Photoionization cross section: Exact expansion over resonances and natural line shape

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(Received 18 April 1989)

The photoionization cross section is analyzed as a sum of resonance contributions plus background. The contribution of each resonance is proportional to the square of a complex transition-dipole matrix element divided by a complex energy denominator and has a natural asymmetric line shape that is the superposition of a dispersive and an absorptive Lorentzian component.

I. INTRODUCTION

Recent photoionization experiments\(^1\)\(^-\)\(^6\) on atomic hydrogen in an electric field have stimulated interest in the detailed structure of the photoionization cross section. In particular, the question of how resonances determine both the positions of peaks and “line shape” near peaks has been raised. Early computations\(^7\) assumed a Lorentzian line shape. Subsequent numerical calculations\(^8\),\(^9\) found non-Lorentzian line shapes for some peaks. More recently,\(^10\),\(^11\) Regge-pole theory has been used to represent the cross section approximately as a sum of resonance contributions plus a background term and to show that “in the vicinity of the resonance the cross section can be well parametrized by Fano’s formula.” These results, however, come after many approximations applied to a Jeffrey-Wentzel-Kramers-Brillouin (JWKB) semiclassical analysis, and the final formulas are complicated. As a consequence, the physical interpretation of the individual terms is not clear, nor is the generality of the result. Most recently,\(^12\) JWKB methods were used to reproduce the experimental results of Ref. 1, but Fano’s formula was found not appropriate and was “disqualified on physical grounds. . . .”

For a number of years it has been possible to calculate resonance eigenvalues and eigenfunctions to high accuracy by complex coordinate methods.\(^13\),\(^14\) As pointed out in Ref. 1, however, “in order to compare calculated values for resonance energies and widths with experimental data, one needs an analytic line-shape expression, or a procedure for weighting the poles in the complex plane to represent phenomena on the real energy axis.” This is the main problem we seek to solve.

Our plan is (i) to derive the decomposition of the photoionization cross section exactly as a sum of resonance contributions plus a background term; (ii) to show that each resonance contribution is essentially the imaginary part of the square of the transition-dipole matrix element between the initial and final complex resonance wave functions, divided by a complex energy denominator, so that the expansion can be numerically calculated term by term; (iii) to show that the line shape of each resonance contribution is exactly given by a superposition of dispersive and absorptive Lorentzian components — what is sometimes called a Fano profile, although here no mechanism of the type invoked by Fano\(^15\) is present (that is, the natural line shape of resonance contributions to the photoionization cross section is asymmetric); (iv) to illustrate how the local line shape is determined by the nearest resonance only when the resonances are sharp, but how it can be completely different from the natural line shape of a single resonance when several resonances overlap; and (v) to discuss families of related expansions and the relevant convergence features.

For purposes of clarity and rigor, we give the derivation first with respect to a specific model system: the symmetric double-$\delta$-well potential.\(^16\),\(^17\) After putting the results in suitable model-independent form, we point out the rigorous generality to standard one-dimensional potentials of finite range. The final forms of the expansion are Eqs. (41), (43), (51), and (52). The line shape of a single resonance is contained in Eq. (45). Application to photoionization of hydrogen in an electric field, our original motivation, is not treated in this paper but will be dealt with in a subsequent publication.

II. DOUBLE-$\delta$ MODEL

It is advantageous to be able to start with a closed-form expression and then go backwards to get its expansion. There is a simple one-dimensional model that has both bound states and an infinite number of resonances and for which the photoionization cross section has closed form. The potential consists of two $\delta$ functions with negative coupling constant:

$$V(x) = -g[\delta(x+a) + \delta(x-a)] .$$

This model has exactly one even-parity bound state and, if $2ga > 1$, exactly one odd-parity bound state. (We adopt units in which $e = m = \hbar = 1$.) We give a brief discussion of the solutions of the Schrödinger equation,

$$-\frac{1}{2} \frac{d^2}{dx^2} + V(x) \psi(x) = E \psi(x) .$$

A. Even-parity bound state

The even-parity bound-state solution (where $N_e$ is a normalization constant) is given by

$$\psi_e(x) = \begin{cases} N_e \cosh \zeta_e a e^{\zeta_e (x + a)}, & x < -a, \\
N_e \cosh \zeta_e a, & -a \leq x \leq +a, \\
N_e \cosh \zeta_e a e^{-\zeta_e (x - a)}, & +a < x, \end{cases}$$

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\[ E_e = -\frac{1}{2} \frac{e^2}{\xi_e} . \]  

The parameter \( \xi_e \) is determined from the matching condition on the logarithmic derivative at \( x = \pm a \),

\[
\left[ \frac{d \ln \psi}{dx} \right]_{x = \pm a + 0} - \left[ \frac{d \ln \psi}{dx} \right]_{x = \pm a - 0} = -2g
\]

which by Eq. (3) is

\[
\frac{\xi_e}{g} - 1 = e^{-2g a} .
\]

Equation (6) has exactly one solution (for \( g > 0 \)), which for large \( g \) is given approximately by

\[
\xi_e \sim g + ge^{-2ga} + \ldots
\]

The normalization integral with Eq. (6) taken into account is

\[
N_e^{-2} = \int_{-\infty}^{+\infty} \psi_e(x)^2 dx = a + \frac{1}{2} \frac{1}{\xi_e - g} .
\]

Illustrative calculations will be given later with \( a = 1 \) and \( g = 5 \), for which the solution of Eq. (6) for \( \xi_e \) is approximately 5.000 226 896 661 257.

### B. Odd-parity bound state

Similarly, the odd-parity bound state, when \( 2ga > 1 \), is given by

\[
\psi_o(x) = \begin{cases} 
-N_e \sinh \xi_o a e^{-\xi_o (x + a)} & x < -a, \\
N_e \sinh \xi_o a, & -a \leq x \leq +a, \\
N_e \sinh \xi_o a e^{-\xi_o (x - a)} & +a < x.
\end{cases}
\]

The matching condition [Eq. (5)] takes a form similar to Eq. (6) but with a sign difference,

\[
\frac{\xi_o}{g} - 1 = -e^{-2g a},
\]

and which has the approximate solution for large \( g \),

\[
\xi_o \sim g - ge^{-2ga} + \ldots.
\]

The normalization integral is

\[
N_o^{-2} = \int_{-\infty}^{+\infty} \psi_o(x)^2 dx = -a + \frac{1}{2} \frac{1}{g - \xi_o} .
\]

As is characteristic of double-well potentials, the energy difference between the odd and even bound states, \( (\xi_o^2 + \xi_e^2)/2 \), is exponentially small \( (\sim 2g^2 e^{-2ga}) \). The numerical value of \( \xi_o \) for \( a = 1 \) and \( g = 5 \), obtained by solving Eq. (10), is 4.999 772 897 223 268.

### C. Odd-parity continuum states

The photoionization of the **ground state**, which is of even parity, only involves the odd-parity continuum. The eigenfunctions that are real for real \( k \) are

\[
\psi_k(x) = \begin{cases} 
\frac{i}{2} F(k)e^{ikx} + \frac{i}{2} F(-k)e^{-ikx} & x < -a, \\
\sin kx, & -a \leq x \leq +a, \\
\frac{i}{2} F(-k)e^{ikx} + \frac{i}{2} F(k)e^{-ikx} & +a < x,
\end{cases}
\]

where the coefficient \( F(k) \), called the Jost function,\(^{16,18} \) is determined by the matching condition, Eq. (5),

\[
F(k) = \frac{k + ig(e^{2ika} - 1)}{k}.
\]

Note that \( F(k) \) satisfies

\[
F(-k) = F(k^*)^* .
\]

The normalization integral for \( \psi_k \) is

\[
\int_{-\infty}^{+\infty} \psi_k(x) \psi_k(x) dx = \pi F(k) F(-k) \delta(k - k^*) .
\]

Care has been taken with Eqs. (8), (12), and (16) to avoid complex conjugation and to maintain analyticity in \( k \).

### III. EXACT FORMULA FOR PHOTOIONIZATION CROSS SECTION \( \sigma \) IN DOUBLE-\( \delta \) MODEL

The photoionization cross section from the bound state \( \psi_e(x) \) to the continuum state \( \psi_k(x) \) in light of circular frequency \( \omega \) is given by\(^2 \)

\[
\sigma = \frac{4\pi^2 \omega c k}{\mu^2} ,
\]

where the transition dipole matrix element \( \mu \) is defined by

\[
\mu = \frac{\int_{-\infty}^{+\infty} \psi_e(x) x \psi_k(x) dx}{\pi F(k) F(-k)} .
\]

The \( k \) in the denominator of Eq. (17) comes from the \( \delta(k - k^*) \) normalization for the continuum wave function [versus \( \delta(E - E') \) normalization, in which case the \( k \) would be absent]. Note that for real \( k \), the functions \( \psi_e(x), \psi_k(x), \) and \( F(k)F(-k) \) are all real, and consequently, so is \( \mu \). Implicit in Eq. (17) is the relation between \( \omega \) and \( k \),

\[
\omega = E - E_e = \frac{1}{2} (k^2 + \xi_e^2) .
\]

Evaluation of the integral in Eq. (18) leads to

\[
\sigma = \frac{4\pi^2 \omega}{ck} \frac{16N_e^2 e^{2\xi_e a}(k \cos k - \xi_e \sin k)^2}{\pi(k^2 + \xi_e^2)^4 F(k) F(-k)} ,
\]

where \( N_e^2 \) and \( F(k) \) may be evaluated from Eqs. (8) and (14).

The photoionization cross section \( \sigma \) [Eq. (20)] is plotted in Fig. 1. One sees a sequence of approximately equally spaced maxima with markedly asymmetric line shapes. Towards understanding the line shape, we compare in Fig. 2 the three \( k \)-dependent factors,

\[
\omega \left( \frac{1}{k^2 + \xi_e^2} \right)^4 \left( \frac{1}{F(k)F(-k)} \right) \left( \frac{(k \cos k - \xi_e \sin k)^2}{k} \right) .
\]

The first factor is monotonically decreasing and accounts for the strong fall off of \( \sigma \) at high \( k \). The second factor provides the sharp resonance character. The product of the second factor with the smoothly oscillating third factor, the oscillations of which reflect the net phase matching or mismatching of the initial and final wave functions, produces the asymmetry in the resonance structure. The
third factor also makes the cross section vanish almost periodically in $k$ [asymptotically at $k \sim (n + 1/2) \pi/a$, for integer $n$]. Each main structural feature, including the zeros, that comes out here as a product of factors has to come out as a single term or sum of overlapping terms in the decomposition of the photoionization cross section as a sum over resonances.

IV. RESONANCE CONTRIBUTIONS TO $\sigma$

A. Location of poles of $\sigma$

Each sharp peak in $\sigma$ corresponds to a peak in $1/F(k)F(-k)$. These in turn are associated with zeros of $F(k)F(-k)$, which can only occur at complex $k(2ga > 1)$, and which are poles of $\sigma$. Consider the zeros of $F(k)$ [Eq. (14)], or more conveniently $kF(k)$, except, of course, for the spurious root introduced at $k = 0$:

$$k = ig(1 - e^{2ika}).$$

(22)

First notice that Eq. (22) is exactly the same as the matching equation for the odd-parity bound state, Eq. (10), with the identification $k = i\xi_0^-$. One root is just this bound state (which is in the upper half $k$ plane). The others are resonances that correspond to outgoing wave boundary conditions at $\infty$ ($e^{ika}$ as $x \to \infty$, $e^{-ika}$ as $x \to -\infty$), as is clear from Eqs. (9) and (13). It is not hard to determine that for large $g$ the roots (other than $i\xi_0^-$) of $F(k)$ are given asymptotically by

$$k_{\pm n} = \pm n \pi \left[ 1 + \frac{1}{2ga} + \cdots \right] - \frac{n^2 \pi^2}{4g^2a^2} + \cdots,$$

$$n = 1, 2, \cdots$$

(23)

all of which are in the lower half plane. Similarly, $F(-k)$ has roots that are the negative of those of $F(k)$ and correspond to incoming wave boundary conditions. Resonance structure in $1/F(k)F(-k)$ is clearly visible in Fig. 2 near $k \sim \pi, 2\pi, 3\pi,$ and $4\pi$. The zeros of $F(k)$ and $F(-k)$ are plotted in Fig. 3.

B. Cauchy formula

We now seek to expand $\sigma$ in terms of contributions from each of the resonances. Our main technique is Cauchy's integral formula. We write

$$\frac{ck\sigma(k)}{4\pi\omega} = \frac{1}{2\pi i} \oint_{|z| = \epsilon} \frac{cz\sigma(z)/4\pi\omega}{z-k} \, dz,$$

(24)

where $\epsilon$ is smaller than the distance of $k$ to any singularity of $z\sigma/\omega$. Note that it is convenient not to expand the $\omega/k$ that is explicit in Eq. (17) for $\sigma$. As discussed above, the numerator has simple poles at $\pm i\xi_0^-$ and at the resonances $k_{\pm n}$ and $-k_{\pm n}$. It has fourth-order poles at $\pm i\xi_0^-$, as is evident from Eq. (20). At $\infty$ the numerator is dominated by an overall $z^{-6}$ factor, except near the $k_{\pm n}$ and $-k_{\pm n}$. There are no branch cuts. Consequently, one can find a sequence of circles, centered at the origin, with radii tending to infinity, on which the integral tends
to zero. We enlarge the integration contour \(|z - k| = \varepsilon\) to the successive circles of this sequence and in the standard way obtain \(ck\sigma(k)/4\pi\omega\) as the negative of a sum of residues,

\[
\frac{ck\sigma(k)}{4\pi\omega} = - \sum_{\text{poles} \atop (z = k)} \text{Res} \left[ \frac{cz\sigma(z)/4\pi\omega}{z - k} \right],
\]

(25)

\[
\frac{ck\sigma(k)}{4\pi\omega} = - \sum_{\text{poles} \atop (z = k)} \text{Res} \left[ 16N_e^2\xi_e^2 e^{2\xi_e}\frac{1}{z - k} \times \frac{(z \cos \alpha - \xi_e \sin \alpha)^2}{(z^2 + \xi_e^2)^4 F(z)F(-z)} \right].
\]

(26)

C. Evaluation of residues

The residues at \(z = \pm i\xi_e\), where \(\xi_e\) corresponds to the even-parity bound state, contribute a rational function of \(k^2\) that is a polynomial of degree 3 in \(k^2\) called \(P_3(k^2)\), divided by \((k^2 + \xi_e^2)^4\). The coefficients of \(k^2\) in \(P_3(k^2)\) are themselves polynomials in \(\xi_e\), \(a\), and \(g\), times the \(2N_e^2\xi_e^2e^{2\xi_e}\). The \(P_3(k^2)\) will not be given here explicitly, but it is included in the total nonresonance contribution plotted below in Fig. 6:

\[
- \text{Res}_{z = i\xi_e} - \text{Res}_{z = -i\xi_e} = \frac{\xi_e P_3(k^2)}{(k^2 + \xi_e^2)^4}.
\]

(27)

Consider next the poles that come from the zeros of \(F(k)\), Eq. (14). There is one on the imaginary axis at \(z = k_0 - ig\) [the odd-parity bound state, Eq. (11)], while the rest (the \(k_{\pm n}\)) all lie in the lower half plane, as indicated by Eq. (23) and the open diamonds in Fig. 3. All are simple poles, so that the residues are given by

\[
- \text{Res}_{z = k_n} = 16N_e^2\xi_e^2 e^{2\xi_e} (k_n\cos k_n a - \xi_e \sin k_n a)^2
\]

\[
(28)
\]

(28)

With the help of the matching condition, Eq. (22), this turns out to be

\[
- \text{Res}_{z = k_n} = 2N_e^2\xi_e^2 e^{2\xi_e} \frac{1}{k - k_n} \frac{1}{(k^2 + \xi_e^2)^4}
\]

\[
\times \frac{-ik_n^2(2g + ik_n - \xi_e)^2}{g(g + ik_n)[-a + \frac{1}{2}(1/(g + ik_n))]}.
\]

(29)

Here \(k_n\) can be any of the zeros of \(F(k)\), including \(k_0\).

Similarly, the contribution from a zero of \(F(-k)\) — denote the root by \(u_n\) — is given by

\[
- \text{Res}_{z = -u_n} = 2N_e^2\xi_e^2 e^{2\xi_e} \frac{1}{k - u_n} \frac{1}{(u_n^2 + \xi_e^2)^4}
\]

\[
\times \frac{iu_n^2(2g - iu_n - \xi_e)^2}{g(g - iu_n)[-a + \frac{1}{2}(1/(g - iu_n))]}.
\]

(30)

But the roots of \(F(-k)\) are just the negative of the roots of \(F(k)\). That is, we can take \(u_n = -k_n\). The two contributions coming from \(k_n\) and \(-k_n\) can be added together to give

\[
\frac{ck\sigma(k)}{4\pi\omega} = \text{Res}_{z = k_n} - \text{Res}_{z = -k_n} = \frac{i\xi_n}{k^2 - k_n^2} c(k_n),
\]

where

\[
c(k_n) = -4N_e^2\xi_e^2 e^{2\xi_e} \frac{1}{(k^2 + \xi_e^2)^4}
\]

\[
\times \frac{k_n^2(2g + ik_n - \xi_e)^2}{g(g + ik_n)[-a + \frac{1}{2}(1/(g + ik_n))]}.
\]

(32)

Now recall that except for the \(k_0 = i\xi_0\), corresponding to the odd-parity bound state, all the \(k_n\) are paired according to Eqs. (15) and (23). If \(k_n\) is a root of \(F(k)\), then so is \(-k_n^*\); i.e.,

\[
k_{-n} = -k_{n}^*.
\]

(33)

Since \(\xi_0, a, g, N_e\) are all real, Eqs. (32) and (33) imply that

\[
\frac{ik_{-n} c(k_{-n})}{k^2 - k_{-n}^2} = \frac{[i\xi_n c(k_n)]^*}{k^2 - k_n^2}.
\]

(34)

and the contributions of the residues at \(k_{\pm n}\) can be combined. In short, we express \(\sigma\) explicitly as a term from the poles at \(k = \pm i\xi_0\) (the bound state), a contribution from the odd-parity bound state at \(k = -i\xi_0\), and a sum over the resonances \(k_n\) in the fourth quadrant \((n = 1, 2, 3, \ldots)\). The result is

\[
\sigma = \frac{4\pi\omega}{c} \left[ \sum_{n = 1}^{\infty} \frac{k_n c(k_n)}{k^2 - k_n^2} - \frac{\xi_0 c(i\xi_0)}{k^2 + \xi_0^2} \right] + i \sum_{n = 1}^{\text{(4th quad. resonance)}} \frac{k_n c(k_n)}{k^2 - k_n^2}.
\]

(35)

Equation (35) is a preliminary form of the desired expansion of \(\sigma\) as background plus resonance contributions. However, it can be put in a much more insightful and model-independent form.

D. \(c(k_n)\) and square of transition dipole with resonance wave functions

Note first that the term in the denominator of Eq. (32) for \(c(k_n)\),

\[
a - \frac{1}{2g + ik_n},
\]

(36)

is exactly the formula for the odd-parity bound-state normalization integral, Eq. (12), with \(\xi_0\) replaced by \(-i\xi_n\). That is, Eq. (36) is the normalization integral obtained by integrating the square (not the modulus squared) of the outgoing-wave resonance wave function (corresponding to \(k_n^*\)) along a path \(\gamma\) on which the integrand vanishes at
A suitable specification for \( \gamma \) is as follows: \( \gamma \) starts at \( x = -a - \infty e^{i\theta} \), runs along a ray of angle \( \theta \) to \( x = -a \), continues along the \( x \) axis from \( -a \) to \( +a \), then runs along a ray of angle \( \theta \) from \( x = a \) to \( x = a + \infty e^{i\theta} \), with \( \tan \theta = -\text{Im} k_n / \text{Re} k_n \). A sketch of one such path appears in Fig. 4.

The resonance wave function is specified by

\[
\psi^{\text{res}}_n(x) = \begin{cases} 
    i N_n \sin k_n x e^{-ik_n(x-a)}, & x < -a, \\
    -i N_n \sin k_n x, & -a \leq x \leq a, \\
    -i N_n \sin k_n x e^{ik_n(x-a)}, & a < x,
\end{cases}
\]

which is the wave function of Eq. (9) and normalization integral of Eq. (12) with \( \zeta_n = -ik_n \). Note that apart from the normalization, Eq. (37) is the same as Eq. (13) since \( F(k_n) = 0 \) and \( F(-k_n) = 1 - \exp(-2ik_n a) \).

It turns out that \( c(k_n) \) is the square of the transition-dipole matrix element between the ground state and the resonance wave function. If one computes the transition dipole between the ground state and the wave function of Eq. (37) along the path \( \gamma \) described in the preceding paragraph, one finds

\[
\mu_{e,k_n} = \int_{\gamma} \psi_e(x) x \psi^{\text{res}}_n(x) dx ,
\]

\[
\mu_{e,k_n} = \frac{-i 2N_e N_n e^{i\omega_n} k_n (2g - \zeta_e + ik_n)}{\zeta_e + k_n^2} .
\]

Taking the square of Eq. (39) and using Eq. (22) to eliminate the \( \exp(2ik_n a) \), one finds that

\[
c(k_n) = \mu_{e,k_n}^2 .
\]

### E. Model-independent form for resonance contributions

Returning now to Eq. (35), we find a formula for \( \sigma \) in which, except for the first background term, the numerator of every contribution is of the form of the square of a transition-dipole matrix element multiplied by \( i \) times a wave vector:

\[
\sigma = \frac{4\pi i \omega}{c} \sum_{n=1}^{\infty} \begin{pmatrix} k_n & \mu_{e,l,k_n}^2 & k_n^* \\ \mu_{e,k_n} & \mu_{e,l,k_n}^2 & k_n \\ k & k^2 - k_n^2 & k
\end{pmatrix} \] .

\[
+ i \sum_{n=1}^{\infty} \begin{pmatrix} k_n & \mu_{e,k_n}^2 & k_n^* \\ \mu_{e,l,k_n} & \mu_{e,k_n}^2 & k_n \end{pmatrix} \] .

\[
(\text{resonances})
\]

Finally, we convert \( \omega \) and the various \( k^2 \) to energies via Eq. (19) and

\[
E = \frac{1}{2} k^2 , \quad E_e = \frac{1}{2} k_n^2 , \quad E_e = -\frac{1}{2} \zeta_e^2 , \quad E_o = -\frac{1}{2} \zeta_o^2 ,
\]

to get \( E \) real,

\[
(\text{lower half-plane resonances})
\]

The form of the resonance contributions in Eqs. (41) and (43) transcend the present model.

### F. Numerical reconstruction of photoionization cross section from background and resonances

To display the practical applicability of the preceding formula, we give in Fig. 5 the graphs corresponding to

![Fig. 4. The path \( \gamma \).](image1)

![Fig. 5. Reconstruction of photoionization cross section from background plus one, two, three, and four resonance terms.](image2)
V. DISCUSSION

A. Behavior of formula at origin

The photoionization cross section is non-negative. In the double-$\delta$ model it is clear from the exact expression, Eq. (20), that as $k$ goes to zero, $\sigma$ goes to zero. In contrast, the formula (41) for the decomposition has an explicit $k^{-1}$ factor. Any truncation of the series can be singular at the origin, (cf. Fig. 5). When more resonance terms are added in, the singularity becomes less and less noticeable, as is also visible in Fig. 5. Individual resonance terms can also cause the truncated sum to be negative. But as additional resonance terms are added, the "wings" build the baseline back up to positive values (cf. Fig. 7).

It is possible to modify the formula (43) so that the partial sums are not singular at the origin, as is shown in Sec. VI. Nevertheless, Eq. (43) is computationally optimum for the double-$\delta$ model.

B. Background terms

The nonresonance contribution consists of two terms in Eq. (43). Only the sum is of interest here. We plot it in Fig. 6, keeping the same scale as in Fig. 5. Note that it has a singularity at $k = 0$, which is cancelled by contributions from the resonance terms, that it approaches zero from positive values as $k$ tends to $\infty$, and that it is otherwise structureless.

C. Line shape of resonance terms

A most important result has to do with the line shape of a single resonance term in Eq. (43).

\[
\sigma_n = -\frac{4\pi(E - E_n)}{c} \text{Im} \left\{ \frac{E_n}{E} \right\}^{1/2} \frac{\mu_e^2 k_n}{E - E_n} \left( \frac{\cos(\theta) - \sin(\theta)(E - \text{Re}E_n)}{(E - \text{Re}E_n)^2 + (\text{Im}E_n)^2} \right),
\]

(44)

The energy-dependent prefactor is slowly varying and does not significantly affect the line shape near the reso- nances (in the example of this paper). The second factor—mainly the $\mu^2/(E-E_n)$—controls the line shape. We put it in a more transparent form

\[
-\text{Im} \left\{ \frac{E_n}{E} \right\}^{1/2} \frac{\mu_e^2 k_n}{E - E_n} = \left( \frac{E_n}{E} \right)^{1/2} \mu_e^2 k_n \frac{\cos(\theta) - \sin(\theta)(E - \text{Re}E_n)}{(E - \text{Re}E_n)^2 + (\text{Im}E_n)^2},
\]

(45)

where $\theta$ is defined by

\[
\theta = \text{arg}(\sqrt{E_n\mu_e^2 k_n}) = \frac{1}{2} \text{arg}E_n + 2 \text{arg}\mu_e k_n.
\]

(46)

The phase $\theta$ is what determines the line shape of the contribution of a single resonance, which is manifestly the sum of a standard absorptive Lorentzian with a dispersive Lorentzian. That is, the natural line shape is essentially that of Fano without a Fano mechanism.

For the four resonances plotted in Fig. 5, the values of $\theta$ are 0.53120, 0.94548, 1.1731, and 1.2995, respectively. For these relatively sharp resonances $\text{arg}E_n$ is quite small ($-0.0604$, $-0.0796$, $-0.0821$, and $-0.0797$, respectively), and $\theta$ is almost entirely due to the complexity of the transition dipole.

D. Local line shape when resonances overlap

It is important to distinguish between the line shape of a single resonance contribution and the local line shape of $\sigma$ near a resonance. When the width of a resonance is narrow compared to the spacing between resonances, then the local line shape near the resonance is dominated by that resonance. When the width is not narrow, then many resonances overlap and contribute to the local line shape, which can be quite different from the line shape of the closest resonance. In particular, in the present example the lowest resonances are sharp, and the four peaks plotted in Fig. 5 have primarily the shape of the nearby resonances. For higher resonances the angle $\theta$ approaches $\pi/2$, and the line shape of each resonance has a dispersive shape not seen directly in the cross-section profile. It is seen indirectly, in the sense that the cross section (cf. Fig. 1) returns to zero approximately at $k = (n + 1/2)\pi/a$, and it is the negative dip in the dispersion profile of the closest resonance on top of the overlapping wings of nearby broad resonances that brings the cross section back to zero.

This phenomenon is illustrated in Fig. 7 where the build up of $\sigma$ near $k_{10}$ is plotted as up to 9, 10, 11, 13, and 20 resonances are added. Note that when the tenth resonance is first added in, its dispersive profile is dominant (near $k = 10.22\pi/a$). The next few contributions change the local line shape to an almost symmetric
profile. But what is especially important is that the peak of this profile comes roughly $\pi/4a$ before the location of the real part of the 10th resonance eigenvalue $10.220909 - \text{i}0.93827$ and the cross section itself has a zero roughly $\pi/4a$ after this real part. That is, neither the maximum nor the zero of $\sigma$ mark the center of the nearest resonance. One might think that in the usual sense these resonances are not so overlapping: their widths are $\sim 1$ while the separation between consecutive resonances is $\sim \pi$. Such a thought is misleading, however, because it tacitly assumes a standard absorptive profile for the resonance. Here the resonance profile is in part dispersion, which falls off more slowly than absorption.

VI. ALTERNATIVE FORMULAS

A. Prefactor

The expansions (41) and (43) arise in a natural way in our derivation because $k\sigma/\omega$ resolves completely and exclusively into partial fractions: not only the resonance terms, but also the background terms. Nevertheless, there is some arbitrariness to the separation of the photoionization cross section into resonances and background. Recall that in the Cauchy integral (24), an explicit $1/k$ that appears in the formulas (17) and (20) is kept as prefactor and is not expanded. If the $1/k$ is included in the function to be expanded,

$$\frac{c\sigma(k)}{4\pi\omega} = \frac{1}{2\pi i} \oint_{|z-k|=\epsilon} \frac{c\sigma(z)/4\pi\omega}{z-k} \, dz,$$

then the end result is that only two changes need to be made to the formulas (41) and (43) for $\sigma$: (i) there are differences in the coefficients of the polynomial $P_1(k^2)$ [call the new one $Q_1(k^2)$]; and (ii) each residue picks up an additional factor $(k/k_n)^2$. That is, Eq. (41) becomes

$$\sigma = \frac{4\pi\omega}{c} \left[ \frac{-k}{\zeta} \frac{Q_1(k^2)}{(k^2 + \zeta^2)^2} + \frac{k}{\zeta} \frac{\mu^2_{\epsilon,k_n}}{k^2 + \zeta^2} \right] + i \sum_{n=1}^{\infty} \left( \frac{k}{k_n} \frac{\mu^2_{\epsilon,k_n}}{k^2 - k_n^2} - \frac{k}{k_n^2} \frac{\mu^2_{\epsilon,k_n}}{k^2 - k_n^2} \right),$$

(48)

This formula improves convergence for small $k$ but slows it for large $k$. Note that Eq. (48) vanishes term by term at $k = 0$, but the background (including the factor $\omega$) increases linearly with $k$ for large $k$. For sharp resonances ($\text{Im} E_n$ small), the local line shape in this formula is almost unchanged, because the phase angle $\theta$, given here by

$$\theta = -\frac{1}{2} \text{arg} E_n + 2 \text{arg} \mu_{\epsilon,k_n},$$

(49)

is again determined mainly by the dipole-matrix element. For broad resonances the local line shape is again the superposition of many contributions.

Equation (48) has an unexpected element: a change of one power of $k$ in what was being expanded made a change of two powers $(k/k_n)^2$ in the final formula. If in fact a change of two powers of $k$ had been made in what was being expanded, exactly the same formula would have resulted. This is because $\sigma(k)$ is an odd function of $k$, and Eq. (48) is valid for all $k$.

B. On the factor $k_n/k$

Of particular interest is the factor $k_n/k = \sqrt{E_n/E}$ in Eqs. (41) and (43) that does not seem to arise if the expansion of the photoionization cross section is obtained by formally applying Rayleigh-Schrödinger perturbation theory to the calculation of the Floquet eigenvalue of the state being ionized.

It is clear from Sec. VIA that this factor is not removed simply by changing the prefactor. If, however, the integration contours described in Sec. IVB are modified at the same time, then inclusion of the $1/k$ in the part to be expanded does result in a different final formula from Eq. (48). The modification to the circular contours that leads to Eq. (50) below is as follows: a semicircle in the right half plane; a line running from $+i\infty + \epsilon$ to $-i\infty + \epsilon$; a semicircle in the left half plane traversed clockwise; and again a line running from $+i\infty + \epsilon$ to $-i\infty + \epsilon$. That is, a horizontal, distorted figure eight. The integrations along the straight line parallel to the imaginary axis remain in the formula as background. Instead of Eq. (48), one obtains

$$\sigma = \frac{\omega}{\pi i} \int_{-i\infty}^{+i\infty} \frac{\sigma(z)/\omega}{z-k} \, dz + \omega \text{Res}_{k = \pm i\epsilon_k, \pm i\epsilon_0} \left( \frac{\sigma(z)/\omega}{z-k} \right)$$

$$+ i \frac{4\pi\omega}{c} \sum_{n=1}^{\infty} \left( \frac{\mu^2_{\epsilon,k_n}}{k^2 - k_n^2} - \frac{\mu^2_{\epsilon,k_n}}{k^2 - k_n^2} \right),$$

(50)
or, calling the first two (nonresonance) terms $b(k)$,

$$\sigma = b(k) + \frac{4\pi \omega}{c} \sum_{\text{res}} \left( \frac{\mu_{e,k}^2}{k^2 - k_n^2} \right) \left( \frac{\mu_{e,k}^*}{k^2 - k_n^*} \right).$$  \hspace{1cm} (51)

Finally, for real positive $E$, Eq. (51) can be written

$$\sigma = b(\sqrt{2E}) - \frac{4\pi (E - E_\ast)}{c} \sum_{\text{res}} \left( \frac{\text{Im} \left( \frac{\mu_{e,k}^2}{E - E_n} \right)}{E - E_n} \right).$$  \hspace{1cm} (52)

Equations (51) and (52) trade a simpler resonance contribution for a background that is not evaluated in closed form (for the present model). Also, parity is not explicitly evident, but is hidden in the background function $b(k)$, which is small for $k$ on the positive real axis, but not on the negative real axis.

If in a numerical calculation one were to ignore the background contributions in Eqs. (41) and (43) versus Eqs. (51) and (52), and add up only the resonance terms, then the only difference between the two sets of formulas (except near $k = 0$) would be a slowly varying separation of baselines.

VII. GENERALIZATIONS

How general are these expansions? The key features of the derivation for the double-$\delta$ model are (i) that the Jost function $F(k)$ is an entire function and consequently has only isolated zeros, and (ii) that there is a sequence of integration contours with radii tending to $\infty$ on which the integral of the Cauchy formula remains bounded. These two features will hold rigorously for any "standard" one-dimensional potential of infinite range. For potentials not of infinite range, and in more than one dimension, one complication is the possibility of branch cuts in the Jost function (e.g., Yukawa potentials). Such complications contribute to the background terms, but the contributions of isolated resonances are expected to be of the forms given in Eqs. (41), (43), (51), and (52). Further complications may arise when the asymptotics are not exponentials.

For example, for hydrogen in a constant electric field the asymptotics are given by Airy functions. Complex dilation turns the spectrum from absolutely continuous to discrete (infinite number of resonances), and we expect an analogous analysis to be valid.

VIII. CONCLUSIONS

The photoionization cross section $\sigma$ has been expressed as a sum over resonances plus background. The contribution of each resonance is proportional to the imaginary part of the square of the (complex) transition dipole between the ground and (complex) resonance wave function, divided by a (complex) energy denominator, and times a slowly varying factor. The derivation was carried out for the specific example of a double-$\delta$ potential, for which the cross section, bound states, and resonances were all obtainable in closed form. The resulting expansion was then generalized. For the case of standard one-dimensional potentials of finite range, the derivation is rigorous, but for more complicated potentials the background term has not been determined. The form of each resonance contribution permits it to be calculated directly from the wave functions of the initial and resonance states, which allows application to problems for which the cross section cannot be found in closed form. When the resonances are sharp, the local line shape of $\sigma$ is essentially the same as that of the nearest resonance. When the resonances are broad, i.e., overlapping, then the local line shape of $\sigma$ includes the superposition of the wings of several resonances and may look very different from the shape of the nearest resonance. The natural line shape of a single resonance is a linear combination of absorptive and dispersive Lorentzians, with the mixture depending primarily on the phase of the transition dipole when the resonance is narrow. Thus one has a characteristically asymmetric line shape without a Fano mechanism.

ACKNOWLEDGMENTS

The authors wish to thank the National Science Foundation for partial support of this work under Grant No. NSF-PHY-85-02383, and the Fulbright Commission.

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