Resonance Broadening of Absorption Lines*

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A general theory of line broadening is used to study the effects of collisions on absorption line shapes when self-broadening is important. Special attention is focused on the role of processes in which an excited atom transfers its electronic excitation to an unexcited atom; it is this process which distinguishes self-broadening from foreign-gas broadening. Several forms for the absorption rate are presented corresponding to particular assumptions about the amplitudes associated with this phenomenon. For example, one approximation leads to a generalized Lorentz-Lorenz law in which the one-atom polarizability is replaced by one that accounts for line broadening. Finally, the importance of many-body effects in the calculation of the linewidth is briefly discussed to determine when simple impact theories are applicable.

I. INTRODUCTION

THE subject of the broadening of spectral lines due to collisions has received extensive investigation. The theoretical analysis has been guided principally by an approach in which one atom is singled out as an absorber and the others are regarded as perturbers.[1] Such a procedure is eminently suited to systems in which foreign-gas broadening predominates; however, for self-broadening this test-particle picture requires closer scrutiny.

Modern many-body techniques were used by the author to develop a general theory of line broadening.[2] In that paper, hereafter referred to as I, the absorption rate is related to the correlation function of the whole gas, i.e., the entire gas is considered the absorber. In the present paper this method is applied to the problem of self-broadening with the primary purpose of determining to what extent the usual foreign-gas broadening theories are applicable. A great deal of confusion exists on this question.[3,4] For example, it has been suggested that a foreign-gas theory can be transcribed into one applicable to self-broadening simply by replacing certain two-particle scattering amplitudes by ones which account for exchange scattering.[5] It will soon be apparent that such is not the case. Indeed, it should be obvious on physical grounds that for a low-density neutral gas the question of whether an atom is a fermion or a boson is quite irrelevant.

The present paper relies on I to a certain extent; however, its reading is not essential to an understanding of this paper. In Sec. II the fundamental equations relating the absorption rate to the propagator formalism are listed. An integral equation is derived in Sec. III whose solution yields an amplitude, the discontinuity of which is directly related to the absorption rate. The

system is specialized to a low-density gas in which broadening in the lower level is negligible. Section IV is devoted to various limiting cases for the integral equation, one of which corresponds to a generalization of the Lorentz-Lorenz law. Section V briefly touches upon the question of self-consistency in the calculation of the self-energy matrix of a given level. Finally, Sec. VI includes a summary and some additional remarks.

II. FUNDAMENTAL EQUATIONS AND DEFINITIONS

A. Absorption Rate

The transition rate per unit volume per unit flux of photons of definite momentum is given by

$$\sigma(\mathbf{p}, \omega) = (2\pi/\omega c)\tfrac{1}{2} \sum_{k} \sum_{n,m} \rho_n \, |\langle m \mid \mathbf{J}\cdot\hat{\boldsymbol{\epsilon}}_k \mid n \rangle|^2$$

$$\times (2\pi)^4 \delta(P_n - P_m + p). \quad (2.1)$$

Except for the density matrix ρ_n representing the average over initial states, Eq. (2.1) is the familiar result of quantum perturbation theory. $\mathbf{J}$ is the electric current operator for the entire gas. Here $\hat{\boldsymbol{\epsilon}}_k$ and p denote, respectively, the polarization and 4-momentum of the incident radiation. Energy and momentum conservation are expressed by the δ function, which restricts transitions to states of 4-momentum for the gas equal to $p + P_n$, where P_n is the 4-momentum of the initial state of the gas. In I it was observed that the Fourier coefficients of the temperature propagator for the electric current field were closely related to $\sigma(\mathbf{p}, \omega)$. These coefficients have the spectral representation

$$\mathbf{P}_{ij}(p) = -\int (d\omega'/2\pi)(\omega' - \omega_p)^{-1}$$

$$\times [1 - \exp(-\beta\omega')] A_{ij}(\mathbf{p}, \omega'), \quad (2.2)$$

where $p = (\mathbf{p}, \omega_p)$, with $\omega_p = i(2\pi\nu_p/\beta)$, $\nu_p = 0, \pm 1, \cdots$. From the form of A_{ij} (see I) it follows that

$$\sigma(\mathbf{p}, \omega) = (2\pi/\omega c)\tfrac{1}{2} \sum_{i,j} (\mathbf{1}_\perp)_{ij} A_{ij}(\mathbf{p}, \omega). \quad (2.3)$$

* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] U. Fano, Phys. Rev. **131**, 259 (1963).

[2] B. Bezzerides, J. Quant. Spectry. Radiative Transfer **7**, 353 (1967).

[3] G. P. Reck, Hisao Takebe, and C. Alden Mead, Phys. Rev. **137**, A683 (1964).

[4] A. W. Ali and H. R. Griem, Phys. Rev. **140**, A1044 (1965).
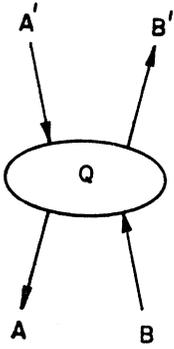
[5] A. Ben-Reuven, Phys. Rev. **145**, 7 (1966).

FIG. 1. Particle-hole propagator in medium.

Thus,

$$\sigma(\mathbf{p}, \omega) = -\frac{i(2\pi/\omega c)}{1-\exp(-\beta\omega)} \{\tfrac{1}{2} \operatorname{Tr}[\mathbf{I}_\perp \cdot \mathfrak{D}_\omega \mathbf{P}] = \tfrac{1}{2}\mathfrak{D}_\omega \mathbf{P}_\perp\},$$

(2.4)

$$\mathbf{I}_\perp = \mathbf{I} - \mathbf{pp}/p^2,$$

where $\mathbf{I}$ is the unit dyad, and $\mathfrak{D}_\omega f = f(\omega^-) - f(\omega^+)$, f being an arbitrary function of complex ω. Hence one need only calculate $\mathbf{P}_\perp$, perform the analytic continuation in ω above and below the real axis, and construct $\mathfrak{D}_\omega \mathbf{P}_\perp$.

B. Propagator Formalism

Since $\mathbf{P}_{ij}$ is a temperature propagator, its calculation may be expressed conveniently in terms of simple diagrammatic rules.[2] In I it is shown that $\mathbf{P}_{ij}$ is given by the contribution of all connected graphs joining two current-measuring vertices. These rules are put into their most advantageous form by a slight variation from the more conventional notation.

In general, atom propagators are matrices in their internal degrees of freedom parametrized by a momentum and a frequency variable. Thus it is useful to introduce a notation which places all degrees of freedom on an equal basis. The variables associated with each vertex are to be summed according to

$$\beta^{-1}\sum_{\omega_a} \int \frac{d^3a}{(2\pi)^3} \sum_\alpha \equiv \int_a \sum_\alpha \equiv \int_A.$$

(2.5)

The capital letter A is taken to denote an extended state $|\,A\,\rangle = |\,\omega_a a\alpha\rangle$, where $\omega_a = (2\nu_a+1)i\pi/\beta$, $\nu_a = 0, \pm1$, $\cdots$, $\mathbf{a}$ is the center-of-mass (c.m.) momentum of an atom, and α is an internal-state label. Correspondingly, an atom propagator is written

$$\langle A \mid G \mid A'\rangle = \delta(a-a')G_{\alpha\alpha'}(a),$$

(2.6a)

explicitly accounting for 4-momentum conservation. The atom–atom and atom–external-field coupling become

$$\langle AB \mid V \mid A'B'\rangle = \delta(a+b-a'-b') \langle \mathbf{ab} \mid V_{\alpha\beta\alpha'\beta'} \mid \mathbf{a'b'}\rangle$$

(2.6b)

and

$$\langle A \mid J_i \mid B\rangle = \delta(a+p-b)\,(J_i)_{\alpha\beta},$$

(2.6c)

respectively.

Above, the 4-conserving δ function denotes

$$\delta(a-a') \equiv (2\pi)^3\delta(\mathbf{a}-\mathbf{a}')\beta\delta_{\omega_a\omega_{a'}}.$$

(2.6d)

Instead of working directly with $\mathbf{P}_{ij}$ it is convenient to express it in terms of the amplitude Q. As illustrated in Fig. 1, Q is essentially a particle-hole propagator of the gas. From the rules,

$$\delta(p-p')\mathbf{P}_{ij}(p) = \int_{A,A',B,B'} \langle A \mid J_j \mid B\rangle$$

$$\times \langle AB \mid Q \mid A'B'\rangle \langle B' \mid J_i \mid A'\rangle. \quad (2.7)$$

Since Q is 4 conserving,

$$\langle AB \mid Q \mid A'B'\rangle = \delta(b'+a-a'-b) \langle ab \mid Q_{\alpha\beta\alpha'\beta'} \mid a'b'\rangle.$$

(2.8)

Then Eq. (2.7) becomes

$$\mathbf{P}_{ij}(p) = \sum_{\alpha,\beta,\alpha',\beta'} \int_{a,a'} (J_j)_{\alpha\beta}$$

$$\times \langle a \; a+p \mid Q_{\alpha\beta\alpha'\beta'} \mid a' \; a'+p\rangle (J_i)_{\beta'\alpha'}. \quad (2.9)$$

The matrix-element notation is merely a convenient device for keeping track of the various dependences of the quantities J, Q, etc.

III. INTEGRAL EQUATION FOR Q

Q satisfies the integral equation illustrated in Fig. 2(a). Thus

$$\langle AB \mid Q \mid A'B'\rangle = \langle A' \mid G \mid A\rangle \langle B \mid G \mid B'\rangle$$

$$+ \int_{A_1,A_2,B_1,B_2} \langle A_1 \mid G \mid A\rangle \langle B \mid G \mid B_1\rangle$$

$$\times \langle A_1B_1 \mid K \mid A_2B_2\rangle \langle A_2B_2 \mid Q \mid A'B'\rangle. \quad (3.1a)$$
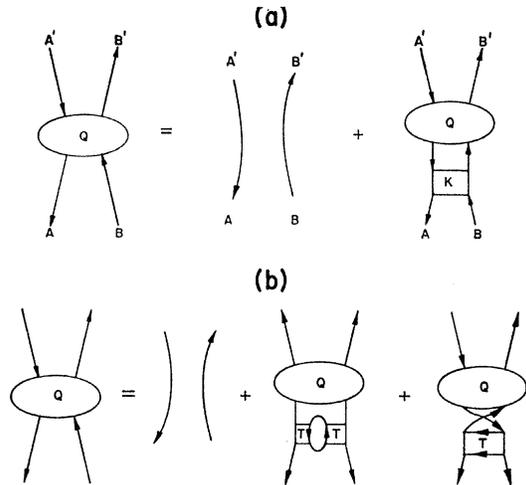

FIG. 2. (a) Integral equation for Q; (b) integral equation for Q in T-matrix approximation.

Equation (3.1b) defines the kernel K. This section is devoted to finding suitable approximations for K.

A. Approximations for K

Once an approximation for the self-energy Σ is prescribed, Q and hence K are fixed,[6] i.e., it is possible to limit one's attention to Σ.

1. T-Matrix Approximation

The system under consideration is a low-density gas of neutral molecules. Hence three-body processes should be unimportant in the determination of Σ, and for this reason Σ is adequately described by the diagram shown in Fig. 3(a), where T is the two-body scattering matrix in the medium. Contributions outside the T-matrix approximation are given in Figs. 3(b) and 3(c). Figure 3(b) describes the simultaneous interaction of three bodies, whereas Fig. 3(c) may be important to collective excitations of the gas analogous to the exciton of solid-state physics.

In the T-matrix approximation Q is given by Fig. 2(b). Thus

$$K = K^{(1)} + K^{(2)}, \qquad (3.1b)$$

where

$$\langle A_1 B_1 \mid K^{(1)} \mid A_2 B_2 \rangle = -\int_{C_1, C_1', C_2, C_2'} \langle C_2 \mid G \mid C_1 \rangle$$

$$\times \langle C_1' \mid G \mid C_2' \rangle \langle C_2 A_2 \mid T \mid C_1 A_1 \rangle \langle C_1' B_1 \mid T \mid C_2' B_2 \rangle$$

$$(3.2a)$$

and

$$\langle A_1 B_1 \mid K^{(2)} \mid A_2 B_2 \rangle = \langle B_1 A_2 \mid T \mid A_1 B_2 \rangle. \quad (3.2b)$$

Equation (3.1b) may be written

$$\langle a\,a+p \mid Q_{\alpha\beta\alpha'\beta'} \mid a'\,a'+p \rangle = \delta(a-a') G_{\alpha'\alpha}(a) G_{\beta\beta'}(a+p)$$

$$+ \sum_{\alpha_1, \alpha_2, \beta_1, \beta_2} G_{\alpha_1\alpha}(a) G_{\beta\beta_1}(a+p)$$

$$\times \int_{a_2} \langle a\,a+p \mid K_{\alpha_1\beta_1\alpha_2\beta_2} \mid a_2\,a_2+p \rangle$$

$$\times \langle a_2\,a_2+p \mid Q_{\alpha_2\beta_2\alpha'\beta'} \mid a'\,a'+p \rangle, \quad (3.3)$$

since K is 4 conserving.

An alternative form for Eq. (3.3) may be obtained by utilizing the notational device of a dyad vector space as introduced in I. In Fano's Liouville-operator
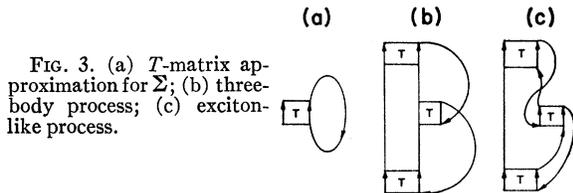
(a)   **(b)**   **(c)**

FIG. 3. (a) T-matrix approximation for Σ; (b) three-body process; (c) exciton-like process.

[6] G. Baym and L. P. Kadanoff, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

formulation of pressure broadening such a notation is used.[4] The dyad vector space is an ordered pair of internal states of an atom. Given an operator S, acting in the space spanned by the internal states of an atom, one may construct two different operators in the dyad space; these operators are defined by

$$\langle \alpha\beta \mid S^{(R)} \mid \alpha'\beta' \rangle = \delta_{\alpha\alpha'} S_{\beta\beta'}, \qquad (3.4a)$$

$$\langle \alpha\beta \mid S^{(L)} \mid \alpha'\beta' \rangle = \delta_{\beta\beta'} S_{\alpha\alpha'}^*. \qquad (3.4b)$$

Thus in the dyad-space notation, with

$$\langle \alpha_1\beta_1 \mid K(a, a_2, p) \mid \alpha_2\beta_2 \rangle \equiv \langle a\,a+p \mid K_{\alpha_1\beta_1\alpha_2\beta_2} \mid a_2\,a_2+p \rangle$$

$$(3.5)$$

and

$$\langle \alpha\beta \mid Q(a, p) \mid \alpha'\beta' \rangle \equiv \int_{a'} \langle a\,a+p \mid Q_{\alpha\beta\alpha'\beta'} \mid a'\,a'+p \rangle,$$

$$(3.6)$$

Eq. (3.3) implies that

$$Q(a, p) = [G^\dagger(a)]^{(L)} G^{(R)}(a+p)$$

$$\times \left(I + \int_{a_1} K(a, a_1, p) Q(a, p) \right). \quad (3.7)$$

The absorption rate of radiation whose energy is in the neighborhood of a level difference of an atom is of primary interest in this paper. A given level may include states of differing energy as well as other quantum numbers. However, the system is limited to gases (1) whose atoms have a level difference sufficiently large that particle-propagator amplitudes connecting states from the two levels may be ignored, and (2) for which the number of atoms in the excited level is negligible compared with those in the lower level. These restrictions imply that the notation used above designating internal states may be taken literally, i.e., α_k [β_m] denotes a state from the lower [upper] level.

2. No Broadening in Lower Level

Equation (3.2a) indicates that $K^{(1)}$ involves the product of two scattering amplitudes, one amplitude representing the quasielastic scattering of two unexcited atoms and the other the quasielastic scattering of an excited and unexcited atom. $K^{(2)}$ is given directly in terms of an inelastic-scattering amplitude.

For foreign-gas broadening, $K^{(2)}$ is unimportant, since the amplitude for the exchange of internal energy is usually quite small. If $K^{(2)}$ is ignored, the resulting integral equation constitutes a generalization of the Anderson-Baranger theory of impact broadening.[2] Since self-broadening is the issue here, the system will be restricted to those situations for which broadening in the lower state is negligible. Then $K = K^{(2)}$ and Eq.

(3.7) reduces to

$$Q(a, p) = [G_{(0)}^\dagger(a)]^{(L)} G^{(R)}(a+p)$$

$$\times \left(I + \int_{a_1} K^{(2)}(a, a_1, p) Q(a_1, p) \right). \quad (3.8)$$

B. Frequency Sums

The frequency sum implicit in Eq. (3.8) is performed in the usual fashion. Since the method is illustrated in I, the treatment here will be brief. With V static, T and hence $K^{(2)}$ are functions of $\omega_a + \omega_{a_1} + \omega_p = \omega_{a+a_1+p}$. From Eq. (3.6), Q is a function of ω_{a_1} and ω_{a_1+p}. Thus the frequency sum of Eq. (3.8) may be written

$$\beta^{-1} \sum_{\omega_{a_1}} K^{(2)}(\omega_{a_1+a+p}) Q(\omega_{a_1}, \omega_{a_1+p})$$

$$= (2\pi i)^{-1} \int_{\Gamma_0} f_+(z) K^{(2)}(\omega_{a+p}+z) Q(z, z+\omega_p), \quad (3.9)$$

where only frequency dependence is explicitly shown. In Eq. (3.9),

$$f_+(z) = [e^{\beta z} + 1]^{-1}. \quad (3.10)$$

The contour Γ_0 encircling the poles of $f_+(z)$ is shown in Fig. 4. The distortion of the contour Γ_0 to $\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3$ reduces the integral in Eq. (3.9) to the sum of contributions from the contours Γ_1, Γ_2, and Γ_3, along the branch singularities at $\text{Im} z = 0$, $\text{Im}(z+\omega_p) = 0$, and $\text{Im}(z+\omega_{a+p}) = 0$, respectively. The contribution of the contour Γ_2 is proportional to the density of excited atoms. The integral along Γ_3 is proportional to the square of the density [this fact is obvious from the spectral representation of $T(z)$]. Thus only the contribution of the Γ_1 contour need be retained.

Define

$$Q^\pm(a_1, p) \equiv Q(a_1^\pm, a_1 + \omega_p) \quad (3.11a)$$

and

$$Q(a_1^-, a_1+p) - Q(a_1^+, a_1+p) \equiv Q^{-+}(a_1, p); \quad (3.11b)$$

then Eq. (3.8) becomes

$$Q(a, p) = [G_{(0)}^\dagger(a)]^{(L)} G^{(R)}(a+p)$$

$$\times \left(I + (2\pi i)^{-1} \int_{a_1} K^{(2)}(a, a_1, p) f_+(a_1) Q^{-+}(a_1, p) \right).$$

$$(3.12)$$

In Eq. (3.12),

$$\int_{a_1} = \int_{a_1} \int_{a_1},$$

with a_1 denoting a real continuous energy variable. It should always be clear from the context when a_1 represents (a_1, a_1) collectively, or just the energy vari-

able itself. It is convenient to introduce Q' through

$$Q^{-+}(a, p) = 2\pi i \delta(H_0^{(L)}(\mathbf{a}) - a) Q'(a, p), \quad (3.13)$$

where $H_0(\mathbf{a})$ is the free Hamiltonian of an atom with c.m. momentum $\mathbf{a}$. Then Eq. (3.12) implies that

$$Q'(a, p) = G^{(R)}(a+p) \left[I + \int_{a_1} K^{(2)}(a, a_1, p) f_+(a_1) \right.$$

$$\times \delta(H_0^{(L)}(\mathbf{a}_1) - a_1) Q'(a_1, p) \bigg]. \quad (3.14)$$

Now $\mathbf{P}_{ij}$ is given by

$$\mathbf{P}_{ij}(p) = \sum_{\alpha, \beta, \alpha, \beta} (J_j)_{\alpha\beta} \langle \alpha\beta | M(p) | \alpha'\beta' \rangle (J_i)_{\beta'\alpha'}, \quad (3.15a)$$

where

$$M(p) \equiv \int_a Q(a, p). \quad (3.15b)$$

The frequency summation may be performed in the same manner as with Eq. (3.9). Here $\Gamma = \Gamma_1 + \Gamma_2$ and the contribution of the Γ_2 contour may again be ignored. Thus

$$M(p) = (2\pi i)^{-1} \int_a f_+(a) Q^{-+}(a, p). \quad (3.16)$$

Equation (3.16) may be rewritten as

$$M(p^\pm) = \int_\mathbf{a} N^{(L)}(\mathbf{a}) Q^\mathbf{a}(p^\pm), \quad (3.17)$$

where

$$Q^\mathbf{a}(p) = Q'(a, p),$$

$$N^{(L)}(\mathbf{a}) = f_+(a), \qquad \text{with } a = H_0^{(L)}(\mathbf{a}). \quad (3.18)$$

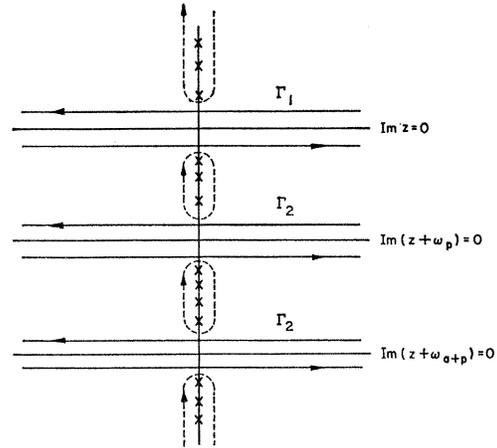From Eq. (3.14) an equation for $Q^\mathbf{a}(p^\pm)$ may be

Fig. 4. Integration contours for Eq. (2.19).

determined. In that equation appears

$$\left\langle \alpha_1\beta_1 \left| \int_{a_1}\int_a \delta(H_0^{(L)}(\mathbf{a})-a)K^{(2)}(a, a_1, \mathbf{p}^{\pm})\delta(H_0^{(L)}(\mathbf{a})-a) \right| \alpha_2\beta_2 \right\rangle$$

$$= \langle \mathbf{a}_1+\mathbf{p}\ \mathbf{a} \mid T_{\beta_1\alpha_2\alpha_1\beta_2}[\epsilon_{\alpha_2}(\mathbf{a})+\epsilon_{\alpha_1}(\mathbf{a}_1)+\omega^{\pm}]\mid \mathbf{a}_1\ \mathbf{a}+\mathbf{p}\rangle. \quad (3.19)$$

For the energy-exchange amplitude of Eq. (3.19), write

$$\langle \alpha_1\beta_1 \mid (\mathbf{a}_1+\mathbf{p}\ \mathbf{a} \mid T_{\mathrm{ex}}^{\pm} \mid \mathbf{a}_1\ \mathbf{a}+\mathbf{p}) \mid \alpha_2\beta_2\rangle. \quad (3.20)$$

Finally,

$$Q^{\mathrm{a}}(\mathbf{p}^{\pm}) = G^{(R)}(a+\mathbf{p}^{\pm})\left[I+\int_{\mathbf{a}_1}(\mathbf{a}_1+\mathbf{p}\ \mathbf{a} \mid T_{\mathrm{ex}}^{\pm} \mid \mathbf{a}_1\ \mathbf{a}+\mathbf{p})N^{(L)}(\mathbf{a}_1)Q^{\mathrm{a}_1}(\mathbf{p}^{\pm})\right], \quad (3.21)$$

where it is understood that

$$G^{(R)}(a+\mathbf{p}^{\pm}) \equiv G^{(R)}(\mathbf{a}+\mathbf{p}, H_0^{(L)}(\mathbf{a})+\omega^{\pm}).$$

It should be emphasized here that the only important restriction of Eq. (3.21) is that it be applied to systems for which broadening in the lower level is negligible.

IV. LIMITING CASES FOR INTEGRAL EQUATION

In this section simple limits of Eq. (3.21) will be discussed to illustrate its content. Indeed, a general solution is impossible without detailed knowledge of T_{ex}.

A. Collision-Dominated Line

If Q^{a_1} in Eq. (3.21) is a smoothly varying function of atomic momentum $\mathbf{a}_1$ compared with T_{ex}, the integral equation reduces to an algebraic one. To investigate this situation expand Q^{a_1} about $\mathbf{a}$.

$$Q^{\mathrm{a}_1} = [\exp(\delta\mathbf{a}\cdot\nabla_{\mathbf{a}})]Q^{\mathrm{a}}, \quad \delta\mathbf{a}\equiv\mathbf{a}_1-\mathbf{a}. \quad (4.1)$$

Then Eq. (3.21) reduces to

$$\{[G^{(R)}(a+\mathbf{p}^{\pm})]^{-1}-\Delta_{\mathbf{p}}^{\pm}(\mathbf{a})-\Delta_{\mathbf{p}}^{\pm}(\mathbf{a})\cdot\nabla_{\mathbf{a}}$$
$$-\Delta_{\mathbf{p}}^{\pm}(\mathbf{a}):\nabla_{\mathbf{a}}\nabla_{\mathbf{a}}/2!-\cdots\}Q^{\mathrm{a}}=I, \quad (4.2)$$

where the moments are defined by

$$\Delta_{\mathbf{p}}^{\pm}(\mathbf{a}) = \int_{\mathbf{a}_1}\langle\mathbf{a}_1+\mathbf{p}\ \mathbf{a} \mid T_{\mathrm{ex}}^{\pm} \mid \mathbf{a}_1\ \mathbf{a}+\mathbf{p}\rangle N^{(L)}(\mathbf{a}_1), \quad (4.3\mathrm{a})$$

$$\Delta_{\mathbf{p}}^{\pm}(\mathbf{a}) = \int_{\mathbf{a}_1}\langle\mathbf{a}_1+\mathbf{p}\ \mathbf{a} \mid T_{\mathrm{ex}}^{\pm} \mid \mathbf{a}_1\ \mathbf{a}+\mathbf{p}\rangle N^{(L)}(\mathbf{a}_1)\delta\mathbf{a}, \quad (4.3\mathrm{b})$$

$$\Delta_{\mathbf{p}}^{\pm}(\mathbf{a}) = \int_{\mathbf{a}_1}\langle\mathbf{a}_1+\mathbf{p}\ \mathbf{a} \mid T_{\mathrm{ex}}^{\pm} \mid \mathbf{a}_1\ \mathbf{a}+\mathbf{p}\rangle N^{(L)}(\mathbf{a}_1)\delta\mathbf{a}\,\delta\mathbf{a}. \quad (4.3\mathrm{c})$$

If the gradient terms are small compared to the contribution of $\Delta_{\mathbf{p}}^{\pm}(\mathbf{a})$, then Eq. (4.2) implies that

$$Q^{\mathrm{a}}(\mathbf{p}^{\pm})\approx Q_{(0)}^{\mathrm{a}}(\mathbf{p}^{\pm}) \equiv \{[G^{(R)}(a+\mathbf{p}^{\pm})]^{-1}-\Delta_{\mathbf{p}}^{\pm}(\mathbf{a})\}^{-1}. \quad (4.4)$$

Thus $\Delta_{\mathbf{p}}^{\pm}$ appears as an additional contribution to the self-energy, augmenting the shift and width of the line. To estimate the importance of the gradient terms it is sufficient to consider a two-state system. Define the corresponding diagonal matrix elements of $Q_{(0)}^{\mathrm{a}}(p)$, $\Delta_{\mathbf{p}}(\mathbf{a})$, and $\Sigma^{(R)}(a+p)$ by $Q_{(0)}$, Σ_{ex}, and Σ_d, respectively. For example,

$$\langle\alpha\beta \mid Q_{(0)}^{\mathrm{a}}(p) \mid \alpha\beta\rangle \equiv Q_{(0)}, \quad (4.5)$$

$$\nabla_{\mathbf{a}}Q_{(0)} = (\mathbf{p}/m+\nabla_{\mathbf{a}}\Sigma)/(\omega-\omega_{\beta\alpha}-\mathbf{a}\cdot\mathbf{p}/m-\Sigma)^2, \quad (4.6)$$

where

$$\Sigma = \Sigma_{\mathrm{ex}}+\Sigma_d.$$

Thus,

$$\mid \mathbf{\Delta}\cdot\nabla_{\mathbf{a}}Q_{(0)}\mid \leq (\mid \mathbf{\Delta}\mid/\Sigma^2)(p/m+\mid\nabla_{\mathbf{a}}\Sigma\mid). \quad (4.7)$$

With $\nabla_{\mathbf{a}}\Sigma\approx\nabla_{\mathbf{a}\epsilon}(\partial/\partial\epsilon)\Sigma$ and $\mathbf{\Delta}\approx\langle a\rangle\Sigma_{\mathrm{ex}}$, Eq. (4.7) implies that

$$\mid \mathbf{\Delta}\cdot\nabla_{\mathbf{a}}Q_{(0)}\mid \lesssim\gamma[p\langle a/m\rangle/\Sigma$$
$$+(\langle a/m\rangle/\langle\lambda\rangle)\hbar(\partial/\partial\epsilon)(\ln t)], \quad (4.8)$$

where

$$\Sigma_{\mathrm{ex}}\approx\gamma\Sigma, \quad \gamma=\Theta(1),$$

$\langle\lambda\rangle$ is the thermal de Broglie wavelength, and t is the elastic-scattering amplitude. Equation (4.8) may be rewritten as

$$\mid \mathbf{\Delta}\cdot\nabla_{\mathbf{a}}Q_{(0)}\mid \lesssim\gamma(\Gamma_{\mathrm{Doppler}}/\Gamma_{\mathrm{Pressure}}+\langle v\rangle t_Q/\langle\lambda\rangle), \quad (4.9)$$

where the collision time-delay $t_Q=\hbar(\partial/\partial\epsilon)(\ln t)$ has been introduced.[7] If the line is collision dominated, the first term is negligible. For most situations $t_Q\approx 0$. Indeed, in the limit of classical motion t_Q is rigorously equal to zero. Similar arguments may be constructed for the higher moments. Hence in the event that Doppler shifting is small compared with collisional broadening, Eq. (4.4) is a good approximate solution to Eq. (3.21). In the static limit this result follows trivially.

B. Hard-Core Correlation

Consider the lowest-order nonzero contribution of the energy-exchange amplitude to $\mathbf{P}$ [see Fig. 5(a)].

[7] M. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964).
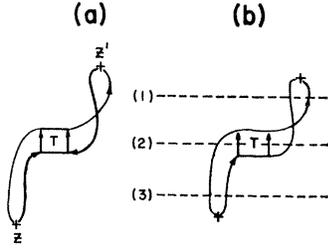
(a)   **(b)**

FIG. 5. (a) First-order contribution of T_{ex} to P; (b) cuts of Fig. 5(a).

The darkened region in coordinate space is equivalent to

$$\sum_{\beta_1,\alpha_2} \int_{x_1,y_1} G_{\alpha'\alpha_2}(z',y_1) G_{\beta\beta_1}(z,x_1) \langle x_1 y_1 \mid T_{\beta_1\alpha_2\alpha_1\beta_2} \mid x_2 y_2 \rangle. \tag{4.10}$$

This amplitude has a particularly simple form in the limit of hard-core correlations. The two-particle propagator in the T-matrix approximation is shown in Fig. 6(a). The corresponding relationship between G^{II} and T is shown in Fig. 6(b), which implies that

$$\langle XY \mid G^{II} V \mid X_2 Y_2 \rangle = \int_{X_1,Y_1} \langle X \mid G^I \mid X_1 \rangle$$

$$\times \langle Y \mid G^I \mid Y_1 \rangle \langle X_1 Y_1 \mid T \mid X_2 Y_2 \rangle. \tag{4.11}$$

The capital letters collectively denote the internal-state label and the space-time coordinate. Since V is local and static, Eq. (4.11) indicates that Eq. (4.10) may be replaced by

$$\sum_{\beta_1,\alpha_2} \langle zz' \mid G_{\beta\alpha'\beta_1\alpha_2}{}^{II} \mid x_2 y_2 \rangle \delta(\tau_{x_2} - \tau_{y_2}) V_{\beta_1\alpha_2\alpha_1\beta_2}(\mathbf{x}_2 - \mathbf{y}_2). \tag{4.12}$$

In the event that the two-particle propagator may be approximated by hard-core correlations,

$$\langle zz' \mid G_{\beta\alpha'\beta_1\alpha_2}{}^{II} \mid x_2 y_2 \rangle$$

$$= H(\mid \mathbf{x}_2 - \mathbf{y}_2 \mid) G_{\beta\beta_1}(z, x_2) G_{\alpha'\alpha_2}(z', y_2) \tag{4.13}$$

in Eq. (4.12).

$$H(\mid \mathbf{x} \mid) = 0, \qquad \mid \mathbf{x} \mid \leq a$$

$$H(\mid \mathbf{x} \mid) = 1, \qquad \mid \mathbf{x} \mid > a. \tag{4.14}$$

For the general case, Eqs. (4.12) and (4.13) show that in Eq. (3.21) T_{ex} is to be replaced by

$$V_{ex}'(\mathbf{p}) = \int_x V_{ex}(\mathbf{x}) H(\mid \mathbf{x} \mid) \exp(-i\mathbf{p}\cdot\mathbf{x}). \tag{4.15}$$

Thus,

$$Q^a(p^\pm) = G^{(R)}(a+p^\pm)\left[I + V_{ex}'(\mathbf{p})\int_{a_1} N^{(L)}(\mathbf{a}_1) Q^{a_1}(p^\pm)\right] \tag{4.16}$$

or

$$M(p^\pm) = \frac{\int_a N^{(L)}(\mathbf{a}) G^{(R)}(a+p^\pm)}{\left[I - \int_a N^{(L)}(\mathbf{a}) G^{(R)}(a+p^\pm) V_{ex}'(\mathbf{p})\right]}. \tag{4.17}$$

Only the long-range part of the interaction between two atoms need be included in Eq. (4.15). In the dipole approximation,

$$V(\mathbf{x}_1 - \mathbf{x}_2) = \mathbf{d}_1 \cdot \Lambda_{12} \cdot \mathbf{d}_2, \tag{4.18}$$

where $\mathbf{d}$ is the dipole moment operator of a single atom, and

$$\Lambda_{12} \equiv \nabla_{x_1}\nabla_{x_2} \mid \mathbf{x}_1 - \mathbf{x}_2 \mid^{-1}. \tag{4.19}$$

$$\int_{|x|<a} \exp(-i\mathbf{p}\cdot\mathbf{x}) V(\mathbf{x})$$

$$= -\int_{|x|<a} \exp(-i\mathbf{p}\cdot\mathbf{x}) \nabla_x\nabla_x \mid \mathbf{x} \mid^{-1} = -\int_{|x|<a} \nabla_x\nabla_x \mid \mathbf{x} \mid^{-1}, \tag{4.20}$$

since $pa \ll 1$. From isotropy,

$$\int_{|x|<a} \nabla_x\nabla_x \mid \mathbf{x} \mid^{-1} = C\mathbf{I}, \tag{4.21}$$

where

$$C = \int_{|x|<a} \nabla^2 \mid \mathbf{x} \mid^{-1} \Big/ \mathrm{Tr}\mathbf{I} = \frac{1}{3}\int_{|x|<a} 4\pi\delta(\mathbf{x}) = \frac{4}{3}\pi. \tag{4.22}$$

With

$$\int \Lambda_{12} \exp(-i p \cdot x) = 4\pi \mathbf{pp}/p^2 = 4\pi \mathbf{I}_{||}, \tag{4.23}$$

Eq. (4.15) becomes

$$V_{ex}'(\mathbf{p}) = \mathbf{dd} : \left(\tfrac{4}{3}\pi\mathbf{I} + 4\pi\mathbf{I}_{||}\right). \tag{4.24}$$

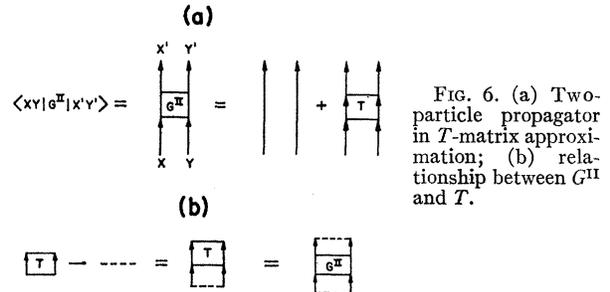The longitudinal contributions in Eq. (4.24) may be neglected due to the isotropy of the system and the

(a)

$$\langle xy|G^{II}|x'y'\rangle =$$

FIG. 6. (a) Two-particle propagator in T-matrix approximation; (b) relationship between G^{II} and T.

(b)

definition of $P_\perp$. In Eq. (4.24),

$$\langle \alpha'\beta' \mid \mathbf{dd} \mid \alpha\beta\rangle \equiv \langle \alpha \mid \mathbf{d} \mid \beta\rangle\langle\beta' \mid \mathbf{d} \mid \alpha'\rangle. \quad (4.25)$$

From Sec. II,

$$[P_\perp(p^\pm)]/\omega_{\beta\alpha}{}^2 = \tfrac{1}{2} \operatorname{Tr}[M(p^\pm)\mathbf{dd}]:\mathbf{l_\perp}, \quad (4.26)$$

where the trace is taken over a complete set of dyad vector states, and $\omega_{\beta\alpha}$ is the frequency of the absorption line. Thus, upon defining

$$N\alpha_\perp(p^\pm) \equiv \int_a N^{(L)}(\mathbf{a})G^{(R)}(a+p^\pm)\mathbf{dd}:\mathbf{l_\perp}, \quad (4.27)$$

$$[P_\perp(p^\pm)]/\omega_{\beta\alpha}{}^2 = \tfrac{1}{2} \operatorname{Tr}\left[\frac{N\alpha_\perp(p^\pm)}{I-(4\pi/3)N\alpha_\perp(p^\pm)}\right], \quad (4.28)$$

Eq. (4.28) has a very suggestive form. The above assumption of pure hard-core correlation results in an expression for $P_\perp$ which has a formal equivalence to the Lorentz–Lorenz law usually derived from the viewpoint of macroscopic electrodynamics.[8] The essential difference is that the one-atom polarizability is replaced by one which explicitly accounts for pressure broadening and Doppler shifting.

C. $\mathfrak{D}\Sigma_{ex}$ Small Compared with $\mathfrak{D}\Sigma_d$

At times a direct procedure for calculating $\mathfrak{D}P$ or the absorption rate is useful. Again consider Fig. 5(a). Direct calculation shows that the amplitude corresponding to this graph contributes three terms to $\mathfrak{D}P$, each characterized by the product of various spectral functions for the lines and an associated amplitude [see Fig. 5(b)]. For example, one term is to be identified with the "cut" labeled (1), where the two intersected particle lines contribute spectral functions, and the remaining portion of the diagram yields an amplitude calculated in the usual fashion. Cut (3) provides a similar contribution. Cut (2), however, may be ignored whenever $\mathfrak{D}\Sigma_{ex}\ll\mathfrak{D}\Sigma_d$ or, equivalently, when the discontinuity of the energy-exchange amplitude is small compared with the total cross section for scattering. Recall that in Sec. III $\mathfrak{D}T_{ex}=0$, since T_{ex} was approximated by a purely static correlation. In general, all possible cuts of all possible graphs must be counted.[9]

The result of the procedure described above may be put in a convenient form by introducing generalized atomic-dipole operators:

$$\mathbf{D}_{\beta\alpha}{}^\alpha(p^\pm) \equiv \sum_{\alpha',\beta'} \langle\beta' \mid \mathbf{d} \mid \alpha'\rangle V_{\alpha\beta\alpha'\beta'}{}^\mathbf{a}(p^\pm), \quad (4.29)$$

where in dyad-space notation

$$V^\mathbf{a}(p^\pm) = I + \int_{\mathbf{a_1}} (\mathbf{a_1}+\mathbf{p\,a} \mid T_{ex}{}^\pm \mid \mathbf{a_1}\,\mathbf{a}+\mathbf{p})$$

$$\times N^{(L)}(\mathbf{a_1}) V^{\mathbf{a_1}}(p^\pm). \quad (4.30)$$

Then

$$\mathfrak{D}(P_\perp/\omega_{\beta\alpha}{}^2) = \tfrac{1}{2} \operatorname{Tr}\left[\int_\mathbf{a} N^{(L)}(\mathbf{a})\mathfrak{D}(G^{(R)}(a+p))\right.$$

$$\left.\times \mathbf{D^a}(p^+)\,(\mathbf{D^a}(p^+))^\dagger\right]:\mathbf{l_\perp}. \quad (4.31)$$

When D is set equal to $\mathbf{d}$, Eq. (4.31) reduces to the usual foreign-gas result. Thus one may regard self-broadening as identical to foreign-gas broadening with a renormalized coupling between the external radiation field and a given atom of the gas. V allows for the transfer of the optical excitation to another atom through the energy-exchange amplitude.

V. SELF-CONSISTENCY IN Σ

In the previous sections, no essential restrictions were placed on T. It is tempting to replace this scattering amplitude in the medium by its zero-density analog, the two-particle scattering matrix in vacuum. It has been observed, however, that Σ cannot be expressed as an analytic expansion in powers of the density in the core of the line,[1] and this observation thereby questions the validity of simple-impact theories.[3] The issue is the importance of self-consistency in the calculation of Σ. The arguments, however, assumed the static limit from the outset, and it is conceivable that the appearance of any divergences may be spurious (note that no divergence results if Σ is given in terms of the free-scattering amplitude).

The scattering amplitude in the medium may be written[6]

$$\langle\mathbf{ab} \mid \mathfrak{I}_{\alpha\beta\alpha'\beta'}(\omega_p) \mid \mathbf{a'b'}\rangle = \langle\mathbf{ab} \mid \mathfrak{V}_{\alpha\beta\alpha'\beta'} \mid \mathbf{a'b'}\rangle$$

$$+ \sum_{\alpha_1,\alpha_2,\beta_1,\beta_2} \int_{a_1,b_1} \langle\mathbf{ab} \mid \mathfrak{V}_{\alpha\beta\alpha_1\beta_1} \mid \mathbf{a_1b_1}\rangle$$

$$\times \frac{A_{\alpha_1\alpha_2}(a_1) A_{\beta_1\beta_2}(b_1)}{\omega_p-a_1-b_1} \langle\mathbf{a_1b_1} \mid \mathfrak{I}_{\alpha_2\beta_2\alpha'\beta'}(\omega_p) \mid \mathbf{a'b'}\rangle, \quad (5.1)$$

where

$$\omega_p = \omega_{a+b}$$

and

$$\langle\mathbf{ab} \mid \mathfrak{V}_{\alpha\beta\alpha'\beta'} \mid \mathbf{a'b'}\rangle$$

$$= (2\pi)^3\delta(\mathbf{a}+\mathbf{b}-\mathbf{a'}-\mathbf{b'}) V_{\alpha\beta\alpha'\beta'}(\mathbf{a}-\mathbf{a'}). \quad (5.2)$$

In the limit of no broadening in the lower level, resonating contributions to the intermediate-state sum of Eq. (5.1) arise for (α_1, α_2) $[(\beta_1, \beta_2)]$ chosen from the

[8] L. Rosenfeld, *Theory of Electrons* (North-Holland Publishing Company, Amsterdam, 1951).

[9] J. S. Langer, Phys. Rev. **127**, 5 (1962); D. F. DuBois, V. Gilinsky, and M. G. Kivelson, *ibid.* **129**, 2376 (1963).

lower [upper] or upper [lower] levels. Thus either $A_{\alpha_1\alpha_2}$ or $A_{\beta_1\beta_2}$ may be approximated by the uncorrected spectral function.

It is convenient to introduce the self-energy operator

$$\Sigma = I \otimes \Sigma^{(1)} + \Sigma^{(1)} \otimes I, \qquad (5.3)$$

such that

$$\langle \beta b \alpha a \,|\, \Sigma(z) \,|\, \beta' b \alpha' a \rangle = \langle \alpha a \beta b \,|\, \Sigma(z) \,|\, \alpha' a \beta' b \rangle$$

$$\equiv \delta_{\alpha\alpha'} \Sigma_{\beta\beta'} [z - \epsilon_\alpha(a), b]. \quad (5.4)$$

Here (α, α') $[(\beta, \beta')]$ are chosen from the lower [upper] level, and $\Sigma^{(1)}$ is the usual atom self-energy. In Eq. (5.3) the right- and left-hand outer products of $\Sigma^{(1)}$ with the unit operator I appear. With Eqs. (5.3) and (5.4), Eq. (5.1) may be written as an operator equation:

$$\mathfrak{I}(z) = \mathfrak{V} + \mathfrak{V} G_\Sigma(z)\mathfrak{I}(z), \qquad (5.5)$$

where

$$G_\Sigma = [z - H_0 - \Sigma(z)]^{-1}. \qquad (5.6)$$

The question of self-consistency then reduces to determining the relationship between $\mathfrak{I}(z)$ and

$$\mathfrak{I}_f(z) = \mathfrak{V} + \mathfrak{V} G_0(z)\mathfrak{I}_f(z), \qquad (5.7)$$

i.e., with $\Sigma = 0$. It is a simple matter to show that

$$\mathfrak{I}(z) = \mathfrak{I}_f(z)[1 + G_0 R_\Sigma \mathfrak{I}(z)], \qquad (5.8)$$

where

$$R_\Sigma = \Sigma + \Sigma G_\Sigma \Sigma. \qquad (5.9)$$

Thus,

$$\mathfrak{I}(z) = \mathfrak{I}_f(z) + \Delta_1(z) + \Delta_2(z) + \cdots, \qquad (5.10)$$

where the first correction term is

$$\Delta_1(z) = \mathfrak{I}_f(z) G_0 \Sigma G_0 \mathfrak{I}_f(z). \qquad (5.11)$$

Since only an order-of-magnitude estimate of Eq. (5.11) is required, take $z = \epsilon_\beta(b) + \epsilon_\alpha(a)$ above. A given contribution to an expansion of Eq. (5.11) in intermediate states is bounded from above by

$$\int_{a_1,b_1} \frac{\langle ba \,|\, \mathfrak{I}_{\beta\alpha\beta_1\alpha_1} \,|\, b_1 a_1 \rangle \Sigma_{\beta_1\beta_2}(b) \langle b_1 a_1 \,|\, \mathfrak{I}_{\beta_2\alpha_1\beta'\alpha} \,|\, ba \rangle}{[\epsilon(a) + \epsilon(b) - \epsilon(a_1) - \epsilon(b_1) + i\eta]^2}.$$

$$(5.12)$$

Note that either the elastic or the energy-exchange amplitude may appear here. An order-of-magnitude evaluation of Eq. (5.10)[7] yields

$$\mathfrak{I} = \mathfrak{I}_f \left[1 + \mathfrak{O}\left(\left| \frac{f}{\langle \lambda \rangle} \frac{\Sigma/2}{\langle \epsilon \rangle} \right| \right) \right], \qquad (5.13)$$

where f is the scattering amplitude and $\langle \lambda \rangle$ the thermal deBroglie wavelength.

Consider an example taken from absorption experiments of Lauriston and Welsh.[10] For Na $(3S^{1/2} - 3P^{1/2})$ at a density of 0.34×10^{-18} atoms/cc and $T = 891°$K, they measure a damping constant $\gamma_1 = 2.3 \times 10^{11}$ sec^{-1}. Thus $\langle \epsilon \rangle = 0.1$ eV, $\langle \lambda \rangle = 0.03$ Å, and $\Sigma \approx \hbar\gamma_1/2 = 7.5 \times 10^{-5}$ eV. With $f \approx \sigma^{1/2}$ and $\sigma \approx 1.4 \times 10^4 a_0^2$ (see Ref. 11), $f \approx 2 \times 10^2 a_0$. Thus,

$$\left| \frac{f}{\langle \lambda \rangle} \frac{\Sigma/2}{\langle \epsilon \rangle} \right| \approx 1.3.$$

Clearly self-consistency cannot be ignored in this case. For H $(1S-2P)$ $f_{\rm H}/\langle \lambda_{\rm H} \rangle \approx 0.05 f_{\rm Na}/\langle \lambda_{\rm Na} \rangle$; thus, even if the same collisional width were measured, the correction would be less than 7%. Actually this estimate is an extreme upper bound since the corresponding cross sections differ by at least an order of magnitude. Hence, self-consistency for H is closer to a 1% correction and the simple impact theories are relevant.

VI. CONCLUDING REMARKS

The applicability of the simple-impact theories has been the primary concern of this paper. At least in the limit of negligible broadening in the lower level, it is always possible to make formal contact with the results of such theories as shown in Sec. IV. However, it should be clear that the energy-exchange amplitude results in a qualitative difference between self- and foreign-gas broadening. Thus, the relative importance of $T_{\rm ex}$ to the quasielastic scattering amplitudes must be understood. Several limits of the general integral equation have been discussed, but they certainly do not represent an exhaustive collection.

The question of self-consistency is a difficult one which must not be ignored for certain systems. The work of Reck et al.[3] may be interpreted as an attempt at a self-consistent calculation of Σ in the static limit. They were motivated primarily by the rather confusing experimental situation, but Sec. V indicates that motional effects may be of great importance and result in considerable simplification in spite of the anomalously large resonance-scattering amplitudes.

Finally, it should be clear that the contact between self- and foreign-gas broadening is not made simply by accounting for exchange scattering. Indeed, if exchange scattering is included above, nothing is significantly changed.

[10] A. C. Lauriston and H. L. Welsh, Can. J. Phys. **29**, 217 (1951).

[11] T. Watanabe, Phys. Rev. **138**, A1573 (1965).