internal molecular motion. Taking Ångström's measurements, corrected for the dispersion of air, he found them to be the twentieth, twenty-seventh and thirty-second harmonics, respectively, of a fundamental vibration whose wavelength in vacuo would be 131,277.14 x 10^{-10} meters. This is illustrated in the following table.

Table 1

Observed wavelengths reduced to wavelengths in vacuo (Å)	Calculated values (Å)	Differences
h = 4102.37	1/32 x 131277.14 = 4102.41	+ 0.04
F = 4862.11	1/27 x 131277.14 = 4862.12	+ 0.01
C = 6563.93	1/20 x 131277.14 = 6563.86	- 0.07

Å is the Ångström unit = 10^{-10} m, for which Stoney proposed the name "tenthetmetre". The differences between the measured and calculated values were less than 10^{-11} and thus beyond the limit of accuracy of measurement. The fourth visible line H γ did not fit into the series of harmonics, nor were any further harmonics to be found. He hoped, however, that these would in time be discovered. He also used the theory of harmonic series to explain the appearance of fluted band spectra, suggesting that these patterns were made up of lines, or harmonics, ruled in very close succession. Thus one of the two fluted patterns observed in the nitrogen band spectrum he believed to be the harmonic series from the 1960th to the 1995th of a certain molecular vibration. Stoney's paper,

first presented to the BA in 1870, was published in full in the following year in the *Philosophical Magazine.* It attracted much interest; both the astrophysicist William Huggins and the chemist Henry Enfeld Roscoe appended it to works on spectrum analysis (Schellen, ed. Huggins 1872; Roscoe 1873).

Shortly after this, Stoney published the second part of this inquiry jointly with James Emerson Reynolds, the analyst of the RDS and keeper of its mineral department (Stoney and Reynolds 1871). In most of his other investigations Stoney was content to make use of the published results of others; on this occasion he carried out with Reynolds a laboratory investigation of the absorption spectrum of the vapour of chlorochromic anhydride (chromyl chloride CrO_2Cl_2) which they thought might be accounted for by a single molecular motion. In testing the theory of simple harmonic ratios, Stoney and Reynolds used a scale of inverse wavelengths in preference to ordinary wavelengths. This proved to be a significant innovation, arising from the theory of simple harmonic ratios; harmonics, where they existed, would be equally spaced on such a scale, and the interval between successive harmonics would equal the value of the fundamental.

With a spectroscope, made by the Dublin instrument makers Thomas and Howard Grubb, they measured the angular deviations of 31 of the 106 lines observed in the spectrum of chromyl chloride, and by graphical interpolation they deduced the inverse wavelengths of these lines. They then calculated the corresponding positions of the lines on the assumption that they were equally spaced on the inverse scale. Finding the differences between calculated and observed values to be within the limits of observational error, they concluded they had found a harmonic series in this spectrum: the observed lines were considered to be the 628th and succeeding harmonics of a certain fundamental. They also observed a periodic variation in the intensities of the lines, which they tried to represent by a sine curve; the squares of the ordinates of this curve gave the intensities of the lines of the observed pattern.

Stoney's theory of simple harmonic ratios and harmonic series dominated the thinking in the field for the next decade. At the 1871 meeting of the BA, Stoney outlined the advantages of an inverse scale, and he presented a table of wave numbers for the principal lines of the solar spectrum. A committee was set up to produce a catalogue of spectral rays on a wave number scale. It took seven years to complete its task of establishing precisely and cataloguing the wave numbers of all known lines of the solar spectrum and of the spectra of the elements. At the Dublin meeting of the Association in 1878 the catalogue was presented and published in the report of the meeting. In the meantime others, including Jacques Louis Soret of Geneva and the German-born Manchester physicist Arthur Schuster, discovered and published harmonic series for other elements similar to Stoney's hydrogen series. In 1877 and 1878 the American Pliny Earl Chase published tables of harmonic relations for as many as twenty elements (see Maier 1964, 62-81).

In a series of studies, published between 1879 and 1883, the Cambridge chemists George Downing Liveing and James Dewar provided certain fundamental clarifications about the nature of spectra. By close inspection of the spectra of the alkali metals they were able to make distinctions between the multitude of lines by grouping those having a similar appearance. They effectively formulated the criterion of "homologous" series, according to which only lines of the same physical character could be placed in the same group. The identification of members of homologous series was greatly assisted by a discovery made in 1883 by the Dublin chemist Walter Noel Hartley. Taking his cue from Stoney in using wave numbers rather than wavelengths, Hartley recognised that many

doublet and triplet series had roughly the same separation of their component lines (Hartley 1883). Liveing and Dewar also found a number of impressive simple harmonic relationships to exist within some of the sequences, though whole series could not be represented as harmonics of single fundamental vibrations.

The discovery of further lines in the ultraviolet region of the hydrogen spectrum towards the end of the decade presented a new challenge to Stoney's theory. Hermann Wilhelm Vogel, of Berlin-Charlottenburg, discovered five new hydrogen lines in 1879 and, in the following year, William Huggins in England discovered twelve strong lines in the spectra of a number of white stars, three of which coincided with known hydrogen lines of the solar spectrum. The remaining nine lines he designated by letters of the Greek alphabet, alpha through iota. Huggins communicated his results to Stoney and included the latter's reply when he published his results (Huggins 1880, 678-81).

The central issue for Stoney was whether or not these lines could be related by a single law, that is whether or not the points lay exactly on or just close to a specific curve. He therefore plotted all 14 lines against their wave frequencies, i.e. the reciprocals of the wavelengths, and obtained the following curve (see Fig.1).

RECIPROCAL OF WAVELENGTH
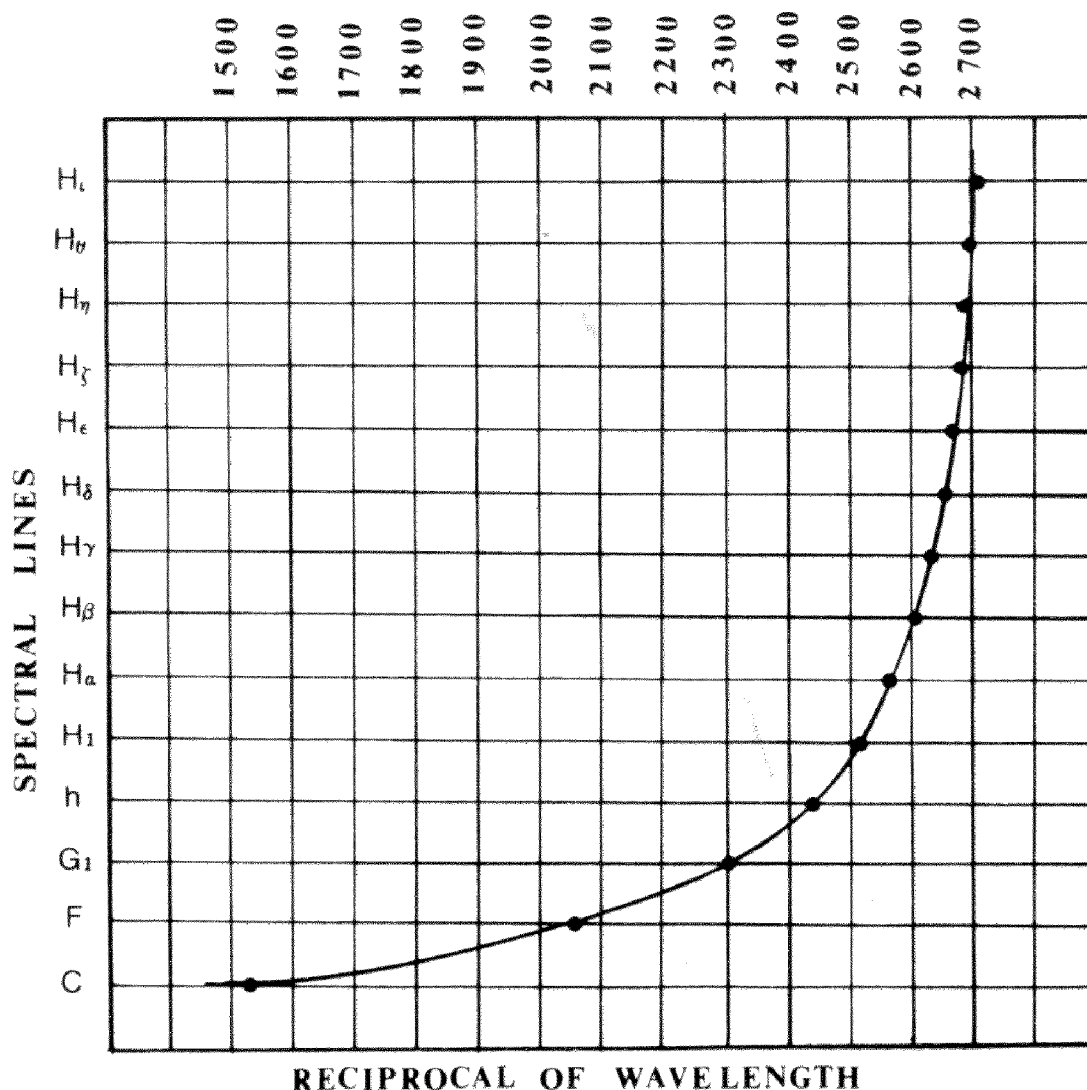
(Figure 1)

If the lines lay exactly on the curve and obeyed an exact mathematical law they could be regarded as the successive partial tones of an atomic or molecular vibration. On the other hand, if the points were close to but not exactly on the curve, then he could attribute the lines observed to a harmonic series, most of whose members are invisible or suppressed. To decide between these alternatives he constructed a table of first and second differences (Table 2), since if the curve represented a second order polynomial these second differences would be constant.

Table 2

Line	Wavelength (in air)	Wave freq.	First diff.	Second diff.
C	6562.1	1523.9		
F	4860.7	2057.3		
G$_1$	4340.1	2304.1		
			134.2	
h	4101.2	2438.3		52.4
H$_1$	3968.1	2520.1		29.6
			52.2	
α	3887.5	2572.3		16.3
			35.9	
β	3834.0	2608.2		9.1
			26.8	
γ	3795.5	2654.3		3.7
			15.6	
ε	3745.5	2669.9		4.5
			11.1	
ζ	3730.0	2681.0		2.1
			9.0	
η	3717.5	2690.0		1.8
			7.2	
θ	3707.5	2697.2		1.0
			6.2	
ι	3799 [sic]	2703.4		

On the grounds of the irregularity of the second differences he rejected the possibility of an exact mathematical law. He concluded that the points were close to but not exactly on a definite curve and therefore that Huggins' lines were to be regarded not as consecutive members of a single series but rather as members of one or more series with positions near the curve. Stoney thus failed to find the law for the hydrogen series and the first spectral series formula. He was unwilling to attribute the irregularities of the second differences to errors of observation on the part of Huggins. But his adherence to the law of harmonic ratios also seems to have predisposed him to the view that such a mathematical law did not exist. For, if one were admitted for the hydrogen series, then he would have to dispense with his theory of simple harmonic ratios and, as regards a physical explanation, the simple acoustical analogy would have to be replaced by a more complex one.

While many remarkable harmonic series had been discovered, physicists were now beginning to doubt the validity of Stoney's law. In 1879 Arthur Schuster suggested that the true law had not yet been found and that the harmonic relationships discovered might be accidental (Schuster 1879). In a major mathematical study of the spectra of magnesium, sodium, copper, barium and iron, Schuster produced evidence that made the theory almost untenable (Schuster 1881). On the assumption of random distribution of spectral lines, he showed that the number of small integer (i.e. less than 100) ratios obtained was almost the same as the number of harmonic ratios actually observed in the spectra. Schuster's results were in the main unfavourable to the theory of simple harmonic ratios but did not refute it entirely. Schuster thus concluded that some hitherto undiscovered law existed, which in special cases resolves itself into the law of harmonic ratios. The effect of the investigation was, however, to dampen the enthusiasm for the theory of harmonic ratios and the simple acoustical analogy, which were accordingly modified and generalised.

But Stoney was not alone in failing to find the formula for the hydrogen lines. Schuster and all other physicists who studied the problem were equally unsuccessful. In the end it was Johann Jacob Balmer, a sixty-year-old Swiss schoolmaster, who solved this mathematical puzzle. Stoney's simple numerical relationships convinced Balmer that some kind of simple law existed, and he eventually succeeded in relating all four lines in the visible hydrogen spectrum by the four proper fractions 9/5, 4/3, 25/21, and 9/8 to a key-note or "fundamental number", viz. 3645.6×10^{-7} mm. These fractions do not in fact form a series, and a law only became apparent when the numerator and denominator of the second and fourth fractions were multiplied by 4, giving: 9/5, 16/12, 25/21, 36/32. The series is then given by $m^2/(m^2-n^2)$ where n = 2 and m is the series of integers beginning with 3 (see Balmer 1885) .

The fractions and the formula expressed the four hydrogen wavelengths to a high degree of precision. The fractions were however not those of a harmonic series; the overtones were all greater in wavelength than the fundamental, whereas in a harmonic series of the acoustical type they would be smaller. Although Balmer had not found a simple harmonic relationship such as that associated with a vibrating string, it is evident that he had been greatly assisted by Stoney's acoustical analogy. He had modified Stoney's approach and sought a much smaller number for his fundamental (see McGucken 1969, 133). Even after the publication of Balmer's law, Stoney continued to insist that his relationship of 1870-71 for the three hydrogen lines represents a particular case of this law (see Stoney 1891, 566f.).

All in all, the analogy to acoustics was not destroyed by Schuster's investigation and the discovery of Balmer's law; instead attention turned to an analogy with more complicated acoustical cases such as bars, bells and elastic jars, where the mathematical relationships were more complex. Balmer suggested that his formula might be a special case of a more general formula applicable to other series in other elements. In this he was on the right track, but neither he nor Stoney were to play a significant role in the quest for further spectral series formulae. The major contributors here were Johannes Robert Rydberg of Lund and the Hanover team of Heinrich Kayser and Carl Runge. Their work was carried out within the context of the complex acoustical analogy. They and others failed, however, to produce a successful atomic model to account for spectral series (see Maier 1964, 88-132).

Electrodynamics/Electromagnetic theory

Following Heinrich Hertz's discovery of the photoelectric effect (in 1887), and his verification of Maxwell's prediction (in 1887/88) that light is a form of electromagnetic radiation, physicists began to think in terms of an electric or electromagnetic explanation of optical and spectral phenomena. Here the atom or quantum of electricity, as conceived by Stoney and Helmholtz, was to play a significant role. In the early 1890s there was a series of important contributions from Arthur Prince Chattock of Bristol, Hermann Ebert of Erlangen, Franz Richarz of Bonn, Arthur Schuster, and even from Helmholtz himself (see Romer 1941; Maier 1964, 268-282; McGucken 1969, 184-194). The most elaborate and most important was, however, the paper of Stoney "On the cause of double lines and of equidistant satellites in the spectra of gases", read at the RDS on the 26 March and 22 May 1891. It also represents the culmination of his work on kinetic theory, electrochemistry and spectroscopy (Stoney 1891).

Consistent with his earlier theory, Stoney argued that spectral phenomena arose from undulations in the luminiferous ether created by periodic vibrations occurring within molecules. He held both gaseous molecules and chemical atoms to be elaborate systems within which highly complex but periodic changes were constantly taking place. At first, he accounted for line spectra using a kinematical model, treating the molecule as a dynamical system like the solar system (see Figure 2).

A point P, that acts on the ether, is considered to move along an orbit in a molecule M as a result of an intermolecular encounter. The actual course of P is found by first establishing the dominant orbit and then subjecting this to perturbations. Having treated the subject in the first chapter under this "crude dynamical hypothesis", he proceeded in the following chapter to make certain corrections in order to convert the investigation into one under the electromagnetic theory. To accomplish this, he resorted to his conception of a quantum of electric charge associated with each chemical bond. This entity he now refers to as an "electron" in place of his previous term E_1 (Stoney 1891, 583). This was the first time the term was used in modern scientific literature.

According to Stoney, there are in each atom at least two, and possibly several, such electrons. They cannot be removed from the atom, but their presence is disguised when the atoms chemically unite. The motions of electrons in perturbed elliptical orbits create the electromagnetic undulations in the ether which the spectroscope resolves as spectral lines. The actual orbit of the electron might be more complicated than the simple ellipse but, in mathematical treatment, it could be resolved into elliptical partials by application of Fourier's theorem. To illustrate his idea, Stoney again resorts to an acoustical analogy, this time comparing an entire spectrum to a chord played by an orchestra: "each molecule of the gas corresponds to the entire orchestra; and the orbits described within it by its several electrons are what correspond to the vibrations of the sounding-boards, columns of air, &c., of the instruments, these being the parts of the orchestra which act directly on the surrounding medium" (Stoney 1891, 592). The whole spectrum is thus likened to an optic chord being played by the molecules; a spectral series represents one of the notes of this chord being played by a single electron; and the individual lines are the partials of a note (Ibid. 595).

An apsidal shifting of the partial would give rise to a double line in the spectrum and the observation of series of doublets could thus provide information about each elliptical motion. He attempted therefore to apply his model to account for the line spectra of hydrogen and the alkali metals which he named "monads" or "light monad
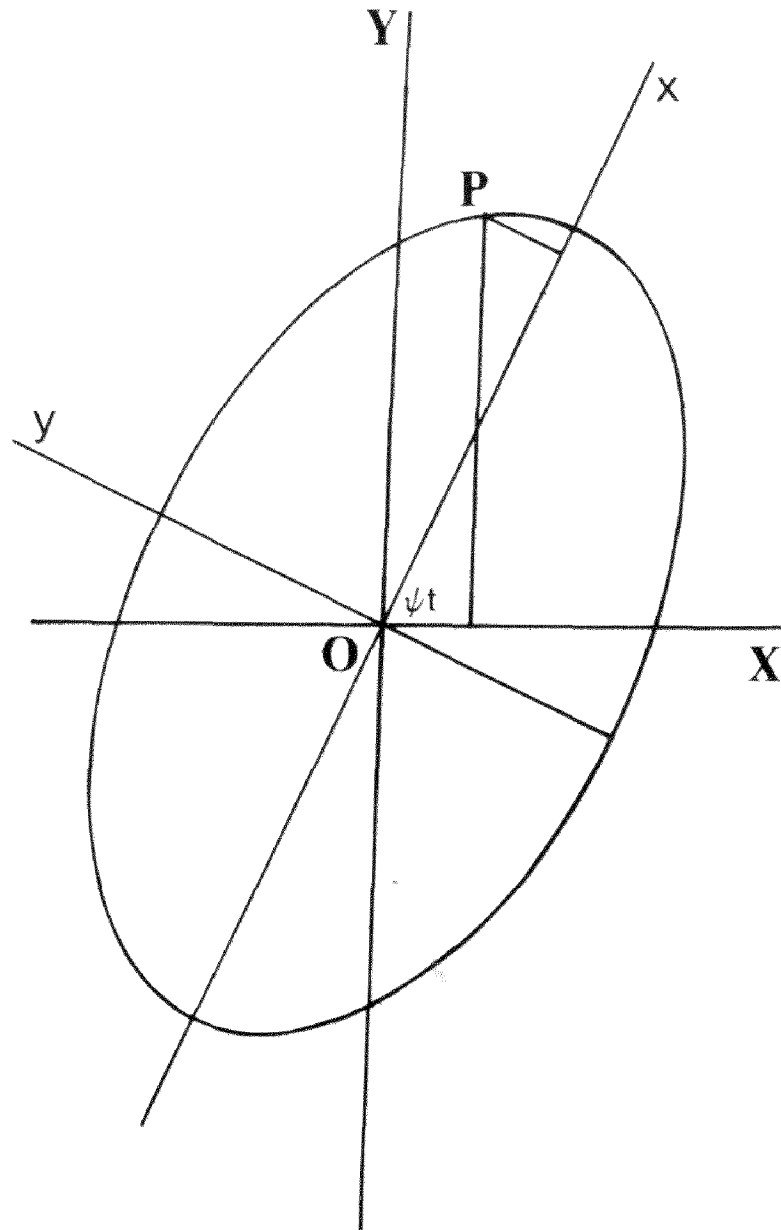
(Figure 2)

elements", each of which had been shown by Rydberg to consist of three series of double lines, designated "sharp", "diffuse" and "principal".

According to Stoney's theory, an unperturbed partial gives rise to a single spectral line. The frequency of the light is the frequency with which the orbiting point completes its revolutions, and its intensity is represented by $a^2 + b^2$, where a and b are the semi-major and semi-minor axes, respectively, of the unperturbed harmonic partial. The perturbing forces lead to apsidal shifting of the ellipse, i.e. a slow shifting in their planes, and accordingly the original harmonic is split into two ellipses whose frequencies are the sum and difference, respectively, of the original and shifting frequencies. The positions and relative intensities of the doublet components depend, firstly, on whether the apsidal motion takes place in the same or opposite direction to the revolution of the point P and, secondly, on the ellipticity of the partial. In this way

Stoney explained the origin and the intensity relations of the doublets in the sharp series of the alkali metals. The diffuse and principal series doublets arise from the same general cause, additional perturbations leading to the less sharp character of these lines.

Stoney also considered a number of other perturbations and the corresponding effects that would result in the spectrum. These included a precessional shifting of the plane of the partial with respect to the reference plane that results in the formation of triplets in the spectrum; a periodic change in the inclination of the two planes; a periodic change of ellipticity; and a nutation superimposed upon the precessional motion.

Two aspects of Stoney's model require comment. In contrast to the later use of the term "electron", which referred to a specific type of electrically charged particle, Stoney used the term only with reference to the unit of charge. Furthermore, neither the sign of the charge nor its mass play a role in his considerations. He had previously established the magnitude of the charge involved, but he never contemplated the significance of the charge to mass ratio. Stoney's "electron" is therefore not yet a sub-atomic particle, and it would certainly be wrong to portray him as discoverer of the electron.

The second point that deserves comment is Stoney's use of the term "monad", or "monad element", for hydrogen and the alkali metals. At the end of the nineteenth century this term was generally being used in the sense of Leibniz's philosophy. Stoney did have philosophical interests but he was probably resorting — to borrow a term from Faraday — simply to the "phraseology" of monadology or monadism. We should bear in mind, however, that Stoney's "electron" could not be removed from the molecule or atom, which was therefore not susceptible of further division. This was in harmony with the received view at the time that free electrons cannot exist except at the electrodes in an electrolytic bath. In fact it was George Francis FitzGerald of Trinity College Dublin, Stoney's nephew, who first, in the wake of J.J.Thomson's verification of the particulate nature of cathode rays, suggested the possibility of free electrons, and thus broke with orthodox thinking on the question (FitzGerald, 1897).

Historians who have discussed Stoney's theory have given very different assessments of it. John Heilbron for example has described it as an "elegant kinematical theory" (Heilbron 1964, 94). According to Clifford Maier, a new approach of fundamental significance was introduced by Stoney; furthermore the foundations of a new theoretical context in which to tackle the problem of line spectra were laid by him in this work (Maier 1964, 273 & 276). On the other hand, William McGucken considers Stoney's introduction of orbiting electrons and his advocacy of the electromagnetic theory of spectra to be the only positive aspects of the work. His explanation of doublets and triplets did not agree with observation and was ignored (McGucken 1969, 188). Against McGucken's opinion that Stoney's theory was quickly disgarded, it will be argued here that Stoney's approach did have a significant influence on further developments that culminated in the discovery of the electron at the end of the decade. Furthermore a continuity in the lines of research followed is evident.

Following his presentation to the RDS in 1891, Stoney published further papers promoting his theory of spectra (Stoney 1892a, 1893-98, 1895a, 1895b). He gained an audience for his ideas, but also met with opposition. Carl Runge of Hanover, for example, debated with him in the pages of *Nature* about the suggestion that all motions could be resolved into elliptical partials and analysed by the methods of Fourier (Runge 1892; Stoney 1892b). Stoney also had to defend his priority over the atom or quantum of electricity against assertions made by Hermann Ebert (Ebert 1894; Stoney 1894).

Stoney had rejected the idea that line spectra might be caused by Hertzian discharges within or between molecules, since the variety of chance conditions under which such discharges might occur could not account for the exactitude of observed line spectra (Stoney 1891, 584). In a paper of 1893, Ebert pictured line spectra as arising from charged spherical oscillators of atomic dimensions (Ebert 1893). This time it was FitzGerald who defended the interpretation of Stoney by pointing out in a note presented to the BA meeting in that year that the frequency of such an oscillator would be many times greater than the observed frequencies; if line spectra were to be attributed to charged oscillators, then these would have to be of subatomic dimensions (FitzGerald 1893).

At the BA meeting in 1894, and in a series of letters in *Nature* during the following months, one of the basic themes underlying Stoney's theory, namely the difficulty of reconciling kinetic theory with line spectra, was debated. In the course of this debate, Arthur Schuster proposed yet another model involving the oscillation in a molecule of unit electric charges about points of equilibrium (Schuster 1894-95). A basic feature of Stoney's theory had been the idea that an atom or molecule constantly emits all the lines observed in the spectrum. Schuster now departed from this view and assumed that the molecule emits only one or a few of the wavelengths at a given instant. The entire spectrum is nevertheless produced because all the molecules are simultaneously emitting different wavelengths. Furthermore, the intensities of the observed lines depend not on the amplitudes of vibration, as Stoney thought, but on the number of molecules giving rise to them. Schuster's explanation rather than Stoney's is the one that has come to be accepted (see McGucken 1969, 192). It is however significant that Schuster used both Stoney's concept of the electron, i.e. a quantum of charge, and Stoney's own term "electron". Schuster ends by expressing his belief in the existence of the electron with the words: "In the existence of the 'electron' I firmly believe".

As the concept of the electron became increasingly accepted, mathematical and theoretical physicists attempted to develop an electron theory, that is one based on small electrically-charged particles which would establish the various relations between electricity, light and matter. The most important of these electron theories were those of Joseph Larmor and Hendrik Antoon Lorentz. The former has been described by Alfred Romer as a "a curiously Irish creation" (Romer 1941, 680). Larmor was an Ulsterman and, like Stoney, had been professor in Galway before going to Cambridge where he became Lucasian professor. Larmor's electron theory was inspired by a theory of the propagation of light, developed by James MacCullagh at Trinity College Dublin between 1836 and 1841, and reinterpreted in terms of Maxwell's electromagnetic theory by FitzGerald in 1880. Here Larmor's theory will be considered only to the extent of documenting Stoney's influence (see Heilbron 1964, 90-93; Maier 1964, 285-289; McGucken 1969, 192-194).

Larmor first presented his theory to the Royal Society of London in December 1893. It was however in a section entitled "Introduction to free electrons", added some months later on the suggestion of FitzGerald (see Larmor 1905) who had refereed the paper, that Larmor proposed a theory of spectra derived from that of Stoney. The essential innovation here is Larmor's conception of "discrete electric nuclei", which were to be thought of as "centres of radial twist" in the ether (Larmor 1894; 1929, 515-516). His exact words are that such "monad charges — or electrons, as we may call them after Doctor Johnstone Stoney — must circulate very rapidly, in fact with velocities not many hundred times smaller than the velocity of radiation". Larmor's understanding of the electron is however quite different from that of Stoney; in fact Larmor's electron corresponds to the

monads of Stoney's theory: "the electron would be chemically an atom of very simple type such as e.g. that of hydrogen" (*Ibid.*). On the other hand, Larmor's electron, unlike Stoney's, is conceived of as a particle and not just a quantum of charge. There can be no doubt that Larmor adopted the idea of the electron from Stoney, a fact often not heeded by historians (e.g. Falconer 1987); some do stress, however, the influence of FitzGerald on Larmor's introduction of discrete electric charges, or "electrons", into electromagnetic theory (e.g. Warwick 1991).

In a second paper, whose title was extended by the addition "Part II: Theory of electrons", Larmor proposed a system of positive and negative electrons revolving about one another. Such a system would be "roughly of the type of a ring of positive electrons revolving round an inner ring of negative ones" (Larmor 1895; 1929, 597). He believed that the origin of the numerous spectral lines of certain molecules could be illustrated by such a system. His model here is similar to the planetary model of Stoney and he writes: "Thus in the analogous astronomical system of the Sun, Earth, and Moon, which has only nine coordinates, three for each body, there exist the much larger number of periodic inequalities or oscillations that are discussed in the Lunar Theory. The fact is that the oscillations of the coordinates of the system are not themselves harmonic or even exactly periodic; it is only when they are analysed by the mathematical processes suitable to vibrations, or by a physical instrument such as a spectroscope which yields the same results, that the lines of the spectrum come into existence." (*Ibid.*) Thus Larmor's basic approach seems to have been inspired by Stoney's earlier theory (see Maier 1964, 288; McGucken 1969, 194).

Larmor's theory furthermore yielded a prediction of the effect observed by Pieter Zeeman in the following year, namely the broadening and splitting of spectral lines in a magnetic field. In his 1895 paper, Larmor considered an electron of charge e and mass m describing an elliptical orbit about an equilibrium point where the central attractive force is proportional to the displacement, and he predicted what would happen if a uniform magnetic field was applied. In a treatment that is very reminiscent of Stoney, he described the results in terms of precessions of the axis of rotation about the direction of the magnetic field (Larmor 1895; 1929, 597). Thus, even before the Zeeman effect was discovered experimentally, Larmor had examined the question theoretically and he had recognised that the magnitude of the magnetic frequency separation would be proportional to the charge to mass ratio of the electron producing the line. However, he wrongly assumed that the mass of the electron was of the order of magnitude of a hydrogen atom, and he therefore expected the effect to be over a thousand times smaller than that eventually observed (see Heilbron 1964, 93 & 103; Maier 1964, 288f., 298f.; Whittaker 1962, 411).

It was to Lorentz's ion theory, published in 1892 and 1895, that Zeeman turned after he successfully observed in August 1896 the widening of the D lines of sodium and the red lines of lithium in a strong magnetic field (see Heilbron 1964, 100-103; Maier 1964, 289-300; McGucken 1969, 194-198). A direct influence of Stoney on the development of Lorentz's ideas cannot be established. However Zeeman, in his main publication that appeared in an English translation in March 1897, indicated in a footnote that he only subsequently learned of Stoney's earlier attempts to explain doublets and triplets in terms of perturbing forces on the elliptical orbits of electron charges (Zeeman 1897a, 234). He had thus opted for Lorentz's explanation based on the latter's theory of ions. The predictions of this theory were wonderfully confirmed by Zeeman's observations. It also provided a means of determining the ratio of charge to mass of the ion. In his first paper,

Zeeman estimated this ratio to be of the order of magnitude of 10^7 electromagnetic C.G.S. units (Zeeman 1897a, 235). But, in a more precise measurement in 1897, he obtained the value 1.6 x 10^7 for the sodium lines (Zeeman 1897b, 256). Also in the same year Lorentz found the value 1.2 x 10^7 for zinc lines (Lorentz 1897, 24). These values were in good agreement with values later generally accepted (1.7592 $\pm$ 0.0005 x 10^7). However, the charge to mass ratio for the ions of the chemical atoms, determined from electrolytic data, was only of the order of magnitude of 10^4. This discrepancy could be accounted for by assuming the charge of the particle producing spectral lines to be much larger or its mass much smaller, or perhaps both.

Since the ratio of the square of the charge to mass also appeared in his equations for other phenomena, Lorentz was able to determine the approximate magnitude of the mass separately (Lorentz 1897, 25), and he concluded that the charge on a hydrogen ion in an electrolyte and the charge on the ion producing the spectral lines were of the same order of magnitude and that this "lightion" was only a small part of the hydrogen molecule, having only about 1/350th of the mass of a hydrogen atom. Lorentz's theory could also indicate, from the polarisations of the outer lines of a Zeeman triplet, the sign of the charge of the "lightion". In his original paper, Zeeman stated that the revolving ion would be positive but, in the next paper, he corrected his results and concluded that the radiation was chiefly due to the motion of negatively charged particles (Zeeman 1897a, 235; 1897b, 58).

For a short time, the agreement between theory and observation for the Zeeman effect seemed perfect. In December 1897, however, Thomas Preston presented a paper to the RDS (Preston 1897) that contained new experimental discoveries which eventually led to the abandonment of the simple classical explanation of the Zeeman effect. He had discovered that not all lines split into the normal triplets predicted by theory, and that certain lines in the zinc and cadmium spectra became quadruplets. This he followed up in a series of other papers over the next two years (see Maier 1964, 300-311; Weaire and O'Connor 1987). A number of other workers soon confirmed the existence of such anomalous Zeeman effects. It was thus established that the Zeeman effect for different spectral lines varied considerably within the same elementary spectrum. Some lines separated into distinct triplets, others resolved into doublets, quartets, sextets, octets and other multiplets.

In a final effort to reintroduce some organisational clarity, Preston resorted in 1899 to Stoney's 1891 approach (see BA Report 1899, 63f.). Stoney had attributed each of the three homologous series found in the sodium spectrum to the action of an individual electron. Preston now grouped the members of the Zeeman triplets, found in spectra like that of zinc, into series of firsts, seconds and thirds. As all the members of each group suffered similar perturbations in a magnetic field, the e/m ratio was considered to be the same for all the lines of the same group but not the same for all the lines of the spectrum as a whole. In other words, each group must be due to the action of an individual particle. This was the last lease on the life of Stoney's model. Its demise did not however mean that something better had taken its place; in fact none of the various attempts to account for the variety of observations surrounding the Zeeman effect on a classical basis ever proved satisfactory (see Maier 1964, 808f.).

Gas discharge phenomena and cathode rays

Whereas the electron had been all but discovered by 1897 in the course of spectral investigations, the actual experimental discovery was only achieved with the

resolution of the controversy about the nature of cathode rays that had developed in about 1882. One of the roots of this debate is to be found in the concept of the so-called "fourth state of matter" or "radiant matter" that can be traced back to Humphrey Davy and Michael Faraday. This concept reached its greatest refinement in the studies of William Crookes who was the first to apply it directly as the basis of the first coherent theory of the nature of electric discharge in vacuum tubes (see Turpin 1980, 116-152).

Crookes' theory developed out of his work between 1873 and 1876 on the radiometer. This well-known device consisted of an arm with pith balls at either end mounted on a pivot within a vacuum tube. In his initial paper Crookes believed that the motion of the balls was due to radiation (Crookes 1876a, 338). However, in 1876, he changed his viewpoint in favour of one which attributed the motion to the effects of the residual gas (Crookes 1876b). Earlier in that year, Stoney had asserted that, in a very rarefied state, when the mean free paths of the molecules were inordinately large, the residual gas caused the movement of the radiometer vanes (Stoney 1876). Adopting Stoney's idea, Crookes then proposed that the "fourth state of matter" had been attained when the mean free path was of the order of the dimensions of the vessel, and he explained the action of the radiometer in terms of a variable region of molecular pressure in front of the pith balls.

In a paper of 1882, Crookes then applied his concept of the fourth state to electrical effects in rarefied gases in general. In 1838, Michael Faraday had observed the appearance of distinct glows at the cathode and anode with an intervening dark space. Crookes now related the dark space observed around the cathode to the layer of molecular pressure causing the movement of the radiometer. This dark space varied with pressure in the same way as the layer of molecular pressure in the radiometer had varied, and he concluded that this represented the mean free path of the molecules of the residual gas. At high exhaustions, the dark space extended the entire length of the tube and the molecules travelled unimpeded, being stopped only by the glass at the opposite end of the tube. The phosphorescence observed was attributed to corpuscular impact and not radiation (Crookes 1882). It was Crookes' theory, the essential element of which was Stoney's mean-free-path concept adapted from the explanation of the radiometer, that triggered off the cathode ray controversy.

Stoney took no part in the debate about the nature of cathode rays between 1882 and 1897, but it is likely that he was a supporter of the corpuscular conception. This view was opposed by a number of German physicists, the most important of whom were Eugen Goldstein, Eilhard Wiedemann and Heinrich Hertz, who advocated an ether-wave interpretation. The most formidable obstacles to the acceptance of the corpuscular interpretation came from Hertz; his investigations failed to reveal an electrostatic deflection of the rays, and showed an apparent divergence of the paths of the rays and the current within the discharge tube (Hertz 1883). When in 1892 Hertz and Philipp Lenard showed that cathode rays pass through thin metal foils a further difficulty was raised for the particle interpretation (Hertz 1892).

It was J.J. Thomson who now emerged as the leading figure in the effort to vindicate the corpuscular interpretation. Between 1883 and 1895 he carried out a series of investigations on the conduction of electricity through gases before turning in 1894 to the study of cathode rays as such. Historians have naturally tended to concentrate their interest on Thomson's investigations of cathode rays; however recent studies (Turpin 1980, 153-180; Falconer 1987) have stressed the importance of his early work on gas discharge for the discovery of the electron. Here we also find a certain continuity with the

earlier researches of Faraday and Stoney.

In 1883, Thomson put forward a theory of the nature of the discharge of electricity, based on an analogy with conduction in liquids. According to this electrolytic analogy, electricity was assumed to be concentrated in definite quantities, charging with definite amounts the carriers which conveyed the current. For the next ten years, his efforts in this area essentially amounted to a search for evidence of permanent dissociation of gases. By the time he took up the study of cathode rays, his investigations of the electrolysis of steam and other gases had provided an understanding of the nature of the discharge of electricity through gases. Before discharge, a certain number of molecules in the gas were considered to exist in a condition close to dissociation. The application of an electric field of sufficient intensity would then lead to the dissociation of the gas molecules. The resulting ions, each of which carries a charge equal to that of the electrolytic ion of hydrogen, are then diffused through the gaseous volume.

The discovery of Röntgen- or x-rays in 1895 considerably simplified the method of rendering gases conductive, and Thomson's experiments on gases exposed to these rays led to further important results (see Turpin 1980, 180-207). In 1894, Thomson started his studies of cathode rays, and showed their velocity to be less than a thousandth that of light which supported the view that the rays were streams of charged atoms rather than etherial waves (Thomson, 1894). In the following year, Jean Perrin, in France, demonstrated that cathode rays were charged with negative electricity and that the paths of the current and the cathode rays coincide (Perrin 1895), thereby overcoming one of the main stumbling blocks for the corpuscular theory arising from Hertz's work.

In early 1897, Thomson then repeated Hertz's 1883 experiment, which had failed to reveal the electrostatic deflection of cathode rays. The flaw he found to lie in the fact that the cathode rays in passing through a gas make it a conductor that then screens off the electric force from the charged particles. The solution to the problem lay in repeating Hertz's experiment at high exhaustions. These results were first announced at the Royal Institution on April 30, 1897 (Thomson 1897a), and were published in same year (Thomson 1897b). This work effectively resolved the cathode ray controversy by removing the major obstacles in the path of the acceptance of the particle theory. It was during his Royal Institution lecture that he first proposed that the "cathode rays are charged particles moving with high velocities" and that "the size of the carriers must be small compared with the dimensions of ordinary atoms or molecules". Thomson called these negatively-charged subatomic particles "corpuscles". Citing William Prout, who in 1815 had suggested that the atoms of all the elements were built up of hydrogen atoms, Thomson proposed that atoms of ordinary matter were made of corpuscles. His "corpuscle" was thus a building block of nature. Finally, he devised a method for measuring the ratio of the mass to charge (m/e) of the corpuscle in cathode rays. The value he found was of the same order of magnitude as that deduced by Zeeman (i.e. about 10^{-7}) and was independent of the nature of the gas. Faced with a discrepancy of a factor of a 1000 between the mass to charge ratio for the cathode ray corpuscles and the electrolytic hydrogen ion, he concluded that the former were smaller than the atoms of hydrogen.

Zeeman's results had been published a month before Thomson's lecture. Furthermore, at least two others measured the charge to mass ratio of cathode ray particles before Thomson. As early as 1890, Arthur Schuster had measured this ratio from experiments on the deflection of cathode rays in a magnetic field (Schuster 1890a; 1890b). In 1897, Walter Kaufmann at the University of Berlin also established that the e/m ratio for

cathode rays was about 1000 times that of the electrolytic hydrogen ion (Kaufmann 1897). Both Schuster and Kaufmann failed to make the deduction from this discrepancy that the charge carriers were much smaller than hydrogen atoms. Both had thrown the baby out with the bath water (see Heilbron 1964, 79). Yet another German, Emil Wiechert of Königsberg, undertook magnetic deflection experiments on cathode rays and found their e/m to lie between the limits of 400 to 4000 times that of electrolytic hydrogen, the uncertainty being due to the estimated error in determining the velocity of the rays (Wiechert 1897a; 1897b). The magnitude of the ratio proved to his satisfaction that cathode rays could not be charged chemical atoms, and he concluded that they were streams of atoms of electricity. The largeness of the e/m ratio implied the smallness of m, which Wiechert understood to be entirely electromagnetic in nature. He anticipated that its radius was sufficiently small to account for its ability to penetrate thin metal foils (see Heilbron 1964, 95-96).

Thus, in early 1897, two different entities were proposed as solutions to the cathode ray impasse, namely Thomson's "corpuscle" and Wiechert's "atom of electricity", which was probably more akin to the earlier conceptions of Stoney and Helmholtz. As regards the "corpuscle", it was FitzGerald rather than Thomson who first broke with the sanction against free atoms of electricity; on hearing of Thomson's Royal Institution lecture he suggested: "we are dealing with free electrons in these cathode rays" (Fitz-Gerald 1897; cf. Whittaker 1962, 362). The acceptance of the hypothesis of free electrons by the turn of the century was largely due to the advocacy of FitzGerald, Larmor and Oliver Lodge of Liverpool. Furthermore, the acceptance of Thomson's corpuscle was facilitated by its identification with the "electron" of Larmor's theory and the "ion" of the Lorentz theory (see Heilbron 1964, 96f.).

There is a fairly general consensus that J.J. Thomson was the discoverer of the electron. However, if we take as a definition of discovery the measurement of the charge to mass ratio accompanied by an explanation of the discrepancy with the corresponding ratio for the electrolytic hydrogen ion in terms of an entity having a mass much smaller than the hydrogen atom, then Zeeman and Lorentz and possibly Wiechert emerge as rival discoverers. Early 1897 is the earliest date at which the electron can be considered as discovered. However, in 1897 a crucial question was still left unanswered. All Thomson, or his rival discoverers, had was the value of the m to e ratio for the cathode rays, from which it was concluded that it was the value of m in the ratio that was small, not the value of e that was large. On this basis Thomson announced his discovery of the "corpuscle". But, until he could determine the value of either quantity independently, his theory would remain incomplete. The measurement of these two quantities for cathode rays and in the photoelectric effect formed the subject of two papers which he published in 1898 and 1899. Hence, it would be more correct to set the date of the discovery of the electron as 1899 rather than 1897 (see Turpin 1980, 202).

Conclusion

It only remains to assess Stoney's role in the discovery of the electron. Fifty years ago Alfred Romer wrote two papers (Romer 1941; 1942) in which he considered the discovery of the electron in two periods: the speculative history of atomic charges in the period from 1873 to 1895 was followed by the history of the experimental discovery. Here Romer's division has been followed in considering a period of the conceptual discovery followed by one of the experimental discovery. In the first period, Stoney emerges as one

of the central figures but, when the time came for the electron to be experimentally discovered, he had been superseded by a younger generation of physicists. Nevertheless, he made a significant contribution in each of the five avenues along which progress leading to the discovery of the electron was made. His most important contribution was his interpretation of Faraday's laws of electrolysis in terms of a fundamental quantum of electricity, the magnitude of whose charge he was the first to to determine. In spectroscopy he failed to discover Balmer's law, but his law of simple harmonic ratios gave the initial impulse in the search for spectral series formulae. His kinematical model of 1891, with an orbiting electron in a molecule, was probably the most sophisticated model for the explanation of line spectra that was developed within classical physics.

Finally, it seems appropriate to turn to the anniversary being celebrated, namely the naming of the electron in 1891. It has been suggested that Stoney presented his 1891 paper to the Royal Dublin Society for patriotic reasons (Romer 1941, 678f.). It has also been suggested that Stoney coined the term "electron" from his term "electrine" of 1881, which may in turn have been constructed by adopting the Irish diminutive. It would of course be incorrect to portray Stoney as an Irish nationalist. His relationship to Ireland was probably characterised by a certain ambivalence after the disappointments of his career. Stoney never wrote a monograph himself but, in 1906, he contributed a preface (Stoney 1906) and a frontispiece photograph of himself to a popular book by Edmund Edward Fournier D'Albe entitled *The Electron Theory*. This book contains the following dedication:

"Do cum glóire Dé agus onóra na h-Eireann".

Fournier D'Albe, a physicist and popular scientific writer, was active in the Gaelic and Celtic revival and author of an Irish-English dictionary; the dedication was surely his. But Stoney seems to have had no problem in associating himself with the sentiments expressed.

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