Parameterization of Absorption-Line Profiles

*

Scientific Report # 23

Bruce W. Shore

Harvard College Observatory

November 1967

ABSTRACT

The parameterization

$$\sigma(E) = C + \sum_K \frac{(\frac{1}{2}\Gamma_K)\, B_K + (E - E_K)\, A_K}{(E - E_K)^2 + (\frac{1}{2}\Gamma_K)^2}$$

for attenuation cross-sections is discussed, with attention to the following details: prescriptions for "exact" calculation of profile parameters, in which the effects of "distortions" are separated from the effects of multiple "scatterings"; the validity of assuming independent (non-interfering) resonances; the specific case of autoionizing lines; connections with alternative parameterizations; the prohibition on negative cross-sections assured by unitarity; behavior at threshold; and the applicability of this parameterization to emission lines.

I. INTRODUCTION

Observations of photon (or neutron) attenuation typically disclose cross-sections with the energy dependence [1]

$$Q(E) = C(E) + \sum_K \frac{(\frac{1}{2}\Gamma_K)\ B_K + (E - E_K)\ A_K}{(E - E_K)^2 + (\frac{1}{2}\Gamma_K)^2} \ . \tag{1.1}$$

Applied to photon projectiles, incident with energy ω on an atom in state I, this attenuation cross-section reads

$$\sigma(I,\omega) = C(\omega) + \sum_K \frac{(\frac{1}{2}\Gamma_K)\ B_K + (\omega - \omega_{IK})\ A_K}{(\omega - \omega_{IK})^2 + (\frac{1}{2}\Gamma_K)^2} \ . \tag{1.2}$$

(Here, and throughout this paper, I use atomic units, $e = \hbar = m = 1;\ c = 1/\alpha \cong 137$). The rapid variation of $\sigma(I_o,\omega)$ with photon energy near the resonance energies $\omega_{IK} = E_K - E_I$ traces the profile of an absorption line.

Nuclear physicists have, for many years, used such parameterizations, although the validity of formula (1.1) is by no means restricted to nuclear collisions. Until the recent revival of interest in ultraviolet spectroscopy, atomic spectroscopists had little need for such elaborate parameterization: for non-autoionizing lines, the parameter A_K vanishes, B_K is equal to $2\pi\alpha$ times the oscillator strength, and the observed width Γ_K

reflects conditions in the absorbing medium rather than the natural radiative width. For autoionizing lines, the profile parameters A_K, B_K, Γ_K, and E_K each have empirical and physical utility[2], just as do the more familiar parameters of quantum defect and oscillator strength.

Equation (1.1) is only one of several mathematically equivalent representations (parameterizations) of Q(E). Other expressions have also been suggested. Burke[3], Smith[4], and Peterkop and Veldre[5] have recently reviewed the theories for explaining resonance structure in collision cross-sections for electron and photon scattering; Burke[3] and Smith[4] summarize the presently available values for profile parameters. To date, there has been little effort to determine, either theoretically or experimentally, profile parameters other than resonance width and resonance position. I hope the present article will stimulate experimental tests of formula (1.2) for the description of complicated photoionization cross-sections and will encourage computation of profile parameters.

Before we judge the usefulness of formula (1.1) for fitting and predicting cross-sections, several points deserve attention. Are the resonances really independent, or is there interference between resonances? How does formula (1.1) compare with other commonly used parameterizations? Is formula (1.1) consistent with the unitary property of the scattering matrix or will it give erroneous negative cross-sections? Do autoionizing lines seen in emission have the same profiles as absorption lines? The present paper addresses these questions, and provides a more refined prescription for the computation of profile parameters than the formulas given in reference 1.

II. BASIC DEFINITIONS[6]

For a system comprising projectile and target, whose composite quantum numbers are a and whose combined energy is E, the attenuation cross-section $\sigma(a,E)$ is

$$\sigma(a,E) = \frac{2\pi}{F_a} \int_{c \neq a} \delta(E_a - E_c)\ |T_{ca}|^2 , \tag{2.1}$$

where F_a denotes the projectile flux corresponding to the choice of normalization for the incident wave ψ_a, $T_{ca} \equiv \langle \psi_c | T | \psi_a \rangle$ is the transition amplitude linking initial state ψ_a with final state ψ_c, and $\int_c$ denotes a generalized sum over final states (a sum over discrete labels and an integration over continuous labels). Making use of the unitary property of the scattering matrix $S_{ba} = \delta_{ba} - 2\pi i\ \delta(E_a - E_b)\ T_{ba}$, one can write (2.1) in the alternative form

$$\sigma(a,E) = -\frac{2}{F_a} \operatorname{Im} T_{aa} . \tag{2.2}$$

The optical theorem, Eq. (2.2), expresses mathematically what experimenters long ago recognized: in studying neutral projectiles it is simpler to measure beam attenuation in the forward direction than to collect the scattered flux from all directions.

It should be clear that $\sigma(a,E)$ has the form $Q(E)$ of Eq. (1.1) if T_{aa} can be written

$$\frac{2\pi}{F_a} T_{aa} = \sum_{K} \frac{B_K - iA_K}{E - E_K + i\frac{1}{2}\Gamma_K} + D - iC. \qquad (2.3)$$

Thus if the scattering amplitude can be expressed as the sum of independent resonance contributions, attenuation cross-sections will display the energy dependence $Q(E)$ of equation (1.1), with no interference between resonances.

III. THE DEFINITION OF INDEPENDENT OVERLAPPING RESONANCES[6]

Methods for breaking the operator

$$T \equiv V + V \frac{1}{E^{+}-H} V \equiv V + VGV \qquad (3.1)$$

into resonant (T_Q) and non-resonant (T_P) parts, $T = T_P + T_Q$, have been discussed by Fonda and Newton[7], Feshbach[8], and Zhivopistsev[9] amongst others. The resonance structure can be brought out most readily by the use of projection operators,

$$1 = P + Q \qquad PP = P \qquad QQ = Q \qquad PQ = QP = 0 \qquad (3.2)$$

such that Q projects resonance states, and P projects possible initial and final states[10]. The introduction of an operator[1]

$$t = V + VP\,[E^{+} - H^{\circ} - PVP]^{-1}\,PV \qquad (3.3)$$

then permits one to write

$$T = V + V\,[E^{+} - H^{\circ} - V]^{-1}\,V$$

$$= t + tQ\,[E - H^{\circ} - QtQ]^{-1}\,Qt \qquad (3.4)$$

and so to identify the non-resonant part (elastic scattering and direct processes)

$$T_P = t \tag{3.5}$$

and the resonant part

$$T_Q = tQ\,[E - H^\circ - QtQ]^{-1}\,Qt \tag{3.6}$$

We can now introduce[1], at least formally, a set of resonance states Φ_K,

$$Q\,\Phi_K = \Phi_K, \qquad P\,\Phi_K = 0, \tag{3.7}$$

which satisfy the equation

$$[H^\circ + QtQ - \mathcal{E}_K]\,\Phi_K = 0 \tag{3.8}$$

with complex eigenvalue

$$\mathcal{E}_K = E_K + i\tfrac{1}{2}\Gamma_K. \tag{3.9}$$

Since t is not Hermitian, the familiar orthogonality theorem for eigenstates having different eigenvalues applies to $\langle\Phi_K^\dagger|\Phi_L\rangle$ rather than to the usual $\langle\Phi_K|\Phi_L\rangle$, where $\Phi^\dagger$ is the adjoint of Φ. By using the fact that

$$Q[H^\circ+t]Q = Q[H^\circ+\mathcal{P}VP\frac{1}{E-PHP}PV - i\pi\, VP\delta(E-H)PV]Q$$

$$\equiv Q[H^\circ + VG_PV - i\pi\, V\, I_P\, V]Q \qquad (3.10)$$

($\mathcal{P}$ denotes principal value) where H° and QVVQ are real, one can show that[12] $\Phi_K^\dagger = \Phi_K^*$. The bi-orthogonal expansion is therefore

$$Q = \sum_K \frac{|\Phi_K\rangle\langle\Phi_K^*|}{\langle\Phi_K^*|\Phi_K\rangle}, \qquad \frac{\langle\Phi_K^*|\Phi_L\rangle}{\langle\Phi_K^*|\Phi_K\rangle} = \delta_{KL}. \qquad (3.11)$$

Just as with conventional calculations of atomic structure, states of different energy are orthogonal, but degenerate states need not be. Equation (3.11) requires that we determine our degenerate states to diagonalize the interaction QtQ within a manifold of degenerate states. This requirement can be met with conventional approaches employing angular-momentum coupling and/or the diagonalization of comparatively small matrices. The resonance part of the scattering amplitude can now be written

$$\langle\psi_b|T_Q|\psi_a\rangle = \sum_K \frac{\langle\psi_a|t|\Phi_K\rangle\ \langle\Phi_K^*|t|\psi_a\rangle}{(E-\mathcal{E}_K)\ \langle\Phi_K^*|\Phi_K\rangle}\ . \qquad (3.12)$$

We thereby obtain, as desired, the resonance scattering amplitude as a sum over independent (though not necessarily well-separated) resonance terms.

To determine the resonance parameters, it proves convenient to write

$$t = V \sum_{n=0}^{\infty} (G_P^\circ V - i\pi g_P V)^n \tag{3.13}$$

where

$$g_P \equiv P\,\delta(E - H^\circ)P$$

$$G_P^\circ \equiv \mathcal{P}\left[P \frac{1}{E - H^\circ} P\right]$$

$$G_Q^\circ \equiv \mathcal{P}\left[Q \frac{1}{E - H^\circ} Q\right] . \tag{3.14}$$

We can then write a perturbation-theory solution of Eq. (3.8) as

$$\Phi_K = \left[1 + G_Q^\circ V \sum_{n=0}^{\infty} (G_Q^\circ V + G_P^\circ V - i\pi g_P V)^n \right]\varphi_K \tag{3.15}$$

where, as in reference 1, φ_K is a combination of degenerate **eigenstates** of H° chosen to diagonalize V within a degenerate manifold. We may also write Eq. (3.15) as

$$\Phi_K = \left[1 + G_Q^\circ V \left(1 - G_Q^\circ V - G_P^\circ V - i\pi g_P V \right)^{-1} \right] \varphi_K . \qquad (3.16)$$

The preceding prescription yields an unnormalized state Φ_K which satisfies the condition

$$\langle \varphi_K | \Phi_K \rangle = 1 \qquad \text{since} \quad \langle \varphi_K | \varphi_K \rangle = 1. \qquad (3.17)$$

Similarly, the complex value $\mathcal{E}_K$ can be written

$$\mathcal{E}_K \equiv E_K + i\tfrac{1}{2}\Gamma_K = \langle \varphi_K | H^\circ + t \,|\, \Phi_K \rangle . \qquad (3.18)$$

The preceding expressions, extensions of previous results[13], do not separate explicitly the real and imaginary parts of Φ_K. For that purpose, it is useful to introduce (real) states Ψ_K,

$$\Psi_K = \sum_{n=0}^{\infty} (G_Q^\circ V + G_P^\circ V)^n \, \varphi_K \equiv \Lambda \varphi_K . \qquad (3.19)$$

This expression for Ψ_K, taken with the requirement that degenerate Ψ_K have diagonal elements of V,

$$\langle \varphi_K | V | \varphi_L \rangle = 0 \qquad \text{if } E_K = E_L \text{ and } K \neq L, \qquad (3.20)$$

is a description of the states obtained in conventional calculations of bound states; all integrations over continuum states require principal values. These Ψ_K contain mixtures of configurations, including continuum functions, whose energy differs from E_K. Thus unlike the Φ_K states they do not belong exclusively to the Q set:

$$Q\Psi_K + P\Psi_K = \Psi_K \qquad \text{but } P\Psi_K \neq 0. \tag{3.21}$$

By rearranging sums, one can then obtain the formulas

$$E_K = \langle \varphi_K | H^\circ + V | \Psi_K \rangle + O(V^3) \tag{3.22a}$$

$$\Gamma_K = 2\pi \langle \Psi_K | V g_P V | \Psi_K \rangle + O(V^4) \tag{3.23a}$$

$$A_K = \frac{4\pi}{F_a} \langle \Psi_K | V g_P V\Lambda | \psi_a \rangle \langle \psi_a | V | \Psi_K \rangle^* + O(V^5) \tag{3.24a}$$

$$B_K = \frac{2}{F_a} \left\{ |\langle \Psi_K | V | \psi_a \rangle|^2 - \pi^2 |\langle \Psi_K | V g_P V\Lambda | \psi_a \rangle|^2 \right\} + O(V^6), \tag{3.25a}$$

where $O(V^n)$ indicates that further terms involve n products of V. Such corrections are of the form

$$V\Lambda \cdot (-i\pi g_P V\Lambda)^{n-1},$$

and thus they describe the effects of multiple scatterings between equal-energy states. In contrast, the operators VG_pV, VG°_QV, and Λ describe "distortions" which mix configurations of different energy. Formulas (3.22) - (3.25) therefore give a prescription for profile parameters which separates the effects of distortion and of multiple scattering.

In obtaining the preceding formulas I have neglected corrections to the normalization of Φ_K:

$$\langle\Phi_K{}^*|\Phi_K\rangle^{-1} = 1 - \sum_N \frac{|\langle\Psi_K|V|\varphi_N\rangle - i\pi\langle\Psi_K|Vg_pV|\Psi_N\rangle|^2}{(e_K - e_N)^2}$$

$$+ O(V^4)/(e_K - e_N)^4$$

$$\cong 1. \tag{3.26}$$

Here e is the eigenvalue of an unperturbed state: $H^\circ\varphi_K = e_K\varphi_K$. As we shall note in section VI, this approximation is consistent with unitarity restrictions.

It is also useful to introduce (real) distorted "continuum" states Ψ_a, the counterparts of the "bound" states Ψ_K:

$$\Psi_a = \sum_{n=0}^{\infty} (G^\circ_Q V + G^\circ_p V)^n \psi_a \equiv \Lambda\psi_a. \tag{3.27}$$

The Ψ_a states are the Ψ^1 states of Lippmann and Schwinger[14]; the wavefunctions are standing waves. Like the Ψ_K states, the Ψ_a states do not belong exclusively to the P or the Q class:

$$P\Psi_a + Q\Psi_a = \Psi_a \qquad \text{but} \qquad Q\Psi_a \neq 0. \tag{3.28}$$

With the introduction of these distorted continuum states, we can write the profile parameters as

$$E_K = \langle \varphi_K | H^\circ + V | \Psi_K \rangle + O(V^3) \tag{3.22b}$$

$$\Gamma_K = 2\pi \int_c \delta(E - E_c) \, | \langle \Psi_K | V | \psi_c \rangle |^2 + O(V^4) \tag{3.23b}$$

$$A_K = \frac{4\pi}{F_a} \langle \psi_c | V | \Psi_K \rangle^* \int_c \delta(E - E_c) \, \langle \Psi_K | V | \psi_c \rangle \, \langle \psi_c | V | \Psi_a \rangle + O(V^5) \tag{3.24b}$$

$$B_K = \frac{2}{F_a} \left\{ | \langle \Psi_K | V | \psi_a \rangle |^2 - \pi^2 \left| \int_c \delta(E - E_c) \, \langle \Psi_K | V | \psi_c \rangle \, \langle \psi_c | V | \Psi_a \rangle \right|^2 \right\} + O(V^6). \tag{3.25b}$$

These are the required generalizations of expressions in reference 1. Matrix elements here involve the use of "exact, distorted" excited states Ψ_K, incorporating configuration mixing in the usual sense, and "zero-order, unperturbed" continuum states ψ_a. This asymmetry in the exactness of dextral and sinistral wavefunctions is the counterpart of the familiar result[14]

$$\langle \psi_b | T | \psi_a \rangle = \langle \psi_b | V | \Psi_a^+ \rangle = \langle \Psi_b^- | V | \psi_a \rangle . \tag{3.29}$$

The background may be expressed in a similar way, if we introduce the expansion

$$\begin{aligned} t &= V \sum_{n=o}^{\infty} (G_p^0 V - i\pi g_p V)^n \\ &= V\Lambda_p \sum_{n=o}^{\infty} (-i\pi g_p V \Lambda_p)^n \end{aligned} \tag{3.30}$$

where

$$\Lambda_p = \sum_{n=o}^{\infty} (G_p^0 V)^n . \tag{3.31}$$

We then obtain

$$\begin{aligned} C &\equiv \frac{-2}{F_a} \operatorname{Im} \langle \psi_a | t | \psi_a \rangle \\ &= \frac{2\pi}{F_a} \langle \psi_a | V\Lambda_p \cdot g_p \cdot V\Lambda_p | \psi_a \rangle + O(V^4) \\ &= \frac{2\pi}{F_a} \int_c \delta(E - E_c) \, | \langle \psi_c | V\Lambda_p | \psi_a \rangle |^2 + O(V^4) . \end{aligned} \tag{3.32a}$$

The matrix element here requires either a distorted initial continuum function, $\Psi_a^P = \Lambda_p \psi_a$, or distorted final functions $\Psi_c^P = \Lambda_p \psi_c$, but not both. Thus we can write

$$C = \frac{2\pi}{F_a} \int_c \delta(E - E_c) \,|\, \langle \psi_c | V | \Psi_a^P \rangle |^2 + O(V^4)$$

$$= \frac{2\pi}{F_a} \int_c \delta(E - E_c) \,|\, \langle \Psi_c^P | V | \psi_a \rangle |^2 + O(V^4). \tag{3.32b}$$

In summary, we see that the attenuation cross-section may be written

$$\sigma(a) = C + \sum_K \frac{b_K + \epsilon_K a_K}{(\epsilon_K)^2 + 1}$$

$$= \frac{2\pi}{F_a} \langle \Psi_A^P | V g_p V | \Psi_A^P \rangle +$$

$$+ \frac{2}{F_a} \sum_K \frac{1}{(\epsilon_K)^2 + 1} \frac{[\langle \Psi_K | V | \psi_a \rangle |^2 - |\pi \langle \Psi_K | V g_p V | \Psi_A \rangle |^2]}{2\pi \langle \Psi_K | V g_p V | \Psi_K \rangle}$$

$$+ \frac{4\pi}{F_a} \sum_K \frac{\epsilon_K}{(\epsilon_K)^2 + 1} \frac{\langle \Psi_K | V | \psi_a \rangle \langle \Psi_a | V g_p V | \Psi_K \rangle}{2\pi \langle \Psi_K | V g_p V | \Psi_K \rangle} \tag{3.33}$$

where

$$a_K = A_K/(\tfrac{1}{2}\Gamma_K), \qquad b_K = B_K/(\tfrac{1}{2}\Gamma_K),$$

$$\epsilon_K \quad (E - E_K)/(\tfrac{1}{2}\Gamma_K). \tag{3.34}$$

For the case of an isolated resonance, or of degenerate resonances, there is no distinction between Ψ_a and Ψ_a^P, and we can write

$$\sigma(a) = C_K + \frac{b_K + \epsilon_K a_K}{(\epsilon_K)^2 + 1} \tag{3.35}$$

where

$$\begin{aligned} C_K &= \frac{2\pi}{F_a} \left\langle \Psi_a \middle| V g_p V \middle| \Psi_a \right\rangle + O(V^4) \\ &= \frac{2\pi}{F_a} \int_c \delta(E - E_c) \left| \left\langle \Psi_a \middle| V \middle| \psi_c \right\rangle \right|^2 + O(V^4). \end{aligned} \tag{3.36}$$

IV. PHOTON ATTENUATION PROFILES

The preceding formulas apply quite generally to attenuation. For the specific application to photon attenuation, discussed in reference 1, we must distinguish two contributions to the interaction $V \equiv H - H^{\circ}$: the inter-electron (Coulomb, spin-orbit, etc.) interaction, which we shall call v, and the interaction with the radiation field, manifested through the atomic dipole-moment operator D. The parameters of Eq.(1.2) are then[1]

$$\Gamma_K = \Gamma_K^{\text{rad}} + \Gamma_K^{\text{auto}} \tag{4.1}$$

$$\Gamma_K^{\text{rad}} = \sum_{N<K} \frac{4}{3} (\alpha\omega)^3 \frac{|\langle \Psi_N \| \underset{\sim}{D} \| \Psi_K \rangle|^2}{\varpi_K} \tag{4.2}$$

$$\Gamma_K^{\text{auto}} = \int_c \delta(E_I+\omega-E_c)\,.\,2\pi\,|\langle \Psi_K | v | \Psi_c \rangle|^2 \tag{4.3}$$

$$A_K = \frac{8}{3}\pi^2\alpha\omega \int_c \delta(E_I+\omega-E_c)\, \frac{\langle \Psi_I \| \underset{\sim}{D} \| \Psi_K \rangle}{\sqrt{\varpi_I}} \langle \Psi_K | v | \psi_c \rangle \frac{\langle \Psi_I \| \underset{\sim}{D} \| \Psi_c \rangle^*}{\sqrt{\varpi_I}} \tag{4.4}$$

$$B_K = \frac{4}{3}\frac{\pi\alpha\omega}{\varpi_I} \left\{ |\langle \Psi_I \| \underset{\sim}{D} \| \Psi_K \rangle|^2 - \pi^2 \left| \int_c \delta(E_I-\omega-E_c)\, \langle \Psi_K | v | \Psi_c \rangle\, \langle \psi_c \| \underset{\sim}{D} \| \Psi_I \rangle \right|^2 \right\} \tag{4.5}$$

$$C = \frac{4}{3}\pi\alpha\omega \int_c \delta(E_I + \omega - E_c)\, \frac{|\langle \Psi_I \| \underset{\sim}{D} \| \psi_c \rangle|^2}{\varpi_I} \;. \tag{4.6}$$

The use of reduced matrix elements $\langle \Psi_I \| D \| \Psi_K \rangle$ and intrinsic weights $\varpi_I = 2J_I + 1$ eliminates all reference to magnetic quantum numbers, because the Coulomb interaction is independent of these numbers.

As pointed out previously[1], these quantities depend explicitly on the photon energy ω. In application to resonance profiles, one may replace ω by the resonance frequency $\omega_{KI} = E_K - E_I$ without introducing appreciable error. However, when one examines the cross-section very far from resonance, as is done in deriving the Rayleigh scattering formula, it is essential to recognize that ω rather than ω_{IK} appears in the formulas.

All the preceding formulas may, of course, be written in terms of a bound-bound oscillator strength,

$$f(I \rightarrow K) \equiv f_{IK} \equiv \frac{2}{3} \omega_{KI} \frac{|\langle \Psi_I \| \underset{\sim}{D} \| \Psi_K \rangle|^2}{\varpi_I} \qquad (4.7)$$

and a bound-free (photoionization) oscillator strength,

$$\frac{df_{Ic}}{d\omega} \equiv \frac{2}{3} \omega_{cI} \frac{|\langle \Psi_I \| \underset{\sim}{D} \| \psi_c \rangle|^2}{\varpi_I} \qquad (4.8)$$

as was done previously[1], or they could be written in terms of radiative transition probabilities.

$$A^{rad}(K \rightarrow I) = \frac{4}{3} |\alpha\omega_{KI}|^3 \frac{|\langle \Psi_K \| \underset{\sim}{D} \| \Psi_I \rangle|^2}{\varpi_K} . \qquad (4.9)$$

We can then see that B_K is $2\pi\alpha$ times the bound-bound oscillator strength <u>less</u> an amount attributable to interference with the photoionization background.

Formulas (4.3) - (4.6) show that the line profile of an autoionizing line depends on the amplitude for bound-bound transition,

$$\langle \Psi_I \| \underset{\sim}{D} \| \psi_K \rangle$$

the amplitude for autoionization,

$$\langle \Psi_K | v | \psi_c \rangle$$

and the amplitude for bound-free photoionization,

$$\langle \Psi_I \| \underset{\sim}{D} \| \psi_c \rangle .$$

The present arrangement of these three quantities into the four quantities A_K, B_K, C, and Γ_K is done to simplify the algebraic expression for σ; one could as well use matrix elements directly as the basic quantities.

V. ALTERNATIVE EXPRESSIONS

It is easy to see that expression (3.33) may be written in the form

$$\sigma(a) = \sigma'_b + \sum_K \sigma_{aK} \frac{(q_K + \epsilon_K)^2}{(\epsilon_K)^2 + 1} \tag{5.1}$$

where

$$\sigma_{aK} = \frac{2\pi^2}{F_a} \left| \int_c \delta(E-E_c) \; \langle \Psi_K | V | \psi_c \rangle \;\; \langle \psi_c | V | \Psi_a \rangle \right|^2 \tag{5.2}$$

$$q_K = \frac{\langle \Psi_K | V | \psi_a \rangle}{\pi \int_c \delta(E-E_c) \; \langle \Psi_K | V | \psi_c \rangle \langle \psi_c | V | \Psi_a \rangle} \tag{5.3}$$

$$\sigma'_b = \frac{2\pi}{F_a} \int_c \delta(E-E_a) \, | \langle \Psi^P_a | V | \psi_c \rangle |^2 + \sum_K \sigma_{aK} . \tag{5.4}$$

Expression (5.1) is a possible generalization of the isolated-resonance formula suggested by Fano[16]:

$$\sigma = \sigma_b + \sigma_a \frac{(q + \epsilon)^2}{\epsilon^2 + 1} . \tag{5.5}$$

However, σ'_b is not physically meaningful, because it contains the infinite quantity $\sum \sigma_{aK}$. [The background C of expression (3.33) contains no such divergent sum.]

An alternative generalization may be obtained by recasting the resonance portion T_Q of the T operator,

$$T_Q = PtQ \frac{1}{E - H^\circ - QtQ} \cdot QtP \tag{5.6}$$

into a slightly different form. A recent paper by Feshbach[12] suggests a simple means for carrying out this rearrangement. We first write t as

$$\begin{aligned} t &= V + VG_P V - i\pi\, V\, I_P\, V \\ &\equiv VP\, \Omega^{(+)} \equiv \Omega^{(-)}\, PV \end{aligned} \tag{5.7}$$

where

$$G_p \equiv \mathcal{P} \frac{1}{E - PHP}\ , \qquad I_p \equiv P\delta(E - H)P. \tag{5.8}$$

This permits us to write

$$T_Q = \Omega^{(-)}\, PVQ\, [E - H^Q + i\pi\, QV\, I_p\, VQ]^{-1}\, QVP\ ^{(+)} \tag{5.9}$$

$$= \Omega^{(-)} PVQ \frac{1}{1 + i\pi\left[\frac{1}{E-H^Q}\ QVP\right] I_p VQ} \cdot \left[\frac{1}{E-H^Q} \cdot QVP\right] \Omega^{(+)}$$

where

$$H^Q \equiv H^\circ + QVQ + QVG_PVQ. \tag{5.10}$$

A simple rearrangement, using the identity

$$\frac{1}{1 + AB} A = A \frac{1}{1 + BA} , \tag{5.11}$$

then gives

$$T_Q = \Omega^{(-)} PVQ \left[\frac{1}{E-H^Q} QVP \right] \frac{1}{1 + i\pi\ I_P VQ \left[\frac{1}{E-H^Q} \cdot QVP \right]} \cdot \Omega^{(+)} . \tag{5.12}$$

We can now introduce a reaction operator[12]

$$K = PVQ\ [E - H^Q]^{-1}\ QVP$$

$$\equiv PVQ\ [E - H^\circ - QVQ - QVG_PVQ]^{-1}\ QVP \tag{5.13}$$

and so write the T_Q operator as

$$T_Q = \Omega^{(-)} K\ [1 + i\pi\ I_P\ K]^{-1}\ \Omega^{(+)} . \tag{5.14}$$

To proceed, I shall assume that either PVP is diagonal in the continuum of Ψ_a, or that only a single continuum occurs. This permits us to write $\Omega^{(-)}K$ as $\Omega^{(-)}I_PK$. We need next to introduce eigenstates of I_PK:

$$\langle \Upsilon_c | I_P \, V \frac{1}{E-H^Q} V | \Upsilon_{c'} \rangle = 0 \quad \text{if } c \neq c' . \tag{5.15}$$

We can then write the resonance amplitudes as

$$\begin{aligned} \langle \psi_b | T_Q | \psi_a \rangle &= \sum_c \frac{\langle \psi_b | \Omega^{(-)} I_P K | \Upsilon_c \rangle \langle \Upsilon_c | \Omega^{(+)} | \psi_a \rangle}{1 + i\pi \langle \Upsilon_c | I_P K | \Upsilon_c \rangle} \\ &= \sum_c \langle \Psi_b^- | \Upsilon_c \rangle \langle \Upsilon_c | \Psi_a^+ \rangle \\ &\qquad \times \frac{\langle \Upsilon_c | VQ \frac{1}{E-H^Q} QV | \Upsilon_c \rangle}{1 + i\pi \langle \Upsilon_c | VQ \frac{1}{E-H^Q} QV | \Upsilon_c \rangle} . \end{aligned} \tag{5.16}$$

Let us now define ϵ by

$$\frac{1}{\epsilon} \equiv \pi \langle \Upsilon_c | VQ \frac{1}{E-H^Q} QV | \Upsilon_c \rangle = \sum_K \frac{\pi | \langle \Upsilon_c | VQ | \Psi_K \rangle |^2}{E - E_K} . \tag{5.17}$$

Here I have made use of the fact that the Ψ_K states of the preceding section are eigenstates of H^Q:

$$[H^o + V + VG_PV - E_K] \, \Psi_K = 0 . \tag{5.18}$$

Next note that, because $\Psi_a^P = (1 + G_P V)\psi_a$, we can write

$$\langle \Psi_a^- | \Upsilon_c \rangle \langle \Upsilon_c | \Psi_a^+ \rangle$$

$$= \langle \psi_a | 1 + VG_P - i\pi\, VI_P | \Upsilon_c \rangle$$

$$\times \langle \Upsilon_c | 1 + G_P V - i\pi\, I_P V | \psi_a \rangle$$

$$= | \langle \Psi_a^P | \Upsilon_c \rangle |^2 - \pi^2 | \langle \Psi_a^P | VI_P | \Upsilon_c \rangle |^2$$

$$-2\pi i \langle \Psi_a^P | VI_P | \Upsilon_c \rangle \langle \Upsilon_c | \Psi_a \rangle \;. \qquad (5.19)$$

Thus we obtain the resonant part of the cross-section as

$$-\frac{2}{F_a} \operatorname{Im} \langle \psi_a | T_Q | \psi_a \rangle = \frac{2}{F_a} \sum_{K} \frac{1}{\epsilon^2+1} \; | \langle \Psi_a^P | \Upsilon_c \rangle |^2 - \pi^2 | \langle \Psi_a^P | VI_P | \Upsilon_c \rangle |^2$$

$$\times \frac{4\pi}{F_a} \sum_{K} \frac{\epsilon}{\epsilon^2+1} \cdot \langle \Psi_a^P | VI_P | \Upsilon_c \rangle \langle \Upsilon_c | \Psi_a^P \rangle \;.$$

$$(5.20)$$

In keeping with our assumption that only a single continuum contributes, we write the cross-section as

$$\sigma(a) = \frac{2\pi}{F_a} \langle \Psi_a^P | V.g_P.V | \Psi_a^P \rangle + \frac{2}{F_a} \cdot \frac{1}{\epsilon^2+1} \cdot \left\{ | \langle \Psi_a^P | \Upsilon_a \rangle |^2 - \pi^2 | \langle \Psi_a^P | V | \Upsilon_a \rangle |^2 \right\}$$

$$+ \frac{4\pi}{F_a} \cdot \frac{\epsilon}{\epsilon^2+1} \cdot \langle \Psi_a^P | VI_P | \Upsilon_a \rangle \langle \Upsilon_a | \Psi_a^P \rangle \;. \qquad (5.21)$$

We thereby obtain formula (5.5), with

$$\sigma_b' = \frac{2\pi}{F_a} \int_c \delta(E-E_c) \left\{ |\langle \psi_a|V|\Psi_c\rangle|^2 - |\langle \psi_a|V|\Upsilon_c\rangle|^2 \right\} \tag{5.22}$$

$$\sigma_a = \frac{2\pi}{F_a} |\langle \Upsilon_a|V|\psi_a\rangle|^2 \tag{5.23}$$

$$q = \frac{\langle \Psi_a^P|\Upsilon_a\rangle}{\pi \langle \Upsilon_a|V|\psi_a\rangle} \tag{5.24}$$

and ε given by Eq. (5.18). These expressions have the form of those derived by Comes and Sälzer[17], who fit observations of Krypton by Huffmann et. al[18] to formulas (5.5) and (5.18).

The preceding discussion is intended to indicate possible connections between the many-resonance formula (3.3) and previous formulas used in discussions of autoionization, not as a prescription for computing σ_a, σ_b, and q. It seems likely that the more explicit energy structure evidenced in formula (3.3) and the simple physical and mathematical significance of those profile parameters will make that formula more useful than (5.1) or (5.5) for overlapping resonances. Ultimately, of course, the validity of any parameterization must rest on empirical evidence.

VI. UNITARITY

In accord with observations, formulas (3.24) - (3.25) give B_K and A_K that may be positive, negative, or zero. The attenuation cross-section of Eq. (2.1) cannot, of course, become negative. If our approximation to the scattering amplitude T_{aa} yields a unitary scattering matrix, then Eq. (2.2) will also give non-negative cross-sections. To see that the preceding formulas are consistent with this restriction, let us write

$$\langle \psi_a | V | \Psi_K \rangle = \beta \cdot \pi \int_c \delta(E-E_c) \; \langle \Psi_a | V | \psi_c \rangle \; \langle \psi_c | V | \Psi_K \rangle . \tag{6.1}$$

To get a negative B_K we assume that $|\beta|^2 < 1$. The attenuation cross-section can then be written as

$$\begin{aligned} \sigma(a) = \frac{2\pi}{F_a} \left\{ \int_c \delta(E-E_c) \; | \langle \Psi_a^P | V | \psi \rangle |^2 \right. \\ -\pi \sum_K \left| \int_c \delta(E-E_c) \; \langle \Psi_a | V | \psi_c \rangle \langle \psi_c | V | \Psi_K \rangle \right|^2 \\ \times \frac{(1-\beta^2)(\frac{1}{2}\Gamma_K) + 2\beta(E-E_K)}{(E-E_K)^2 + (\Gamma_K/2)^2} \quad . \end{aligned} \tag{6.2}$$

Now if we define "vectors" $\underset{\sim}{a}$, $\underset{\sim}{a}^{P}$ and $\underset{\sim}{K}$ having the "components"

$$a_c \equiv \delta(E-E_c) \langle \Psi_a | V | \psi_c \rangle$$

$$a_c^P \equiv \delta(E-E_c) \langle \Psi_a^P | V | \psi_c \rangle$$

$$K_c \equiv \delta(E-E_c) \langle \Psi_K | V | \psi_c \rangle \qquad (6.3)$$

then we can write

$$\int_c \delta(E-E_c) \quad \langle \Psi_a | V | \psi_c \rangle \langle \psi_c | V | \Psi_K \rangle = \underset{\sim}{a} \cdot \underset{\sim}{K} \qquad (6.4)$$

$$\Gamma_K = 2\pi |\underset{\sim}{K}|^2 . \qquad (6.5)$$

The cross-section then takes the form

$$\sigma(a) = \frac{2\pi}{F_a} \left\{ |\underset{\sim}{a}^P|^2 - \sum_K \frac{|\underset{\sim}{a} \cdot \underset{\sim}{K}|^2}{|\underset{\sim}{K}|^2} \cdot \frac{(\frac{1}{2}\Gamma_K)^2 - \beta^2(\frac{1}{2}\Gamma_K) + 2\beta(\frac{1}{2}\Gamma_K)(E-E_K)}{(E-E_K)^2 + (\frac{1}{2}\Gamma_K)^2} \right\} .$$

The most extreme value occurs if all resonances occur at the same energy E_K. The Q collection then consists of those degenerate bound states corresponding to energy E_K, and there is no distinction between $\Psi_a^P = \Lambda_P \psi_a$ and $\Psi_a = \Lambda \psi_a$. Under these conditions the minimum, which occurs when $\beta = 0$, is

$$\sigma(a) = \frac{2\pi}{F_a} \left\{ |\underset{\sim}{a}|^2 - \sum_{K} \frac{|\underset{\sim}{a}\cdot\underset{\sim}{K}|^2}{|\underset{\sim}{K}|^2} \right\} . \tag{6.7}$$

The summation cannot exceed $|\underset{\sim}{a}|^2$, because it is the sum of the "direction cosines" in a set of independent "directions." That is, the summation goes over a set (the entire Q collection) of independent (orthogonal) states. Thus the cross-section cannot become negative. The minimum value (zero) occurs, as Fano noted[16], when the resonance states interact with only a single continuum, because then

$$|\underset{\sim}{a}\cdot\underset{\sim}{K}|^2 = |\langle \Psi_a|V|\psi_c\rangle\langle\psi_c|V|\Psi_K\rangle|^2 = |\underset{\sim}{a}|^2 x |\underset{\sim}{K}|^2 . \tag{6.8}$$

The photon continuum is independent of the electron continuum, so that (6.8) holds also when a single photon continuum and a single electron continuum are both present. The preceding arguments apply to overlapping degenerate resonances as well as to a sum of isolated resonances.

VII. THRESHOLDS

The basic division into P states (open channels) and Q states (closed channels) adopted in the present discussion is energy-dependent. With increasing projectile energy, channels that once were closed become accessible for reactions. As a simple example, we might progress from consideration of $(1s)^2\ 2p$ to $1s\ 10s\ 2p$ to the continuum of $1s\ \epsilon s\ 2p$. At the ionization limit $1s\ \infty s\ 2p$ (or $1s\ 0s\ 2p$) the influence of these states must be transferred from the resonance amplitude T_Q into the "direct" background amplitude T_P. The presence of a new continuum manifests itself as a threshold for an additional process.

Just below threshold, in an energy interval Δ which includes numerous resonances converging to a limit at the threshold energy, the energy-averaged cross-section is

$$\begin{aligned}
\Delta^{-1}\int dE\ \sigma(a) &= \Delta^{-1}\left[\int dE\ C + \sum_K \pi\ B_K\right] \\
&= \Delta^{-1}\ \frac{2\pi}{F_a}\Bigg\{\int dE\ \mathop{\mathsf{S}}_c \delta(E-E_c)\,|\langle\Psi_a|V|\psi_c\rangle|^2 \\
&\qquad + \sum_K |\langle\Psi_a|V|\Psi_K\rangle|^2 \\
&\qquad -\pi^2 \sum_K \Big|\mathop{\mathsf{S}}_c \delta(E-E_c)\,\langle\Psi_a|V|\psi_c\rangle\langle\psi_c|V|\Psi_K\rangle\Big|^2\Bigg\}\ . \qquad (7.1)
\end{aligned}$$

Because of the negative interference term, the cross-section can be quite small. In the absence of appreciable contribution from the continuum ψ_c, this expression reads

$$\Delta^{-1} \int dE\ \sigma(a) = \Delta^{-1} \frac{2\pi}{F_a} \sum_K | \langle \Psi_a | V | \Psi_K \rangle |^2 . \qquad (7.2)$$

Just above threshold, the resonance states Ψ_K become continuum states, say Ψ_b, and we have

$$\Delta^{-1} \int dE\ \sigma(a) = \Delta^{-1} \frac{2\pi}{F_a} \left\{ \int dE \int_c \delta(E-E_c) | \langle \Psi_a | V | \psi_c \rangle |^2 + \int dE \int_b \delta(E-E_b) | \langle \Psi_a | V | \psi_b \rangle |^2 \right\} . \qquad (7.3)$$

The interference is now absent. Formulas (7.2) and (7.3) show that cross-sections need not display a discontinuous threshold behavior, even though the influence of a particular configuration transfers abruptly from T_Q to T_P.

It may happen, however, that the entire series occurs over a very brief energy interval, so that the cross-section may, for practical purposes, be considered as changing abruptly. This situation occurs with X-ray attenuation: absorption coefficients are customarily regarded as increasing discontinuously at thresholds, because the allowed Rydberg series occupies only a short interval below the threshold.

Note that the present formulas permit the occurrence of a series of autoionizing lines overlying the region near an ionization limit. Since the resonance states are independent, the cross-section appears as a superposition of the threshold behavior of Eqs. (7.1) - (7.3) and the resonance structure of formula (1.2). However, the present approach does not explicitly display the interesting intensity variations, attributable to configuration mixing of bound states, which occur in a Rydberg series.

VIII. ENERGY VARIATION OF PARAMETERS

Formula (1.1) will be of use when the quantities A_K, B_K, and E_K and Γ_K vary little with energy E over the interval of interest. Under what conditions can we consider these quantities to be constant parameters?

The possible energy variation, as shown by formulas (3.19), (3.22) - (3.25) and (4.1) - (4.6), comprises two types: the energy variation caused by distortion (and expressed as principal value integrals involving the varying energy), and an energy variation caused by the change of continuum integrals such as $\langle \Psi_K | V | \Psi_a \rangle$. (For photon processes, there is also an explicit dependence on photon energy.) We expect the distortion change to be small over the energy interval spanned by a resonance, so that the major variation of A_K, B_K, and C with E may be attributed to the change of the continuum wavefunction. Such slow variations have been previously studied with the quantum defect formulation[18], although the same structure should emerge from computations that employ an effective potential. For the autoionizing lines hitherto identified, the continuum varies sufficiently slowly over a few widths Γ_K that we can expect A_K and B_K to be constants characteristic of each resonance. Verification of this assumption [and the utility of formula (1.2)] will require detailed examination of observational data.

There are, of course, regularities in successive values of A_K, B_K, and Γ_K as one progresses along a series of lines. In part, these variations come from the continuum structure just mentioned. In part, the regularities reflect variations of single-particle orbitals, such as the $n^{-3/2}$ behavior of the hydrogenic wavefunction $P_{n\ell}$. And in part, the variations may be manifestations of the configuration mixing of bound states. These influences deserve further attention, although I shall not discuss them here.

IX. EMISSION PROFILES

The absorption profile (1.2) is observed in the limit of a cold, gaseous, optically thin absorbing medium; under these conditions the specific monochromatic intensity passing through a thickness dx diminishes according to the formula

$$-dI(\omega) = dx \sum_{I_0} N(I_0)\ \sigma(I_0,\ \omega) \qquad (9.1)$$

where $N(I_0)$ is the number of atoms per unit volume in state I_0

The derivation of Eq. (1.2) from scattering theory made clear the applicability to autoionizing-line profiles observed in absorption spectroscopy. The same profiles should usually be observed in emission spectroscopy. That is, the monochromatic specific intensity emitted by an optically thin source of thickness dx, containing N_e free electrons per unit volume and $N(I_1)$ ions per unit volume in ground state I_1, is

$$dI(\omega) = dx\ \frac{N_e}{\varpi_e}\ \frac{N(I_1)}{\varpi(I_1)}\ \frac{2\pi\alpha^2\omega^3}{(2\pi kT)^{3/2}} \sum_{I_0} \exp(-E/kT)\ \varpi(I_0)\ \sigma(I_0,\omega), \qquad (9.2)$$

where I_0 denotes a state of the atom, formed by electron capture followed by photon decay, and ϖ_e, $\varpi(I_1)$, and $\varpi(I_0)$ are the intrinsic statistical weights of electron, target ion, and product atom respectively. The exponential energy E is

$$E = E(I_o) + \omega - E(I_1). \tag{9.3}$$

Equation (9.2) is most easily obtained by writing

$$dI(\omega) = \frac{\omega}{4\pi} \cdot dx \int_c N(c) \sum_{I_o} \delta(E(I_o)+\omega-E(c))\, v \cdot \sigma(c \to I_o, \omega) \tag{9.4}$$

and assuming that the electrons have a Maxwellian velocity distribution and the ion states I_1' are populated as in equilibrium:

$$\int_c N(c) = \sum_{I_1'} \int_C \int d\epsilon \left\{ N(I_1)\, \frac{\varpi(I_1')}{\varpi(I_1)}\, \exp(-\Delta/kT) \right\} \times \left\{ N_e\, \frac{4\pi v^2}{(2\pi kT)^{3/2}}\, \exp(-\epsilon/kT)\, \frac{dv}{d\epsilon} \right\}. \tag{9.5}$$

Here $\Delta \equiv E(I_1') - E(I_1)$, and C refers to quantum numbers of the composite system of electron plus ion. One can then use the reciprocity relation

$$\sigma(I_1'\, C, \epsilon \to I_o, \omega) = \frac{2\pi\alpha^2\omega^2}{v^2} \cdot \frac{\varpi(I_o)}{\varpi_e \varpi(I_1)} \cdot \sigma(I_o, \omega \to I_1' C, \epsilon) \tag{9.6}$$

and the fact that, for the profiles of interest, photon scattering is negligible (that is, the autoionizing widths greatly exceed the "natural" radiative widths). Substitution of Eqs. (9.5) and (9.6) into (9.4) then gives formula (9.2).

Formulas (9.1) and (9.2) state that (as one expects from simple thermodynamic arguments) an emission spectrum and the corresponding absorption spectrum show the same profiles, apart from a numerical factor. The absorption profiles of autoionizing lines, as parameterized in Eq. (1.2), may appear as "windows" ($B_K < 0$) or as asymmetric profiles ($A_K \neq 0$). Such profiles, often referred to as Beutler-Fano profiles, occur because of interference between direct photoionization and photoexcitation followed by autoionization. Autoionizing lines in emission are superposed on a background of free-bound and free-free emission. Beutler-Fano profiles then occur because of interference between free-bound emission and electron capture followed by photon emission. Thus transitions which appear as bright features ("window" resonances) in absorption will appear, in emission, as dark features. (Bright or dark here refer to greater or less intensity than adjacent continuum.)

However, Eq. (9.2) does not always apply. In particular, when radiative widths are comparable to autoionizing widths, we can no longer identify photoionization $\sigma(I_0, \omega \rightarrow I_1' C, \varepsilon)$ with the attenuation cross-section $\sigma(I_0, \omega)$. The simplification permitted by the optical theorem no longer obtains, and the profiles may show interference between resonances.

ACKNOWLEDGEMENTS

I am indebted to Dr. David Ederer for questioning the possibility of negative cross-sections from Eq. (1.2), to Dr. George Rybicki for discussing bi-orthogonal expansions, and to Dr. Eugene Avrett for explaining radiative transfer equations. I have also benefitted from numerous conversations with Dr. David Burgess.

This work has been supported by the NASA through grant NsG-438.

FOOTNOTES

[1] B.W. Shore, Rev. Mod. Phys. **39**, 439 (1967) (Paper I).

[2] B.W. Shore, J. Opt. Soc. Am. **57**, 881 (1967) Paper II).

[3] P.G. Burke, Advances in Physics **14**, 521 (1965).

[4] K. Smith, Reports on Progress in Physics **29**, 373 (1966).

[5] R. Peterkop and V. Veldre; in Advances in Atomic and Molecular Physics (Academic Press, New York) **2**, 263 (1966).

[6] Reference 1 gives a more complete discussion of the basic quantities used here. In summary, ψ_a, ψ_b, and ψ_c are continuum eigenstates of $H^\circ \equiv H-V$, $\delta(x)$ is the Dirac delta, and E^+ stands for $E + i\eta$ where $\eta \rightarrow 0+$.

[7] L. Fonda and R.G. Newton, Ann. Phys. (N.Y.) **10**, 490 (1960).

[8] H. Feshbach, Ann. Phys. (N.Y.) **19**, 287 (1962).

[9] F.A. Zhivopistsev, Yadernaya Fiz. **1**, 600 (1965), English transl.: Soc. J. Nucl. Phys. **1**, 429 (1965).

[10] Most of the results require only that Q should exclude the initial state. The present definition, discussed in reference 1, proves useful when applying perturbation theory.

[11] cf. P.A.M. Dirac, The Principles of Quantum Mechanics (Oxford University Press, London, 1958) 4th. ed. p.32.

[12] H. Feshbach, Ann. Phys. (N.Y.) **43**, 416 (1967).

[13] Paper 1 paid insufficient attention to the complex nature of the bi-orthogonal expansion and normalization; in effect, it replaced Φ_K by the zero-order approximation φ_K. That deficiency is here corrected.

[14] B.A. Lippmann and J. Schwinger, Phys. Rev. 79, 469 (1950).

[15] Reference 1 denoted these quantities as $\bar{A}_K$, $\bar{B}_K$, and $\bar{C}$, in order to emphasize averaging over polarization and orientation. The weight ϖ was denoted by g in reference 1.

[16] U. Fano, Phys. Rev. **124**, 1866 (1961).

[17] F.J. Comes and H.G. Sälzer, Phys. Rev. **152**, 29 (1966).

[18] R.E. Huffman, Y. Tanaka, and I.C. Larrabee, J. Chem. Phys. **39**, 902 (1963).

[19] For example A . Burgess and M.J. Seaton, Mon. Not. Roy. Ast. Soc. **120**, 121 (1960); G. Peach, Mon. Not. Roy. Ast. Soc. **124**, 371 (1962).