Width and Shift of Spectral Lines Due to Dissipative Interaction

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(Received December 10, 1956)

The theory of line width due to dissipative interactions, such as collisions, is examined for the case of weakly coupled systems (weak collisions). It is shown that the apparent paradox that the width of the energy of the total system is of the order of Avogadro's number is resolved by a substraction procedure. The width of a spectral line is the *difference* in widths of the two macroscopic states before and after the transition. This should be contrasted to the case of natural line width where the width of the line is the sum of the widths of the two states involved. The physical reason for the difference in sign is discussed.

1. INTRODUCTION

A PROBLEM often encountered in spectroscopy is the width of a line due to the fact that transitions among the states of a system render its energy uncertain because of relaxation effects. Much thought has gone into this effect in gases under the title of pressure broadening. The line is broadened due to collisions. The gas system is quite complicated, however, as one must consider the exchange between the internal energy of a molecule and translational energy. This complication necessitates approximation and it is not always possible to keep track of the nature of the errors committed. It is also difficult to trace the physics through.

A simple problem of equal physical interest is presented by the following situation. Consider phonons in a slightly anharmonic crystal. The anharmonicity can be shown to give rise to "collisions" among the phonons in such a way that a nonequilibrium situation goes to the equilibrium distribution. This was first carried through by Peierls[1] in 1929 and later made rigorous in quantum mechanics by Van Hove[2] and in classical mechanics by Prigogine and the author.[3] Now suppose radiation is incident on the crystal in such a way that it changes the population of, say, phonon k (k includes both wave vector and polarization). Then because of its interaction with all the other phonons, phonon k can be expected to exhibit a line width and a line shift. A similar situation arises in neutron scattering from crystals. For a pure harmonic crystal Placzek and Van Hove[4] have shown that one-phonon coherent scattering leads to the scattering of neutrons of only a few discrete energies at given scattering angle. Phonon collisions will make these lines shift and have width. This effect was pointed out by Van Hove[5] and in fact was the starting point of the present work.

A similar situation arises when radiation induces transitions in the population of any kind of excitation, spin waves, excitons, etc., which are in interaction. The general problem is to calculate the line width and shift.

Our intuition tells us that if the collisions yield a mean lifetime of γ_k^{-1} for the kth mode of excitation, then the line width should be γ_k. This is best seen by considering a given exciton to be in interaction with the rest of the system. This interaction not only causes an energy shift as in time-independent perturbation theory, but a width as well. The latter is a result of the fact that the lifetime of the excitation renders its energy uncertain by the Heisenberg uncertainty principle ($\Delta E\,\gamma_k^{-1}=1\,;\hbar=1$). It is our aim to verify this result. That this is not trivial may be seen by reference to the classical paper of Wigner and Weisskoff[6] on natural line breadth. For a multi-level atom, it is found that a transition $a\rightarrow b$ has a line width

$$\Gamma_{ab}=\Gamma_a+\Gamma_b, \tag{1.1}$$

where Γ_a, Γ_b are the inverse lifetimes of the levels a, b, respectively, due to the radiation itself. This result is reasonable. If there is a width associated with level a and another with level b, one expects the width of a line to be the sum of the two.

If this reasoning is then naively extended to the case of relaxing media, the line width for the transition between states, $\{n_1\cdots n_k{}^{(2)}\cdots n_\rho\}\rightarrow\{n_1\cdots n_k{}^{(1)}\cdots n_\rho\}$, would be

$$\Gamma_{\text{trans}}=|\Gamma_{\{n_1\cdots n_k{}^{(1)}\cdots n_\rho\}}+\Gamma_{\{n_1\cdots n_k{}^{(2)}\cdots n_\rho\}}|. \tag{1.2}$$

This result is absurd for the reason that $\Gamma_{\{n\}}$ is an extensive quantity of the order of Avogadro's number. That is, for a very large system, the probability that *any* exciton change its state in a given time interval, no matter how small, is very large if the system becomes big enough. For example, in the case of phonons in an anharmonic crystal, we have

$$\Gamma=\tfrac{1}{2}\sum_{kk'k''}\{C_{kk'k''}\times[(n_k+1)(n_{k'}+1)(n_{k''})+n_kn_{k'}(n_{k''}+1)]\times\delta(\omega_k+\omega_{k'}+\omega_{k''})\delta(k+k'+k''-K)\}, \tag{1.3}$$

where K is a vector in the reciprocal lattice. The lifetime of a single phonon k may be equated with the

[1] R. Peierls, Ann. Physik **3**, 1055 (1929).
[2] L. Van Hove, Physica **21**, 517 (1955).
[3] R. Brout and I. Prigogine, Physica **22**, 35 (1956).
[4] G. Placzek and L. Van Hove, Phys. Rev. **93**, 1207 (1954).
[5] L. Van Hove, *Brussels Conference on Irreversible Processes, 1955* (unpublished).
[6] E. Wigner and V. Weisskoff, Z. Physik **63**, 54 (1930).

difference

$$\Gamma\{n_1\cdots n_k+1\cdots n_\rho\}-\Gamma\{n_1\cdots n_k\cdots n_\rho\}\equiv\gamma_k. \quad (1.4)$$

Thus the reasoning of Wigner and Weisskoff in the physical interpretation of Eq. (1) fails. The problem must be attacked on a new basis using known information about dissipative systems. These systems have been studied in the limit of weak coupling by Van Hove[2] and we shall find that his formalism leads automatically to the correct answer. It is found that, to within a constant factor,

$$\Gamma_{\text{trans}}=\gamma_k. \quad (1.5)$$

In this case it is then the *difference* of Γ's rather than the sums as in Eq. (1) that gives the correct width.

In the course of the analysis it will be made clear how our problem differs from that of natural line width. It turns out that the two problems answer entirely different questions.

For convenience we shall treat the problem of spontaneous emission, and then indicate how to apply the result to absorption.

2. SPONTANEOUS EMISSION

In finding the intensity formula we use standard first order perturbation theory in the interaction between the radiation (or neutron) field and the system. The Hamiltonian is

$$H=H_s+H_r+H_{\text{int}}, \quad (2.1)$$

where H_s=Hamiltonian of the system, H_r=Hamiltonian of the radiation field, and H_{int}=interaction between system and radiation. We shall treat systems for which (reference 2)

$$H_s=H^0+\lambda V; \quad |\lambda V|\ll H^0, \quad (2.2)$$

where V couples the modes of excitation in the manner of "collisions." We work in the representation that diagonalizes H^0+H_r (i.e., numbers of modes of excitation and photons). We begin with photon vacuum 0 and go to a one-photon state ω. For the specification of the system we adopt a convenient notation, remarking that we are primarily interested in the transition induced by H_{int} in changing the population of a particular mode of excitation, say k. It will be convenient to isolate this particular mode of excitation in the notation, but to lump all the others in a single index α, i.e., the index α specifies the populations $n_1\cdots n_{k-1}n_{k+1}\cdots n_\rho$; ρ labels the last mode of excitation. In first order in H_{int} we have ($\hbar=1$)

$$\psi(t)=\psi(0)+i\int_0^t dt_1 \exp[i(H_s+H_r)(t-t_1)]H_{\text{int}}\times\exp[i(H_s+H_r)t_1]. \quad (2.3)$$

Using (2.3), we have for a given spontaneous emission

$$\langle N_k^f;\alpha;\omega|\psi(t)\rangle=i\sum_{\alpha';\alpha^0;N_k^0}\int_0^t dt_1 \times\langle N_k^f;\alpha|\exp[iH_s(t-t_1)]|N_k-1;\alpha'\rangle \times\exp[i\omega(t-t_1)]\langle N_k-1;\omega|H_{\text{int}}|N_k\rangle \times\langle N_k;\alpha'|\exp[iH_st_1]|N_k^0;\alpha^0\rangle\langle N_k^0;\alpha^0|\psi(0)\rangle. \quad (2.4)$$

In the amplitude $\langle N_k^f;\alpha;\omega|\psi(t)\rangle$, only those contributions which contain $\langle N_k-1;\omega|H_{\text{int}}|N_k\rangle$ are included, for these are the only ones that contribute to the line in question. In (2.4) the index $N_k^f;\alpha$ labels the final state to which the system has evolved after its radiative transition to $N_k-1;\alpha'$ at t_1. In general, $N_k^f\neq N_k-1$. The intensity of the line is the square of (2.4) summed over N_k^f and α and finally integrated over ω for the integrated line intensity.

In the expression (2.4) appear matrix elements of the type $\langle N_k;\alpha|\exp[iH_st]|N_k';\alpha'\rangle$. These matrix elements have been studied by Van Hove[2] for H_s of the type (2.2), where V, in dissipative systems, has characteristic diagonal singularities in its even powers. In the lowest nonvanishing order in λ, which is λ^2, Van Hove has found (we call β the index of the whole system $\beta=n_k;\alpha$)

$$\langle\beta|\exp[iH_st]|\beta'\rangle=U_\beta\delta_{\beta\beta'}+i\lambda\int_0^t dt_1U_\beta(t-t_1)V_{\beta\beta'}U_{\beta'}(t_1)+\cdots \quad (2.5)$$

$$+(i\lambda)^\nu\sum_{\beta_2\cdots\beta_\nu}\int_0^t dt_\nu\cdots\int_0^{t_2}dt_1 \times[U_\beta(t-t_\nu)V_{\beta\beta_\nu}U_{\beta_\nu}(t_\nu-t_{\nu-1})\cdots V_{\beta_2\beta'}U_{\beta'}(t_1)] +\cdots, \quad (2.6)$$

where

$$U_\beta(t)=\exp\{i[E(\beta)+\Delta(\beta)+i\Gamma(\beta)]t\}, \quad (2.7)$$

$$\Gamma_\beta=\pi\lambda^2\sum_{\beta'}|\langle\beta|V|\beta'\rangle|^2\delta(E_\beta-E_{\beta'}), \quad (2.8)$$

$$\Delta_\beta=\lambda^2\sum_{\beta'}|\langle\beta|V|\beta'\rangle|^2[1/(E_\beta-E_{\beta'})]_P, \quad (2.9)$$

E_β=unperturbed eigenvalue of H_0.

In Eq. (2.9), $(\,)_P$ means the principal part. Equation (2.6) further has the proviso that all β indexes are kept successively two by two unequal; all of these diagonal terms are absorbed in the Γ and Δ of Eq. (2.7). The operator U may be thought of as a renormalized propagation operator after all the diagonal singularities in V^2 have been separated out. $\Delta(\beta)$ is the shift in energy of the state due to the interaction and $\Gamma(\beta)$ is the width.

Substitution of Eq. (2.6) into (2.4) is the formal answer to our problem. Let us first look at a trivial

case to gain familiarity with the nature of the terms involved. Suppose that the mode of excitation k is uncoupled from the system. In this case N_k is a redundant index in the matrix element of $\exp(iH_st)$ except insofar as it enters into the U, defined by (2.7). In this case we have

$$U_\beta(t)=\exp\{i[E(\alpha)+\Delta(\alpha)+i\Gamma(\alpha)]t\}\times\exp(iN_k\epsilon_kt). \quad (2.10)$$

From the expansion (2.6), we then see that the factors $\exp(iN_k\epsilon_kt_\nu)$ successively cancel through the U factors, leaving only a factor $\exp(iN_k\epsilon_kt)\langle\alpha|\exp(iH_s't)|\alpha'\rangle$, where H_s' does not contain the mode of excitation k. For this case, Eq. (2.4) becomes

$$\begin{aligned}\langle N_k-1;\alpha;\omega|\psi(t)\rangle=&\sum_{\alpha'\alpha^0}\exp[i\omega t]\\&\times\int_0^t dt_1\langle N_k-1;\alpha|\exp[iH_s(t-t_1)]|N_k-1;\alpha'\rangle\\&\times\langle N_k-1;\omega|H_{\rm int}|N_k;0\rangle\exp[i(\omega-\epsilon_k)t_1]\\&\times\langle N_k-1;\alpha'|\exp(iH_st_1)|N_k-1;\alpha^0\rangle\\&\times\langle N_k;\alpha^0|\psi(0)\rangle, \quad (2.11)\end{aligned}$$

where for future comparison we have deliberately written the matrix elements in terms of H_s rather than H_s'. In Eq. (2.11), the matrix element of $\exp(iH_st_1)$ has had the index N_k changed to N_k-1, and the factor $\exp(i\epsilon_kt_1)$ removed. This is convenient to do as it then permits summation over all intermediate indexes in a very simple manner. It is the trick that simplifies the real case considerably.

Summing over α' and α^0 gives

$$\begin{aligned}&\langle N_k-1;\alpha;\omega|\psi(t)\rangle\\&\quad=\exp\{i[\omega+(N_k-1)\epsilon_k]t\}\int_0^t dt_1C_\alpha(t)C_{N_k}(0)\\&\qquad\times\exp[i(\omega-\epsilon_k)t_1]\langle N_k-1;\omega|H_{\rm int}|N_k\rangle. \quad (2.12)\end{aligned}$$

Squaring (2.12) and summing over α ($\sum|C_\alpha|^2=1$) gives the standard first order perturbation theory for an isolated system. The principal point that we would like to bring out is the introduction of the phase shift ϵ_kt_1 in the exponential due to the "interaction at t_1." This has a strong analog in the coupled problem, but the phase shift is then complex owing to the nonvanishing of γ_k in Γ_β for the coupled case. This is the circumstance that gives rise to the width.

For the real case, we use the full U as given by Eq. (2.7). It is then desired to express the matrix element $\langle N_k;\alpha|\exp[iH_st_1]|N_k^0;\alpha^0\rangle$ in terms of $\langle N_k-1;\alpha|\exp(iH_st_1)|N_k^0-1;\alpha^0\rangle$ just as was done for the uncoupled case. In order to do this, two approximations will be made, neither of them serious. Consider a typical successive product of U's that arises in the matrix element of $\exp(iH_st_1)$. This will contain terms like

$$\begin{aligned}&\cdots U_{\alpha^\nu;N_k{}^\nu}(-t_\nu)U_{\alpha^{\nu-1};N_k{}^{\nu-1}}(t_\nu)\cdots\\&\quad=\cdots\exp\{i[E_{\alpha^\nu;N_k{}^\nu}-E_{\alpha^{\nu-1};N_k{}^{\nu-1}}+\Delta_{\alpha^\nu;N_k{}^\nu} \quad (2.13)\\&\quad-\Delta_{\alpha^{\nu-1};N_k{}^{\nu-1}}+i(\Gamma_{\alpha^\nu;N_k{}^\nu}-\Gamma_{\alpha^{\nu-1};N_k{}^{\nu-1}})]t_\nu.\end{aligned}$$

This we wish to compare with $\cdots U_{\alpha_\nu;N_k{}^\nu-1}(-t_\nu)\times U_{\alpha_{\nu-1};N_k{}^{\nu-1}-1}(t_\nu)\cdots$. These are the same except for a factor

$$\begin{aligned}&\exp\{i[\Delta_{\alpha_\nu;N_k{}^\nu}-\Delta_{\alpha_{\nu-1};N_k{}^{\nu-1}}-\Delta_{\alpha_\nu;N_k{}^\nu-1}\\&\quad+\Delta_{\alpha_{\nu-1};N_k{}^{\nu-1}-1}+i(\Gamma_{\alpha_\nu;N_k{}^\nu}-\Gamma_{\alpha_{\nu-1};N_k{}^\nu-1}\\&\quad-\Gamma_{\alpha_\nu;N_k{}^\nu-1}+\Gamma_{\alpha_{\nu-1};N_k{}^{\nu-1}-1})]t_\nu\} \quad (2.14)\\&=\exp\{i[\delta_k(\alpha_\nu)-\delta_k(\alpha_{\nu-1})+i(\gamma_k(\alpha_\nu)-\gamma_k(\alpha_{\nu-1}))]t_\nu\},\\&\qquad\delta_k(\alpha)=\Delta_{N_k;\alpha}-\Delta_{N_k\alpha-1;},\\&\qquad\gamma_k(\alpha)=\Gamma_{N_k;\alpha}-\Gamma_{N_k-1;\alpha}. \quad (2.15)\end{aligned}$$

[In (2.14) note that the unperturbed eigenvalues $E_{\alpha_\nu;N_k}$ cancel by additivity just as in the uncoupled case.] $\delta_k(\alpha)$ and $\gamma_k(\alpha)$ are, respectively, the shift and width of the mode of excitation k, given α. We now assert that (2.14) can be replaced by 1. This is so because α_ν differs from $\alpha_{\nu-1}$ by the population of a few modes of excitation only, whereas $\delta_k(\alpha)$ and $\gamma_k(\alpha)$ depend on the population of all the excitons in α. Therefore, the differences of the δ's and γ's are negligible compared to the δ's and γ's themselves.

The other approximation will be the replacement of $\langle\alpha_\nu;N_k{}^\nu|V|\alpha_{\nu-1};N_k{}^{\nu-1}\rangle$ by $\langle\alpha_\nu N_k{}^\nu-1|V|\alpha_{\nu-1};N_k{}^{\nu-1}-1\rangle$. For those matrix elements which do not involve a change of N_k, this is exact. For the relatively few that do involve N_k, the error is usually negligible. With these approximations, we have

$$\begin{aligned}&\langle N_k;\alpha'|\exp(iH_st_1)|N_k{}^0;\alpha^0\rangle\\&\quad=\exp\{i[\epsilon_k+\delta_k(\alpha')+i\gamma_k(\alpha')]t_1\}\\&\qquad\times\langle N_k-1;\alpha'|\exp[iH_st_1]|N_k{}^0-1;\alpha^0\rangle, \quad (2.16)\end{aligned}$$

so that (2.4) becomes

$$\begin{aligned}\langle N_k{}^f;\alpha;\omega|\psi(t)\rangle=&\sum_{\alpha';\alpha^0;N_k{}^0}\exp[i\omega t]\\&\times\int_0^t dt_1\langle N_k{}^f;\alpha|\exp[iH_s(t-t_1)]|N_k-1;\alpha'\rangle\\&\times\langle N_k-1;\alpha'|\exp[iH_st_1]|N_k{}^0-1;\alpha^0\rangle\\&\times\exp\{i[\omega-\omega_k(\alpha')+i\gamma_k(\alpha')]t_1\}\\&\times\langle N_k-1;\omega|H_{\rm int}|N_k\rangle\langle N_k{}^0;\alpha^0|\psi(0)\rangle, \quad (2.17)\end{aligned}$$

where $\omega_k(\alpha)=\epsilon_k+\delta_k(\alpha)$. The main difference that the coupling has introduced in comparison with the uncoupled case is the introduction of the shift $\delta_k(\alpha')$ in

the phase shift at t_1 together with the imaginary part $\gamma_k(\alpha')$. This latter produces the width of the line.

It is the square of (2.17) summed over $N_k{}^f;\alpha$ that gives us our transition probability. This is

$$P_{N_k\to N_k-1}(\omega;t)=\sum_{\alpha';\alpha''}\sum_{N_k{}^f;\alpha}\sum_{N_k{}^0;\alpha_0}\int_0^t dt_1\int_0^t dt_2$$
$$\times\langle N_k-1;\alpha''|\exp[iH_s(t-t_2)]|N_k{}^f;\alpha\rangle$$
$$\times\langle N_k{}^f;\alpha|\exp[iH_s(t-t_1)]|N_k-1;\alpha'\rangle$$
$$\times\langle N_k-1;\alpha'|\exp[iH_st_1]|N_k{}^0-1;\alpha^0\rangle$$
$$\times\langle N_k{}^0-1;\alpha^0|\exp[iH_st_2]|N_k-1;\alpha''\rangle$$
$$\times|\langle N_k-1;\omega|H_{\rm int}|N_k\rangle|^2|\langle N_k{}^0;\alpha^0|\psi(0)\rangle|^2$$
$$\times\exp\{i[(\omega-\omega_k(\alpha')+i\gamma_k(\alpha'))t_1$$
$$-(\omega-\omega_k(\alpha'')-i\gamma_k(\alpha''))t_2]\},\quad(2.18)$$

where we have used the assumption that the initial phases are chosen at random, i.e.,

$$\langle\psi(0)|N_k{}^0;\alpha^0\rangle\langle N_k{}'^0;\alpha'^0|\psi(0)\rangle_{\rm Av}$$
$$=\delta_{N_k{}^0N_k{}'^0}\delta_{\alpha^0\alpha'^0}|\langle N_k{}^0;\alpha^0|\psi(0)\rangle|^2.$$

The sum over $N_k{}^f;\alpha$ is easily carried out. The sum over $N_k{}^0;\alpha^0$ requires a bit more care. If we assume statistical equilibrium we may write [with $P_{N_k{}^0;\alpha^0}=|\langle N_k{}^0;\alpha^0|\psi(0)\rangle|^2$]

$$P_{N_k{}^0;\alpha^0}=P_{N_k{}^0-1;\alpha^0}\eta_k,\quad(2.19)$$

where η_k may be taken independent of α_0 and $N_k{}^0$ (for a canonical ensemble $\eta_k=\exp[-\beta\epsilon_k]$. Further, equilibrium means

$$P_{N_k{}^0-1;\alpha^0}=P(E_0),\quad(2.20)$$

where E_0 is the unperturbed energy of the state $N_k{}^0-1;\alpha_0$. The sum over $N_k{}^0;\alpha^0$ can be then carried out by replacing $P(E_0)$ by the diagonal operator $P(H_0)$ so that (2.18) becomes

$$P_{N_k\to N_k-1}(\omega;t)$$
$$=\sum_{\alpha'\alpha''}\int_0^t dt_1\int_0^t dt_2|\langle N_k-1;\omega|H_{\rm int}|N_k\rangle|^2\eta_k$$
$$\times\langle N_k-1;\alpha''|\exp[iH_s(t_2-t_1)]|N_k-1;\alpha'\rangle$$
$$\times\langle N_k-1;\alpha'|\exp[iH_st_1]P(H_0)\exp[-iH_st_2]|$$
$$\times N_k-1;\alpha''\rangle\exp\{i[(\omega-\omega_k(\alpha')+i\gamma_k(\alpha'))t_1$$
$$-(\omega-\omega_k(\alpha'')-i\gamma_k(\alpha''))t_2]\}.\quad(2.21)$$

In reality the use of Eq. (2.20) is an approximation, always used in weakly coupled systems. To this approximation, it is permissible to commute $\exp(-iH_st_2)$ with $P(H_0)$ in Eq. (2.21) and bring out at a factor $P(E_0)$, where $P(E_0)=P_{N_k-1;\alpha'}=P_{N_k-1;\alpha''}$. The neglected commutator gives a contribution of $0(\lambda)$ to the total intensity which is very small, compared to our final result. This then leads to

$$P_{N_k\to N_k-1}(\omega;t)$$
$$=\sum_{\alpha';\alpha''}\int_0^t dt_1\int_0^t dt_2|\langle N_k-1;\omega|H_{\rm int}|N_k\rangle|^2P_{N_k;\alpha'}$$
$$\times|\langle N_k-1;\alpha''|\exp[iH_s(t_1-t_2)]|N_k-1;\alpha'\rangle|^2$$
$$\times\exp\{i[(\omega-\omega_k(\alpha')+i\gamma_k(\alpha'))t_1$$
$$-(\omega-\omega_k(\alpha'')-i\gamma_k(\alpha''))t_2]\},\quad(2.22)$$

where we have used (2.19). The square of the matrix element of $\exp[iH_s(t_2-t_1)]$ is the transition probability $P_{N_k-1;\alpha'\leftarrow N_k-1;\alpha''}(t_2-t_1)$. This quantity vanishes unless the transition conserves energy. It obeys a Poisson-type stochastic equation, referred to as either the transport equation or the master equation (Van Hove[2]).

Equation (2.22) is exact in the weakly coupled sense and is the formal solution to the problem. Its evaluation is properly carried out by substituting in the solution of the transport equation for $P_{N_k-1;\alpha''\leftarrow N_k-1;\alpha'}$. This is a difficult and unrewarding task. We shall rather use an approximation which makes physical sense and allows for a simple evaluation of (2.22). The fact that both $\gamma_k(\alpha)$ and $\delta_k(\alpha)$ are small compared to ω_k should be borne in mind. Further, they are slowly varying functions of α. For almost all α on the energy surface the populations of the various exons are near to the equilibrium populations so that $\gamma_k(\alpha)$ and $\delta_k(\alpha)\approx\bar\gamma_k$ and $\bar\delta_k$ for most α. With this in mind we shall consider a reasonable approximation to $P_{N_k-1;\alpha''\leftarrow N_k-1;\alpha'}(t_2-t_1)$. First of all most of the integral in (2.22) comes from $t_2<\gamma_k{}^{-1};t_1<\gamma_k{}^{-1}$ or $|t_2-t_1|<\gamma_k{}^{-1}$. In this time interval it is unlikely that the population of the mode of excitation k undergoes more than one change. Thus $P_{N_k-1;\alpha''\leftarrow N_k-1;\alpha'}(t_2-t_1)$ may be considered as the probability of transition $\alpha'\to\alpha''$ and the mode of excitation k undergoes no transition.

Now in the time interval $|t_2-t_1|=O(\gamma_k{}^{-1})$ there are many transitions that take place among the states α. As most α' are typical near equilibrium states on the energy shell, most transitions go to similar such states. Therefore, for most transitions we expect that α'' will again be a typical equilibrium state. As $|t_2-t_1|\ll\Gamma_{\rm syst}{}^{-1}$ we then expect that the system displays its ergodic character as far as the α indices are concerned with but rare exception. We thus approximate

$$P_{N_k-1;\alpha''\leftarrow N_k-1;\alpha'}(t_2-t_1)=P_{\alpha'}{}^{\rm eq}\times\text{the probability}$$
$$\text{that the mode of excitation } k \text{ undergoes no}$$
$$\text{transitions in } (t_2-t_1).\quad(2.23)$$

The second factor in (2.23) may be approximated by the following argument. For $|t_2-t_1|\ll\gamma_k{}^{-1}$ it is unity. For $|t_2-t_1|\gg\gamma_k{}^{-1}$ it is $P_{N_k-1}{}^{\rm eq}$. We are interested in

$|t_2-t_1|=O(\gamma_k^{-1})$ so that neither of the above applies. Rather, we think of the probability that a single mode of excitation k does not decay in times somewhat less than γ_k^{-1} (the probability that two or more modes of excitation decay in this time is very small) so that we expect the second factor in (2.23) to be $\exp[-\bar{\gamma}_k \times(t_2-t_1)]$. $\bar{\gamma}_k$ is the mean value of $\gamma_k(\alpha)$, averaged over α. In summary we put

$$|\langle N_k-1;\alpha''|\exp[iH_s(t_2-t_1)]N_k-1;\alpha'\rangle|^2 \approx P_{\alpha''}{}^{\text{eq}}\exp[-\bar{\gamma}_k|t_2-t_1|]. \quad (2.24)$$

We consider the first factor in Eq. (2.24) a very good approximation. The second factor is reasonable, but not as firmly based as the first. Putting (2.24) into (2.22), we have the sum

$$\sum P_{\alpha'}{}^{\text{eq}}\exp\{i[\omega-\omega_k(\alpha')+i\gamma_k(\alpha')]t_1\} =\langle\exp\{i[\omega-\omega_k(\alpha')+i\gamma_k(\alpha')]t_1\}\rangle. \quad (2.25)$$

Now $P_{\alpha'}{}^{\text{eq}}$ is very highly peaked about the equilibrium values of the populations of the modes of excitation so that the mean of the exponential is well approximated by the exponential of the mean. Thus (2.25) is approximately[7]

$$\langle\exp\{i[\omega-\omega_k(\alpha')+i\gamma_k(\alpha')]t_1\}\rangle =\exp[i(\omega-\bar{\omega}_k+i\bar{\gamma}_k)t_1]. \quad (2.26)$$

Putting this into (2.22) together with (2.24), we have

$$P_{N_k\to N_k-1}(\omega;t)=|\langle N_k-1;\omega|H_{\text{int}}|N_k\rangle|^2P_{N_k} \times\int_0^t dt_1\int_0^t dt_2\exp[-\bar{\gamma}_k|t_1-t_2|-\bar{\gamma}_k(t_1+t_2) +i(\omega-\bar{\omega}_k)(t_1-t_2)]. \quad (2.27)$$

Integration over (2.27), for $t\gg\bar{\gamma}_k^{-1}$, gives the spontaneous emission line shape:

$$P_{N_k\to N_k-1}(\omega)=\frac{|\langle N_k-1;\omega|H_{\text{int}}|N_k\rangle|^2P_{N_k}}{(2\bar{\gamma}_k)} \times\left[\frac{2\bar{\gamma}_k}{(\omega-\bar{\omega}_k)^2+(2\bar{\gamma}_k)^2}\right]. \quad (2.28)$$

Equation (2.28) is in standard line-shape form with half-width $2\bar{\gamma}_k$. Our main point, as asserted in the introduction, is that the fundamental quantity which enters into the calculation is the difference of the Γ_{syst} between initial and final states, in order to get the line width. The line shift is $\bar{\delta}_k$.

In order to treat absorption problems, one handles the situation as a scattering problem in which case the technique of resonance fluorescence is employed. As is well known, for incident radiation of frequency range broad compared to the line breadth, the cross section is then a product of the total probability of absorption multiplied by the rate of spontaneous emission. Since the line shape of absorption is the same as emission, the former part will just reproduce the same formulas as derived for emission. The rate of emission is then merely proportional to the square of the matrix element of H_{int} with no resonance denominators. The result is a shape which is the same as for emission.

[7] An alternative procedure to get to this point is to use the fact that $\delta_k(\alpha)$ and $\gamma_k(\alpha)$ are slowly varying in α to more advantage, by replacing the exponentials in (2.22) by the exponentials of the means, i.e., replace $\delta_k(\alpha')$, $\delta_k(\alpha'')$, $\gamma_k(\alpha')$, $\gamma_k(\alpha'')$ by their mean values. The sum over α' and α'' then yields the probability that N_k-1 does not change in (t_2-t_1), which we take to be $\exp[-\bar{\gamma}_k|t_2-t_1|]$ for $|t_2-t_1|=0(\bar{\gamma}_k^{-1})$. This procedure leads to (2.27) as well.

3. DISCUSSION

This problem is different from the problem of natural line width in the following way. In the natural line width problem of a three-level atom, one looks for the asymptotic component of the wave function after all photons are emitted. If one then wants the line shape of the emission line from the highest to the next highest level, one must integrate over the frequencies of all other lines that might appear in the asymptotic component of the wave function. The result of the calculation is to give a width equal to the sum of the widths associated with each level. Here the width is caused by the interaction with the radiation.

For the case we have discussed it is the system Hamiltonian that gives rise to the width. Thus, we focus attention on the particular mode of excitation undergoing a transition. The fate of all other modes of excitation is of no interest and subtracts out in the final answer, hence the difference of the Γ's. In the natural line width of the multi-level atom, we are very much concerned with the fate of the intermediate state to which a transition has been made since the radiation is the cause of all transitions. These sequential transitions are not statistically independent; the joint distribution of the frequencies of all lines is not factorized. The observed line width must then take into account all transitions involved.

Finally it should be pointed out that the natural line width could be added in to our expression by just continuing the expansion of H_{int} in (2.3). Then restricting ourselves to the states $|0;N_k\rangle$; $|\omega;N_k-1\rangle$ we collect all the diagonal singularities that arise in powers of H_{int}. These just sum up into an exponential expressing a width and a shift which would then be included in the U_β of Eq. (2.7). The natural line width and the collision line width *add*.

ACKNOWLEDGMENTS

I would like to express my gratitude to Professor H. A. Bethe for his reading of the manuscript coupled with his very cogent and helpful criticism. I should also like to thank Professor A. W. Overhauser for pointing out the fact that Γ_{syst} is an extensive quantity, thereby putting the whole problem into its proper framework.