Quantum Theory of Spectral Line Broadening[*,†]

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Simple radiation theory is used to derive a formula proposed earlier by P. W. Anderson, for calculating the intensity within a collision-broadened spectral line. The problem is considered, first from the point of view of molecular transitions, and then by computing the work done by the light wave. The general result for absorption is stated in Eq. (18), wherein the first double integral represents true absorption, the second induced emission.

THE variety of treatments of the line-broadening problem is so great as to be bewildering, and it is often difficult to see whether different approaches describe, or do not describe, the same effects. A single starting point, not too far back in the equations of radiation theory but general enough for extensive use, would aid greatly in synthesizing this field of optics. Such a starting point was suggested by Anderson[1] who, following mainly the work of Lindholm[2] and Foley,[3] called attention to what he appropriately termed the quantum-mechanical generalization of the classical Fourier formula or, briefly, the Fourier-integral formula for computing line contours.

Anderson reasons as follows. The intensity spectrum of a classical charge of varying dipole moment $\mu(t)$ is given by

$$I(\omega) = \frac{2\omega^4}{3\pi c^3} \left| \int_{-\infty}^{\infty} dt \mu(t) e^{-i\omega t} \right|^2. \tag{1}$$

Using the quantum rule for the expectation value of a classical observable Q; namely $\bar{Q} = \mathrm{Tr}(\rho Q)$, he rewrites Eq. (1) in the form

$$I(\omega) = \frac{2\omega^4}{3\pi c^3} \mathrm{Tr} \left\{ \rho \int_{-\infty}^{\infty} dt \mu(t) e^{-i\omega t} \int_{-\infty}^{\infty} dt \mu(t) e^{i\omega t} \right\}, \tag{2}$$

and takes ρ to be the statistical matrix for the atomic states at the beginning of the radiation process; $\mu(t)$ is the time-dependent ("Heisenberg") form of the dipole matrix and Tr designates the diagonal sum. This very plausible method needs of course some justification beyond an appeal to the correspondence principle in view of the highly derivative nature of the operator that is being transcribed, and Anderson provides it in his thesis,[4] employing the elaborate technique of quantum radiation theory. Nor is the passage from Eq. (1) to (2) unique, for the matrix $\mu(t)$ does not commute with itself at different times and this leaves the order

in which the two integrals occur quite arbitrary. Furthermore, and this is one point of the present paper, a formula like (2), if correct, should be derivable by the simple methods of semiclassical radiation theory that have been widely used earlier in this field, provided the formula is applied to absorption. The quantum character of the photon field can hardly matter in a problem which ignores the natural line width. In the following we give two simple derivations of a formula similar to (2) for absorption and discuss its relevance. Crucial in this analysis is the use of certain "collision-smeared" atomic states, which previous investigators seem to have overlooked with the result of finding only approximations to the quantum Fourier formula.

I. METHOD OF MOLECULAR TRANSITIONS

Let the stationary eigenstates of a molecule, so long as it is unperturbed by other molecules and by light, be denoted by φ_λ. The functions satisfy

$$H_0 \varphi_\lambda = E_\lambda \varphi_\lambda.$$

When exposed to other molecules which exert energy perturbations $C(t)$ during collisions, and also to a light wave adding the energy $F(t)$, the states of an absorbing molecule, $\Psi(t)$, must obey

$$i\hbar \partial \Psi / \partial t = (H_0 + C + F)\Psi. \tag{3}$$

Instead of expanding Ψ directly in terms of the φ we consider first the Schrödinger equation in the absence of the light wave:

$$i\hbar \partial \Phi / \partial t = [H_0 + C(t)]\Phi,$$

but instead of dealing with a single Φ we introduce the set

$$\{\Phi_i(t)\},$$

formed by the expansion

$$\Phi_i = \sum_\lambda U_{\lambda i}(t) \varphi_\lambda. \tag{4}$$

We impose the condition that at time t_0

$$\Phi_i(t_0) = \varphi_i; \quad \text{i.e.,} \quad U(t_0) = 1.$$

The time-development matrix U obeys the Schrödinger equation,

$$i\hbar \dot{U} = (H_0 + C)U,$$

[1] P. W. Anderson, Phys. Rev. **76**, 647 (1949).
[2] E. Lindholm, Arkiv. Mat. Astron. Fysik **32**, 17 (1945).
[3] H. M. Foley, Phys. Rev. **69**, 616 (1946).
[4] P. W. Anderson dissertation, Harvard University (1949), unpublished.

and is unitary, $U^\dagger U = 1$. Hence it may be seen that the Φ_i form a complete orthonormal set at every instant. It is therefore proper to expand the solutions of Eq. (3) in terms of them;

$$\Psi = \sum_\lambda a_\lambda(t)\Phi_\lambda(t).$$

The coefficients are then subject to the equation

$$i\hbar \dot{a}_k = \sum_\lambda F_{k\lambda} a_\lambda, \tag{5}$$

with

$$F_{k\lambda} = \int \Phi_k^* F \Phi_\lambda dv.$$

But the F's may be transformed back to the stationary base $\{\varphi_i\}$. Any operator P whose matrix in the Φ-base is P_{ij} can be expressed in the stationary base as follows:

$$P_{ij} = \int \Phi_i^* P \Phi_j dv = \sum_{\lambda\mu} U_{\lambda i}^* U_{\mu j} \int \varphi_\lambda^* P \varphi_\mu dv = (U^\dagger P^s U)_{ij}.$$

The matrix on the left is in a Heisenberg representation which includes the time dependence resulting from molecular collisions in its basis, though not the light wave. On the right we have P^s in the stationary or Schrödinger representation. Henceforth we shall write P^H for $U^\dagger P^s U$ and understand that all matrices appearing in subsequent equations are in the φ-base.

Equation (5) reads, in vector form,

$$i\hbar \dot{a} = F^H a. \tag{6}$$

and will be solved by successive approximation. First, however, we take note of an alternative procedure which, though erroneous, is not without interest.

It is possible to expand the solution of Eq. (3) directly in terms of the stationary states in the manner:

$$\Psi(t) = \sum_\lambda b_\lambda(t)\varphi_\lambda,$$

and then to compute the amplitudes b. The usual methods of treating time-dependent perturbations would have us do precisely this and ask us to regard the quantity $|b_k|^2$ as the probability of a jump from the initial state to the state k. This is indeed what it signifies, but the jump in question results from *both* perturbing agencies, collisions and radiation field. This is easily seen from the fact that the b's do not vanish in the absence of F. What interests us is the probability of a jump caused by F alone, and this is $|a_k|^2$.

Theories[5] based on a calculation of the b's yield answers which are *adiabatic* approximations to the correct one. This is because, when the molecular collisions are supposed to produce no transitions between atomic states (adiabatic hypothesis), the light wave remains the only agency to do so. In our complete picture, the collisions "smear out" the energy levels via Eq. (4), and we ask what is the probability that a light wave will induce a jump between these collision-smeared

[5] See reference 3, and M. Mizushima, Phys. Rev. **83**, 94 (1951).

states $\{\Phi_i(t)\}$ in time $t - t_0$. This probability is given by $|a_k|^2$. The smearing is the result not only of static perturbations but also of diabatic effects.

Returning now to Eq. (6) we find that its solution can be expressed in the iterated form,

$$a(t) = \left[1 + \sum_{s=1}^\infty I^{(s)}(t)\right]a(t_0), \tag{7}$$

where

$$I^{(s)}(t) = (i\hbar)^{-s} \int_{t_0}^t dt_s \int_{t_0}^{t_s} dt_{s-1} \int_{t_0}^{t_{s-1}} \cdots$$
$$\times \int_{t_0}^{t_2} dt_1 F^H(t_s) \cdots F^H(t_1).$$

Since $1 + \sum I^{(s)}$ is unitary,

$$\sum_s (I^{(s)\dagger} + I^{(s)}) = -\sum_{rs} I^{(s)\dagger} I^{(r)}; \tag{8}$$

and this yields the useful relations

$$I^{(1)\dagger} + I^{(1)} = 0,$$
$$I^{(2)\dagger} + I^{(2)} + I^{(1)\dagger} I^{(1)} = 0, \text{ etc.}$$

The transition probabilities are

$$|a_k(t)|^2 = |a_k|^2 + \sum_\lambda \sum_{s=1}^\infty (a_k a_\lambda^* I_{k\lambda}^{(s)*} + a_\lambda a_k^* I_{k\lambda}^{(s)})$$
$$+ \sum_{\lambda\mu} a_\lambda a_\mu^* \sum_{rs} I_{k\lambda}^{(s)} I_{k\mu}^{(r)*}. \tag{9}$$

The a's on the right denote initial values. The statistical matrix for the absorbing molecule is defined by $\rho_{ij}(t) = b_i(t) b_j^*(t)$, but since $\Phi_i(t_0) = \varphi_i$, we may also write $a_i a_j^* = \rho_{ij}(t_0)$. Because of the random distribution of the phases among the amplitudes a, the statistical matrix is effectively diagonal, and we have

$$\rho_{ij}(t_0) = \rho_i \delta_{ij}.$$

In view of this, and with the use of Eq. (8), the expression for the probabilities becomes

$$\rho_k(t) = \rho_k + \sum_\lambda \rho_\lambda \sum_{rs} I_{k\lambda}^{(s)} I_{k\lambda}^{(r)*}$$
$$- \sum_\lambda \rho_k \sum_{rs} I_{\lambda k}^{(s)} I_{\lambda k}^{(r)*}.$$

Now $I^{(s)}$ is of the order s in F, and hence of order s in the electric field strength of the light wave; we shall retain in $|a_k(t)|^2$ only terms of second order, as is customary. This limits us to the integrals $I_{k\lambda}^{(1)} I_{k\lambda}^{(1)*}$, and

$$\rho_k(t) = \rho_k + \sum_\lambda (\rho_\lambda - \rho_k)|I_{k\lambda}^{(1)}(t)|^2. \tag{10}$$

The explicit form of the field perturbation in the dipole approximation is

$$F(t)^H = -\boldsymbol{\varepsilon} \cdot \mathbf{u}^H \cos(\omega t + \alpha),$$

and

$$I^{(1)}(t) = (i\hbar)^{-1} \int_{t_0}^t F^H(\tau) d\tau.$$

When we set $\mathcal{E} \cdot \mathbf{u}^H = \mathcal{E}\mu^H \cos\theta$, average over θ and over the random phase angle α, we obtain

$$\rho_k(\infty) - \rho_k = \frac{\mathcal{E}^2}{12\hbar^2} \sum_\lambda (\rho_\lambda - \rho_k) \left\{ \left| \int_{-\infty}^{\infty} dt \mu_{k\lambda}{}^H(t) e^{i\omega t} \right|^2 + \left| \int_{-\infty}^{\infty} dt \mu_{k\lambda}{}^H(t) e^{-i\omega t} \right|^2 \right\}. \quad (11)$$

This expression represents the increment in population of the kth level resulting from the light wave; not all of it is due to absorption. The meaning of the various terms becomes clear if we decompose the sum on the right and regard each term in λ as representing an individual spectral line. This decomposition is of course not meaningful physically when collisions cause the individual lines to overlap.

When decomposition is permissible, the dipole moment μ^H, which satisfies

$$-i\hbar\dot{\mu}^H = (H_0+C)^H \mu^H - \mu^H (H_0+C)^H, \quad (12)$$

is approximately given by

$$\mu_{k\lambda}{}^H = \mu_{k\lambda}{}^s e^{i\omega_{k\lambda}t}$$

(where $\omega_{k\lambda} = (E_k - E_\lambda)/\hbar$ represents the unperturbed molecular frequencies), since that is the solution of Eq. (12) when C is absent. Hence the first integrand in Eq. (11) has approximately the exponential factor $e^{i(\omega+\omega_{k\lambda})t}$, the second the factor $e^{i(\omega_{k\lambda}-\omega)t}$. If $E_k > E_\lambda$ the second of these produces resonance and the first can be neglected; otherwise their role is reversed. In that case,

$$\rho_\lambda \left| \int_{-\infty}^{\infty} dt \mu_{k\lambda}{}^H(t) e^{-i\omega t} \right|^2 \quad (13)$$

represents absorption, and

$$-\rho_k \left| \int_{-\infty}^{\infty} dt \mu_{k\lambda}{}^H(t) e^{-i\omega t} \right|^2$$

represents induced emission. When (13) is summed over all k and λ we find the formula to which Eq. (2) reduces when ρ is taken to be diagonal.

The symmetry of Eq. (11) is noteworthy. Both sets of terms, those in $e^{i\omega t}$ and those in $e^{-i\omega t}$, are necessary in absorption since, as we have seen, one set is important when $E_k > E_\lambda$ and the other when $E_\lambda > E_k$.

II. WORK DONE BY THE LIGHT WAVE

There is another way of obtaining Eq. (11). Because it is physically interesting and involves the same mathematical tools as the preceding section we present it briefly here. While thus far we have studied the effect of the light wave on the molecule, we shall now compute the work done by the light wave.

The electric vector is again given by $\mathcal{E} \cos(\omega t + \alpha)$. The work done by the wave on an absorbing molecule

in the time interval $t - t_0$ is

$$W = \mathcal{E} \cdot \int_{t_0}^{t} dt' \cos(\omega t' + \alpha) \frac{d}{dt'} \langle \mathbf{u}(t') \rangle, \quad (14)$$

provided $\langle \mathbf{u} \rangle$ is the quantum mechanical expectation value of the dipole moment,

$$\langle \mathbf{u}(t) \rangle = \mathrm{Tr}[\rho(t)\mathbf{u}] = \mathrm{Tr}[a(t)a^\dagger(t)\mathbf{u}^H(t)],$$

if we use our earlier representation. The a's are known from Eq. (7). In this analysis only terms of the first order in F need be retained, since W already has a factor $\mathcal{E}$ aside from those in $\langle \mu \rangle$. Hence

$$\langle \mathbf{u}(t) \rangle = \mathrm{Tr} \left\{ \left[1 + (i\hbar)^{-1} \int_{t_0}^{t} dt F^H \right] \times a a^\dagger \left[1 - (i\hbar)^{-1} \int_{t_0}^{t} dt F^H \right] \mathbf{u}^H \right\} = \mathrm{Tr}[\rho \mathbf{u}^H(t)] + (i\hbar)^{-1} \mathrm{Tr} \left\{ \rho \left[\mathbf{u}^H(t) \int_{t_0}^{t} dt' F^H(t') - \int_{t_0}^{t} dt' F^H(t') \mathbf{u}^H(t) \right] \right\}, \quad (15)$$

where $a = a(t_0)$ and $\rho = \rho(t_0)$. The first term on the right of Eq. (15) is independent of F and represents the mean dipole moment of the absorbing molecule in the presence of the perturbers only. Thus, when W is averaged over a random distribution of phases α of the light wave, this term contributes nothing. We therefore neglect it at once.

Referring to Eq. (14) and integrating by parts, we write

$$W = \mathcal{E} \cdot \langle \mathbf{u}(t) \rangle \cos(\omega t + \alpha) \Big|_{t_0}^{t} + \omega \mathcal{E} \cdot \int_{t_0}^{t} dt' \sin(\omega t' + \alpha) \mathbf{u}^H(t').$$

Since $\int_{t_0}^{t} dt F^H$ vanishes at t_0, we see that the integrated term vanishes at the lower limit. Furthermore, although the damping factor which would describe the natural breadth in absorption has been omitted as being small compared to the collision broadening effects, this damping term makes the integrated term in W vanish at the upper limit when $t \to \infty$. Thus the mean value with respect to α is

$$\langle W \rangle_\alpha = -\frac{i}{\hbar} \left\langle \omega \mathcal{E} \cdot \int_{t_0}^{t} dt' \sin(\omega t' + \alpha) \times \mathrm{Tr} \left\{ \rho \left[\mathbf{u}^H(t') \int_{t_0}^{t'} dt'' F^H(t'') - \int_{t_0}^{t'} dt'' F^H(t'') \mathbf{u}^H(t') \right] \right\} \right\rangle_\alpha.$$

On inserting F^H we find (omitting henceforth the uperscript H on μ)

$$\langle W \rangle_\alpha = \frac{i}{\hbar}(\mathscr{E}\cos\theta)^2\omega\left\langle \mathrm{Tr}\left\{\rho\left[\int_{t_0}^{t}dt'\,\sin(\omega t'+\alpha)\mu(t')\right.\right.\right.$$

$$\times \int_{t_0}^{t'}dt''\cos(\omega t''+\alpha)\mu(t'') - \int_{t_0}^{t}dt'\,\sin(\omega t'+\alpha)$$

$$\left.\left.\left.\times\int_{t_0}^{t'}dt''\cos(\omega t''+\alpha)\mu(t'')\mu(t')\right]\right\}\right\rangle_\alpha.$$

The second double integral can be transformed to

$$\int_{t_0}^{t}dt'\cos(\omega t'+\alpha)\mu(t')\int_{t_0}^{t}dt'\sin(\omega t'+\alpha)\mu(t')$$

$$-\int_{t_0}^{t}dt'\cos(\omega t'+\alpha)\mu(t')\int_{t_0}^{t'}dt''\sin(\omega t''+\alpha)\mu(t'').$$

When this expression is substituted and the average over α is taken, two of the three double integrals cancel, the result being

$$\langle W \rangle_\alpha = -\frac{i\omega}{2\hbar}(\mathscr{E}\cos\theta)^2\,\mathrm{Tr}\left\{\rho\left[\int_{t_0}^{t}dt'\,\cos\omega t'\mu(t')\right.\right.$$

$$\times\int_{t_0}^{t}dt'\,\sin\omega t'\mu(t') - \int_{t_0}^{t}dt'\,\sin\omega t'\mu(t')$$

$$\left.\left.\times\int_{t_0}^{t}dt'\,\cos\omega t'\mu(t')\right]\right\}$$

$$=\frac{\omega}{4\hbar}(\mathscr{E}\cos\theta)^2\,\mathrm{Tr}\left\{\rho\left[\int dt\mu(t)e^{i\omega t}\int dt\mu(t)e^{-i\omega t}\right.\right.$$

$$\left.\left.-\int dt\mu(t)e^{-i\omega t}\int dt\mu(t)e^{i\omega t}\right]\right\}. \quad (16)$$

From the signs of the two integrals in brackets we see that the first represents true absorption, the second the energy returned to the light wave, i.e., induced emission, in accord with the conclusions of the preceding section. The coefficient too agrees with that of Eq. (11); for if $\rho_k(\infty)-\rho_k$ is multiplied by $\hbar\omega$, its coefficient becomes identical with that of (16), provided $\langle\cos^2\theta\rangle$ is replaced by $\frac{1}{3}$.

The present method is perhaps superior to that of Sec. I because it yields the trace expression directly and requires for its interpretation no decomposition into separate spectral lines.

III. DETAILED BALANCING BETWEEN ABSORPTION AND EMISSION

Such decomposition is necessary, however, for a discussion of detailed balancing between absorption and spontaneous emission. Furthermore, absorption must be assumed to take place from a radiation bath of many frequencies with energy density $P(\omega)$. The relation between P and our former $\mathscr{E}$ is this:

$$\mathscr{E}^2 = 8\pi P(\omega)d\omega. \quad (17)$$

The mean work done by the light wave per unit frequency interval, i.e., the intensity of net absorption, is given by $\langle W \rangle_{\alpha,\theta}/d\omega$ as t_0 and t tend to $-$ and $+\infty$, respectively; in view of Eqs. (16) and (17) it is

$$I_A(\omega) = \frac{2\pi\omega P}{3\hbar}\,\mathrm{Tr}\left\{\rho\left[\int_{-\infty}^{\infty}dt\mu(t)e^{i\omega t}\int_{-\infty}^{\infty}dt\mu(t)e^{-i\omega t}\right.\right.$$

$$\left.\left.-\int_{-\infty}^{\infty}dt\mu(t)e^{-i\omega t}\int_{-\infty}^{\infty}dt\mu(t)e^{i\omega t}\right]\right\}. \quad (18)$$

When ρ is diagonal this expression will be seen to take the form

$$I_A(\omega) = \frac{2\pi\omega P}{3\hbar}\sum_{km}(\rho_m-\rho_k)J_{km},$$

whereas Anderson's emission formula [Eq. (2)] becomes

$$I_E(\omega) = \frac{2\omega^4}{3\pi c^3}\sum_{km}\rho_k J_{km},$$

where

$$J_{km} \equiv \left|\int_{-\infty}^{\infty}dt\mu_{km}(t)e^{-i\omega t}\right|^2.$$

These formulas describe the entire spectrum; the ρ's are the initial occupation numbers of the molecular states. We now associate every term of these summations with a single atomic transition, the one involving μ_{km} with a transition of frequency ω_{km}. The number of absorptive transitions within $d\omega$ is then $I_A/\hbar\omega$, the reverse number $I_E/\hbar\omega$. The principle of detailed balancing requires these to be equal. Hence, if

$$A = (2\omega^3/3\pi\hbar c^3)J_{km}$$

and

$$B = (2\pi/3\hbar^2)J_{km},$$

it is necessary that $(\rho_m-\rho_k)P(\omega)B=\rho_k A$. We are thus led to the universal relation,

$$A/B = \hbar\omega^3/\pi^2 c^3,$$

between the Einstein coefficients A and B. In this sense detailed balancing has been proved.

In a more specific sense, however, the problem is not solved. For if we take $P(\omega)$ to be a Planck distribution, the occupation numbers ρ_i do not conform to the Boltzmann law, $\rho_i \cong e^{-E_i/kT}$, with unperturbed atomic energies E_i. This can hardly be a fault of the decomposition of the trace; it is probably indicative of a residual lack of refinement in our work. Perhaps it should be added that the use of quantum radiation theory does not remove this feature, for it leads to precisely the same results.