

Effects of Configuration Interaction on Intensities and Phase Shifts

One of the enduring goals of scientific work at the National Institute of Standards and Technology (NIST) has been the expression of measurements in terms related directly to natural phenomena of an invariant and absolute character.

For example, the unit of time, the second, is now defined as exactly 9,192, 631, 770 periods of oscillation of the radiation associated with a specified quantum transition between states of the ^{133}Cs atom. This makes it possible, in principle, for any laboratory to realize the value of the second by preparing a sample of ^{133}Cs in conditions that make it resemble a group of identical atoms unperturbed by their immediate environment.

Of course, such an ideal realization is not attainable in practice. This permanent fact of life has provided steady stream of work over the years for theoretical physicists at NIST: there is always a need for models that can provide better quantitative links between realistic and ideal situations.

Ugo Fano (1912–) is believed to be the first theoretical physicist hired by NIST, and he has certainly been one of the most influential to date. His 1961 paper *Effects of Configuration Interaction on Intensities and Phase Shifts* [1] is one of the most frequently referenced journal articles by a NIST author, having been cited over 3200 times in the scientific literature. This paper treats a subject of fundamental interest to metrology and physics: the excitation spectra of quantum-mechanical systems. Its key result, the simple formula given in Eq. (3) below, is now well known to physicists as the “Fano profile” or “Fano line shape.” It addresses the challenge of expressing observed phenomena in a concise manner that can be derived from first principles. 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. These aspects are discussed in turn below, though they cannot be entirely disentangled.

Among the phenomena key to the early development of quantum mechanics were atomic spectra, i.e., the colors of light absorbed or emitted by free atoms. Such light was found to consist largely of discrete frequencies whose distribution is a characteristic property of the atomic species involved (see Fig. 1). The existence of these discrete frequencies led Niels Bohr [2] to postulate a model of atomic structure in which the atom can subsist only in certain states of well-defined energy,

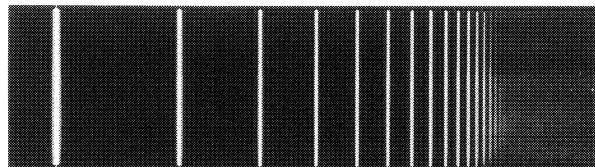


Fig. 1. Visible emission spectrum of the hydrogen atom (spectral lines of the Balmer series). The atomic radiation has been dispersed by a spectral grating and projected onto a photographic plate, to show the discrete frequency components of the radiation. The frequency increases to the right, with white indicating higher intensity (i.e., this is a photographic positive). If viewed by the eye, these lines would appear blue-violet. Figure courtesy of Prof. C. R. Vidal.

although transitions between such states can be induced. Transitions between two states may be associated with accompanying optical radiation, of angular frequency $\omega_0 = 2\pi\Delta E/h$, where ΔE is the difference in energies of the two states, and h is Planck’s constant. At this level of detail, the modern concept of atomic structure is the same as Bohr’s. Thus, accurate data on intrinsic atomic frequencies has great fundamental and practical value. For example, as noted above, such frequencies now provide the legal definition of the second. NIST has for many years maintained a program to generate, evaluate, and maintain a database of relevant atomic spectral properties; that effort is summarized elsewhere in this volume.

Bohr’s basic idea, that transitions between atomic states are associated with radiation of a definite frequency, needs to be broadened somewhat to describe phenomena actually encountered in the laboratory. For example, if one prepares a sample of atoms in a high-energy state, they may make transitions to a lower-energy state by emission of optical radiation. This process will take place over some period of time. Under simplifying but widely applicable assumptions, Viktor Weisskopf and Eugene Wigner [3] showed that quantum mechanics describes the time dependence of the intensity of emitted radiation, $I(t)$, as following the law of *exponential decay*,

$$I(t) \sim \exp(-\Gamma t), \quad (1)$$

where t is the time, measured from the moment of state preparation, and Γ is a rate constant that can be regarded as the inverse of the lifetime of the higher state. This law

expresses a simple idea: the instantaneous probability of decay of a given atom is independent of the time t at which it occurs. Exponential decay is encountered in a number of physical systems, such as the natural transmutation of radioactive elements.

An alternative mode of observation of exponential decay is the resolution of its frequency spectrum. This is a straightforward and convenient practice in optical spectroscopy, where the various frequency components of radiation may be spatially dispersed by reflecting it from a diffraction grating, or by passing it through a prism, and projecting it onto a screen, photographic plate, or detector array. By this means, the spectrum of a white light source is spread out into the familiar rainbow pattern. On the other hand, the spectrum of an atomic radiation governed by the decay law of Eq. (1), exhibits the ‘‘Lorentzian’’ profile, or line shape,

$$I(\omega) \sim 1/[(\omega - \omega_0)^2 + (T/2)^2], \quad (2)$$

where $I(\omega)$ is the intensity at the angular frequency ω , and ω_0 , as stated above, is proportional to the difference in energy between atomic states. In this representation, T plays the role of the ‘‘width’’ of the spectral feature. This expresses Heisenberg’s uncertainty principle: the energy of a state is indeterminate by an amount inversely proportional to its lifetime. For most optical spectra generated by atoms, the ratio T/ω_0 is of the order 10^{-6} . Thus the human eye would perceive the spectrum of Eq. (2) as being a remarkably pure (monochromatic) and bright color, localized at the appropriate position on the viewing screen. However, if examined in detail, atomic spectra can exhibit significant deviations from the form of Eq. (2). The differences are due to the actions of physical processes neglected in the simplifying assumptions mentioned above.

Fano’s 1961 treatment deals with one of the more important classes of such processes: those in which there are alternative pathways for a transition between atomic states. In quantum mechanics, the existence of alternative pathways invariably gives rise to the phenomenon of *interference*: the probability amplitudes associated with travel along the different paths combine with a phase relationship, just as the crests and troughs of classical wave motion can combine to yield a null displacement. In the model considered by Fano, which has been found to have broad applicability, the interference phenomenon inevitably gives rise to a ‘‘dark spot,’’ i.e., the spectral intensity vanishes at a particular frequency. The line shape formula derived by Fano, in his chosen notation, takes the form

$$I(\varepsilon) \sim (q + \varepsilon)^2 / (1 + \varepsilon^2), \quad (3)$$

where $\varepsilon = 2(\omega - \omega_0)/T$ is the angular frequency, measured from the line center ω_0 in units of T , and q is a parameter that describes the interference between pathways. When q is much greater than 1, one of the pathways has the predominant transition amplitude, and Eq. (3) becomes equivalent to Eq. (2) in the region where the signal is strongest.

Fano was first motivated to understand this phenomenon 25 years previously, as a student of Enrico Fermi in Rome. Fermi suggested to Fano that, as a research project, he should try to understand photo-absorption spectra of the noble gases that had recently been observed by Hans Beutler of the University of Berlin [4].

Beutler’s spectra exhibited broad, highly asymmetric absorption series, quite uncharacteristic of atomic spectra known at the time. In contrast to the well-separated, sharp features visible in Fig. 1, Beutler’s spectra showed structures whose width was comparable to their separation.

The origin of this phenomenon was correctly proposed by Beutler to be associated with the phenomenon of *autoionization*, which had previously been identified in atomic spectra by Ettore Majorana [5] and Allen Shenstone [6].

Autoionization occurs upon excitation of an electronic configuration that has an energy higher than that needed to ionize (i.e., remove one electron from) the atom. For example, two atomic electrons may be excited, with a total energy that is sufficient to access an alternative configuration, in which one of the electrons relaxes to a state of lower energy, while the other escapes from the atom. This phenomenon is analogous to a possible, though we hope unlikely, rearrangement of the Solar System, in which the energy released by a contraction of the orbit of Jupiter could be used to liberate the Earth from its orbit about the Sun. In the simplest case of autoionization of a state of two excited electrons, the two interfering quantum-mechanical pathways may be envisaged as follows. One involves the direct ejection of one electron from the atom, leaving behind a positively-charged ion; the other generates a state of two excited electrons, which then relaxes by energy exchange to yield the same final state, a free electron and a positive ion.

In a paper published in 1935 [7], Fano showed that spectral profiles of the type observed by Beutler could indeed be generated by quantum mechanical interference in autoionization, and he presented a formula equivalent to that of Eq. (3). However, his presentation did not involve a quantitative analysis of Beutler’s data, which was quite complicated, and still, in its time, somewhat of an anomaly in atomic spectroscopy. When Fano returned to this class of problems in 1961, key developments in experimental technique had elevated it to a frontier research area of atomic physics.

The new experimental situation of the 1960s evolved along two fronts, on both of which NIST made pioneering contributions that would be adopted world-wide: high-resolution electron spectroscopy, and the application of synchrotron radiation.

John Simpson and Chris Kuyatt led the electron spectroscopy effort in the Electron Physics Section at NIST. They designed electron current sources and detectors that enabled electron scattering by atoms to be investigated in unprecedented detail [8]. Among the signal achievements of this technique was the identification of numerous “negative ion resonances” analogous to the doubly-excited electronic states encountered in photoabsorption. An electron colliding with an atom can lose energy by exciting an atomic electron, and be captured by the field of the residual ion. This can give rise to a transient state in which the incident and excited electrons orbit the positively charged ion core, which subsequently decays by the capture of one electron and the release of the other. This situation provides for interference of two quantum-mechanical amplitudes: one for direct scattering of the incident electron, the other involving the temporary capture/excitation process, which results eventually in a scattered electron. The experimental data treated explicitly by Fano in his 1961 paper were in fact provided by such an experiment. The formation of these resonances was mediated by *correlation* of electronic motions, a phenomenon not encompassed by the traditional “mean field” concepts of atomic structure. The study of such resonances therefore provided insight into unexplored avenues of atomic and molecular physics, which developed as a major research theme in the 1960s with interest extending to the present day.

In the early 1960s the emergence of synchrotron radiation sources greatly expanded the range of optical spectroscopy. At NBS, which played a leading role in the field, the development of a synchrotron radiation source was an offshoot of a program of investment in betatron electron accelerators which started in the late 1940s. The betatrons were originally obtained to provide high-energy electron beams for the production of x rays. These accelerators also yielded, at first as an unappreciated byproduct, a broad band of synchrotron radiation spanning the electromagnetic spectrum from the radio to the x-ray domains. This broad-band capability was not matched by any other laboratory-based radiation source; in particular, synchrotron radiation provided exceptional coverage of the far ultra-violet spectral region, i.e., radiation with wavelengths between about 5 nm and 150 nm, vs the 500 nm wavelength characteristic of visible light. Far ultraviolet radiation has sufficient energy to cause multiple electron excitation in all elements, so that electronic states of the type observed by Beutler would become ubiquitous rather than exceptional.

Robert Madden was hired by NBS to head the Far Ultraviolet Physics Section and was charged with converting one of the betatron machines into a dedicated source of synchrotron radiation for far ultraviolet spectroscopy and radiometry, the Synchrotron Ultraviolet Radiation Facility (SURF). In collaboration with Keith Codling, David Ederer, and others, Madden made numerous pioneering explorations of this spectral region. The first major results of this work are shown in Fig. 2: the absorption spectra of helium, neon, and argon gas [9]. The helium spectra were particularly striking, because they confounded initial theoretical expectations that two series of lines would be observed, rather than the single one displayed here. A companion publication by John Cooper, Fano, and Francisco Prats [10] showed that effects of electron correlation would tend to favor strongly transitions to one of the two series. This result hinted at the existence of characteristic features of two-electron dynamics that might be found in other spectra; this became a prominent theme in atomic physics during the next two decades and is still of interest today.

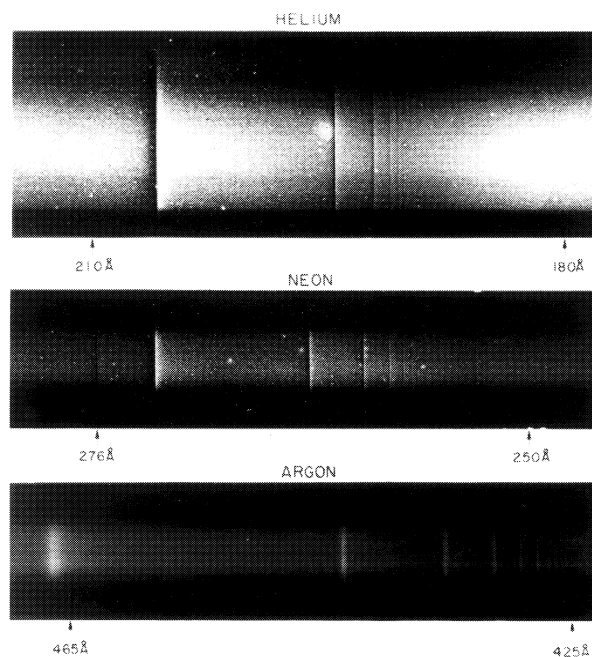


Fig. 2. Absorption spectra of helium, neon, and argon atoms in the extreme ultraviolet spectral region, from [9]. These are images of photographic plates exposed to radiation from the NBS electron synchrotron (now the Synchrotron Ultraviolet Radiation Facility—SURF). The synchrotron radiation was passed through a gas cell and then dispersed by a diffraction grating to show the dependence of absorption upon wavelength (which is indicated in Ångstrom units: $1 \text{ \AA} = 10^{-10} \text{ m}$). Increased blackness indicates increased absorption by the gas. Note that in contrast to Fig. 1, these spectral lines clearly exhibit asymmetric profiles.

An example [11] of the application of the Fano profile formula to the synchrotron radiation data is shown in Fig. 3. The quantitative determination of the parameters q , ω_0 , and Γ that are obtained from this type of analysis is essential for comparison of experiment and theory, or for comparison of experiments of two different types. For example, Fig. 3 describes an atomic state excited by photoabsorption; the same state can be excited by other means—in fact, it was this very same state, produced by electron-impact excitation, that was analyzed in Fano's 1961 paper—but the values of ω_0 and Γ should be independent of the mode of excitation since they are intrinsic characteristics of the excited state.

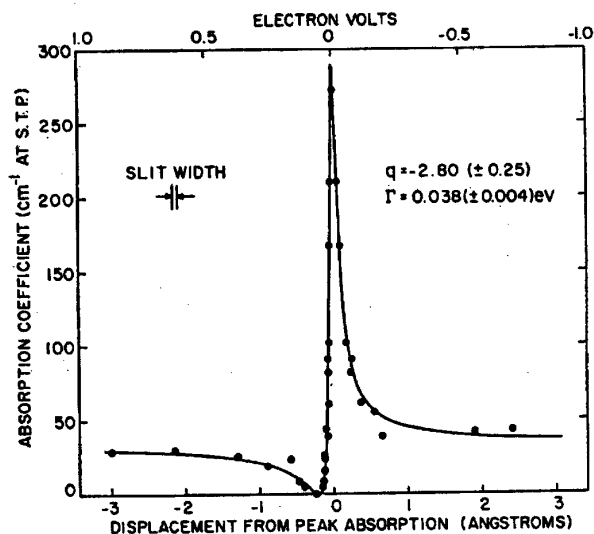


Fig. 3. The absorption coefficient vs. wavelength for the strongest absorption feature of helium (around 206 Å) shown in Fig. 2, from [11]. Note that wavelength increases to the right here, opposite to the display of Fig. 1. The points are experimental data; the solid line is a fit to the Fano profile formula (Eq. 2), with the values q and Γ as indicated. This feature is associated with excitation of the $2s2p\ ^1P^0$ state of the helium atom.

Ugo Fano, who did his graduate work in Italy under Fermi in the early 1930s, was hired by NBS in 1946 with a charge to build up the fundamental science base of the x-ray program. In his 19 years at NBS he provided guidance and inspiration to many of the Bureau's physicists and chemists. After moving to the University of Chicago in 1965, he led his graduate students in the detailed analysis of noble-gas photoabsorption spectra. The analysis of these spectra was a noteworthy achievement of multichannel quantum defect theory, developed by Fano and coworkers along lines laid out by Michael Seaton. This theory had a pronounced influence on high-resolution laser spectroscopy in the 1970s and

1980s; its development is summarized in two articles in the February 1983 issue of *Reports on Progress in Physics* [12].

At NIST, the Fano profile formula evokes memories of a remarkably productive era of atomic and electron physics, one in which there was strong interplay between theory and experiment, as well as between electronic and optical spectroscopy. Many legacies of this era are visible in NIST programs today. For example, the Electron Physics Section spawned the topografiner project, work on resonance tunneling in field emission, and the development of spin-polarized electron sources and detectors—all of which are described elsewhere in this volume. The success of the SURF synchrotron source inspired to the worldwide development of synchrotron radiation as a research tool. SURF has since gone through two major upgrades and today serves as the nation's primary standard for source-based radiometry over a wide region of the optical spectrum. Fano's theory of spectral line shapes continues to be applied to a wide range of physical problems: his 1961 paper was cited over 150 times in the scientific literature in 1999.

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