

Emission versus Absorption in Resonance Pressure Broadening*

William D. Lyon[†] and C. Alden Mead

Chemistry Department, University of Minnesota, Minneapolis, Minnesota 55455

(Received 2 September 1969)

For a transition in a monatomic gas, it is shown that certain processes in which excitation is transferred from one atom to another lead to different resonance-broadened line shapes in emission and absorption. The absorption line shape is determined by an averaged diagonal matrix element of the resolvent operator (in the representation of the unperturbed states), while in emission some off-diagonal elements contribute. The differences are exhibited formally in terms of resolvent-operator theory, and also worked out explicitly for the case of pure impact broadening with the classical path approximation. In this case, the main effect is a shift of the emission line toward the red, relative to the absorption, by an amount of the same order of magnitude as the width. In the case where the lower level in emission is the one undergoing resonance broadening, the line shapes for emission and absorption (with the same final states) are the same.

I. INTRODUCTION

Although the distinction is frequently ignored in line-shape theory, there are important differences between absorption and emission processes, which in some cases can cause an absorption line shape to differ from the (supposedly) corresponding emission shape. There are two chief causes of this difference.

The first difference is that absorption is in general a much more precisely defined process than emission. In an absorption problem, one can start with an initial state (photon moving toward absorbing medium, which is in its ground state or some other well-defined state) which is asymptotically an eigenstate of some readily identifiable zero-order Hamiltonian \mathcal{H}_0 . One then calculates the electric field and polarization in the medium as the state evolves under the interaction, arriving at a frequency-dependent complex susceptibility, and hence a formula for the absorption line shape. Essentially the same thing can be done in a time-independent formalism, by forming a dressed (scattering) photon state which approaches the eigenstate of \mathcal{H}_0 in the limit of zero interaction. The problem is thus as well defined as an ordinary scattering problem, and can be treated in principle by the same methods. In emission, however, the situation is different. If one wishes to assume that the initial state (e.g., a single atom of a gas excited, no photon present) is an eigenstate of some \mathcal{H}_0 , then there is no unambiguous way of choosing \mathcal{H}_0 , as there is no \mathcal{H}_0 whose eigenstates asymptotically approach those of \mathcal{H} and include the assumed initial state. Thus, different ways of dividing the Hamiltonian up into zero-order and interaction parts correspond to different assumptions about the initial state, and hence, in general, different line shapes. To settle this unambiguously, one must consider the way in

which the initial excited state was actually created in the physical problem under study. An elementary example of this is considered in the well-known textbook by Heitler,¹ where it is shown that an isolated atom excited by a band of radiation narrow compared with its natural linewidth will emit with a linewidth the same as that of the exciting radiation; while if the exciting radiation is very broad, the emission will have the natural linewidth. Thus, any theory of emission must start with some assumption about the initial state, and the results in general will depend on this assumption.

Even after one has chosen an initial state, however, there remain differences in the treatment. In absorption, one is normally measuring a susceptibility, i. e., a relation between polarization and field; while in emission, one is interested directly in a transition probability: Given an initial state, what is the probability that a photon of given frequency will be present at a later time? The two problems are not obviously (and, in view of the above, not in fact) identical. In particular, consider the effect of processes in which the excitation is transferred from one atom to another in a gas prior to emission (or subsequent to absorption). Such processes certainly play an important role in resonance-broadening problems in gases. In emission, it is certainly clear that, if the initial state has the excitation localized on a single atom, these excitation transfer processes will contribute substantially to the propagation of the excitation from the interior to the surface of the sample, and hence presumably to the line shape. In absorption, such processes contribute both to electric field and polarization in the gas. Their contribution to the susceptibility, therefore, is not easy to determine. *A priori* it is possible that it could be zero due to cancellation (and in fact, something like this does apparently happen). In resonance broadening,

therefore, one might expect that the contribution of excitation transfer will be different for absorption and emission. For nonresonant broadening, where excitation transfer plays no appreciable role, one would not expect this problem to arise.

In this article, we shall make the customary choice of initial state (excitation shared incoherently between atoms of the gas, thermal equilibrium with respect to other degrees of freedom), and concentrate on the different effects of excitation transfer. It will be shown that this choice of initial state leads to an emission line shape different from that for absorption. However, the question of the choice of initial state can never be completely ignored. The reader should bear in mind that our results, like those of any emission theory, depend on the choice of initial state; and, no doubt, there exists a choice which would emit a line identical to the absorption.

Among the standard treatments of pressure broadening, those of Baranger,² and Fano³ are set up in terms of emission (though the distinction is not stressed), but are difficult to apply directly to resonant broadening since they consider the autocorrelation function for the dipole moment of a single emitting atom rather than of the whole gas. The treatment of Ross,⁴ based on modern many-body theory, is formulated in terms of absorption, as is the many-body treatment of resonance broadening by Bezzrides.⁵ Zaidi⁶ has given a treatment of resonance broadening in emission, but concentrates mainly on a case in which the two are essentially the same (to be treated in Sec. III B of the present paper).

Resonant broadening in absorption has been treated in terms of resolvent-operator theory by Reck, Takebe, and Mead.⁷ There, it was shown that the frequency- and wave-number-dependent susceptibility $F(\nu, \kappa)$ could be expressed in terms of an averaged diagonal matrix element of the resolvent operator $R(\nu)$, as follows:

$$F(\nu, \kappa) = -4\pi\mathfrak{N}\mu^2\epsilon_j \overline{\langle A_j, \vec{\kappa}(A) | R_+(\nu) | A_k, \vec{\kappa}(A) \rangle} \epsilon_k, \quad (1)$$

where μ^2 is \hbar^{-1} times the square of the usual transition dipole matrix element; \mathfrak{N} is the density in atoms/cm³; $\vec{\epsilon}$ is a polarization unit vector perpendicular to $\vec{\kappa}$; and $|A_j, \vec{\kappa}(A)\rangle$ denotes a state in which atom A has become excited, with polarization along the j direction, and has acquired a momentum $\hbar\vec{\kappa}$ in addition to what it had before absorption. The bar denotes averaging, the Hamiltonian is in angular frequency units (so that R has the dimensions of time), and repeated indices are summed over (notation will be explained more fully in Sec. II). If the wave-number of dependence of F

is negligible, then the refractive index $n(\nu)$ is given by

$$n^2(\nu) - 1 = 4\pi\chi(\nu) = F(\nu, \nu_0/c), \quad (2)$$

where ν_0 is the isolated atom resonant frequency. The imaginary part, of course, gives the absorption. It should be noticed that only *diagonal* elements of the resolvent appear in (1). In a sense, therefore, some of the contributions of excitation transfer to field and polarization do indeed cancel out in this case; although one needs to take such processes into account in evaluating the diagonal matrix element of R , they do not lead to the appearance of off-diagonal elements. As we shall see presently, excitation transfer causes off-diagonal elements of R to appear in the expression for the emission line shape. Subsequently, Eq. (1) has been applied, together with various types of approximations, to the calculation of resonance-broadening line shapes and comparison with experiment.^{7,8}

In the present paper, we show that the emission line shape contains contributions from off-diagonal elements of R which do not appear in (1), and their contribution is explicitly calculated for a special case. The plan of the paper is as follows.

In Sec. II, the notation and Hamiltonian are discussed, and it is shown how emission line shapes are to be expressed in principle in terms of resolvent-operator theory. Also, a preliminary transformation is carried out to eliminate the necessity of considering virtual photon states in evaluating resolvent matrix elements.

In Sec. III A, the case of emission is considered, and it is shown that off-diagonal resolvent matrix elements do indeed appear. Section III B considers another type of emission, in which the lower state (final state of atom after emission) is the one subject to resonance broadening. Here, it is shown that, as in absorption, only diagonal elements of R appear.

In Sec. IV, the contribution of various final states to the over-all emission line shape is analyzed, especially with regard to their behavior as functions of the gas density. In an expansion of the emission line shape in powers of the density, it is shown at which order (of \mathfrak{N}) each type of final state makes its first contribution. Even to first order in \mathfrak{N} (and in all higher orders), the off-diagonal terms contribute.

Section V contains an explicit calculation of the emission line shape in the classical path impact limit. For this case, it is shown that the effect of the off-diagonal terms is to shift the line toward the red, by an amount of the same order of magnitude as the resonance linewidth.

There is some discussion in Sec. VI.

II. PRELIMINARIES

A. Notation and Hamiltonian

The notation to be used is essentially that of Refs. 7 and 8. The system is a gas of N atoms of mass m enclosed in volume V with periodic boundary conditions. We are interested, of course, in the limit $N, V \rightarrow \infty$, with $\mathfrak{N} = N/V$ constant. We neglect effects of quantum statistics, treating the atoms as distinguishable, though identical. Each atom has a nondegenerate S ground state, and a triply degenerate P excited state with energy separation $\hbar\nu_0$. In addition, a higher excited S state is considered in Sec. III B. The atoms do not interact in the ground state, and interact through resonant dipole-dipole forces in the excited state.

The symbol $|0\rangle$ denotes a state in which all atoms are in their ground state, with each atom A having a designated momentum \vec{p}_A , these being distributed according to a Boltzmann distribution. The symbol A_j within a ket indicates that atom A has become excited, with dipole polarization j . $\vec{\kappa}(A)$ means that A has momentum $\hbar\vec{\kappa}$ in addition to what it has in $|0\rangle$. $\vec{\kappa}$ by itself means that one or more atoms (unspecified) have acquired excess momentum. A Greek letter, e.g., λ , denotes the presence of a photon of wave vector $\vec{\kappa}_\lambda$ and polarization $\vec{\epsilon}_\lambda$. Thus, for example, $|A_j, \vec{\kappa}_1(A), \vec{\kappa}_2(B)\rangle$ denotes a state in which A is excited with j polarization, atoms A and B have excess momentum $\hbar\vec{\kappa}_1$ and $\hbar\vec{\kappa}_2$, respectively (in addition to their initial momenta \vec{p}_A, \vec{p}_B), no photons are present, and all atoms other than A and B are in the same state as in $|0\rangle$.

Since we are considering resonant effects, we can restrict our attention to states close to each other in energy. Thus, we consider only states in which either one atom is excited, or one photon is present, with frequency close to ν_0 , in addition to arbitrary changes in momentum distribution. Thus, only states of the form $|A_j, \vec{\kappa}\rangle$ and $|\lambda, \vec{\kappa}\rangle$ are considered.

The Hamiltonian (in angular frequency units) may be written as follows:

$$\mathfrak{H} = T + \mathfrak{U} + \mathfrak{H}_f + \mathfrak{H}_{\text{int}}, \quad (3)$$

$$\text{where } T = \frac{\hbar}{2m} \sum_B \nabla_B^2 - \sum_B \frac{p_B^2}{2m\hbar}, \quad (4)$$

$$\mathfrak{U} = \sum_{A \neq B} \frac{\mu^2}{r_{AB}^3} |A_j\rangle \left(\delta_{jk} - 3 \frac{r_{ABj} r_{ABk}}{r_{AB}^2} \right) \langle B_k|, \quad (5)$$

$$\mathfrak{H}_f = \sum_\lambda |\lambda\rangle \omega_\lambda \langle \lambda| (\omega_\lambda = \nu_\lambda - \nu_0), \quad (6)$$

$$\mathfrak{H}_{\text{int}} = i \left(\frac{2\pi\nu_0}{V} \right)^{1/2} \mu \sum_{A, \lambda} \epsilon_{\lambda j} [|\lambda\rangle \exp(-i\vec{\kappa}_\lambda \cdot \vec{r}_A) \langle A_j|$$

$$- |A_j\rangle \exp(i\vec{\kappa}_\lambda \cdot \vec{r}_A) \langle \lambda|] . \quad (7)$$

We have subtracted $\sum p^2/2m\hbar + \nu_0$ from \mathfrak{H} so that the (zero-order) energy of $|A_j\rangle$ is zero. Operators such as ∇, r_A , etc., operate only on the translational degrees of freedom, while $|A_j\rangle \langle B_k|, |A_j\rangle \langle \lambda|$, etc., affect only the internal and/or photon degrees of freedom. In arriving at (7), we have used the assumption that ν_λ is close to ν_0 , by assuming $|\omega_\lambda| \ll \nu_0$. Otherwise there would be an additional factor ν_0/ν_λ in each term.

B. Resolvent and Asymptotic States

For any scattering problem with Hamiltonian

$$\mathfrak{H} = \mathfrak{H}_0 + \mathfrak{H}_{\text{int}},$$

with zero-order eigenstate $|\omega\rangle, \mathfrak{H}_0|\omega\rangle = \omega|\omega\rangle$, the corresponding scattering state $|\bar{\omega}\rangle$ (such that $\mathfrak{H}|\bar{\omega}\rangle = \omega|\bar{\omega}\rangle$) is given by^{9, 10}

$$|\bar{\omega}\rangle_\pm = |\omega\rangle + R_\pm(\omega) \mathfrak{H}_{\text{int}} |\omega\rangle, \quad (8)$$

where R is the resolvent operator

$$R(\omega) = (\omega - \mathfrak{H})^{-1},$$

$$R_\pm(\omega) = \lim_{\epsilon \rightarrow 0^+} (\omega \pm i\epsilon - \mathfrak{H})^{-1}. \quad (9)$$

The $+$ sign corresponds to the "retarded" solution: $|\bar{\omega}\rangle_+$ approaches $|\bar{\omega}\rangle$ for large negative times. If the minus sign is chosen, $|\bar{\omega}\rangle_-$ is the state that would approach $|\omega\rangle$ in the distant future. (More accurately, nearly stationary wave packets made up of $|\bar{\omega}\rangle_\pm$ will approach $|\omega\rangle$ in the remote past/future).

In this article, we will be interested in states $|\vec{\kappa}\lambda\rangle_-$, i.e., states which in the remote future will have a photon λ and the gas in some altered momentum distribution. This is the situation which corresponds to emission.

C. Preliminary Transformation of Resolvent

In the succeeding sections, we will have to calculate resolvent matrix elements such as $\langle A | R | B \rangle$, and it will be convenient for this purpose to transform the resolvent somewhat so as to formally eliminate the photon states. Consider then the problem of calculating the resolvent of a Hamiltonian coupling two manifolds of states (in our case g , the manifold of excited atom states, and λ , the manifold of photon states). The Hamiltonian and resolvent (to be solved for) may be written as

$$\mathcal{H} = \begin{pmatrix} \mathcal{H}_g & \mathcal{H}_{\text{int}} \\ \mathcal{H}_{\text{int}}^\dagger & \mathcal{H}_\lambda \end{pmatrix}; R(\omega) = \begin{pmatrix} R_g & \rho \\ \rho' & R_\lambda \end{pmatrix}, \quad (10)$$

where each entry is, of course, a matrix. From (10) and $(\omega - \mathcal{H})R = 1$, we find

$$(\omega - \mathcal{H}_g)R_g - \mathcal{H}_{\text{int}}\rho' = 1; \quad (11a)$$

$$(\omega - \mathcal{H}_g)\rho - \mathcal{H}_{\text{int}}R_\lambda = 0; \quad (11b)$$

$$-\mathcal{H}_{\text{int}}^\dagger R_g + (\omega - \mathcal{H}_\lambda)\rho' = 0; \quad (11c)$$

$$-\mathcal{H}_{\text{int}}^\dagger \rho + (\omega - \mathcal{H}_\lambda)R_\lambda = 1. \quad (11d)$$

Solving (11c), we find

$$\rho' = (\omega - \mathcal{H}_\lambda)^{-1} \mathcal{H}_{\text{int}}^\dagger R_g. \quad (12)$$

Now one can substitute (12) into (11a), obtaining

$$[\omega - \mathcal{H}_g - \mathcal{H}_{\text{int}}(\omega - \mathcal{H}_\lambda)^{-1} \mathcal{H}_{\text{int}}^\dagger] R_g = 1. \quad (13)$$

Since we are only interested in R_g , (13) is the relation we desire.

The diagonal part of the additional term in (13) is given by

$$\begin{aligned} & \langle A_j | \mathcal{H}_{\text{int}} (\omega - \mathcal{H}_\lambda)^{-1} \mathcal{H}_{\text{int}}^\dagger | A_k \rangle \\ &= \frac{2\pi\nu_0 \mu^2}{V} \sum_\lambda \frac{\epsilon_{\lambda j} \epsilon_{\lambda k}}{\omega - \omega_\lambda}, \end{aligned} \quad (14)$$

where we have made use of (7) and omitted the kinetic energy contribution. To evaluate (14), one replaces the sum by an integral in the usual way, and takes a contour below or above the pole at $\omega = \omega_\lambda$, according to whether we are evaluating R_+ or R_- . The real part is essentially a self-energy term which can be eliminated by standard procedures.¹¹⁻¹³ The imaginary part (if $|\omega| \ll \nu_0$) is just the natural linewidth Δ_0 . Hence, the right-hand side of (14) becomes

$$\mp i \Delta_0 \delta_{jk} = \mp i \frac{2\nu_0^3 \mu^2}{3c^3} \delta_{jk}. \quad (15)$$

The off-diagonal part of $\mathcal{H}_{\text{int}}(\omega - \mathcal{H}_\lambda)^{-1} \mathcal{H}_{\text{int}}^\dagger$ represents processes in which excitation is transferred from one atom to another via emission of a virtual photon. We will omit these terms, assuming that the electrostatic dipole-dipole interaction is the

dominant mechanism in excitation transfer. This is admittedly an approximation, but it is one that is nearly always made in line-broadening theory, so it is appropriate to make it in order to compare our results for emission with previously derived absorption results depending on the same approximation. With this approximation and (15), we now see that

$$R_{g\pm}(\omega) = (\omega \pm i \Delta_0 - \mathcal{H}_g)^{-1}. \quad (16)$$

Hence, the radiation field is taken into account simply by adding $\pm i \Delta_0$ to ω in the resolvent. According to (3), $\mathcal{H}_g = T + \mathcal{V}$.

III. GENERAL FORMULAS FOR EMISSION INTENSITY

A. Upper State Broadened

Here we assume an initial state in which one atom is excited, and attempt to calculate the probability of final states. As pointed out in the Introduction, there is some arbitrariness in choice of initial state. Our choice will be probably the most natural one: excitation shared incoherently and with equal probability between all atoms, thermal equilibrium with respect to translational degrees of freedom. The assumed initial state is therefore just $|A_j\rangle$, and the intensity must be averaged over A, j . This seems to be the most natural choice, and is certainly the one usually made, tacitly or otherwise. However, it should be borne in mind that the subsequent results do depend on this choice. Before applying them to any experimental situation, one should first convince oneself that the choice of initial state is appropriate for the problem under study.

The final state after emission will consist of a photon λ , and perhaps an altered momentum distribution in the gas, i. e., it will be of the form $|\lambda \vec{k}\rangle$. The probability amplitude that the final state will be a particular $|\lambda \vec{k}\rangle$ is clearly just the amplitude for $|A_j\rangle$ being a state that will become $|\lambda \vec{k}\rangle$ in the distant future, in other words $\langle A_j | \overline{|\lambda \vec{k}\rangle} \rangle$. To get the total probability that a photon λ will be emitted, we must square this, sum over \vec{k} (since we are only going to observe the photon, not the final momentum distribution), and average over A, j . Hence, the total intensity (probability) for emission of a particular photon λ is given by

$$g(\lambda) = \frac{1}{3N} \sum_{A, j, \vec{k}} |\langle A_j | \overline{|\lambda \vec{k}\rangle} \rangle|^2. \quad (17)$$

From (7) and (8), we have for $|\overline{|\lambda \vec{k}\rangle} \rangle$:

$$\overline{|\lambda \vec{k}\rangle} = |\vec{k} \lambda\rangle - i\mu \left(\frac{2\pi\nu_0}{V} \right)^{1/2}$$

$$\times R_-[\omega_\lambda + K(\vec{\kappa})] \sum_B |B_\lambda, \vec{\kappa} + \vec{\kappa}_{\lambda B}\rangle . \quad (18)$$

Here, $K(\vec{\kappa})$ is just the added kinetic energy associated with $\vec{\kappa}$:

$$\begin{aligned} K(\vec{\kappa}) &= \sum_B \vec{\kappa}_B \cdot \vec{p}_B / m + \hbar \kappa_B^2 / 2m \\ &= \vec{\kappa} \cdot \vec{v} + \hbar \kappa^2 / 2m , \end{aligned}$$

where $\vec{v} = \vec{p}/m$, and the last equality represents simply shorthand notation. B_λ denotes polarization in direction of $\vec{\epsilon}_\lambda$, and $\vec{\kappa} + \vec{\kappa}_\lambda B$ indicates that the excited atom B has acquired an additional momentum $\hbar \vec{\kappa}_\lambda$ in addition to whatever momentum it may have in $\vec{\kappa}$. From now on, the subscript on ω will be omitted.

Since $\langle A_j | \vec{\kappa}_\lambda \rangle = 0$, we have, from (17) and (18),

$$\begin{aligned} g(\lambda) &= \frac{2\pi\nu_0\mu^2}{3NV} \sum_{A, B, C, \vec{\kappa}} \\ &\times \langle A_i | R_-[\omega + K(\vec{\kappa})] | B_\lambda, \vec{\kappa} + \vec{\kappa}_{\lambda B} \rangle \\ &\times \langle C_\lambda, \vec{\kappa} + \vec{\kappa}_{\lambda C} | R_+[\omega + K(\vec{\kappa})] | A_i \rangle . \quad (19) \end{aligned}$$

The reader's attention is called to the presence of the off-diagonal elements in (19), representing final emission by an atom other than the one initially excited. Note also that there are cross terms. That is, different atoms may interfere with one another in emission, as long as the final state (including $\vec{\kappa}$) is the same.

The presence of the off-diagonal terms in (19), which are absent in (1), indicates that the resulting line shape will be different. In Secs. IV and V some of the effects of this will be analyzed in more detail. First, however, we pause to consider another emission problem, in which the final state is the one subject to resonance broadening.

B. Lower State Broadened

Here we consider the case where each atom possesses an additional excited state X (assumed to be an S state for definiteness) with energy $\hbar(\nu_0 + \nu_1)$ relative to the ground state, which is coupled to our excited P state, but not to the ground state. We consider emission from X down to the P state, with photons emitted with frequencies close to ν_1 . Since X is not coupled to the ground state, there will be no resonant broadening of the upper state. The emission line will be affected, however, by the resonant broadening of the lower (P) state. Eventually, a second photon will be emitted with frequency near ν_0 as the gas returns to its ground electronic state. We can embody all this in our Hamiltonian by adding the terms

$$\mathcal{H}_X = \nu_1 \sum_A |A_X\rangle \langle A_X| , \quad (20)$$

$$\begin{aligned} \text{and } \mathcal{H}'_{\text{int}} &= i\mu_1 \left(\frac{2\pi\nu_1}{V} \right)^{1/2} \sum_{A, \eta} \epsilon_{\eta j} [|A_j, \eta\rangle \\ &\times \exp(-i\vec{\kappa}_\eta \cdot \vec{r}_A) \langle A_X | \\ &- |A_X\rangle \exp(i\vec{\kappa}_\eta \cdot \vec{r}_A) \langle A_j, \eta |] . \quad (21) \end{aligned}$$

We use η to denote a photon in the frequency range around ν_1 and μ_1 for the transition dipole matrix element. As before, we assume that the initial state is just $|A_X\rangle$. In the final state after emission, a photon η has appeared and the rest of the system is in one of the eigenstate of \mathcal{H}_3 , the Hamiltonian of Eq. (3). These are presumably of the form $|\vec{\kappa}\lambda\rangle$, but we don't need their explicit form for this subsection, so they are denoted simply by α . Our final states, therefore, are of the form $|\eta, \alpha\rangle$, where

$$\mathcal{H}_3 |\alpha\rangle = E_\alpha |\alpha\rangle ;$$

$$|\alpha\rangle = \sum_{B, \kappa} |B_j, \vec{\kappa}\rangle \langle B_j, \vec{\kappa} | \alpha \rangle + \sum_{\lambda, \kappa} |\lambda, \vec{\kappa}\rangle \langle \lambda, \vec{\kappa} | \alpha \rangle . \quad (22)$$

The emission intensity in this case is given by

$$g(\eta) = \sum_\alpha |\langle A_X | \overline{\eta\alpha} \rangle_-|^2 . \quad (23)$$

From (8), (21), and (22), we have

$$\begin{aligned} |\overline{\eta\alpha} \rangle_- &= |\eta\alpha\rangle - i\mu_1 \left(\frac{2\pi\nu_1}{V} \right)^{1/2} R_-(\nu_\eta + E_\alpha) \\ &\times \sum_{B, \vec{\kappa}} |B_X, \vec{\kappa} + \vec{\kappa}_{\eta B}\rangle \langle B_\eta, \vec{\kappa} | \alpha \rangle . \quad (24) \end{aligned}$$

Now since $|A_X\rangle$ is not coupled to anything except the manifold of photon states, we find after doing the transformation of Sec. II C,

$$\begin{aligned} R_-(\nu_\eta + E_\alpha) |B_X, \vec{\kappa}\rangle \\ = (\nu_\eta + E_\alpha - i\Delta_X - \nu_1)^{-1} |B_X, \vec{\kappa}\rangle , \quad (25) \end{aligned}$$

where Δ_X is the natural linewidth of X . Using (24) and (25), and introducing $\omega' = \nu_\eta - \nu_1$, we now obtain

$$\begin{aligned} \langle A_X | \overline{\lambda\alpha} \rangle_- &= -i\mu_1 \left(\frac{2\pi\nu_1}{V} \right)^{1/2} (\omega' + E_\alpha - i\Delta_X)^{-1} \\ &\times \langle A_\eta, -\vec{\kappa}_\eta | \alpha \rangle , \quad (26) \end{aligned}$$

since of all the terms in the sum in (24), the only one that contributes (because of 25) is the one with $B=A$, $\vec{k}=-\vec{k}_\eta(A)$.

From (23) and (26), we now find for the intensity

$$\mathcal{I}(\eta) = \frac{2\pi\nu_1}{V} \mu_1^2 \sum_\alpha \langle A_\eta, -\vec{k}_\eta(A) | \alpha \rangle \times [(\omega' + E_\alpha)^2 + \Delta_X^2]^{-1} \langle \alpha | A_\eta, -\vec{k}_\eta(A) \rangle . \quad (27)$$

But since

$$\sum_\alpha | \alpha \rangle (-\omega' - E_\alpha + i\Delta_X)^{-1} \langle \alpha | = R(-\omega' + i\Delta_X) ,$$

with the resolvent taken with respect to \mathcal{H}_0 , (27) becomes

$$\mathcal{I}(\eta) = -\frac{2\pi\nu_1}{V} \mu_1^2 \frac{1}{\Delta_X} \text{Im} \langle A_\eta, -\vec{k}_\eta(A) | \times R(-\omega' + i\Delta_X) | A_\eta, -\vec{k}_\eta(A) \rangle$$

or, since

$$\Delta_X = \frac{2\nu_1^3}{c^3} \mu_1^2 ,$$

$$\mathcal{I}(\eta) = -\frac{\pi c^3}{\nu_1^2 V} \text{Im} \langle A_\eta, -\vec{k}_\eta(A) | \times R(-\omega' + i\Delta_X) | A_\eta, -\vec{k}_\eta(A) \rangle . \quad (28)$$

In the limit $\Delta_X \rightarrow 0$ (negligible broadening of upper state), this becomes identical with the imaginary part of (1) except for trivial constant factors and the change in the sign of ω' , which corresponds to the fact that high frequency emission corresponds to a lower final state, instead of a higher one as in absorption. The conclusion, therefore, is that results for absorption, involving only diagonal resolvent matrix elements, may be taken over bodily for this kind of emission. A similar result has been obtained by Zaidi.⁶ This case is of interest because the many careful experiments of the Oxford group¹⁴ on resonant broadening in rare-gas emission are of this type.

We will not pursue this further, since it has been treated in detail by Zaidi,⁶ and since the main result is simply to justify the usual practice of comparing theoretical line shapes derived for absorption to emission problems of this type.⁸ We now return to the emission from the P state, where the results are different.

IV. ANALYSIS OF CONTRIBUTIONS

A. Diagrammatic Notation

According to (4), (5), and (16), a matrix element of R between two states in which an atom is excited may be formally expanded as follows:

$$\langle A | R | B \rangle = \frac{\delta_{AB}}{W} + \frac{1}{W} \langle A | \mathcal{V} | B \rangle \frac{1}{W'} , \\ + \frac{1}{W} \sum_c \langle A | \mathcal{V} | C \rangle \frac{1}{W''} \langle C | \mathcal{V} | B \rangle \frac{1}{W'} + \dots , \quad (29)$$

where the W 's are energy denominators. Thus, the matrix element $\langle A | R | B \rangle$ may be pictured as consisting of a sum of contributions of various paths by which the excitation is transferred from the initial state $|A\rangle$ to the final excitation state $|B\rangle$, from which emission occurs. Each step represents a transfer of momentum as well as excitation. If an intermediate atom [such as C in (29)] has the same momentum in initial and final states, then different C will lead to the same final state and C is to be summed over. On the other hand, if the specification of the final state includes an altered momentum for a specific atom C , it cannot be summed over. It is convenient to represent this state of affairs by a diagrammatic notation similar to that used in Ref. 7. We use a circle with a capital letter inside to represent an atom, and a line connecting two circles to denote a single step in an expansion such as (29), in which the excitation is transferred from one atom to another. An asterisk (*) by an atom means that that atom is required to have the same momentum in initial and final states, and hence can be summed over. Thus, Fig. 1 shows some of the diagrams which contribute to the matrix element $\langle A_j | R | B_j, \vec{k}(B), -\vec{k}(A) \rangle$. We are interested in the dependence of the contributions of the various diagrams on N , V , and the density $\mathfrak{N} = N/V$. For this purpose, we do not have to consider the factors of μ^2 , energy denominators, etc.

One easily arrives at the following rules for the contribution of a particular diagram.

- (i) The Fourier transform of Eq. (5) leads to

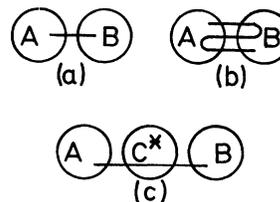


FIG. 1. Some of the diagrams contributing to $\langle A_j | R | B_j, \vec{k}(B), -\vec{k}(A) \rangle$.

$$\langle A_j | v | B_{\vec{k}}, -\vec{k}(A)\vec{k}(B) \rangle = \frac{4\pi\mu^2}{V} \frac{\kappa_j \kappa_{\vec{k}}}{\kappa^2} .$$

Hence, each line in the diagram contributes a factor V^{-1} , and if there are l lines in all, this makes V^{-l} . (ii) The final momentum of each of a atoms appearing in the diagram is specified. Since *total* momentum is automatically conserved, however, this leads to only $(a-1)$ restrictions on the momentum transfers. The remaining (if any) $(l-a+1)$ transfers can be summed over; each of these contributes a factor V , giving an over-all factor V^{l-a+1} . (iii) Starred atoms are summed over, giving a factor N^s , where s is the number of starred atoms.

Putting all this together, one sees that the contribution D of the diagram goes as

$$D \propto N^s V^{-a+1} = \mathfrak{N}^s V^{-q+1} , \quad (30)$$

where $q = a - s$ is the number of unstarred atoms. It is easy to see that q is a property only of the initial and final states, being the number of atoms which *either* are excited in the initial and/or final state, or have their momentum altered between initial and final state, *or both*. For given initial and final state, one can write diagrams with any number of starred intermediates from zero to infinity. Hence, summing over all diagrams will give some function $\mathfrak{F}(\mathfrak{N})$, where in general $\mathfrak{F}(0) \neq 0$. Of course, \mathfrak{F} will be different for different initial and final states, but we need not indicate this specifically in our notation.

For example, we see that

$$\langle A_j | R | A_j \rangle \propto \mathfrak{F}(\mathfrak{N}) , \quad (31)$$

$$\langle A_j | R | A_j, \vec{k}_n \rangle \propto V^{-n} \mathfrak{F}(\mathfrak{N}) , \quad (32)$$

where \vec{k}_n means that n atoms other than A have altered momentum. According to our rules, $q=1$ in (31) and $q=n+1$ in (32), independently of wheth-

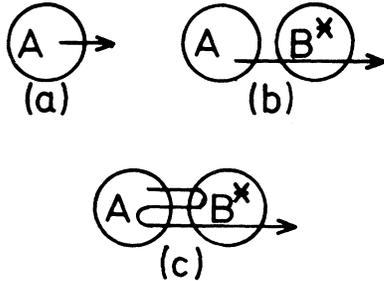


FIG. 2. Some of the diagrams contributing to $\langle A_j | \lambda, -\vec{k}_\lambda(A) \rangle_-$.

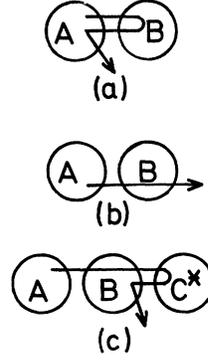


FIG. 3. Some of the diagrams contributing to $\langle A_j | \lambda, \vec{k}_1(A), \vec{k}_2(B) \rangle_-$.

er A also has altered momentum or not. Similarly,

$$\langle A_j | R | B_{\vec{k}}, \vec{k}_n \rangle \propto V^{-n-1} \mathfrak{F}(\mathfrak{N}) , \quad (33)$$

where here n is the number of atoms other than A and B with altered momentum. Here $q = n + 2$, regardless of the initial and final momentum of A and B . We now proceed to apply this analysis to the contributions to the emission intensity.

B. Contributions to Emission

According to (17) and (18), the emission amplitude to a particular final momentum distribution $\langle A_j | \vec{k}_\lambda \rangle$ is proportional to a sum of matrix elements $\langle A_j | R | B_\lambda, \vec{k} + \vec{k}_\lambda \rangle$. Their contributions to emission can be indicated diagrammatically by simply appending an arrow to a diagram to indicate final emission of a photon. If the emitting atom $B \neq A$ is left after emission with the same momentum as in the initial state, then the final state after emission is independent of B , so B can be starred and summed over, giving a factor of N . Otherwise, the dependence on N and V is the same as for the diagram without the arrow. Figure 2 gives some of the contributions to $\langle A_j | \lambda, -\vec{k}_\lambda(A) \rangle$. It is of interest to note that the contribution of Fig. 2(b) is actually zero, since the momentum transfer to B must be exactly \vec{k}_λ , causing B to be polarized along \vec{k}_λ , hence perpendicular to ϵ_λ and unable to emit. This would not be true if we had kept the virtual-photon excitation transfer terms dropped in Sec. II C, and is not true in any event for Fig. 2(c).

Consider then the contributions to the amplitude $\langle A_j | \lambda, \vec{k}_n \rangle$ (where n is the number of atoms *other than* A with altered momentum) from the various $\langle A | R | B \rangle$. One finds the following. (a) The term with $B=A$ goes as $\mathfrak{F}(\mathfrak{N})V^{-n}$, from (32). An example of this with $n=1$ is the diagram of Fig. 3(a). (b) If $B \neq A$ is one of the n , as in Fig. 3(b) for $n=1$, the contribution goes as $\mathfrak{F}(\mathfrak{N})V^{-n}$, according to (33). Recall that n in (33) is the number of

atoms *other than A and B* with altered momentum.

(c) If *B* is different from *A* and not one of the *n*, as in Fig. 3(c), we get $\mathcal{F}(\mathfrak{X})V^{-n-1}$ from the resolvent and *N* from summing over *B*, in all $\mathfrak{X}\mathcal{F}(\mathfrak{X})V^{-n}$.

Thus, the entire amplitude goes as $\mathcal{F}(\mathfrak{X})V^{-n}$. To get the intensity, we must square this and sum over $\vec{\kappa}$. Squaring gives V^{-2n} . Summing over the final momenta of the *n* atoms plus *A*, with the restriction of over-all momentum conservation gives V^n , and summing over the *n* atoms gives N^n . The total contribution to the intensity of final states in which *n* atoms other than *A* have altered momentum is, therefore,

$$g_n(\lambda) \propto \mathfrak{X}^n \mathcal{F}(\mathfrak{X}) \quad (34)$$

[Remember that \mathcal{F} is just some function of \mathfrak{X} which is finite at $\mathfrak{X}=0$, not necessarily the same function in each of Eqs. (31)–(34).] Thus, if the intensity is expanded in powers of \mathfrak{X} , the lowest order to which states $\vec{\kappa}_n$ will contribute is the *n*th. Note that *A* must also be permitted to have an altered momentum. The expansion of g may be related to that of the width Δ and shift *S* by writing the normalized g as

$$g = \frac{1}{\pi} \frac{\Delta}{(\omega - S)^2 + \Delta^2} \quad .$$

Hence, the same conclusion applies to expansions of $\Delta = \Delta_0 + \mathfrak{X}\Delta_1 + \dots$, and $S = \mathfrak{X}S_1 + \dots$: If Δ (or *S*) is desired only to the *n*th order in \mathfrak{X} , then we can restrict our attention to final states in which no more than *n* atoms (other than *A*) have their momentum altered.

Another important question is where the contributions of the off-diagonal elements of *R* come in. It is easy to see from the above analysis that they make a contribution at $n=0$ [e.g., Fig. 2(c)] which, however, is at least of first order in \mathfrak{X} , since, for example, *B* is starred in Fig. 2(c). They also contribute at $n=1$, as shown by Fig. 3(b), and all higher orders. In the density expansion, therefore, they contribute to all orders from the first on up. Hence, even if one only wants the broadening (shift) to lowest order in the density, one should include the off-diagonal terms and should expect the emission line shape in general to be different from the absorption.

In Sec. V, we calculate this difference explicitly for a special case.

V. SOLUTION FOR CLASSICAL PATH IMPACT LIMIT

A. Differential Equation for Resolvent and Classical Path Limit

The treatment in this section will be closely related to that of Secs. 3, 4.1, and 4.4 of Ref. 8.

The main difference is that there only diagonal matrix elements of *R* were considered, while we must now be concerned with the off-diagonal ones. We will not discuss the limitations on the main approximations made, since that has already been done in Ref. 8.

As shown in Sec. II C, we can evaluate *R* with respect to the gas Hamiltonian $\mathcal{H}_G = T + \mathcal{V}$ only, as long as we add $\pm i\Delta_0$ to the argument. To obtain a differential equation for a resolvent matrix element, we write explicitly the integration over translational coordinates. With the aid of (3)–(5) and (9), we obtain

$$\langle A_j | R(\eta) | B_k, \vec{\kappa} + \vec{\kappa}_\lambda B \rangle = V^{-N} \times \int \dots \int \langle A_j | \mathcal{R}(\eta) | B_k \rangle d^3N \mathbf{r}, \quad (35)$$

$$\mathcal{R}(\eta) = \exp\left(-\frac{i}{\hbar} \vec{p} \cdot \vec{r}\right) \left(\eta + \frac{\hbar}{2m} \nabla^2 + \frac{p}{2m\hbar} - \mathcal{V}\right)^{-1} \times \exp i \left[\left(\frac{\vec{p}}{\hbar} + \vec{\kappa} \right) \cdot \vec{r} + \vec{\kappa}_\lambda \cdot \vec{r}_B \right], \quad (36)$$

where $\mathcal{R}(\eta)$ is a matrix in the internal coordinates which is a function of position. We have used the shorthand notation introduced after Eq. (18).

If we multiply both sides of (36) by $\exp[(i/\hbar)\vec{p} \cdot \vec{r}]$, apply $(\eta - \mathcal{H})$ to both sides, and finally multiply by $\exp[(-i/\hbar)\vec{p} \cdot \vec{r}]$, we obtain the differential equation satisfied by the matrix \mathcal{R} :

$$\left(\eta + \frac{\hbar}{2m} \nabla^2 + \hbar \vec{v} \cdot \nabla - \mathcal{V}\right) \mathcal{R} = \exp i(\vec{\kappa} \cdot \vec{r} + \vec{\kappa}_\lambda \cdot \vec{r}_B) \quad (37)$$

In our case, referring to (19) and (16), we see that

$$\eta = \omega + \vec{v} \cdot \vec{\kappa} + (\hbar/2m)\kappa^2 \pm i\Delta_0. \quad (38)$$

The classical path approximation is obtained⁸ by letting \hbar approach zero in (37) and (38). In this limit, therefore, we have

$$(\omega + \vec{v} \cdot \vec{\kappa} \pm i\Delta_0 + i\vec{v} \cdot \nabla - \mathcal{V}) \mathcal{R}_\pm = \exp i(\vec{\kappa} \cdot \vec{r} + \vec{\kappa}_\lambda \cdot \vec{r}_B). \quad (39)$$

The differential equation (39) is satisfied by⁸

$$\mathcal{R}(\vec{r}) = -i \int_0 U(\vec{r} | \vec{r} - \vec{v}t) \exp i[\eta t + \vec{\kappa} \cdot (\vec{r} - \vec{v}t) + \vec{\kappa}_\lambda \cdot (\vec{r}_B - \vec{v}t)] dt, \quad (40)$$

where *U* is a time-displacement operator in the internal coordinates for a process in which the gas begins at the position $\vec{r} - \vec{v}t$ and moves at constant velocity \vec{v} for time *t* to the final position \vec{r} . It for-

mally satisfies the relations

$$i(\partial/\partial t)U(\vec{r}|\vec{r}-\vec{v}t)=U\mathcal{U}(\vec{r}-\vec{v}t) \quad (43)$$

$$U(\vec{r}|\vec{r})=UU^\dagger=1 \quad ,$$

$$U(\vec{r}|\vec{r}-\vec{v}t)U(\vec{r}-\vec{v}t|\vec{r}-\vec{v}t')=U(\vec{r}|\vec{r}-\vec{v}t') \quad , \quad (41)$$

$$i(\partial/\partial t)U(\vec{r}+\vec{v}t|\vec{r})=\mathcal{U}(\vec{r}+\vec{v}t)U(\vec{r}+\vec{v}t|\vec{r}) \quad ,$$

from which it follows that

$$i\vec{v}\cdot\nabla U(\vec{r}|\vec{r}-\vec{v}t)=\mathcal{U}(\vec{r})U-U\mathcal{U}(\vec{r}-\vec{v}t) \quad , \quad (42)$$

Using (42) and (43), one can verify (40) directly.

The upper limit in (40) must be chosen in such a way that the integral converges with the exponential going to zero, i. e., it must be $-\infty$ for R_- , $+\infty$ for R_+ . Also, according to (38), η contains a term in $\vec{v}\cdot\vec{k}$ which cancels another such term in the exponent in (40). Thus, we obtain, from (35) and (40),

$$\begin{aligned} \langle A_j | R_-[\omega + K(\vec{k})] | B_\lambda, \vec{k} + \vec{k}_\lambda B \rangle &= -\frac{V^{-N}}{i} \int \cdots \int d^{3N}r \int_0^\infty dt \\ &\times \langle A_j | U(\vec{r}|\vec{r}+\vec{v}t) | B_\lambda \rangle \exp[(-i\omega - \Delta_0)t + i\vec{k}\cdot\vec{r} + i\vec{k}_\lambda\cdot(\vec{r}_B + \vec{v}_B t)] \quad . \quad (44) \end{aligned}$$

$$\begin{aligned} \text{Similarly, } \langle C_\lambda, \vec{k}_\lambda C | R_+[\omega + K(\vec{k})] | A_j \rangle &= \frac{V^{-N}}{i} \int \cdots \int d^{3N}r' \int_0^\infty dt' \langle C_\lambda, \vec{k}_\lambda C | \vec{r}' - \vec{v}t' | A_j \rangle \\ &\times \exp[(i\omega - \Delta_0)t' - i\vec{k}\cdot(\vec{r}' - \vec{v}t') - i\vec{k}_\lambda\cdot\vec{r}'_C] \quad . \quad (45) \end{aligned}$$

Combining (19), (44), and (45), we obtain

$$\begin{aligned} g(\lambda) &= \frac{2\pi\nu_0\mu^2}{3N} V^{-(2N+1)} \sum_{A,B,C,\vec{k}} \int \cdots \int d^{3N}r d^{3N}r' \int_0^\infty dt \int_0^\infty dt' \times \langle A_j | U(\vec{r}|\vec{r}+\vec{v}t) | B_\lambda \rangle \\ &\times \langle C_\lambda | U(\vec{r}'|\vec{r}'-\vec{v}t') | A_j \rangle \exp[i\omega(t'-t) - \Delta_0(t'+t) + i\vec{k}_\lambda\cdot(\vec{r}_B + \vec{v}_B t - \vec{r}'_C) + i\vec{k}\cdot(\vec{r} - \vec{r}' + \vec{v}t')] \quad . \quad (46) \end{aligned}$$

The sum over \vec{k} just gives the Dirac δ function $V^N\delta^{3N}(\vec{r}-\vec{r}'+\vec{v}t')$, which in turn makes the r' integration easy. Thus, (46) becomes

$$\begin{aligned} g(\lambda) &= \frac{2\pi\nu_0\mu^2}{3N} V^{-(N+1)} \sum_{ABC} \int \cdots \int d^{3N}r \int_0^\infty dt \int_0^\infty dt' \langle A_j | U(\vec{r}|\vec{r}+\vec{v}t) | B_\lambda \rangle \langle C_\lambda | U(\vec{r}+\vec{v}t|\vec{r}) | A_j \rangle \\ &\times \exp[i\omega(t'-t) - \Delta_0(t'+t) + i\vec{k}_\lambda\cdot(\vec{r}_B + \vec{v}_B t - \vec{r}_C - \vec{v}_C t')] \quad . \quad (47) \end{aligned}$$

We can now perform a closure on A and make use of (41) to obtain

$$\begin{aligned} g(\lambda) &= \frac{2\pi\nu_0\mu^2}{3N} V^{-(N+1)} \sum_{B,C} \int \cdots \int d^{3N}r \int_0^\infty dt \int_0^\infty dt' \langle C_\lambda | U(\vec{r}+\vec{v}t'|\vec{r}+\vec{v}t) | B_\lambda \rangle \\ &\times \exp[i\omega(t'-t) - \Delta_0(t'+t) + i\vec{k}_\lambda\cdot(\vec{r}_B + \vec{v}_B t - \vec{r}_C - \vec{v}_C t')] \quad . \quad (48) \end{aligned}$$

Equation (48) may be simplified further as follows: First, in the region $t' > t$, make the substitutions $\tau = t' - t$, $\vec{\rho} = \vec{r} + \vec{v}t$. Apart from the external constants, the contribution of this region to (48) then becomes

$$\sum_{B,C} \int \cdots \int d^{3N}\rho \int_0^\infty dt \int_0^\infty d\tau \langle C_\lambda | U(\vec{\rho} + \vec{v}\tau | \vec{\rho}) | B_\lambda \rangle \exp[(i\omega - \Delta_0)\tau - 2\Delta_0 t + i\vec{k}_\lambda\cdot(\vec{\rho}_B - \vec{\rho}_C - \vec{v}_C \tau)]$$

$$= \frac{1}{2\Delta_0} \sum_{B,C} \int \cdots \int d^{3N} \rho \int_0^\infty d\tau \langle C_\lambda | U(\vec{\rho} + \vec{v}\tau | \vec{p}) B_\lambda \rangle \exp[(i\omega - \Delta_0)\tau + i\vec{k}_\lambda \cdot (\vec{\rho}_B - \vec{\rho}_C - \vec{v}_C\tau)] ,$$

where the second form is obtained by performing the integration over t . Now, in the other region, $t > t'$, let $\tau = t - t'$, $\vec{\rho} = \vec{r} + \vec{v}t'$, and interchange the dummy indices B and C . Doing this, one obtains

$$g(\lambda) = \frac{\pi c^3}{v_0^2 N} V^{-(N+1)} \text{Re} \sum_{B,C} \int \cdots \int d^3 r \int_0^\infty dt \langle C_\lambda | U(\vec{r} + \vec{v}t | r) B_\lambda \rangle \exp[(i\omega - \Delta_0)t - i\vec{k}_\lambda \cdot (\vec{r}_C + \vec{v}_C t - \vec{r}_B)] , \quad (49)$$

where we have gone back to using r, t instead of ρ, τ . Equation (49) represents a considerable simplification over (46), but is still too complicated to evaluate in closed form without further approximations. Accordingly, in Sec. VB we consider the impact limit of (49).

B. Two-Body Impact Limit

In this approximation as discussed in Ref. 8, one considers U to be simply a product of U 's representing independent instantaneous two-body collisions. The assumption of two-body collisions means that one of these separate U 's, e.g., U_{AB} , representing a collision between A and B , is just what one would calculate in the absence of all other atoms. Thus, it refers only to the internal coordinates of A and B and is a function only of their relative position \vec{r} . Choosing the z axis in the direction of the relative velocity v , the instantaneous assumption means that $U_{AB}(\vec{r} + \vec{v}t | \vec{r})$ is taken equal to the S matrix $S_{AB} = U_{AB}(\infty | -\infty)$ if $z < 0$, $z + vt > 0$, while otherwise it is assumed to be equal to the unit matrix. Independent means that separate collisions are averaged independently, and that processes in which the excitation is transferred away from an atom in a collision and returned to it in a subsequent one, or in which the same atom collides twice with atoms carrying the excitation, etc., are ignored.

With this approximation, the U matrix element in (49) may be thought of as made up of a sum of contributions from all possible paths (i.e., all possible sequences of excitation transfers) by which the excitation can be brought from B to C in time t . Since, however, we intend to integrate over t and sum over C , we can think of the full (49) as made up of contributions from all paths beginning on B , regardless of duration or end point.

Now let us evaluate the contribution from the totality of paths containing a given number, n , of transfer collisions. Such a path can be divided up into $(n+1)$ segments, in each of which there is no transfer. The n points dividing the segments from

just the complex conjugate of the above expression. Putting all this together, and also using (15), one finally transforms (48) into

one another represent transfer collisions. We denote the time between the $(j-1)$ st and the j th collisions by t_j , and that between the n' th (and final) collision and the end of the path by t_f . All the t_j and t_f are to be integrated over. Now the analysis of Ref. 8 shows that integration over the coordinates of the $(N-n-1)$ atoms not involved in any excitation transfer collision leads to a factor $V^{(N-n-1)} \exp(-\frac{1}{2}\mathfrak{R}v\sigma t)$, where σ is the total collision cross section. According to Ref. 8,

$$\frac{1}{2}v\sigma = \frac{2}{3}\pi^2\mu^2 . \quad (50)$$

Since $\sum_j t_j + t_f = t$, this can be thought of as a product of contributions from the separate sequences (including f), each contributing $\exp(-\frac{1}{2}\mathfrak{R}v\sigma t_j)$. This is to be thought of as the amplitude for the absence of excitation transfer along the j th segment. The assumption of independent collisions prevents any complications from the fact that the over-all path here is zigzag while that considered in Ref. 8 is straight. Similarly, the factor $\exp(i\omega - \Delta_0)t$ can be thought of as a product of such factors from each segment.

The quantity $\vec{r}_C + \vec{v}_C t - \vec{r}_B$ in (49) is just the over-all displacement of position of the excitation along the path. This too can be treated as a sum of independent contributions of the segments, since during each segment the excitation is carried a distance $\vec{v}_j t_j$, where \vec{v}_j is the velocity of the atom having the excitation in the j th segment. In addition, there is a contribution \vec{b}_j for each collision, where \vec{b}_j is the (vector) impact parameter, since the instantaneous transfer moves the excitation by \vec{b}_j . Putting all this together, we see that each segment contributes a factor

$$U_j = \exp(i\omega - \Delta_0 - \frac{1}{2}\mathfrak{R}v\sigma - i\vec{k}_\lambda \cdot \vec{v}_j)t_j . \quad (51)$$

Each collision contributes the following factors: (i) a factor $\exp(-i\vec{k}_\lambda \cdot \vec{b}_j)$ from the excitation, as discussed in the preceding paragraph; (ii) a transfer S -matrix element $s(b)$; (iii) from the

integration over the relative coordinates of the colliding atoms (part of the $d^3N\mathbf{r}$), a factor $v dt_j$ (v = relative velocity) representing the range of z for which the collision takes place between t_j and $t_j + dt_j$, and also d^2b from the other two coordinates; (iv) A factor of N , from summing over all possible choices of atoms that might collide.

Finally, we must integrate over r_B in (49) and sum over B , giving a factor NV . Putting all this together and carrying out the independent integrations and averages over the t_j , we find for the total contribution of all n -transfer paths:

$$\mathcal{G}_n(\lambda) = \frac{\pi c^3}{\nu_0^2 V} \text{Re} \times \left[\left\{ \frac{-1}{i\omega - \Delta_0 - \frac{1}{2} \mathfrak{N} v \sigma - i \vec{\kappa}_\lambda \cdot \vec{v}} \right\}^{n+1} \mathfrak{N}^n F^n \right], \quad (52)$$

where the curly brackets denote velocity averaging over the Boltzmann distribution, and

$$F = [v \int d^2b s(b) \exp(-i \vec{\kappa}_\lambda \cdot \vec{b}) d^2b]. \quad (53)$$

To evaluate F , we approximate $s(b)$ by its asymptotic form,^{15, 16}

$$s_{xx} = -s_{yy} = (2i\mu^2/vb^2), \quad (54)$$

where the x direction is that of b , and all other elements of s are zero. We also assume that, after velocity averaging, there will be no contribution from transfers in which the polarization changes. This means that the polarization must always be λ , and we can also average over the two possible polarizations for given κ_λ , since they are equivalent on the average. In this way, we can replace $s(b)$, which is really a matrix, by the scalar quantity

$$\begin{aligned} s'(b) &= \frac{1}{2} [Trs(b) - \hat{\kappa}s(b)\hat{\kappa}] \\ &= (i\mu^2/vb^2) \sin^2\theta (\sin^2\phi - \cos^2\phi), \end{aligned} \quad (55)$$

where $\hat{\kappa}$ denotes a unit vector in the direction of $\vec{\kappa}_\lambda$, θ is the angle between $\vec{\kappa}_\lambda$ and the z axis (which is in the direction of \vec{v}), and ϕ is the angle between b and the projection of $\vec{\kappa}_\lambda$ on the xy plane. We now have for F , using (53) and (55),

$$\begin{aligned} F &= i\mu^2 \sin^2\theta \int_0^\infty \frac{db}{b} \int_0^{2\pi} \\ &\times (1 - 2 \cos^2\phi) \exp(-i \vec{\kappa}_\lambda \cdot b \sin\theta \cos\phi) d\phi. \end{aligned} \quad (56)$$

The integral over ϕ is closely related to well-known integral representations of Bessel functions,¹⁷ and gives the result

$$F = 2\pi i \mu^2 \sin^2\theta \int_0^\infty \frac{d\rho}{\rho} [J_0(\rho) + 2J_0''(\rho)], \quad (57)$$

where $\rho = \kappa_\lambda b \sin\theta$.

Making use of the differential equation satisfied by J_0 , and its behavior for small ρ , one easily finds that the ρ integration in (57) gives $\frac{1}{2}$. For $\sin^2\theta$, clearly, we must take its average value, $\frac{2}{3}$. We therefore have, finally,

$$F = \frac{2}{3} \pi i \mu^2. \quad (58)$$

Inserting (58) into (52) and summing over n after some rearrangement, we find

$$\begin{aligned} \mathcal{G}(\lambda) &= \frac{\pi c^3}{\nu_0^2 V} \text{Re} \left\{ \frac{-1}{i(\omega - \vec{\kappa}_\lambda \cdot \vec{v} + i\Delta_0 + \frac{1}{2} i \mathfrak{N} v \sigma)} \right\} \sum_{n=0}^{\infty} Z^n \\ &= \frac{\pi c^3}{\nu_0^2 V} \text{Re} \left\{ \frac{-1}{i(\omega - \vec{\kappa}_\lambda \cdot \vec{v} + i\Delta_0 + \frac{1}{2} i \mathfrak{N} v \sigma)} \right\} (1 - Z)^{-1}, \end{aligned} \quad (59)$$

$$\text{where } Z = \left\{ \frac{2/3 \pi \mu^2}{\omega - \vec{\kappa}_\lambda \cdot \vec{v} + i\Delta_0 + \frac{1}{2} i \mathfrak{N} v \sigma} \right\}. \quad (60)$$

The velocity averaging gives a Voigt profile:

$$\mathcal{G}(\omega; \Delta; \kappa) = \left(\frac{\beta}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} \frac{\exp(-\beta v^2) dv}{\omega + i\Delta - \kappa v} \quad (61)$$

(where $\beta = \frac{1}{2} m/kT$),

so that our full expression for the emission intensity is

$$\mathcal{G}(\lambda) = \frac{\pi c^3}{\nu_0^2 V} \text{Re} \left(\frac{i \mathcal{G}(\omega; \Delta_0 + \frac{1}{2} \mathfrak{N} v \sigma; \kappa_\lambda)}{1 - \frac{2}{3} \pi \mathfrak{N} \mu^2 \mathcal{G}(\omega; \Delta_0 + \frac{1}{2} \mathfrak{N} v \sigma; \kappa_\lambda)} \right). \quad (62)$$

The meaning of the result is a bit more transparent, however, if we assume that all velocities are small enough to be neglected. This corresponds to restricting our attention to the true resonance broadening and ignoring Doppler broadening. In this limiting case, one finds immediately

$$\begin{aligned} \mathcal{G}(\lambda) &= \frac{\pi c^3}{\nu_0^2 V} \text{Re} \left(\frac{i}{\omega + i(\Delta_0 + \frac{1}{2} \mathfrak{N} v \sigma) + \frac{2}{3} \pi \mathfrak{N} \mu^2} \right) \\ &= \frac{\pi c^3}{\nu_0^2 V} \frac{\Delta_0 + \frac{1}{2} \mathfrak{N} v \sigma}{(\omega + \frac{2}{3} \pi \mathfrak{N} \mu^2)^2 + (\Delta_0 + \frac{1}{2} \mathfrak{N} v \sigma)^2}. \end{aligned} \quad (63)$$

This is the same impact line shape as for ab-

sorption^{2,8} except that the line is shifted to the red by $\frac{2}{3}\pi\eta\mu^2$. According to Eq. (50), this shift is smaller than the width by a factor of π^{-1} , and might be expected to be difficult to see. Nevertheless, the theory definitely predicts that the shift should be present in the emission line provided that our choice of initial state is valid under the conditions of the experiment and that the various approximations made in this section are satisfied. It also predicts that, when Doppler and resonant broadening are both present in emission, they do not combine into a simple Voigt profile, but into the more complicated expression (62). This has to do with the fact that the velocity distributions of all the intermediate atoms which carry the excitation before emission contribute to the profile.

It is perhaps appropriate at this point to say a few words about some of the approximations made in this subsection, which might seem at first glance to go beyond the impact approximation. These have to do in particular with the evaluation of the collision contributions in Eqs. (53)–(58).

First, the separate averaging for the segment and collision contributions, including velocity averaging, might seem at first glance to be an impermissible separate averaging of absolute velocities of the atoms in a collision (for the segment contribution) and their relative velocity (for the collision contribution). Here, though, the situation is saved by the fact that v drops out of the expression for F in (56).

If the assumption that excitation transfer with change of polarization does not contribute is accepted, then the replacement of the remainder of s by its average in Eq. (55) is certainly permissible even without velocity averaging, since we integrate b over the xy plane. The neglect of polarization change on the average is clearly correct for any one collision, but not necessarily for the combined contribution of two or more, since the deviations, which depend on the velocities of the atoms involved in the collisions, may be correlated in successive collisions. If, however, one is only interested in getting the shift and/or width to first order in the density, then the analysis of Sec. IV shows that one can, indeed, limit oneself to single collisions. Corrections to this approximation, therefore, may well affect the detailed line shape but not the term linear in the density. They really represent corrections for the nonindependence of collisions, and are thus somewhat outside the spirit of the impact approximation.

Finally, there is the replacement of s by its asymptotic form. In terms of diagrams, this means that transfer collisions are treated only to first order, i. e., diagrams such as those of Figs. 1(b) and 2(c) are omitted. This is valid in the region $b^2 \gg \mu^2/v$ or, referring to (50), $b^2 \gg \sigma$. The question then is whether this criterion is satisfied

in the range of ρ which makes the main contribution to the integral (57). The carrying out of the ϕ integration in (56), of course, does not depend on (54). The approximation is valid, therefore, if the region in which it breaks down corresponds only to very small ρ , i. e., if

$$\kappa_{\lambda}^2 \sigma \ll 1.$$

Another way of putting this is that the square of the emitted wavelength must be much greater than a collision cross section. If this is not satisfied, however, one would not use the impact approximation in any case. This approximation has greater validity here than in the usual case¹⁵ where one tries to use it to calculate the total cross section. There, the integral over b diverges and a cutoff must be introduced, while here the exponential factor causes the integral to converge.

We conclude, therefore, that the results of this section depend only on the validity of the impact approximation.

Zaidi⁶ has treated this problem under a somewhat different set of assumptions, arriving at an expression valid in the wings of the line.

VI. DISCUSSION

The conclusions of this article may be summarized as follows, (a) For resonant broadening of the lower state in emission, the emission line shape is the same as that for absorption from the ground state to the resonant-broadened state. (b) For emission from the resonant-broadened state to the ground state, however, this is not the case; the off-diagonal matrix elements of the resolvent contribute to emission but not to absorption, for our particular choice of initial emitting state. (c) In the impact limit, this difference manifests itself in a small shift of the emission line toward the red. We do not know of any existing experimental results which provide a test of this. It would be desirable to do an experimental check, however; the situation is favorable at least in that the predicted ratio between shift and width is subject only to the impact approximation and not to uncertainties over the value of μ .

As has been mentioned several times already, the emission results would be different for different assumptions about the initial state. In our case, the assumption responsible for the main results is that in the initial state the excitation is shared *incoherently* among the atoms of the gas. If there were coherent sharing, e. g., if the initial state were of the form

$$|I\rangle = \sum_A a_A |A_i\rangle,$$

then Eq. (19) would contain terms proportional to

$$\langle A_i | R_- | B_\lambda \rangle \langle C_\lambda | R_+ | D_i \rangle a_A^* a_D,$$

which vanish in the incoherent case because of random phases among the coefficients a_A . It is also the incoherence which enables us to perform the closure with respect to A which leads from Eq. (47) to (48). Thus, different assumptions about coherence of excitation sharing would lead to substantially different results.¹⁸ Different assumptions about initial momentum distribution, however, would affect only the detailed treatment of the Doppler broadening. In an absorption experiment, the excitation probability amplitude is proportional to the polarization vector, so there is coherent sharing in this case, the details of which are different for different frequencies of exciting radiation (because of the different values of the refractive index). Hence, our assumed initial state differs, in general, from what one would have immediately after an absorption, and the latter in turn depends on the nature of the exciting radiation. If initial excitation is brought about by electron impact, or some similar means, it seems reasonable to assume that our initial state should describe the situation fairly well.

Since the off-diagonal resolvent matrix elements represent excitation transfer processes, it is clear

that their role in nonresonant broadening, where excitation transfer can only be a virtual process, should be much less significant. For nonresonant broadening, therefore, the difference between absorption and emission corresponds to a higher order effect than in the case considered here.

The resolvent method which we have used is not as general, and perhaps not as elegant, as the Green's-function methods used in Refs. 4-6 and 19. In particular, our formulation requires the neglect of quantum statistics. When these are unimportant, however, the present method has its advantages. It is sufficiently rigorous in formulation to permit a careful study of the validity of some of the standard approximations, and at the same time often leads to a fairly transparent intuitive picture of what is happening in a line broadening process. It also seems to be easier to express some kinds of approximations in the present formalism.

ACKNOWLEDGMENTS

One of us (CAM) would like to thank the Alfred P. Sloan Foundation for a fellowship which was in effect during much of the time when this work was being carried out. He would also like to thank Dr. A. Omont for calling to his attention the discrepancy mentioned in Ref. 16.

*Research supported in part by the National Science Foundation through Grant No. GP-7552.

†Present address: Chemistry Department, University of Akron, Akron, Ohio.

¹W. Heitler, The Quantum Theory of Radiation (Clarendon Press, Oxford, England, 1954), 3rd ed., pp. 201-204.

²M. Baranger, *Phys. Rev.* **111**, 481 (1958); **111**, 494 (1958); **112**, 855 (1958).

³U. Fano, *Phys. Rev.* **131**, 259 (1963).

⁴D. W. Ross, *Ann. Phys. (N. Y.)* **36**, 458 (1966).

⁵B. Bezzerides, *Phys. Rev.* **159**, 3 (1967).

⁶H. R. Zaidi, *Phys. Rev.* **173**, 123 (1968).

⁷G. P. Reck, H. Takebe, and C. A. Mead, *Phys. Rev.* **137**, A683 (1965).

⁸C. A. Mead, *Intern. J. Theoret. Phys.* **1**, 317 (1968).

⁹A. Messiah, Quantum Mechanics, translated by J. Potter (John Wiley & Sons, New York, 1966), Vol. II, pp. 712-15, 819, and 994.

¹⁰P. Roman, Advanced Quantum Theory (Addison-Wesley Publishing Co., Reading, Mass., 1965), pp. 392-403. Our Eq. (8) is equivalent to Roman's equations (4)-(394a), (394b), p. 401.

¹¹Reference 1, pp. 348-353.

¹²E. Arnous and K. Bleuler, *Helv. Phys. Acta* **25**, 581 (1952).

¹³C. A. Mead, *Phys. Rev.* **120**, 854 (1960).

¹⁴H. G. Kuhn, E. L. Lewis, and J. M. Vaughn, *Phys. Rev. Letters* **15**, 687 (1965); J. M. Vaughn, *Proc. Roy. Soc. (London)* **A295**, 164 (1966); H. G. Kuhn and E. L. Lewis, *ibid.* **A299**, 423 (1967).

¹⁵F. W. Byron, Jr., and H. M. Foley, *Phys. Rev.* **134**, A625 (1964); A. W. Ali and H. R. Griem, *ibid.* **140**, A1044 (1965).

¹⁶The matrix elements given in Table I, Ref. 8, do not have the right asymptotic form and are therefore incorrect.

¹⁷A. Sommerfeld, Partial Differential Equations in Physics, translated by E. G. Straus (Academic Press Inc., New York, 1964), pp. 84-92.

¹⁸The effect of coherent sharing on the natural linewidth has been discussed by H. G. Kuhn, E. L. Lewis, and J. M. Vaughn, Ref. 14, and by Y. C. Lee and D. L. Lin, *Phys. Rev.* **183**, 147 (1969); **183**, 150 (1969).

¹⁹B. Bezzerides, *Phys. Rev.* **181**, 379 (1969).