Fano Line Shapes Reconsidered: Symmetric Photoionization Peaks from Pure Continuum Excitation

U. Eichmann,[1,2] T. F. Gallagher,[1,3] and R. M. Konik[3]

[1]*Max-Born-Institute for Nonlinear Optics and Short Pulse Spectroscopy, D-12489 Berlin, Germany*
[2]*Institut für Atomare Physik und Fachdidaktik, Technical University Berlin, D-10623 Berlin, Germany*
[3]*Department of Physics, University of Virginia, Charlottesville, Virginia 22904-4714, USA*

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In a photoionization spectrum in which there is no excitation of the discrete states, but only the underlying continuum, we have observed resonances which appear as symmetric peaks, not the commonly expected window resonances. Furthermore, since the excitation to the unperturbed continuum vanishes, the cross section expected from Fano's configuration interaction theory is identically zero. This shortcoming is removed by the explicit introduction of the phase shifted continuum, which demonstrates that the shape of a resonance, by itself, provides no information about the relative excitation amplitudes to the discrete state and the continuum.

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Quantum interference occurs whenever there exist two coherent paths from an initial state to a final state. Particularly fascinating is the case in which one of the two paths is via a resonance, for in this case the presence of the resonance is manifested in a wide variety of line shapes. In the case of optical absorption they are often termed Fano line shapes [1]. One of the earliest examples occurred in the absorption spectrum of Ar, Kr, and Xe [2]. Above the first ionization limit the rare gas atoms can be photoionized either directly or via the doubly excited states, which are coupled to the ionization continuum. The absorption cross section due to the doubly excited states does not simply add to the continuum photoionization cross section, as might be naively expected for a Breit-Wigner resonance [3]. Rather, the amplitudes for excitation of the doubly excited state and the continuum must be added, often leading to asymmetric resonances. Such asymmetric resonances are ubiquitous in the photoionization of atoms and molecules [4], and their existence prompted Fano to develop his seminal theory of configuration interaction between a discrete state and a continuum.

As it becomes possible to preserve quantum mechanical coherence in more complex systems, it is likely that Fano's theory will find increasingly wide application. For example, photoabsorption in quantum well systems exhibits interference which is essentially identical to that observed in atomic photoionization [5,6]. Somewhat different manifestations occur in the conductance through magnetic impurity atoms [7] and single electron transistors [8]. Extensions of Fano's theory have been worked out for these problems [9] and for its application to chaotic systems [10].

Here we report an experiment which reveals a shortcoming of the straightforward application of Fano's theory. In particular, we describe a photoionization experiment in which the excitation amplitudes to a series of discrete states vanish, yet we see symmetric peaks at their locations, not the commonly expected window resonances, or dips, in the photoionization cross section. More problematic, the excitation amplitude to the unperturbed continuum also vanishes, leading the theory to predict no excitation at all. In fact, the theory is not completely correct for long range Coulomb potentials and thus fails to describe photoionization. In the sections which follow we describe our experiment, review Fano's theory, point out the source of the problem, and suggest the correct form for the photoionization cross section.

In the experiment Sr atoms in a beam are excited to the doubly excited $5d17l$ state with $l = 12$ using four pulsed lasers and a Stark switching technique, as shown in the energy level diagram of Fig. 1 and described in detail elsewhere [11]. Sr atoms in the $5d17l$ state are then exposed to a fifth, 550 nm, laser pulse which excites them to the energy range between the Sr^+ $5f$ and $5g$ ionization limits. This excitation could imaginably produce either directly a Sr^+ $5f$ ion together with a free electron or a $5gnl'$ atom. This latter state autoionizes quickly (in roughly 1 ns), thus producing a free electron and so would again leave the ion predominantly in the excited Sr^+ $5f$ state. The same 550 nm laser pulse then ionizes the Sr^+ $5f$ ion to produce Sr^{++} [12]. The production of Sr^{++} is proportional to the excitation by the first 550 nm photon. Approximately 100 ns after the laser pulse we apply a 1 kV/cm electric field pulse which drives the Sr^{++} ions to a dual microchannel plate detector. The detector signal is recorded with a gated integrator as the wavelength of the 550 nm laser is slowly scanned over many shots of the lasers. The observed photoionization spectrum is shown in Fig. 2. In it a clear series of symmetric, apparently Lorentzian peaks, at the locations of the $5gnl'$ states ($l' = 11, 13$), is quite evident, and there is no photoionization between the peaks. At first glance it seems obvious that we are exciting only the $5gnl'$ states

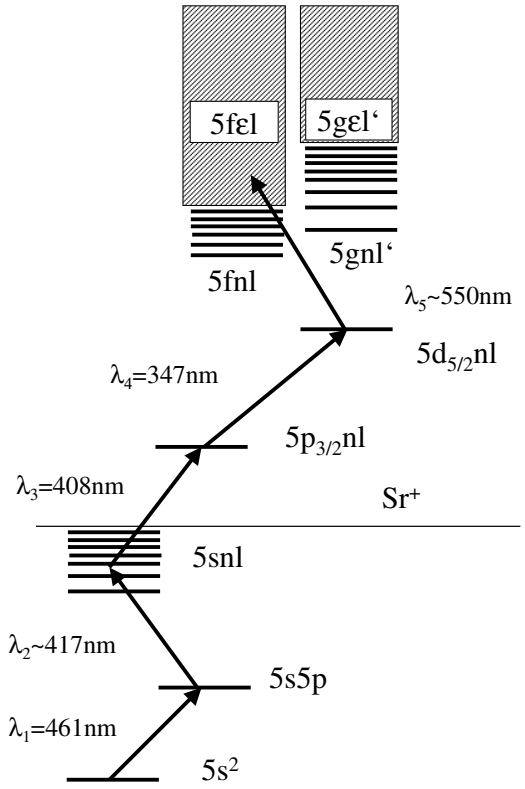

FIG. 1. Excitation scheme of the experiment. The excitation of the Sr $5d17l$ state is done with four fixed frequency lasers and Stark switching. The frequency of the final fifth laser is swept through the energy from the Sr^+ $5f$ to $5g$ limits. As shown, there is no excitation amplitude to the $5gnl'$ states, only to the $5f\epsilon l$ continuum.

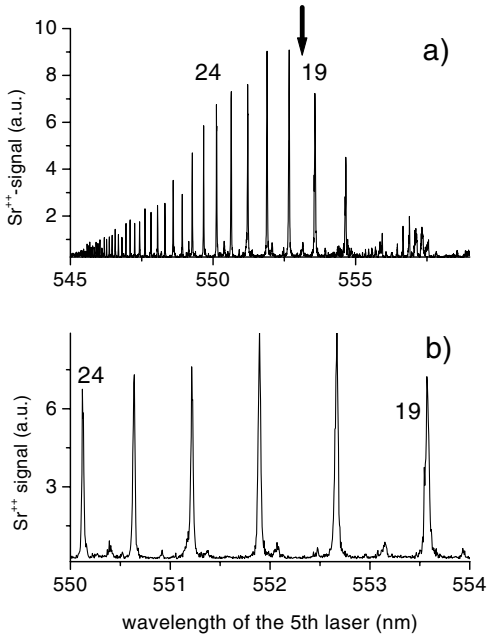

FIG. 2. Photoionization spectrum observed by scanning the fifth laser (a) from slightly below the $5f$ limit, shown by the arrow, to the vicinity of the $5g$ limit at about 544 nm. The resonances corresponding to $5g19l'$ and $5g24l'$ states have the numbers 19 and 24, respectively, above them. (b) Expanded view of the $5g19l'$–$5g24l'$ resonances.

and not exciting the $5f\epsilon l$ continuum at all. However, after more careful consideration it becomes apparent that quite the opposite is true. The initial $5d17l$ state is well represented by an independent particle picture, i.e., a Sr^+ $5d$ ion with a hydrogenic nl electron bound to it, and the wave function is the product of these two wave functions. There is evidently no electric dipole coupling from the $5d17l$ state to the $5gnl'$ state. In contrast, the dipole coupling from the $5d17l$ state to the $5f\epsilon l$ continuum is allowed. In particular, the Sr^+ ion makes the $5d$–$5f$ transition, and the nl spectator electron is shaken off to the ϵl continuum, resulting in the $5f\epsilon l$ final state [13–15]. However, shakeoff to the unperturbed hydrogenic $5f\epsilon l$ continuum, ψ_E, is everywhere forbidden, and we observe the excitation to the $5f\epsilon l$ continuum only where it is phase shifted by its interaction with the $5gnl'$ states.

Fano's theory describes the excitation from an initial state i to a final state f, which consists of a discrete state ϕ at energy E_ϕ and the degenerate continuum ψ_E, which we assume to be energy normalized. (We follow the notation of Ref. [1].) It is most often the case that the coupling from the discrete state to the continuum, V_E, is energy independent, and we here consider this case. This coupling broadens the discrete state so that it has a width (FWHM), $\Gamma = 2\pi|V_E|^2$, and the natural energy scale for the problem is the reduced energy, $\epsilon = 2(E - E_\phi)/\Gamma$. In addition to broadening the discrete state, ϕ, the coupling V_E also produces a phase shift Δ in the radial phase of the continuum wave function, and as we pass from far below to far above the discrete state at E_ϕ there is a phase shift of π. In particular, Δ is given by $\Delta = \cot^{-1}(\epsilon)$, so that far below, at, and far above the resonance at E_ϕ, $\Delta = 0$, $\pi/2$, and π, respectively. Well removed from the resonance the continuum wave function is described by its unperturbed solution $\psi_E \sim \sin(kr + \phi_{\rm bg})$, where k is the continuum electron's wave number and $\phi_{\rm bg}$ is a background phase. At the resonance, E_ϕ, it is described by its phase shifted solution, Λ_E, with asymptotic form $\sim\cos(kr + \phi_{\rm bg})$, and in general by $\psi_E\cos(\Delta) + \Lambda_E\sin(\Delta)$ with asymptotic form $\sin(kr + \phi_{\rm bg} + \Delta)$ [1,16]. The resulting continuum wave function has the same asymptotic amplitude across the resonance. We note that these forms of the continuum wave function, given in Ref. [1], are appropriate for short range potentials.

The photoexcitation cross section is composed of the excitation amplitudes to the discrete state ϕ, the unperturbed continuum ψ_E, and the phase shifted continuum Λ_E. In Fano's theory the phase shifted continuum is represented as a principal part integral over the unperturbed continuum, yielding the following expression:

$$\sigma \propto \left| \frac{\langle \phi|\mu|i\rangle \sin\Delta}{\pi V_E^*} + \frac{1}{\pi V_E^*}\mathbf{P}\int dE' \frac{V_{E'}^*\langle \psi_{E'}|\mu|i\rangle}{(E-E')}\sin\Delta - \langle \psi_E|\mu|i\rangle\cos\Delta \right|^2, \quad (1)$$

where μ is the transition electric dipole moment, $\langle \phi|\mu|i\rangle$ and $\langle \psi_E|\mu|i\rangle$ are the excitation matrix elements to the discrete state and the unperturbed continuum, and $\mathbf{P}$ denotes a principal part integral.

If the excitation amplitude to the continuum $\langle \psi_E|\mu|i\rangle$ is assumed to be energy independent, it appears that the principal part integral can be neglected, and doing so leads to the following common misinterpretation of the theory. Namely, if there is no continuum excitation, there is a symmetric, approximately Lorentzian peak of width Γ centered at E_ϕ. On the other hand, if there is no excitation of the discrete state, $\langle \phi|\mu|i\rangle$, there is a symmetric dip, or window resonance, in the photoionization cross section with vanishing excitation at E_ϕ. If both amplitudes are nonzero the resulting interference term leads to the familiar asymmetric Fano line shape.

In addition to being a source of confusion, writing the continuum Λ_E as the principal part integral of Eq. (1) is incorrect for long range potentials which support bound states. It thus does not correctly represent photoionization, as shown graphically by our experiment. However, it does represent Λ_E correctly for short range potentials, as encountered in photodetachment [17]. There are two straightforward ways to remedy this shortcoming of Fano's theory. The first is to extend the principal part integral of Eq. (1) so that it includes not only the unperturbed continuum ψ_E (here $5f\epsilon l$), but the associated bound states as well (here $5fnl$)[18]. This extension ultimately reflects the fact that the set of continuum states (here $5f\epsilon l$) is not by itself complete in terms of the radial functions. The second is to adopt a more physical approach and rewrite Eq. (1) using the phase shifted continuum explicitly, i.e.,

$$\sigma \propto \left| \frac{\langle \phi|\mu|i\rangle \sin\Delta}{\pi V_E^*} - \langle \psi_E|\mu|i\rangle\cos\Delta - \langle \Lambda_E|\mu|i\rangle\sin\Delta \right|^2. \quad (2)$$

In this form it is apparent that discarding the principal part integral is equivalent to neglecting the excitation amplitude to the phase shifted continuum, Λ_E, which is likely to be comparable to or greater than the excitation amplitude to the unperturbed continuum ψ_E.

The most physically appealing way of writing Eq. (2) is to assume a sinusoidal dependence of the continuum excitation amplitude on the phase Δ and replace $\langle \psi_E|\mu|i\rangle\cos\Delta + \langle \Lambda_E|\mu|i\rangle\sin\Delta$ in Eq. (2) by $\langle \psi_E|\mu|i\rangle_{\max}\cos(\Delta - \phi_i)$. Here $\langle \psi_E|\mu|i\rangle_{\max}$ is the maximum transition amplitude from i to the continuum as a function of the radial continuum phase, and ϕ_i is a measure of the radial phase difference between the initial state and the unperturbed continuum ψ_E. $\langle \psi_E|\mu|i\rangle_{\max}$, assumed to be positive, decreases slowly with energy. Far from the resonance, where $\Delta = 0$ or π, the excitation amplitude to the continuum takes the value $\pm\langle \psi_E|\mu|i\rangle_{\max}\cos\phi_i$, which is in general smaller in magnitude than $\langle \psi_E|\mu|i\rangle_{\max}$. With this modification the cross section is given by

$$\sigma \propto \left| \frac{\langle \phi|\mu|i\rangle \sin\Delta}{\pi V_E^*} - \langle \psi_E|\mu|i\rangle_{\max}\cos(\Delta - \phi_i) \right|^2. \quad (3)$$

With no excitation of the discrete state, i.e., $\langle \phi|\mu|i\rangle = 0$, and only continuum excitation, it is clear that any line shape can be obtained using Eq. (3), and several are shown in Fig. 3 for different positive values of $\phi_i \leq \pi/2$. For negative values the profiles are reflected through $\epsilon = 0$. As shown by Fig. 3, $\phi_i = \pi/2$ leads to symmetric peaks, as seen in our spectrum of Fig. 2.

Why the spectrum of Fig. 2 is a case in which $\phi_i = \pi/2$ is easily understood. If we consider any one of the peaks of Fig. 2, the discrete state ϕ is the $5gnl'$ state and the unperturbed continuum ψ_E is the $5f\epsilon l$ continuum. As we have already stated, the dipole moment from the initial state, $i = 5d17l$, to the discrete state, $\phi = 5gnl'$, vanishes. The dipole matrix element for excitation from the $5d17l$ state to the $5f\epsilon l$ continuum is given by

$$\langle 5f\epsilon l|\mu|5d17l\rangle = \langle 5f|\mu|5d\rangle\langle \epsilon l|17l\rangle, \quad (4)$$

i.e., a product of the ionic dipole matrix element and an overlap integral for the outer electron. In both the unperturbed $5d17l$ state and the unperturbed $5f\epsilon l$ continuum, the outer ($17l$ or ϵl) electron states are hydrogenic and have quantum defects $\delta = 0$. Consequently, the overlap integral $\langle 17l|\epsilon l\rangle$ vanishes due to the orthogonality of the $17l$ and ϵl radial wave functions. Evidently, with no interaction between the discrete state and the continuum there would be no continuum excitation. However, when

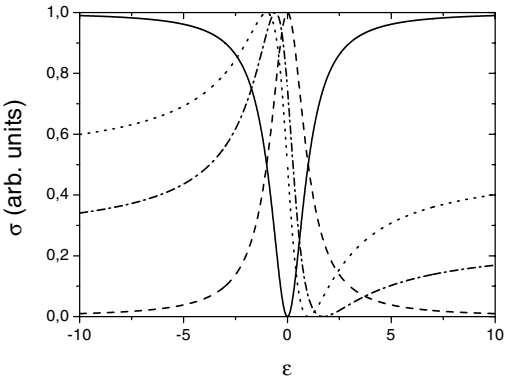

FIG. 3. Relative cross sections for pure continuum excitation assuming the same value of $\langle \psi_E|\mu|i\rangle_{\max}$, or equivalently, the maximum cross section, in all cases. Four values of the initial state continuum phase are shown: $\phi_i = 0$, $\pi/4$, $\pi/3$, and $\pi/2$ corresponding to $q = 0$, -1, -1.732, and $-\infty$. For $\phi < 0$ the profiles are reflected through $\epsilon = 0$.

the configuration interaction is taken into account the continuum excitation is allowed. Specifically, as we pass the energies of the $5gnl'$ states the interaction of the $5f\epsilon l$ continuum with the $5gnl'$ states causes the radial continuum phase to go through a phase shift of π. The change in the radial phase causes the overlap integral of Eq. (4) to depart from zero. In particular, it oscillates sinusoidally with Δ, having the form

$$\langle \epsilon l|17l\rangle = \langle \epsilon l|17l\rangle_{\max} \sin\Delta, \tag{5}$$

where $\langle \epsilon l|17l\rangle_{\max}$ decreases slowly with increasing energy. Clearly the overlap integral reaches its maximum at $\Delta = \pi/2$, the location of the $5gnl'$ states. With this observation we can use Eqs. (4) and (5) to write the second term of Eq. (3) for our spectrum of Fig. 2 as

$$\langle \psi_E|\mu|i\rangle_{\max} \cos(\Delta - \phi_i) = \langle 5f|\mu|5d\rangle\langle \epsilon l|17d\rangle_{\max} \times \cos(\Delta - \pi/2); \tag{6}$$

i.e., the spectrum of Fig. 2 corresponds to the $\phi_i = \pi/2$ case shown in Fig. 3. In spite of the fact that the peaks of Fig. 2 appear to be from excitation of the discrete $5gnl'$ states, they are due only to the phase shifted $5f\epsilon l$ continuum. Asymmetric line shapes attributed to pure continuum excitation have been observed previously, but it was less clear in those cases that there was no excitation to the discrete state [14,15].

It is conventional to express the shape of the resonance as the ratio of the photoionization cross section to the cross section of the unperturbed continuum, i.e., as

$$\left| \frac{\langle f|\mu|i\rangle}{\langle \psi_E|\mu|i\rangle} \right|^2 = \frac{(q + \epsilon)^2}{1 + \epsilon^2}, \tag{7}$$

where we have introduced the Fano shape parameter q, defined as [1,16]

$$q = \frac{\langle \phi|\mu|i\rangle/\pi V_E^* - \langle \psi_E|\mu|i\rangle_{\max} \sin\phi_i}{\langle \psi_E|\mu|i\rangle_{\max} \cos\phi_i}. \tag{8}$$

It is evidently minus the ratio of the coefficients of the $\sin\Delta$ and $\cos\Delta$ terms of Eqs. (1) or (2). If we use the original Fano form of Eq. (1) and ignore the principal part integral, the second term in the numerator of Eq. (8) is missing while the q of the resonance seems to provide immediately the ratio of the amplitudes for discrete and continuum excitation (and is often used as such [19]). However, as shown by Eq. (8), this simple correspondence does not exist. To show the difference more clearly we rewrite Eq. (8) as

$$q = \frac{\langle \phi|\mu|i\rangle}{\pi V_E^* \langle \psi_E|\mu|i\rangle_{\max} \cos\phi_i} - \tan\phi_i, \tag{9}$$

showing that q depends on both the ratio of the amplitudes to the discrete state and the unperturbed continuum and the phase ϕ_i between the initial state and the unperturbed continuum. In the absence of excitation to the discrete state $q = -\tan\phi_i$ and can take any value.

In conclusion, we have observed symmetric peaks in a photoionization spectrum which appear to be due to excitation of only the discrete state. However, they are due to pure continuum excitation, in particular, to the phase shifted continuum Λ_E, since excitation to the unperturbed continuum ψ_E vanishes. More generally, pure continuum excitation can lead to the entire range of Fano profiles so that an asymmetric line shape does not necessarily imply interference between the bound and continuum excitation amplitudes. Consequently, the q of an observed resonance does not, by itself, tell us the ratio of the excitation amplitudes to the discrete state and the unperturbed continuum. While we have here described the photoexcitation at a single resonance using an adaptation of Fano's configuration interaction theory which is applicable to long range potentials, we can also readily develop a quantum defect theory description extending from below the $5f$ limit to above the $5g$ limit [20–22].

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