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## Radiative Decay of Coupled Atomic States

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The radiative decay of an atom with two excited states coupled by an external perturbation is investigated. The differential equations of motion are Fourier transformed and the probability amplitudes are obtained by contour integration. The real parts of the poles in the complex plane are the perturbed energies of the excited states, and the imaginary parts yield the decay characteristics. The decay probabilities of the excited states contain three different decay terms; two exponential decays and one modulated exponential decay. The probabilities of the final states give the frequency distribution of the emitted photons as a function of time. In an Appendix, the Heitler-Ma formalism is used to eliminate the final states of the system, and the resulting equations which contain damping terms are compared with the phenomenological method.

## I. INTRODUCTION

When Weisskopf and Wigner<sup>1</sup> considered the radiative decay of multilevel coupled atomic systems, they showed that for a certain class of decays it is possible to simplify the set of differential equations of motion for the system by eliminating the final states. This procedure yields equations for the decaying states only, with coup-

ling to the final state accounted for by the inclusion of damping terms. Other authors<sup>2-5</sup> have extended this method to cases of two or more excited states which are coupled by external perturbations, and which decay via several channels to a common ground state despite the fact that the original derivation excluded such situations.<sup>6</sup>

A formalism developed by Heitler and Ma<sup>7,8</sup> can

be used to study the radiative decay of coupled atomic levels. By applying this method to the decay of two coupled levels, we obtain those results which have been deduced from the Weisskopf-Wigner method; in addition, we also get information about the frequency distribution of the emitted radiation.

In the Appendix the Heitler-Ma method is used to derive the equations of motion with damping terms which have previously been assumed in the phenomenological theory.

## II. GENERAL THEORY: DECAY OF TWO COUPLED STATES

We consider an atom which has two excited states  $a$  and  $b$  and a ground state  $c$ . Initially the system of atom plus radiation field is in the state  $|o\rangle$  with the atom in state  $|a\rangle$  and no photons present. In the intermediate state  $|j\rangle$  the atom is in state  $|b\rangle$ , and no photons are present. Each final state  $|f\rangle$  consists of the atom in state  $|c\rangle$  and a photon with wave vector  $\vec{k}$  and polarization  $\vec{\sigma}$  emitted.

The Hamiltonian for this system is  $H = H_0 + H + V$ , where  $H_0$  is the unperturbed Hamiltonian for the atom and radiation field,  $H$  represents the interaction of the atom with the radiation field, and  $V$  is a time-independent perturbation.

In relativistic units ( $\hbar = m = c = 1$ )

$$H = \sum_{k_\sigma} \left( \frac{2\pi}{L^3 k_\sigma} \right)^{1/2} \left[ a(k_\sigma) e^{i\vec{k} \cdot \vec{r}} + a^\dagger(k_\sigma) e^{-i\vec{k} \cdot \vec{r}} \right] \hat{e}_\sigma(\vec{k}) \cdot \vec{p},$$

where  $a(k_\sigma)$  and  $a^\dagger(k_\sigma)$  are the annihilation and creation operators, respectively, for a photon with wave vector  $\vec{k}$ , polarization  $\vec{\sigma}$ , and polarization direction  $\hat{e}_\sigma(\vec{k})$ . In the interaction representation with  $H_{\text{interaction}} = H + V$ , the state of the system at time  $t$  is

$$|U(t)\rangle = b_o(t) e^{-iE_o t} |o\rangle + b_j(t) e^{-iE_j t} |j\rangle + \sum_f b_f(t) e^{-iE_f t} |f\rangle. \quad (1)$$

In Eq. (1) the state vectors are

$$|o\rangle = |a\rangle |o\rangle_{\text{rad}}, \quad |j\rangle = |b\rangle |o\rangle_{\text{rad}}, \\ |f\rangle = |c\rangle |\vec{k}_\sigma\rangle_{\text{rad}},$$

with energies  $E_o = E_a$ ,  $E_j = E_b$ ,  $E_f = E_c + k_\sigma$ , where  $\sum_f$  is the sum over final states which includes sums over frequency, direction, and polarization of the radiation field.

The differential equations for the probability amplitudes are

$$i \dot{b}_o(t) = H_{o_j} e^{i(E_o - E_j)t} b_j(t) + \sum_f H_{of} e^{i(E_o - E_f)t} b_f(t) + i\delta(t), \quad (2a)$$

$$i \dot{b}_j(t) = H_{j_o} e^{i(E_j - E_o)t} b_o(t) + \sum_f H_{jf} e^{i(E_j - E_f)t} b_f(t), \quad (2b)$$

$$i \dot{b}_f(t) = H_{f_o} e^{i(E_f - E_o)t} b_o(t) + H_{f_j} e^{i(E_f - E_j)t} b_j(t), \quad (2c)$$

where  $H_{nm} = \langle n | H_{\text{interaction}} | m \rangle$ .

The last term in Eq. (2a) states the initial condition that at  $t = 0$  the system is in state  $|o\rangle$ .

To solve Eq. (2), the  $b$ 's can be transformed as<sup>9</sup>

$$b_n(t) = (-1/2\pi i) \int_{-\infty}^{\infty} dE G_n(E) e^{i(E_n - E)t}, \quad (3)$$

$$i\delta(t) = (-1/2\pi i) \int_{-\infty}^{\infty} dE e^{i(E_o - E)t}. \quad (4)$$

Substituting these expressions into Eq. (2) gives

$$(E - E_o)G_o = H_{o_j} G_j + \sum_f H_{of} G_f + 1, \quad (5)$$

$$(E - E_j)G_j = H_{j_o} G_o + \sum_f H_{jf} G_f, \quad (6)$$

$$(E - E_f)G_f = H_{f_o} G_o + H_{f_j} G_j. \quad (7)$$

The set of Eqs. (5)–(7) can most easily be solved for the  $G$ 's by introducing the following definitions:

$$-\frac{1}{2} i \gamma_{nm} = \sum_f H_{nf} H_{fm} / (E - E_f), \quad (8)$$

$$H'_{nm} = H_{nm} - \frac{1}{2} i \gamma_{nm}. \quad (9)$$

The resulting expressions for the  $G$ 's are

$$G_j = \frac{H'_{j_o}}{(E - E_o + \frac{1}{2} i \gamma_{oo})(E - E_j + \frac{1}{2} i \gamma_{jj}) - H'_{j_o} H'_{o_j}}, \quad (10)$$

$$G_o = \frac{E - E_j + \frac{1}{2} i \gamma_{jj}}{(E - E_o + \frac{1}{2} i \gamma_{oo})(E - E_j + \frac{1}{2} i \gamma_{jj}) - H'_{j_o} H'_{o_j}}, \quad (11)$$

$$G_f = \frac{H_{f_j} H'_{j_o} + H_{f_o} (E - E_j + \frac{1}{2} i \gamma_{jj})}{(E - E_f) [(E - E_o + \frac{1}{2} i \gamma_{oo})(E - E_j + \frac{1}{2} i \gamma_{jj}) - H'_{j_o} H'_{o_j}]}. \quad (12)$$

These expressions are now used in Eq. (3) to obtain integral equations for the probability amplitudes  $b_o(t)$ ,  $b_j(t)$ , and  $b_f(t)$ :

$$b_o(t) = \frac{-1}{2\pi i} \times \int_{-\infty}^{\infty} \frac{dE (E - E_j + \frac{1}{2} i \gamma_{jj}) e^{i(E_o - E)t}}{(E - E_o + \frac{1}{2} i \gamma_{oo})(E - E_j + \frac{1}{2} i \gamma_{jj}) - H'_{j_o} H'_{o_j}}, \quad (13)$$

$$b_j(t) = \frac{-1}{2\pi i} \times \int_{-\infty}^{\infty} \frac{dE H'_{j_o} e^{i(E_j - E)t}}{(E - E_o + \frac{1}{2} i \gamma_{oo})(E - E_j + \frac{1}{2} i \gamma_{jj}) - H'_{j_o} H'_{o_j}}, \quad (14)$$

$$b_f(t) = \frac{-1}{2\pi i} \times \int_{-\infty}^{\infty} \frac{dE [H_{f_j} H'_{j_o} + H_{f_o} (E - E_j + \frac{1}{2} i \gamma_{jj})] [e^{i(E_f - E)t} - 1]}{(E - E_f) [(E - E_o + \frac{1}{2} i \gamma_{oo})(E - E_j + \frac{1}{2} i \gamma_{jj}) - H'_{j_o} H'_{o_j}]}. \quad (15)$$

In Eq. (15) the initial condition  $b_f(0) = 0$  has been used.

For atomic systems where  $(E_o - E_j) \ll (E_o - E_c)$ , it can be shown the  $\text{Re}\gamma_{oo}(E)$  and  $\text{Re}\gamma_{jj}(E)$  can be replaced, respectively, by  $\text{Re}\gamma_{oo}(E_o)$  and  $\text{Re}\gamma_{jj}(E_j)$  in Eqs. (13)–(15). Furthermore, the imaginary parts of  $\gamma_{oo}(E)$  and  $\gamma_{jj}(E)$  can be absorbed into  $E_o$  and  $E_j$ , respectively, giving rise to energy shifts.<sup>10</sup> Thus, in Eqs. (13)–(15)

$$E_o - \frac{1}{2}i\gamma_{oo}(E) \rightarrow E_o - \frac{1}{2}i\gamma_o$$

$$\text{and } E_j - \frac{1}{2}i\gamma_{jj}(E) \rightarrow E_j - \frac{1}{2}i\gamma_j,$$

where  $\gamma_o = \text{Re}\gamma_{oo}(E_o)$  and  $\gamma_j = \text{Re}\gamma_{jj}(E_j)$ .

As will be seen,  $\gamma_o$  and  $\gamma_j$  are the radiative decay constants of the unperturbed atomic states  $|a\rangle$  and  $|b\rangle$ , respectively.

If  $|a\rangle$  and  $|b\rangle$  are good angular momentum states, then it can be shown that the cross term  $\gamma_{jo}(E)$  is zero, and thus  $H'_{jo} = H_{jo} = V_{jo}$ .<sup>11</sup> To simplify the expressions for the probability amplitudes, the following definitions are introduced:

$$A = E_o - \frac{1}{2}i\gamma_o, \quad B = E_j - \frac{1}{2}i\gamma_j, \quad C = -|H_{jo}|^2,$$

$$E_1 = \frac{1}{2} \{ (A+B) + [(A+B)^2 - 4(AB+C)]^{1/2} \},$$

$$E_2 = \frac{1}{2} \{ (A+B) - [(A+B)^2 - 4(AB+C)]^{1/2} \}.$$

Therefore,

$$b_o(t) = \frac{-1}{2\pi i} \int_{-\infty}^{\infty} \frac{dE(E - E_j + \frac{1}{2}i\gamma_j)e^{i(E_o - E)t}}{(E - E_1)(E - E_2)}, \quad (16)$$

$$b_j(t) = \frac{-1}{2\pi i} \int_{-\infty}^{\infty} \frac{dE H_{jo} e^{i(E_j - E)t}}{(E - E_1)(E - E_2)}, \quad (17)$$

$$b_f(t) = \frac{-1}{2\pi i} \times \int_{-\infty}^{\infty} \frac{dE [H_{fj}H_{jo} + H_{fo}(E - E_j + \frac{1}{2}i\gamma_j)] [e^{i(E_f - E)t} - 1]}{(E - E_1)(E - E_2)(E - E_f)}. \quad (18)$$

The real parts of the poles  $E_1$  and  $E_2$  are the perturbed energies of the excited states, and the imaginary parts of  $E_1$  and  $E_2$  determine the decay characteristics of the system.

The Eqs. (16)–(18) can be evaluated by contour integration. Since  $\text{Im}(E_1) < 0$  and  $\text{Im}(E_2) < 0$  the path of integration is taken to be a clockwise infinite semicircular contour including the lower half of the complex plane. Using the theory of residues, we find

$$b_o(t) = [(E_1 - E_j + \frac{1}{2}i\gamma_j)e^{i(E_o - E_1)t} - (E_2 - E_j + \frac{1}{2}i\gamma_j)e^{i(E_o - E_2)t}] (E_1 - E_2)^{-1}, \quad (19)$$

$$b_j(t) = [e^{i(E_j - E_1)t} - e^{i(E_j - E_2)t}] (E_1 - E_2)^{-1}, \quad (20)$$

$$b_f(t) = \frac{[H_{fo}(E_1 - E_j + \frac{1}{2}i\gamma_j) + H_{jo}H_{fj}][e^{i(E_f - E_1)t} - 1]}{(E_1 - E_2)(E_1 - E_f)} - \frac{[H_{fo}(E_2 - E_j + \frac{1}{2}i\gamma_j) + H_{jo}H_{fj}][e^{i(E_f - E_2)t} - 1]}{(E_1 - E_2)(E_2 - E_f)}. \quad (21)$$

Finally, the probabilities of the states  $|o\rangle$ ,  $|j\rangle$  and  $|f\rangle$  are obtained by multiplying Eqs. (19)–(21) by their respective complex conjugates:

$$|b_o(t)|^2 = \frac{1}{4}(P^2 + Q^2)^{-1} \left\{ [(\Delta + P)^2 + (X + Q)^2] e^{-(X_o + X_j - Q)t} + [(\Delta - P)^2 + (X - Q)^2] e^{-(X_o + X_j + Q)t} - 2e^{-(X_o + X_j)t} \{ [\Delta^2 + X^2 - P^2 - Q^2]^2 + [(X + Q)(\Delta - P) - (\Delta + P)(X - Q)]^2 \}^{1/2} \cos(Pt - \phi) \right\}, \quad (22)$$

$$|b_j(t)|^2 = 2V_{jo}^2 (P^2 + Q^2)^{-1} e^{-(X_o + X_j)t} [\cosh(Qt) - \cos(Pt)], \quad (23)$$

$$|b_f(t)|^2 = |a_1(\epsilon)|^2 \{ 1 + e^{-(X_o + X_j - Q)t} - 2e^{-1/2(X_o + X_j - Q)t} \cos[\frac{1}{2}(\epsilon - P)t] \} + |a_2(\epsilon)|^2 \{ 1 + e^{-(X_o + X_j + Q)t} - 2e^{-1/2(X_o + X_j + Q)t} \cos[\frac{1}{2}(\epsilon + P)t] \} + 2a(\epsilon) \{ e^{-(X_o + X_j)t} \cos(Pt + \theta) + \cos\theta - e^{-1/2(X_o + X_j - Q)t} \cos[\frac{1}{2}(\epsilon - P)t + \theta] - e^{-1/2(X_o + X_j + Q)t} \cos[\frac{1}{2}(\epsilon + P)t - \theta] \}. \quad (24)$$

In the above equations the following definitions have been used:

$$\Delta = E_o - E_j, \quad V_{j_o} = \langle j | V | o \rangle, \quad X_o = \frac{1}{2} \gamma_o,$$

$$X_j = \frac{1}{2} \gamma_j, \quad X = X_j - X_o,$$

$$P = \left[ (\Delta^2 + X^2)^2 + 16 V_{j_o}^4 + 8 V_{j_o}^2 (\Delta^2 - X^2) \right]^{1/4} \\ \times \cos \left[ \frac{1}{2} \tan^{-1} \left( \frac{-2 \Delta X}{\Delta^2 - X^2 + 4 V_{j_o}^2} \right) \right],$$

$$Q = \left[ (\Delta^2 + X^2)^2 + 16 V_{j_o}^4 + 8 V_{j_o}^2 (\Delta^2 - X^2) \right]^{1/4} \\ \times \sin \left[ \frac{1}{2} \tan^{-1} \left( \frac{-2 \Delta X}{\Delta^2 - X^2 + 4 V_{j_o}^2} \right) \right],$$

$$\phi = \tan^{-1} \left( \frac{2(\Delta Q - X P)}{\Delta^2 + X^2 - P^2 - Q^2} \right), \quad \epsilon = 2E_f - (E_o + E_j),$$

$$a_{1,2}(\epsilon) = \left( [H_{f_o}(\Delta \pm P) - 2V_{j_o}H_{f_j}][\pm(P^2 - Q^2) - \epsilon P + Q(X_o + X_j)] + (X \pm Q)[\pm 2PQ - Q\epsilon - P(X_o + X_j)] \right. \\ \left. + i \{ [H_{f_o}(\Delta \pm P) - 2V_{j_o}H_{f_j}][\mp 2PQ + Q\epsilon + P(X_o + X_j)] + (X \pm Q)[\pm(P^2 - Q^2) - \epsilon P + Q(X_o + X_j)] \} \right) \\ \times \{ (P^2 + Q^2)[(\epsilon \mp P)^2 + (X_o + X_j \mp Q)^2] \}^{-1}, \\ a(\epsilon)e^{i\theta} = a_1(\epsilon)a_2^*(\epsilon).$$

The probabilities of the initial state [Eq. (22)] and the intermediate state [Eq. (23)] contain three different decay terms. Two of them are pure exponential decays while the third is a modulated exponential decay. The decay rates are  $X_o + X_j \pm Q$  for the pure exponential decays, respectively, and the modulated decay rate is  $X_o + X_j$ . The decay

probability of the intermediate state agrees with the result of Wangsness.<sup>5</sup> The probability of the final states [Eq. (24)] increases monotonically as a function of time. A plot of  $|b_f(t)|^2$  as a function of frequency of the emitted photons generally shows two distant peaks. As  $t \rightarrow \infty$ , Eq. (24) can be written as

$$|b_f(\infty)|^2 = \frac{|H_{f_o}|^2 [(K + \Delta)^2 + X_j^2] + |H_{f_j}|^2 V_{j_o}^2 + 2V_{j_o} [(K + \Delta) \operatorname{Re}(H_{f_o}H_{f_j}^*) - X_j \operatorname{Im}(H_{f_o}H_{f_j}^*)]}{K^2(K + \Delta)^2 + X_o^2 X_j^2 + V_{j_o}^4 + X_j^2 K^2 + X_o^2 (K + \Delta)^2 - 2V_{j_o}^2 [K(K + \Delta) - X_o X_j]}, \quad (25)$$

where  $K = k_\sigma - (E_o - E_c)$ ,  $k_\sigma$  is the wave number of the emitted photon, and the other symbols are as defined above.

The frequency distribution for an uncoupled initial state can be obtained from Eq. (25) by setting  $V_{j_o} = 0$ . This yields

$$|b_f(\infty)|^2 = |H_{f_o}|^2 / (K^2 + X_o^2). \quad (26)$$

On the other hand, if one assumes that the decay constant of the initial state vanishes ( $\gamma_o = 0$ ), then

$$|b_f(\infty)|^2 = |H_{f_j}|^2 V_{j_o}^2 / \{ [K(K + \Delta) - V_{j_o}^2]^2 + X_j^2 K^2 \}. \quad (27)$$

To illustrate some of the features of the decay of

two coupled excited states, we have calculated the decay of the  $n = 2$ ,  $j = \frac{1}{2}$  states in atomic hydrogen coupled by an electric field. In this case the  $2S_{1/2}$  state is the initial state  $|o\rangle$ , and the  $2P_{1/2}$  state the intermediate state  $|j\rangle$ . In Fig. 1 we have plotted the time dependence of the two excited states. An electric field of 100 V/cm produces a  $V_{j_o}$  of  $2.2\gamma_j$ . Fig. 2 gives the frequency distribution of emitted photons. This curve shows the two peaks characteristic of this type of decay.

#### APPENDIX

It is possible to use the Heitler-Ma method to derive the differential equations of motion for the states  $|o\rangle$  and  $|j\rangle$  which contain damping terms

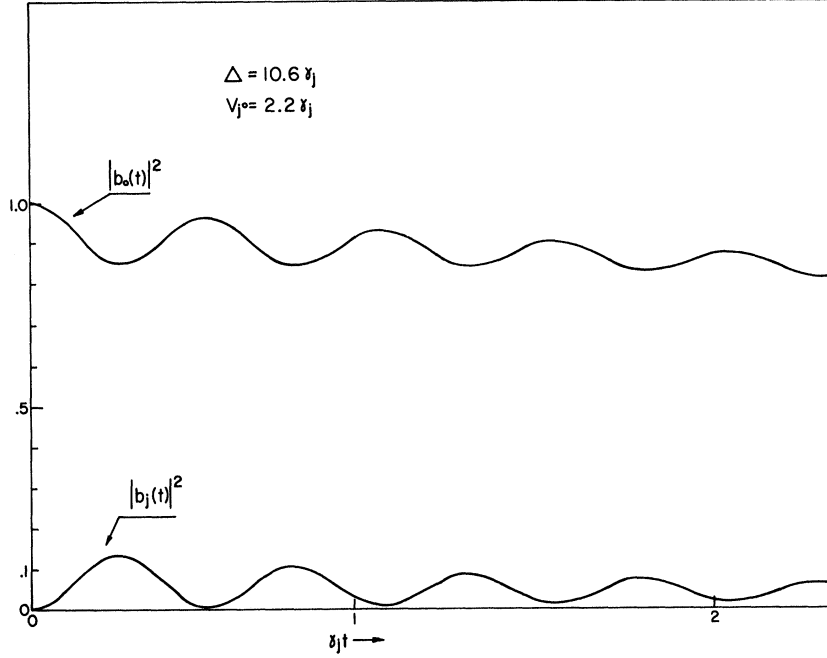


FIG. 1. Probabilities of the excited states  $|o\rangle$  and  $|j\rangle$  as a function of time for the case  $\gamma_{00} = \gamma_{j0} = 0$ . Time is in units of the natural decay time  $\gamma_j^{-1}$  of the unperturbed state  $|j\rangle$ .  $\Delta = E_0 - E_j$  is the unperturbed energy separation of the excited states.

to account for the coupling to the final states. For reference Eqs. (5)–(7) are listed:

$$(E - E_0)G_o = H_{oj}G_j + \sum_f H_{of}G_f + 1, \quad (5)$$

$$(E - E_j)G_j = H_{jo}G_o + \sum_f H_{jf}G_f, \quad (6)$$

$$(E - E_f)G_f = H_{fo}G_o + H_{fj}G_j. \quad (7)$$

Equation (7) can be solved for  $G_f$ :

$$G_f = H_{fo}G_o + H_{fj}G_j / (E - E_f). \quad (A1)$$

Using Eqs. (A1) and (8), Eqs. (5) and (6) can be rewritten to yield the following expressions:

$$(E - E_0)G_o = [H_{oj} - \frac{1}{2}i\gamma_{oj}(E)]G_j - \frac{1}{2}i\gamma_{oo}(E)G_o + 1, \quad (A2)$$

$$(E - E_j)G_j = [H_{jo} - \frac{1}{2}i\gamma_{jo}(E)]G_o - \frac{1}{2}i\gamma_{jj}(E)G_j. \quad (A3)$$

Both sides of Eq. (A2) are now multiplied by  $-1/2\pi i e^{i(E_0 - E)t}$  and integrated over  $E$  to give

$$\begin{aligned} & (-1/2\pi i) \int_{-\infty}^{\infty} dE (E - E_0) [G_o e^{i(E_0 - E)t}] \\ &= (-1/2\pi i) e^{i(E_0 - E_j)t} \int_{-\infty}^{\infty} dE [H_{oj} - \frac{1}{2}i\gamma_{oj}(E)] \\ &\quad \times G_j e^{i(E_j - E)t} - \frac{1}{2}i \left[ - (1/2\pi i) \int_{-\infty}^{\infty} dE \gamma_{oo}(E) \right. \\ &\quad \times G_o e^{i(E_0 - E)t} \left. + \left[ - (1/2\pi i) \int_{-\infty}^{\infty} dE e^{i(E_0 - E)t} \right] \right]. \end{aligned} \quad (A4)$$

Since  $\gamma_{oo}(E)$  and  $\gamma_{oj}(E)$  vary slowly with  $E$ , they are treated as constants and taken outside the integrals in Eq. (A4). Now using Eqs. (3) and (4), it follows that

$$\begin{aligned} \frac{d}{dt} b_o(t) = & -i(H_{oj} - \frac{1}{2}i\gamma_{oj})e^{i(E_0 - E_j)t} b_j(t) \\ & - \frac{1}{2}\gamma_o b_o(t) + \delta(t). \end{aligned} \quad (A5)$$

In the same manner Eq. (A3) can be multiplied by  $-(1/2\pi i)e^{i(E_j - E)t}$  and integrated over  $E$  to give

$$\begin{aligned} \frac{d}{dt} b_j(t) = & -i(H_{jo} - \frac{1}{2}i\gamma_{jo})e^{i(E_j - E_o)t} b_o(t) \\ & - \frac{1}{2}\gamma_j b_j(t), \end{aligned} \quad (A6)$$

where  $\gamma_{jj}(E)$  and  $\gamma_{jo}(E)$  are taken to be the constants  $\gamma_j$  and  $\gamma_{jo}$ . As was pointed out above,  $\gamma_{jo}(E) = \gamma_{oj}(E) = 0$  if  $|a\rangle$  and  $|b\rangle$  are good angular momentum states. Equations (A5) and (A6) then reduce to the following:

$$\begin{aligned} \frac{d}{dt} b_o(t) = & -iH_{oj}e^{i(E_0 - E_j)t} b_j(t) \\ & - \frac{1}{2}\gamma_o b_o(t) + \delta(t), \end{aligned} \quad (A7)$$

$$\frac{d}{dt} b_j(t) = -iH_{jo}e^{i(E_j - E_o)t} b_o(t) - \frac{1}{2}\gamma_j b_j(t). \quad (A8)$$

These are the differential equations of motion which are assumed in the phenomenological theory for the system of two coupled decaying states.

The solution of Eqs. (A7) and (A8) yields the decay characteristics of the initial state  $|o\rangle$  and the intermediate state  $|j\rangle$  coupled to a set of final states  $|f\rangle$ . The initial conditions as represented by the  $\delta$  function are  $b_o(0) = 1$  and  $b_j(0) = b_f(0) = 0$ . The real parts of  $\gamma_o$  and  $\gamma_j$  are the damping constants of the isolated states  $|o\rangle$  and  $|j\rangle$ , respec-

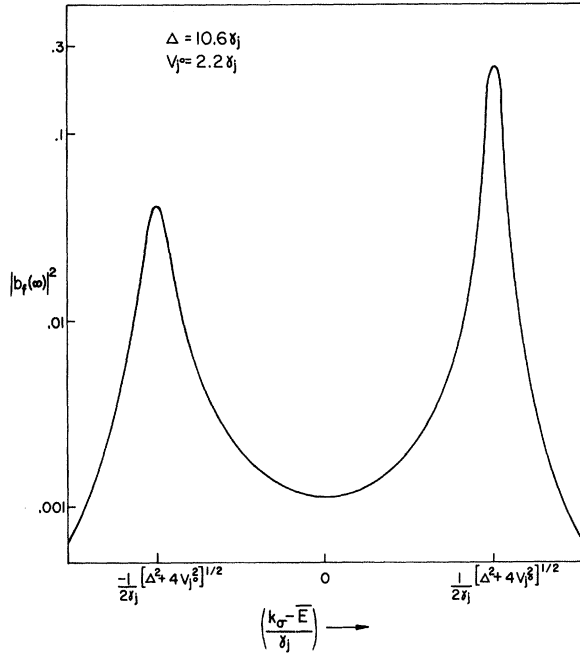


FIG. 2. Frequency distribution of final states for the case of  $\gamma_{00} = \gamma_{j0} = 0$ . The frequency is in units of the natural linewidth  $\gamma_j$  of the unperturbed state  $|j\rangle$ ;  $\bar{E} = \frac{1}{2}[(E_0 - E_c) + (E_j - E_c)]$  is the average energy of the excited atomic states above the ground state;  $\Delta = E_0 - E_j$  is the energy separation of the excited states when  $V_{j0} = 0$ ; and  $(\Delta^2 + 4V_{j0}^2)^{1/2}$  is the approximate perturbed energy separation of the excited states.

tively. For more than two excited states, the elimination of the final states proceeds in exactly the same way, and the resulting expressions are similar to Eqs. (A7) and (A8).

The line shape of the emitted radiation can be obtained from the solutions<sup>12</sup> of Eqs. (A7) and (A8) by using the following procedure.

The inverse of Eq. (3) is

$$G_n(E) = -i \int_{-\infty}^{\infty} b_n(t) e^{i(E - E_n)t} dt. \quad (\text{A9})$$

Inserting Eq. (A9) into Eq. (A1) gives

$$G_f(E) = \frac{1}{E - E_f} \left[ H_{f0} \int_{-\infty}^{\infty} b_0(t) e^{i(E_0 - E)t} dt + H_{fj} \int_{-\infty}^{\infty} b_j(t) e^{i(E_j - E)t} dt \right]. \quad (\text{A10})$$

The intensity of radiation is proportional to  $|b_f(\infty)|^2$ , and it can be shown that<sup>8</sup>

$$b_f(\infty) = [(E - E_f)G_f(E)]_{E=E_f}. \quad (\text{A11})$$

The resulting expression for  $|b_f(\infty)|^2$  agrees with Eq. (25) above.

<sup>1</sup>V. Weisskopf and E. Wigner, *Z. Physik* **63**, 54 (1930).

<sup>2</sup>H. Bethe, *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Springer Verlag, Berlin, 1933), 2nd ed., Vol. 24/1, p. 455.

<sup>3</sup>P. Kusch and V. W. Hughes, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), 3rd ed., Vol. 37/1, p. 72.

<sup>4</sup>H. Wieder and T. G. Eck, *Phys. Rev.* **153**, 103 (1967).

<sup>5</sup>R. K. Wangness, *Phys. Rev.* **149**, 60 (1966).

<sup>6</sup>Reference 1, p. 67.

<sup>7</sup>W. Heitler and S. T. Ma, *Proc. Roy. Irish Acad.*

*A52*, 109 (1949).

<sup>8</sup>W. Heitler, *The Quantum Theory of Radiation* (Oxford U. P., London, 1954), pp. 163-174.

<sup>9</sup>Reference 8, p. 165.

<sup>10</sup>Reference 7, pp. 115-116.

<sup>11</sup>G. Breit, *Rev. Mod. Phys.* **5**, 91 (1933); see the discussion on p. 118. There are, however, atomic systems where  $\gamma_{j0}$  does not vanish; see J. W. Czarnik and P. R. Fontana, *J. Chem. Phys.* **50**, 4071 (1969).

<sup>12</sup>These solutions are carried out in Ref. 5. The results are Eqs. (19) and (20) given above.