Colloquium: Ettore Majorana and the birth of autoionization

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In some of the first applications of modern quantum mechanics to the spectroscopy of many-electron atoms, Ettore Majorana in 1931 solved several outstanding problems by developing the theory of autoionization. Later literature makes only sporadic references to this accomplishment. After reviewing his work in its contemporary context, we describe subsequent developments in understanding the spectra treated by Majorana and extensions of his theory to other areas of physics. Several puzzles are found concerning the treatment of Majorana’s work in the subsequent literature and the way in which the modern theory of autoionization was developed.

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I. INTRODUCTION

Ettore Majorana (Fig. 1) ceased to be an active member of the physics community on or about March 27, 1938 at the age of 31. His subsequent fate is unknown, as discussed by Amaldi (1966).

Majorana was regarded by Enrico Fermi, his doctoral thesis supervisor, as being comparable to Galileo and Newton in his capability for original scientific contributions. He published only nine papers; these have been reprinted, along with English translations and commentaries, in a volume commemorating the centenary of his birth (Bassani and The Council of the Italian Physical Society, 2006). He left a large number of unpublished scientific manuscripts, and several of them have been published recently (Esposito et al., 2003, 2008). Some of his contributions to theoretical physics have been recently reviewed by Wilczek (2009).

His scientific work focused on two main topics: nuclear and elementary particle physics and atomic and molecular physics. His doctoral thesis in July 1929 was a theoretical study of the structure of the nucleus and the mechanism of alpha decay. In 1932 he published brilliant and pioneering results on the unitary representations of the Lorentz group (Majorana, 1932b) that received scant attention and were rediscovered years later (Fradkin, 1966). He is probably best known in physics as a whole for his theory of the neutrino (Majorana, 1937). A Majorana neutrino is its own antiparticle, and it has yet to

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FIG. 1. Ettore Majorana, date unknown. (Photo reproduced with permission of E. Recami and F. Majorana.)
be determined whether the known neutrinos are Dirac or Majorana particles. Present experiments on neutrinoless double beta decay seek to settle this issue (Avignone et al., 2008). Furthermore, Majorana fermions have recently become of much interest in the theory of topological quantum computing, the quantum Hall effect, and exotic forms of superconductivity (Nayak et al., 2008). On the other hand, Majorana’s most influential paper (Majorana, 1932a), as measured by citations, concerns the motion of atoms in an inhomogeneous magnetic field. This subject emerged in the center of modern physics ca. 1990 as a key element of the technology of trapping ultracold atoms. This area of research has been recognized by Nobel Prize awards in 1997, 2001, and 2005, has opened new vistas on quantum degenerate matter, and has facilitated measurements of unprecedented precision which are establishing impressive bounds on the time variation of the fundamental constants.

Majorana’s genius is displayed throughout his work on atomic physics, which exhibits keen physical insight and remarkable technical virtuosity. His first paper (Gentile and Majorana, 1928) and a conference presentation from the same year (Majorana, 1929) present first-principles calculations of the spectra of complex atoms—cesium, gadolinium, and uranium—in the context of Fermi’s statistical model of the atom, which had first been published only eight months previously (Fermi, 1927). The scope of these papers is most impressive, encompassing substantial numerical calculations, quantitative treatment of the spin-orbit interaction, comparison with experimental data, and introduction of corrections to Fermi’s statistical potential to attain better agreement with fine-structure data. Atomic spectroscopy and dynamics remained a preoccupation of Majorana in the following years. The present work explores one of his signal contributions to this field, the identification of the effect of autoionization in atomic spectra.

Majorana’s contributions to autoionization are presented in two papers dealing with atomic energy levels lying above the first ionization limit, published in 1931 only 24 pages apart in the same volume of the same journal (Majorana, 1931a, 1931b). The first of these investigations the doubly excited $2s^2, 2s2p$, and $2p^2$ electron configurations of the helium atom. These all have sufficient energy to induce spontaneous ionization (Majorana termed “ionizzazione spontanea”), in which one electron makes a transition into the ground state of He⁺ and the other carries off the excess energy. The second of these papers, dealing with $np^2 \ ^3P$ electron configurations above the ionization limit in zinc, cadmium, and mercury, is widely acknowledged as a pioneering work on “...the importance of autoionization in atomic spectra in the optical region...” (Condon and Shortley, 1935). Although the first of these papers also treats autoionization in a highly insightful and original manner, it has very rarely been cited in the now extensive literature on this subject. Majorana’s great contribution to understanding autoionization was the identification of symmetry principles and their practical application to the spectroscopy of nonstationary states.

Introductory treatments of quantum mechanics focus on the role of “stationary states,” the quiescent states of isolated systems. Understanding the properties of such systems plays a foundational role in quantum physics. However, the observable evidence available in the early days of quantum mechanics involved transitions between nominally stationary states, such as atomic and molecular spectra presented as sharp lines. The regular patterns observed in such spectra provided key clues to decoding the underlying mechanisms of atomic structure—yet such clues are occasionally obscured by anomalies. Majorana was the first to identify one pervasive mechanism that clouds otherwise clear spectral signatures: autoionization.

Analogues of autoionization are found throughout physics and are usually described in terms of a “discrete state embedded in a continuum” (Fano, 1961). The theoretical understanding of autoionization seems to have been developed independently at least twice in Enrico Fermi’s group within the course of a few years: first by Majorana and later by Ugo Fano (1935). The Fano formulation is the one most widely known today. There is no public record of communication between these two developments, and Fano’s 1935 paper does not cite Majorana’s work of 1931.

In this paper we review the scientific development of the concept of resonance between discrete and continuum states in the spectra of various quantum-mechanical systems, ranging from early atomic spectroscopy to work of the present day. Section II presents the state of atomic spectroscopy ca. 1931, introducing the importance of the “displaced” (primed) terms in the development of atomic theory, and the observation and classification of transitions of the $p-p’$ type. Section III presents the symmetry considerations underlying Majorana’s analyses of atomic spectra. Section IV reports the main results of the 1931 papers by Majorana, emphasizing his contributions to the identification of broad principles governing atomic spectroscopy, to energy-level analysis of spectra, and identification of the effects of autoionization. Section V discusses the contemporary identification of autoionization by Shenstone and subsequent foundational work on autoionization. Section VI discusses later work on doubly excited states in zinc, cadmium, and mercury, and Sec. VII reviews double excitation in helium. Section VIII concludes with a review of analogs of autoionization in different branches of physics.

II. THE STATE OF ATOMIC SPECTROSCOPY CA. 1931

A. Observed spectra

Majorana’s famous paper on autoionization (Majorana, 1931b) deals with a distinctive type of triplet multiplet observed in the atomic spectra of Zn, Cd, and Hg. In modern notation, these multiplets are classified as \( nsp^2 \ ^3P - np^2 \ ^3P \) transitions, with \( n=4, 5, \) and 6 for Zn,
Cd, and Hg, respectively. During the period 1924–1926, experimental spectroscopists had confidently assigned lines to each of these multiplets even though in each case the expected two lines from the upper np^2 3P_1 level were missing or were thought to be missing (Fig. 2). A short account of the earlier theoretical and experimental work will help explain this remarkable confidence.

In his study of the spectra of Ca and Sr, Rydberg (1894) arranged the wave numbers of certain groups of lines into arrays exhibiting constant fine-structure splittings within each array. By 1921, it was known that selection rules allow only six transitions between the three levels of an upper 3P term and those of a lower 3P term, and Landé’s theory gave the predicted Zeeman splitting for these lines. Using these results and the available observations, Götze (1921) was able to classify the lines of one of Rydberg’s arrays in each of the Ca and Sr spectra as transitions from the levels of a new upper 3P term to levels of a known lower 3P term. He also classified the equivalent multiplet for Ba. Götze’s designation of the upper levels of these multiplets as P’ terms, indicating that they do not belong to any of the usual Rydberg series, was generally adopted for other spectra and was used by Majorana.

Wentzel (1923, 1924), following a suggestion by Bohr, and Russell and Saunders (1925) first explained the origin of the primed terms in atomic spectra. Wentzel’s study of a P series in calcium and the interpretations by Russell and Saunders of P’ terms in calcium, strontium, and barium led to the conclusion that the P’ terms might have energies greater than the principal ionization energy of the atom. They thus concluded that such P’ terms involve the excitation of two electrons from the ground state. Interpretation of the origin of such double-excitation terms was a significant part of a broader development of atomic spectroscopy theory during the period 1920–1925 by Landé, Heisenberg, Hund, Pauli, Laporte, Russell and Saunders, Wentzel, and others [see Bowen and Millikan (1925), Shenstone (1926), and Sawyer (1926), for example].

As a result Ruark and Chenault (1925) were able to classify the four observed lines of the Cd 5s5p 3P’–5p^2 3P multiplet at 223.9–232.9 nm (Fig. 2) based on the occurrence of the known 5s5p 3P’ fine-structure separations in the multiplet and on the observed Zeeman-effect triplet for the 3P’_1=3P’_0 line (Paschen, 1911). Ruark (1925) noted that this Zeeman pattern “fixes the character of the whole group.” He gave negative “term values” for the upper 3P’_0 and 3P’_1 levels with respect to the ionization energy, thus recognizing their positions above the 2S limit. Foote et al. (1925) were able to observe these four lines in absorption; to explain the missing 5p^2 3P_2 lines they suggested that the 5p^2 3P_1 and 3P_2 levels “may practically coincide.” The Cd multiplet they recorded in absorption is shown in Fig. 3.

Following these Cd identifications, Sawyer and Beese (1925) classified the corresponding four lines of the Zn 4s4p 3P’–4p^2 3P multiplet and noted the occurrence of two additional lines on the spectogram that might be transitions from the otherwise missing 4p^2 3P_2 level. They hesitated to assign the two lines, however, because of their diffuse appearance, in contrast to the sharpness of the four classified lines. Figure 4 shows a high-resolution reproduction of this multiplet taken from much later work (Martin and Kaufman, 1970). Sawyer and Beese (1926) later classified the two diffuse lines as transitions from the 4p^2 1D_2 level, which they reasoned...
would combine with the 4s4p $^3P^o_2$ and $^3P^o_s$ levels “to give a diffuse doublet.” In a third paper, from which Majorana took the data for Zn, Sawyer (1926) retained this interpretation of the diffuse Zn lines. Sawyer (1926) and Sawyer and Beese (1926) also classified three lines of the Hg spectrum as transitions from the 6p$^2$ $^3P^o_1$ level to the 6s6p $^3P^o_s$ levels, but their suggested classification of a line at 190.01 nm as the 6s6p $^3P^o_s$–6p$^2$ $^3P^o_0$ level was later shown to be incorrect.

Observations and energy-level analysis of the spectrum of neutral copper published in 1926 were important for an independent recognition of autoionization phenomena in 1931. Improvements in analysis of complex atomic spectra initiated by the discovery of multipliclets by Catalán (1922), together with Zeeman-effect observations for copper, allowed confident assignment of copper lines of very different widths to the same quadruplet multiplet (Beals, 1926; Shenstone, 1926; Sommer, 1926). The fact that the multipliclets having this puzzling character involved upper terms lying above the principal ionization limit led Allen Shenstone to introduce ideas of autoionization in atomic spectra (Sec. V).

The experimental background for the paper of Majorana (1931a) on doubly excited states of helium is much simpler and will be summarized in Sec. III.

B. Theories of unstable electronic states

The interaction of light and charged particles with atoms provided many of the clues to the origin of atomic structure and dynamics and also suggested that radiationless conversions of internal atomic energies could occur in the form of a time-reversed inelastic electron collision process (Klein and Rosseland, 1921). In striking observations made in a Wilson-type cloud chamber beginning in 1923, Pierre Auger noticed that atoms from which a K-shell electron was ejected by x-ray absorption would often emit a second electron with an energy $E$ related to the K- and L-shell binding energies: $E=\frac{E_K}{2}−2E_L$ (Auger, 1923). Thus, the production of an electron vacancy in the K shell is followed by a transition in which one L electron falls into the K hole and another is ejected from the atom; this transition is mediated by the Coulomb interaction between the two L-shell electrons. Auger (1926) appears to have been the first to refer to this process as “auto-ionisation.”

Wentzel (1927) presented a theoretical description of the experimental results of the Auger effect, the photo-excitation of an electron in a K orbit accompanied by the ejection of a second electron. This behavior requires a transfer of internal energy between the electrons, with the excitation of an electron to a level located above the lower ionization threshold. Wentzel described the radiationless process of spontaneous ionization of an excited atom (Wentzel: “spontaneous Ionisation”). He expressed the ejected electron wave function as a coherent mixing of the excited state and another state represented by an outgoing spherical wave, the mixing due to electron-electron interactions. The rate of the spontaneous ionization is determined by the matrix element of the interaction energy between the wave functions composing the mixed state. Wentzel did not present specific calculations of the matrix elements, a task which was by no means routine at that time. Majorana significantly advanced this understanding of autoionization through successful analysis of several outstanding problems of atomic spectroscopy, in which he introduced symmetry considerations and parametric treatment of the interaction between discrete and continuum states.

III. SYMMETRY CONSIDERATIONS FOR DOUBLY EXCITED STATES

Majorana’s statements of the symmetry principles governing interactions between discrete and continuum states are a major feature of his 1931 papers. The helium paper (Majorana, 1931a) deals with doubly excited 2s$^2$, 2s2p, and 2p$^2$ terms lying high above the 1s $^3S$ ionization energy. Thus the basic considerations in the spectra studied by Majorana pertain to interactions of these terms with states of the He 1s$^2$es, 1s$^2$ep, and 1s$^2$ed continua and of np$^2$ terms in Zn, Cd, and Hg with ns$^2$ne, nsne, and nse$^2$ continua. Majorana first assumed Russell-Saunders coupling, so that the levels have definite parity, total spin, total orbital angular momentum, and total angular momentum ($\pi$, S, L, and J). The contexts of Majorana’s references to the “symmetry character” of states make it clear that all of these quantum numbers are pertinent. He then states that, in the absence of a radiative transition, the symmetry character of a state is constant; a doubly excited level can autoionize only into a continuum of the same symmetry character. The result is that autoionization is allowed for the 2s$^2$ $^1S$, 2s2p $^3P$ $^o_2$, $^1P$, and 2p$^2$ $^1D$, $^1S$ terms of He and for the np$^2$ $^1D$, $^1S$ terms of Zn, Cd, and Hg but is forbidden for the p$^2$ $^3P$ terms in all these atoms. This fundamental insight was the basis for Majorana’s brilliant analysis of the experimental data in both his 1931 papers.

With regard to the role of parity in the above considerations, it is interesting to note that, following Wigner (1927), Majorana (1931a) divided the doubly excited terms of He into two symmetry classes. The 2s$^2$ $^1S$, 2s2p $^3P$ $^o_2$, $^1P$, and 2p$^2$ $^1D$ and $^1S$ terms were “normal” in the sense that the wave function parity (odd or even) was the same as the parity of the L value. The 2p$^2$ $^3P$ term was, however, a “reflected” term: the parity is even, but the L value is odd. Since the available 1s$^2$e continua all have normal character (including the pertinent 1s$^2$ep $^3P$ continuum), autoionization from the 2p$^2$ $^3P$ term is forbidden in the Russell-Saunders approximation.

IV. ANALYSES OF THE OBSERVED DOUBLE-EXCITATION SPECTRA

Having given the experimental background and an account of the pertinent symmetry requirements, we now complete our account of Majorana’s 1931 spectroscopy papers. His awareness of the Auger effect and of its the-
oretical analysis (Wentzel, 1927) led to his important implicit assumption in both papers that observation of radiative transitions from atomic levels having sufficient energy to undergo spontaneous ionization required explanation.

A. Double excitation in helium

Compton and Boyce (1928) first measured a new line of neutral helium at 32.038 nm in spectra obtained using electron-impact excitation. The proximity of the line to the He \(^{+}\) 1s-2p resonance line at 30.4 nm suggested a screened 1s-2p transition from an upper \(2pnl\) level to a lower 1snl term. Compton and Boyce gave 1s2s-2s2p as a possible classification. Working in F. Paschen’s laboratory, Kruger (1930) observed this line in the spectrum of a hollow-cathode discharge and suggested the classification 1s2p \(^3P\) - 2p \(^3P\) as “very likely.” Majorana (1931a) gave this classification a firm theoretical basis by first pointing out that the broadening of levels from which autoionization is allowed should be “perfectly observable” or so great as to make any detection of their radiative transitions very difficult. This consideration, together with pertinent symmetry requirements and the experimental wave number of the sharp line at 32.04 nm, rendered any alternative to Kruger’s 1s2p \(^3P\) - 2p \(^3P\) classification extremely unlikely. With regard to a line observed by Kruger at 35.75 nm, Majorana rejected Kruger’s suggested classification 1s2s \(^1S\) - 2s2 \(^1S\). After also rejecting several other possible classifications involving two-electron excitation, he concluded that “attribution” of the 35.75 nm line to helium was “doubtful.”

The apparent lack of awareness of this major contribution to theoretical atomic physics by later researchers on two-electron excitation in helium and autoionization processes in general is extraordinary, especially since only 24 pages separate the paper from the famous paper of Majorana (1931b) on autoionization. None of the papers on double-excitation states in helium published in the 1930s, following Majorana’s 1931 papers, cited Majorana or gave any evidence of knowledge of the \(LS\)-coupling requirements for autoionization already explained by Majorana and Shenstone (1931a, 1931b); see, for example, Fender and Vinti (1934), Wu (1934), Wilson (1935), Kiang et al. (1936), and Bundy (1937). Indeed, some of these papers suggested classifications for the 32 nm line that Majorana had already shown to be physically unrealistic. Only in the mid-1940s did Wu (1944) reconfirm Kruger’s classification of the 32 nm line using new calculations of autoionization widths and of the energies of pertinent two-electron-excitation levels, together with a statement of the symmetry-based conditions necessary for autoionization. Wu failed to cite the 1931 papers of Majorana or Shenstone. Almost all later authors, including one of us, who referred to earlier work have cited only Wu’s 1944 paper as providing the theoretical basis for Kruger’s classification of the 32 nm line, with no mention of Majorana (1931a) (see, e.g., Moore (1949), Martin (1960), Madden and Codling (1965), Aashamar (1970), Burrow (1970), Berry et al. (1971), and Tech and Ward (1971)).

B. The incomplete \(np^2 \, ^3P\) terms in zinc, cadmium, and mercury

The paper of Majorana (1931b) was stimulated by the apparently missing transitions from the \(np^2 \, ^3P\) level in each of these spectra (Sec. II). Applying the symmetry considerations described in Sec. III and again considering the relatively high probabilities of allowed Auger transitions, Majorana assumed that the \(np^2 \, ^1D_2\) and \(^3S_1\) levels in these atoms would autoionize so rapidly that observation of any radiative transitions from these levels would be very unlikely. Moreover, even a small coherent mixing of the \(p^2 \, ^1D_2\) state into the wave function of the nominal \(^3P_2\) level or of the \(^3S_0\) state into the \(p^2 \, ^3P_0\) wave function might allow autoionization from these \(^3P\) levels sufficient to affect their radiative transitions. Majorana’s key point here was that inclusion of the spin-orbit interactions of the \(p\) electrons in the energy matrices resulted in just such mixings. Thus, he explained in the Cd and Hg spectra the “instability” of the \(p^2 \, ^3P_2\) level due to mixing with the autoionizing \(^1D_2\) level must be large enough to account for the absence of the \(^3P_2\) lines in the observed \(P-P''\) multiplet.

Majorana further concluded that the expected two lines from the \(4p^2 \, ^3P_2\) level in Zn were in fact just the two diffuse lines classified by Sawyer (1926) as transitions from the \(4p^2 \, ^1D_2\) level (see Fig. 4). Majorana noted that these lines were “weaker and of a different aspect” compared to the other four lines of the multiplet due to autoionization from the \(4p^2 \, ^3P_2\) level. He pointed out that the previously suggested explanations of the missing \(p^2 \, ^3P_2\) levels in Zn and Cd, as described in Sec. II, were based on physically unrealistic energy-level structures for the \(np^2\) configurations.

As a large part of this effort Majorana calculated the mixing wave function. Previous work by Goudsmit (1930) concentrated on the determination of the atomic energies in the intermediate coupling case, and Bartlett (1929) derived the mixed wave function. Apparently unaware of these works, Majorana independently derived the spectrum and wave functions of a two-electron atom in the case of intermediate coupling.

For a description of Majorana’s calculations, it is convenient to begin with an account of more modern methods. For specificity we now discuss the case of Cd \(5p^2\), whose energy-level diagram is shown in Fig. 2, although identical methods are also applicable to Zn \(5p^2\) and Hg \(5p^2\). The autoionization rate of the \(^1P\) levels may be derived following the treatments of Fano (1961) and Aymar et al. (1986). In accounting for the spin-orbit interaction between the Cd \(5p^2\) levels, the wave function of the \(^3P_2\) level is expressed as
\[
\langle \phi(5p^2 3P_2) \rangle = \alpha(5p^2 3P_2) + \beta(5p^2 1D_2).
\]

The \( \alpha, \beta \) mixing coefficients can be determined from the experimental energies of the three \( \text{3}P_j \) levels. Following the approach introduced by Fano (1961), the mixing of a discrete state \( \phi \) with a continuum of states \( \psi_{E'} \) produces an eigenvector \( \Psi_E \) of the atomic Hamiltonian \( H \) with the form

\[
\Psi_E = \phi + P \int dE' \frac{V_{E', \psi_{E'}}}{E - E'},
\]

where \( V_{E', \psi_{E'}} \) is the matrix element expressing the coupling of the discrete and continuum states,

\[
V_{E'} = \langle \psi_{E'} | H | \phi \rangle,
\]

and \( P \) designates the principal part of the integral. Thus the discrete state \( \phi \) is modified by a coherent mixing of the continuum states.

For the case of the \( \text{Cd I} \ 5s^3 \text{P}_2 \) level, owing to the symmetry properties presented in Sec. III, the only nonvanishing interaction matrix element is between the \( 5p^2 1D \) component of the state \( \phi \) and the adjacent continuum \( 5s\text{ed} 1D_2 \). The absorption-emission processes between two quantum states have a probability determined by the squared matrix element of a suitable transition operator between those states. The continuum mixing modifies that probability. In conclusion, the autoionization width \( \Gamma \) of the \( 5p^2 3P_2 \) level is determined by the \( \beta \) coefficient in Eq. (1), i.e., the amplitude of the \( 5p^2 1D \) component of the state \( \phi \) and by the matrix element for the Coulomb interaction between the \( 5p^2 1D_2 \) component of the state \( \phi \) and the adjacent continuum \( 5s\text{ed} 1D_2 \).

The Majorana analysis starts with Eq. (1) and the mixing coefficients. However, instead of describing the continuum through a continuous distribution of states, Majorana imposes a mixing between the \( np^2 3P_2 \) discrete level having a negligible autoionization rate and the \( np^2 1D_2 \) level having a large decay rate to the continuum. Majorana does not derive the transition probability for the absorption process terminating on the mixed state and does not calculate the spontaneous-ionization absorption spectra. Instead, determining the mixing coefficients from the spin-orbit Hamiltonian diagonalization, he links the autoionization rate \( \Gamma \) to the decay rate of the mixed \( np^2 3P_2 \) level, concluding that \( \Gamma \) depends on the mixing coefficient and on the decay rate of the \( np^2 1D_2 \) level.

Although Majorana’s treatment does not include a description of the detailed line shape, the diagonalization of his perturbation matrix would lead to the characteristic Fano autoionization profile (Fano, 1961)

\[
I(\epsilon, q) = \frac{(q + \epsilon)^2}{1 + \epsilon^2},
\]

where \( \epsilon \) is the energy measured in units of \( \Gamma \) and \( q \) is a parameter characterizing the interference of amplitudes for transitions involving the discrete and continuum components of \( \Psi_E \). A derivation of the autoionization line shape based on a treatment similar to the Majorana one was reported by Shore (1967, 1968).

V. CONTEMPORARY AND SUBSEQUENT WORK ON AUTOIONIZATION

A. Shenstone’s contemporary identification of autoionization

Shenstone (1931a) gave his first account of autoionization at a meeting of the American Physical Society at the National Bureau of Standards, Washington, D.C. He pointed out that in complex spectra having two ionization limits “a term built on the ion of higher energy may be above the lower of the two limits. It is then possible for the atom to dissociate spontaneously into an ion plus an electron if there is a correct relationship between the quantum numbers of the term and those of the ion and electron.” Drawing on his ongoing analysis of the copper spectrum Shenstone (1926, 1948) gave the levels of the nominal \( 3d^4s(\text{4}D)5s \, \text{4}D, \, \text{2}D \) and \( (\text{1}D)5s \, \text{2}D \) terms, which lie above the \( 3d^{10} 1S \) ionization energy, as examples of the effect. Because the available \( D \)-term continuum is \( 3d^{10}(1S)\text{ed}(2D) \), autoionization from the \( 3d^4s5s \) levels is allowed only for those levels having some \( \text{2}D \) character, i.e., from the four \( \text{2}D \) levels and, owing to deviations from the Russell-Saunders coupling, from the nominal \( \text{4}D \) levels having \( J \) values 3/2 and 5/2. Thus the emission lines from these levels were “extremely weak in low-pressure sources and very diffuse under high pressure” due to autoionization.

In a paper published later in the same year, Shenstone (1931b) discussed ultraionization energies in atoms, i.e., ionization resonances observed at energies above the principal ionization energy in electron-ion spectroscopy. Regarding such “hyper-ionization potentials” observed in mercury, Shenstone suggested that the ultraionization resonances were “not a direct result of the electron impact but that the primary process is one of excitation to a negative level [i.e., a level lying above the ionization energy], followed by auto-ionization.” In support of the assumption that such negative levels must exist in mercury, Shenstone suggested that a new \( 3P_2 \) level discovered in mercury by Takamine and Suga (1930) and confirmed by Paschen (1930) belonged to the \( 5d^{6}s^{6}6p \) configuration. He then showed that the energy of this level, \( 15295 \text{ cm}^{-1} \) below the \( 5s^2 1S_2 \) limit, almost certainly meant that some of the higher levels of this configuration lay above the first ionization energy.

Shenstone cited the theory of predissociation by Kro nig (1930) as showing that in molecules “such radiationless transitions can take place only under very stringent quantum conditions.” In connection with “certain peculiarities of the copper arc spectrum,” Shenstone again outlined the energy considerations for autoionization and then wrote “A comparison of this case with that of predissociation... makes it very probable that such transitions from a given state can occur if there exists a con-
tinuum characterized by the same \( L, S, J \), and parity as the state in question. 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.” (Shenstone was apparently unaware that Auger himself had already suggested this name for the effect discovered by him.)

The insight into autoionization processes by Majorana and Shenstone foreshadowed an entire branch of atomic spectroscopy.

**B. Subsequent foundational work on autoionization**

In an important later work Beutler (1935) published a detailed investigation of the absorption spectra of noble gases for levels above the ionization limit. In that study, Beutler ascribed the observed strong asymmetric absorption lines to the autoionization process and referred to previous work of Kronig and Shenstone but not to Majorana’s. In their classic book *The Theory of Atomic Spectra, Condon and Shortley (1935)* recognized the simultaneous and independent contributions of Majorana and Shenstone in identifying the autoionization concept. In the same year, Beutler’s work caught the attention of Emilio Segré in Enrico Fermi’s group in Rome. Fermi suggested to his junior associate, Ugo Fano, that he find a specific explanation for the line shapes seen by Beutler. In fact, as described by Fano himself (Fano, 2000), the hypothesis of autoionization alone does not provide the full description of the asymmetrically broadened lines observed by Beutler. Soon Fano (1935) produced a theoretical analysis of the mixing of a discrete level with a continuum. This work and his more complete analysis (Fano, 1961) introduced the Beutler-Fano autoionization profile, a line-shape formula that has found wide applicability in many branches of physics. Work of Fano (1961) and the contemporaneous development in experimental techniques for extreme ultraviolet spectroscopy and electron collisions with atoms and molecules elevated the Beutler-Fano line shapes to a frontier research topic in atomic physics. Autoionization has played an important role in the progress of spectroscopy because it is observed in a large variety of atomic and molecular spectra, and in some cases autoionization rates differ by orders of magnitude between states of the same electronic configuration.

It is worth noting that Majorana derived independently many of the important results of Fano’s 1935 paper and also an effect not discussed explicitly then by Fano but revisited by him in 1961, the shift in the energy of the resonance due to interaction with the continuum, which is the rightmost term in Eq. (2). This was pointed out by Di Grezia and Esposito (2008), who have summarized work found in Majorana’s unpublished research notebooks of 1930. It seems clear that Majorana then had an understanding of the theory of autoionization similar to that of the present day, but he did not express it in detail in his 1931 paper nor (it seems) did he communicate it explicitly within Fermi’s group—where, presumably, it would have been brought to Fano’s attention within the next few years. Fano (2000) credited Fermi with providing some of the essential ideas in his 1935 paper during personal conversations but does not mention Majorana’s work in this context.

**VI. CONTINUING STORY OF \( P-P' \) SPECTROSCOPY FOR ZINC, CADMIUM, AND MERCURY**

The autoionization section of Condon and Shortley (1935) included a description of Majorana’s treatment of the \( np^2 \, 3P \) terms in Zn, Cd, and Hg. Unfortunately they missed his identification of the \( 4p^2 \, 3P_2 \) level in Zn, writing that “in all cases the \( 3P_0 \) and \( 3P_1 \) levels are known but the \( 3P_2 \) cannot be found.” This oversight has been repeated over the years in practically all papers referring to earlier identifications of the \( 4p^2 \, 3P_2 \) level in Zn. The \( 4p^2 \) levels for Zn in *Atomic Energy Levels* by Moore (1952) derive from the interpretation of Sawyer (1926), with the broadened \( J=2 \) level misidentified as \( 4p^2 \, 1D_2 \) and the corresponding \( 3P_2 \) level shown as missing. The paper of Majorana (1931b) was not cited.

In considering the relation of Shenstone’s work on autoionization to that of Majorana, one is led to still another peculiarity in the history of the interpretation of the Zn \( 4p^2 \, 3P_2 \) level. It will be remembered that Sawyer and Beese (1926) had mistakenly designated this level as \( 4p^2 \, 1D_2 \) because of the “diffuse” character of its transitions to the \( 4s4p \, 3P_2 \) and \( 3P_1 \) levels, as compared with the four sharp lines comprising the \( 4p^2 \, 3P_1 \) and \( 3P_0 \) transitions. In their 1925 report, Sawyer and Beese noted that although the \( 3P_2 \) designation would give a “normal pp’ triplet group….We hesitate to make this assignment.” Referring to the possibility that the \( 3P_2 \) level “has a diffuse nature,” they wrote “We know, however, of no similar example of this sort.” But an “example of this sort” was given in reports published that same year; both Shenstone (1926) and Beals (1926) described the anomalously diffuse nature of the Cu I lines from just two of the four \( 3d^94s5s \, 4D \) levels, namely, the \( 4D_{3/2} \) and \( 4D_{5/2} \) levels. In view of the general ignorance of Majorana’s correct assignment of the Zn \( 4p^2 \, 3P_2 \) level after 1931, it is surprising that no spectroscopist of that era correctly identified this Zn level by analogy with the Cu I \( 3d^94s5s \, 4D \) term as interpreted in 1926 and/or on the basis of explanations by Shenstone (1931a, 1931b) of the anomalous broadening of two of the \( 4D \) levels. We note that a paper by Selwyn (1929) giving new ultraviolet wavelengths for 13 elements included the Zn I \( P-P' \) multiplet, with correct, although tentative, classifications for the two lines from the \( 4p^2 \, 3P_2 \) level “suggested as completing the group.” Selwyn did not refer to Sawyer’s earlier discussions of the classifications of these lines and, in any case, his tentative classifications played no role in the subsequent history of the question.

Based on their new observations of the \( P-P' \) multiplets in Zn, Cd, and Hg and on improved knowledge of pertinent spectroscopic regularities, Garton and Rajaratnam (1955) confirmed and extended previous analy-
ses by giving the classifications of all six lines of the multiplets in Zn and Cd and correctly locating the 6p2 3P0 level in Hg. In addition to measuring and classifying the two broad lines from the Cd 5p2 3P2 level, Garton and Rajaratnam determined the autoionization probability of this level as 3.32 ¥ 10^{-13} \text{s}^{-1}. Although they cited the paper of Majorana (1931b), they accepted the summary by Condon and Shortley of his results for Zn by referring to “the missing p2 3P2 level in Zn 1, Cd 1, and Hg 1" in their introduction. The convincing discussion by Garton and Rajaratnam led to subsequent citations of their paper for identification of the Zn 4p2 3P2 level, usually without recognition of Majorana’s strongly argued and much earlier identical assignment.

The first new wavelengths published for the six Zn 4s4p 3P−4p2 3P lines since the measurement by Selwyn (1929) were a result of observations of the Zn spectrum by Martin and Kaufman (1970) (see Fig. 4). Accurate values for the 4p2 3P levels were determined, and measurement of the width of the 4s4p 3P1−4p2 3P2 transition gave an autoionization probability of 4.1 ¥ 10^{-12} \text{s}^{-1} for the 4p2 3P2 level. A predicted position and width were given for the strongly autoionizing 4p2 1D2 “level” and for the 1S0 level. Almost 40 years after the paper of Majorana (1931b), Martin and Kaufman brought attention to his original identification of the Zn 4p2 3P2 level, but a lack of recognition of this notable feature of his analysis has continued in the literature.

Shore (1968) applied his theory for the parametrization of attenuation cross sections to obtain expressions for the resonance parameters for the transitions of the nominal np2 3P2 level to the nsnp 3P2, 3P1, and 1P1, levels of Zn, Cd, and Hg. His prediction of Lorentzian profiles for the transitions to the 3P2 and 3P1 levels was consistent with the observations for Zn (Martin and Kaufman, 1970; Parkinson and Reeves, 1972) and for Cd (Garton and Rajaratnam, 1955; Parkinson and Reeves, 1972). Parkinson and Reeves (1972) applied Shore’s theory to their absolute measurements of autoionization-resonance profiles for the np2 3P transitions in Zn and Cd and obtained profile parameters not only for the nsnp 3P2, 3P1 transitions but also for the asymmetric profiles of the transitions to the nsnp 1P1 level. In the Fano formulation of Eq. (4) the profile is generically asymmetric but becomes Lorentzian in the limit of q ¥ 1. More recent calculations of cross sections for photoionization from the Zn 4s4p levels by Froese Fischer and Zatsarinny (2007) gave energies, shapes, and widths for all of the 4s4p → 4p2 resonances.

Research groups in Orsay and Caen have measured the autoionization widths of p2 3P levels of Cd I (Aymar et al., 1986), Zn I (Chantepie et al., 1988), and Hg I (Chéron et al., 1989) using optogalvanic detection. The high resolution of these measurements gave the striking result that not only do the p2 3P levels undergo autoionization but their widths are greater than those of the corresponding 3P0 levels. Values of the widths of the 3Pj levels in all three atoms as calculated with inclusion of relativistic and/or higher-order effects agreed satisfactorily with the measurements. The Cd I optogalvanic spectra of Fig. 5 show the different line widths of the multiplet. All the lines belonging to the p2 configuration suffer perturbations by autoionization, large or small, following precisely the scheme predicted by Majorana. Direct comparison of the spectra shown in Figs. 3–5 illustrates the increased spectroscopic resolution of more or less typical measurements over a period of some 60 years. However, the low resolution of the 1925 spectra did not limit the physical intuition of Majorana.

The strong interaction of a p2 1D term with an sd term is a pervasive effect in atomic spectra. It can be seen from a different perspective in the behavior of the np2 terms of the alkaline earths, which, like their counterparts in Zn, Cd, and Hg, nominally consist of two equivalent p electrons outside a closed shell. However, the np2 1D term lies below the ionization limit in the alkaline earths, so it is not “embedded in a continuum” of nsed states into which it can autoionize. It is, however, embedded in a series of nsn’d Rydberg states with which it interacts strongly. Indeed, it seems that in Mg the 3p2 1D term cannot be identified as a distinct state at all; instead it seems to be distributed among the members of the 3snd Rydberg series (Lu, 1974; Froese Fischer, 1975).

VII. CONTINUING STORY OF DOUBLE EXCITATION IN HELIUM

The experimental identification of the 2p2 3P term by Kruger (1930) and, much more conclusively, by Majorana (1931a) was brought into question for a brief period in 1970–1971. A variational-perturbation calculation by
Aashamar (1970) of the $2p^2 \, 3P$ energy including mass-polarization, relativistic, and radiative contributions gave a predicted wavelength of 32.0290 nm for the transition to the $1s2p \, 3P$ term. The corresponding wave number is about 100 cm$^{-1}$ greater than the wave number corresponding to Kruger’s measured wavelength of 32.039 nm for the transition. Given the expected accuracy of his calculation, Aashamar concluded that “we cannot regard the theoretical result as a conclusive verification that the line in question has been correctly identified.” This matter was soon settled by Tech and Ward (1971), whose new measurement of the line gave an experimental wave number of 481301.5 cm$^{-1}$, which is 0.1 cm$^{-1}$ less than Aashamar’s result. Errors of 0.009 and 0.010 nm in the measurements by Compton and Boyce (1928) and by Kruger (1930), respectively, are not surprising given the lack of accurate wavelength standards near 32 nm at that time.

Calculations for the $2p^2 \, 3P$ term by Drake and Dalgarno (1970) included transition probabilities for the radiative decay of this state to the $1s2p \, 3P$, $1s3p \, 3P$, and $1s4p \, 3P$ terms. The lifetime of the $2p^2 \, 3P$ term is dominated by the radiative transition to the $1s2p \, 3P$ term, and the lifetime obtained from the sum of the calculated probabilities for these three transitions, 0.083 ns, is in good agreement with the experimental value of 0.09(1) ns (Knystautas and Drouin, 1973). It is clear that radiative transitions comprise the only significant decay modes for the $2p^2 \, 3P$ term, thus confirming to a high degree Majorana’s brilliant original argument that autoionization from this term is forbidden.

It is noteworthy that the first observations of any new transitions to doubly excited levels in the optical spectrum of helium were published some 35 years after the original measurement of the $1s2p \, 3P – 2p^2 \, 3P$ line by Compton and Boyce (1928). Increased interest in double excitation and autoionization began in the 1960s, stimulated in large part by new experimental results such as the observations by Madden and Codling of two-electron and inner-shell absorption spectra in rare gases, beginning with helium (Madden and Codling, 1963, 1965). A review by Fano (1969) included references for both experimental and theoretical results up to 1968 and a compilation by Martin (1973) gave energies for “48 levels or resonances observed above the He$^+$ 1s $2S$ limit that have been assigned to expected terms.” We note here that the compiled data included energies for all the $2s^2$, $2s2p$, and $2p^2$ terms discussed by Majorana (1931a).

VIII. AUTOIONIZATION AS A PERVASIVE EFFECT IN PHYSICS

Interest in atomic autoionization increased dramatically in the 1960s, due to the development of synchrotron light sources and high-resolution electron scattering...
apparatus (Clark, 2002), was stepped up again in the 1970s with the development of laser spectroscopy (Ay- 
mar et al., 1996), and remains an active topic today with 
particular relevance to ultracold atomic physics (Köhler 
et al., 2006). Moreover, the theory of atomic autoioniza-
tion as developed by Fano in 1935 and 1961 has been 
widely applied throughout physics: the 1961 paper had 
been cited over 5400 times by early 2009 and is one of 
the most frequently cited papers in the original Physical 
Review series.

A key event in the revival of interest in atomic auto-
ionization was the observation of series of autoionizing 
resonances in the noble gases. Figure 6 shows the pho-
toabsorption spectra of several noble gases above their 
ionization limits. As mentioned, a central role in the 
story was played by the doubly excited states of helium 
previously investigated by Majorana. Figure 7 depicts an 
alYSIS of the strongest feature visible in Fig. 6, which 
shows remarkable agreement with the Fano line-shape 
formula, including the noteworthy vanishing of the ab-
sorption coefficient on the long-wavelength side of the 
resonance. This interference effect is a consequence of 
the quantum mixing introduced by Majorana.

A schematic of this interference phenomenon is 
shown in Fig. 8, in which the left top frame depicts the 
doubly excited states of helium considered by Majorana. 
The subsequent frames of this figure show how this basic 
concept is used to discuss recent experiments on laser 
excitation of semiconductor quantum dots by Kroner 
et al. (2008). Figure 9 shows the dependence on laser inten-
sity of the line profiles observed in this experiment. The 
accompanying fits to a Fano line-shape formula suggest 
the continuing validity of this picture well into the re-
gime of nonlinear optical response. A nonlinear gener-
alization of the Fano model of autoionization has been 
presented by Miroshnichenko et al. (2005) and Zhang 
et al. (2006).

Another recent phenomenon with line shapes de-
scribed by the autoionization formula, outside atomic 
physics and even quantum mechanics, involves light 
propagation in photonic crystals (Galli et al., 2009). Fig-
ure 10 shows two different Fano profiles associated with 
the scattering of light incident on a nanocavity in such a 
crystal, the interference in this case being associated 
with coupling of a confined cavity mode with a propa-
gating mode in the crystal. We note that this phenom-
enon is strictly classical in origin.

Quantum interference is a key element of the 
quantum-mechanical structure underlying all physical 
systems. Majorana’s work in 1931 identified the effects...
of quantum interference in the low-resolution atomic spectra available at that time. The dramatic increase since then in spectroscopic resolution has demonstrated that the interference associated with the superposition of discrete and continuum states is pervasive in atomic and molecular physics. The control recently achieved through improved experimental techniques in other areas of physics has demonstrated that quantum interference will continue to play a major role in our full understanding of nature.

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