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Calculation of Resonance Broadening*

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The line-shape function is expressed in terms of three boundary functions related to the two-particle Green's function. The transverse as well as the longitudinal interaction among atoms is considered, using the photon propagator approach. The broadening of one of the radiative states through the resonance interaction with the ground state is considered in detail. The contributions of multiple transfer of excitation and of two-body scattering are calculated separately. Several validity conditions are also obtained which clarify the approximations in the existing results. The velocity dependence of the width parameter is investigated in some detail; our results differ considerably from the existing results because we have included higher-order contributions. The extreme low-density region [where (collision width) ~ (natural width)] is also considered; the linewidth is found to be nonlinear in the number density. The additional contribution of the coupling between the radiative states is also calculated in a special case.

I. INTRODUCTION

In this paper we calculate the contributions to resonance broadening which arise from multiple transfer of excitation and from two-body scattering. In addition to width results, quantitative conditions are obtained which help in selecting the important terms in various situations of interest. These validity conditions also help in understanding the nature of approximations in the existing results.[1-3] A "photon propagator" approach is used to treat the interaction among atoms. This method simplifies the calculations, and permits a unified treatment of longitudinal and transverse interactions.

The line-shape function is expressed in terms of three boundary functions related to the two-particle Green's function. The particular case of a transition $\nu \rightarrow \mu$, in which only the level μ is broadened appreciably by resonance with perturbers in the ground state $\bar{\nu}$, is considered in detail. (This is the situation in the important experiments of Kuhn *et al.*[4]) In this case width and shift are given by a single parameter Σ_μ.

At high densities, multiple transfer is important and Σ_μ has a nonlinear dependence on the number density. (A result similar to that obtained by Reck *et al.*[2] arises when additional assumptions are made.) In the impact regime, only two-body scattering is important, but the lowest-order contribution to the T matrix is usually not sufficient. (In fact, the perturbation series may diverge.) We have obtained a solution of the integral equation for the T matrix which includes all orders of dipole-dipole interaction. The velocity dependence of Σ_μ is investigated in detail, and its effect on the line shape is discussed. The result obtained by Mizushima[3] is found to be inadequate in the experimental situation of interest.[4] (Mizushima considered only the lowest-order two-body contribution, using a classical path approach.)

At extremely low densities, when the collision width ~ the natural width, we find that Σ_μ again becomes nonlinear in the number density, because the transverse interaction is also important. This effect may be responsible for the "residual width" observed by Kuhn *et al.*[4]

The situation when $\bar{\nu} = \nu$ is also considered briefly. In this case the line shape is more complicated because of the coupling between the radiative states μ and ν. The additional contribution to the width and shift parameter is obtained under a specific set of assumptions.

In many of the results we have retained the frequency dependence of the width and shift parameter. This dependence can be important in the wings of the line, when $\Delta\omega^{-1} >>$ average duration of a collision.

II. BASIC RELATIONS

Consider an isolated resonance transition $\nu \rightarrow \mu$ with unperturbed frequency $\omega_{\mu\nu}$, where μ and ν denote the two internal energy states of the atoms comprising the gas. The line shape is essentially given by the following function of frequency, ω.[5]

$$\chi_{\mu\nu}(\vec{k}, \omega, \beta) = \int_{-\infty}^{+\infty} d(t-\bar{t}) \times e^{i\omega(t-\bar{t})} \chi_{\mu\nu}(\vec{k}, t, \bar{t}, \beta). \quad (1)$$

$$\chi_{\mu\nu}(\vec{k}, t, \bar{t}, \beta) = (2\pi)^{-6} \times \int d\vec{p}\, d\bar{\vec{p}}\, \langle a_i^{\dagger}(t) a_j(t) a_k^{\dagger}(\bar{t}) a_l(\bar{t}) \rangle_{\beta}, \quad (2)$$

where a_i ($a_i^{\dagger}$) represents the annihilation (creation) operator of state i with $i = (\nu, \vec{p} - \vec{k}/2)$, $j = (\mu, \vec{p} + \vec{k}/2)$, $k = (\mu, \bar{\vec{p}} + \vec{k}/2)$, and $l = (\nu, \bar{\vec{p}} - \vec{k}/2)$; $\beta = 1/k_{\beta}T$, and an average over Gibbs's ensemble at temperature T is implied by the angular brackets in (2). Here we have denoted the momenta of the center of mass of the atom by $\vec{p} \pm \vec{k}/2$, where $\vec{k}$ is the momentum of the photon. (We assume $\hbar = 1$.)

We define the one- and two-particle temperature Green's functions as follows,[6,7] assuming translational invariance in space and time.

$$g_1(12, t_1 t_2, \beta) = -i \langle \tau [a_1(t_1) a_2^{\dagger}(t_2)] \rangle_{\beta} = (-i\beta)^{-1} \sum_{\epsilon_1} g_1(\mu_1 \mu_2, \vec{p}_1, \epsilon_1) \times \exp[-i\epsilon_1(t_1 - t_2)] \delta_{\vec{p}_1, \vec{p}_2}, \quad (3)$$

$$g_2(12\,3\,4, t_1 t_2 t_3 t_4, \beta) = -\langle \tau [a_1(t_1) a_2(t_2) a_3^{\dagger}(t_3) a_4^{\dagger}(t_4)] \rangle_{\beta} = (-iB)^{-2} \sum_{\epsilon \bar{\epsilon} \omega} g_2(\mu_1 \mu_2 \mu_3 \mu_4, \vec{p}\,\bar{\vec{p}}\vec{k}, \epsilon \bar{\epsilon} \omega) \times \exp\{-i[\epsilon(t_1 - t_3) + \bar{\epsilon}(t_2 - t_4) + \omega(t_1 - t_2 + t_3 - t_4)/2]\} \delta_{\vec{p}_1 + \vec{p}_2, \vec{p}_3 + \vec{p}_4}, \quad (4)$$

where $1 = (\mu_1, \vec{p}_1)$ etc.; $\vec{p}_1 = \vec{p} + \vec{k}/2$, $\vec{p}_2 = \bar{\vec{p}}_2 - \vec{k}/2$, $\vec{p}_3 = \vec{p} - \vec{k}/2$, and $\vec{p}_4 = \bar{\vec{p}} + \vec{k}/2$; $\epsilon, \bar{\epsilon} = i(2n+1)\pi/\beta$, $\omega/2 = i\,2n\pi/\beta$, $n = 0, \pm 1, \pm 2, \ldots$. Here the Fourier series expansions involve the imaginary time domain, and τ is the fermion time-ordering operator. (For definiteness we assume the atoms to be fermions.) We shall use the same variables for real and imaginary values of the frequencies ($\epsilon \bar{\epsilon}\, \omega$) and times ($t_1 t_2 t_3 t_4$). In the final result we need only the analytic continuation to real values.

Following Picman,[7] we define a function F for $\mathrm{Im}\omega > 0$.

$$F(\mu_1 \mu_2 \mu_3 \mu_4, \vec{p}\vec{k}, \epsilon\omega, \beta) = \lim_{i(t_4 - t_2) \to 0_+} \frac{1}{2\pi i} \int \frac{d\bar{\vec{p}}}{(2\pi)^3} \times \sum_{\bar{\epsilon}} g_2(\mu_1 \mu_2 \mu_3 \mu_4, \vec{p}\,\bar{\vec{p}}\vec{k}, \epsilon\bar{\epsilon}\omega, \beta) \times \exp[-i\bar{\epsilon}(t_2 - t_4)]. \quad (5)$$

Also let F_1, F_2, and F_3 be the branches of F as $\mathrm{Im}(\epsilon - \omega/2) \to 0_+$, $\mathrm{Im}(\epsilon - \omega/2) \to 0_-$, and $\mathrm{Im}(\epsilon + \omega/2) \to 0_-$, respectively. The function $\chi_{\mu\nu}$, defined by (2), involves a particular branch of g_2 in the real-time domain. We follow Picman's procedure,[7] and make analytic continuations to real frequencies and times. Then from (1), (2), (4), and (5) we obtain the following general formula for the line-shape function.

$$\chi_{\mu\nu}(\vec{k}, \omega, \beta) = 2(1 - e^{-\beta\omega}) \mathrm{Im} \bar{\chi}_{\mu\nu}(\vec{k}, \omega, \beta). \quad (6)$$

$$\bar{\chi}_{\mu\nu}(\vec{k}, \omega, \beta) = \int [d\vec{p}/(2\pi)^3] \int_{-\infty}^{+\infty} d\epsilon [(F_1 - F_2) \times \bar{f}(\epsilon - \omega/2) + (F_2 - F_3) \bar{f}(\epsilon + \omega/2)]. \quad (7)$$

$$\bar{f}(\epsilon) = (1 + e^{\beta\epsilon})^{-1}. \quad (8)$$

Here $F_m = F_m(\mu\nu\nu\mu, \vec{p}\vec{k}, \epsilon\omega, \beta)$, $m = 1, 2, 3$.

Starting from the temperature-dependent Bethe-Salpeter integral equation for g_2, Picman also derived a set of coupled integral equations for the functions F_m. For our case, this set can be written as follows.

$$F_m(\vec{p}, \epsilon) = F_m^{\,0}(\vec{p}, \epsilon) \left(1 + \int \frac{d\vec{p}\,'}{(2\pi)^3} \int_{-\infty}^{+\infty} d\epsilon' \times \sum_{n=1}^{3} K_{mn} F_n(\vec{p}\,', \epsilon') \right). \quad (9)$$

Here $K_{mn} = K_{mn}(\mu\nu\nu\mu, \vec{p}\vec{p}\,'\vec{k}, \epsilon\epsilon'\omega, \beta)$, which involves the various branches of the vertex function K of the Bethe-Salpeter equation.[8] The functions, $F_m^{\,0}$ denote the respective branches of the "zero-order function," F^0, defined as follows.

$$F^0(\mu\nu\nu\mu, \vec{p}\vec{k}, \epsilon\omega) = (2\pi i)^{-1} g_{1\mu}(\vec{p} + \vec{k}/2, \epsilon + \omega/2) \times g_{1\nu}(\vec{p} - \vec{k}/2, \epsilon - \omega/2). \quad (10)$$

Here $g_{1\mu} = g_1(\mu\mu)$, which is defined by (3). If $g_1(\mu' \neq \mu)$ is negligible, the following result is obtained in terms of the self-energy, Σ.

$$g_{1\mu}(\vec{p}, \epsilon, \beta) = [\epsilon + U - E_{\mu} - p^2/2m - \Sigma_{\mu}(\vec{p}, \epsilon, \beta)]^{-1}, \quad (11)$$

where U is the chemical potential, and m is the mass of the atom. As Σ vanishes, g_1 approaches the free-atom propagator, $g_1^{\,0}$.

The line-shape function χ consists of the "irreducible hole-particle propagator," since the coupling K cannot include one-photon reducible diagrams.[5] This coupling represents the correlations between the two radiative states μ and ν. The zero-order function χ^0 involves only the uncoupled propagators for these two states, as seen from (7) and (10). The integral equations (9) are equivalent to the equation for χ shown in the diagram of Fig. 1.

Now we consider specific situations. First, we assume that almost all the perturbing atoms are in the ground state $\bar{\nu}$, and that the transition $\bar{\nu} \to \nu$ is forbidden. Therefore, only the resonance broadening of state μ caused by transitions $\bar{\nu} \to \mu$,

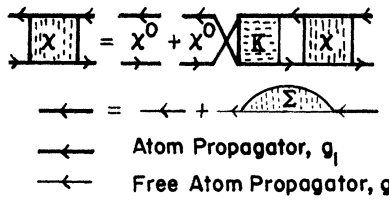

FIG. 1. The equation for the "hole-particle propagator" χ.

is important. As we shall see, in this case the contribution of the coupling K is not important, and the zero-order functions $F_m{}^0$ are sufficient. In the next section we consider the resulting "zero-order line shape." We shall also assume an isotropic system, so that an average over the polarizations of the atoms can be performed.

III. ZERO-ORDER LINE SHAPE

Since broadening of state ν is assumed to be small, the integral over ϵ in (7) can be evaluated at the pole of $g_{1\nu}{}^0$ [See Eq. (10)]. Further, assuming $\beta\omega \gg 1$, we obtain

$$\chi_{\mu\nu}{}^0(\vec{k}, \omega, \beta) \approx 2\mathrm{Im}\bar{\chi}_{\mu\nu}{}^0(\vec{k}, \omega, \beta), \tag{12a}$$

$$\bar{\chi}_{\mu\nu}{}^0(\vec{k}, \omega, \beta) = \int \frac{d\vec{p}}{(2\pi)^3} \frac{-f_\nu(\vec{p} - \vec{k}/2)}{\omega - \omega_{\mu\nu} - \vec{p}\cdot\vec{k}/m - \Sigma_\mu(\vec{p}\,\vec{k}\,\omega\beta)}, \tag{12b}$$

$$\Sigma_\mu(\vec{p}\,\vec{k}\,\omega\beta) = \Sigma_\mu(\vec{p} + \vec{k}/2, \omega + E_\nu + |\vec{p} - \vec{k}/2|^2/2m - U + i\delta, \beta), \tag{12c}$$

$$f_\nu(\vec{p}) = \{1 + \exp[\beta(E_\nu + p^2/2m - U)]\}^{-1}, \tag{12d}$$

where $\delta \to 0_+$. Here $\vec{p}\cdot\vec{k}/m$ represents the Doppler shift, and Σ_μ represents the width and shift parameter of the state μ. If Σ_μ is independent of ω and $\vec{p}$, Eq. (12) reduces to a Voigt profile which consists of a convolution integral of a Lorentzian and a Gaussian profile. We shall see that these conditions are not always satisfied. Now we calculate various contributions to Σ_μ which are important in different physical situations.

A. Contribution of the Multiple Transfer of Excitation

The perturbing interaction can be represented by the second-quantized operators for the 4-potential, $A_\alpha(\vec{r})$, $\alpha = 0, 1, 2, 3$, where A_0 represents the longitudinal part and A_i, $i = 1, 2, 3$, represents the transverse part. We shall calculate the contribution to Σ_μ of the multiple-transfer diagrams shown in Fig. 2. In the dipole approximation this contribution can be written as follows.[9]

$$\Sigma_\mu(\vec{p}, \epsilon) = i\int \frac{d\vec{q}}{(2\pi)^3} \frac{1}{-i\beta} \sum_\Delta \sum_{ij\nu'} d_{\mu\nu'}{}^i d_{\mu\nu'}{}^{j*} \times E_{ij}(\vec{q}, \Delta)\, g_{1\nu'}(\vec{p} + \vec{q}, \epsilon + \Delta), \tag{13}$$

where $\Delta = i2n\pi/\beta$, $n = 0, \pm 1, \pm 2, \ldots$, $d_{\mu\nu'}{}^i$ is the component of the electric dipole matrix element, $i = 1, 2, 3$, and E_{ij} is related to the photon propagators $D_{\alpha\beta}$ as follows.[6]

$$E_{ij}(\vec{q}, \Delta) = \Delta^2 D_{ij}(\vec{q}, \Delta) + q_i q_j D_{00}(\vec{q}, \Delta). \tag{14}$$

$$\mathcal{D}_{\alpha\beta}(\vec{r}, \vec{r}', t, t', \beta) = -i\langle \bar{\tau}[A_\alpha(\vec{r}, t) A_\beta(\vec{r}', t')]\rangle_\beta = \int [d\vec{q}/(2\pi)^3](-1/i\beta) \sum_\Delta \exp[i\vec{q}\cdot(\vec{r} - \vec{r}') - i\Delta(t - t')] D_{\alpha\beta}(\vec{q}, \Delta, \beta), \tag{15}$$

where $\bar{\tau}$ is the boson time-ordering operator. The photon propagators $D_{\alpha\beta}$ can be expressed in terms of the polarization operator Π, which represents the effect of the presence of the other atoms. For an isotropic system, Π is a scalar and we have[10]

$$D_{ij}(\vec{q}, \Delta) = 4\pi[\Delta^2 - c^2q^2 - 4\pi\Pi(\vec{q}, \Delta)]^{-1} \times (\delta_{ij} - q_i q_j/q^2), \tag{16a}$$

$$D_{00}(\vec{q}, \Delta) = (4\pi/q^2)[1 - 4\pi\Pi(\vec{q}, \Delta)/\Delta^2]^{-1} \tag{16b}$$

As Π vanishes, $D_{\alpha\beta}$ approaches the free photon propagator, $D_{\alpha\beta}{}^0$. The contribution to Π arises from the irreducible hole-particle propagator χ. In the dipole approximation we obtain

$$\Pi(\vec{q}, \Delta) \approx -\Delta^2 \sum_{\mu'\nu'} \rho\, |d_{\mu'\nu'}|^2 \bar{\chi}_{\mu'\nu'}(\vec{q}, \Delta). \tag{17}$$

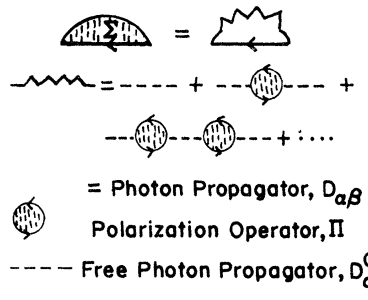

FIG. 2. The multiple transfer diagrams which contribute to the self-energy Σ.

The factor ρ results from averaging over the polarizations in an isotropic system. ($\vec{\chi}_{\mu'\nu'}$ is defined by (7), with Δ imaginary.)

Using analytic continuation in the Δ plane, we can change the summation over Δ in (13) to an integral along the branch lines of E_{ij} and $g_{1\nu'}$. The main part of collision and natural width are contained in the contribution arising from the branch line of E_{ij}; on evaluating the integral over Δ at the pole of $g_{1\nu'}$ this contribution reduces to the following result [see also (12c)].

$$\Sigma_\mu(\vec{p}\vec{k}\omega\beta) \approx i\int \frac{d\vec{q}}{(2\pi)^3} \sum_{ij\nu'} (e^{-\beta\omega'}-1)^{-1} d_{\mu\nu'}{}^{i} d_{\mu\nu'}{}^{j*} \times \mathrm{Im}E_{ij}(\vec{q}, -\omega'+i\delta), \quad (18a)$$

$$\omega' = \omega + E_\nu - E_{\nu'} + (|\vec{p}-\vec{k}/2|^2 - |\vec{p}+\vec{k}/2+\vec{q}|^2)/2m. \quad (18b)$$

We shall separately consider the contribution of the longitudinal (Coulomb) interaction, $\Sigma_\mu{}^{c}$, and that of the transverse interaction $\Sigma_\mu{}^{t}$. From (14) it is clear that we can write

$$\Sigma_\mu = \Sigma_\mu{}^{c} + \Sigma_\mu{}^{t}.$$

1. *Longitudinal Interaction*

Setting $e^{-\beta\omega'} \approx 0$ in (18a), then using (14) and (16b) we obtain

$$\Sigma_\mu{}^{c}(\vec{p}\vec{k}\omega\beta) \approx -i(2\pi^2)^{-1} \sum_{\nu'} \rho |d_{\mu\nu'}|^2 \int d\vec{q} \times \mathrm{Im}[1 - S(\vec{q}, \omega, \beta)]^{-1}, \quad (19)$$

$$S(\vec{q}, \omega, \beta) = 4\pi\Pi(\vec{q}, -\omega'+i\delta, \beta)/\omega'^2 \approx 4\pi\rho |d_{\mu\nu'}|^2 \int \frac{d\vec{p}'}{(2\pi)^3} \frac{f_{\nu'}(\vec{p}'+\vec{q}/2)}{\omega - \omega_{\mu\nu}' - i\gamma}, \quad (20a)$$

$$\omega_{\mu\nu}' = \omega_{\mu\nu} + (\vec{p}+\vec{q}/2-\vec{p}')\cdot\vec{q}/m + (\vec{p}+\vec{q}/2)\cdot\vec{k}/m. \quad (20b)$$

In obtaining (20a) we have used (17) and (12b), replacing Σ_μ by $-i\gamma$. ($\mathrm{Re}\Sigma_\mu$ is small for resonance broadening.) The parameter γ represents the damping of the intermediate state during the collision. In this notation, $\Sigma_\mu[-i\gamma]$ represents the self-energy of the radiating atom [perturbing atom] in state μ. We are using this notation to emphasize the fact that the dominant contributions to Σ_μ and $-i\gamma$ can be quite different in some physical situations.

In impact regime $t_c \gg \tau_c$, where t_c is the average time interval between the collisions and τ_c is the average duration of a collision. The lifetime of the radiating atom in state μ is essentially determined by t_c, so that $-\mathrm{Im}\Sigma_\mu \sim 1/t_c$, a result well known from the impact theory of line broadening. At the same time $t_c \gg \tau_c$ implies that a collision with a third atom is not likely to contribute to γ. Therefore, the first-order diagram of Fig. 2 should make the dominant contribution to γ; this contribution is of the order of natural linewidth, as we shall see later. In this case, the lifetime of the intermediate state of the perturbing atom is mainly determined by the two-body contribution rather than by γ. On the other extreme we have the quasistatic limit in which $t_c \ll \tau_c$. This condition implies that $l \ll D_0$, where l is the average interatomic spacing and D_0 is the "optical collision diameter," a measure of the range of the interaction. In this case the many-body collisions will be dominant, and the contributions to the self-energies of the radiator and the perturber will essentially be the same, so that $-i\gamma = \Sigma_\mu \approx \Sigma_\mu{}^{c}$. The dominant process in the many-body collisions should be the multiple transfer of excitation because of the large cross-section of excitation transfer.

In most cases it will be necessary to cut off the integral over q (momentum transfer during the intermediate states of the collision) in (19) at an upper limit q_0, such that $1/q_0 \sim d_0$, the gas-kinetic collision diameter of the colliding atoms. This cutoff will take account of the hard cores of the atoms. The integral in (19) is not divergent, however, and the cutoff is necessary only if the effective range of integration covers the hard-core region. The kinetic factors in (20b) are of the order of $v_{\mathrm{th}}q_0$ if $q_0/m \ll v_{\mathrm{th}}$ and of the order of $1/\beta$ if $q_0/m \sim v_{\mathrm{th}}$, where v_{th} is the thermal average of the relative velocity, $\vec{v}_r = (\vec{p}-\vec{p}')/m (k \approx \omega/c \ll q_0)$. In the following approximations we shall also use our initial assumption, *viz.* $n_{\nu'} \approx 0$ if $\nu' \neq \bar{\nu}$, where $\bar{\nu}$ is the ground state. We also assume that the angular momentum of state $\mu(\bar{\nu})$ is 1(0). In this case $\rho = 1/9$ in (19) and (20a). (In subsection III. B we will see that a more careful treatment of hardcore correlations gives a somewhat different value for the averaging factor, ρ.)

In the impact regime, we are interested in the region where $\gamma \ll |\Sigma_\mu| \sim (\omega - \omega_{\mu\nu}) \ll 1/\tau_c \sim v_{\mathrm{th}}/D_0 < v_{\mathrm{th}}q_0$. The last inequality is valid because $D_0 > d_0 \sim 1/q_0$ for the dipole-dipole interaction. Further assuming $q_0/m \ll v_{\mathrm{th}}$, we obtain from (20a):

$$S(q) \approx i(4\pi^2/9q)\bar{n}_{\bar{\nu}}(v_q)|d_{\mu\bar{\nu}}|^2, \quad (21a)$$

where $\bar{n}_{\bar{\nu}}(v_q)$ is the number density of atoms with velocity component v_q along $\vec{q}$.

In the quasistatic regime we can neglect the kinetic factors in (20b), replace $-i\gamma$ by $\Sigma_\mu{}^{c}$, and obtain from (20a):

$$S(\omega) \approx (4\pi/9)n_{\bar{\nu}}|d_{\mu\bar{\nu}}|^2 \times [\omega - \omega_{\mu\nu} + \Sigma_\mu{}^{c}(\omega)]^{-1}. \quad (21b)$$

In this case, (19) gives

$$\Sigma_\mu{}^c(\omega) \approx -i(2/27\pi)q_0{}^3|d_{\mu\bar{\nu}}|^2 S_i(\omega) \times \{[1-S_\gamma(\omega)]^2 + S_i{}^2(\omega)\}^{-1}, \quad (22)$$

where $S = S_\gamma + iS_i$. This result represents an algebraic equation for $\Sigma_\mu{}^c(\omega)$, and it includes all the multiple-transfer processes shown in Fig. 2. If $|S|^2 \ll 1$, we can neglect S_γ and S_i in the denominator, and the result represents only the contribution of the second-order diagram in Fig. 2 (it is also the lowest-order diagram for two-body scattering); furthermore, near resonance $\omega - \omega_{\mu\nu} \approx 0$, and the solution of (22) in this approximation is

$$\Sigma_\mu{}^c \approx -i(8n_{\bar{\nu}}q_0{}^3/81)^{\frac{1}{2}}|d_{\mu\bar{\nu}}|^2. \quad (23a)$$

That is, the width parameter is proportional to the square root of the number density, a result similar to that obtained by Reck *et al.*[2] The validity condition $|S|^2 \ll 1$ now becomes

$$18\pi^2(n_{\bar{\nu}}/q_0{}^3) \ll 1. \quad (23b)$$

With $q_0 \sim 1/d_0$, this condition cannot be satisfied simultaneously with the condition $l \ll D_0$ unless D_0 is very much larger than d_0. Therefore in many cases the complete Eq. (22) may be required in the quasistatic situation. In addition to a more complicated nonlinear dependence on the number density, this equation predicts a line shape different from the Voigt profile, since the width and shift parameter will have an appreciable dependence on $(\omega - \omega_{\mu\nu})$.

In the impact regime, the condition $|S|^2 \ll 1$, when S is given by (21a), is likely to be satisfied, so that the effect of the multiple transfer can be neglected. However, the higher-order two-body processes can be more important in this case. We shall calculate this contribution in subsection III.B.

2. *Transverse Interaction*

From (14), (16a), (18a), and (20a), on setting $\exp -\beta\omega' \approx 0$ and performing the angular integrations, we obtain

$$\Sigma_\mu{}^t(\omega) \approx -i(4/\pi)\sum_{\nu'}\rho|d_{\mu\nu'}|^2 \int_0^\infty dq q^2 \omega'^4 \times S(\omega)/[(\omega'^2 - c^2q^2)^2 + \omega'^4 S^2(\omega)], \quad (24a)$$

$$\omega' \approx \omega + E_\nu - E_{\nu'}, \quad (24b)$$

$$S(\omega) \approx 4\pi \mathrm{Im}(\omega - \omega_{\mu\nu} - i\gamma)^{-1} \times \sum_{\nu'}\rho n_{\nu'}|d_{\mu\nu'}|^2. \quad (24c)$$

We have neglected ReS, since it is small near resonance. We have also neglected the q dependence of S and ω', since the contribution of kinetic factors is small in (24a). [Only "weak" collisions, with $q \sim k \approx \omega/c$, contribute appreciably to (24a).] The integral over q can be evaluated by contour integration in the complex q-plane. The result is:

$$\Sigma_\mu{}^t = -i\sum_{\nu'}\rho(\omega'/c)^3|d_{\mu\nu'}|^2 \times \sqrt{2}\, S[(1+S^2)^{\frac{1}{2}} - 1]^{-\frac{1}{2}} \quad (25a)$$

At very low densities, when $S \ll 1$, a binomial expansion gives

$$\Sigma_\mu{}^t \approx -i\sum_{\nu'}2\rho(\omega'/c)^3|d_{\mu\nu'}|^2(1 + S^2/8). \quad (25b)$$

The first term gives the natural width whereas the second term gives the first correction arising from transverse atom-atom interactions. As seen from (24c), S is linear in the number density n at very small densities, since γ approaches a constant value of the order of natural width. However at somewhat higher densities, in the impact regime for example, γ is also proportional to n, and therefore S is relatively independent of n, at least near the line center. Therefore, the correction to the natural width is proportional to n^2 at very low densities, and it approaches a constant value at relatively higher densities. Hence the total width, $-\mathrm{Im}(\Sigma_\mu{}^c + \Sigma_\mu{}^t)$, should decrease faster than the first power of n when the collision width is of the order of natural width. This is a possible explanation of the "residual widths" observed by Kuhn *et al.*,[4] when they made a linear extrapolation of the measured resonance widths to the zero density. It should be noticed that the line shape in this region (without Doppler broadening) is not Lorentzian because of the appreciable dependence of $\Sigma_\mu{}^t$ on ω through $S(\omega)$.

B. Contribution of the Two-Body Scattering

This contribution is completely taken into account through the two-body T matrix. The general framework is discussed elsewhere.[5,11] Here we shall calculate the T matrix for the longitudinal dipole-dipole interaction which arises from the resonance between states μ and $\bar{\nu}$. In this case we must consider the effects of hard-core correlations more carefully. A cutoff at an upper limit of the momentum transfer, q_0, is required, where $1/q_0 \sim d_0$, the gas-kinetic collision diameter. At the same time, the effect of the singularity of the potential in coordinate space[9] should also be excluded. Hence we can write the dipole-dipole interaction in momentum space as follows.

$$\langle \bar{\nu}\mu | \overline{W}(\vec{q}) | \mu\bar{\nu}\rangle = 4\pi\sum_{ij} d_{\mu\bar{\nu}}{}^i d_{\mu\bar{\nu}}{}^{j*} \times (q_i q_j/q^2 - \delta_{ij}/3). \quad (26a)$$

We shall assume the conservation of the total internal angular momentum of the two atoms, and specialize to the case when the state $\mu[\bar{\nu}]$ has an angular momentum quantum number 1 [0]. Then the total internal angular momentum has projections +1, 0, and −1. In the usual diagonal representation the three values of the matrix elements in (26a) can be easily calculated. Choosing the quantization axis normal to the plane of the collision we obtain

$$W(\sigma) = (4\pi\sigma/9)\,|d_{\mu\bar{\nu}}|^2, \tag{26b}$$

where $\sigma = +\frac{1}{2}, -1$, and $+\frac{1}{2}$ for the projection states +1, 0, and −1, respectively. Let us now define the direct and transfer T-matrix elements as follows.

$$T_d(\vec{p}\,\bar{\vec{p}}\,\vec{q}, \epsilon+\bar{\epsilon}, \sigma) = \langle \mu\vec{p}+\vec{q}, \bar{\nu}\bar{\vec{p}}-\vec{q}\,|\,T(\epsilon+\bar{\epsilon}, \sigma)\,|\,\mu\vec{p}, \bar{\nu}\bar{\vec{p}}\rangle.$$

$$T_e(\vec{p}\,\bar{\vec{p}}\,\vec{q}, \epsilon+\bar{\epsilon}, \sigma) = \langle \bar{\nu}\vec{p}+\vec{q}, \mu\bar{\vec{p}}-\vec{q}\,|\,T(\epsilon+\bar{\epsilon}, \sigma)\,|\,\mu\vec{p}, \bar{\nu}\bar{\vec{p}}\rangle.$$

Figure 3 shows the diagrams contributing to T_d and T_e. These diagrams lead to the following equations.

$$T_d(\vec{p}\,\bar{\vec{p}}\,\vec{q}, \epsilon+\bar{\epsilon}, \sigma) = T_d{}^0(\vec{p}\,\bar{\vec{p}}\,\vec{q}, \epsilon+\bar{\epsilon}, \sigma) + \int [d\vec{q}'/(2\pi)^3] \times T_d{}^0(\vec{p}+\vec{q}', \bar{\vec{p}}-\vec{q}', \vec{q}-\vec{q}', \epsilon+\bar{\epsilon}, \sigma) \times \bar{F}(\vec{p}\,\bar{\vec{p}}\,\vec{q}', \epsilon+\bar{\epsilon}) T_d(\vec{p}\,\bar{\vec{p}}\,\vec{q}', \epsilon+\bar{\epsilon}, \sigma). \tag{27a}$$

$$T_d{}^0(\vec{p}\,\bar{\vec{p}}\,\vec{q}, \epsilon+\bar{\epsilon}, \sigma) = W^2(\sigma)(2\pi)^{-3} \times \int d\vec{q}'\, \bar{F}(\bar{\vec{p}}\,\vec{p}\,\vec{q}', \epsilon+\bar{\epsilon}). \tag{27b}$$

$$\bar{F}(\vec{p}\,\bar{\vec{p}}\,\vec{q}, \epsilon+\bar{\epsilon}) = i(-i\beta)^{-1} \sum_{\Delta} g_{1\mu}(\epsilon+\Delta, \vec{p}+\vec{q}) \times g_{1\bar{\nu}}(\bar{\epsilon}-\Delta, \bar{\vec{p}}-\vec{q}). \tag{27c}$$

$$T_e(\vec{p}\,\bar{\vec{p}}\,\vec{q}, \epsilon+\bar{\epsilon}, \sigma) = W(\sigma)\{1 + \int [d\vec{q}'/(2\pi)^3] \times \bar{F}(\vec{p}\,\bar{\vec{p}}\,\vec{q}', \epsilon+\bar{\epsilon}) T_d(\vec{p}\,\bar{\vec{p}}\,\vec{q}', \epsilon+\bar{\epsilon}, \sigma)\}. \tag{28}$$

Here Δ denotes the even frequencies as defined earlier. Eq. (27a) is like the usual integral equation for the T matrix, except that $T_d{}^0$ has taken the place of the first-order interaction. The contribution of the two-body scattering to Σ_μ can be written as follows [see (12c)].

$$\Sigma_\mu(\vec{p}, \omega) = \int [d\bar{\vec{p}}/(2\pi)^3] f_{\bar{\nu}}(\bar{\vec{p}}) \times \tfrac{1}{3}\sum_\sigma T_d(\vec{p}\,\bar{\vec{p}}\,0, \epsilon+\bar{\epsilon}, \sigma). \tag{29a}$$

$$\epsilon+\bar{\epsilon} = \omega + E_\nu + E_{\bar{\nu}} + (p^2 - \bar{p}^2)/2m - 2U + i\delta. \tag{29b}$$

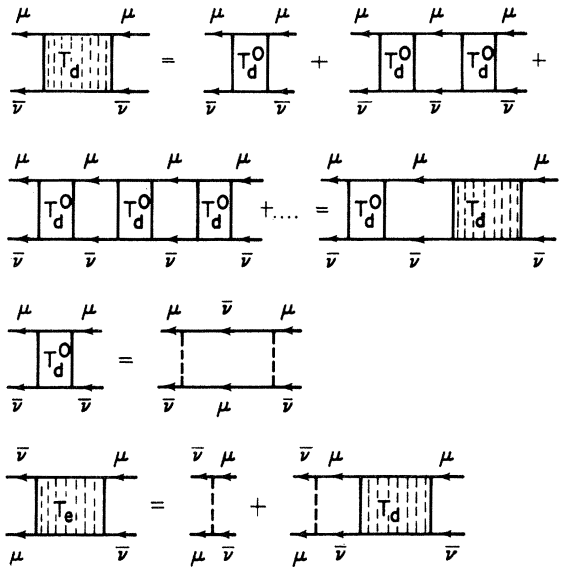

FIG. 3. The resonance contributions to the T matrix

T_e does not contribute to Σ_μ, because two atoms in different internal states behave as distinguishable particles and the pair wave function has symmetric as well as antisymmetric parts.[12] [Anyway the contribution of T_e is small at low densities if $q_0 \ll$ (thermal momenta).]

The summation over Δ in (27c) is performed by changing to an integral as before, and small terms are neglected. Then using (29b) we obtain

$$\bar{F}(\vec{p}\,\bar{\vec{p}}\,q, \omega) = (\omega - \omega_{\mu\nu} - \vec{v}_\gamma \cdot \vec{q} - q^2/m + i\gamma)^{-1}, \tag{30a}$$

where $\vec{v}_\gamma = (\vec{p} - \bar{\vec{p}})/m$ (30b)

is the relative velocity. We have again replaced Σ_μ by $-i\gamma$ as in Eq. (20a). The kinetic factors in (30a) are of the order of $v_{\text{th}} q_0$ if $q_0/m \ll v_{\text{th}}$, and are of the order of $1/\beta$ if $q_0/m \sim v_{\text{th}}$, where v_{th} is the thermal average of v_γ. When the kinetic factors are negligible, (27b) and (30a) give

$$T_d{}^0(\omega, \sigma) = (6\pi^2)^{-1} W^2(\sigma) \times q_0{}^3(\omega - \omega_{\mu\nu} + i\gamma)^{-1}. \tag{31}$$

On the other hand, when γ and $(\omega - \omega_{\mu\nu}) \ll v_{\text{th}} q_0$ (with $q_0/m \ll v_{\text{th}}$), we obtain

$$T_d{}^0(v_\gamma, \sigma) = -i(8\pi v_\gamma)^{-1} W^2(\sigma) q_0{}^2. \tag{32}$$

(In the latter case there is no exchange of energy between the internal and external degrees of freedom; therefore the magnitude of the relative velocity, v_γ, remains unchanged during the collision.) Now from (27a) and (30a) it follows that

T_d is a function of $\omega[v_r]$ when Eq. (31) [Eq. (32)] is valid. In both cases the integral equation reduces to an algebraic equation and we can write the solutions in the following form.

$$T_d = WR(1-R'^2)^{-1}. \tag{33}$$

$$T_e = W[1+R'^2(1-R'^2)^{-1}]. \tag{34}$$

Corresponding to (31) and (32) respectively, we have

$$R(\omega,\sigma) = (6\pi^2)^{-1} W(\sigma) q_0^3 (\omega - \omega_{\mu\nu} + i\gamma)^{-1}, \tag{35a}$$

$$R(v_r,\sigma) = -i(8\pi v_r)^{-1} W(\sigma) q_0^2. \tag{35b}$$

R' is also defined by (35a) and (35b) with a different cutoff, q_0'. From the nature of our approximations it is expected that q_0' will be somewhat smaller than q_0. As stated earlier, in the impact regime $\gamma \sim$ natural width; while in the quasistatic regime, $-i\gamma \sim \Sigma_\mu$.

If $|R'^2| \ll 1$, R'^2 can be neglected in (33) and (34), and only the lowest-order contribution to the T matrix remains. If $|R'^2| > 1$, the perturbation series in the powers of interaction diverges.

When (35a) is valid, we obtain from (29) and (33):

$$\Sigma_\mu(\omega) = (n_{\bar\nu}/3) \sum_\sigma W(\sigma) \times R(\omega,\sigma)[1 - R'^2(\omega,\sigma)]^{-1}. \tag{36}$$

This result is valid (assuming $q_0/m \ll v_{\rm th}$) when $\Delta\omega = (\omega - \omega_{\mu\nu}) \gg v_{\rm th} q_0 > v_{\rm th}/D_0 \sim 1/\tau_c$. (Here D_0 is the optical collision diameter, and τ_c is the average duration of a collision.) This region of validity is outside the usual impact regime in which it is assumed that $\Delta\omega \ll 1/\tau_c$, a condition which may not be satisfied in the wings of some broad lines. Physically the dependence of Σ_μ on $\Delta\omega$ in (36) results from collisions which could not be completed in the radiation lifetime $\sim(\Delta\omega)^{-1}$. This dependence on $\Delta\omega$ will cause a deviation of the line shape from the Voigt profile in the wings.

When (35b) is valid, Σ_μ shall have velocity dependence. We shall examine this case in some detail. Using the classical Boltzmann distribution function for $f_{\bar\nu}(p)$ in (29a), performing some integrations, and changing over to a more convenient set of variables, we can write the result as follows.

$$\Sigma_\mu(V) = -i \sum_\sigma \Delta_0(\sigma) \psi(V,\sigma), \tag{37a}$$

$$\psi(V,\sigma) = V^{-1}[\mathrm{erf}(V) + \Delta_1(\sigma)\phi(V,\sigma)], \tag{37b}$$

$$\mathrm{erf}(V) = 2\pi^{-\frac{1}{2}} \int_0^V dX e^{-X^2}, \tag{37c}$$

$$\phi(V,\sigma) = 2\pi^{-\frac{1}{2}} \int_0^\infty dX X e^{-X^2} \times \{\tan^{-1}[|V-X|/\Delta_1(\sigma)] - \tan^{-1}[|V+X|/\Delta_1(\sigma)]\}, \tag{37d}$$

$$V = (\beta/2m)^{\frac{1}{2}} p, \quad X = (\beta/2m)^{\frac{1}{2}} \bar p, \tag{37e}$$

$$\Delta_0(\sigma) = 2\pi(m\beta/2)^{\frac{1}{2}} n_{\bar\nu} \sigma^2 |d_{\mu\bar\nu}|^4 q_0^2/243, \tag{37f}$$

$$\Delta_1(\sigma) = (m\beta/2)^{\frac{1}{2}} |\sigma| |d_{\mu\bar\nu}|^2 q_0'^2/18. \tag{37g}$$

The first term in (37b), which contains the error function erf(V), results from the contribution of the lowest-order forward scattering (T_d^0); it has the same velocity dependence as obtained by Mizushima,[3] who used a classical path approach. The second term in (37b) contains the higher-order contributions to the forward scattering; the parameter Δ_1 is a measure of this contribution. Using numerical integration, the function $\psi(V)$ was calculated for several values of Δ_1. The results are shown in Fig. 4. It is obvious that the velocity dependence can be quite different from Mizushima's result ($\Delta_1 = 0$) in the important region around $V = 1$.

The line shape is given by Eq. (12). When Doppler broadening is negligible, we obtain for a classical gas:

$$\chi_{\mu\nu}{}^0(\Delta\omega) = 8\pi^{-\frac{1}{2}} n_\nu \int_0^\infty dV\, V^2 e^{-V^2} \times \Delta(V)[\Delta\omega^2 + \Delta^2(V)]^{-1}, \tag{38}$$

where $\Delta\omega = \omega - \omega_{\mu\nu}$, and $\Delta(V) = -\mathrm{Im}\Sigma_\mu(V)$.

If Doppler broadening is included, Eq. (12a) gives:

$$\chi_{\mu\nu}{}^0(\Delta\omega) = 4n_\nu \frac{c}{\omega}\left(\frac{m\beta}{2\pi}\right)^{\frac{1}{2}} \int_0^\infty dV\, V e^{-V^2} \times \left(\tan^{-1}\frac{\Delta\omega + Y}{\Delta(V)} - \tan^{-1}\frac{\Delta\omega - Y}{\Delta(V)}\right), \tag{39}$$

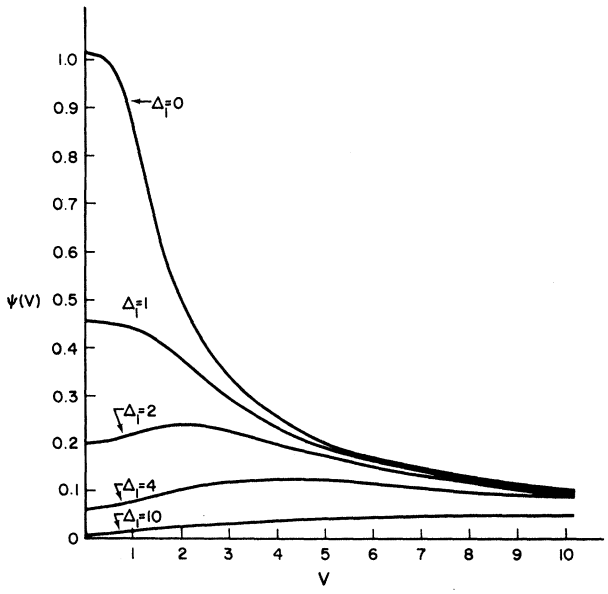

FIG. 4. The velocity dependence of the width parameter.

where $Y=(2/m\beta)^{1/2}V\omega/c$. Integrating once by parts we obtain from (39):

$$\chi_{\mu\nu}{}^{0}(\Delta\omega)=2\pi^{-\frac{1}{2}}n_{\nu}\int_{-\infty}^{\infty}dV\,e^{-V^2}\times\Delta[(\Delta\omega-Y)^2+\Delta^2]^{-1}+I(\Delta\omega)\,, \quad (40a)$$

$$I(\Delta\omega)=2n_{\nu}\frac{c}{\omega}\left(\frac{m\beta}{2\pi}\right)^{\frac{1}{2}}\int_{0}^{\infty}dV\,e^{-V^2}\frac{d\Delta}{dV}\times\left(\frac{\Delta\omega-Y}{(\Delta\omega-Y)^2+\Delta^2}-\frac{\Delta\omega+Y}{(\Delta\omega+Y)^2+\Delta^2}\right) \quad (40b)$$

If Δ is independent of velocity, $I=0$, and (40a) gives a Voigt profile. Mizushima[3] considered only the first term in (40a) as the generalization of the Voigt profile; the correction $I(\Delta\omega)$ does not appear in his line-shape function.

Now we make contact with the experimental results.[4] Consider, for example, the broadening of 2^1P state of helium. (Although 2^1P is the lower radiative state, our results are still applicable.) The experiments give a collision half width, $\frac{1}{2}\Delta\omega_{1/2}\sim 8\times10^{8}$ rad/sec at $n\sim10^{17}$ atoms/cm^3 and $T=80^{\circ}$K. In this case the optical collision diameter $D_0\sim16$ Å, kinetic collision diameter $d_0\sim3$ Å, $v_{th}\sim9\times10^{4}$ cm/sec, and $1/\tau_c\sim4\times10^{11}$ rad/sec. A direct check shows that all the validity conditions for (37a) are satisfied. Although the contribution of the multiple transfer is negligible, the higher-order two-body scattering is important. With $1/q_0'\sim4$ Å we obtain $\Delta_1(\pm1)\sim2$ and $\Delta_1(\pm\frac{1}{2})\sim1$. From Fig. 4 it is seen that, in the important region around $V=1$, the velocity dependence in this case is less sharp compared to Mizushima's result ($\Delta_1=0$).[3] Therefore the deviation from a Voigt profile of the line shape given by (39) will be smaller. Our results give a half width of the order of the experimental value for $1/q_0\sim2$ Å.

The width parameter in (37a) depends on the cutoff parameters for which only an order-of-magnitude estimate ($1/d_0$) is available. In the previous calculations,[1,13,14] this cutoff has not been taken into account, and a straight line trajectory approximation is made. The assumption of straight-line trajectories is equivalent to a high-energy approximation which is valid when the kinetic energy$\gg$ the potential energy (it is also equivalent to the Born approximation for the phase shifts which is valid when the phase shifts are small.) At low velocities this approximation is not valid. At high velocities, the effect of the cutoff becomes more important. In the experimental situation considered, the kinetic energy at the thermal velocities ~ the potential energy at the cutoff (this is also the cause of the velocity dependence of Σ_μ). In the next stage of refinement the cutoff procedure should be improved by taking proper account of the other short-range interactions. (Within the present approximation, the additional contribution of the hard cores can be calculated separately using the hard-sphere collision diameter; but this contribution is small since $D_0^2\gg d_0^2$). At the same time the mixing of the orbital and the internal angular momenta, caused by the noncentral interaction potential, should also be considered. This effect is present in the collisions in which the polarization of the excited atom is changed because the orbital and internal angular momenta are not separately conserved. Watanabe[14] considered the change of polarization but he made the straight line trajectory approximation. (In this subsection we have made the "fixed-atom approximation," to use his terminology.)

Finally, let us compare the relative importance of the multiple transfer and the two-body processes. Both contributions to Σ_μ contain the second-order diagram of Fig. 2. If we neglect R'^2 in the denominator of (36) and $S_\gamma{}^2$ and $S_i{}^2$ in the denominator of (22), we obtain the same result within a factor of $\frac{1}{2}$ which arises from a more careful consideration of the hard-core correlations in (26a). This result is the common contribution of the second-order diagram. [Similar result is obtained if (21a) is used, and the result is compared with (37a) with $\Delta_1=0$.] As stated earlier, the higher-order multiple transfer processes are negligible if $|S|^2\ll1$, and the higher-order two-body processes are negligible if $|R'^2|\ll1$. Thus the two-body processes are more important than the multiple transfer if $|R'|>|S|$. Using Eqs. (21a) and (21b) and (35a) and (35b) this condition can be written as follows in these two special cases: $q_0'{}^3>8\pi^2 v_\gamma\bar{n}_{\bar{\nu}}(v_z)$ when kinetic factors are important and $q_0'{}^3>6\pi^2 n_{\bar{\nu}}$ when the kinetic factors are negligible.

IV. COUPLING BETWEEN THE RADIATIVE STATES

In this section we consider the situation when $\bar{\nu}=\nu$, i.e., the ground state is the lower radiative state. In this case the coupling K in Fig. 1 is also important. The general framework of the T approximation for K was discussed in Ref. 11. Here we shall make use of our calculation of the T matrix to obtain the additional contributions to the width and shift parameter in a particular case. T_d should be excluded from K for the same reason that T_e was excluded from Σ_μ in Eq. (29). In addition, the first-order component in T_e along $\vec{k}$ does not contribute to K in an isotropic system. Thus we obtain from (34) and (35a):

$$K(\mu\nu\nu\mu,\omega)\approx\tfrac{1}{3}\sum_{\sigma}\{W(\sigma)R'^2(\omega,\sigma)\times[1-R'^2(\omega,\sigma)]^{-1}-|W(\sigma)|\}. \quad (41)$$

In this case K is independent of $\vec{p}$, $\vec{p}\,'$, ϵ, and ϵ'; therefore the kernels K_{mn} in (9) differ from each other only by factors $\bar{f}(\epsilon\pm\omega/2)$,[8] and the coupled set of integral equations reduce to a single algebraic equation with the solution:

$$\bar{\chi}_{\mu\nu}(\vec{k},\omega)=\bar{\chi}_{\mu\nu}{}^{0}(\vec{k},\omega)\times[1-\bar{\chi}_{\mu\nu}{}^{0}(\vec{k},\omega)K(\mu\nu\nu\mu,\omega)]^{-1}. \quad (42)$$

Neglecting Doppler broadening and using (12b), (36), and (41) we obtain the following line-shape function from (6) and (42).

$$\chi_{\mu\nu}(\omega) = -2n_\nu \operatorname{Im}[\omega - \omega_{\mu\nu} - \Delta_{\mu\nu}(\omega)]^{-1}, \quad (43a)$$

$$\Delta_{\mu\nu}(\omega) = (n_\nu/3) \times \sum_\sigma [W(R - R'^2)(1 - R'^2)^{-1} + |W|], \quad (43b)$$

where W is given by (26b), and R and R' are given by (35a) with $\bar{\nu} = \nu$. The last term in this expression for the width and shift parameter ($\Delta_{\mu\nu}$) represents the Lorentz-Lorenz correction.[11]

Equation (43b) is valid when $\Delta\omega \gg v_{\text{th}} q_0 > 1/\tau_c$, a condition which may be satisfied in the wings of a broad line. In the line core at low densities the kinetic factors are likely to dominate, and (35b) should be used; but in this case the integral equation does not reduce to an algebraic equation. However, if the velocity dependence of Σ_μ is not sharp, the integral equation can again be reduced to an approximate algebraic equation with a solution similar to (43a) in form. This situation is quite possible in some cases as is clear from Fig. 4.

The results of this section are applicable to the resonance lines proper, e.g., 1^1S–2^1P transition in helium. However this transition has not been directly investigated because of the short wavelength. Other resonance transitions involving the ground state have been measured, e.g., in alkali vapors; but the resonance width and shift have not been clearly isolated to warrant a detailed comparison with the theory at this stage. (References to the experimental work are given by Reck *et al.*[2])

It should also be noticed that, in general, the contribution of K to $\Delta_{\mu\nu}$ is of the order $n_\nu K$. Therefore, if $\bar{\nu} \neq \nu$ and $n_{\bar{\nu}} \gg n_\nu$, this contribution is negligible. This is the justification for using the "zero-order line shape" for the transitions measured by Kuhn *et al.*[4]

V. CONCLUSIONS

Starting from the general line-shape function we have calculated the important contributions to the resonance broadening. At the same time we have attempted to clarify the validity of various approximations in the existing calculations[1–3,13,14] and made contact with a specific experimental situation.[4] In particular, it is found that the contribution of higher-order two-body processes and their effect on the velocity dependence of the width parameter can be quite important in the impact regime. It is also found that, at extremely low densities, the resonance width becomes nonlinear in the number density. At high enough densities, the multiple transfer of excitation should become the dominant process because of the large excitation transfer cross section. Therefore the use of "effective resonance interaction"[9] is appropriate in this situation. Equations (19) or (22), and (25a) give the first-order contribution in the effective resonance interaction.

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[9]For example, the Coulomb dipole-dipole potential can be written as follows.

$$\langle \mu\nu' | \tilde{W}(r) | \nu\mu' \rangle = r^{-3} [\vec{d}_{\mu\nu} \cdot \vec{d}_{\nu'\mu'} - 3r^{-2} (\vec{d}_{\mu\nu} \cdot \vec{r})(\vec{d}_{\nu'\mu'} \cdot \vec{r})]$$

$$= \int [d\vec{q}/(2\pi)^3] \sum_{ij} (d_{\mu\nu}{}^i d_{\mu'\nu'}{}^{j*} \times 4\pi q_i q_j / q^2) e^{i\vec{q}\cdot\vec{r}} .$$

Comparing with Eqs. (14) and (16b), we see that

$$\sum_{ij} (d_{\mu\nu}{}^i d_{\mu'\nu'}{}^{j*} E_{ij})$$

represents the transfer matrix elements of the dipole-dipole potential if $\Pi = 0$; the polarization Π takes into account the presence of other atoms. Hence $\sum_{ij} (d_{\mu\nu}{}^i d_{\mu'\nu'}{}^{j*} E_{ij})$ represents the "effective resonance interaction" in dipole approximation.

[10]See Eqs. (28·26c) and (28·27c) in Ref. 6. (We have used the relation $\epsilon(\vec{q}, \Delta) = 1 - 4\pi\Pi(\vec{q}, \Delta)/\Delta^2$, where ϵ is the dielectric constant.) We are using the gauge with $\nabla \cdot \vec{A} = 0$; however E_{ij} is a gauge invariant quantity.

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Therefore, for a pair of distinguishable atoms the two contributions cancel, as the pair wave function contains equal parts of symmetrized and antisymmetrized components.]

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Electron Broadening of Isolated Spectral Lines*

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The electron broadening of an isolated atomic transition is calculated using the propagator approach. Electron correlations are included, and therefore the divergences arising in the impact-limit calculations are eliminated. The general expression for width reduces to previously obtained results if the correlations are neglected. The case of plasmon broadening is also considered. In this case, the width parameter has resonance-type frequency dependence, resulting in considerable deviation from Lorentz profile. Under suitable conditions "sidebands" appear about a "forbidden line."

I. INTRODUCTION

Broadening of atomic spectral lines in a plasma is of considerable interest at present. While a quasistatic approximation can be used for ion broadening, the dynamics must be considered for electron broadening.[1] The long-range Coulomb interaction causes special problems in the calculation of electron broadening in the impact limit, since a binary collision approximation is not strictly valid. Griem *et al.* employed a cutoff to avoid the divergence that arises in the linewidth calculation based on the impact limit.[2] Lewis further investigated the validity of these results and obtained a different cutoff, suitable for the wings of the line.[3] Recently, Smith and Hooper[4,5] treated the problem more generally, using the resolvent technique, and showed that the divergences do not arise. Moreover, the width parameter has an appreciable dependence on frequency, which leads to a deviation from a Lorentz profile, including asymmetry.

The purpose of this paper is to apply the "propagator technique" to the case of an isolated line. The necessary formalism has been developed in an earlier paper,[6] in which an application to resonance broadening was considered. (This paper will be referred to as I.) We derive a formula for the width parameter which includes the electron correlations; it does not involve any divergence. In the limit of no electron correlations, this formula reduces to the result of Griem *et al.*[2] near the line center, and to the result of Smith and Hooper[4] in the line wings.

We also consider the interesting case of the "plasmon broadening." In this case, the electron correlations give rise to collective excitations. The resulting width parameter has a resonance type of frequency dependence and the line shape is basically different. Under suitable conditions this line shape will exhibit fine structure. In particular, it could include "sidebands" about a neighboring "forbidden line." The possibility of such sidebands was earlier predicted by Baranger and Mozer[7] by calculating the probability of a second-order transition caused jointly by plasmons and photons. In our treatment this result arises as one of the consequences of "plasmon broadening."

The main advantage of the formalism employed in this paper is the automatic inclusion of all electron correlations. This makes the actual calculations simpler. In addition, contact is made with the standard work on the many-electron problem,[8,9] which permits the use of existing results to treat other interesting cases in electron broadening, e.g., the impurity spectrum in metals. Ion broadening can also be treated within this general framework, if the quasistatic approximation is not sufficient and ion dynamics should be included.

II. BASIC RELATIONS

In I, the general line-shape function was related to the irreducible "hole-particle propagator," χ. [See Eq. (6) and Fig. 1 in I.] Some of the diagrams which can contribute (in electron broadening) to the self-energy part Σ and the vertex function K are shown in Fig. 1. We shall consider only the first-order diagrams in the "effective interaction" since the contribution of higher-order diagrams is small. (We have also neglected the transverse photon propagator since its contribution is of the order of natural width.) The first-order diagram for K, shown in Fig. 1, results in a nonresonant contribution to the propagator χ