Spectral Line Shape in the Presence of Weak Collisions and Intense Fields

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A general treatment of the resolvent operator in Liouville space using the Goldberger-Watson approach is presented. Exact, formal expressions for the matrix elements of the resolvent, as well as approximate expressions based on an iteration procedure, are given. The formalism is then applied to the study of the line shape of atomic transitions in the presence of both weak collisions and an intense radiation field. The dependence of the line shape on the intensity and spectral composition of the field is discussed, and expressions for shifts and widths are derived.

1. INTRODUCTION

A LARGE class of line-shape problems might be abstracted as follows: Two uncoupled systems are brought into interaction at time $t=0$. As a result of this interaction, one or more particles (or quasiparticles) are emitted, scattered, or absorbed. The line-shape problem is to find out how the probability of such processes depends on the energy of the particles (or quasiparticles) involved.

From a theoretical standpoint, the simplest line-shape problem is that of an isolated atom in an excited state, making a spontaneous radiative transition to the ground state. Heitler[1] has developed a method to treat this problem; namely, his theory of damping phenomena. What causes the line to shift and broaden in this case is the coupling of the atom to the vacuum radiation field. We are talking here about the nonrelativistic problem, although Heitler has treated the fully relativistic case. The idea of the damping theory is quite simple. Starting with an initial state containing the vacuum field and the excited atom, one calculates the probability that the atom is in the ground state and a photon of energy $\hbar\omega$ is present. This probability is a function of the time t. Taking the limit for $t\rightarrow\infty$, one obtains a function of ω which is the line-shape function. If the transition takes place via an intermediate level and two photons are emitted, one calculates the probability that the atom is in the ground state and two photons are present. Summing over all possible frequencies of the photon emitted in one of the transitions, one obtains the line shape of the other transition. In a similar fashion one can treat many other problems such as absorption, resonance fluorescence, scattering, etc. Heitler's method is a particular way of handling the time-evolution operator e^{-iHt} which determines the time development of a quantum-mechanical system whose Hamiltonian is H. This method, in a more general and elegant mathematical form, has been discussed extensively by Goldberger and Watson.[2]

In actual experimental situations, one never has an isolated atom. As a consequence, the line shape of radiative transitions is usually determined by factors other than the radiation field, such as collisions with other atoms, Doppler effect, external fields, etc. Consider, for example, the problem of collision broadening of spontaneous radiative transitions in a gas in thermal equilibrium. Since it is the collisions that keep the gas in equilibrium, the effect of the vacuum field is negligible compared to the effect of the collisions. Thus, in such problems, the natural broadening can normally be neglected. As far as collision (pressure) broadening is concerned, there has been a considerable amount of work, but no attempt will be made here to give a complete list of references. For a review of the older work, the reader is referred to Breene's[3] book. More recently, Baranger[4] was really the first to present a fully quantum-mechanical treatment of the problem. Although his approach is fairly general (within the frame of the impact approximation), the emphasis is on applications in plasmas where the long-range forces pose special problems. Later, Fano[5] approached the problem from a different point of view. He used the Liouville representation, as developed by Zwanzig,[6] to study the motion of the density operator of the gas. Attention is focused upon one atom which is undergoing the radiative transition and an average over the degrees of freedom of the rest of the gas (which is regarded as the thermal bath) is taken. A similar approach to the problem of quantum relaxation (of which pressure broadening is an example) is that of Lax.[7] The main difference between this and Fano's work is that Lax does not use the Liouville representation and works in the time domain while Fano works in the frequency domain. Otherwise, both authors study the density matrix and eliminate the bath variables. In addition, Lax is more

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[2] M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), Chap. 8.

[3] R. G. Breene, Jr., *The Shift and Shape of Spectral Lines* (Pergamon Press, Inc., New York, 1961).

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[6] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960); and in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Interscience Publishers, Inc., New York, 1961).

[7] M. Lax, J. Phys. Chem. Solids **25**, 487 (1964).

interested in broadening due to anharmonic effects in crystals rather than in pressure broadening, although the two problems are quite similar. Finally, a slightly different treatment of pressure broadening in the impact approximation has been given by Cooper[8] and also by Davis.[9] Both authors use the density-matrix formalism.

Problems such as pressure broadening, broadening in neutron scattering by anharmonic crystals, etc., have one basic feature in common which distinguishes them from the problem of natural broadening. In the first class of problems, the broadening is caused by an interaction different from the one that induces the transition; in the case of natural broadening it is the same interaction that causes the transition as well as the broadening, as Brout[10] has pointed out. Now, although natural broadening is usually negligible when other broadening effects are present, it is not generally true that the broadening due to the Hamiltonian that induces the transition is also negligible. The existence of high-intensity light sources (lasers) makes it possible to observe[11] transitions in which the effect of an optical frequency field is comparable to that of the collisions. This is because the initial field state contains a large number of photons and it is not the vacuum state as in natural broadening. Karplus and Schwinger[12] have discussed an analogous phenomenon in the microwave region using a different approach.

It is the purpose of this paper to present a method for treating line-shape problems, in which broadening caused by the Hamiltonian that induces the transitions and broadening caused by other interactions are treated on an equal footing. The present approach, which has been motivated by Fano's[5] work, exploits the formal similarity between the time-evolution operator $\exp(-iHt)$ governing the time development of the wave function, and the time-evolution operator $\exp(-iLt)$ in the Liouville representation governing the time development of the density matrix. A treatment of the line-shape problem in slow neutron scattering by anharmonic crystals using the techniques of damping theory and cast in terms of the operator $\exp(-iHt)$ has been given by Akcasu and Osborn.[13]

In Sec. 2 we study the relevent operator in Liouville space. The analysis proceeds along lines similar to those of Goldberger and Watson[2] and results in a set of integral equations satisfied by the matrix elements of the resolvent operator. These equations are then used for a perturbation calculation to lowest nonvanishing order.

As an application of the method, we study in Sec. 3 the line shape of induced optical transitions in a gas taking into account both broadening caused by the radiation field and broadening due to weak collisions. The assumption is that the collisions are weak so that a calculation to the lowest nonvanishing order is a good first approximation. What we have in mind are collisions between neutral atoms where no long-range forces are involved. Most of the time the atom suffers weak collisions that perturb its state very little. Strong collisions must be well separated in time; i.e., the time between strong collisions must be large compared to the duration of the collision. Under these conditions and as long as the interaction is small enough not to cause overlapping of the lines, perturbation theory can be used (see, for example, Baranger's[4] third paper, Sec. 4). Thus, as far as collisions are concerned, we have rederived with a different method Baranger's result for isolated lines for the case in which both initial and final state are perturbed. But at the same time, we allow for broadening effects due to the radiation field and study the dependence of such effects on the intensity and spectral composition of the field.

2. FORMULATION

The total Hamiltonian of the problems we shall be concerned with can generally be written as

$$H=H^S+H^P+H^R+V^C+V^{SR}+V^{PR}, \qquad (2.1)$$

where H^S shall be referred to as the "system" Hamiltonian, H^P as the "perturber" Hamiltonian, and H^R as the "radiation" Hamiltonian. It will be understood that the total Hamiltonian is broken up in such a fashion that the eigenstates and eigenvalues of H^S, H^P, and H^R can be found. The term V^C represents the interaction between system and perturber; V^{SR} represents the interaction between the system and the radiation, while V^{PR} stands for the interaction between perturber and radiation. In some cases, the total Hamiltonian can be broken up so that V^{PR} either vanishes or can be neglected. Here, however, we shall retain it for the sake of consistency. Introducing the notation

$$H^0\equiv H^S+H^P+H^R \qquad (2.2a)$$

and

$$V\equiv V^C+V^{SR}+V^{PR}, \qquad (2.2b)$$

(2.1) reads

$$H=H^0+V. \qquad (2.3)$$

Let $|a\rangle$, $|b\rangle$, $\cdots$ be the eigenstates of H^0 with energies ω_a, ω_b, $\cdots$, i.e.,

$$H^0|a\rangle\equiv\omega_a|a\rangle. \qquad (2.4)$$

It is assumed throughout this paper that all Hamiltonians have been divided by $\hbar$.

If now $\rho(t)$ is the total density operator, its time evolution is governed by the Schrödinger equation

$$(d/dt)\rho(t)=-i[H,\rho(t)]. \qquad (2.5)$$

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[9] J. Davis, Proc. Phys. Soc. (London) **90**, 283 (1967).
[10] R. Brout, Phys. Rev. **107**, 664 (1957).
[11] E. B. Aleksandrov *et al.*, JETP Pis'ma v Redakstiyu **3**, 85 (1966) [English transl.: Soviet Phys.—JETP Letters **3**, 53 (1966)].
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Introducing the Liouville operator L defined by[5,14]

$$L_{ab;\,a'b'}\equiv H_{aa'}\delta_{bb'}-H_{bb'}{}^{*}\delta_{aa'}\,, \tag{2.6}$$

where the asterisk denotes complex conjugation, (2.5) can be written as

$$(d/dt)\rho(t)=-iL\rho(t)\,. \tag{2.7}$$

Note that in matrix form this equation reads

$$(d/dt)\rho_{ab}(t)=-i\sum_{a'b'}L_{ab;a'b'}\rho_{a'b'}(t)\,. \tag{2.8}$$

One can now write the formal solution

$$\rho(t)=\mathfrak{U}(t)\rho(0) \tag{2.9}$$

of (2.7), where $\mathfrak{U}(t)$ is a Liouville time-evolution operator defined by

$$\mathfrak{U}(t)\equiv e^{-iLt}. \tag{2.10}$$

Since L is a Hermitian operator, $\mathfrak{U}(t)$ is unitary. It should also be noted that L can be written as

$$L^{S}+L^{P}+L^{C}+L^{R}+L^{SR}+L^{PR}\equiv L^{0}+L^{I}, \tag{2.11}$$

where the meaning of the symbols become self-evident when compared to Eqs. (2.2).

Taking the Laplace transform of (2.10) one is led to the resolvent operator

$$\mathcal{G}(z)\equiv 1/(z-L) \tag{2.12}$$

in terms of which $\mathfrak{U}$ is expressed as

$$\mathfrak{U}(t)=\frac{1}{2\pi i}\int_{C}e^{-izt}\mathcal{G}(z)dz\,, \tag{2.13}$$

where the contour C on the z plane runs from $i\epsilon+\infty$ to $i\epsilon-\infty$ with ϵ being a positive number. That this is the appropriate contour is easily seen if one recalls that H has real eigenvalues which, by virtue of (2.6), implies that $\mathcal{G}(z)$ has all its singularities on the real axis. For $t>0$, (2.13) becomes

$$\mathfrak{U}(t)=-\frac{1}{2\pi i}\int_{-\infty}^{+\infty}dx\,e^{-ixt}\mathcal{G}(x^{+})\,, \tag{2.14}$$

where

$$\mathcal{G}(x^{\pm})\equiv\lim_{\epsilon\to+0}\mathcal{G}(x\pm i\epsilon) \tag{2.15}$$

and x is a real variable. Thus, the problem of calculating matrix elements of the time-evolution operator is reduced to one of calculating the corresponding matrix element of the resolvent and then computing the inversion integral. However, often one is not interested in the inversion integral because the resolvent operator itself can be used directly to give the line shape.

Now we proceed to study the matrix elements of $\mathcal{G}(z)$. First, we observe that, in the representation that diagonalizes H^{0}, the Liouville operator L^{0} is also diagonal, i.e.,

$$L_{ab;\,a'b'}{}^{0}=(\omega_a-\omega_b)\delta_{aa'}\delta_{bb'}\,, \tag{2.16}$$

from which it follows that

$$\left(\frac{1}{z-L^{0}}\right)_{ab;\,a'b'}=\frac{1}{z-\omega_a+\omega_b}\delta_{aa'}\delta_{bb'}\,. \tag{2.17}$$

Using a well-known operator identity, $\mathcal{G}(z)$ can be written as

$$\mathcal{G}(z)=\frac{1}{z-L^{0}-L^{I}}=\frac{1}{z-L^{0}}+\frac{1}{z-L^{0}}L^{I}\mathcal{G}(z)\,, \tag{2.18}$$

from which we obtain

$$\mathcal{G}_{ab;\,cd}(z)=\frac{1}{z-\omega_a+\omega_b}\times\{\delta_{ac}\delta_{bd}+\sum_{a'b'}L_{ab;\,a'b'}{}^{I}\mathcal{G}_{a'b';\,cd}(z)\}\,, \tag{2.19}$$

where we have used (2.17).

Consider diagonal matrix elements for which (2.19) gives

$$\mathcal{G}_{cd;\,cd}(z)=\frac{1}{z-\omega_c+\omega_d}\{1+L_{cd;\,cd}{}^{I}\mathcal{G}_{cd;cd}+\sum_{a'b'(\neq cd)}L_{cd;\,a'b'}{}^{I}\mathcal{G}_{a'b';\,cd}(z)\}\,. \tag{2.20}$$

For off-diagonal matrix elements $\mathcal{G}_{ab;\,cd}$ (with $ab\neq cd$), we introduce the operator $F(z)$ defined by

$$\mathcal{G}_{ab;\,cd}(z)\equiv F_{ab;\,cd}(z)\mathcal{G}_{cd;\,cd}(z) \tag{2.21a}$$

and

$$F_{cd;\,cd}(z)\equiv 1\,. \tag{2.21b}$$

Substituting into Eqs. (2.20) and (2.19), we obtain

$$F_{ab;\,cd}(z)=\frac{1}{z-\omega_a+\omega_b}\{L_{ab;\,cd}{}^{I}+\sum_{a'b'(\neq cd)}L_{ab;\,a'b'}{}^{I}F_{a'b';\,cd}(z)\} \tag{2.22}$$

and

$$\mathcal{G}_{cd;\,cd}(z)\{z-\omega_c+\omega_d-L_{cd;cd}{}^{I}-\sum_{a'b'(\neq cd)}L_{cd;\,a'b'}{}^{I}F_{a'b';\,cd}\}=1\,. \tag{2.23}$$

At this point it is convenient to introduce a set of orthogonal projection operators P^{ab} defined by

$$P_{a'b';\,a''b''}{}^{ab}\equiv\delta_{a'a}\delta_{a''a}\delta_{b'b}\delta_{b''b}\,. \tag{2.24}$$

It is easy to verify that they have the property

$$P^{ab}P^{cd}=P^{ab}\delta_{ac}\delta_{bd} \tag{2.25}$$

which shows that they indeed are orthogonal projection

[14] U. Fano, Rev. Mod. Phys. **29**, 74 (1957).

operators. If Ω is any operator in Liouville space, one can show that

$$(P^{ab}\Omega)_{a'b';\ a''b''}=\Omega_{ab;\ a''b''}\delta_{a'a}\delta_{b'b} \tag{2.26a}$$

and

$$(\Omega P^{ab})_{a'b';\ a''b''}=\Omega_{a'b';\ ab}\delta_{a''a}\delta_{b''b}. \tag{2.26b}$$

We shall also need a set of projection operators Q^{ab} defined by

$$Q^{ab}\equiv\sum_{a'b'(\neq ab)}P^{ab}. \tag{2.27}$$

That these operators have the projection property $Q^{ab}Q^{ab}=Q^{ab}$ is a consequence of Eq. (2.25). Finally, one can readily verify that P^{ab} as well as Q^{ab} commute with L^0 or any other operator diagonal in the $\{|a\rangle\}$ representation.

Let us now introduce the operator $R(z)$ defined by

$$R(z)\equiv L^IF(z). \tag{2.28}$$

Because of Eqs. (2.21b) and (2.22), we can write

$$F=\frac{1}{z-L^0}L^IF=\frac{1}{z-L^0}R, \tag{2.29}$$

from which it follows that

$$F_{ab;\ cd}(z)=\frac{1}{z-\omega_a+\omega_b}R_{ab;\ cd}(z). \tag{2.30}$$

Note that the last two equations are good for calculating off-diagonal matrix elements only. Substituting now (2.30) into (2.22) and using the projection operator Q^{cd} we obtain

$$R(z)=L^I+L^IQ^{cd}\frac{1}{z-L^0}R(z) \tag{2.31}$$

which is an integral equation for $R(z)$. This operator can also be used in (2.23) if we observe that the last two terms inside the brackets are nothing else but $R_{cd;\ cd}(z)$. Thus Eq. (2.23) immediately gives

$$\mathcal{G}_{cd;\ cd}(z)=\frac{1}{z-\omega_c+\omega_d-R_{cd;\ cd}(z)}. \tag{2.32}$$

As for the off-diagonal matrix elements of $\mathcal{G}(z)$, from Eqs. (2.21a) and (2.30) we obtain

$$\mathcal{G}_{ab;\ cd}(z)=\frac{1}{z-\omega_a+\omega_b}R_{ab;\ cd}(z)\times\frac{1}{z-\omega_c+\omega_d-R_{cd;\ cd}(z)}. \tag{2.33}$$

Now we have expressed all matrix elements of the resolvent in terms of $R(z)$ and we have an integral equation for R.

The structure of Eq. (2.32) suggests that $R_{cd;\ cd}$ plays the role of a shift-width function, except that it does not refer to a single level but to a pair of levels. In fact, it will be seen later that it is a combination of the shifts and widths of the levels $|c\rangle$ and $|d\rangle$. In order to separate shifts from widths, we need to study the operator $R(z)$ somewhat further.

By introducing the operator

$$L^Q\equiv L^0+Q^{cd}L^IQ^{cd}, \tag{2.34}$$

which is a Hermitian operator commuting with Q^{cd}, one can show that

$$R(z)=L^I+L^IQ^{cd}\frac{1}{z-L^Q}Q^{cd}L^I, \tag{2.35}$$

from which it is obvious that

$$R^\dagger(z)=R(z^*). \tag{2.36}$$

Now, starting with Eq. (2.31) and following a procedure similar to that of Ref. 2, we obtain

$$R(z)-R^\dagger(z)=-2iR^\dagger(z)\times\frac{\mathrm{Im}z}{(\mathrm{Re}z-L^0)^2+(\mathrm{Im}z)^2}Q^{cd}R(z). \tag{2.37}$$

Because of (2.36) we can write

$$\lim_{\epsilon\to+0}R_{cd;\ cd}(x\pm i\epsilon)\equiv D_{cd}(x)\mp\Gamma_{cd}(x). \tag{2.38}$$

Combining this with (2.37) and using the identity

$$\lim_{\epsilon\to+0}\frac{\epsilon}{(x-L^0)^2+\epsilon^2}=\pi\delta(x-L^0),$$

we obtain

$$\Gamma_{cd}(x)=\pi\{R^\dagger(x^+)\delta(x-L^0)Q^{cd}R(x^+)\}_{cd;\ cd}, \tag{2.39}$$

which is positive definite and represents a width. The shift $D_{cd}(x)$ can be calculated through the dispersion relation[2]

$$D_{cd}(x)=L_{cd;\ cd}{}^I-\frac{\mathrm{P}}{\pi}\int_{-\infty}^{+\infty}\frac{\Gamma_{cd}(x')dx'}{x'-x}, \tag{2.40}$$

where P denotes the Cauchy principal value. Introducing (2.38) into (2.32), we obtain

$$\lim_{\epsilon\to+0}\mathcal{G}_{cd;\ cd}(x\pm i\epsilon)=\frac{1}{x-\omega_c+\omega_d-D_{cd}(x)\pm i\Gamma_{cd}(x)}. \tag{2.41}$$

For the off-diagonal matrix elements of $\mathcal{G}(z)$, one has Eq. (2.33), where $R_{ab;\ cd}$ is still to be calculated. For this we have the integral equation (2.31) which we can iterate and truncate after a certain term depending on the process under consideration and provided the

coupling is weak enough for the perturbation calculation to be meaningful. The iteration proceeds as follows:

From Eq. (2.31) we have

$$R_{ab;\,cd}=L_{ab;\,cd}{}^{I}+\sum_{a'b'}M_{ab;\,a'b'}R_{a'b';\,cd}$$
$$=L_{ab;\,cd}{}^{I}+M_{ab;\,ab}R_{ab;\,cd}+\sum_{a'b'(\neq ab)}M_{ab;\,a'b'}R_{a'b';\,cd}, \quad (2.42)$$

where, for simplicity, we have set

$$M\equiv L^{I}Q^{cd}[1/(z-L^{0})]. \quad (2.43)$$

Iterating Eq. (2.42) once, we obtain

$$R_{ab;\,cd}=L_{ab;\,cd}{}^{I}+M_{ab;\,ab}R_{ab;\,cd}+\sum_{a'b'(\neq ab)}M_{ab;\,a'b'}L_{a'b';\,cd}{}^{I}$$
$$+\sum_{a'b'(\neq ab)}\sum_{a''b''}M_{ab;\,a'b'}M_{a'b';\,a''b''}R_{a''b'';\,cd}, \quad (2.44)$$

which, upon separating the term for $a''b''=ab$, becomes

$$R_{ab;\,cd}=L_{ab;\,cd}{}^{I}+\{M_{ab;\,ab}+\sum_{a'b'(\neq ab)}M_{ab;\,a'b'}M_{a'b';\,ab}\}\times R_{ab;\,cd}+\sum_{a'b'(\neq ab)}M_{ab;\,a'b'}L_{a'b';\,cd}{}^{I}$$
$$+\sum_{a'b'(\neq ab)}\sum_{a''b''(\neq ab)}M_{ab;\,a'b'}M_{a'b';\,a''b''}R_{a''b'';\,cd}. \quad (2.45)$$

This process can be repeated. With every iteration, one obtains a new term containing $R_{ab;\,cd}$ as well as other terms. The terms containing $R_{ab;\,cd}$ give contributions to the shift-width function. To see this, we neglect the last term in Eq. (2.45). This term is of order higher than the second in L^{I}. Solving then for $R_{ab;\,cd}$ we obtain

$$R_{ab;\,cd}=\frac{L_{ab;\,cd}{}^{I}+\sum_{a'b'(\neq ab)}M_{ab;\,a'b'}L_{a'b';\,cd}{}^{I}}{1-W_{ab;\,cd}}, \quad (2.46)$$

where we have introduced

$$W_{ab;\,cd}(z)\equiv M_{ab;\,ab}+\sum_{a'b'(\neq ab)}M_{ab;\,a'b'}M_{a'b';\,ab}. \quad (2.47)$$

It is evident now that $W_{ab;\,cd}$ is a shift-width function and that further iterations will contribute terms of higher order to both the numerator and the denominator of (2.46). This equation represents an approximate expression for $R_{ab;\,cd}$ up to second order in L^{I}. Also, $W_{ab;\,cd}$ is calculated up to second order in L^{I}, which is quite satisfactory for many practical applications. The numerator, however, must be calculated to higher order in some cases. For example, in the case of Raman scattering by a crystal the lowest nonvanishing term in the numerator will be of sixth order in L^{I} (recall that L^{I} contains all interactions between the unperturbed parts of the Hamiltonian).

In the following sections we apply this formalism to the study of a line-shape problem. There are a few mathematical questions concerning the analytic properties of $\mathcal{G}(z)$ and $R(z)$ not touched upon at all. The reason for this omission is that Goldberger and Watson[2] have examined these problems in connection with the resolvent $(z-H)^{-1}$ and the associated R operator. Their considerations can be carried over to the present formalism almost verbatim.

3. LINE SHAPE OF INDUCED ATOMIC TRANSITIONS IN THE PRESENCE OF WEAK COLLISIONS

As an application of the formalism, we study in this section the spectrum of the induced transitions between atomic states, for the case in which the radiating atom undergoes collisions with other atoms. We think of a gas and focus our attention upon one atom (the atom of interest) which is undergoing a radiative transition. This atom—to be referred to hereafter as the system—can at the same time interact with the rest of the gas via collisions. We adopt the usual model used by Baranger,[4] Fano,[5] and others. The total Hamiltonian may be written as

$$H=H^{S}+H^{P}+V^{C}+H^{R}+V^{SR},$$

where H^{S} is the free Hamiltonian of the atom of interest (system); H^{P} is the sum of the free Hamiltonians of the atoms of the rest of the gas; V^{C} contains the interaction between system and the rest of the gas, as well as the interaction between the atoms of the rest of the gas; H^{R} is the Hamiltonian of the free radiation field and V^{SR} the interaction between system and radiation. We shall also use the notation

$$H^{0}\equiv H^{S}+H^{P}+H^{R}, \quad (3.1a)$$
$$V\equiv V^{C}+V^{SR}. \quad (3.1b)$$

Tht total Liouville operator is now written as

$$L\equiv L^{S}+L^{P}+L^{R}+L^{C}+L^{SR}\equiv L^{0}+L^{I}, \quad (3.2)$$

where the meaning of the symbols is obvious.

The starting point for the study of the spectrum will be the Fourier transform of the autocorrelation function of the dipole-moment operator, as discussed by Baranger.[4] Thus the quantity we wish to calculate is

$$\Phi(\omega)\equiv\pi^{-1}\,\mathrm{Re}\int_{0}^{\infty}dt\,e^{i\omega t}\,\mathrm{Tr}\{yy(t)\rho\}, \quad (3.3)$$

where y is the dipole operator of the atom, ρ is the total density operator at $t=0$, and $\mathrm{Im}\omega\rightarrow+0$. Fano[5] notices that

$$\mathrm{Tr}\{yy(t)\rho\}=\mathrm{Tr}\{ye^{-iLt}(\rho y)\}, \quad (3.4)$$

from which it easily follows that the spectrum is

$$\Phi(\omega)=\pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}\{y\mathcal{G}(x^{+}=\omega)(\rho y)\}. \quad (3.5)$$

If the initial state contains $N(\omega)$ photons per unit frequency, the power absorbed, or emitted by induced emission, in frequency interval $d\omega$ about ω, is $P(\omega)\,d\omega$, where

$$P(\omega)\equiv(4\omega^4/3c^3)N(\omega)\Phi(\omega). \tag{3.6}$$

We shall follow Baranger[4] and others in calling $\Phi(\omega)$ "the spectrum" although, strictly speaking, the spectrum is $P(\omega)$. This equation does not contain spontaneous emission. The spectrum of spontaneous emission is obtained from (3.6) by letting $N=1$. The effect of collisions is contained in $\Phi(\omega)$ as shown in Refs. 4 and 5. But $\Phi(\omega)$ also depends on $N(\omega)$. This gives rise to the natural line shape in the case of spontaneous emission when the initial state of the radiation field is the vacuum state. The focal point of this section is to find the dependence of $\Phi(\omega)$ on the initial state of the field taking into account at the same time the effect of collisions. Thus, from here on and throughout this section we study $\Phi(\omega)$.

Let us consider the representations that diagonalize H^S, H^P, and H^R, and denote the eigenstates by $|\alpha\rangle$, $|\beta\rangle$, $\cdots$, $|p\rangle|p'\rangle$, $\cdots$, and $|n\rangle,|m\rangle$, $\cdots$, respectively. The respective energies will be denoted by ω_α, $\omega_\beta\cdots$, ω_p, $\omega_{p'}\cdots$, ω_n, $\omega_m\cdots$. We mean by $|n\rangle$ the photon number representation. Consequently, n stands for a whole set of numbers specifying the number of photons in all modes. We shall make the usual assumption[5] that initially there is no significant correlation between the system, the rest of the gas, and the field. In addition, we shall assume that the system and the rest of the gas are in thermal equilibrium. Then we can write

$$\rho=\rho^S\rho^P\rho^R, \tag{3.7}$$

where ρ^S is diagonal in the α representation and ρ^P is diagonal in the p representation. The same assumption can not be made about ρ^R because, for laser light, ρ^R will in general possess off-diagonal matrix elements in the photon number representation. However, one can show[15] that the presence of these matrix elements is of neither mathematical nor physical consequence in the case of single-photon emission or absorption. We shall therefore treat ρ^R as if it were diagonal.

Noting now that y operates on system states only, (3.5) gives

$$\Phi(\omega)=-\pi^{-1}\,\mathrm{Im}\sum_{\beta,\alpha}|y_{\beta\alpha}|^2\rho_{\alpha\alpha}{}^S \times\sum_p\sum_n\rho_{pp}{}^P\rho_{nn}{}^R\mathcal{G}_{\alpha pn,\beta pn;\ \alpha pn,\beta pn}(x^+=\omega). \tag{3.8}$$

To compress notation somewhat, we shall use the single index a instead of αpn, the index b for βpn, etc. Note that a and b differ only in the system indices, and this is due to the fact that y operates on system states only. We shall also use the notation $\mathcal{G}_{ab}$ instead of $\mathcal{G}_{ab;\ ab}$ for the diagonal matrix elements of $\mathcal{G}$. Introducing now the quantity

$$\langle\mathcal{G}_{ab}(\omega)\rangle\equiv\sum_p\sum_n\rho_{pp}{}^P\rho_{nn}{}^R\mathcal{G}_{ab;\ ab}(x^+=\omega), \tag{3.9}$$

the spectrum reads

$$\Phi(\omega)=-\pi^{-1}\,\mathrm{Im}\sum_{\beta,\alpha}|y_{\beta\alpha}|^2\rho_{\alpha\alpha}{}^S\langle\mathcal{G}_{ab}(\omega)\rangle. \tag{3.10}$$

The summation over α and β represents a sum over all lines of the atom. The shape of each line is determined by $\langle\mathcal{G}_{ab}\rangle$.

We now turn to the study of $\langle\mathcal{G}_{ab}(x^+)\rangle$. Using Eq. (2.41) and making use of the fact that $\omega_a-\omega_b=\omega_\alpha-\omega_\beta$, we obtain

$$\mathcal{G}_{ab}(x^+)=\frac{1}{x-\omega_\alpha+\omega_\beta-D_{ab}(x)+i\Gamma_{ab}(x)}. \tag{3.11}$$

To calculate $\Gamma_{ab}(x)$, we use Eq. (2.39) and limit ourselves to the lowest-order nonvanishing contribution. For this we approximate R by L^I [see Eq. (2.35)]. Substituting into (2.39) and recalling the definition of the projection operators we find

$$\Gamma_{ab}(x)=\pi\sum_{a'b'\neq ab}L_{ab;\ a'b'}{}^IL_{a'b';\ ab}{}^I \times\delta(x-L_{a'b';\ a'b'}{}^0). \tag{3.12}$$

From the definition of $L_{ab;\ a'b'}{}^I$, one can show that, for $a'b'\neq ab$, we have

$$L_{ab;\ a'b'}{}^IL_{a'b';\ ab}{}^I=|V_{aa'}|^2\delta_{bb'}+|V_{bb'}|^2\delta_{aa'},$$

which if substituted into (3.12) yields

$$\Gamma_{ab}(x)=\pi\sum_{a'\neq a}|V_{aa'}|^2\delta(x-L_{a'b';\ a'b}{}^0) +\pi\sum_{b'\neq b}|V_{bb'}|^2\delta(x-L_{ab';\ ab'}{}^0). \tag{3.13}$$

Recalling that $L_{a'b';\ a'b}{}^0=\omega_{a'}-\omega_b$ and $L_{ab';\ ab'}{}^0=\omega_a-\omega_{b'}$, we can write (3.13) as

$$\Gamma_{ab}(x)=\pi\sum_{a'\neq a}|V_{a'a}|^2\delta(x-\omega_{a'}+\omega_b) +\pi\sum_{b'\neq b}|V_{bb'}|^2\delta(x-\omega_a+\omega_{b'}). \tag{3.14}$$

Consider now $D_{ab}(x)$ as given by (2.40). First, note that $L_{ab;\ ab}{}^I=V_{aa}-V_{bb}$. Often these diagonal matrix elements will vanish; for example, in nonrelativistic radiation problems. Here, we shall neglect them, assuming that they vanish or that the ω's have been so redefined as to incorporate them. Substituting $\Gamma_{ab}(x)$ into (2.40) and performing the integration over x', we obtain

$$D_{ab}(x)=\mathrm{P}\sum_{a'\neq a}\frac{|V_{a'a}|^2}{x-\omega_{a'}+\omega_b}+\mathrm{P}\sum_{b'\neq b}\frac{|V_{b'b}|^2}{x-\omega_a+\omega_{b'}}. \tag{3.15}$$

[15] P. Lambropoulos, C. Kikuchi, and R. K. Osborn, Phys. Rev. **144**, 1081 (1966).

Having now expressed D_{ab} and Γ_{ab} in terms of the interaction V we can substitute into (3.11) and then into (3.10), thus obtaining

$$\Phi(\omega)=\pi^{-1}\sum_{\beta,\alpha}|y_{\beta\alpha}|^2\rho_{\alpha\alpha}{}^S \times\left\langle\frac{\Gamma_{ab}(\omega)}{(\omega-\omega_{\alpha\beta}-D_{ab}(\omega))^2+\Gamma_{ab}{}^2(\omega)}\right\rangle, \quad (3.16)$$

where $\omega_{\alpha\beta}=\omega_\alpha-\omega_\beta$, and the brackets indicate a statistical average as in (3.9). If one can replace averages of functions by functions of averages, and if $D(\omega)$ and $\Gamma(\omega)$ are slowly varying functions of ω, (3.16) becomes a superposition of Lorentzians each of which represents one atomic line.

Let us now calculate the widths and shifts more explicitly. Using the expansion in terms of the modes inside a cubic box of volume Ω, the Hamiltonian of the free radiation field reads[16]

$$H^{\mathbf{R}}=\sum_{\mathbf{k}\lambda}\omega_{\mathbf{k}}(a_{\mathbf{k}\lambda}{}^\dagger a_{\mathbf{k}\lambda}+\tfrac{1}{2}), \quad (3.17)$$

where $\mathbf{k}$ denotes the photon wave vector, λ is the polarization index taking on the values 1 and 2, and the creation and annihilation operators obey the usual boson commutation relations. The single-mode states are defined by

$$a_{\mathbf{k}\lambda}{}^\dagger a_{\mathbf{k}\lambda}|n_{\mathbf{k}\lambda}\rangle=n_{\mathbf{k}\lambda}|n_{\mathbf{k}\lambda}\rangle, \quad (3.18)$$

where $n_{\mathbf{k}\lambda}$ assumes non-negative integral values. The interaction between system and radiation field can now be written as[16]

$$V^{SR}=-\left(\frac{2\pi e^2}{m^2\hbar}\right)^{1/2}\Omega^{-1/2}\sum_{\lambda\mathbf{k}}\frac{\mathbf{p}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}}{(\omega_{\mathbf{k}})^{1/2}}(a_{\mathbf{k}\lambda}{}^\dagger+a_{\mathbf{k}\lambda}), \quad (3.19)$$

where $\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}$ is the unit polarization vector of the $\mathbf{k}\lambda$ mode and $\mathbf{p}$ is the momentum operator of the electrons of the atom of interest in the center-of-mass system (barycentric system).[2] In writing V^{SR} as in (3.19), we have neglected the term which is quadratic in the vector potential $\mathbf{A}$ of the field and have made the dipole approximation $e^{\pm i\mathbf{k}\cdot\mathbf{r}}\simeq 1$. At the end we shall let the volume of the box approach infinity and shall replace the summation over $\mathbf{k}\lambda$ by integration. The states of the radiation field are now written as $/\cdots n_{\mathbf{k}\lambda},\ n_{\mathbf{k}'\lambda'},\cdots\rangle$ or $|\{n_{\mathbf{k}\lambda}\}\rangle$ for short. The energy of such a state is $\omega_n=\sum_{\mathbf{k}\lambda}\omega_k n_{\mathbf{k}\lambda}$, where $\omega_k=kc$ and c is the speed of light.

Recall now that V is the sum of V^{SR} and V^c, where the first commutes with variables of the rest of the gas while V^c commutes with variables of the radiation field. Then, in a matrix element of the form $V_{a'a}$ appearing in (3.14), there will be contributions of two kinds. First, there will be contributions diagonal in the photon states in which V^{SR} does not contribute, and second there will be contributions diagonal in states of the rest of the gas in which V^c does not contribute because of the assumptions we have made earlier. Thus $V_{a'a}$ will contain contributions of the form $\langle\alpha'\langle\{n_{\mathbf{k}\lambda}'\}||V^{SR}|\alpha,\{n_{\mathbf{k}\lambda}\}\rangle$ summed over α' and $\{n_{\mathbf{k}\lambda}'\}$, and contributions of the form $\langle\alpha'\langle p'|V^c|\alpha,p\rangle$ summed over α' and ρ'. Similar considerations apply to $V_{b'b}$, except that α and α' are replaced by β and β', respectively. It is clear now that $\Gamma_{ab}(x)$ can be written as the sum of two contributions $\Gamma_{ab}{}^c(x)$ and $\Gamma_{ab}{}^R(x)$, where the first contains matrix elements of V^c and the second contains matrix elements of V^{SR}. For $\Gamma_{ab}{}^c(x)$, we have

$$\Gamma_{ab}{}^c(x)=\pi\sum_{\alpha'p'(\neq\alpha p)}|V_{\alpha'p',\alpha p}{}^c|^2\delta(x-\omega_{\alpha'}-\omega_{p'}+\omega_\beta+\omega_p) +\pi\sum_{\beta'p'(\neq\beta p)}|V_{\beta'p',\beta p}{}^c|^2 \times\delta(x-\omega_a-\omega_p+\omega_{\beta'}+\omega_{p'}), \quad (3.20)$$

where V^c will not be specified further for the time being.

To calculate $\Gamma_{ab}{}^R(x)$, we take V^{SR} as given by (3.19a) and calculate matrix elements of the form $V_{\alpha'\{n\mathbf{k}\lambda'\},\alpha\{n\mathbf{k}\lambda\}}{}^{SR}$. We then substitute into (3.14), express the matrix elements of the position operator $\mathbf{r}$, replace the summation over $\mathbf{k}$ by integration according to

$$\sum_{\mathbf{k}}\to\frac{\Omega}{8\pi^3c^3}\int_0^\infty\int_\Omega\omega_k{}^2d\omega_k d\boldsymbol{\Omega},$$

where Ω is the volume of the box and $d\boldsymbol{\Omega}$ is the differential of the solid angle, i.e., $d\boldsymbol{\Omega}=\sin\vartheta d\vartheta d_p$. After some straightforward manipulations, we obtain

$$\begin{aligned}\Gamma_{ab}{}^R(x)=&\xi\sum_{\alpha',\lambda}\omega_{\alpha'\alpha}{}^2\int\int d\omega_k d\boldsymbol{\Omega}\omega_k|\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}\cdot\mathbf{r}_{\alpha'\alpha}|^2\delta(x-\omega_{\alpha'}-\omega_k+\omega_\beta)\\ &+\xi\sum_{\alpha',\lambda}\omega_{\alpha'\alpha}{}^2\int\int d\omega_k d\boldsymbol{\Omega}\omega_k n_\lambda(\omega_k,\Omega)|\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}\cdot\mathbf{r}_{\alpha'\alpha}|^2[\delta(x-\omega_{\alpha'}-\omega_k+\omega_\beta)+\delta(x-\omega_{\alpha'}+\omega_k+\omega_\beta)]\\ &+\xi\sum_{\beta',\lambda}\omega_{\beta'\beta}{}^2\int\int d\omega_k d\boldsymbol{\Omega}\omega_k|\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}\cdot\mathbf{r}_{\beta'\beta}|^2\delta(x-\omega_\alpha+\omega_{\beta'}+\omega_k)\\ &+\xi\sum_{\beta',\lambda}\omega_{\beta'\beta}{}^2\int\int d\omega_k d\boldsymbol{\Omega}\omega_k n_\lambda(\omega_k,\boldsymbol{\Omega})|\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}\cdot\mathbf{r}_{\beta'\beta}|^2\cdot[\delta(x-\omega_\alpha+\omega_{\beta'}+\omega_k)+\delta(x-\omega_\alpha+\omega_{\beta'}-\omega_k)], \quad (3.21)\end{aligned}$$

[16] L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed.

where $n_\lambda(\omega_k,\Omega)$ is another notation for $n_{k\lambda}$, i.e., the number of photons per unit frequency, per unit solid angle, and of polarization λ. The constant ξ is defined by

$$\xi \equiv e^2/4\pi\hbar c^3. \tag{3.22}$$

In order to simplify (3.21) somewhat, we shall introduce the quantity $N(\omega_k)$ defined by

$$N(\omega_k)|\mathbf{r}_{\alpha'\alpha}|^2 \equiv \sum_\lambda \int_\Omega d\Omega n_\lambda(\omega_k,\Omega)|\boldsymbol{\varepsilon}_{k\lambda}\cdot\mathbf{r}_{\alpha'\alpha}|^2. \tag{3.23}$$

Obviously, $N(\omega_k)$ depends on the spectral composition of the state of the radiation field. Assuming now that $N(\omega_k)$ is not singular, we can perform the integrations over ω_k. The result is written conveniently in terms of the step function $\eta(x)$ defined by

$$\begin{aligned} \eta(x)&=1 \quad \text{for} \quad x>0 \\ &=0 \quad \text{for} \quad x<0. \end{aligned} \tag{3.24}$$

For this definition to be consistent with the properties of the delta function, we shall take $\eta(x=0)=\frac{1}{2}$. Lastly, we note that in the first and third terms (which are independent of the initial photon flux) we have the quantity

$$\sum_\lambda \int d\Omega |\boldsymbol{\varepsilon}_{k\lambda}\cdot\mathbf{r}_{\alpha'\alpha}|^2.$$

This can be simplified if one calls ϑ the angle between $\mathbf{k}$ and $\mathbf{r}_{\alpha'\alpha}$. Then,

$$|\boldsymbol{\varepsilon}_{k\lambda}\cdot\mathbf{r}_{\alpha'\alpha}|^2 = |\mathbf{r}_{\alpha'\alpha}|^2 \sin^2\vartheta.$$

One can now perform the integration over the solid angle obtaining $(8\pi/3)|\mathbf{r}_{\alpha'\alpha}|^2$. With this result and Eq. (3.23) we have eliminated (at least formally) the dependence on angle. The integrations over frequency can now be performed using the step function. The result is

$$\begin{aligned} \Gamma_{ab}{}^R(x) &= (8\pi/3)\xi \textstyle\sum_{\alpha'} \omega_{\alpha'\alpha}{}^2|\mathbf{r}_{\alpha'\alpha}|^2(x-\omega_{\alpha'}+\omega_\beta)\eta(x-\omega_{\alpha'}+\omega_\beta)+\xi\sum_{\alpha'}\omega_{\alpha'\alpha}{}^2|\mathbf{r}_{\alpha'\alpha}|^2 \\ &\times\{(x-\omega_{\alpha'}+\omega_\beta)N(x-\omega_{\alpha'}+\omega_\beta)\eta(x-\omega_{\alpha'}+\omega_\beta)+(\omega_{\alpha'}-x-\omega_\beta)N(\omega_{\alpha'}-x-\omega_\beta)\eta(\omega_{\alpha'}-x-\omega_\beta)\} \\ &+(8\pi/3)\xi\textstyle\sum_{\beta'}\omega_{\beta'\beta}{}^2|\mathbf{r}_{\beta'\beta}|^2(\omega_\alpha-x-\omega_{\beta'})\eta(\omega_\alpha-x-\omega_{\beta'})+\xi\sum_{\beta'}\omega_{\beta'\beta}{}^2|\mathbf{r}_{\beta'\beta}|^2 \\ &\times\{(\omega_\alpha-x-\omega_{\beta'})N(\omega_\alpha-x-\omega_{\beta'})\eta(\omega_\alpha-x-\omega_{\beta'})+(x-\omega_\alpha+\omega_{\beta'})N(x-\omega_\alpha+\omega_{\beta'})\eta(x-\omega_\alpha+\omega_{\beta'})\}. \end{aligned} \tag{3.25}$$

It is now trivial to write experssions for the shifts if we use Eq. (3.15). Again, to lowest order in V, we obtain the sum of two contributions: the collision contribution $D_{ab}{}^c(x)$ and the radiation contribution $D_{ab}{}^R(x)$. The first is given by

$$D_{ab}{}^c(x) = \mathrm{P}\sum_{\alpha'p'(\neq\alpha p)} \frac{|V_{\alpha'p',\alpha p}{}^c|^2}{x-\omega_{\alpha'}-\omega_{p'}+\omega_\beta+\omega_p} + \mathrm{P}\sum_{\beta'p'(\neq\beta p)} \frac{|V_{\beta'p',\beta p}{}^c|^2}{x-\omega_\alpha-\omega_p-\omega_{\beta'}+\omega_{p'}}, \tag{3.26}$$

and the second is given by

$$\begin{aligned} D_{ab}{}^R(x) = {}& \frac{8\pi}{3}\xi\sum_{\alpha'}\omega_{\alpha'\alpha}{}^2|\mathbf{r}_{\alpha'\alpha}|^2\mathrm{P}\int_0^\infty d\omega_k \frac{\omega_k}{x-\omega_{\alpha'}-\omega_k+\omega_\beta} \\ &+\xi\sum_{\alpha'}\omega_{\alpha'\alpha}{}^2|\mathbf{r}_{\alpha'\alpha}|^2\left\{\mathrm{P}\int_0^\infty d\omega_k\frac{\omega_k N(\omega_k)}{x-\omega_{\alpha'}-\omega_k+\omega_\beta}+\mathrm{P}\int_0^\infty d\omega_k\frac{\omega_k N(\omega_k)}{x-\omega_{\alpha'}+\omega_k+\omega_\beta}\right\} \\ &+\frac{8\pi}{3}\xi\sum_{\beta'}\omega_{\beta'\beta}{}^2|\mathbf{r}_{\beta'\beta}|^2\mathrm{P}\int_0^\infty d\omega_k\frac{\omega_k}{x-\omega_\alpha+\omega_{\beta'}+\omega_k} \\ &+\xi\sum_{\beta'}\omega_{\beta'\beta}{}^2|\mathbf{r}_{\beta'\beta}|^2\left\{\mathrm{P}\int_0^\infty d\omega_k\frac{\omega_k N(\omega_k)}{x-\omega_\alpha+\omega_{\beta'}+\omega_k}+\mathrm{P}\int_0^\infty d\omega_k\frac{\omega_k N(\omega_k)}{x-\omega_\alpha+\omega_{\beta'}-\omega_k}\right\}. \end{aligned} \tag{3.27}$$

This completes the derivation of expressions for shifts and widths to lowest order in perturbation theory. Although this approximation is quite adequate for a large class of line-shape problems in atomic and molecular processes, one can straightforwardly obtain higher-order corrections by continuing the iteration of (2.35).

To elucidate the results we have obtained thus far let us look at a special case. Assume that Γ_{ab} and D_{ab} are much smaller than $\omega_{\alpha\beta}$. Then, the averaged quantity in (3.16) will be a function of ω highly peaked at $\omega=\omega_{\alpha\beta}$. If, at the same time, $\Gamma_{ab}(\omega)$ and $D_{ab}(\omega)$ are functions slowly varying in the vicinity of $\omega_{\alpha\beta}$, one might replace them by their value at $\omega_{\alpha\beta}$. Note that a necessary condition for $\Gamma(\omega)$ and $D(\omega)$ to be slowly varying is that $N(\omega_k)$ be slowly varying. From (3.25) and (3.27) we

find that the radiation contributions to Γ and D at $\omega_{\alpha\beta}$ are

$$\Gamma_{ab}{}^{R}(\omega_{\alpha\beta})=(8\pi/3)\xi\sum_{\alpha'}\omega_{\alpha\alpha'}{}^{3}|\mathbf{r}_{\alpha'\alpha}|^{2}\eta(\omega_{\alpha\alpha'})+\xi\sum_{\alpha'}\omega_{\alpha\alpha'}{}^{3}|\mathbf{r}_{\alpha'\alpha}|^{2}\{N(\omega_{\alpha\alpha'})\eta(\omega_{\alpha\alpha'})-N(\omega_{\alpha'\alpha})\eta(\omega_{\alpha'\alpha})\}$$
$$+(8\pi/3)\xi\sum_{\beta'}\omega_{\beta\beta'}{}^{3}|\mathbf{r}_{\beta'\beta}|^{2}\eta(\omega_{\beta\beta'})+\xi\sum_{\beta'}\omega_{\beta\beta'}{}^{3}|\mathbf{r}_{\beta\beta'}|^{2}\{N(\omega_{\beta\beta'})\eta(\omega_{\beta\beta'})-N(\omega_{\beta'\beta})\eta(\omega_{\beta'\beta})\} \quad (3.28)$$

and

$$D_{ab}{}^{R}(x)=\frac{8\pi}{3}\xi\sum_{\alpha'}\omega_{\alpha\alpha'}{}^{2}|\mathbf{r}_{\alpha'\alpha}|^{2}\mathrm{P}\int_{0}^{\infty}d\omega_{k}\frac{\omega_{k}}{\omega_{\alpha\alpha'}-\omega_{k}}+\xi\sum_{\alpha'}\omega_{\alpha\alpha'}{}^{2}|\mathbf{r}_{\alpha'\alpha}|^{2}\left\{\mathrm{P}\int_{0}^{\infty}d\omega_{k}\frac{\omega_{k}N(\omega_{k})}{\omega_{\alpha\alpha'}-\omega_{k}}+\mathrm{P}\int_{0}^{\infty}d\omega_{k}\frac{\omega_{k}N(\omega_{k})}{\omega_{\alpha\alpha'}+\omega_{k}}\right\}$$
$$-\frac{8\pi}{3}\xi\sum_{\beta'}\omega_{\beta\beta'}{}^{2}|\mathbf{r}_{\beta'\beta}|^{2}\mathrm{P}\int_{0}^{\infty}d\omega_{k}\frac{\omega_{k}}{\omega_{\beta\beta'}-\omega_{k}}-\xi\sum_{\beta'}\omega_{\beta\beta'}{}^{2}\mathbf{r}_{\beta'\beta}\left\{\mathrm{P}\int_{0}^{\infty}d\omega_{k}\frac{\omega_{k}N(\omega_{k})}{\omega_{\beta\beta'}-\omega_{k}}+\mathrm{P}\int_{0}^{\infty}d\omega_{k}\frac{\omega_{k}N(\omega_{k})}{\omega_{\beta\beta'}+\omega_{k}}\right\}. \quad (3.29)$$

The collision contributions to Γ and D are obtained from (3.20) and (3.26) by setting $x=\omega_{\alpha\beta}$. Thus we obtain

$$\Gamma_{ab}{}^{c}(\omega_{\alpha\beta})=\pi\sum_{\alpha'p'(\neq\alpha p)}|V_{\alpha'p',\alpha p}{}^{c}|^{2}\delta(\omega_{\alpha\alpha'}-\omega_{p'p})$$
$$+\pi\sum_{\beta'p'(\neq\beta p)}|V_{\beta'p',\beta p}{}^{c}|^{2}\delta(\omega_{\beta\beta'}-\omega_{p'p}) \quad (3.30)$$

and

$$D_{\alpha\beta}{}^{c}(\omega_{\alpha\beta})=\mathrm{P}\sum_{\alpha'p'(\neq\alpha p)}\frac{|V_{\alpha'p',\alpha p}{}^{c}|^{2}}{\omega_{\alpha\alpha'}-\omega_{p'p}}$$
$$-\mathrm{P}\sum_{\beta'p'(\neq\beta p)}\frac{|V_{\beta'p',\beta p}{}^{c}|^{2}}{\omega_{\beta\beta'}-\omega_{p'p}}. \quad (3.31)$$

To the extent that the assumptions made are valid, the spectrum (3.16) becomes a superposition of Lorentzians. The widths and shifts are now seen to consist of the widths and shifts of the levels α and β of the system. Consider, for example, Eq. (3.29). The first term is the natural width of the state $|\alpha\rangle$. Because of the step function $\eta(\omega_{\alpha\alpha'})$, only terms for which $\omega_{\alpha}>\omega_{\alpha'}$ give nonvanishing contributions to the sum. This is to be expected since the natural width is due to the fact that the state $|\alpha\rangle$ can make spontaneous transitions but to lower levels only. Similarly, the third term represents the natural width of the state $|\beta\rangle$. The second term represents the width of the state $|\alpha\rangle$ due to the presence of photons. The first term inside the curly brackets contributes only for $\omega_{\alpha}>\omega_{\alpha'}$, while the second contributes only for $\omega_{\alpha}<\omega_{\alpha'}$. Clearly, the first is due to emission of photons and the second is due to absorption. The two contributions are additive. Similar considerations apply to the fourth term which refers to the state $|\beta\rangle$. Each of the terms analyzed above has its corresponding term in the expression for the shift $D_{ab}{}^{R}(\omega_{\alpha\beta})$. Here, however, the vacuum shifts lead to infinities—a well-known fact—which can be eliminated by cutoff procedures. The simplest way to do this in the nonrelativistic approximation is by using Bethe's[17] method. The induced shifts—the second and the third term—will not lead to infinities as long as the integral

$$\int_{0}^{\infty}N(\omega)d\omega$$

is finite. This will generally be true for actual light sources since the integral represents the total energy of the initial state of the field. The total radiation width of the spectral line $\alpha\rightarrow\beta$ is the sum of the widths of the two states $|\alpha\rangle$ and $|\beta\rangle$ while the total shift is the difference of the shifts.

In a similar fashion, the collisional width of the line consists of the sum of the collisional widths of the states $|\alpha\rangle$ and $|\beta\rangle$ as shown by (3.30); the collisional shift is given by the difference of the two shifts as shown by (3.31). Finally, the collisional width is added to the radiation width, and the collisional shift is added to the radiation shift.

The fact that the final collisional width is the sum of the widths of the states $|\alpha\rangle$ and $|\beta\rangle$ stems from the approximations made in calculating the widths. It was assumed that V^{c} connected only different atomic states and Γ as given by (2.39) was calculated to the lowest order, which implies that $R(z)$ was approximated by L^{I} (see Eq. (2.31). The meaning of these approximations is that we have considered only inelastic scattering and it is natural, as Baranger[4] has shown, for the probabilities (or cross sections) to add incoherently. Additional effects come into play, however, when one considers elastic scattering as well. In that case the transition amplitudes for scattering from the two atomic states subtract and the absolute square of their difference gives an additional contribution to the width.[4] This is analogous to the phase-broadening effects discussed by McCumber[18] and Lax.[19] The way to obtain such contributions in the present formalism is to calculate $\Gamma(x)$ more accurately and allow for elastic scattering (see, for example, Fano's procedure in Ref. 5, Sec. 5). Note that $R(z)$ [see Eq. (2.31)] is essentially a transition amplitude and broadening from elastic scattering will come through matrix elements of R diagonal in atomic states.

One still has to perform the averaging indicated by the brackets in (3.16). The quantities that depend on the statistical variables are the shifts and widths. The crudest way of handling this problem is to replace averages of functions by functions of averages. We then

[17] H. Bethe, Phys. Rev. **72**, 339 (1947).

[18] D. E. McCumber, Phys. Rev. **135**, A1676 (1964).

[19] M. Lax, Phys. Rev. **145**, 110 (1966), Appendix A.

obtain

$$\Phi(\omega)=\pi^{-1}\sum_{\beta,\alpha}|y_{\beta\alpha}|^2\rho_{\alpha\alpha}{}^{S}\frac{\langle\Gamma_{ab}{}^{c}(\omega_{\alpha\beta})\rangle+\langle\Gamma_{ab}{}^{R}(\omega_{\alpha\beta})\rangle}{[\omega-\omega_{\alpha\beta}-\langle D_{ab}{}^{c}(\omega_{\alpha p})\rangle-\langle D_{ab}{}^{R}(\omega_{\alpha\beta})\rangle]^2+[\langle\Gamma_{ab}{}^{c}(\omega_{\alpha\beta})\rangle+\langle\Gamma_{ab}{}^{R}(\omega_{\alpha\beta})\rangle]^2}. \tag{3.32}$$

The vacuum radiation shifts and widths can be taken out of the brackets. The average induced radiation shifts and widths are obtained from (3.28) and (3.29) by simply replacing $N(\omega)$ by $\langle N(\omega)\rangle$. This averaged spectral density is a quantity that one can determine experimentally by measuring the energy of the light source as a function of frequency. To compute the averaged collisional shifts and widths, it is usually adequate to use an expansion in powers of the gas density. If we write V^c as a sum of binary interactions, then, to lowest order in perturbation theory, we obtain shifts and widths that are linear in the gas density. In fact, one obtains expressions similar to those for the induced radiation shifts and widths except that $\langle N(\omega)\rangle$ is replaced by the gas density and the dipole matrix elements (with the associated constants) are replaced by scattering cross sections (see Ref. 4 and 5).

Now let us consider the various assumptions we have made and discuss the manner in which the spectrum will be affected if they are not valid.

Replacing the average of a function by the function of the averages can be regarded as a first approximation. If the deviations of the shifts and widths from their average values are not sufficiently small, the approximation can be improved to any desired order by expanding the function in a Taylor series around the average values. For example, to second order in the deviations from their average values, the shifts in (3.32) give rise to an additional contribution to the width. It appears, however, that, as far as collision and radiation broadening are concerned, Eq. (3.32) will often be satisfactory.

The above statistical approximation could be made directly in (3.16). Then, we would have an expression in which the averaged shifts and widths would be frequency-dependent, while in (3.32) they have been replaced by their values at $\omega=\omega_{\alpha\beta}$. The vacuum radiation shifts and widths [see (3.25) and (3.27)] are indeed slowly varying functions of x so that replacing them by their values at $\omega_{\alpha\beta}$ is an excellent approximation. The dependence of the induced shifts and widths on x is mainly determined by the function $N(\omega_k)$. If this function does not vary slowly in the vicinity of $\omega_{\alpha\beta}$, then the averaged shifts and widths will be frequency-dependent. Thus, the presence of a strong radiation field appears to have two effects. First, it may shift and broaden the line because of its intensity. This is the type of phenomenon observed by Aleksandrov *et al.*,[11] who report a shift of an optical transition in potassium vapor due to the influence of a ruby-laser pulse. The broadening of the line is analogous to the effect that Karplus and Schwinger[12] studied in connection with microwave absorption. The second effect that the strong field may have is to make shifts and widths strongly frequency-dependent, thereby altering the shape of the line. As pointed out earlier, for this to happen $\langle N(\omega)\rangle$, should be a function rapidly varying in the vicinity of $\omega_{\alpha\beta}$. For laser sources, one would expect $\langle N(\omega)\rangle$ to be something like a Lorentzian or a Gaussian; generally a peaked function. Depending on the width of this function and the position of its center with respect to $\omega_{\alpha\beta}$, it may be possible to observe a change of the shape of $\Phi(\omega)$. Such changes could be observed in absorption experiments and resonance fluorescence, as well as in stimulated emission. It should be pointed out that the induced broadening is a resonance phenomenon in the sense that only photons of certain frequencies—determined by the spectrum of the system—are effective in causing it. This can be seen from Eq. (3.28) where only values of $N(\omega)$ evaluated at the frequencies $\omega_{\alpha\alpha'}$ and $\omega_{\beta\beta'}$ appear. Of course, this is a consequence of the fact that the width reflects the probability for the atom to make real transitions out of a certain state. The shift, however, is associated with virtual transitions and, although Eq. (3.29) does contain resonance denominators, it is an integral over the whole spectrum that determines its value. The resonance denominators simply cause certain parts of the spectrum to weigh more than others. In view of the above remarks it is evident that a light source with a narrow spectrum that does not coincide with a transition may cause a shift but leave the width unaffected. This seems to be the case in Ref. 11, although no line-shape measurements have been reported.

Before closing this section, we should note that in a gas as envisaged here Doppler broadening will, in general, be important. This means that we have to include the motion of the center of mass of the system. The recoil of the center of mass leads to the Doppler shift which when averaged over all possible directions gives rise to an effective width. Its inclusion into the present formalism is straightforward.