Interference between radiative emission and autoionization in the decay of excited states of atoms

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An excited state of an atom which can autoionize can also undergo radiative decay. We consider the interaction between the final states resulting from these two modes of decay, and its effects on such quantities as the fluorescence yield of the excited state, excitation profile of the excited state, and the spectra of the emitted photons and electrons. It is shown that the fraction of decays of the excited state resulting in a photon (fluorescence yield) is particularly sensitive to the details of the final-state interaction. In lowest order in the final-state interaction, the fluorescence yield is increased by a factor $(1 + 1/q^2)$ from the traditional value, where q is the Fano q parameter relating to the excited state and the final atomic state.

I. INTRODUCTION

An excited state of an atom which can autoionize can also decay to a lower-lying state of the atom via spontaneous emission of a photon. For neutral atoms, the lifetimes of these excited states due to allowed autoionization (typically 10^{-15}–10^{-13} sec) are shorter by many orders of magnitude than the lifetimes due to allowed $E1$ transitions (typically 10^{-9} sec). In these cases one is quite justified in neglecting the emission process in theoretical[1] and experimental[2] analysis of these states. However, if the excited state is forbidden to autoionize in the LS coupling scheme the rates of these two processes can become comparable[3]— or the spontaneous emission rate may even become dominant. In addition, the two rates may become comparable in excited states of highly stripped ions. This occurs because autoionizing rates are roughly Z independent (Z is the effective nuclear charge), while dipole rates vary roughly as Z^4. For the same reason, in heavy atoms, the emission rate may dominate the ionization rate for excited states involving one or more inner-shell excitations[4]; this is reflected in a fluorescence yield of the order of $\frac{1}{2}$ or greater. Recently developed techniques for carrying out Stark studies of autoionizing states also hold promise of allowing studies in regimes where autoionizing and spontaneous decay rates are comparable, since both rates can be "tuned" through application of electric fields.[5]

Traditional theoretical analyses of the autoionization process either do not consider the possibility of spontaneous emission of the excited state,[1] or assume that the two processes are additive.[6] However, as we shall show below these processes should not, in many cases, be treated as simply additive. Rather, there is competitive interference between the two processes which greatly complicates the problem and may cause significant corrections to the usual expressions for the fraction of atoms decaying either via autoionization or via spontaneous emission.

In the following we will use the word "atom" to indicate either an atom or an ion and the word "ion" to indicate the next stage of ionization.

In Sec. II, we consider the problem of an atom in an excited state $|a\rangle$ which can decay either via autoionization to an ionic state $|i\rangle$ or via spontaneous emission to an atomic state $|f\rangle$. In Sec. III, we will approximate the rather complicated results of Sec. II in order to indicate the magnitude of the effects which can be expected. In Sec. IV, we consider several experiments which could be carried out on a system such as discussed in Sec. II. In Sec. V, we extend the results of Secs. II and III to the more general (and realistic) case in which the state $|a\rangle$ can decay via spontaneous emission to a set of states $|f_i\rangle$; in Sec. VI, we consider the case in which the state $|a\rangle$ can decay via autoionization to a set of states $|i_j\rangle$. Finally, in Sec. VII, we present our conclusions.

II. THEORY: TWO-LEVEL ATOM

Let us consider the case of an excited state $|a\rangle$ of an atom which can decay either via autoionization to the state $|i\rangle$ of the ion, emitting an electron of energy e, or via spontaneous emission of a photon having a definite angular momentum and energy ω ($\hbar = 1$) leaving the atom in the state $|f\rangle$. We denote the former state of ion plus electron by $|ie\rangle$, and the latter state of atom plus photon by $|f\omega\rangle$. For later use, we shall specify that $|ie\rangle$ and $|f\rangle$ are all given in terms of time-independent position state wave functions; $|\omega\rangle$ is, as usual, a state in the occupation number representation. We shall further assume that $|ie\rangle$ can also decay to $|f\omega\rangle$ through action of the atom-field Hamilton-

ian H_{AF}. We shall generalize to the case in which many final states $|f\omega)$ of the atom exist, or in which many possible states of the ion plus electron exist, in following sections.

The Hamiltonian for this system can be written in the form

$$H = H_A + H_F + H_{AF},\qquad(1)$$

where H_A is the atomic term; H_F the field term; and H_{AF} the atom-field interaction. The states $|a)$, $|f\omega)$, and $|ie)$ will be assumed to satisfy

$$(a|H|a) = E_a,$$
$$(f\omega|H|f\omega') = \delta(\omega - \omega')(E_f + \omega) \equiv E_\omega \delta(\omega - \omega'),$$
$$(ie|H|ie') = \delta(e - e')(E_i + e) \equiv E_e \delta(e - e'),$$
$$(a|H|f\omega) = (a|H_{AF}|f\omega) \equiv H_{a\omega},$$
$$(a|H|ie) = (a|H_A|ie) \equiv H_{ae},$$
$$(ie|H|f\omega) = (ie|H_{AF}|f\omega) \equiv H_{e\omega}.$$

(2)

We will take both $|ie)$ and $|f\omega)$ to have δ-function normalization

$$(f\omega|f\omega') = \delta(\omega - \omega'),$$
$$(ie|ie') = \delta(e - e').$$

(3)

Let us first consider the case in which the atom is in the state $|a)$ at $t = 0$. At $t > 0$ the wave function can be expanded as

$$|\psi) = \alpha_a(t)|a) + \int de\,\alpha_e(t)|ie) + \int d\omega\,\alpha_\omega(t)|f\omega)$$

(4)

and satisfies

$$H|\psi) = i\frac{\partial}{\partial t}|\psi).\qquad(5)$$

Note that both $|ie)$ and $|f\omega)$ belong to continua of states with, in the former case, the energy of the emitted electron belonging to a continuum, and, in the latter, the energy of the photon belonging to a continuum. This fact, plus the fact that $(ie|H_{AF}|f\omega) \neq 0$, greatly complicates the solution of this problem. To see this we substitute (4) into (5) and manipulate further to obtain [using (1)]

$$i\dot{\alpha}_a(t) - E_a\alpha_a(t) = \int de\,\alpha_e(t)H_{ae}$$
$$+ \int d\omega\,\alpha_\omega(t)H_{a\omega} + i\delta(t),$$
$$i\dot{\alpha}_e(t) - E_e\alpha_e(t) = \alpha_a(t)H_{ea} + \int d\omega\,\alpha_\omega(t)H_{e\omega},$$
$$i\dot{\alpha}_\omega(t) - E_\omega\alpha_\omega(t) = \alpha_a(t)H_{\omega a} + \int de\,\alpha_e(t)H_{\omega e}.$$

(6)

We Fourier transform Eqs. (6) according to[7]

$$\alpha_j(t) = -\frac{1}{2\pi i}\int_{-\infty+i\epsilon}^{+\infty+i\epsilon} G_j(z)e^{-izt}\,dz\qquad(7)$$

obtaining the algebraic equations

$$(z - E_a)G_a = \int de\,H_{ae}G_e + \int d\omega\,H_{a\omega}G_\omega + 1,$$
$$(z - E_e)G_e = H_{ea}G_a + \int d\omega\,H_{e\omega}G_\omega,$$
$$(z - E_\omega)G_\omega = H_{\omega a}G_a + \int de\,H_{\omega e}G_e.$$

(8)

Unfortunately, these equations are not easily solved due to the coupling between the two continua.[7a] It is therefore more convenient to start not with $|ie)$ and $|f\omega)$ but with two sets of new states $|1E\}$ and $|2E\}$ which are already diagonal with respect to H_{AF}. The decay of $|a)$ into these states can then easily be evaluated, using the technique of Fourier transformation just described, as there will be no coupling between these two new continua.

One of the most straightforward techniques for "diagonalizing" continua involves the use of the so-called "reaction" or K matrix.[8,9] A detailed discussion of this approach can be found in Refs. 8 and 9. Briefly, we are searching for a wave function $|E\}$ satisfying:

$$H|E\} = E|E\},\qquad(9)$$

where $|E\}$ is composed of states from the continua $|f\omega)$ and $|ie)$. In particular, it can be shown that Eq. (9) is satisfied by

$$|E\} = \sum_l \left(|lE) + \sum_j \mathcal{P}\int dE'\,\frac{|jE')K_{jE',lE}}{E - E'}\right)B_l(E),$$

(10)

where $|lE)$ is either the state $|f\omega)$ of energy $E_\omega = E$, or the state $|ie)$ of energy $E_e = E$, $\mathcal{P}$ indicates principal value integration, and the K-matrix element $K_{jE',lE}$ satisfies the integral equation

$$K_{jE',lE} = (jE'|H_{AF}|lE)$$
$$+ \sum_k \mathcal{P}\int dE''\,\frac{(jE'|H_{AF}|kE'')K_{kE'',lE}}{E - E''}.\qquad(11)$$

Equation (9) is satisfied for any value of the constants $B_l(E)$; we shall choose them such that the wave functions $|E\}$ have the desired asymptotic form.

Physically, it is clear that, at large distances from the atom, one of the solutions (10) should correspond to an ion in the state $|i)$ plus an outgoing electron of energy e, and the other solution should correspond to the atom in the state $|f)$ plus a photon of energy ω. Mathematically, this means that as we let the coordinates of one electron, the nth, for example, in an n-electron atom, go to

infinity, we will get in the former case an asymptotic dependence of the type

$$|1E\} \xrightarrow[r_n \to \infty]{} |i; r_1, r_2, \ldots, r_{n-1})(C_i/r_n) \sin(kr_n + \delta_k)$$

(12)

and, in the latter case,

$$|2E\} \xrightarrow[r_n \to \infty]{} |f^{-1}; r_1, r_2, \ldots, r_{n-1})C_f e^{-\kappa r_n},$$

(13)

where in (12) k is the momentum of the outgoing electron (in the continuum) and δ_k is the total phaseshift associated with this electron. $|f^{-1}; r_1, \ldots, r_{n-1})$ is the wave function for the atom with its nth electron removed; the wave function of this electron has an asymptotic dependence $e^{-\kappa r_n}$, where κ is real and positive.

Inserting these asymptotic values into Eq. (10) and carrying out the principal-value integrals, one finds that the solution of (9) which has the asymptotic form of an ion plus electron is

$$|1E\} = \Delta(E)^{-1}\{[1 - i\pi K_{\omega\omega}(E)]|ie\rangle + i\pi K_{\omega e}(E)|f\omega\rangle\}$$

$$\xrightarrow[r \to \infty]{} |ie)$$

(14)

and the solution which has the asymptotic form of an atom plus photon is

$$|2E\} = \Delta(E)^{-1}\{[1 - i\pi K_{ee}(E)]|f\omega\rangle + i\pi K_{e\omega}(E)|ie\rangle\}$$

$$\xrightarrow[r \to \infty]{} |f\omega).$$

(15)

In Eqs. (14) and (15) $K_{ab}(E)$ is an "on the energy shell" element of the K matrix[9]

$$K_{ab}(E) = K_{aE, bE}.$$

(16)

$|ie\rangle$ and $|f\omega\rangle$ are the states $|ie)$ and $|f\omega)$, respectively, modified by admixtures of other continuum states:

$$|ie\rangle = |ie) + \mathcal{P} \int de' \frac{|ie')K_{e'E', eE}}{E - E'}$$

$$+ \mathcal{P} \int d\omega' \frac{|f\omega')K_{\omega'E', eE}}{E - E'},$$

(17)

$$|f\omega\rangle = |f\omega) + \mathcal{P} \int de' \frac{|ie')K_{e'E', \omega E}}{E - E'}$$

$$+ \mathcal{P} \int d\omega' \frac{|f\omega')K_{\omega'E', \omega E}}{E - E'}$$

(18)

and

$$\Delta(E) = \det|1 - i\pi K(E)|,$$

$$= [1 - i\pi K_{ee}(E)][1 - i\pi K_{\omega\omega}(E)] + \pi^2 |K_{e\omega}(E)|^2.$$

(19)

The states $|1E\}$ and $|2E\}$ satisfy the orthonormality condition (see Appendix)

$$\{iE | jE'\} = \delta(i, j)\delta(E - E').$$

(20)

One can now calculate the decay of the state $|a)$ into the two continua $|1E\}$ and $|2E\}$. With the system being at state $|a)$ at $t = 0$, its wave function at $t > 0$ will be given by

$$|\psi\rangle_t = \alpha_a(t)|a) + \int dE_1 \alpha_{1E_1}(t)|1E\}$$

$$+ \int dE_2 \alpha_{2E_2}(t)|2E\}.$$

(21)

Proceeding as before one obtains the Green's function equations:

$$(z - E_a)G_a = \int dE_1 H_{a, 1E_1} G_{1E_1}$$

$$+ \int dE_2 H_{a, 2E_2} G_{2E_2} + 1,$$

$$(z - E_1)G_{1E_1} = H_{1E_1, a} G_a,$$

$$(z - E_2)G_{2E_2} = H_{2E_2, a} G_a.$$

(22)

Solving the last two of equations (22) for G_{iE_i} and substituting in the first, one obtains

$$[z - \omega_a(z) + i\gamma_a(z)/2]G_a(z) = 1$$

(23)

with

$$\omega_a(z) = E_a + \mathcal{P} \int dE_1 \frac{|H_{a, 1E_1}|^2}{z - E_1} + \mathcal{P} \int dE_2 \frac{|H_{a, 2E_2}|^2}{z - E_2},$$

$$\gamma_a(z) = 2\pi[|H_{a, 1E}|^2_{E=z} + |H_{a, 2E}|^2_{E=z}].$$

(24)

We shall make the usual assumption[7,10] that the matrix elements in (24) are varying with energy E slowly enough that one can replace z by E_a in both $\omega_a(z)$ and $\gamma_a(z)$. We shall comment on the validity of this assumption below. With this approximation we replace $\omega_a(z)$ and $\gamma_a(z)$ by

$$W_a = \omega_a(z = E_a),$$

$$\Gamma_a = \gamma_a(z = E_a),$$

(25)

and (23) becomes

$$(z - W_a + i\Gamma_a/2)G_a(z) \cong 1.$$

(26)

Inserting the value of $G_a(z)$ obtained from (26) into the Fourier transform (7) we find the probability of being in the state $|a)$ as a function of time:

$$P(t) = |\alpha_a(t)|^2 = e^{-\Gamma_a t}.$$

(27)

We can further calculate what fraction of the decay produces an electron $[|a) \to |1E\}]$ and what fraction produces a photon $[|a) \to |2E\}]$. Using Eqs. (22) and (23) one finds

$$G_{1E_1} = [H_{1E_1, a}/(z - E_1)]G_a$$

$$= \frac{H_{1E_1, a}}{(z - E_1)[z - \omega_a(z) + i\gamma_a(z)/2]}.$$

(28)

We need only find the components of α_{1E_1} which survive as $t \to \infty$, since these correspond to what

will be measured. Using the method of residues one obtains

$$\alpha_{1E_1}(t \to \infty) = \frac{H_{1E_1,a}}{E_1 - \omega_a(E_1) + i\gamma_a(E_1)/2} e^{-iE_1 t}.$$ (29)

The total probability of finding an emitted electron as $t \to \infty$ is then

$$\mathfrak{F}_e = \int dE_1 \, |\alpha_{1E_1}(t \to \infty)|^2$$

$$= \int dE_1 \, \frac{|H_{1E_1,a}|^2}{(E_1 - \omega_a(E_1) + i\gamma_a(E_1)/2)(E_1 - \omega_a(E_1) - i\gamma_a(E_1)/2)}$$

$$= \frac{2\pi |H_{1E_1,a}|^2_{E_1 \simeq W_a}}{\Gamma_a} \equiv \frac{\Gamma_1}{\Gamma_a},$$ (30)

where $\omega_a(E_1)$ and $\gamma_a(E_1)$ can be obtained from (24). In obtaining the last part of Eq. (30), we have again supposed that the quantities $\omega_a(E_1)$, $\gamma_a(E_1)$, and $H_{1E_1,a}$ are not strong functions of the energy E_1, and that they can be treated as constants equal to W_a, Γ_a and $H_{1E_1,a}|_{E_1=W_a}$, respectively, in the integration over E_1. Finally, using Eq. (14) one finds

$$\Gamma_a \mathfrak{F}_e = |\Delta(E)|^{-2} 2\pi\{(1 + \pi^2 |K_{\omega\omega}|^2)|(a|H|ie)|^2$$
$$+ \pi^2 |K_{\omega e}|^2 |(a|H|f\omega)|^2$$
$$+ 2\pi \, \text{Im}[(1 - i\pi K_{\omega\omega})K^*_{\omega e}$$
$$\times \langle f\omega|H|a)(a|H|ie\rangle]\},$$ (31)

where the "on energy shell" elements of the K matrix are evaluated at $E = E_a$.

In a like manner, we find that the fluorescence yield, or relative probability of decaying into the states $|2E\}$—emitting a photon—is just

$$\Gamma_a \mathfrak{F}_p = \frac{2\pi |H_{2E_2,a}|^2_{E_2 \simeq W_a}}{\Gamma_a} \equiv \frac{\Gamma_2}{\Gamma_a},$$ (32)

which becomes, using Eq. (15),

$$\Gamma_a \mathfrak{F}_p = |\Delta(E)|^{-2} 2\pi\{(1 + \pi^2 |K_{ee}|^2)|(a|H|f\omega)|^2$$
$$+ \pi^2 |K_{e\omega}|^2 |(a|H|ie)|^2$$
$$+ 2\pi \, \text{Im}[(1 - i\pi K_{ee})K^*_{e\omega}$$
$$\times \langle ie|H|a)(a|H|f\omega\rangle]\}.$$ (33)

At this point we introduce a parameter q_f by extending Fano's analogous definition[1]:

$$q_f = \frac{(a|H|f\omega)}{\pi(a|H|ie)K_{e\omega}}\bigg|_{E=E_a}.$$ (34)

Examining the definition of the matrix elements (2) and of the K matrix (11) we note that $K_{ee}, K_{\omega\omega}$, and q_f are real quantities. Now using the definition (34), we write

$$\pi K_{e\omega} = (1/q_f)(a|H|f\omega)/(a|H|ie);$$ (34')

introducing this in Eqs. (31) and (32) we obtain the compact expressions

$$\Gamma_a \mathfrak{F}_p = \frac{2\pi |(a|H|ie)|^2}{|\Delta(E)|^2}$$
$$\times \left[1 + \left(\pi K_{\omega\omega} - \frac{1}{q_f} \frac{|(a|H|f\omega)|^2}{|(a|H|ie)|^2}\right)^2\right]$$ (35)

and

$$\Gamma_a \mathfrak{F}_p = \frac{2\pi |(a|H|f\omega)|^2}{|\Delta(E)|^2} \left[1 + \left(\pi K_{ee} - \frac{1}{q_f}\right)^2\right].$$ (36)

Now, since we have simply "diagonalized an energy matrix" in going from the continua $|f\omega)$ and $|ie)$ to the new continua $|1E\}$ and $|2E\}$, the transformation between the two sets must be unitary. Thus we must also have that

$$\Gamma_a = \Gamma_a^0 \equiv 2\pi[|(a|H|f\omega)|^2_{E_\omega=E_a} + |(a|H|ie)|^2_{E_e=E_a}],$$ (37)

i.e., the total probability of decay of $|a)$ should be invariant under a basis set transformation. Any lack of equality between Γ_a^0 and Γ_a is an indication that the approximations used in resolving Eqs. (22) are in error. That is, that one cannot treat $\gamma_a(z)$ and $\omega_a(z)$ as constants.

Even though the total decay probability should be equal for the two "representations" this is not necessarily true for the relative probabilities in (30) and (32). Thus $\mathfrak{F}_e$ and $\mathfrak{F}_p$ can differ from the traditional fractions going into each of the decay channels

$$F_e = 2\pi |(a|H|ie)|^2_{E_e=E_a}/\Gamma_a^0$$ (38)

and

$$F_p = 2\pi |(a|H|f\omega)|^2_{E_\omega=E_a}/\Gamma_a^0.$$ (39)

In Sec. III, we shall consider this point in more detail. (We shall henceforth leave off the subscripts which indicate the energy at which the matrix elements are to be evaluated, since it is always at the energy conserving value.)

III. APPROXIMATE BRANCHING RATIOS

In order to investigate the differences between the usual branching ratios F_e and F_p, and the more complicated ratios $\mathfrak{F}_e$ and $\mathfrak{F}_p$ derived in Sec. II, we shall consider an approximation to the K matrix defined by Eq. (11). In particular we will keep only the lowest-order term in an expansion of K in powers of H_{AF}. Thus

$$K_{\omega E, eE'} \cong (f\omega, E | H_{AF} | ie, E'), \tag{40a}$$

$$K_{\omega E, \omega'E'} \cong K_{eE, e'E'} \cong 0, \tag{40b}$$

and from Eq. (19)

$$|\Delta(E)|^2 = (1 + \pi^2 |H_{e\omega}|^2)^2 \tag{41}$$

In this limit, the definition of q_f [Eq. (34)] becomes identical to that of Fano.[1]

Since, from Eqs. (25), (30), (32), and (37)

$$\mathfrak{F}_e + \mathfrak{F}_p = 1,$$

Γ_a can be obtained in this approximation by adding together the resulting (35) and (36).

$$\Gamma_a = \Gamma_a(\mathfrak{F}_e + \mathfrak{F}_p)$$

$$= \frac{2\pi}{1 + \pi^2 |H_{e\omega}|^2} [|(a|H|ie)|^2 + (a|H|f\omega)|^2]. \tag{42}$$

Since this is not obviously equal to Γ_a^0, it is not clear that unitarity is preserved at this level of approximation. However, it will be approximately preserved if $\pi^2 |H_{e\omega}|^2 \ll 1$, i.e., if the final-state interaction is small.

If we now further approximate $(a|H|ie)$ and $(a|H|f\omega)$ by their first terms (omit principal value integrals), we find

$$\pi^2 |H_{e\omega}|^2 = \frac{1}{q_f^2} \frac{|(a|H|f\omega)|^2}{|(a|H|ie)|^2} = \frac{1}{q_f^2} \frac{F_p}{F_e} \tag{43}$$

and

$$\Gamma_a = \Gamma_a^0 \left(1 + \frac{1}{q_f^2} \frac{F_p}{F_e}\right)^{-1}.$$

Then

$$\Gamma_a \mathfrak{F}_e \cong \left[2\pi |(a|H|ie)|^2 \Big/ \left(1 + \frac{1}{q_f^2} \frac{F_p}{F_e}\right)^2 \right]$$

$$\times \left(1 + \frac{1}{q_f^2} \frac{|(a|H|f\omega)|^4}{|(a|H|ie)|^4} \right),$$

or

$$\mathfrak{F}_e = \left[F_e \Big/ \left(1 + \frac{1}{q_f^2} \frac{F_p}{F_e}\right) \right] \left[1 + \frac{1}{q_f^2} \left(\frac{F_p}{F_e}\right)^2 \right] \tag{44}$$

and

$$\mathfrak{F}_p = \left[F_p \Big/ \left(1 + \frac{1}{q_f^2} \frac{F_p}{F_e}\right) \right] \left(1 + \frac{1}{q_f^2}\right). \tag{45}$$

Equations (44) and (45) indicate that, if q_f is small,

the correction to the radiative fraction (fluorescence yield) can be quite large independent of F_p/F_e. If F_p/F_e is larger than 1, then the correction to F_e can also be large. However, as noted above, if $(1/q_f^2)(F_p/F_e)$ is large, unitarity may be strongly violated and Eqs. (44) and (45) may be seriously in error. It is nevertheless interesting to note that in the very strong final-state interaction limit, $(1/q_f^2)(F_p/F_e) \gg 1$, $\mathfrak{F}_e \to F_p$ and $\mathfrak{F}_p \to F_e$.

IV. THREE-LEVEL ATOM

We will now consider the case in which the atom plus field is in the state $|g, \vec{k}_0\rangle$ at $t = 0$, where the state $|g\rangle$ is connected to the states $|a\rangle$ and $|ie\rangle$ by the atom-field Hamiltonian H_{AF}. The wave function $|\vec{k}_0\rangle$ indicates, in the occupation number representation, the wave function for a photon of momentum $\vec{k}_0$ and energy ω_0, with $E_a - E_g \cong \omega_0$. We assume that $|g\rangle \neq |f\rangle$, and that the radiative decay from $|a\rangle$ and $|ie\rangle$ to $|g\rangle$ is insignificant compared to the analogous decay to $|f\rangle$. We will make calculations corresponding to a number of experiments which can be performed on such a system.

First of all, let us consider the probability of absorption of the photon ω_0 as a function of ω_0. Proceeding as before [Eqs. (22)–(25)] we have that at $t > 0$ the system wave function will be given by

$$|\psi\rangle_t = \alpha_g(t) | g\vec{k}_0\rangle + \alpha_a(t) |a\rangle$$

$$+ \int dE_1 \alpha_{1E_1}(t) | 1E_1\} + \int dE_2 \alpha_{2E_2}(t) | 2E_2\}. \tag{46}$$

Fourier transforming, we obtain the Green's-function equations:

$$[z - (E_g + \omega_0)]G_g = \int dE_1 H_{g, 1E_1} G_{1E_1}$$

$$+ \int dE_2 H_{g, 2E_2} G_{2E_2} + H_{ga} G_a + 1, \tag{47a}$$

$$(z - E_a)G_a = H_{ag} G_g + \int dE_1 H_{a, 1E_1} G_{1E_1}$$

$$+ \int dE_2 H_{a, 2E_2} G_{2E_2}, \tag{47b}$$

$$(z - E_1)G_{1E_1} = H_{1E_1, g} G_g + H_{1E_1, a} G_a, \tag{47c}$$

$$(z - E_2)G_{2E_2} = H_{2E_2, g} G_g + H_{2E_2, a} G_a. \tag{47d}$$

Solving the last two equations for G_{iE_i}, $i = 1, 2$ and substituting in the first two, one obtains

$$[z - \omega_g(z) + i\gamma_g(z)/2]G_g(z)$$

$$= [\omega_{ga}(z) - i\gamma_{ga}(z)/2]G_a(z) + 1,$$

$$[z - \omega_a(z) + i\gamma_a(z)/2]G_a(z) \tag{48}$$

$$= [\omega_{ag}(z) - i\gamma_{ag}(z)/2]G_g(z),$$

with

$$\omega_g(z) = E_g + \omega_0 + \mathcal{P} \int dE_1 \frac{|H_{g,1E_1}|^2}{z - E_1}$$
$$+ \mathcal{P} \int dE_2 \frac{|H_{g,2E_2}|^2}{z - E_2},$$

$$\gamma_g(z) = 2\pi[\, |H_{g,1E_1}|^2_{E_1=z} + |H_{g,2E_2}|^2_{E_2=z}\,],$$

$$\omega_a(z) = E_a + \mathcal{P} \int dE_1 \frac{|H_{a,1E_1}|^2}{z - E_1}$$
$$+ \mathcal{P} \int dE_2 \frac{|H_{a,2E_2}|^2}{z - E_2}, \tag{49}$$

$$\gamma_a(z) = 2\pi[\, |H_{a,1E_1}|^2_{E_1=z} + |H_{a,2E_2}|^2_{E_2=z}\,],$$

$$\omega_{ga}(z) = H_{ga} + \mathcal{P} \int dE_1 \frac{H_{g,1E_1}H_{1E_1,a}}{z - E_1}$$
$$+ \mathcal{P} \int dE_2 \frac{H_{g,2E_2}H_{2E_2,a}}{z - E_2},$$

$$\gamma_{ga}(z) = 2\pi[(H_{g,1E_1}H_{1E_1,a})_{E_1=z}$$
$$+ (H_{g,2E_2}H_{2E_2,a})_{E_2=z}].$$

$\omega_{ag}(z)$ and $\gamma_{ag}(z)$ are obtained from ω_{ga} and γ_{ga} by interchanging $a \longleftrightarrow g$. The matrix elements not previously defined are

$$H_{ga} = (g\vec{k}_0 | H_{AF} | a),$$
$$H_{ge} = (g\vec{k}_0 | H_{AF} | ie), \tag{50}$$
$$H_{g\omega} = (g\vec{k}_0 | H_A | f\omega).$$

We again make the assumption that the matrix elements in (49) are slowly varying functions of energy and we replace z by $E_a \simeq E_g + \omega_0$. We denote the resulting γ's and ω's with the corresponding capital letters, and Eqs. (48) become

$$(z - W_g + i\Gamma_g/2)G_g(z) = (W_{ga} - i\Gamma_{ga}/2)G_a(z) + 1,$$
$$(z - W_a + i\Gamma_a/2)G_a(z) = (W_{ag} - i\Gamma_{ag}/2)G_g. \tag{51}$$

Solving the second equation for $G_a(z)$ and inserting in the first one obtains:

$$\left(z - W_g + i\frac{\Gamma_g}{2} - \frac{(W_{ga} - i\Gamma_{ga}/2)(W_{ag} - i\Gamma_{ag}/2)}{z - W_a + i\Gamma_a/2}\right)G_g(z) = 1. \tag{52}$$

This equation can be introduced in (7) and the resulting problem solved exactly. However, it is convenient to consider an approximate solution valid for $|H_{ga}|$, $\Gamma_g \ll \Gamma_a$. This corresponds to the usual experimental conditions. Then z in the denominator of (52) can be replaced by W_g leading to

$$G_g(z) \cong \left(z - W_g + i\frac{\Gamma_g}{2}\right.$$
$$\left. - \frac{(W_{ga} - i\Gamma_{ga}/2)(W_{ag} - i\Gamma_{ag}/2)}{W_g - W_a + i\Gamma_a/2}\right)^{-1}. \tag{53}$$

This can be separated into real and imaginary parts, using $\delta \equiv W_g - W_a$:

$$\frac{(W_{ga} - i\Gamma_{ga}/2)(W_{ag} - i\Gamma_{ag}/2)}{\delta + i\Gamma_a/2} = \left(\delta^2 + \frac{\Gamma_a^2}{4}\right)^{-1}\left\{\delta\left(|W_{ga}|^2 - \frac{|\Gamma_{ga}|^2}{4}\right) - \frac{\Gamma_a}{2}\operatorname{Re}(\Gamma_{ga}W_{ag})\right.$$

$$\left. - i\left[\frac{\Gamma_a}{2}\left(|W_{ga}|^2 - \frac{|\Gamma_{ga}|^2}{4}\right) + \delta\operatorname{Re}(\Gamma_{ga}W_{ag})\right]\right\}$$

$$= \left(\delta^2 + \frac{\Gamma_a^2}{4}\right)^{-1}\left\{\delta\left(|W_{ga}|^2 - \frac{|\Gamma_{ga}|^2}{4}\right) - \frac{\Gamma_a}{2}\operatorname{Re}(\Gamma_{ga}W_{ag})\right.$$

$$\left. - i\left|W_{ga} + \delta\frac{\Gamma_{ga}}{\Gamma_a}\right|^2\frac{\Gamma_a}{2}\right\} + i\frac{|\Gamma_{ga}|^2}{2\Gamma_a}. \tag{54}$$

Consequently, use of Eq. (7) leads to

$$|\alpha_g(t)|^2 = e^{-\sigma t}, \tag{55}$$

where

$$\sigma = \Gamma_g - \frac{|\Gamma_{ga}|^2}{\Gamma_a} + \frac{\Gamma_a |W_{ga} + \delta\Gamma_{ga}/\Gamma_a|^2}{\delta^2 + \Gamma_a^2/4}. \tag{56}$$

If we further define a "q parameter"

$$q_g \equiv 2W_{ag}/\Gamma_{ag} \tag{57}$$

σ becomes

$$\sigma = \Gamma_g - \frac{|\Gamma_{ga}|^2}{\Gamma_a} + \frac{|\Gamma_{ga}|^2}{\Gamma_a}\frac{|\frac{1}{2}\Gamma_a q_a + \delta|^2}{\frac{1}{4}\Gamma_a^2 + \delta^2}. \tag{58}$$

That is, the absorption spectra will display the

familiar Beutler-Fano profile.[1,11] There are, however, several differences between Eq. (58) and the corresponding results of Fano.[1] First, the detuning δ contains both a shift in the energy of $|a)$ due to the interactions with the final states $|f\omega)$ and $|ie)$, and also a shift in the energy of $|g)$ due to the interaction with the ionization continuum $|ie)$: In the approximation of Sec. III we have

$$\delta \cong E_g + \omega_0 - E_a + \mathcal{P} \int \frac{|H_{ge}|^2}{E_g + \omega_0 - E_e} de$$
$$- \mathcal{P} \int \frac{|H_{a\omega}|^2}{E_a - E_f - \omega} d\omega - \mathcal{P} \int \frac{|H_{ae}|^2}{E_a - E_e} de.$$

The shift in the energy of $|a)$ due to $|f\omega)$ is just

the Lamb shift of $|a\rangle$ in the approximation that the decay to $|g\rangle$ is negligible. The decay probability Γ_a appearing in (58) is the total probability of decay—not just the one due to autoionization. Finally, q_g defined by Eq. (57) does not reduce, in the limit of Sec. III, exactly to the corresponding q parameter of Fano,[1] which we denote by q_g^F. Instead

$$q_g \cong q_g^F[1 + (1/q_f^2)(F_p/F_e)]. \tag{57'}$$

Finally, we note that, due to the approximation made below Eq. (52), the present results hold also if $|g\rangle = |f\rangle$.

Now we can further calculate the profile of the emitted electron (the final state being $|1E_1\rangle \to |ie\rangle$ as well as that of the emitted radiation (the final state being $|2E_2\rangle \to |f\omega\rangle$, the limits representing $r \to \infty$). From (47c) we have

$$G_{1E_1} = \frac{H_{1E_1,g}}{z - E_1} G_g + \frac{H_{1E_1,a}}{z - E_1} G_a$$

$$= \frac{1}{z - E_1} \left(H_{1E_1,g} + H_{1E_1,a} \frac{W_{ag} - i\Gamma_{ag}/2}{z - W_a + i\Gamma_a/2} \right) G_g$$

$$= \frac{H_{1E_1,g}(z - W_a + i\Gamma_a/2) + H_{1E_1,a}(W_{ag} - i\Gamma_{ag}/2)}{(z - E_1)[(z - W_g + i\Gamma_g/2)(z - W_a + i\Gamma_a/2) - (W_{ga} - i\Gamma_{ga}/2)(W_{ag} - i\Gamma_{ag}/2)]} . \tag{59}$$

We insert now (59) in (7) and retain, as before the component of $\alpha_{1E_1}(t)$ which does not decay exponentially with time:

$$\alpha_{1E_1}(t \to \infty) = \frac{H_{1E_1,g}(E_1 - W_a + i\Gamma_a/2) + H_{1E_1,a}(W_{ag} - i\Gamma_{ag}/2)}{(E_1 - W_g + i\Gamma_g/2)(E_1 - W_a + i\Gamma_a/2) - (W_{ga} - i\Gamma_{ga}/2)(W_{ag} - i\Gamma_{ag}/2)} e^{-iE_1 t} \tag{60}$$

or

$$|\alpha_{1E_1}(t \to \infty)|^2 = \frac{|H_{1E_1,g}(\delta_a + i\Gamma_a/2) + H_{1E_1,a}(W_{ag} - i\Gamma_{ag}/2)|^2}{(\delta_a \delta_g - \Gamma_a\Gamma_g/4 - |W_{ag}|^2 + |\Gamma_{ag}|^2/4)^2 + [\delta_a\Gamma_g/2 + \delta_g\Gamma_a/2 + \text{Re}(\Gamma_{ga}W_{ag})]^2} \tag{61}$$

with $\delta_g = E_1 - W_g$, $\delta_a = E_1 - W_a$.

In a similar manner we have from (47d):

$$G_{2E_2} = (z - E_2)^{-1}(H_{2E_2,g}G_g + H_{2E_2,a}G_a)$$

$$= \frac{H_{2E_2,g}(z - W_a + i\Gamma_a/2) + H_{2E_2,a}(W_{ag} - i\Gamma_{ag}/2)}{(z - E_2)[(z - W_g + i\Gamma_g/2)(z - W_a + i\Gamma_a/2) - (W_{ga} - i\Gamma_{ga}/2)(W_{ag} - i\Gamma_{ag}/2)]} \tag{62}$$

which substituted in (7) results in

$$\alpha_{2E_2}(t \to \infty) = \frac{H_{2E_2,g}(\delta_a + i\Gamma_a/2) + H_{2E_2,a}(W_{ag} - i\Gamma_{ag}/2)}{(\delta_g + i\Gamma_g/2)(\delta_a + i\Gamma_a/2) - (W_{ga} - i\Gamma_{ga}/2)(W_{ag} - i\Gamma_{ag}/2)} e^{-iE_2 t} \tag{63}$$

with $\delta_g = E_2 - W_g$ and $\delta_a = E_2 - W_a$. Finally,

$$|\alpha_{2E_2}(t \to \infty)|^2 = \frac{|H_{2E_2,g}(\delta_a + i\Gamma_a/2) + H_{2E_2,a}(W_{ag} - i\Gamma_{ag}/2)|^2}{(\delta_g\delta_a - \Gamma_g\Gamma_a/4 - |W_{ga}|^2 + |\Gamma_{ga}|^2/4)^2 + [\delta_g\Gamma_a/2 + \delta_a\Gamma_g/2 + \text{Re}(\Gamma_{ga}W_{ag})]^2} . \tag{64}$$

If we expand the K matrix, as in Sec. III above, we obtain for (61) and (64) $(H_{g\omega} = 0)$

$$|\alpha_{1E_1}(t \to \infty)|^2 = \frac{|\Gamma_{ag}|^2}{4\pi^2 q_f^2 |H_{ea}|^2(1 + \pi^2|H_{e\omega}|^2)^2 D} \left[\left(q_g q_f - \frac{F_p}{F_e} + \frac{\Gamma_a}{\Gamma_{ag}} \frac{H_{eg}}{H_{ea}} q_f x \right)^2 + \left(q_f + q_g \frac{F_p}{F_e} - \frac{\Gamma_a}{\Gamma_{ag}} \frac{H_{eg}}{H_{ea}} q_f \right)^2 \right] \tag{65}$$

and

$$|\alpha_{2E_2}(t \to \infty)|^2 = \frac{|\Gamma_{ag}|^2 |H_{\omega a}|^2}{4\pi^2 q_f^2 |H_{ea}|^4(1 + \pi^2|H_{e\omega}|^2)^2 D} \left[\left(q_g q_f - 1 + \frac{\Gamma_a}{\Gamma_{ag}} \frac{H_{eg}}{H_{ea}} \right)^2 + \left(q_f + q_g - \frac{\Gamma_a}{\Gamma_{ag}} \frac{H_{eg}}{H_{ea}} x \right)^2 \right], \tag{66}$$

where

$$D = \left(\delta_g x - \frac{\Gamma_g}{2} - \frac{|W_{ag}|^2}{\Gamma_a/2} + \frac{|\Gamma_{ag}|^2}{4} \frac{2}{\Gamma_a} \right)^2 + \left(\frac{\Gamma_g}{2} x + \delta_g + \frac{\Gamma W_{ag}}{\Gamma_a/2} \right)^2 \tag{67}$$

and

$$x = \delta_a/(\Gamma_a/2). \qquad (68)$$

If we further make the approximation that $|W_{ag}|^2 \ll \Gamma_a$ and $\Gamma_{aa} \cong 2\pi H_{ae}H_{eg}$, then Eq. (66) reduces to the result obtained earlier by Armstrong and Beers[12] when the limit $\Gamma_q \to 0$ is taken. Specifically we have

$$|\alpha_{1E_1}(t \to \infty)|^2 = \frac{|H_{eg}|^2}{q_f^2} \frac{1}{(1 + \pi^2 |H_{e\omega}|^2)^2 D}$$
$$\times \left[\left(q_g q_f - \frac{F_p}{F_e} + q_f x \right)^2 + \left(q_g \frac{F_p}{F_e} \right)^2 \right] \qquad (69)$$

$$|\alpha_{2E_2}(t \to \infty)|^2 = \frac{|H_{eg}|^2}{q_f^2} \frac{F_p}{F_e} \frac{1}{(1 + \pi^2 |H_{e\omega}|^2)^2 D}$$
$$\times [(q_g q_f)^2 + (q_g + q_f - x)^2] \qquad (70)$$

with

$$D = (\delta_g x - 2|W_{ag}|^2/\Gamma_a)^2 + (x\Gamma_g/2 + \delta_g + 2\Gamma_{ga}W_{ag}/\Gamma_a)$$
$$\cong (\delta_g x)^2 + (x\Gamma_g/2 + \delta_g)^2 \cong \delta_g^2(1 + x^2). \qquad (71)$$

Both Eqs. (61) and (64) are quite complicated and it is difficult to make general statements concerning the shape of the spectrum of either the electron or photon. However, it is clear that if $\delta_a = \delta_g$ (that is, if $W_a = W_g$), and for large values of W_{ga}, the states $|a)$ and $|g\omega_0)$ will form Autler-Townes doublets,[13] and asymmetrical doublet structure will be observed in both electron and photon spectra. However, the value of W_{ga} at which the doublet structure appears is not easily obtainable from these complicated equations.

V. MANY FINAL STATES

Let us now generalize the theory of Secs. II and III to the situation in which there are a number of lower energy atomic states $|f_i)$ into which the excited atom can decay radiatively. We assume there are n such atomic states; when the outgoing photon states $|\omega_i)$ are included, there are n continua $|f_i\omega_i)$. The states are assumed to satisfy relations similar to those given in Eq. (2).

If one proceeds as in Sec. II and takes the Fourier transform of the time-dependent coefficients $\alpha_j(t)$, one arrives at a set of $(n + 2)$ coupled equations similar to those in Eq. (8). As before, decoupling of the equations is achieved by the K-matrix method. In the present case, the $(n + 1)$ eigenstates of H are given by

$$|\Lambda E\} = \sum_{l=1}^{n+1} \left(|lE) + \sum_j \mathcal{P} \int \frac{|jE')K_{jE',lE}}{E - E'} dE' \right) B_l^\Lambda(E)$$
$$\equiv \sum_{l=1}^{n+1} B_l^\Lambda(E)|lE\rangle, \qquad (72)$$

where the elements of the K matrix are given by Eq. (12), with

$$|1E) = |ie) \quad \text{and} \quad |lE) = |f_e\omega_e)$$
$$\text{for } 2 \leq l \leq n+1. \qquad (73)$$

In Eq. (72), $\Lambda = 1$ corresponds to the eigenstates asymptotically describing an ion plus an outgoing electron, and $\Lambda = 2, \ldots, n+1$ correspond to the n eigenstates asymptotically describing an atom in state $|f_\Lambda)$ plus an emitted photon of frequency ω_Λ. From the boundary conditions and the orthonormality of the eigenstates $|\Lambda E\}$, (see Appendix) one obtains the equations satisfied by the $B_l^\Lambda(E)$:

$$\sum_l (1 - i\pi K)_{\Lambda l} B_l^\Lambda = \delta(\Lambda, \Lambda') \qquad (74)$$

or

$$B_l^\Lambda = \text{cofactor}(T_{\Lambda l})/|T| \qquad (75)$$

where $T \equiv 1 - i\pi K$.

With the formal solution of the eigenstates, one has the decoupled equations

$$(z - E_a)G_a = 1 + \sum_\Lambda \int dE_\Lambda H_{a, \Lambda E_\Lambda} G_{\Lambda E_\Lambda} \qquad (76)$$

$$(z - E_\Lambda)G_{\Lambda E_\Lambda} = H_{\Lambda E_\Lambda, a} G_a, \quad \text{all } \Lambda,$$

which lead to the expression

$$[z - \omega_a(z) + \tfrac{1}{2} i\gamma_a(z)]G_a(z) = 1, \qquad (77)$$

where

$$\omega_a(z) = E_a + \sum_\Lambda \mathcal{P} \int dE_\Lambda \frac{|H_{a, \Lambda E_\Lambda}|^2}{z - E_\Lambda}, \qquad (78)$$

$$\gamma_a(z) = 2\pi \sum_\Lambda |H_{a, \Lambda E_\Lambda}|^2_{E_\Lambda = z}.$$

We make the same simplifying assumptions as in Sec. II thus introducing into Eq. (77) $W_a = w_a(E_a)$ and $\Gamma_a = \gamma_a(E_a)$. Then proceeding through the same steps that led to equations (30) and (31), one finally arrives at

$$\mathcal{F}_e = (2\pi/\Gamma_a)|H_{a, 1E_1}|^2 \qquad (79)$$

$$\mathcal{F}_{p\Lambda} = (2\pi/\Gamma_a)|H_{a, \Lambda E_\Lambda}|^2, \quad \Lambda \geq 2 \qquad (80)$$

where $\mathcal{F}_e$, $\mathcal{F}_{p\Lambda}$ are the fractional probabilities of decay into $|1E\}$ and $|\Lambda E\}$. The usual fractional probabilities for transition into the various channels are, in this case,

$$F_e = (2\pi/\Gamma_a^0)|(a|H|ie)|^2 \qquad (81)$$

$$F_{pl} = (2\pi/\Gamma_a^0)|(a|H|f_l\omega_l)|^2, \qquad (82)$$

where

$$\Gamma_a^0 = 2\pi \left[|(a|H|ie)|^2 + \sum_{l=2}^{n+1} |(a|H|f_l\omega_l)|^2 \right]. \qquad (83)$$

Now let us make the same first-order approximation as in Sec. III, so as to investigate the character of solutions for many final states. If we keep only the first-order contributions to the K matrix, then only K_{l1} and K_{1l}, $l \geq 2$ are nonvanishing and explicitly evaluating the matrix T in this approximation, one finds

$$|T| = 1 + \pi^2 \sum_{l=2}^{n+1} |K_{1l}|^2 ,$$

$$\text{cofactor}(T_{l1}) = i\pi K_{1l}, \quad l \neq 1$$

$$\text{cofactor}(T_{1l}) = i\pi K_{1l}, \quad l \neq 1$$

$$\text{cofactor}(T_{11}) = 1, \quad (84)$$

$$\text{cofactor}(T_{ll}) = |T| - \pi^2 |K_{1l}|^2, \quad l \neq 1$$

$$\text{cofactor}(T_{kl}) = -\pi K_{1k}K_{1l}, \quad k,l, \neq 1, \ k \neq l$$

Then, the eigenstates have the form

$$|1E\} = |T|^{-1} \left(|1E\rangle + i\pi \sum_{l=2}^{n+1} K_{1l} |lE\rangle \right) \quad (85)$$

and

$$|\Lambda E\} = |\Lambda E\rangle + |T|^{-1} \left(i\pi K_{1\Lambda} |1E\rangle \right.$$
$$\left. - \pi^2 \sum_{l=2}^{n+1} K_{1\Lambda}K_{1l} |lE\rangle \right). \quad (86)$$

The evaluation of the fractional probabilities is now quite straightforward.

In order to express the quantities $\mathfrak{F}_e$ and $\mathfrak{F}_p$ in a form analogous to the previous result, we introduce the Fano q parameter for each state $|lE\rangle$, $l \geq 2$

$$q_l = (a|H|lE\rangle/\pi(a|H|1E\rangle K_{1l}. \quad (87)$$

Before calculating $\mathfrak{F}_e$ and $\mathfrak{F}_p$ we must find the relationship between Γ_a and Γ_a^0. It is readily found that

$$\Gamma_a \mathfrak{F}_e = \frac{\Gamma_a^0 F_e}{|T|^2} \left[1 + \left(\frac{1}{F_e} \sum_{k=2}^{n+1} \frac{F_{pk}}{q_k} \right)^2 \right] \quad (88)$$

and

$$\Gamma_a \mathfrak{F}_{p\Lambda} = \frac{\Gamma_a^0 F_{p\Lambda}}{|T|^2} \left\{ \frac{1}{q_\Lambda^2} + \left[1 + \frac{1}{F_e} \sum_{k=2}^{n+1} \left(\frac{F_{pk}}{q_k} \frac{q_\Lambda - q_k}{q_\Lambda} \right) \right]^2 \right\} \quad (89)$$

Summing over Λ in the above equation and adding to this the expression above it, we find

$$\Gamma_a = \Gamma_a^0 \left\{ 1 - \frac{1}{|T|} \left[\frac{1}{F_e} \left(\sum_k \frac{F_{pk}}{q_k} \right)^2 + \sum_k \frac{F_{pk}}{q_k^2} \right] \right\}. \quad (90)$$

Let us denote ϵ the proportionality constant relating the Γ's so that

$$\epsilon = \frac{\Gamma_a^0}{\Gamma_a} = |T| \left\{ |T| - \left[\frac{1}{F_e} \left(\sum_k \frac{F_{pk}}{q_k} \right)^2 + \sum_k \frac{F_{pk}}{q_k^2} \right] \right\}^{-1}. \quad (91)$$

The fractional probabilities then are given by

$$\mathfrak{F}_e = \frac{\epsilon F_e}{|T|^2} \left[1 + \left(\frac{1}{F_e} \sum_k \frac{F_{pk}}{q_k} \right)^2 \right] \quad (92)$$

$$\mathfrak{F}_{p\Lambda} = \frac{\epsilon F_{p\Lambda}}{|T|^2} \left\{ \frac{1}{q_\Lambda^2} + \left[1 + \frac{1}{F_e} \sum_{k=2}^{n+1} \left(\frac{F_{pk}}{q_k^2} \frac{q_\Lambda - q_k}{q_\Lambda} \right) \right]^2 \right\}. \quad (93)$$

The above expressions for the fractional probabilities are quite complicated. Their deviation from the usual F_e and F_p depends on $(1/F_e)(F_{pl}/q_l)$ or $1/q_\Lambda^2$ not being very small for some value of l.

VI. TWO OR MORE ELECTRON CONTINUA

In this section we examine the case of an excited state $|a\rangle$ which can decay to state $|f\rangle$, by emitting a photon of frequency ω, and also can autoionize to a number of states $|k\rangle$, $k = 1, 2, \ldots$ by emitting an electron with energy e. We will limit our calculation to two states, $|ie\rangle$ and $|je\rangle$, of the latter kind for the sake of simplicity. Generalization to more states is straightforward.

First following Fano,[1] we construct two new states $|1e\rangle$ and $|2e\rangle$:

$$|1e\rangle = (2\pi/\Gamma_e)^{1/2} [|ie\rangle(ie|H|a) + |je\rangle(je|H|a)] \quad (94)$$

$$|2e\rangle = (2\pi/\Gamma_e)^{1/2} [|ie\rangle(je|H|a) - |je\rangle(ie|H|a)] ,$$

where

$$\Gamma_e = 2\pi [|(a|H|ie)|^2 + |(a|H|je)|^2], \quad (95)$$

The new states have the properties

$$(me|ne') = \delta(m,n)\delta(e - e'), \quad m,n = 1,2$$

and

$$(a|H|2e) = 0.$$

As in the previous sections we employ the K-matrix method to diagonalize the Hamiltonian with respect to states $|1e\rangle$, $|2e\rangle$, and $|f\omega\rangle$. The new states are given by expressions analogous to Eq. (72) and the pertinent expansion coefficients are given by Eq. (75). Repeating the procedure which led from Eq. (21) to Eq. (32) and making the same type of approximations we obtain

$$\mathfrak{F}_{ie} = (2\pi/\Gamma_a) |(a|H|ie\}|^2, \quad i = 1,2$$
$$\mathfrak{F}_p = \frac{2\pi}{\Gamma_a} |(a|H|f\omega\}|^2 \quad (96)$$

with

$$\Gamma_a = 2\pi \{ |(a|H|1e\}|^2 + |(a|H|2e\}|^2 + |(a|H|f\omega\}|^2 \}.$$

To obtain a first-order expression for $\mathfrak{F}$ and Γ_a we consider the same approximation to the K ma-

trix as in Sec. III. Namely, we will consider only the lowest-order term in an expansion of K in powers of H_{AF}. Thus the resulting T matrix is

$$T = 1 - i\pi K = \begin{bmatrix} 1 & 0 & -i\pi K_{1\omega} \\ 0 & 1 & -i\pi K_{2\omega} \\ -i\pi K_{\omega 1} & -i\pi K_{\omega 2} & 1 \end{bmatrix} \qquad (97)$$

and

$$\Delta = \det |T| = 1 + \pi^2(|K_{1\omega}|^2 + |K_{2\omega}|^2). \qquad (98)$$

Introducing the approximate expressions for $|1e\rangle$, $|2e\rangle$, and $|f\omega\rangle$ in Eqs. (96) we obtain

$$\mathfrak{I}_{1e} \cong \frac{2\pi}{\Gamma_a \Delta^2} \left| (1 + \pi^2 |K_{2\omega}|^2)(a|H|ie\rangle + i\pi K_{\omega 1}(a|H|f\omega\rangle \right|^2,$$

$$\mathfrak{I}_{2e} \cong \frac{2\pi}{\Gamma_a \Delta^2} \left| -\pi^2 K_{1\omega} K_{\omega 2}(a|H|1e\rangle + i\pi K_{\omega 2}(a|H|f\omega\rangle \right|^2, \qquad (99)$$

$$\mathfrak{I}_p \cong \frac{2\pi}{\Gamma_a \Delta^2} \left| i\pi K_{i\omega}(a|H|1e\rangle + (a|H|f\omega\rangle \right|^2.$$

If we define a profile parameter

$$q = (a|H|f\omega\rangle / \pi(a|H|1e\rangle K_{1\omega} \qquad (100)$$

and

$$T_b = \pi^2 |K_{2\omega}|^2 \qquad (101)$$

Eqs. (99) become

$$\mathfrak{I}_{1e} = \frac{1}{\Delta^2} \frac{\Gamma_a^0}{\Gamma_a} F_{1e} \left[(1 + T_b)^2 + 1/q^2 \left(\frac{F_p}{F_{1e}} \right) \right],$$

$$\mathfrak{I}_{2e} = \frac{1}{\Delta^2} \frac{\Gamma_a^0}{\Gamma_a} F_p T_b \left(1 + \frac{1}{q^2} \right), \qquad (102)$$

$$\mathfrak{I}_p = \frac{1}{\Delta^2} \frac{\Gamma_a^0}{\Gamma_a} F_p \left(1 + \frac{1}{q^2} \right),$$

and

$$\Gamma_a = \frac{\Gamma_a^0}{\Delta} (1 + T_b F_{1e}), \qquad (103)$$

$$\Delta = 1 + \frac{1}{q^2} \frac{F_p}{F_{1e}} + T_b^2 . \qquad (104)$$

Finally, we have for the fraction of decays resulting in a photon

$$\mathfrak{I}_p = (F_p/\Delta)(1 + 1/q^2)(1 + T_b F_{1e})^{-1} \qquad (105)$$

and for the fraction resulting in an electron

$$\mathfrak{I}_e = \mathfrak{I}_{1e} + \mathfrak{I}_{2e} = F_{1e} \left[1 + T_b + \frac{T_b}{\Delta} \left(\frac{F_p}{F_b} - T_b^2 \right) \right].$$

As discussed by Fano,[1] any number of electron continua can be handled in a straightforward fashion by making combinations of states analogous to those defined in Eq. (94). We shall therefore not discuss the many electron-continua problem.

VII. CONCLUSIONS

We have studied the effects of final-state interactions on the decay of (highly) excited states of atoms which can autoionize. It is shown that this final-state interaction can affect the relative probabilities of autoionization and of radiative decay of such states. Physically, this is due to the fact that, in the case of autoionization, the resulting electron and ion can undergo dielectronic recombination, leading to a final-state atom plus emitted photon; in the case of spontaneous emission, the photon can be reabsorbed, resulting in the emission of an electron. Thus, as can be seen in Eqs. (43) and (44), the probability of autoionization is reduced by a factor $(1 + \pi^2 |H_{e\omega}|^2)^{-1} \cong 1 - \pi^2 |H_{e\omega}|^2$ which describes the loss due to recombination, and increased by an amount $\sim \pi^2 |H_{a\omega} H_{\omega e}|^2$, which describes the rate of reabsorption of emitted photons. Exactly parallel statements can be made concerning the probability for spontaneous emission of a photon.

The approximate expressions obtained for $\mathfrak{I}_e$ and $\mathfrak{I}_p$ in Sec. III show that these quantities can differ from the usual expression F_e and F_p if $1/q_f^2$ is of the order of unity, or if $(1/q_f^2)(F_p/F_e)$ is large. As discussed in Sec. III in the latter case the final-state interaction is so large that the approximate Eqs. (43) and (44) may be suspect and the more complicated expressions of Sec. II should be used. However, if $(1/q_f^2)(F_p/F_e) \ll 1$, then Eqs. (43) and (44) should be quite adequate to describe the effects of final-state interactions. Perhaps the most striking prediction of these equations is that, even when $(1/q_f^2)(F_p/F_e)$ is very small, there can be a large difference between $\mathfrak{I}_p$ and F_p if $1/q_f^2$ is large. That is, the fluorescence yield is particularly sensitive to the effects of final-state interactions.

In Sec. IV, we showed that the absorption spectrum of the autoionizing state will be qualitatively similar to that predicted by theories having no final-state interaction.[1] However, it was noted that q_g, which parameterizes the absorption spectra [Eqs. (57) and (58)], is defined somewhat differently from the q's which parametrize the emission spectra [Eqs. (34), (88), and (100)]. These emission q's go, in the limit discussed in Sec. III, to the q parameter of Fano[1]; the absorption q_g does not, however, being related in this limit to a "Fano-type" q_g^F by

$$q_g \cong q_g^F [1 + (1/q_f^2)(F_p/F_e)].$$

Although the difference between these terms is small in the limit in which this approximation is most nearly correct, it does indicate that in general q parameters measured in emission will be slightly different from those measured in absorption.

In Sec. IV, we also showed that this final-state interaction caused the spectra of both the emitted electron and emitted photon to be quite complicated. However, because of their complicated form these spectra can be used to obtain a great deal of information concerning the final-state interaction; in particular, they can be used to determine the q parameters of both the initial and the final atomic (ionic) states.

The calculations of Secs. V and VI can also be done in an alternative manner which makes the computationally equivalent to the problem considered in Secs. II and III. This alternative consists of first using the K matrix to diagonalize H_{AF} with respect to all of the possible "ion + electron" and "atom + photon" states. Then, following Fano,[1] from that subset of diagonalized states which asymptotically look like the atom plus a photon, one can make one linear combination which interacts with $|a\rangle$, with all the other orthogonal combinations having zero matrix elements with $|a\rangle$. Similar combinations can be made using the subset of diagonalized states which asymptotically go to ion plus electron. Then, the state $|a\rangle$ interacts with only a single combination of states which are asymptotically atom + photon, and only a single combination which are asymptotically ion plus electron, just as in Sec. II. The resulting expressions, al-

though more compact than those of Secs. V and VI, may be less convenient to use. For example, although this approach would easily give the total fluorescence yield, it would not lead in a straight-forward way to the fluorescence yield to a particular final state. In addition, the resulting q parameters would be quite complicated functions of Fano-like q parameters.

APPENDIX

The requirement that the wave functions constructed by the K-matrix technique described in Sec. II be orthonormal leads to requirements on the set of coefficients $B_l^\alpha(E)$. We note that the operator H_{AF} is a Hermitian operator so

$$V_{jE',iE} \equiv \langle jE'|H_{AF}|iE\rangle$$
$$= V_{iE,jE'}^* . \tag{A1}$$

The orthonormality condition requires that

$$\{\alpha E | \beta E'\} = \delta(\alpha, \beta)\delta(E - E'). \tag{A2}$$

It follows that

$$\delta(\alpha, \beta)\delta(E - E') = \sum_{l,m} B_l^{\alpha*}(E)B_m^\beta(E')\left(\langle lE|mE'\rangle + \sum_j \mathcal{P}\int dE'' \langle jE''|mE'\rangle \frac{K_{jE'',lE}^*}{E - E''} \right.$$

$$+ \sum_k \mathcal{P}\int dE'' \langle lE|kE''\rangle \frac{K_{kE'',mE'}}{E' - E''}$$

$$+ \sum_{j,p} \mathcal{P}\int dE'' \mathcal{P}\int dE''' \frac{K_{jE'',lE}^*}{E - E''} \frac{K_{kE''',mE'}}{E' - E'''} \langle jE''|kE'''\rangle \right)$$

$$= \sum_{l,m} \left(\delta(l,m)\delta(E - E') + (E - E')^{-1}(K_{lE,mE'} - K_{mE',lE}^*) \right.$$

$$\left. + \sum_j \mathcal{P}\int dE'' \frac{K_{jE'',lE}^* K_{jE'',mE'}}{(E - E'')(E' - E'')} \right) B_l^{\alpha*}(E)B_\omega^\beta(E'). \tag{A3}$$

But Fano[1] has shown that

$$\mathcal{P}\int dE'' \frac{f(E'')}{(E - E'')(E'-E'')} = \mathcal{P}\int dE''f(E'')\left\{ \frac{1}{E - E'}\left(\frac{1}{E'-E''} - \frac{1}{E-E''} \right) + \pi^2\delta(E - E')\delta(E - E'') \right\} \tag{A4}$$

so that the principal value integral in Eq. (A3) becomes

$$(E - E')^{-1}\int dE'' K_{jE'',lE}^* K_{jE'',mE'}(1/(E' - E'') - 1/(E - E'')) + \pi^2 K_{jE,lE}^* K_{jE,mE'}\delta(E - E').$$

The integral may be simplified by expansion of the K-matrix elements as before

$$\left(\frac{1}{E-E'}\right)\sum_j\left(\mathcal{P}\int dE''\frac{K^*_{jE'',1E}K_{jE'',mE'}}{E'-E''}-\mathcal{P}\int dE''\frac{K^*_{jE'',1E}K_{jE'',mE'}}{E-E''}\right)$$

$$=\left(\frac{1}{E-E'}\right)\sum_j\mathcal{P}\int dE''\left[\frac{K_{jE'',mE'}}{E'-E''}\left(V^*_{jE'',1E}+\sum_s\mathcal{P}\int d\epsilon\,\frac{V^*_{jE'',s\epsilon}K^*_{s\epsilon,1E}}{E-\epsilon}\right)\right.$$

$$\left.-\frac{K^*_{jE'',1E}}{E-E''}\left(V_{jE'',mE'}+\sum_s\mathcal{P}\int d\epsilon\,\frac{V_{jE'',s\epsilon}K_{s\epsilon,mE'}}{E'-\epsilon}\right)\right]$$

$$=\left(\frac{1}{E-E'}\right)\left[\sum_j\mathcal{P}\int dE''\left(\frac{V^*_{jE'',1E}K_{jE'',mE'}}{E'-E''}-\frac{V_{jE'',mE'}K^*_{jE'',1E}}{E-E''}\right)\right.$$

$$\left.+\sum_{j,s}\mathcal{P}\int dE''\,\mathcal{P}\int d\epsilon\,\frac{1}{(E'-E'')(E-\epsilon)}\,(V_{s\epsilon,jE'}K^*_{s\epsilon,1E}K_{jE'',mE'}-V_{s\epsilon,jE'}K^*_{s\epsilon,1E}K_{jE'',mE'})\right],$$

$$(A5)$$

where jE'' and $s\epsilon$ have been interchanged in the second term in the integrand of the double integral. There-
fore, the double integral vanishes, while the first integral is equal to an expansion of $(K_{1E,mE'}-K^*_{mE',1E})$
$/(E-E')$. Summing up terms, we find

$$\delta(\alpha,\beta)\delta(E-E')=\sum_{l,m}\left(\delta(l,m)\delta(E-E')+\pi^2\sum_j K^*_{jE,1E}K_{jE,mE'}\delta(E-E')\right)B^{\alpha*}_l(E)B^\beta_m(E').\qquad(A6)$$

The orthonormality condition then reduces to

$$\delta(\alpha,\beta)=\sum_{l,m}\left(\delta(l,m)+\pi^2\sum_j K^*_{jl}(E)K_{jm}(E)\right)$$

$$\times B^{\alpha*}_l(E)B^\beta_m(E)$$

$$=\sum_{l,m,j}\left(\{[\delta_{jl}-i\pi K_{jl}(E)]B^\alpha_l(E)\}^*\right.$$

$$\left.\times\{[\delta_{jm}-i\pi K_{jm}(E)]B^\beta_m(E)\}\right).\qquad(A7)$$

A sufficient condition for orthonormality then is

$$\sum_l[\delta_{jl}-i\pi K_{jl}(E)]B^\alpha_l(E)=\delta(j,\alpha).\qquad(A8)$$

Defining the matrix T by

$$T(E)\equiv\underline{1}-i\pi K(E)\qquad(A9)$$

it follows that $B^{(\Lambda)}_l$ is given by Eq. (75).

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