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Statistical theory of Fano resonances in atomic and molecular photoabsorption

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A statistical theory of Fano resonances is presented for highly excited atomic and molecular systems with a classical chaotic limit. The probability distribution of the Fano parameter, which characterizes the asymmetry profile of a single resonance, is derived both for the case when the quantum system obeys time-reversal symmetry and when time-reversal symmetry is broken. Applications of the theory to photodissociation spectra of molecules and autoionization of Rydberg atoms are discussed.

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I. INTRODUCTION

Resonance phenomena are ubiquitous in highly excited quantum systems. Typical examples are autoionizing atomic resonances [1], photodissociation of rovibrational molecular states [2], excitons in semiconductor quantum wells [3], and resonant transport through nanostructures [4]. Since the seminal work of Fano [5] it is known that the line shapes of resonances may differ considerably from the Breit-Wigner form in a resonant excitation process. Interference between the indirect and the direct decay process results in a Beutler-Fano resonance profile of the photoabsorption cross section [1,6].

This Rapid Communication is aimed towards a statistical theory of Fano resonances in highly excited quantum systems. From a classical point of view, these systems often exhibit chaotic behavior. It is now common practice to extract information from such quantum systems by analyzing their statistical properties [7–9]. Work so far has concentrated on level spacing statistics [10], resonance width distributions [11,12], and correlation functions [13]. Fano resonances on the other hand are best characterized by their asymmetry properties since maxima or minima in the resonant part of the cross section do not coincide with the formal energy positions of resonances, which are difficult to determine. A statistical description of Fano resonances is also motivated by the increased availabilty of high-resolution experiments on highly excited atomic systems, such as the diamagnetic hydrogen atom [14], and small molecules, such as NO_2 and SO_2 [15]. Furthermore, it will be demonstrated that even low-resolution experiments which do not fully resolve the line shape of individual resonances contain significant information on the statistics of line shapes.

The theory is formulated within the framework of photodissociation of molecules. Since photoabsorption can be viewed as a half collision process we anticipate that it can easily be related to full scattering problems such as quantum transport through nanodevices [16]. In order to demonstrate the broad applicability of the theory, we discuss briefly the diamagnetic Kepler problem, a paradigmatic atomic system, as a further potential candidate in order to test our predictions.

II. THEORY

For the process of molecular photodissociation, Fig. 1 depicts schematically the situation envisaged. Consider a triatomic molecule with two-dimensional potential surfaces in the diabatic representation. The molecule is coherently laser excited from the ground state or a low-lying state $|0\rangle$ of energy E_0 onto two two-dimensional electronic potential surfaces. The transition is accomplished by the dipole operator D. Electronic surface $S1$ is the open channel—the energy E of the molecular complex is above the dissociation threshold—while the motion on the potential surface $S2$ is bound (closed channel). The dipole matrix element for transition to the open channel is given by $d_1 \equiv \langle 0|D|\psi_E^{(\mathrm{reg})}\rangle$, where $|\psi_E^{(\mathrm{reg})}\rangle$ is the regular continuum solution at energy E in the open channel, normalized in energy. When E coincides with the energy E_n of a bound state $|\phi_n\rangle$ in channel 2, the closed channel carries the transition amplitude $\langle 0|D|\phi_n\rangle$ in the absence of coupling to the continuum. In the following it is assumed that transitions between the two excited manifolds are possible. In the diabatic representation the coupling between the two surfaces is given by a nondiagonal potential V. Then the eigenstate $|\phi_n\rangle$ turns into a resonance with width $\Gamma_n = 2\pi|\langle \psi_E^{(\mathrm{reg})}|V|\phi_n\rangle|^2$.

In the regime $\Gamma_n \ll \Delta$ of isolated resonances (Δ being the mean energy spacing of resonances) the oscillator strength $Df(E)$ for the dipole transition is given by [1]

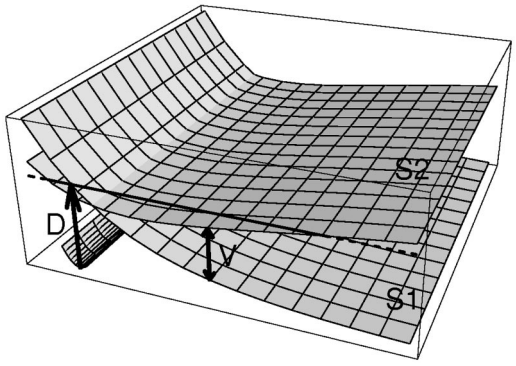

FIG. 1. Schematic sketch of the photodissociation process: Laser excitation takes place from a low-lying electronic potential surface (dipole operator D). The classical dynamics on surface $S2$ is bound and chaotic. Dissociation can take place directly by dipole excitation to channel 1 or indirectly by excitation to channel 2, with the coupling V between the surfaces $S1$ and $S2$.

$$Df(E)=Df^{(\mathrm{bg})}\frac{|q_n+\epsilon_n|^2}{1+\epsilon_n^2}, \tag{1}$$

where $Df^{(\mathrm{bg})}\equiv 2\mu(E-E_0)|d_1|^2/\hbar^2$ is the background oscillator strength for the transition to the open channel in the absence of coupling to the closed channel, μ is the reduced mass of the excited complex, and the reduced energy is denoted by $\epsilon_n\equiv 2(E-E_n-\Delta_n)/\Gamma_n$. The energy shift Δ_n of the resonance is neglected in the following. The line shape of the resonance is parametrized by the Fano parameter q_n. For a nondegenerate continuum it is given by [1]

$$q_n=\frac{\langle 0|D|\phi_n\rangle}{\pi d_1\langle\psi_E^{(\mathrm{reg})}|V|\phi_n\rangle}+\bar{q}\quad \bar{q}=-\frac{\langle 0|D|\psi_E^{(\mathrm{irr})}\rangle}{\langle 0|D|\psi_E^{(\mathrm{reg})}\rangle}. \tag{2}$$

$|\psi_E^{(\mathrm{irr})}\rangle$ is the irregular continuum solution whose phase is shifted asymptotically by $\pi/2$ with respect to the regular solution $|\psi_E^{(\mathrm{reg})}\rangle$ [1]. It appears in the expression for q_n because near resonance the wave function in the open channel acquires a strong admixture of the irregular continuum solution. Both d_1 and $\bar{q}$ depend only weakly on E and are assumed to be constant within the energy window over which a sample of resonances is taken. From Eq. (2) it is seen that the distribution of a set of Fano parameters $\{q_n\}$ taken over a stretch of the energy spectrum is determined by the statistical properties of the set of eigenstates $\{|\phi_n\rangle\}$ of the closed channel.

The distribution of the Fano parameter is derived under the following two conditions: First, the classical motion of the excited molecular complex on the electronic surface $S1$ of the closed channel is chaotic. This ensures that the statistical properties of generic wave functions in chaotic systems apply and that the closed channel subspace can be modeled by random matrix theory [7]. Second, the excitation process and the coupling between the two electronic surfaces are assumed to be spatially well separated: the overlap of the initial wave packet $\langle\mathbf{r}|D|0\rangle$ and the coupling potential $V(\mathbf{r})$ in coordinate representation is negligible. Therefore $x\equiv\langle 0|D|\phi_n\rangle/d_1$ and $y\equiv\pi\langle\psi_E^{(\mathrm{reg})}|V|\phi_n\rangle$ can be taken as statistically independent random variables.

III. DISTRIBUTION OF THE FANO PARAMETER

The calculation of the probability distribution $P(q)$ of the Fano parameter is now straightforward. (The index n of the resonance is omitted in the following.) In the case of time-reversal symmetry the wave functions and therefore x and y can be chosen real. The closed-channel subspace is modeled by $N\times N$ matrices taken from the Gaussian orthogonal ensemble (GOE). All results are understood in the limit $N\to\infty$, where x and y are Gaussian random variables with zero mean and variances σ_x^2 and σ_y^2. The probability distribution is given by

$$P_{\mathrm{GOE}}(q)=\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\,P_{\sigma_x}(x)P_{\sigma_y}(y)\,\delta\left(q-\bar{q}-\frac{x}{y}\right) \tag{3}$$

and $P_{\sigma_x}(x)$ is the probability distribution of x (and likewise for y). Integrating Eq. (3) results in

$$P_{\mathrm{GOE}}(q;s)=\frac{1}{\pi}\frac{s}{s^2+(q-\bar{q})^2},\quad s\equiv\sigma_x/\sigma_y. \tag{4}$$

The probability distribution of the Fano parameter in the GOE case thus turns out to be Lorentzian with mean value $\bar{q}$ and width s.

The width s of the probability distribution is related to the coupling strength V between the closed channel and the continuum channel and the ratio of the dipole transition matrix elements in both channels. Assume that V can be written in the form $V=\lambda V_0$, where λ characterizes the coupling strength and V_0 is fixed. Then $\sigma_y\sim\lambda$ and therefore $s\sim 1/\lambda$. For strong coupling to the continuum, the Lorentz distribution acquires a small width centered around $\bar{q}$. The same holds if direct photoexcitation dominates over the indirect process, since then σ_x becomes small.

In the case of broken time-reversal symmetry the Hamiltonian of the closed channel is modeled by $N\times N$ matrices from the Gaussian unitary ensemble (GUE). In this case x and y are complex Gaussian random variables with independent real and imaginary parts and the Fano parameter is, in general, complex. Most conveniently the distribution of q is characterized by the probability distribution of the phase φ_q and the modulus r_q of the quantity $q-\langle q\rangle$. The phases φ_x of x and φ_y of y are uniformly distributed, mod(2π), and the same holds for $\varphi_q=\varphi_x-\varphi_y$. Denoting the modulus of x by r_x and of y by r_y the probability distribution $P_{\mathrm{GUE}}(r_q)$ is given by

$$P_{\mathrm{GUE}}(r_q)=\int_0^{\infty}dr_x\int_0^{\infty}dr_y P(r_x)P(r_y)\,\delta\left(r_q-\frac{r_x}{r_y}\right), \tag{5}$$

where r_x (and likewise r_y) has the probability distribution $P(r_x)=\sigma_{r_x}^{-2}r_x\exp(-r_x^2/2\sigma_{r_x}^2)$. [Notice that $P(r_x^2)\sim\exp(-r_x^2/2\sigma_{r_x}^2)$ has the form of a Porter-Thomas distribution for GUE.] The final result for Eq. (5) reads

$$P_{\mathrm{GUE}}(r_q)=\delta(r_q)+\frac{s_r^2 r_q}{(s_r^2+r_q^2)^2}\quad (r_q\geqslant 0), \tag{6}$$

where $s_r\equiv\sigma_{r_x}/\sigma_{r_y}$. The distribution is δ–peaked at $r_q=0$ and has a local maximum at $r_q^{(0)}=s_r/\sqrt{3}$ with $P(r_q^{(0)})=3\sqrt{3}/(16s_r)$. Again, as discussed for the GOE case, the width s_r of the probability distribution $P_{\mathrm{GUE}}(r_q)$ is determined by the strength of the coupling between the two channels and the ratio of the strength between the dipole transition to the closed and to the open channel.

IV. PROFILE AREA DISTRIBUTION FOR GOE

In low-resolution experiments the experimental quantity of interest often is the distribution of the profile area attributed to a single resonance rather than the distribution of the Fano parameter itself. To be more specific, assume that the

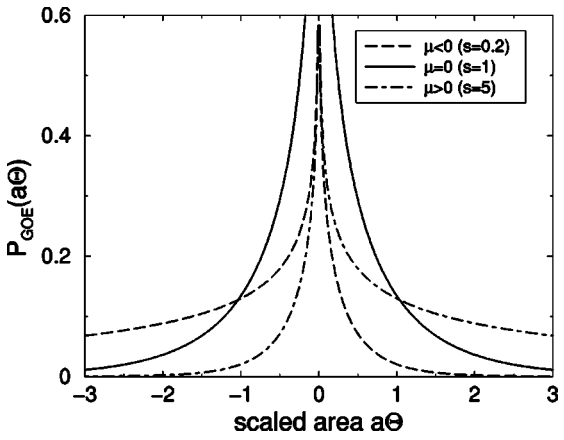

FIG. 2. Distribution $P(\hat{\Theta})$ of the scaled resonance area $\hat{\Theta}=a\Theta$, see discussion after Eq. (10). The average value of the Fano parameter is fixed at $\overline{q}=0$ and s is varied.

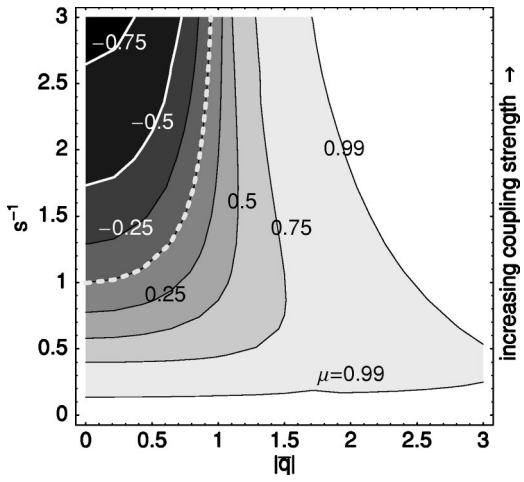

FIG. 3. Asymmetry parameter μ of the area distribution, Eq. (10), as a function of the average shape parameter $\overline{q}$ and s^{-1}. The white dashed line marks the values $(\overline{q}, 1/s)$, where $\mu=0$.

bandwidth δE of the exciting laser beam is larger than the width Γ of the resonance but still smaller than the mean spacing Δ between adjacent resonances ($\Gamma<\delta E<\Delta$). Assuming a rectangular laser profile, the excess oscillator strength averaged over the resonance profile with respect to the background strength is given by [17]

$$\overline{Df^{(\mathrm{res})}}(E)=\frac{1}{\delta E}\int_{E-\delta E/2}^{E+\delta E/2} Df^{(\mathrm{bg})}(E')[F(q;\epsilon)-1]dE', \tag{7}$$

where $F(q;\epsilon)\equiv|q+\epsilon|^2/(1+\epsilon^2)$ is the profile function of the resonance [cf. (1)]. Since $\Gamma<\delta E$, the range of integration in Eq. (7) can be extended to infinity and $\overline{Df^{(\mathrm{res})}}(E)$ is given by

$$\overline{Df^{(\mathrm{res})}}(E)=Df^{(\mathrm{bg})}\frac{\Gamma}{2\,\delta E}\int_{-\infty}^{\infty}\frac{q^2+2q\epsilon-1}{1+\epsilon^2}d\epsilon, \tag{8}$$

which, after performing the integration, gives $\overline{Df^{(\mathrm{res})}}/Df^{(\mathrm{bg})}=\pi\Gamma(q^2-1)/2\equiv\Theta$. In the following, the statistical distribution of the observable Θ is discussed. It can be written as $\Theta=x^2+2\overline{q}xy+(\overline{q^2}-1)y^2\equiv f(x,y)$ in terms of the matrix elements x, y and the mean value $\overline{q}$ of the Fano parameter. The probability distribution of Θ is given by

$$P(\Theta)=\int_{-\infty}^{\infty}dx\,P_{\sigma_x}(x)\int_{-\infty}^{\infty}dy\,P_{\sigma_y}(y)\,\delta(\Theta-f(x,y)). \tag{9}$$

Introducing the scaled area $\hat{\Theta}\equiv a\Theta$ with $a=(\sigma_x\sigma_y)^{-1}\sqrt{1/4+b^2}$ and $b=[s+s^{-1}(\overline{q^2}-1)]/4$, the distribution $P(\hat{\Theta})$ can be written as

$$P(\hat{\Theta})=\frac{1}{\pi\sqrt{1+4b^2}}\exp(\mu\hat{\Theta})K_0(|\hat{\Theta}|), \tag{10}$$

where K_0 is the MacDonald function. Additionally the *asymmetry parameter* $\mu=b[\frac{1}{4}+b^2]^{-1/2}$ has been introduced, which determines how much $P(\hat{\Theta})$ deviates from a symmetric distribution. $P(\hat{\Theta})$ diverges logarithmically as $\hat{\Theta}$ approaches zero.

Figure 2 demonstrates the dependence of $P(\hat{\Theta})$ at fixed $\overline{q}=0$ in the three characteristic regimes $\mu<0$, $\mu=0$, and $\mu>0$ by varying s. For $\mu=0$ the probability distribution is symmetric with respect to $\hat{\Theta}=0$ (solid line). For $\mu<0$ the area distribution is asymmetric with the flat side at negative values of $\hat{\Theta}$ (dashed line). The opposite holds for $\mu>0$ (dot-dashed line).

Since μ depends both on s and $\overline{q}$, a contour plot of μ as a function of $(\overline{q},1/s)$ is presented in Fig. 3. The variable $1/s$ instead of s has been chosen for purposes of discussion since $1/s\to\infty$ corresponds to the limit of strong coupling between the closed and the continuum channel. The range of μ is $-1<\mu<1$. The white dashed line marks the subspace of parameters where $P(\hat{\Theta})$ is symmetric ($\mu=0$), given by $\overline{q}^2+s^2=1$. If $|\overline{q}|\geqslant 1$ the asymmetry parameter μ is always positive regardless of $1/s$. For fixed $|\overline{q}|<1$ and weak coupling ($1/s$ small) the asymmetry parameter μ is positive, too. If the coupling is enlarged μ becomes negative above a certain value of $1/s$ which depends on $\overline{q}$.

The expectation value of the scaled area distribution is given by $\langle\hat{\Theta}\rangle=\mu(1+4b^2)$. Thus $\langle\hat{\Theta}\rangle$ is always positive when $|\overline{q}|\geqslant 1$. Note that the area under an *individual* resonance is positive if $|q|>1$ holds for its Fano parameter. When $|q|<1$ the area associated with an individual resonance is negative. In contrast $\langle\hat{\Theta}\rangle$ can either be positive or negative for $|\overline{q}|<1$ depending on the coupling strength to the continuum. Strong coupling to the continuum ($1/s\to\infty$) results in a negative value of $\langle\hat{\Theta}\rangle$. In the limit $\mu\to+1$ Breit-

Wigner resonances dominate the spectrum. For fixed $|\overline{q}|>1$ this limit is reached both for weak and large coupling to the continuum. For $|\overline{q}|<1$ the Breit-Wigner limit is reached only for weak coupling $(1/s\rightarrow 0)$. For $|\overline{q}|<1$ and strong coupling to the continuum $(1/s\rightarrow\infty)$ the expectation value of the area distribution is negative and window resonances with negative area dominate the spectrum in the limit $\mu\rightarrow -1$.

V. POSSIBLE EXPERIMENTAL TESTS

While the theory was formulated for molecular photoabsorption it is applicable to any quantum system with a closed subspace coupled to a single open channel, provided the classical motion in the closed subspace is chaotic. Here we focus on another prominent example, the hydrogen atom in a uniform magnetic field. Diamagnetic Rydberg atoms belong to the experimentally best studied systems in quantum chaos, and high-precision measurements of photoabsorption spectra are available [14]. The system can be described as a set of coupled Rydberg series with each series converging to a single Landau threshold in each subspace of given azimuthal symmetry [1]. At intermediate magnetic-field strengths the different Rydberg series overlap (the spacing between neighboring Landau thresholds is proportional to the magnetic-field strength). The corresponding classical system behaves chaotically in this regime. At energies between the first and second Landau threshold a single channel is open and the Rydberg electron forms an autoionizing state. The set of closed channels can be modeled as a Gaussian orthogonal ensemble [11]. The situation is then analogous to the case of molecular photodissociation discussed above. If one fits the resonances between the first and second threshold to Fano profiles, the statistical distribution of the Fano parameters is expected to obey Eq. (4).

VI. SUMMARY

A statistical theory of Fano resonances for highly excited atomic and molecular systems is presented. It provides a criterion to test the predictions of quantum chaos through the statistical distribution of the Fano parameter. The broad applicability of the theory to mesoscopic, molecular, and atomic resonance phenomena is emphasized. Two potential applications, photodissociation of triatomic molecules and autoionization of the diamagnetic hydrogen atom, have been discussed in detail. It has been shown that even low-resolution experiments are capable of providing valuable information on the statistical properties of Fano resonances.

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