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Historical Background to one of the Most Cited and Influential Papers in Physics: Ugo Fano on Configuration Interaction, 1961

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Abstract
In the December 15, 1961 issue of Physical Review Ugo Fano, then at the National Bureau of Standards in Washington, D.C., published a paper entitled, “Effects of configuration interaction on intensities and phase shifts.” (Fano, 1961) That paper has become one of the most cited papers in American physics. The impetus for the paper was an experimental result, in 1954, by Silverman on an unusual behavior of the continuum of helium in the neighborhood of a discrete peak, under electron impact, reported in a Scientific Report by Silverman and Lassettre in 1957 under an Air Force grant, reported at a conference in 1958, and finally published in the open literature in 1964. The 1957 Report had been brought to Fano’s attention by Robert Platzman, a friend and colleague (Fano, 1977, and Fano, personal communication). Fano recognized the shape of the electron impact spectrum as similar to the qualitative characteristics of optical spectra of some of the rare gases (but not including helium) reported in 1935 by Beutler. Fano, in his first post-doctoral paper, published in Il Nuovo Cimento (1935) had outlined a theory to describe these characteristics. Until the measurement of Silverman there had been no measurement, either optical or by electron impact, sufficiently well resolved or defined to serve as a quantitative test of theory. Fano updated his 1935 paper in a paper in 1961, using the Silverman and Lassettre experimental results as a test of his theory. Fano’s 1961 paper has become one of the most cited papers in American physics.
In the December 15, 1961 issue of Physical Review Ugo Fano, then at the National Bureau of Standards in Washington, D.C., published a paper (Fano, 1961) (the paper will be referred to as Fano61 in the remainder of this paper) entitled, “Effects of configuration interaction on intensities and phase shifts.” The impetus for the paper was an experimental result, first noted in 1954 (see Appendix A), by Silverman of an unusual behavior of the continuum of helium in the neighborhood of a discrete peak, under electron impact, reported in a Scientific Report (see Appendix B) by Silverman and Lassettre in 1957 under an Air Force grant, and finally published in the open literature in 1964 (Silverman and Lassettre, 1964). The 1957 Report had been brought to Fano’s attention by Robert Platzman, a friend and colleague. Fano recognized the shape of the electron impact spectrum as similar to the qualitative characteristics of optical spectra of some of the rare gases (but not including helium) reported in 1935 by Beutler. Fano, in his first post-doctoral paper, published in Il Nuovo Cimento, the same year, had outlined a theory to describe these characteristics. Until the measurement of Silverman there had been no measurement, either optical or by electron impact, sufficiently well resolved or defined to serve as a quantitative test of theory.

Fano’s paper in 1961 was essentially a new paper, rather than simply a reformulation of his 1935 paper. Fano61 developed a theory for configuration interaction, that is, when a system has two
pathways open to it because of the existence of two possible configurations of equal energy. Fano’s treatment reduced the result into one involving three parameters which could be fitted to an experimental result, without the need of evaluating many complex integrals. Fano’s theory has found applications in many areas of physics other than the two-electron excitation in helium, which gave rise to it. A recent in-depth, thorough discussion of the Fano equation and its applicability in atomic, molecular and optical physics; various condensed matter systems; and nuclear, especially particle physics, can be found in Rau (2004) (see also Rau, 2000, for a description of Fano’s lifetime activities).

Fano61 has become one of the most cited papers in physics, with more than 1000 citations through June 2003 in the Physical Review family of journals, (Redner, 2005), and, by 20 October 2019, 11,374 citations in the broader group of journals covered by Google Scholar. The paper is also listed as having had the third greatest impact in the Physical Review group of journals (Redner, 2004, Table III). As such it deserves a study of its background and the details of its conception and implementation. As scientists we tend to believe that we must eliminate the human aspect of our work – objectivity requires replication by others, thus eliminating human faults. History, however, demonstrates that how we do our work, what we accept as results, that for these, human aspects enter in. In this paper I will try to indicate at least some of the ways these enter in.

Many lessons on the history of how science is done can be learned from such an exercise. The present paper is an effort to do so. I have relied on published documents, my own memories of the events and of conversations with Prof. Lassettre, and my memories of Fano’s description of his role in a supper-time conversation in the early 1960s, and on such documents as I have been able to obtain from the University of Chicago archives, and those of the Ohio State University Research Foundation. I have also used some published memoirs of others to confirm or supplement the above sources.

For the present paper we must remember that the Fano61 paper was restricted to the shape of line profiles resulting from the interaction of configurations of two states of equal energy. I have limited myself, except for historical antecedents, to papers which include discussions of line shapes, and to a few papers which followed closely on publication of Fano61. To do otherwise would involve a much broader and more extensive discussion of matters irrelevant to the history of Fano61, the subject of the present paper.

The physics background in 1935.
I will not dwell on the expansion of knowledge which began in 1900 with Max Planck’s use of quantal changes in physical phenomena. What we are primarily interested in is the situation where two states of a system lead to an interaction of these states. In particular we are interested in the situation where, for atoms, one of these states involves the emission of an electron which can have a continuous range of kinetic energies, or, for molecules, one of the states may lead to dissociation or ionization. The process by which this happens is known as the Auger Effect, named after Pierre Auger, who described it in 1923. An earlier notice of the effect was given by Lise Meitner in a paper in 1922, where, however, it was incidental to the major focus of the paper, and therefore neglected (for this discussion of the Meitner-Auger priorities, see Duparc 2009).

The study of spectra was a major focus of attention in the late 1920s. In particular a noticeable difference in many bands of the same molecule, between sharp and diffuse bands occurred. Bonhoeffer and Farkas (1927) and Kronig (1928) were the first to explain that for many diffuse molecular spectra the Auger effect is responsible for the diffuseness, and this results, in a molecule, from the overlapping of discrete energy levels by a continuum (Herzberg, 1950, p. 409). Henri and Teves (1924, p. 895) had previously defined a process of molecular dissociation which they termed “predissociation”:

“These interesting results obtained for the sulphur molecule lead us to a general discussion of different kinds of transformations of any given molecule. We know by the electronic impacts that at a given minimum potential the impacts are no longer elastic; this occurs at the resonance potential of the molecule. It means that certain electrons jump from the normal orbit into the next one. But now we see that before this state is reached the molecule can be modified in its internal structure: the atoms are driven apart, the bonds are weakened, the molecule becomes more reactive, and the rotational movements are no longer quantified. This first modification is a preliminary preparation of the molecule for its total dissociation, and it is necessary to introduce a new term for this change. We propose to denote it by the term predissociation of the molecule.”

Among later studies was that of Gibson and Rice (1929) for iodine monochloride. Their study indicated strongly that the convergence limit of one band corresponded to the dissociation of the molecule into normal chlorine and excited iodine atoms. A second continuum also corresponded to this same process. In the first band the rotation lines were sharp near the head, but showed a marked increase in width for large rotational quantum numbers. The next following bands were diffuse and faded out in the region of the continuum. They concluded that this was the same effect that had been observed by Henri, and labeled by him predissociation. The diffuseness was created by the
interaction of the discrete states and the continuum. Wentzel (1928) had similarly accounted for the diffuseness of lines in a similar situation. The interest of these various theoretical and experimental studies was in the broadening of the discrete levels, the weakening of the emission from these levels, and the transition probabilities of the radiationless decomposition of the system (see the summary by Herzberg, 1950, p. 407). In the period before 1935 only one study, by Rice, of the line shape of discrete lines in a continuum appeared.

In a 1929 paper (Rice, 1929a, p.748) Rice summarized the situation:

“IT HAS been recognized for some time that, when a molecule is raised by absorption of light to an excited state from which subsequent decomposition may occur, the resultant vibration bands may be diffuse, i.e., the rotation lines may be broad and blur into each other. Several recent writers have described the situation more specifically as follows. The molecule is originally in some initial state, with definite electronic, rotational, and vibrational quantum numbers. Through the absorption of radiation it jumps to a higher electronic state, changing at the same time its vibrational and rotational quantum numbers (the rotational in accordance with a

2 Oscar Knefler Rice (1902-1978). Rice’s life and career are presented by Widom and Marcus (1989) and Widom (1979). The facts in this paragraph are taken from those sources. Rice was born in Chicago on February 12, 1903. He never knew his father, Oscar Guido Rice, who had died six months after the marriage. He shared such a background with Isaac Newton, also a posthumous birth, and it is likely that this fact played a major part in his subsequent intellectual development (see, e.g., Silverman, 1974). The given name of his mother, Thekla Knefler Rice, may indicate a connection to the first female Christian martyr, St. Thekla, a contemporary of St. Paul, who lived in what is now Maaloula, Syria (for the history of St. Thekla, see, e.g., Johnson, 2006). Rice was brought up by his mother and her sister, who helped him to complete his education despite their difficult financial situation. Rice attended San Diego Junior College from 1920 to 1922, transferring then to the University of California, Berkeley, where he obtained the B.S. degree in 1924, and the Ph.D. in 1926. He then spent an additional year at Berkeley, then, as a National Research Fellow, at the California Institute of Technology (1927-1929), and a year at the Institut für Theoretische Physik der Universität, Leipzig (1929-1930). He then spent several fruitful years at Harvard (1930-1935) as an Instructor in Chemistry, a year at Berkeley as a Research Associate, and finally in 1936, moved to the University of North Carolina, where he continued for the remainder of his career. Despite his accomplishments at Harvard he seems not to have been very happy there. A.O. Allen (cited by Widom and Marcus, 1989) “believes that the social sophistication of Harvard may not have been well suited to Rice’s quiet, solitary, and contemplative style. Later, at Chapel Hill, he found him to be more relaxed and at peace—although otherwise unchanged.” He died on May 7, 1978.

His scientific work covered many areas of physical chemistry: quantum theory, chemical kinetics, equilibrium and non-equilibrium thermodynamics, and statistical mechanics. Of interest here was his fundamental work on predissociation and diffuse spectra. His book, *Electronic Structure and Chemical Binding*, (1940) was one of the earliest on the subject for students. He also published *Statistical Mechanics, Thermodynamics, and Kinetics* (1967). A fuller description of the originality of his work, tributes to it, including one in 1932 by the future Nobel Prize laureate Lev Landau, and a selective bibliography, can be found in Widom and Marcus (1989).
selection principle). The upper electronic state has a certain dissociation limit; for smaller energies than the energy of dissociation there is a discrete set of vibration-rotation levels, for larger energies a continuous set. In the cases where predissociation occurs there are two higher electronic states to which the molecule might jump, and some of the discrete vibration-rotation levels of one of these electronic states have their energies in the continuous range for the other electronic state. The broadness of the lines has been connected with the short life period of a molecule in a discrete state, when there is the possibility of its making a radiationless transition to a state of dissociation. … It is the purpose of this paper to make a calculation of the width of the line directly in terms of the perturbation matrices without employing the assumption connecting width and life period. The total absorption over the line is also calculated.” [citations omitted]

In a second 1929 paper (Rice, 1929b) Rice noted that the description of the process involved the interaction of two configurations: “Here activation is by light, and after a lapse of time the molecule decomposes. It is shown that, under some circumstances which are discussed in detail, the wave function immediately after the excitation by light may be completely and correctly described as the wave function of a discrete state, which interacts with a continuum.” In 1930 (Rice, 1930a) he extended his theory to radioactive decay, and, for the first time, included a discussion of the resulting line shape. A second paper in 1930 (Rice, 1930b, p. 1552), immediately following the other paper, elaborates the theory for the shape of the line in predissociation, and concludes: “Hence the shape of the broadened discrete line is the same in the case of predissociation as in the case of radioactive decay or dissociation by rotation.” In Rice’s final paper on the subject (Rice, 1933) he attempts a quantitative description of what happens “in the neighborhood of the crossing point of two potential energy curves in a particularly simple case of predissociation. We shall find” he says, “that a given rotation level is not only broadened, but is somewhat distorted in shape, is shifted in position, and has a rather complicated secondary structure.” He attempts to apply the results to iodine monochloride, but concludes: “I think it may be said that while it does not seem possible to account quantitatively for the predissociation phenomena in iodine chloride, progress has been made in understanding and interpreting them, and affording a basis for their discussion.” (Rice, 1933, p.375)

In the years from 1933 to 1961 two papers (according to Google Scholar) in the literature cited Rice’s work. Mulliken (1934) cites the 1933 paper only for its connection to the spectra given by
Brown and Gibson. Breit and Wigner cite it in connection with their treatment of the capture of slow neutrons. Stepanov (1945), extends Rice’s treatment. Stepanov (Stepanov, 1945, p. 317) summarizes the situation at the time: “The most full mathematical treatment of this phenomenon has been given by Rice, who proposed a method of determining the shape of the spectral line in the presence of predissociation. However, Rice has considered only one special case most frequently observed for diatomic molecules - the interaction of only one discrete energy level with a set of continuous levels. All other levels are in that case situated so far that the halfwidth of the predissociated level is much smaller than the distance between them and their distorting effect may be disregarded.

“In the present paper is considered a more general case met with for the predissociation of adjacent rapidly converging vibrational levels near the predissociation limit for the vibrations of heavy polyatomic molecules, for the predissociation of energy levels of weak bonds … “The method of calculation is similar to that of Rice.”

Herzberg’s 1950 discussion of line shapes consists entirely of the following (Herzberg, 1950, p. 410): “The line shape of a line made diffuse by predissociation has been discussed by Rice and Stepanov.” (citations omitted). He does not cite or discuss Beutler’s 1935 paper which cites the work of Rice on line shape in predissociation, nor Fano’s 1935 paper providing a theoretical basis for Beutler’s results.

Autoionization.

Not long after the recognition of predissociation in molecules the analogous phenomenon of autoionization in atomic spectra was noted. Shenstone (September 1, 1931) wrote: “There is a well-known effect in band spectra which is called predissociation. The effect is an automatic dissociation of a molecule when the sum of its vibrational and electronic energies exceeds the energy necessary for dissociation in some lower electronic system.” Wigner suggested to him that some peculiarities of the copper arc spectrum could be explained by a parallel action in an atom. Thus, “it is possible for an atom, by the excitation of two electrons, to exist in a state of energy-content more than sufficient to ionize it by the removal of the first electron. In such a state, there is the possibility of a radiationless transition carrying the excited atom into the state where it exists as an ion plus an electron. … This effect has been referred to as the Auger effect from its analogy to the effect in x-rays discovered by Auger; but I believe that it could much more logically be called auto-ionization.” White
(1931a), a week later, submitted on September 9, applied Shenstone’s insight to the spectra of the noble gases krypton and xenon, and the alkaline earths, calcium, strontium and barium, and the resulting differences, whether sharp or diffuse, of the spectral lines. White (1931b, p.2016) expanded his discussion in a later paper, submitted on October 19, published on December 1, explained the process: “The transition from the discrete energy state into the continuum may be interpreted as a ‘resonance’ phenomenon between two states of the same energy, which results in the spontaneous ejection of an electron with kinetic energy and the return of the atom to a lower series limit. Several good examples of this process of autoionization are to be found in the alkaline earth elements.” White also discusses the explanation for the observations in the inert gases, proposing that “excitation into these negative atomic states takes place first and that ionization without radiation is a secondary process.” I note here, without discussion, the important insights into autoionization in the 1931 papers of that mysterious genius, Ettore Majorana (see e.g., Arimondo, et al., 2010).

Beutler’s spectroscopic results

Hans Beutler, working in Berlin, had studied highly diluted flames from 1923 to 1927, from 1927 to 1932, elementary processes in atoms and molecules, and from 1932 until he left Germany in 1936, studies of excitation of electrons from inner shells of atoms and the hydrogen molecule. Initially these were carried out at the Kaiser Wilhelm Institute under Franz Haber, until the new Nazi government in April 1933 forced out Haber and others of Jewish background from governmental positions. Beutler also, from 1930, had carried out his experimental work at the University of Berlin, and this continued until 1935 or 1936. Judging by his acknowledgments in published papers,
he was enabled to continue his work at the University with the support of Friedrich Paschen and the help of Max Bodenstein, until they too were pushed out in 1935 (Nye, 2011, Chapter 2). The last paper he published in the Zeitschrift für Physik, with Jünger, on the dissociation and ionization energies of the hydrogen molecule, was submitted on May 14, 1936. Beutler then emigrated to the United States.

In 1935 Beutler published a study of the absorption spectra of Argon, Krypton and Xenon. In his introductory remarks (p. 178) he discusses the absence of transition lines in the continuum in emission, but not in absorption. This is due to the great differences in transitions to lower levels and to autoionization, analogous to predissociation. The much greater transition probability for autoionization also leads to broadening of the lines. He cites White’s explanation for these results.

But what is new in Beutler’s work are his observations of the shapes of the lines. He noted (p. 181 and Figure 1) the appearance of diffuse absorption lines which fell off more rapidly on the shorter wavelength side (“… machen sich einige unscharfe Absorptionslinien bemerkbar, deren Intensität nach kurzen Wellen zu schnell abnimmt.”) Later in his discussion (p. 188) he cites Rice, that the form of a line can become unsymmetrical, and even suffer a displacement if the line is strongly broadened (“Die Form der Linie kann nach Rice unsymmetrisch warden, ausserdem kann eine Verschiebung des Terms auftreten, wenn dieser stark verbreitert wird.). Furthermore, the form of the new lines shows a very pronounced falling off on the shorter wavelength side. According to Rice, an asymmetry is possible, but it was hardly to be expected that this asymmetry would be so strong (“Die Form der neuen Linien zeigt eine ganz ausgesprochene Abschattierung nach kurzen Wellen zu. Nach Rice war eine Unsymmetrie möglich, aber es war kaum zu vermuten, dass sie so stark sein wurde.”).

Following the publication of Fano’s 1935 paper Beutler (possibly Fano had sent him a copy of this paper, though this has not been documented) re-stated his interpretation of his results in terms of Fano’s theory. In a 1935 paper on the absorption spectrum of hydrogen (Beutler, Deubner and Jünger, 1935, p. 186) he cited the Nuovo Cimento paper for the asymmetric form of autoionization lines (“… und für diese Terme besteht die Möglichkeit des Zerfalls durch Autoionisation; infolgedessen sind sie verbreitert), with the footnote, (“Die unsymmetrische Form dieser Linien wurde von U. Fano, Nuovo Cim. 12, 1, 1935, gedeutet.”) In a later paper (Beutler and Jünger, 1936, p. 84), also on the absorption spectrum of hydrogen, he cited Fano’s paper again, explaining his 1935 results on asymmetric broadening of the autoionization lines. “Die bei Ar, Kr und Xe beobachtete asymmetrische Verbreiterung des autoionisierender Term wurde von Fano quantummechanisch gedeutet.”.
Fano’s 1935 paper

Fano received his doctorate in 1934 at the University of Turin, where his father, Gino Fano, was on the faculty of the mathematics department, in a position that had been created specifically for him. As seems typical of the period he then went for a post-doctoral in Enrico Fermi’s laboratory in Rome (a summary of Fano’s professional history and a bibliography of his publications is given by Inokuti and Rau, 2003). The story of his encounter with Beutler’s paper has been given in several places, often with errors or distortions. I heard the story from Fano himself at a dinner following a lecture by him at Harvard, probably in the early 1960s, though I do not remember the exact date, to which I had been invited, presumably as the one who had done the experiment which led him to his 1961 paper. Here it seems best to give the story as he wrote it in his memoirs for his children and grandchildren in 2000. The story begins when Fermi said to him, go to the library and read papers and find something to explain. “Emilio Segrè came to me in the library where I was working, dumping a bundle of reprints in front of me, saying, ‘I understand you are looking for problems; these works by good experimentalists may well contain something that needs explaining.’ Within a day or so, I was struck by the tooth-shaped intensity distribution of an absorption spectrum, rising sharply at intervals, followed by smooth decays. The behavior reminded me of the ‘anomalous dispersion’ of refractive indices, whose sign reverses sharply at successive resonant frequencies. Indeed each ‘tooth’ of the absorption spectrum corresponded to one line of a discrete spectral series interfering with the continuous spectrum of a related series. On a Sunday morning I remember outlining this analogy to Fermi, who commented, ‘It sounds reasonable but now you will have to prove it.’ I felt lost upon that encouraging comment, having no notion of how to proceed. The next morning Fermi’s head appeared through a door, saying enigmatically, ‘Fano, you were right.’ During several sessions Fermi introduced me to the relevant theory, and thus I was able to submit a draft paper within a couple of weeks. My initial satisfaction subsided, however, when later, peeking into Fermi’s notebook, I found my whole calculation had been done by him on the Monday morning previous to his ‘you were right.’ “ (Fano, 2000). “The only difference between Fano’s solution and Fermi’s was not in the notation at all; Fano had solved an integral by partial fractions (again an echo of his early training by his father), while Fermi had done a numerical five-point integration.” (Berry et al., 2009). Fano told me of this incident: “Some people go jogging before breakfast every day, Fermi would solve a problem before breakfast every day. He had gone home and worked it all out after his conversation with me.” It’s a beautiful story, demonstrating Fermi’s character.
Fano’s paper contains only two references, the first to the Beutler 1935 paper with its observation of the unusual line shapes, and the second a listing of Beutler’s previous papers on excitation of inner electrons. There are no references to the work of Rice or anyone else. Clearly Fano had not done a careful or complete literature search. Fano reproduces Beutler’s Figure for the spectrum of Xenon (on p. 584 of the English translation of Fano’s 1935 paper) and then, following his theoretical treatment, says, in italics to emphasize the conclusion, (ibid., p. 586), that values for the parameters that determine the curve, that these can be chosen such that “the curve itself can have a behavior that justifies theoretically the results obtained by Beutler.” The definitive theoretical fitting of an experimental result only came 25 years later with the experimental result of Silverman and Lassetre.

Fano’s paper (1935) was published in Italian in the Italian Physical Society publication, Nuovo Cimento, and Fano, and everyone else, then “dropped the matter” (Fano, 1977). It was, as Fano told me, his first post-doctoral paper. Fermi’s, and his laboratory’s, interests had switched about that period, from atomic physics to nuclear physics (see e.g. DiGrezia and Esposito, 2008, p. 229). Fermi, considering his almost off-handed way of solving the problem, may have seen it as more an exercise than as something serious. Apparently, so did Fano. Segrè, in his autobiography (1993, Chapter 4), describes Fermi’s approach to publication: “Fermi observed strict rules concerning the publication of his work and that of his students. He did not permit publication of completely insignificant results. Results of little importance appeared only in Italian. He allowed publication in the Zeitschrift für Physik, or as a letter to Nature, only of papers he considered important. This wise policy was motivated by his desire to establish an international reputation for our Rome group. He did not want any foreign reader to be disappointed in reading one of our papers; there should always be something interesting in them. He applied this rule strictly; and his judgment on the quality of an investigation rarely erred.” Segrè’s first three papers, incidentally, two of which dealt with anomalous dispersion, were also published in Italian. I note parenthetically that the most important journals were considered to be the Zeitschrift für Physik, Nature, and the Proceedings of the Royal Society, and did not include any American journal.

The rapid intellectual growth and independent spirit of Fano in the next few years, as well as his penchant for challenges, can be seen in the papers he produced and where they were published. Following the publication of the paper explaining Beutler’s results Segrè steered him to some questions on anomalous diffraction gratings. His next two papers (numbers 4 and 5 in the Inokuti and Rau (2003) listing) were on this subject. Fano bypassed the “respectable” journals in the list noted above by Segrè, and published them, not in Italian, but in English in the American journal, Physical Review. He then spent a year with Heisenberg in Germany, and the two following papers resulting
from this visit, one on quadrupole moments in nuclei (1937), the other on anomalies in the intensity of diffraction (1938), were in German, both in well-known journals, Naturwissenschaften, and in Annalen der Physik. These were followed by a paper in Italian on thermodynamical concepts in nuclear physics (1938), and one in French on the breakdown of very heavy nuclei into two lighter nuclei (1939). The diversity in areas of physics is quite remarkable in these few years. Thereafter all his work was done in the United States.

But to return to the 1935 paper: in any event everyone did drop it. Other than the two references to Fano’s paper in Beutler’s work, likely to be no more than courtesies, I find only one reference in Google Scholar, in a book by Wolfgang Finkelnburg, Kontinuierliche Spektren, (p. 36), published in 1938, during the period from 1935 to 1961. Fano’s 1935 paper is listed as number 3 in the Inokuti and Rau bibliography, the first two papers being, apparently, the results of his doctoral thesis, both also in Italian. No notice of it is taken by anyone else in the years from 1935 to Fano61, including by Fano himself. His 1961 paper is listed as number 91 of his publications, so it is clear that he himself did nothing further on the subject until he was made aware of the Silverman and Lassettre work. Google Scholar, on October 25, 2019, lists 306 citations of the 1935 paper, all coming after the publication of the 1961 paper. What has happened is the situation described by Borges (1964): “The fact is that every writer creates his own precursors. His work modifies our conception of the past, as it will modify the future.”

The Whiddington experiments

In the early 1930s Whiddington and his students, at the University of Leeds, England, carried out
4 Richard Whiddington (25 November 1885-7 June 1970). The biographical information in the following is taken, unless otherwise noted, from the essay by Feather (1971). Whiddington was born in London, an only son, with two sisters. He entered St. John’s College at Cambridge in 1905, where he did some extra-curricular Mendelian experiments with rats, which he kept in his college rooms. Then, as Feather puts it: “The college authorities, when they became aware of the situation, very naturally regarded the outcome of this adventure of the enquiring mind as unconducive to good order and discipline, and the experiment had to be abandoned.” Thereafter he limited himself to physics, and began research in the Cavendish laboratory. He received the degree of D.Sc. from the University of London in 1911. In 1912 he published what has become known as Whiddington’s Law: that the minimum velocity of an electron needed to excite the characteristic X-rays of an element was proportional to the atomic weight of the element. Niels Bohr used Whiddington’s law in his first published paper using Planck’s quantum hypothesis (Thorsen, 1987). Until the onset of war in 1914 Whiddington continued his work at the Cavendish laboratory. In September of that year he joined the Royal Flying Corps, and from then until the end of the war he worked on communication between airplanes and ground. Following the war he returned to the Cavendish laboratory for a time. After Thomson left Cavendish, and was succeeded by Rutherford, and after his marriage in 1919, Whiddington left to take up the Chair of Physics at the University of Leeds. The department was small, the building it was in was old and congested. Whiddington gradually built up the department. In 1925 the Leeds Philosophical and Literary Society, more than a century old, decided to publish its own journal in two parts, one scientific and one literary. Whiddington became the honorary editor of the
a number of experiments on electron impact of gases. Of these we are concerned here with those reporting two new transitions in helium far out in the continuum. A loss was first reported in 1933 as being at approximately three successive collisions, each being from the state \(1^1S\) to \(2^1P\) (Whiddington, June 24, 1933). It was later recognized, with more precise measurements (Whiddington, 1934), that this could not be the case, the energy difference between the measured transition and that for a three-collision situation being too great. The new line was thus something new, possibly “that it may be due to some simultaneous excitation or ionization plus excitation process within the atom.” Shortly thereafter (Whiddington and Priestley, 1934, Received February 27, 1934) they reported the line as being at an energy loss of 59.25 volts, and visually broader than the reference line. They also suggested that “a double excitation to this state \(2P\) involving both the \(s\) electrons would in all likelihood be also the most probable transition of this kind.” A year later they reported (Priestley and Whiddington, 1935, Received February 20, 1935) a second double excitation loss at 62.27 volts. The first line was to be associated with a transition to the level \((2s2p)P\) (which they had previously wrongly attributed to the forbidden transition to the \((2p, 2p)\) level), the second to a transition to

the level \((2s3p)P\). A later remeasurement (Swift and Whiddington, 1937) gave the positions as 59.73 eV and 63.25 eV for the transitions. The Whiddington values for these two transitions were later corrected to 60.0 and 63.5 eV by Silverman and Lassettre by using a newer value for the conversion from wave numbers to electron volts. This was necessary since the Whiddington energy losses were determined relative to the \(1^1S\) to \(2^1P\) transition in helium, the excitation energy for this transition being obtained from emission spectra.

The Whiddington papers have nothing to say about the line shapes. This is probably due to the limits of their experimental setup. They do say (Whiddington and Priestley, 1934): “Photometry, with a line of so low a density as this, is very difficult on account of the complicating influence of the background; but so far as we have been able to go in this direction there do seem to be indications of structure in the line which our apparatus is not quite competent to resolve.” Nor do they mention Beutler’s work – but Beutler had nothing to say about helium, not having a radiation source suitable

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scientific section, and he and his students thereafter often published the first, and sometimes the only, results of their research in that journal. In the mid-1920s he began the study of electrons passing through gases. His first study of interest in the present context was a note (with H. Jones) in 1927 on energy losses of electrons passing through gases. Studies on energy losses on electron impact in other gases followed until 1939, a paper (with A. H. Lee) on excitation potentials in mercury, published in the Leeds Proceedings. A new war, beginning on September 1, 1939 then intervened. From then until 1945 he was engaged in the war effort. After the war he returned to Leeds, where his duties were primarily administrative. He retired in the summer of 1951. After 1945 there were only three research papers in 1949 and one in 1950, all as co-author. He died in 1970. His publication list comprises 76 items.
The 1954 electron impact measurements

In June of 1952 I received my Ph.D. from the Chemistry Department at Ohio State University, under the supervision of Professor Edwin N. Lassettre. Lassettre had initiated a program of measuring electron impact cross sections after the end of World War II. I stayed on until January, 1955 as a post-doctoral fellow, and continued to carry on measurements of collision cross-sections in atmospheric gases. The work was carried on with a grant from the Air Force Cambridge Research Laboratories. From the Spring of 1954 personnel consisted of myself and one other graduate student.

The \( ^1S \) to \( ^3P \) transition of helium was used to calibrate the measured energy losses. The procedure was to make a run on the target gas, then one on helium, then another on the target gas. It was thus relatively simple to extend the energy loss spectrum to greater energies. I do not remember whether I did this with helium out of curiosity or because I was aware of the Whiddington experiments and decided to confirm them. The results were given in a progress report. These were sent to the grantor quarterly. In the report for the quarter ending March 14, 1954, dated April 15, 1954 (Quarterly Report No. 11, of the Ohio State University Research Foundation, under Contract No. AF19(122)642, dated April 15, 1954, for the period December 15, 1953 to March 14, 1954) the following was included:

“Helium spectra have been obtained at each of several scattering angles out to 80 ev excitation energy. Peaks are found in the spectrum at 60.1 and 63.6 volts. These peaks have been previously reported by Swift and Whiddington [W. Swift and R. Whiddington, Proc. Leeds Phil. Lit. Soc. Sci. Sect. 3, 262 (1937)]. When their results are corrected, using more recent values for the charge on the electron, the peak positions found by them are 59.93 and 63.45 volts. These are in fair agreement with our measurements. The peak at 63.6 volts is small but definitely present. These transitions have been ascribed by Whiddington to the simultaneous excitation of both electrons in helium. The two excitations are therefore superposed on the continuum which results from the excitation of one electron above the ionization potential. Our experiments indicate, however, that a simple superposition of a transition between discrete states on a continuum does not adequately account for the appearance of the curve of scattered current vs excitation energy. In passing through the transition the continuum changes abruptly. If the continuum which precedes the transition is extrapolated be-
Beyond the transition, then the extrapolated curve is much higher than that observed. The occurrence of a transition in which two electrons are excited therefore has a pronounced influence on the probability of the alternative transition in which only one electron is excited. This is an interesting point which previous experimental work has not raised because the spectrum could not be studied with enough accuracy. The spectrum is being further studied to obtain cross section measurements in this interesting region.” (Appendix A)

I was not at the time familiar with the concept of autoionization, or with Beutler’s work – Beutler had not studied helium, and my literature searches were limited to work on helium. And, like everyone else, I was not familiar with Fano’s work, published in what at the time was an obscure journal. But the basic phenomenon was clearly stated.

In the next quarter (Quarterly Report, No. 12, for the period March 15 to June 14, 1954, dated July 30, 1954) cross sections for the 60 eV peak and two points, one on each side of the peak, were measured – the results being parallel, it was clear that all were part of the same phenomenon. But the interpretation was not evident. The report read:

“The initial objective of the present investigation was a study of the ionized continua for both nitrogen and helium. It seemed, at the outset, logical to group the two together since the primary objective was the study of the continuous spectra. As the work progresses it becomes evident that this grouping is not a satisfactory one since transitions are found in the helium continuum at 60.1 and 63.6 volts which are apparently due to the simultaneous excitation of two electrons while such transitions are not found, or not recognized, in the nitrogen spectrum. The study of helium is therefore continuing along lines which differ from the study of nitrogen. It was reported in Progress Report No. 11 that the continuum changed abruptly in passing through the peak at 60.1 volts. This has been further confirmed during the present quarter. Collision cross-section measurements have been made, as a function of angle, for the 60.1 volt peak and for two points in the continuum, one volt above and below the peak, respectively. The trend of cross-sections for these three excitations is very similar indeed. Generalized oscillator strengths when plotted as a function of $(\Delta P)^2$ (square of the momentum change of the colliding electron) give straight lines of positive slope which are very nearly parallel for the three transitions. Extrapolation leads to nonvanishing optical oscillator strengths thus indicating that the 60.1-volt transition is allowed in both absorption and emission. A search of the literature reveals that no emission or absorption line has been found in the optical spectrum, as far as we know, although attempts have been made to detect such a line. The cross-section runs described above show that the peak at 60.1 volts does not tend to become either more or
less pronounced as the scattering angle increases. Although the scattering falls off with increase in angle, the peak neither increases nor decreases relative to adjacent portions of the spectrum although some relative change might be expected for a transition to a discrete state in comparison to transitions to states in an ionized continuum. The precise interpretation of the results in terms of a simple model for the structure of the atom is not evident. Further experimental study has been temporarily delayed in the hope that further consideration of the problem will provide the basis for a better organized experimental study.”

In the next quarter the work on helium was inactive. The quarter after this (Quarterly Report, No. 14, for the period September 15 to December 14, 1954, dated January 10, 1955), my last quarter before leaving for a new position at the University of Toledo, Ohio, additional cross sections were run for several points on the continuum, from 28 to 54 eV, with the comment, “The experimental work on helium is concluded and the calculations are completed, although considerable work remains to be done in the preparation of a report.” I rejoined the project on a part time basis in the Spring of 1956, to assist in the preparation of scientific reports (Progress Report No. 20). A rough draft of the scientific report on collision cross sections for helium was completed in the Spring of 1957, and the finished product became Scientific Report 9, Additional Collision Cross Sections for Helium, Especially in the Ionized Continuum, by Sam Silverman and E.N. Lassettre, July 1957 (see Appendix B and Figure 2).

I thought the result was interesting enough to warrant publication even before the other papers were submitted – those were waiting for the results of the Francis and Jones theses to be written up, to provide the basics for all the others, and Lassettre was taking a long time to write them up. They were eventually published in 1964. In order to get around this obstacle I wrote the helium results up as a note with, basically, only the figure showing the phenomenon, but without any quantitative data, which would have involved the results of the Francis and Jones papers. I don’t have a copy of that manuscript. Eventually, in July 1957 the results were included in Scientific Report No. 9 under the contract. For reasons detailed below in this paper the results given in that paper did not reach the open literature until 1964 (Silverman and Lassettre, 1964) where a footnote cited the contractual support, and stated that the work was “Abstracted in part from Scientific Report 9,” but did not give the dates of the report or the contractual support. The 1964 paper is generally, word for word, that of the 1957 report, with minor revisions and some deletions. The data in the 1964 paper, however, is exactly the same as given in the 1957 Report. With regard to the 60 ev and neighboring peak some of the discussion of the 1957 Report has been deleted, perhaps because of the fuller discussion in the 1961 Fano paper. The 1964 paper noted Fano’s work only in the last sentence: “A theory of line
shape, which accounts well for the shape of the spectrum, has been worked out by Fano who used the data of Fig. 4 to illustrate the theory.”

The results given in Scientific Report 9 were, however, reported, in an abstract, at an international conference on the physics of electronic and atomic collisions held at New York University, New York City, N.Y., on January 27 and 28, 1958. Participants included S. Burch, S.J. Smith, and L. M. Branscomb, from the National Bureau of Standards. Two papers with results on electron impact cross sections in helium were presented, the first on three transitions in helium, given by Silverman and Lassettre, the second, entitled “Electron collision cross sections and oscillator strengths for the double excitation and the ionized continuum in helium,” by Lassettre and Silverman. For the latter paper, the abstract, after noting the two peaks at 60.0 and 63.5 eV and the continuum measurements, stated: “These show the unexpected and surprising result that the intensity of the continuum drops by about twenty percent as the peak is traversed. The 60.0 ev peak has a shape and half-width approximating that of an atomic transition. Electron impact energy spectra show that the discontinuity of the continuum on the two sides of the peak also occurs for the 63.5 ev peak. Cross sections for the 60.0 ev peak and two points in the neighboring continuum measured as a function of angle show that the effect is the same for all angles within the experimental range. There is, at present, no theoretical treatment for the discontinuity in the continuum. It is obvious, however, that the doubly excited states to which the peaks are attributed exert a strong perturbing effect on the neighboring continuum, an effect extending for several volts on either side of the peaks.” No one at the conference, nor, apparently, anyone they may have spoken to subsequently, seemed particularly interested in the result, nor was there any rush to provide a theoretical basis for it.

I left the University of Toledo and began work at the Air Force Cambridge Research Laboratory in Massachusetts in June 1957. Thereafter I was occupied with research on the airglow and aurora. My only contribution to collision theory thereafter was a paper on a theorem for generalized oscillator strengths (1958).

It was the data in Scientific Report 9 which became the basis of the Fano 1961 paper. The line shape reported here was the first one, either optically or by electron impact, which was sufficiently precise and with sufficient resolution to use for the purpose of testing theory.

**Platzman returns from Paris**

The 1957 Report eventually, somehow, found its way to Robert L. Platzman. Platzman (23 August
1918 – 2 July 1973), according to a memoir by Mitio Inokuti (2001), was one of the founders of radiation physics and chemistry. He joined Purdue University in Indiana about 1948, went from there to Argonne National Laboratory in 1958, and then, in 1965, became Professor of Physics and Chemistry at the University of Chicago. While at Argonne he received a Fulbright Fellowship and Visiting Professorship at the University of Paris, and traveled to Paris many times. I remember somehow that it was at the time when he was at Purdue University that he saw the Report containing data on electron collision cross sections for helium, including the data on the 60 eV transition, which would place the date in late 1957 or early 1958. He would have been especially interested in that report, since he had assigned to Miller, one of his graduate students, the Ph.D. thesis topic, completed in 1956, of a comprehensive study of ionization and excitation of helium gas, for which electron-collision cross-sections were better known than for other gases. Platzman and Fano were good friends, and Fano contributed a discussion of Platzman’s work to a memorial service after his death (Fano, 1974).

Platzman, on returning from Europe from one of his visits – I don’t know the exact date, it must have been about 1958, though possibly as late as 1960 (letters from Fano to other scientists in the Spring of 1961 in the University of Chicago Archives indicate the later date), and Fano places it in late 1960 (Fano, 1977) – stopped in Washington to visit his friend Fano. He brought with him Scientific Report 9. Platzman pointed to Fig. 5.1 on p. 13, showing the number of counts for energy losses between 58 and 64 ev, with peaks at 60.0 and 63.5 ev, and an interesting behavior of the continuum in the neighborhood of these peaks. The report noted (p. 1, 12) that the two peaks at 60.0 and 63.5 ev had been previously reported by Whiddington et al. The report later noted (p 12): “The spectrum also shows one remarkable feature not previously reported: an apparent discontinuity in the continuum when the peaks are traversed. The continuum on the high energy loss side of the two peaks is about 20% lower than on the low energy loss side of the peaks. It should be noted also that both peaks have a shape and half-width which is to be expected for a typical atomic transition. This observation suggests at once that the spectral region around 60 ev is not merely the result of superposition of two alternative transitions, one to a discrete state and the other to a continuum. Instead a considerable portion of the spectrum is affected.” Further discussion of the data supported these views. The section concluded with (p. 16): “No theoretical explanation for the peculiar behavior of the continuum is at present available. It is obvious that a strong perturbing effect of the doubly excited states on the continuum exists. Previous treatments of two energy states of this sort have dealt primarily with the perturbing effect on the discrete level (i.e., diffuse levels, auto-ionization) rather than on the continuum.” The report, however, did not take note of the asymmetric shape of the peak, clearly shown on the Figure. Platzman suggested to Fano that there was something interest-
ing to explain here. Fano looked at the materials, turned to Platzman, and said: “I already explained
that behavior in 1935,” and told him the story which has been recounted in an earlier section of
this paper. In the 1961 paper Fano acknowledges Platzman’s role: “This work, and in particular the
analysis of the He excitation, were stimulated by Dr. R. L. Platzman, whose advice and sustained
interest are gratefully acknowledged.”

The path to publication of Fano 1961

Fano’s attention now returned to the problem he had considered earlier in 1935. In the interim be-
tween 1935 and 1961 Google Scholar shows only one citation, other than the two by Beutler, but no
other citation, by Fano or anyone else, of that earlier 1935 paper. His interests had moved in other
directions. Nor had much notice been taken of the 1935 paper of Beutler, which had led to Fano’s
1935 paper. There are three citations of the Beutler paper, neither of which mentions the question of
the shapes of the lines. Fano’s interest in such questions was thus clearly renewed by the results of
the Silverman and Lassettre paper detailing the results of electron impact on helium.

Fano apparently had a draft of the paper by the Spring of 1961. He then sent copies to several peo-
ple for comments (copies of some of these letters are in the Archives of the University of Chicago,
in the Ugo Fano Papers, Box 10, Series 5). On April 3, 1961 Fano writes to Ta You Wu, apparently
with a copy of the paper. From the data of the Silverman and Lassettre paper (though he mentions
only Lassettre) he has fitted the data with three parameters, $E=60.1$ eV above ground state, $\Gamma$ ap-
proximately $0.04$ eV, corresponding to a transition probability of $6 \times 10^{13}$ sec$^{-1}$, and another, later
denominated $q$, approximately $-2.3$. He is not certain of the sign of the latter. He wonders whether
Wu has any theoretical estimates later than what he has published in the past. Wu replies on April
6, 1961, commenting on the sign and on several calculations of transition probability, and gives his
personal belief that all perturbation theory calculations for Auger transition probabilities for light
atoms are not quantitative.

An exchange of letters, which had begun in January with A.G. Shenstone, on a different matter, be-
gins with a letter from Fano on May 9, 1961, which contains a copy of his manuscript. Fano seems
particularly desirable to obtain the perspective of an experimental spectroscopist. “The coupling
between different configurations is treated in my work as a semi-empirical parameter, … that is,
no attempt has been made by me to evaluate this coupling from first principles.” Shenstone had
wanted to “understand from first principles why the interaction was strong in some instances and
weak in others. I fear that my paper will be of no help to you in this connection.” Fano makes clear
his motivation: “I am concerned not only with the accuracy of the paper, but also with the question whether it achieves its main purpose, namely, to develop the formalism to the point where it can be utilized by experimentalists.” Here we have the key to a major reason for the popularity of the 1961 paper in later years. The experimentalist does not have to plow through a complex series of complicated integrals and mathematics – he can match his experimental curve to three parameters and gain useful knowledge. Shenstone replies on May 16, 1961. He finds Fano’s paper very interesting, “even though I do not any longer try to follow the mathematics required in such work. I am especially glad that there is theoretical work of high caliber being done on perturbed series and auto-ionization.” He asks if Fano’s results imply that all lines broadened by auto-ionization should be unsymmetrical? Fano replies on May 23, 1961, that this is not the case. “… the degree of asymmetry should vary greatly and should tend to zero in the limit where the line is infinitely more intense than the continuum to which it is coupled.”

On May 12, 1961 W.R.S. Garton writes to Fano, who has written to him together with a copy of the manuscript of the paper. Garton is enthusiastic: “This is magnificent!” he says. He has a number of illustrative cases, with q both positive and negative. “Your paper, when I am able to absorb it in detail will encourage me to seek quantitative shapes of these odd spectral features.” Fano responds on May 23, 1961, that he was “particularly happy to hear that my paper may really prove useful to you.”

Publication priority questions

Having run his draft past several knowledgeable scientists Fano was now ready to proceed with publication. He wrote to Professor Lassettre on July 24 (this letter is not in the University of Chicago Archives) asking for permission to publish the figure showing the helium electron impact energy loss spectrum in the vicinity of 60 eV. Fano clearly felt that the impact of the theory he had developed rested on the confirmation by testing against the only experimental result available which was sufficiently resolved and detailed. Lassettre replied on July 28, stating his preference that Fano not publish that figure. He noted that a note had already been written (the draft which I had prepared) before receiving Fano’s letter, which omitted references to the earlier papers of the projected series, and which contained the figure in question. He proposed that a revision of that earlier draft, which he had now extensively revised, be submitted for publication to the Journal of Chemical Physics, and which would then be available for quotation by Fano. On August 5, 1961 Lassettre wrote to Fano with a copy of the proposed Letter to the Editor of the Journal of Chemical Physics, to be submitted in about a week, and asking for any comments from Fano. Fano replied to the letter of
July 28 from Italy. He was not sure whether Lassettre agreed that he, Fano, could publish the Figure after it had first been published by Lassettre, or whether Lassettre did not want him to publish the figure at all. “Complete deletion of that figure,” Fano said, “would detract from my paper, I think. Would you want me to modify it, and, if so, how? Do you also have any objection to my Fig. 3 in which your data have been replotted together with my curves?” The University of Chicago Archives contain an undated handwritten note signed by “John,” probably John Cooper, offering to help in whatever way he could, “like expedite getting him to get his letter published quickly.” The note also includes a P.S.: “S.M. Silverman is at Air Force Cambridge in case you want to write to him also,” and giving my address. Fano never did contact me – apparently he felt it was sufficient to deal only with the director of the project, and it was not necessary to include the person who, as one could conclude, as first author of the Report, had actually done the work.

Lassettre then duly submitted the paper to the Journal of Chemical Physics. The then editor of the journal, J. W. Stout, was on vacation, and Norman Nachtrieb, whose specialty was electrochemistry (Obituary, Chicago Tribune, September 13, 1991) was acting editor. Nachtrieb wrote to Lassettre on 14 September 1961 (see Appendix C) explaining that the Communications category, for which the manuscript had been submitted, was restricted to “only a very few manuscripts reporting preliminary results of research of current and extreme interest to large numbers of workers in a field.” and “It did not seem to me that your letter was suitable for publication in this category. I therefore showed your manuscript to an expert in the field. He has informed me that he is in agreement with my opinion.” Nachtrieb suggested that the manuscript be submitted as a Note: “The only special requirement for Notes is that they stand as complete reports of research in themselves and are not preliminary accounts of work which is to be published in detail later.” But the complete account was to appear later as part of the series, and the manuscript was thus never re-submitted at the time, being published finally in 1964, several years after Fano’s 1961 paper. In retrospect Nachtrieb appears as a poor prophet of the importance and general interest of the work. In his defense, that only became apparent after and because of the publication of Fano’s theory.

Apparently Lassettre never informed Fano that the manuscript was not to be published. Fano wrote to Lassettre on September 28, 1961 that his paper had just been accepted by the Physical Review. He expected that the Letter to the Journal of Chemical Physics would appear before his paper, and he would then amend the reference to that work accordingly. His paper then appeared in the December 15, 1961 issue of the Physical Review. Fano appended an asterisk at the end of the title, adding a note in proof: “The most relevant material of this reference is to be published by E.N. Lassettre and S.M. Silverman. I thank Professor Lassettre for permitting me to publish his data and for
having shown me his paper ahead of publication.” Thus the first publication of the figure showing the effect of configuration in helium appeared in Fano’s paper. In retrospect it would seem that it would have been better for Lassettre to submit the paper to Physical Review to be printed together with and preceding the Fano paper.

Apparently people find it easier to cite rather than to read papers, such as Fano’s, very carefully. One recent paper, for example, reproduces a figure showing the absorption spectrum of Xe from a paper by Beutler, but attributes it to helium. Another example: I was at Queen’s University in Belfast, Northern Ireland in 1963-1964 on what was the equivalent of a sabbatical. A well known English spectroscopist came to give a guest lecture. He referred to Fano’s paper, stating that it was one of the rare occasions in physics when the theory preceded the experiment. After prodding by my host I got up to correct him. Similarly, a recent paper in 2009 states that Madden and Codling, in 1963, used synchrotron radiation on helium expecting transparency, and were surprised to find those strange shapes. Actually, their experiment was to check optically the Silverman and Lassettre electron impact results. There was no surprise, nor did they claim any.

The 1961 paper

As in 1935 the question was one of configuration interaction. Fano (1961) reviewed his earlier paper and that of Beutler, modified the theory of that earlier paper, and applied it to the electron impact results. He began the paper with a discussion of configuration interaction: “Electronic states of atoms and molecules are usually classified as belonging to various configurations, according to the independent-particle approximation. The actual stationary states may be represented as superpositions of states of different configurations which are ‘mixed’ by the ‘configuration interaction,’ i.e., by terms of the Hamiltonian that are disregarded in the independent-particle approximation. The effects of configuration interaction are particularly conspicuous at energy levels above the lowest ionization threshold, where states of different configurations coincide in energy exactly since at least some of them belong to a continuous spectrum. The mixing of a configuration belonging to a discrete spectrum with continuous spectrum configurations gives rise to the phenomenon of autoionization. The exact coincidence of the energies of different configurations makes the ordinary perturbation theory inadequate, so that special procedures are required for the treatment of autoionization and of related phenomena.”

He noted, as he had not done in the earlier paper, which referenced only the Beutler paper, that a basic treatment of the problem had been carried out by O. K. Rice in 1933, [discussing predissoci-
ation in molecules], and that, as his earlier paper showed, such autoionization levels in continuous spectra show themselves as very asymmetric peaks. There was new interest in this phenomenon as a result of recent work using far-ultraviolet light (W. R. S. Garton and K. Codling, 1960) [autoionization in barium], electron impact spectra, and energy transfer in molecular collisions (R. Platzman, 1960). The objective of the modified theory, Fano said, “is to present procedures that can be applied to the quantitative analysis of experimental data and to point out the significance of the parameters obtained from such analysis.” (Fano, 1961, p. 1866) The centerpiece of the paper, after developing the theory, was the application of the theory to the electron impact data in helium (ibid., section 3, and figures 2 and 3): “Silverman and Lassettre have observed the cross section for forward inelastic scattering of 500-ev electrons by He. The results obtained by them in the region of 60-ev energy losses are shown in Fig. 2. There seems to be little doubt that the main peak in the experimental curve is associated with the 2s2p \(^1\)P level autoionized level of double excitation. The discussion of the data in [the Silverman and Lassettre paper] emphasized the asymmetry of the results on either side of the main peak and remarked that they are not merely the ‘superposition of two alternative transitions, one to a discrete state and the other to a continuum.’ This effect appears to be just of the type to be expected on the basis of [the present theory] and of the earlier equivalent treatment of [the earlier paper].” Fano then fits the experimental data to the theory. His Fig. 3 shows a good fit (though not perfect) between theory and experiment. The following section presents the modified theory applicable to the Beutler spectroscopic results, but the experimental data are insufficiently resolved for an attempt at a fit to be made: “This result accounts at least in part for the fact, noted [earlier], that the intensity of the rare-gas optical absorption spectra’ never appear to vanish altogether in the range between the two series limits. The interaction of different discrete levels could not be responsible for this result, as will be seen in the next section. The experimental data also show some blurring, presumably due to limited resolving power and no attempt will be made here to account for them in detail.”

In short, the first actual fitting of a theory of configuration interaction in the autoionization situation to experiment, is that of the Fano theory to the experimental data in the Silverman and Lassettre paper. The importance of the Silverman and Lassettre paper on electron impact on helium is shown by a footnote added in proof, and indicated by a “*” at the end of the title, Effects of Configuration Interaction on Intensities and Phase Shifts. The footnote read: “* The most relevant material of this reference is to be published by E. N. Lassettre and S. M. Silverman. I thank Professor Lassettre for permitting me to publish his data and for having shown me his paper ahead of publication.” The paper he was referring to was, presumably, a revision by Lassettre of the short note I had written in the attempt to get it published early, I had, by 1960, been gone from the project since January 1955.
A copy of the revised paper can be found in the archives of the University of Chicago.

The 1961 Fano treatment was applied subsequently to double excitations in helium using optical spectroscopy by Madden and Codling (1963, 1965, with preliminary results fitting the data to the Fano equation at a 1963 conference) with a resolution twenty times greater than the electron impact results of Silverman and Lassettre, and by Mehlhorn (1966), using 4 keV electrons and a scattering angle of 54°. Mehlhorn compared the values of the first double excitation energy loss and the Fano q-factor for the three measurements: for the energy loss, 60.0 eV for Silverman and Lassettre, and Mehlhorn, by electron impact, and 60.123 from optical absorption, by Madden and Codling; and q-values of -1.87 by Fano from the Silverman and Lassettre data; -1.60 or -1.90 by Mehlhorn, depending on the assumed level of the background continuum; and -2.80 by Madden and Codling. An example of a more recent, considerably more complex and sophisticated, paper derivative from the Fano approach is that of Domke, et al. (1996), which includes an extensive review of theory and experiment up to that date.

Discussion and conclusions

There is much that can be learned from this detailed discussion of the history of the background to the Fano 1961 paper. All the ingredients were present in 1935 – both Rice and Fano had provided theoretical models for the interaction of two states with equal energies, but attention was focused on identification of spectral lines with particular energy levels in the atom or molecule, on the selection rules governing transitions between these levels, on the probabilities of transitions, and on the roles of spectral line widths. By 1961 these were fairly well established, at least in their general outlines. As Rau has noted (personal communication, email, 20 May 2014): “Fano was always phenomenological and thinking in experimental terms.” As Fano stated (1977), on the success of his 1961 paper: “The paper appears to owe its success to accidental circumstances, such as the timing of its publication and some successful features of its formulation. The timing coincided with a rapid expansion of atomic and condensed matter spectroscopy, both optical and collisional. The formulation drew attention to the generality of the ingredients of the phenomena under consideration. In fact, however, the paper was a rehash of work done 25 years earlier and its context still needs extension and clarification.” Clark (2001, p. 116) has summarized the basis for the paper’s continuing popularity: “The celebrity enjoyed by this formula derives from the basic importance of the systems it describes, its wide-ranging practical utility, and the historical context in which it emerged.” Thus, very few developments in science should be discussed in isolation. Rather, the context needs to be considered as a basic component of any history.
The history of Fano61 also raises some interesting questions on when does an observation rise to the level of a discovery. Beutler, in 1935, noted an asymmetry in spectral lines resulting from autoionization in several of the noble gases. This was the only paper of his, and the only substances, in which such an asymmetry was noted in the description of experimental results. Beutler’s last papers, before leaving Germany, were on the spectroscopy of the hydrogen molecule. In two of these (discussed above), in 1935 and 1936, possibly after receiving a copy of Fano’s paper, he notes the asymmetric character of the lines in the earlier paper on the noble gases, and notes Fano’s interpretation. In the final paper, Beutler and Jünger (1936), devoted to a discussion of predissociation and autoionization in the hydrogen molecule, Fano and asymmetric line profiles as a characteristic of autoionization is not mentioned at all. The cornerstone of the scientific method is that the validity of a theory or hypothesis is tested by predicting a result which is found to be correct either observationally or experimentally. Qualitatively this was true for the Beutler observation and the Fano interpretation. Fano showed that his theory showed that the Beutler observation could be interpreted by his theory, but still needed a quantitative theoretical calculation of an observed line or lines. But the Beutler observations were not sufficiently resolved for such a determination. Thus we might consider the situation in 1935 as one in which a conditional proof was available. The definitive proof came only later, in 1961, with Fano’s calculated line shape fitting the Silverman and Lassettre electron impact spectrum of helium. The theory alone, like the recent story of the Higgs boson, would be an interesting result, waiting for an experimental confirmation. That Fano understood this can be inferred by his comment in his letter to Lassettre of July 28, that complete deletion of the experimental figure would detract from his paper. It is perhaps unnecessary to add that the subsequent developments in which Fano’s paper is cited, are dependent only on his paper, and not at all on the work that stimulated its origin.

One other matter concerning the timing of publication of a discovery. As mentioned earlier I had recognized after noting the twenty percent lesser amplitude of the continuum on the high energy side compared to the lower energy side that there was something at least interesting, and possibly important, about this observation. I tried from time to time to get others interested in the result, but failed. Like everyone, until Fano, in 1960, nobody was interested. When it came to publication Lassettre wanted to wait until the first papers in the series, which outlined the basics of the methodology, were published. These included the work of Stanley Francis, who received his Ph.D. in 1947, and Ernest Jones, who received his Ph.D. in 1948. Those works provided the basic information on the methodology and theory of the measurements. The thesis work of the others, all on electron impact, of the first post-war group of students, George John (Ph.D., 1949, thesis on methane), Walter Edmisten (Ph.D. 1949, thesis on low speed electrons on methane and ethane), George Begun (Ph.D.,
1950, thesis on cyclic and unsaturated hydrocarbons and a forbidden transition in ethane) and Abra-
ham Berman (Ph.D., 1949, thesis on argon and neon) was never published, though it is noted in
Ausma Skerbele’s Ph. D. thesis, 1960). I do not know why these were never published. Perhaps he
felt that their work was or would be superseded by the new apparatus, or perhaps he was too busy
with the work involved in the design and building of the new apparatus.

The first public notice of the quantitative results on the unusual behavior of the continuum in heli-
um in the area of a discrete peak came in an international conference in New York in January 1958.
Some workers at the National Bureau of Standards presented at that conference. I do not know
whether others from NBS were in the audience. I also do not know whether Fano saw our abstract,
or, if he did, whether he paid any attention to it. In any event he did nothing about it until Platzman
drew his attention in 1960 or 1961 to the Ohio State Report of 1957. The first publication of the fig-
ure showing the configuration interaction in helium came in Fano61, and the publication of Madden
and Codling that followed soon after must have convinced Lassettre of the necessity of earlier pub-
lication of the experimental results of his group. Publication of the group of papers with the results
on the new apparatus followed in 1964. In 1962 Lassettre left Ohio State and its teaching duties and
went to what was then the Mellon Institute in Pittsburgh, Pennsylvania where he could devote his
time and energy to research alone, and the results of himself and his collaborators were thereafter
published in reasonable times after the work was done.

When I began my thesis work, in 1950, I was one of two new students. A new apparatus was par-
tially built, largely designed by Lassettre and Berman, though I was responsible for the design of
some of the lesser components. The story of the efforts to publish the results on helium which led to
the Fano61 paper has been given above. A group of papers was finally published in the Journal of
Chemical Physics in 1964. These included the work of Francis and Jones. Thus the interval between
the Francis thesis and the publication of the paper depending on it was some seventeen years. Las-
settre was clearly less concerned with priority than with being sure that the experiments were done
properly and with as good accuracy as could be achieved.

What then, is the role of the experiment that leads to a theoretical paper with great impact on our
understanding? The answer to this can be taken from the “but for” standard in United States juris-
prudence in a Supreme Court opinion: “The defendant must show that there is a reasonable prob-
ability that, but for counsel’s unprofessional errors, the result of the proceeding would have been
different.” Strickland v. Washington, 466 U.S. 668, 694 (1984). That is, if not for this, that would
not have happened. Fano61 would not have been written, with its formulation appealing to exper-
imentalists, and all the resulting works, if the experiment of Silverman and Lassettre had not been done, and not brought to Fano’s attention by Platzman, at a ripe time.

One aspect of academic scientific research as it has been practiced in the contemporary period is the role of the post-doctoral fellow and his relationship to the senior person. Pre-doctoral students are there to learn how to do research and, in a well-run laboratory, also to learn how to think critically. But once he has received his Ph.D., is he still a creature of the senior member? For many senior researchers students and others in his group are considered to be merely extensions of himself. They are there to extend the work to be done, but not to initiate or carry out ideas of their own. Thus, for example, any paper published with work done by any member of the group must include the name of the senior individual as one of the authors. In other groups he is expected to define his own research interests, as long as those are within the broad area in which the laboratory is engaged. In Fermi’s laboratory, for example, Fano was told, he tells us, by Fermi to go to the library and find something to explain. Fano did this, got an idea, and presented it to Fermi, who then helped him with nomenclature and in working out the problem – a problem which, unbeknownst to Fano at the time, Fermi had already solved. Fermi refused co-authorship, and the result was Fano’s first post-doctoral paper. Lassettre was a very good theoretical physicist and an excellent researcher. He felt burdened by the duties and responsibilities of standard academic life, and finally was able to find a situation where he could concentrate on research. His group consisted mostly, if not entirely, at least originally, of former students of his. While he was at Ohio State the only post-doctorals he had were Berman and myself. I had a good deal of flexibility in what I did outside of what was required to keep the grantor happy. The measurement of the autoionization situation in helium was my own idea. Lassettre was never really interested in that result – in his final report on the grant he summarized a few “significant” results – the configuration interaction was not among them. Nor, in his subsequent work at the Mellon Institute, did he ever return to that area. Fano, in getting permission to reprint the figure in his 1961 paper did not feel the need to go any further than the senior person, Lassettre. Had he paid attention to the 12 Scientific Reports resulting from the grant that he cited he might have noticed that I was co-author or first author on eight of the twelve. He might then have paid more attention to the suggestion made by John [Cooper?] that he might wish also to write to me. Similarly, in his 1935 paper he notes the studies of Beutler “in a series of important works,” with no mention of Beutler’s collaborators in these papers.

In any event, in the final analysis, it is Fano’s paper that is important, and that has led to all the subsequent work. In the initial papers after Fano61 (see, e.g., Madden and Codling, 1963, 1965) reference is made to the Beutler-Fano profiles. Beutler, like myself, has now disappeared from view. It is
now the Fano profile and the Fano q-factor, and, in my view, rightly so.

Acknowledgments
I thank Dr. Charles Deehr for his helpful and informative compliments, and especially Dr. Ravi Rau for his many helpful comments and suggestions on Fano and his work – Dr. Rau was Prof. Fano’s first graduate student at the University of Chicago. I wish also to express my gratitude to the archivists at the University of Chicago and the Ohio State University Research Foundation for the locating and provision of documents used in the preparation of this paper.
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Redner, S., Citation statistics from more than a century of Physical Review, arXiv: Physics/0407137v2, 6 October 2004.


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Figure 1

Absorption spectrum of Xenon

Fig. 2. Absorption des Xe im Gebiet der Seriengrenzen 1022–922 Å des Bogenspektrums. In Richtung der Ordinate steigt die Absorption an; die Wellenlängen sind an der Abszisse vorzeichnet. — Die Figur wurde so gewonnen, daß Aufnahmen bei verschiedenen Xe-Drucken ausgemessen und die Breiten der Absorptionslinien auf Parallelen zur Abszisse abgetragen wurden.
Figure 2

Electron impact spectrum of Helium
58 – 64 ev
The Ohio State University Research Foundation
Scientific Report 9
July 1957
Helium Spectrum - Zero Angle
Accelerating Voltage 504
First Peak 60.0 ± .1
Second Peak 63.5 ± .2

Fig. 5.1 Helium Spectrum in the 60-65 ev region
Figure 3

Comparison of theoretical and experimental line shape of electron impact spectrum of Helium for electron impact energy loss in range of 58 – 64 ev

Fig. 3. Theoretical line shapes corrected for finite instrumental resolving power [Eq. (28)] and fitted to the Silverman-Lassettre data. Experimental points from Fig. 2 reduced in scale 1:7500 counts/10 sec.
APPENDIX A

Extracts from The Ohio State University Research Foundation

December 15, 1853 – March 14, 1954
March 15, 1954 – June 14, 1954
REPORT

By
THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION
COLUMBUS 10, OHIO

To
AIR FORCE CAMBRIDGE RESEARCH CENTER
Cambridge, Massachusetts
Contract No. AF19(122)642
E.O. No. 114-16A1 Phase V

On
Collisional Cross Sections

For the period
December 15, 1953 - March 14, 1954

Submitted by
R. E. Lassettre
Department of Chemistry

Date
April 15, 1954
COLLISIONAL CROSS SECTIONS

1. ABSTRACT

Calculation of collision cross sections from the experimental data on oxygen has been completed. The fraction of collisions which excite the 6.46 eV state has been calculated as well as the fraction of collisions which lead to ionization. Total collision cross sections as functions of incident kinetic energy have also been computed from the data and extrapolated to low energies using the Born approximation. The work on oxygen is now complete except for the study of elastic scattering.

The carbon dioxide spectrum in the region of 9.1 and 11 eV has been further studied. Data suitable for cross section calculations have been obtained. The investigation is continuing.

The ionized continua of both helium and nitrogen are under investigation in the region from 85 to 60 eV. The experimental work on nitrogen is nearly complete and that on helium is well advanced. Two transitions in helium at 60.1 and 63.6 eV have been found. These check the previous work of Swift and McDermott and provide, for the first time, accurate measurements of scattered current in this region. The shape of the spectrum is quite unusual. Further investigation of this region of the helium spectrum is continuing.
2. INVESTIGATIONS IN PROGRESS

During the present quarter attention has been devoted to, (a) completion of calculations of oscillator strengths and cross sections for oxygen, (b) experimental study of the ionised continuum for nitrogen and helium, (c) further experimental study of carbon dioxide.

2.1 Miscellaneous Investigations

2.1.5 Reactivation of Electron Multiplier

As was stated in an earlier progress report, it has been necessary to reactivate the electron multiplier. The multiplier became deactivated when a leak developed in the Knudsen vacuum gauge. The leak was repaired after considerable difficulty, and the multiplier was reactivated. The magnitude of voltage pulses produced by the multiplier was increased very considerably beyond the best obtained during the past two years. The resulting improvement in counting efficiency makes it possible to extend the angular range over which cross section measurements can be made.

2.2 Inelastic Collision Cross Sections for Oxygen in the Spectral Region Between 11 ev and 60 ev

The calculation from experimental data of cross sections and generalized oscillator strengths for inelastic scattering in oxygen have been completed. As stated in Progress Report No. 10 these quantities have been integrated over the spectral region around each peak (from minimum to minimum) in order to facilitate application of the data. According to theory the sum of the generalized oscillator strengths
over the spectrum (for fixed values of \((AP)^2\), the square of the momentum change of the colliding electron) should equal the number of electrons in the molecule. This is called the generalized oscillator sum rule. In the present experiment the only portion of the spectrum covered is that due to excitation of valence electrons. Inner shell electrons are not excited. In this case the sum of the generalized oscillator strengths should exceed the number of valence electrons and be less than the total number. For oxygen the sum should lie between 12 and 16. The magnitudes found by experiment are given in the following table.

<table>
<thead>
<tr>
<th>((AP)^2)</th>
<th>Oscillator</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>11.61</td>
</tr>
<tr>
<td>0.1</td>
<td>11.77</td>
</tr>
<tr>
<td>0.2</td>
<td>11.80</td>
</tr>
<tr>
<td>0.3</td>
<td>12.02</td>
</tr>
<tr>
<td>0.4</td>
<td>12.38</td>
</tr>
</tbody>
</table>

The range of actual measurement is 0 to 60 eV, and, in addition, an extrapolation to higher energies was also made and is included in the above sum. The first three sums are slightly low (i.e. below 12), but by an amount which is within the experimental error involved in the determinations. On the whole the theory seems to be satisfactorily confirmed.

The optical oscillator strengths \((AP = 0)\) were also used to calculate the refractive indices of oxygen at several wavelengths. To our surprise the calculated values of \(n-1\) (\(n = \text{refractive index}\)) are
almost thirty per cent higher than the observed. These calculations
also involve a summation over the spectrum and the fact that a high
result is obtained seems inconsistent with the oscillator sum de-
scribed above, which are, if anything, too low. Either the theory
of refractive indices has been incorrectly employed or the expan-
dated oscillator strengths found here are not accurately equal to
the optical oscillator strengths (i.e. there is a failure of the Born
approximation). Considerable time was spent in re-examination of the
theory of refractive indices, the influence of forbidden transitions
etc., but no reason for the discrepancy could be found. The accuracy
of the experimental data seems to be good. For the present the ques-
tion of the reason for the discrepancy must remain open. We do not
believe that it is due to experimental error.

In a telephone conversation with R. A. Hopleton some time ago,
an interest was expressed in having total collision cross sections,
i.e. cross sections integrated over scattering angle. Dr. Hopleton
also stated that cross sections obtained at low energies would be
highly desirable. We have therefore calculated total collision cross
sections at 500 eV incident kinetic energy (that for which measure-
ments were made) throughout the spectrum. When these are summed over
the spectrum, the total inelastic cross section is obtained. At
500 eV this proves to be 6.1 atomic units. The elastic cross section
was also computed in the usual way, using atomic scattering factors,
from the Born approximation. This proves to be 9.2 atomic units.
This figure is approximate because of the rather rough theory. It will be replaced by a measured value when the experimental study of elastic scattering is complete. The sum $6.1 + 9.2 = 15.3$ gives the total collision cross section for collisions of every type. It is interesting to compare this with the ionization cross section of 5.73 atomic units (at 900 eV) calculated by Missey and Burhop from the data of others. This shows that 37% of these electrons, with 900 eV incident energy, which collide with $O_2$ molecules result in ionization of the molecules.

It is of further interest that the total cross section for exciting the Schumann-Runge transition by electron impact (900 eV electrons) is 0.60 atomic unit, and hence 3.9% of all colliding electrons result in excitation of this state. Since virtually all of the excited molecules decompose into atoms, it follows that the number of oxygen atoms produced (by this excitation) per hundred colliding electrons is 7.9.

This figure is still tentative because of the approximate elastic cross section. The error is probably not large, however. It is known from the work of others, that half of the atoms produced in this way are in $3^p$ states and half in $3^D$ states. It seems highly likely that these data will be useful in the interpretation of atmospheric phenomena.

The present apparatus cannot be used to measure collision cross sections at low energies. By employing the measured data at 900 eV together with the assumptions obtained from the Born approximation, that oscillator strengths depend only on $(AP)^2$, it is possible to compute cross sections at both lower and higher energies. At low energies this procedure may lead to error due to failure of the Born approximation. Nevertheless, there is an improvement over previous theoretical.
calculations which involve not only the Born approximation but, in addition, rather rough approximations to atomic or molecular wave functions. In order to test the procedure some calculations were first made of the total cross sections for the \( 1s \rightarrow 3p \) transition in helium. Using our data these cross sections were calculated and compared with the experimental results of Low and of Enros. The agreement with experiment is considerably better than is provided by wave mechanical calculations based on screening constant wave functions. The discrepancy at low energies is still considerable but is much less than for the approximate theory. Since the improvement was encouraging, further calculations were made for oxygen at each of six excitation energies. The general trend of the total cross sections is indicated by the results for the 6.44 eV transition and for the 41.5 eV transition. It is found that for the 6.44 eV transition the cross section (integrated over the transition) has a rather sharp maximum of 4.6 atomic units at 16 volts incident kinetic energy and falls to 0.72 atomic unit at 400 volts kinetic energy. At 41.5 volts excitation energy the cross section (integrated over a one volt region of the spectrum) has a broad maximum at 130 volts incident kinetic energy. At the maximum the cross section is 0.10 au and falls to 0.06 au at 400 volts. These results may not be highly accurate at low kinetic energies, through failure of the Born approximation. Until accurate data are obtained they are, however, the best available, and the results will be reported in the final scientific report on oxygen.
The calculations and experiments on inelastic scattering by oxygen are now complete. The results on elastic scattering will be reported as soon as the experiments are complete. The scientific report on oxygen will be temporarily deferred. The electron spectrometer is in exceptionally good operating condition and we wish to collect data on other substances during the immediate future.

2.3 Electron Impact Spectra for Carbon Dioxide: Collision Cross Sections for the 9.1 and 11.1 Volt Transitions

The study of carbon dioxide has been delayed by experimental difficulties encountered during the early part of the quarter. Electron impact spectra have been run, however, in the region around the 9.1 ev peak at several scattering angles but it has not been definitely established that two transitions are superposed in this region of the spectrum although this is suggested by some of the spectra. Further data have also been collected on the scattering by the 9.1 ev peak and the 11 ev peak as a function of scattering angle. Helium runs were made before and after the carbon dioxide measurements for calibration purposes. Cross sections have not yet been calculated. Attention has been concentrated on the study of the continua in nitrogen and helium described in the next section.

2.4 Study of Ionized Continua for Helium and Nitrogen

Our plan to study the nitrogen spectrum beyond 20 ev and the helium spectrum beyond 25 ev has been mentioned in several previous reports. This study was undertaken during the quarter and is now well advanced.
Helium spectra have been obtained at each of several scattering angles out to 60 ev excitation energy. Peaks are found in the spectrum at 60.1 and 63.6 volts. These peaks have been previously reported by Swift and Whiddington. When their results are corrected, using more recent values for the charge on the electron, the peak positions found by them are 59.93 and 63.43 volts. These are in fair agreement with our measurements. The peak at 63.6 volts is small but is definitely present. These transitions have been ascribed by Whiddington to the simultaneous excitation of both electrons in helium. The two excitations are therefore superposed on the continuum which results from the excitation of one electron above the ionization potential. Our experiments indicate, however, that a simple superposition of a transition between discrete states on a continuum does not adequately account for the appearance of the curve of scattered current vs excitation energy. In passing through the transition the continuum changes abruptly. If the continuum which precedes the transition is extrapolated beyond the transition, then the extrapolated curve is much higher than that observed. The occurrence of a transition in which two electrons are excited therefore has a pronounced influence on the probability of the alternative transition in which only one electron is excited. This is an interesting point which previous experimental work has not raised because the spectrum could not be studied with enough accuracy. The spectrum is being further studied to obtain cross section measurements in this interesting region.
After the observations on helium, mentioned above, had been made, the nitrogen spectrum beyond 80 ev was also studied. No peaks could be found which corresponded to the double transitions in helium. Nevertheless, because nitrogen is an important atmospheric gas, the spectral region from 80 to 90 ev has been systematically studied. Angular scattering runs (in duplicate) have been made at each of eight excitation energies between 80 and 90 ev. The 13 ev excitation has been run in each case for comparison. Angular runs on the 14.0 and 15.9 ev peaks have also been made. Elastic scattering has been studied out to a 90° scattering angle. These data, together with data given in a previous report, provide a study of nitrogen comparable with that which has been made on oxygen. A few check runs remain to be done. These will be completed during the coming quarter.

2.5 Scientific Reports

The final draft of Report No. 6 is complete. Otherwise, this aspect of the program has been inactive.

Two papers have been submitted for presentation at the Washington meeting of the American Physical Society, April 29 to May 1, 1954.

3. PLANS FOR FUTURE WORK

The following is planned: (1) further experimental study of carbon dioxide, (2) completion of experimental study of ionized continuum for helium and nitrogen, (3) study of elastic scattering in oxygen, and (4) preliminary studies on other atmospheric gases.

4. PERSONNEL AND ADMINISTRATION

Personnel unchanged from last quarter.
5. FISCAL

Unexpended funds on March 31, 1954 amounted to about $81,948.

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2. Ref. 1 p. 151.


Investigator _______________________________ Date _________________________________

Supervisor _______________________________ Date April 14, 1954

For The Ohio State University Research Foundation

Executive Director _______________________________ Date April 14, 1954
REPORT

By
THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION
COLUMBUS 10, OHIO

To
AEROSPACE CASE ACADEMY RESEARCH CENTER
Cambridge, Massachusetts
Contract No. AFOSR-66-652
D. O. No. 111-1651 Phase V

On
COLLISIONAL CEROS SELECTIONS

For the period
March 15, 1953 to June 14, 1954

Submitted by
J. E. Lennard
Department of Chemistry

Date
July 30, 1954
COLLISIONAL CROSS SECTIONS

1. ABSTRACT

During the present quarter the experimental study of the nitrogen scattering in the spectral region above 20 eV has been completed. Scattering as a function of angle has also been re-determined for several peaks below 20 eV for purposes of comparison with our previous work and the agreement is, in general, good. Considerable calculation remains to be done but experimental work is complete.

The ionised continuum in helium has been further studied. Cross section runs on the peak at 60.1 eV have shown that the transition is optically permitted, although it has apparently not been located optically either in emission or absorption. The investigation is continuing.

The collision cross sections for the 9.1 and 11.1 eV transitions in CO₂ have been determined. The 9.1 eV transition is probably optically permitted, contrary to the theoretical proposals of previous investigators. The study of CO₂ is continuing.

Electron impact spectra for NO₃ have been measured as the first step in a more extensive study.

Three papers were presented at scientific meetings during the quarter.
2. INVESTIGATIONS IN PROGRESS

During the present quarter attention has been devoted to
(a) the further study of the ionized cesium for nitrogen and
helium, (b) further experimental study of carbon dioxide, (c) a
preliminary investigation of the electron impact spectrum of
water.

2.1 Miscellaneous Investigations

2.1.1 Emission Lines of the 8.35 ev

While a symposium paper on the above topic was
being prepared, (see Section 2.5), the distribution of scattered
intensity for the 8.35 volt transition was recomputed using the
formula given in a previous report but employing the more pre-
cise method of Bates to allow for anharmonicity in the excited
state. Agreement between theory and experiment is greatly
improved. This emphasizes again the very close connection between
excitation by electron impact at small scattering angles and exci-
tation by the absorption of radiation.

2.1.2 Electron Impact Spectra for H2O

As a preliminary to a more complete study, spectra
have been obtained at gun angles of 6° and 11° over the energy
loss range from 0 to 50 ev. Five peaks are found in the spectrum
at 6°. The peak voltages are approximately 7.3, 10.2, 11.3, 13.5,
and 17.8 ev, respectively. In the 11° spectrum the first four

2
peak still appear, although with much reduced relative heights, but the fifth is missing. The most interesting feature of the spectrum is the relative intensities of the regions below and above 15 ev. In the 11° spectrum, the intensity of that portion of the spectrum above 15 ev is much greater relative to that below 15 ev than in the case at 6°. The change is so great that the two spectra are hardly recognizable on superficial examination as belonging to the same substance. In this respect the spectrum of water differs greatly from those of the other atmospheric constituents which have thus far been studied although even more exaggerated cases have been found in previous studies, not connected with this contrast, in substances which do not occur in the atmosphere. The systematic study of H2O is of considerable interest, although the investigation will have to be very carefully organized and will probably be time consuming.

2.11 Irradiation of Matter

Complete.

2.2 Elastic Collision Cross Sections

For oxygen in the Spectral Region

between 11 and 60 ev.

Complete.
3.3 Electron Impact Spectra for Carbon Dioxide. Collision Cross Sections for the 9.1 and 11.1 eV Transitions

The study of the 9.1 eV peak and the immediate vicinity of the spectrum has been continued. New, and more precise, determinations of the scattered current as a function of angle have been made for both the 9.1 and 11.1 eV transitions. An absolute cross-section determination on the 11.1 eV transition has also been made by comparing the scattering with that of helium, the helium runs being made both before and after the carbon dioxide experiments. The carbon dioxide scattering has also been studied as a function of pressure in order to determine the electronic mean free path. The absolute cross sections obtained in this way must still be regarded as tentative since a question has arisen, after the experiments were completed, concerning the accuracy of the beam current measurements in two of the four helium runs.

Since the 11.1 eV transition is to be the standard of comparison in the study of the remainder of the spectrum, it is essential that the greatest possible accuracy be obtained in the cross-section measurement. Hence, this transition is being further studied and the investigation was not complete at the end of the quarter.

Absolute cross sections have been calculated from the data for the 9.1 eV transition. Since these calculations depend on comparison with the 11.1 eV transition, the results must still
be considered as tentative in the sense that they depend on a
constant of proportionality which is subject to an error of about
10\%. This error will be reduced as the result of subsequent de-
terminations on the 11.1 ev peak as mentioned above. The work
has progressed far enough, however, to indicate that the transi-
tion is optically permitted since the generalised oscillator
strength extrapolates to a nonvanishing, although small, limit.
This conclusion is contrary to the proposals of several previous
investigators who based their predictions on approximate quantum
mechanical arguments. If, as seems probable at present, the
transition is allowed, then this section of the spectrum must be
re-interpreted. The transition is being further studied in order
to improve the precision of experiment and thus reduce the error
in extrapolation. Very careful work is required since the scatter-
ing at 9.1 ev is much smaller than at 11.1 ev.

The spectrum of CO in the neighborhood of 9.1 ev has been
studied as a function of angle. The results suggest that the
spectrum may contain two peaks very close together, although
scatter in the counting rate data is too great to positively
establish this point at present. The investigation of this point
is continuing.
2.4 Study of Ionized Continua for Helium and Nitrogen

The experimental study of the ionized continua for helium and nitrogen have been continued during the present quarter.

In the case of nitrogen the experimental study of continua has been completed with the measurement of spectra at gas angles from 5° to 15°. In addition, angular runs on each peak in the spectrum have been made and a few, and more precise, determination of absolute cross sections for the 12.65 volt transition has also been made. Agreement of relative cross sections between the present and our previous work seems to be very good and the absolute cross sections agree as well as could be expected. More detailed comparison will be given in the next report when the calculations are further advanced. The experimental data on helium are now complete. Precision and reproducibility are very good. Considerable calculation remains to be done but no further experimental work is contemplated at present.

The initial objective of the present investigation was a study of the ionized continua for both nitrogen and helium. It seemed, at the outset, logical to group the two together since the primary objective was the study of the continua spectrum. As the work progresses it becomes evident that this grouping is not a satisfactory one since transitions are found in the helium
continuum at 60.1 and 60.6 volts which are apparently due to the
continuous excitation of two electrons while such transitions
were not found, or not recognised, in the nitrogen spectrum. The
study of helium is therefore continuing along lines which differ
from the study of nitrogen. It was reported in Progress Report
No. 11 that the continuum changed abruptly in passing through the
peak at 60.1 volts. This has been further confirmed during the
present quarter. Collision cross-section measurements have been
made, as a function of angle, for the 60.1 volt peak and for two
points in the continuum, one volt above and below the peak,
respectively. The trend of cross-sections for these three exci-
tations is very similar indeed. Normalised oscillator strengths
were plotted as a function of $(\psi)^2$ (square of the momentum
change of the colliding electron) give straight lines of positive
slope which are very nearly parallel for the three transitions.
Interpolation leads to new diminishing optical oscillator strengths
thus indicating that the 60.1 volt transition is allowed in both
absorption and emission. A search of the literature reveals that
no emission or absorption line has been found in the optical spec-
trum, as far as we know, although attempts have been made to
deflect such a line. The cross-sections measured above show
that the peak at 60.1 volts does not tend to become either more or
less pronounced as the scattering angle increases. Although the
noting fall off with increase in angle, the peak neither
increases nor decreases relative to adjacent portions of the spec-
trum although some relative change might be expected for a transi-
tion to a discrete state in comparison to transitions to states
in an ionized continuum. The precise interpretation of the
results in terms of a single peak for the structure of the atom
is not evident. Further experimental study has been temporarily
delayed in the hope that further consideration of the problem
will provide the basis for a better organized experimental study.

During the course of the above study some additional data
have been collected on the 1's → 2's transition in helium since
the additional labor involved was slight. Cross-section measure-
ments have been extended to 15°. The cross sections agree well
with our previous measurements at the smaller angles where the
two can be compared. No cross section for the transition
becomes equal to that for the optically allowed 1's → 2p transi-
tion at 15°. These data provide an illuminating sample of
the different angular trends of cross sections for optically
allowed and forbidden transitions respectively.

3.5 Scientific Reports
and Papers

Two papers were presented at the Washington meeting of
the American Physical Society April 20 to May 1, 1954 as follows:


A paper was also presented at the Symposium on Molecular Structure and Spectroscopy at the Rensselaer Polytechnic Institute on June 16, 1974, as follows:

3. Intensity Distribution for the \( \sum_{2}^{1} \rightarrow A \sum_{2}^{1} \) Transition in Carbon Monoxide Excited by Electron Impact, by J. S. Silverman and H. E. Lecomte.

All three of the above papers presented by Dr. Silverman.

3. PLAN FOR FUTURE WORK

The following is planned: (1) further experimental study of carbon dioxide, (2) complete the calculation of collision cross sections for the nitrogen continuum, (3) further experimental study of HgO and preliminary work on additional atmospheric constituents, (4) study of elastic scattering in oxygen as time permits.

4. PERSONNEL AND ADMINISTRATION

Personal is unchanged from last quarter. Two additional part-time employees, both graduate students in physical chemistry, will join the project during the summer.
FEDERAL

Unexpended Salts on June 1, 1954 amounted to $35,600.00.

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Investigator

Date

Supervisor: Edwin M. Landis Date: Aug 6, 1954

For The Ohio State University Research Foundation

Executive Director: Dean C. Woodruff Date: Aug 9, 1954
REPORT
by
THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION
Columbus 10, Ohio

To: AIR FORCE CAMBRIDGE RESEARCH CENTER
Cambridge, Massachusetts
Contract No. AF19(122)-642

On: ADDITIONAL COLLISION CROSS SECTIONS FOR HELIUM,
especially in the ionized continuum

Submitted by: Sam Silverman and E. N. Lassettre
Department of Chemistry

Date: July 1957

The research reported in this document has been sponsored in part by
the Geophysics Research Directorate of the Air Force Cambridge Research
Center, Air Research and Development Command, under Contract No.
AF19(122)-642
ABSTRACT

Additional data on the cross sections for the $1^1S \rightarrow 2^3P$ transition are reported and compared with extended theoretical calculations. Some additional results on the $1^1S \rightarrow 2^1S$ transition are also reported.

Collision cross section and oscillator strengths have been determined for several excitations in the ionized continuum. Oscillator strengths agree well with theory except in the vicinity of the double electron excitations. Two excitations which involve simultaneous excitation of two electrons have been observed. Excitation energies agree with the previous work of Whiddington. A discontinuity in the ionized continuum on passing through a peak corresponding to a double excitation has been observed, apparently for the first time.
CONTENTS

1. INTRODUCTION ........................................... 1
2. THE 1S→2P TRANSITION .................................... 1
3. THE 1S→2S TRANSITION .................................... 4
4. CROSS SECTIONS AND OSCILLATOR STRENGTHS FOR THE HELIUM CONTINUUM .......... 8
5. THE 60.0 AND 63.5 EV PEAKS ......................... 12
6. TOTAL COLLISION CROSS SECTIONS FOR THE 1S 3P TRANSITION .................. 16
7. SUMMARY .................................................. 19

LIST OF TABLES

Table No. ................................................. Page
2.1 Theoretical Generalized Oscillator Strengths, f, for the 1S→2P Transition of Helium 2
3.1 Cross Sections and Oscillator Strengths for the 1S→2S Transition from Angular Scattering at 500 Volts 6
4.1 Differential Oscillator Strengths for the Helium Continuum ..................... 9
4.2 Comparative Oscillator Strengths ............................................. 11
5.1 Cross Sections and Differential Oscillator Strengths for the 60.0 ev Peak and the 58.9 ev and 61.3 ev Excitations from Angular Scattering at 500 Volts 14
6.1 Total Collision Cross Sections for the 1S→3P Transition as a Function of Incident Electron Energy 17
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Oscillator Strength of $1^1S \rightarrow 2^1P$ Transition in Helium</td>
<td>3</td>
</tr>
<tr>
<td>3.1</td>
<td>Energy Spectra for the 21 ev Region for Scattering Angles from 9.3° to 15.3°</td>
<td>5</td>
</tr>
<tr>
<td>3.2</td>
<td>$\sigma$ vs $(\Delta \rho)^2$ for both $2^1S$ and $2^1P$ Transitions</td>
<td>7</td>
</tr>
<tr>
<td>5.1</td>
<td>Helium Spectrum in the 60-65 ev Region</td>
<td>13</td>
</tr>
<tr>
<td>6.1</td>
<td>Calculated and Experimental Total Collision Cross Sections as a Function of Incident Electron Energy</td>
<td>18</td>
</tr>
</tbody>
</table>
ADDITIONAL COLLISION CROSS SECTIONS FOR HELIUM, 
ESPECIALLY IN THE IONIZED CONTINUUM

1. INTRODUCTION

Electron collision cross sections for several discrete transitions and at the ionization limit of helium have been presented in a previous report. Inasmuch as collision cross sections for helium are of great interest from both a theoretical and an experimental viewpoint it was thought worthwhile to extend the previous work to include data at larger angles and in the continuum. Since the $1^1S \rightarrow 2^1P$ transition is used for calibrating the apparatus to obtain absolute cross sections, data for this transition were obtained for angles up to about 15 degrees so that a comparison between the shapes of the theoretical and experimental curves could be made over an extended range. These data are presented in Section 2. The $1^1S \rightarrow 2^1S$ transition is of interest as an example of an optically forbidden transition. Additional data for this transition are presented in Section 3. Two peaks far out in the continuum at 60.0 ev and 63.5 ev had previously been reported by Whiddington et al. The energy loss value for these peaks was confirmed and cross sections were measured for the 60.0 ev peak and the neighboring continuum. These results are listed in Section 5. In order to obtain a more complete picture of the continuum, cross sections were determined at several points between the ionization potential and 60 ev. These results are presented in Section 4. Finally, total collision cross sections were calculated as a function of incident electron energy and compared with the results of some optical determinations. These calculations are given in Section 6. The incident electron kinetic energy is approximately 500 ev for all of the experimental work of this report. The experimental methods and techniques used have been adequately described in preceding reports and will therefore not be further discussed here. The helium used was commercial grade obtained from the Air Reduction Company, as in previous experiments.

2. THE $1^1S \rightarrow 2^1P$ TRANSITION

Electron collision cross sections for this transition are of particular interest since it is these cross sections which are used for apparatus calibration and thus for placing other cross sections on an absolute basis. Earlier work on this transition has now been extended in two ways. The theoretical calculations of Jones have been extended to higher values of $(\Delta P)^2$, the square of the change in momentum of the colliding electron. This was necessary since, with the present electron spectrometer, experimental determinations can be made at angles much larger than those covered by the original calculations. The theoretical formulae were also checked by re-evaluation of the integrals involved in the scattering formulae. The theoretical generalized oscillator strengths are given in Table 2.1. This table
also contains the function \(\sigma(P_1/P_2)(\Delta P)^2\) where \(\sigma\) is the collision cross section, \(P_1, P_2\) are the incident and final momenta of the colliding electron and \((\Delta P)^2\) is the square of the change in momentum of the colliding electron. All quantities are in atomic units. This function is tabulated rather than cross section since it is easier to interpolate. The quantity is also used in some of our scientific reports. Enough significant figures have been given in the table so that higher order interpolation formulae can be employed.

<table>
<thead>
<tr>
<th>((\Delta P)^2)</th>
<th>(\sigma(P_1/P_2)(\Delta P)^2)</th>
<th>(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.687152</td>
<td>0.267818</td>
</tr>
<tr>
<td>0.4</td>
<td>0.382592</td>
<td>0.149115</td>
</tr>
<tr>
<td>0.8</td>
<td>0.223543</td>
<td>0.087126</td>
</tr>
<tr>
<td>1.2</td>
<td>0.136140</td>
<td>0.053060</td>
</tr>
<tr>
<td>1.6</td>
<td>0.085940</td>
<td>0.033495</td>
</tr>
<tr>
<td>2.0</td>
<td>0.055974</td>
<td>0.021816</td>
</tr>
<tr>
<td>2.4</td>
<td>0.037473</td>
<td>0.014605</td>
</tr>
<tr>
<td>2.8</td>
<td>0.025700</td>
<td>0.010017</td>
</tr>
<tr>
<td>3.2</td>
<td>0.018011</td>
<td>0.007020</td>
</tr>
<tr>
<td>3.6</td>
<td>0.012866</td>
<td>0.005015</td>
</tr>
<tr>
<td>4.0</td>
<td>0.008808</td>
<td>0.003433</td>
</tr>
</tbody>
</table>

Experimentally, additional data have been accumulated for angles up to about 15 degrees. Also, since this transition is used for calibrating the apparatus, a good deal of data have been collected in the course of work on other gases. The calibration of the apparatus was carried out so as to give the best fit of the experimental and theoretical generalized oscillator strengths over the entire range. All measurements were carried out at incident kinetic energies of approximately 500 ev. The comparison of theory with experiment is shown in Fig. 2.1. The points in this figure designated by triangles are taken
Oscillator Strength of 1^S - 2^P Transition in Helium
Approximate Accelerating Voltage - 500
Maximum Deviation 6.3%
Mean Deviation 2.2%

Fig. 2.1 Oscillator strength of 1^S → 2^P transition in helium
from a previous report\textsuperscript{1}, the data points represented by solid circles were collected during the present research, and the data represented by open circles were collected by Jerome C. Shiloff during the course of a calibration run on carbon dioxide. Since calibration runs on helium are made during the course of studying each gas a great deal of additional data could be added to the figure without, however, adding anything of importance.

The figure shows, essentially, the agreement in the shape of the experimental and theoretical oscillator strength curves. The agreement between theory and experiment is seen to be quite good. The average deviation of the experimental points is of the order of 2%. Although this agreement is quite good it will be evident from inspection of the figure that small systematic deviations are encountered. This is to be expected since the atomic wave functions employed in the calculation are not exact although the approximation is very good\textsuperscript{2} especially for the ground state.

The generalized oscillator strength changes rather slowly with $(AP)^2$ and hence Fig. 2.1 does not fully indicate the excellence of agreement between theory and experiment. The range covered by this figure involves a change in scattered current of more than a thousand-fold. That theory and experiment should agree within a mean deviation of 2% over such a range of scattered current shows clearly that the theoretically predicted shape of scattering curve is a very good approximation to that obtained by experiment. In view of this fact we believe that the theoretical cross sections for this transition approximate closely to the actual cross sections for the transition. This is an important point since the theoretical cross sections, or oscillator strengths, for this transition are employed for the purpose of placing cross sections for other substances on an absolute basis.

3. \textbf{THE $1^1S \rightarrow 2^1S$ TRANSITION}

The $1^1S \rightarrow 2^1S$ transition is of interest because of its character as an optically forbidden transition. Earlier work on this transition had been restricted to angles smaller than about 9 degrees. Since in this angular range the transition appears usually as a shoulder on the $1^1S \rightarrow 2^1P$ peak a graphical resolution procedure was adopted to determine cross sections.\textsuperscript{1} In the present investigation the angular range was extended to about 15 degrees. Figure 3.1 shows energy spectra for the region around 21 ev for scattering angles from 9.3° to 15.3°. This figure supplements Fig. 3.11 of Ref. 1. It is interesting that the transition probabilities for the $1^1S \rightarrow 2^1S$ transition and the $1^1S \rightarrow 2^1P$ transition are nearly equal at 15.3°.

A new resolution procedure was also adopted for separating the $2^1S$ and $2^1P$ peaks. This procedure is based on the fact that the $b$-value (ratio of area to height for a given peak, as explained in Report No. 2
Fig. 3.1 Energy spectra for the 21 eV region for scattering angles from 9.3° to 15.3°
of this series) should be the same for both elastic and inelastic peaks in the same spectrum when the kinetic energy is as high as 500 ev. Consequently the following procedure was adopted. The b-value was first determined from several measurements on the elastically scattered peak. At the smaller angles where the $2^1P$ peak is much stronger than the $2^1S$ peak the total area under both peaks was then measured. The height of the $2^1P$ peak, in conjunction with the elastic scattering b-value, was then used to calculate the contribution of the $2^1P$ peak to the total area. The remaining area was then used to calculate cross sections and oscillator strengths for the $2^1S$ transition. At the larger angles, where the two peaks were resolved, the height of each peak, together with the b-value, was used to calculate cross sections and oscillator strengths. The effect of the tail of the $2^1P$ peak was corrected for by subtracting from the observed $2^1S$ peak height $0.03 \times 2^1P$ peak height.

Table 3.1 lists the cross sections and oscillator strengths determined in the present investigation. In this table only the data for a scattering angle of 4.73° were calculated by subtracting the $2^1P$ area from the total area.

<table>
<thead>
<tr>
<th>Scattering Angle, °</th>
<th>$(\Delta \rho)^2$</th>
<th>$\sigma$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-9.30</td>
<td>0.9614</td>
<td>0.0575</td>
<td>0.0214</td>
</tr>
<tr>
<td>-10.30</td>
<td>1.1750</td>
<td>0.0446</td>
<td>0.0203</td>
</tr>
<tr>
<td>-11.30</td>
<td>1.4102</td>
<td>0.0330</td>
<td>0.0180</td>
</tr>
<tr>
<td>-12.30</td>
<td>1.6669</td>
<td>0.0238</td>
<td>0.0153</td>
</tr>
<tr>
<td>-13.30</td>
<td>1.9449</td>
<td>0.0184</td>
<td>0.0138</td>
</tr>
<tr>
<td>-14.30</td>
<td>2.2446</td>
<td>0.0129</td>
<td>0.0112</td>
</tr>
<tr>
<td>-15.30</td>
<td>2.5651</td>
<td>0.0090</td>
<td>0.0089</td>
</tr>
<tr>
<td>9.70</td>
<td>1.0443</td>
<td>0.0566</td>
<td>0.0229</td>
</tr>
<tr>
<td>4.73</td>
<td>0.2617</td>
<td>0.1705</td>
<td>0.0173</td>
</tr>
</tbody>
</table>

Figure 3.2 shows graphically the cross sections for both the $2^1S$ and $2^1P$ transitions. Data from the earlier report have been included in this figure. It is evident from the figure that at small angles the $2^1P$ peak will be considerably more intense than the $2^1S$ peak, but that at angles greater than about 15° or 16° the $2^1S$ peak will become the dominant feature of the spectrum in this region. This is in accord with our expectations, since the cross sections for an optically forbidden
Fig. 3.2 $\sigma$ vs $(\Delta P)^2$ for both $2^1S$ and $2^1P$ transitions
transition fall off more slowly with angle than those of an optically allowed transition. This leads, however, to the conclusion that much of the earlier work reported in the literature must now be re-evaluated, since in this earlier work measurements were generally made at rather large angles and the peak at about 21 ev was assumed to be the 2P peak. In actual fact resolution was usually not good enough to separate the 2S and 2P transitions and as a result the angular dependence observed is a combination of the two with 2S predominant at large angles. This was probably the case in the work of Hughes and McMillen on helium.10

Another consequence of this increased importance of the 2S peak at larger angles is the possibility that the total cross section, i.e., the cross sections integrated over all scattering angles, may be appreciable. This would be important for the study of processes in which electron impact plays an important role, such as in gas discharges or upper atmosphere studies.

Because of the indirect way in which cross sections must be obtained from the measured scattered currents the data are too scattered to permit extrapolation of oscillator strengths to (AP)2 = 0. In this respect the situation is unchanged from that previously reported.1

4. CROSS SECTIONS AND OSCILLATOR STRENGTHS FOR THE HELIUM CONTINUUM

In the earlier work on helium, cross sections and oscillator strengths were determined from angular scattering runs for the ionization limit at 24.6 ev. In addition some cross sections and oscillator strengths for the 33.6 ev energy loss were calculated from electron impact energy spectra, though these were of doubtful accuracy, to indicate the order of magnitude of these quantities at this energy loss. It was thought worthwhile to extend the data for the continuum utilizing the experience gained in the investigations of oxygen and nitrogen. Aside from the intrinsic interest of the data this was done for the following reasons. First, theoretical calculations of the optical oscillator strengths are available from the work of Wheeler which can be compared with the experimental data. Secondly, data for the continuum should be directly comparable to the results of the optical investigations reported by Weissler7, et al. because of the absence of other lines or band systems. Finally it was of interest to determine whether the behavior of helium in the continuum was similar to that previously observed for oxygen and nitrogen.

Angular scattering runs were carried out at energy losses of 28.5, 34.5, 41.8, 48.1 and 54.3 ev. The data are listed in Table 4.1. The results given in Table 4.1 have been interpolated linearly from the experimental data at equal intervals in (AP)2. Scatter in the data are preserved by the linear interpolation.
It must be pointed out that the background scattering correction was abnormally large for some of the data in Table 4.1. This arises because scattered current for helium at high excitation energies is considerably less than for other substances, such as nitrogen and oxygen, which have been previously studied and the background correction is correspondingly larger in percentage. During the course of writing this report the method for making background corrections was critically reviewed.

By utilizing background scattering data obtained at various times both before and after the determinations at 41.8, 48.1, 54.3 ev it was verified that the background scattering did not vary significantly with time and, moreover, constituted a nearly constant percentage of the total scattering as the scattering angle is varied. The background correction amounts to as much as 20% of the total and the chance of error in the oscillator strengths is larger than usual although it is difficult to place a reliable bound on the magnitude of this error. The error is probably not excessive in the range of angles for which measurements were made but the extrapolations to \((\Delta P)^2 = 0\) are another matter since these are sensitive to very slight systematic errors which could, in fact, be introduced in making a background correction. Of the gases studied under this contract the above situation arises only for helium. In all other cases the background correction above 40 ev rarely exceeds five percent and hence even rough data on background scattering are sufficient.
to provide an adequate correction. It is estimated that the precision of the data in Table 4.1 is 5% except for the extrapolated points where the uncertainty is higher.

Table 4.2 shows a comparison of the electron impact optical oscillator strengths with those obtained by Lee and Weissler\(^7\) using optical methods and with the theoretical calculations of Huang.\(^{13}\) Comparison with the results of Lee and Weissler shows that the electron impact data are about 25% higher on the average than the optical data. Obviously, from an inspection of Table 4.2 (Part B) the electron impact oscillator strengths are consistently higher than those of Lee and Weissler. A consistent bias in extrapolation might account for part of the discrepancy but not for all of it. The uncertainty arising from large background corrections cannot be a serious factor because all but two of the entries in Part B of the table are at excitation energies below those for which any real uncertainty arises. This leaves either the possibility of failure in the Born approximation, which could mean that the extrapolated electron impact oscillator strength was not equal to the optical oscillator strength, or error in the optical determinations, or both. Since we are not qualified to evaluate critically the techniques involved in the optical determinations the matter must be left at this point. It would be of interest to extend the measurements to smaller angles in order to check the possibility of a failure of the Born approximation but this is not feasible with the equipment now in use.

The comparison between the theoretical oscillator strengths calculated by Huang\(^3\) and those determined in the present experimental study are shown in Part A of Table 4.2. The agreement is good except at 54.3 eV. Unfortunately the data at the latter point are subject to uncertainty due to the background correction mentioned previously. Nevertheless, we believe that a real discrepancy is involved although its magnitude may be smaller than that indicated in the table. Additional evidence in support of this view is given in the next section and the results of this section will be further discussed at that point.

It is of interest that the 25% discrepancy of Table 4.2 is of the same order as that between the electron impact oscillator strengths and the optical data of Watanabe, Inn and Zelikoff for the Schumann-Runge continuum of oxygen\(^{14}\), and for the calculated and experimental indices of refraction for oxygen\(^{11}\) and nitrogen.\(^{12}\) This still cannot be regarded as definitive, however, because the agreement with the work of Ditchburn and Heddle for the oxygen continuum is much better,\(^{14}\) while a test of the oscillator sum rule for oxygen\(^{11}\) leads to satisfactory agreement with theory. Finally, the close agreement with the theoretical calculations of Huang for helium at excitation energies of 48.1 eV or lower also provides some support for the electron impact measurements. In view of this situation it can only be said that the differences between oscillator strengths determined by optical and by electron impact
TABLE 4.2 COMPARATIVE OSCILLATOR STRENGTHS

**Part A: Comparison with the theoretical calculations of Wheeler**

<table>
<thead>
<tr>
<th>W</th>
<th>$f_0^0$ theoretical</th>
<th>$f_0^0$ experimental</th>
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</thead>
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<tr>
<td>24.6</td>
<td>0.068</td>
<td>0.066</td>
</tr>
<tr>
<td>28.5</td>
<td>0.055</td>
<td>0.054</td>
</tr>
<tr>
<td>34.5</td>
<td>0.038</td>
<td>0.040</td>
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<tr>
<td>41.8</td>
<td>0.026</td>
<td>0.025</td>
</tr>
<tr>
<td>48.1</td>
<td>0.019</td>
<td>0.018</td>
</tr>
<tr>
<td>54.3</td>
<td>0.015</td>
<td>0.012</td>
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**Part B: Comparison with the optical measurements of Lee and Weissler**

<table>
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<th>W</th>
<th>$f_0^0$ optical</th>
<th>electron impact*</th>
<th>% deviation</th>
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<tr>
<td>25.00</td>
<td>0.063</td>
<td>0.064</td>
<td>1.5</td>
</tr>
<tr>
<td>25.53</td>
<td>0.056</td>
<td>0.063</td>
<td>11</td>
</tr>
<tr>
<td>27.42</td>
<td>0.054</td>
<td>0.056</td>
<td>3.5</td>
</tr>
<tr>
<td>27.82</td>
<td>0.048</td>
<td>0.055</td>
<td>13</td>
</tr>
<tr>
<td>28.50</td>
<td>0.039</td>
<td>0.054</td>
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<td>28.95</td>
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<td>29.60</td>
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<td>31.33</td>
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<td>33.14</td>
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<td>34.16</td>
<td>0.029</td>
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<td>34.59</td>
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<td>38.30</td>
<td>0.027</td>
<td>0.032</td>
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<tr>
<td>40.51</td>
<td>0.015</td>
<td>0.027</td>
<td>25</td>
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<tr>
<td>43.71</td>
<td>0.010</td>
<td>0.022</td>
<td>55</td>
</tr>
<tr>
<td>50.82</td>
<td>0.009</td>
<td>0.015</td>
<td>40</td>
</tr>
<tr>
<td>51.72</td>
<td>0.009</td>
<td>0.014</td>
<td>36</td>
</tr>
</tbody>
</table>

Av. % dev. = 25

*Interpolated from the data of Table 4.1*
methods may be real but are not proven to be real. It would be of some interest to have a further investigation of the Born approximation to collision cross sections and especially the terms arising from second order perturbation theory. If the discrepancies indicated above are real they most probably originate in these terms. The assumption that the limits of generalized oscillator strengths at \((\Delta P)^2 = 0\) are equal to optical oscillator strengths is based on the first order Born approximation. Examination of the second order terms would be of considerable interest in indicating possible deviations from this result.

5. THE 60.0 AND 63.5 EV PEAKS

In 1935 and 1937 Whiddington, et al.\(^2,3,4,5\) reported the presence of two peaks in helium far out in the continuum. The energy losses for these peaks were given as 60.0 and 63.5 ev* and were ascribed to double excitation, i.e., the simultaneous excitation of both electrons. It seemed worth while to check these results with the electron spectrometer and, if possible, to determine cross sections and oscillator strengths for these peaks.

Figure 5.1 shows the spectrum in the region from about 60 ev to 65 ev at a scattering angle of about zero degrees. Both peaks reported by Whiddington, et al. are clearly evident. Energy losses for the two peaks are 60.0 ev and 63.5 ev, in exact agreement with those previously reported. The spectrum also shows one remarkable feature not previously reported: an apparent discontinuity in the continuum when the peaks are traversed. The continuum on the high energy loss side of the two peaks is about 20% lower than on the low energy loss side of the peaks. It should be noted also that both peaks have a shape and half-width which is to be expected for a typical atomic transition. This observation suggests that once the spectral region around 60 ev is not merely the result of superposition of two alternative transitions, one to a discrete state and the other to a continuum. Instead a considerable portion of the spectrum is affected.

In order to test this view, collision cross sections have been determined for the peak at 60 ev and for two points in the neighboring continuum, at 58.9 and 61.3 ev. Cross sections and differential oscillator strengths for these points are given in Table 5.1. The data of Table 5.1 include points at both positive and negative scattering angles and it is evident that the cross sections (and oscillator strengths as well) at equal positive and negative angles are not accurately equal.

*Whiddington's energy loss values have been corrected by using the newer value for the conversion factor from wave numbers to electron volts. This was necessary since his energy losses were determined relative to the \(^1S\rightarrow^2\text{P}\) transition in helium, the excitation energy for this transition being obtained from emission spectra.
Helium Spectrum – Zero Angle
Accelerating Voltage 504
First Peak 60.0 ± .1
Second Peak 63.5 ± .2

Fig. 5.1 Helium Spectrum in the 60-65 ev region
TABLE 5.1 CROSS SECTIONS AND DIFFERENTIAL OSCILLATOR STRENGTHS FOR THE 60.0 EV PEAK AND THE 58.9 EV AND 61.3 EV EXCITATIONS FROM ANGULAR SCATTERING AT 500 VOLTS

<table>
<thead>
<tr>
<th>Scattering Angle, °</th>
<th>60.0 ev</th>
<th>58.9 ev</th>
<th>61.3 ev</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(AP)²</td>
<td>s</td>
<td>f'</td>
</tr>
<tr>
<td>9.70</td>
<td>1.1283</td>
<td>0.0314</td>
<td>0.0416</td>
</tr>
<tr>
<td>8.70</td>
<td>0.9357</td>
<td>0.0340</td>
<td>0.0374</td>
</tr>
<tr>
<td>7.70</td>
<td>0.7637</td>
<td>0.0368</td>
<td>0.0331</td>
</tr>
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<td>0.6129</td>
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<td>0.0318</td>
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<td>0.0549</td>
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<td>0.4255</td>
<td>0.0627</td>
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<td>0.0319</td>
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<td>0.3358</td>
<td>0.0708</td>
<td>0.0280</td>
</tr>
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<td>0.3836</td>
<td>0.0653</td>
<td>0.0295</td>
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<td>0.4365</td>
<td>0.0662</td>
<td>0.0289</td>
</tr>
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<td>-6.30</td>
<td>0.5583</td>
<td>0.0456</td>
<td>0.0300</td>
</tr>
<tr>
<td>-7.30</td>
<td>0.7009</td>
<td>0.0396</td>
<td>0.0327</td>
</tr>
<tr>
<td>-8.30</td>
<td>0.8645</td>
<td>0.0281</td>
<td>0.0236</td>
</tr>
<tr>
<td>-9.30</td>
<td>1.0488</td>
<td>0.0278</td>
<td>0.0343</td>
</tr>
</tbody>
</table>
This is largely due to a small error in the determination of electron beam direction. If an average of these quantities is taken at equal positive and negative angles then the error in the average due to this factor becomes negligible. The situation described here is essentially similar to that for oxygen and reference is made to that report\textsuperscript{11} for a full description. Since the oscillator strengths vary only slowly with angle the values at equal positive and negative angles (for which the values of (AP)\textsuperscript{2} are equal) can be obtained with sufficient accuracy by means of a linear interpolation. This has been done and the averages are given in Table 5.2 at equal intervals in (AP)\textsuperscript{2}. The results are given only to two significant figures since greater accuracy is not justified. The scattered currents are small in these experiments and it is evident from Table 5.1 that the data are scattered. Background scattering is also an important proportion of the total and correction for this factor introduces an additional uncertainty as discussed previously in Section 4. Despite this fact the data are reported, since no measurements in this region have previously been performed and the trends are not doubt essentially correct. When the differential oscillator strengths are extrapolated to (AP)\textsuperscript{2} = 0 the following results are obtained: for the peak at 60.0 ev - 0.028, for the 58.9 ev transition - 0.017, for the 61.3 ev transition - 0.014. Similar measurements for the 63.5 ev peak have not been attempted because the counting rates are still lower and measurements are subject to such large errors that a quantitative study did not seem worth while.

<table>
<thead>
<tr>
<th>(AP)\textsuperscript{2}</th>
<th>60.0 ev</th>
<th>58.9 ev</th>
<th>61.3 ev</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>0.029</td>
<td>0.019</td>
<td>0.016</td>
</tr>
<tr>
<td>0.35</td>
<td>0.030</td>
<td>0.019</td>
<td>0.016</td>
</tr>
<tr>
<td>0.40</td>
<td>0.030</td>
<td>0.020</td>
<td>0.017</td>
</tr>
<tr>
<td>0.45</td>
<td>0.030</td>
<td>0.021</td>
<td>0.017</td>
</tr>
<tr>
<td>0.50</td>
<td>0.030</td>
<td>0.021</td>
<td>0.018</td>
</tr>
<tr>
<td>0.60</td>
<td>0.031</td>
<td>0.021</td>
<td>0.019</td>
</tr>
<tr>
<td>0.70</td>
<td>0.033</td>
<td>0.023</td>
<td>0.020</td>
</tr>
<tr>
<td>0.80</td>
<td>0.032</td>
<td>0.024</td>
<td>0.020</td>
</tr>
<tr>
<td>0.90</td>
<td>0.033</td>
<td>0.025</td>
<td>0.021</td>
</tr>
<tr>
<td>1.00</td>
<td>0.036</td>
<td>0.027</td>
<td>0.022</td>
</tr>
</tbody>
</table>
The data described in the preceding paragraph provide still further support for the view that the spectral region around 60 volts is far from being merely a superposition of a discrete transition and a continuum. For if the reverse were true then two very different transitions would be involved, one resulting from the simultaneous excitation of two electrons and the other the excitation of one electron into an ionized continuum. Two such different transitions would surely be characterized by quite different trends in oscillator strengths with $(\Delta P)^2$. In fact, however, the data of Table 5.2 show that the trends are very similar. In fact all three sets of data are almost exactly parallel. The relative spectrum must, therefore, change but little with change in scattering angle and this has been verified by the determination of spectra at several angles. The discontinuous change in continuum is observed at all angles for which observations were made.

The comparison between the theoretical oscillator strengths of Huang and those determined in the present experiments (Table 4.2, Part A) are of some interest in the light of the above discussion. Wheeler's calculations do not include any contribution from transitions in which both electrons are simultaneously excited. One electron wave functions are used for the excited state (but not for the ground state). Hence the calculations provide, at least approximately, the expected behavior of oscillator strengths in the absence of double excitations. At excitation energies up to and including 48.1 ev agreement between theory and experiment is good but at 54.3 agreement is poor. This suggests that the continuum is affected over a very considerable region. Unfortunately, the disagreement between theory and experiment occurs in the spectral region for which high background corrections make the data uncertain. In the light of the observations described in the preceding portions of this section it is not especially surprising that theory and experiment should disagree at high excitation energies although the magnitude of disagreement indicated in Table 4.2 may be too great. No theoretical explanation for the peculiar behavior of the continuum is at present available. It is obvious that a strong perturbing effect of the doubly excited states on the continuum exists. Previous treatments of two energy states of this sort have dealt primarily with the perturbing effect on the discrete level (i.e., diffuse levels, auto-ionization) rather than on the continuum.

6. TOTAL COLLISION CROSS SECTIONS FOR THE $1s^2 \rightarrow 3^4P$ TRANSITION

In a previous report it was shown that the total collision cross sections could be calculated as a function of incident electron energy using the data obtained at a single incident electron energy. This calculation assumes that the generalized oscillator strength depends only on $(\Delta P)^2$ which follows from the Born approximation. Thus if independent measurements of the total collision cross sections as a function of incident electron energy are available a comparison of these with the
calculated curve would show at what incident electron energy the Born approximation breaks down.

Total cross sections for this transition have been measured optically by Lees and by Thieme. Their method involved intensity measurements on individual spectral lines with a correction for the cascade effect. Cross sections and oscillator strengths have also been measured in this laboratory and are listed in the previous report on helium. These data were used for the calculation of cross section as a function of incident electron energy using essentially the same method as that of Ref. 11. The Lees and Thieme data were then adjusted to agree with the electron impact data at 400 volts. A comparative listing of the results is given in Table 6.1. The data are shown graphically in Fig. 6.1. From Fig. 6.1 it can be seen that the two curves agree well for incident electron energies down to about 150 volts. This indicates roughly the limit of validity of the Born approximation.

### TABLE 6.1 TOTAL COLLISION CROSS SECTIONS FOR THE $1s^{2} \rightarrow 3^{1}p$ TRANSITION AS A FUNCTION OF INCIDENT ELECTRON ENERGY

<table>
<thead>
<tr>
<th>Part A: Calculated from electron impact data</th>
<th>Part B: From the data of Lees and of Thieme. Adjusted to agree with electron impact data at 400 volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incident Electron Energy - Volts</td>
<td>Total Collision Cross Section</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>500</td>
<td>0.0494</td>
</tr>
<tr>
<td>400</td>
<td>0.0574</td>
</tr>
<tr>
<td>300</td>
<td>0.0691</td>
</tr>
<tr>
<td>200</td>
<td>0.0877</td>
</tr>
<tr>
<td>175</td>
<td>0.0942</td>
</tr>
<tr>
<td>110</td>
<td>0.1162</td>
</tr>
<tr>
<td>61.2</td>
<td>0.1243</td>
</tr>
<tr>
<td>45.2</td>
<td>0.1206</td>
</tr>
</tbody>
</table>
Fig. 6.1 Calculated and experimental total collision cross sections as a function of incident electron energy.
7. SUMMARY

The present investigation has included both theoretical and experimental extensions of previous work on helium. Theoretical cross sections for the $1^1S \rightarrow 2^1P$ transition have been calculated for larger values of $(\Delta P)^2$. This was necessary because the increased sensitivity and the geometry of the new apparatus lead to the measurement of scattering cross sections at larger angles than were heretofore used. Experimentally, the following results were obtained:

a. Generalized oscillator strengths for the $1^1S \rightarrow 2^1P$ transition were measured for angles up to about $15^\circ$. The shapes of the experimental and theoretical curves for this transition are in excellent agreement.

b. Cross sections for the $1^1S \rightarrow 2^3S$ transition were measured for angles up to about $15^\circ$. Cross sections for this transition were found to be appreciable at the larger angles, and, in fact, to become greater than those for the $1^1S \rightarrow 2^1P$ transition at angles larger than about $15^\circ$. At the smaller angles the data were insufficiently accurate to decide on whether or not the oscillator strengths extrapolate to zero at zero $(\Delta P)^2$.

c. The occurrence of two peaks at 60.0 ev and 63.5 ev was confirmed. A strong perturbing influence of the 60.0 ev peak on the surrounding continuum was discovered. Cross sections and oscillator strengths for the 60.0 ev peak and for energy losses of 58.9 and 61.3 ev in the continuum were obtained.

d. Cross sections and oscillator strengths were obtained for energy losses of 28.5 ev, 34.5 ev, 41.8 ev, 48.1 ev and 54.3 ev. These were compared with the theoretical calculations of Huang and the experimental optical measurements of Lee and Weissler. Comparison with the calculation of Wheeler leads to the conclusion that the perturbing effect of the 60.0 ev peak extends as far back as 40 ev energy loss. The general features of the oscillator strength vs $(\Delta P)^2$ curves were found to be similar to those previously observed for oxygen and nitrogen.

e. Total collision cross sections as a function of incident electron energy were calculated for the $1^1S \rightarrow 3^1P$ transition and compared with the experimental optical measurements of Lees and of Thieme.
This comparison indicated that the Born approximation is valid for incident electron energies down to about 150 volts.

REFERENCES


