Many-body treatment of pressure shifts associated with collisional broadening*

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A many-body treatment of pressure shifts associated with foreign-gas broadening is presented. The theory treats the case of electrically neutral molecules interacting through higher-order permanent moments. The line-shape analysis is developed using graphical finite-temperature perturbation theory. It is shown that the simplest application of the method of moments leads to unphysical results for the pressure shift. It is found that, if certain "quasiparticle" approximations are made before computing the spectral moments, physically sensible results obtain. *Explicit* expressions for the pressure shift are given for the case of dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions.

I. INTRODUCTION

The theory of pressure-broadened spectral lines has a long history, and the literature of the field is by now considerable. As there exist several excellent reviews of both the older[1,2] treatments and more recent formulations,[3] and an extensive bibliography[4] of experimental and theoretical papers, we shall attempt no comprehensive review of the literature here. We will be concerned primarily with the problem of pressure shifts in neutral gases due to multipole interactions, and shall make some contact with the important formulation of pressure broadening as developed by Anderson.[5]

Anderson has given an impact theory which includes both phase-shift effects and transition effects, for elastic and inelastic collision processes. In addition, he extended previous work to include the case where both the initial and final states of the interacting molecules are degenerate. Anderson did not treat the case of overlapping lines, and he also used the classical path approximation which assumes that the molecules follow classical straight-line paths except for extremely close collisions. We shall discuss Anderson's work in further detail presently.

A number of the more recent formulations of the problem of pressure broadening and shifts employ the techniques of graphical finite-temperature perturbation theory, and the treatment presented here will make use of similar methods. As representative of the above category of treatments, we mention the very elegant and general formulation of Ross,[6] and similar approaches of Bezzerides[7,8] and Zaidi.[9,10] These papers treat a variety of physical problems, and the approximations and assumptions involved in treating the vertex or T-matrix equation are also rather diverse.

In spite of the recent advances in formulating the problem of pressure broadening in a rigorous fashion, it appears that much of the effort to actually *carry out* linewidth calculations[11-19] (for intermolecular broadening) has been done within the framework of Anderson's theory. Undoubtedly one of the reasons for this is that most of the newer theories are rather formal. Thus, as a practical vehicle of calculation, Anderson's theory has unquestionable value. Furthermore, no discussion of Anderson's work is complete without mentioning the excellent paper of Tsao and Curnette[20] who fully expounded and extended Anderson's methods. Their contributions have resulted in a theory which is now rather generally referred to as Anderson-Tsao-Curnette theory. Henceforth we refer to this treatment as ATC and shall refer to Ref. 20 as TC.

While the ATC formulation of pressure broadening appears to provide a solid base for computing linewidths of molecular transitions, it is less satisfactory for treating the related problem of pressure *shifts*. While the shifts tend to be small in the case of microwave transitions,[3] they become more appreciable for infrared transitions. Furthermore, with the recent advances in laser and tunable laser technology, it has become possible to measure,[21-24] with high accuracy, the pressure shifts associated with infrared transitions. It is these considerations which have motivated the work to be presented in this paper.

We now review, briefly, some of the results of ATC theory. To first order in the intermolecular interaction, ATC theory leads to a quantity called $S_1(b)$ which is purely imaginary and will give the lowest-order shift of the spectral line. To second order in the intermolecular interaction, ATC obtain a quantity called $S_2(b)$ which is purely real and this gives the lowest-order contribution to the linewidth. From Anderson's general discussion it appears that the result which gives only broadening in second order is an approximation which is obtained by neglecting certain contributions due to noncommutativity. One might suppose that any

second-order shift should be small compared to the first-order shift given by $S_1(b)$, and thereby justify neglect of the second-order contribution. The difficulty, as we now show, is that under certain circumstances the result for $S_1(b)$ may vanish. (This point has been discussed by Townes and Schawlow,[25] without giving a precise argument.)

Consider the case of foreign-gas broadening and assume that the intermolecular interaction can be expanded as a multipole series. As given by ATC the quantity $S_1(b)$ involves diagonal matrix elements of the perturbing molecule's dipole, or quadrupole, or octopole moment operator. If the perturbing molecule is linear and has a dipole moment, its diagonal matrix elements vanish. If the perturber is not linear this is no longer true. However, in this case the diagonal matrix element of the dipole moment is proportional to a Clebsch-Gordan coefficient

$$(j_1 1 - m_1 0 | j_1 1 j_1 - m_1) = -m_1[j_1(j_1+1)]^{-1/2}.$$

When this is summed over the degeneracy index (m_1), which is how it enters in $S_1(b)$, the result is seen to vanish. Similarly, if the perturber has a quadrupole moment, its diagonal matrix elements will be proportional to a Clebsch-Gordan coefficient

$$(j_1 2 - m_1 0 | j_1 2 j_1 - m_1) = \frac{3m_1^2 - j_1(j_1+1)}{[(2j_1-1)j_1(j_1+1)(2j_1+3)]^{1/2}}.$$

Again when this is summed over m_1 the result will vanish. More generally one can prove the following result for integer $j_2 > 0$,

$$\text{sum} = \sum_{m_1=-j_1}^{j_1} (j_1 j_2 - m_1 0 | j_1 j_2 j_1 - m_1) = 0.$$

A simple proof[26] goes as follows. First use

$$(j_1\, j_2 - m_1 0 | j_1\, j_2\, j_1 - m_1) = (-1)^{j_1+m_1}\left(\frac{2j_1+1}{2j_2+1}\right)^{1/2}(j_1\, j_1 - m_1\, m_1 | j_1\, j_1\, j_2\, 0).$$

Second, note that the factor $(-1)^{j_1+m_1}$ can be written[27]

$$(-1)^{j_1+m_1} = (2j_1+1)^{1/2}(j_1\, j_1 - m_1\, m_1 | j_1\, j_1\, 0 0).$$

This gives

$$\text{sum} = \frac{2j_1+1}{(2j_2+1)^{1/2}} \sum_{m_1=-j_1}^{j_1} (j_1\, j_1 - m_1\, m_1 | j_1\, j_1\, j_2\, 0) \times (j_1\, j_1 - m_1\, m_1 | j_1\, j_1\, 0 0) = \frac{2j_1+1}{(2j_2+1)^{1/2}}\delta_{j_2,0},$$

i.e., the result vanishes for $j_2 > 0$.

It should be pointed out that there are cases of interest where the above argument has no applicability. An example is the case where the dominant interaction is of the induction type, where the internal coordinates of the perturbing molecule do not enter, and a first-order shift results.[28] Quite a few theoretical papers[29-35] have, in fact, considered the first-order shift of HCl (or DCl) transitions[36-38] perturbed by inert gases through induction forces. Several of these treatments have also extended Anderson's treatment to include the second-order shift contribution for this case.

In this paper we present a many-body treatment of pressure broadening of molecular lines with emphasis placed on obtaining formulas for the shift of the line with pressure. As pointed out previously, this is not the first paper to treat pressure broadening as a many-body problem (which of course it is). Often the many-body aspect of the problem is avoided, e.g., in the ATC formulation, by invoking the fact that the collisions are binary and therefore the broadening is proportional to pressure. We believe that the introduction of field operators to describe various identical molecules is actually a simplification. In particular, one can choose a common axis of quantization for all molecules and never have to worry about quantization relative to the instantaneous axis of collision, as is done in Anderson's classical path approach.

It often happens in considering line-shape problems that it is easier to calculate the moments[39-44] of the spectral function, rather than the function itself. If a line is symmetric (or nearly symmetric) about its peak then a calculation of the first moment is sufficient to yield the location of the peak. Since many spectral lines are found experimentally to be rather symmetric, the technique would appear to be a useful tool in obtaining spectral shifts. Futrelle[45] and Gordon[46] have discussed the application of the moment method to molecular-collision problems, but their methods of application as well as physical models are rather different from those which we shall consider. In spite of the simplicity of the moment method, in general it must be applied with a great deal of caution, and blind application of the method can lead to unphysical results. It is known, for example, in magnetic-resonance theory that, under certain circumstances, the perturbing Hamiltonian can give rise to nonresonant or satellite structure[40] occurring in the far wings of the line, and this structure has little relevance to the main spectral peak of interest. We will consider the method of moments in this paper. We will show, however, that the simplest application of the method leads to unphysical results, and we will therefore be led to consider a modified version of the technique.

We close this section with a discussion of the physical system to be considered, the approximations which will be employed, and the general plan of the remainder of the paper. The physical system is essentially that considered in ATC theory, namely a set of molecules called a's which have a dipole moment and can radiate, and a set of perturbing molecules called b's which have no radiative transitions in the frequency range of interest (we do allow the possibility that the b's have a dipole moment however). The molecules are all assumed to be electrically neutral, but are also assumed to possess higher-order moments. We consider the case of sufficiently high temperatures and low pressures where the actual statistics (Bose, Fermi) of the molecules will ultimately be of no consequence. We also visualize the situation where broadening of the a-molecule lines is due primarily to interaction with the foreign b molecules. Thus, we shall ignore self-broadening and also Doppler broadening. These effects could be treated in essentially the same fashion as the foreign-gas broadening.

The approximations we make are well defined. First, we will not attempt to treat the problem of overlapping lines. Second, we assume that extremely close collisions are rare and that the dominant contribution to broadening and shifts can be obtained from some type of multipole expansion. We assume, in addition, that some form of many-body perturbation theory is valid. We do treat the case of degenerate levels and allow both elastic and inelastic processes to occur. The classical path assumption is not invoked in the present treatment.

We should like to emphasize that we will derive *explicit* expressions for the pressure shift to second order in the intermolecular potential. No attempt to perform detailed calculations will be given here. As in the ATC theory, numerical calculations from these formulas will be nontrivial. Because we do not invoke the classical path approximation, our theory requires more integrations than in ATC, but we show in Sec. V that all but one of the necessary integrations can be performed in closed form.

The organization of the remainder of the paper is as follows. In Sec. II we set up the general formalism needed to obtain the line-shape function. In Sec. III we derive an expression for the pressure shift to second order in the intermolecular interaction using the simplest application of the moment method. We show, however, that this leads to unphysical results for the shift. In Sec. IV we go on to develop the graphical perturbation theory for obtaining the line-shape function. This enables us to identify certain contributions in the ATC theory whose physical meaning has not been adequately noted previously. In particular, we show that the contributions which ATC simply call $S_2(b)_{\text{outer}}$ can be identified as self-energy contributions. Similarly the quantity $S_2(b)_{\text{middle}}$ of ATC is shown to correspond to vertex corrections. In certain simple cases the lowest-order vertex corrections may be shown to vanish. This result has previously been noted by ATC. For the case where vertex corrections can be ignored, we show that if one makes certain "quasiparticle" approximations *before* applying the moment method that a sensible result for the pressure shift is obtained. This calculation suggests a more general modification of the moment calculation and the modification leads to the result that the vertex corrections cancel out in the final expression for the line shift in the dilute-gas limit. Finally, in Sec. V we give some details of reducing the line-shift expression. Taking the dilute-gas limit we use symmetry to perform all summations over the degenerate quantum numbers. This calculation is carried out explicitly for the case of dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions.

II. FORMULATION OF THE PROBLEM

We shall consider the case of absorption of radiation. The absorption coefficient α (in cm^{-1}) is related to the transition probability per unit time, W_{abs}, for absorbing a photon of energy $\hbar\omega$ and polarization $\hat{\epsilon}=\hat{z}$ according to

$$\alpha=\frac{1}{cn(\omega)}(1-e^{-\beta\hbar\omega})W_{\text{abs}}, \tag{2.1}$$

with $\beta=1/k_BT$ and where $n(\omega)$ is the refractive index. If we make the dipole approximation (ignore Doppler effects), and assume that the perturbing molecules (the b's) have no radiative transitions in the frequency range of interest, we can write

$$W_{\text{abs}}=4\pi^2\frac{\omega}{V}\sum_{IF}\rho(E_I)\left|\langle I|\sum_a d_a^z|F\rangle\right|^2 \times\delta(E_F-E_I-\hbar\omega). \tag{2.2}$$

Here $|I\rangle$ and $|F\rangle$ are exact (many-body) eigenstates of the system, and $\rho(\mathcal{H})|I\rangle=\rho(E_I)|I\rangle$, where $\rho(\mathcal{H})=\exp[-\beta(\mathcal{H}-\mu_aN_a-\mu_bN_b-\Omega)]$ is the grand canonical density matrix. Also in Eq. (2.2), the dipole moment operator of the radiating a molecules is given by

$$\vec{d}_a=\sum_\alpha e_{a\alpha}\vec{r}_{a\alpha}, \tag{2.3}$$

where $\vec{r}_{a\alpha}$ is the position of the αth charged particle in the molecule labeled by index a. From electrical neutrality

$$\sum_{\alpha} e_{a\alpha} = 0 , \tag{2.4}$$

and we assume a similar condition for the perturbing b molecules.

We write the Hamiltonian for the system as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} , \tag{2.5}$$

where $\mathcal{H}_0$ is the Hamiltonian for noninteracting molecules and $\mathcal{V}$ is the interaction between molecules. Since we are going to ignore self-broadening, we include in $\mathcal{V}$ only the interaction between radiating and perturbing molecules. Ignoring spin-dependent interactions, this becomes

$$\mathcal{V} = \sum_{ab} \sum_{\alpha\beta} \frac{e_{a\alpha} e_{b\beta}}{|\vec{r}_{a\alpha} - \vec{r}_{b\beta}|} . \tag{2.6}$$

We next introduce the transformation to center of mass and internal generalized coordinates according to

$$\vec{r}_{a\alpha} = \vec{R}_a + \vec{f}_{\alpha}(a) , \tag{2.7}$$

where the center of mass is defined by

$$\vec{R}_a = \frac{\sum_{\alpha} m_{a\alpha} \vec{r}_{a\alpha}}{\sum_{\alpha} m_{a\alpha}} = \frac{1}{M_a} \sum_{\alpha} m_{a\alpha} \vec{r}_{a\alpha} . \tag{2.8}$$

For the Hamiltonian $\mathcal{H}_0$, the center of mass of each molecule moves as a free particle, and we have

$$\mathcal{H}_0 = \sum_{\mu\vec{k}} \epsilon^a_{\mu\vec{k}} a^{\dagger}_{\mu\vec{k}} a_{\mu\vec{k}} + \sum_{\gamma\vec{k}} \epsilon^b_{\gamma\vec{k}} b^{\dagger}_{\gamma\vec{k}} b_{\gamma\vec{k}} , \tag{2.9}$$

where $\vec{k}$ is the center-of-mass wave vector, and μ, γ correspond to internal quantum numbers of the radiating and perturbing molecules, respectively. Thus, the unperturbed energies separate as

$$\epsilon^a_{\mu\vec{k}} = \epsilon^a_{\mu} + \epsilon^a_{\vec{k}} , \quad \epsilon^a_{\vec{k}} = \hbar^2 k^2 / 2M_a , \tag{2.10}$$

and similarly for $\epsilon^b_{\gamma\vec{k}}$. Also in Eq. (2.9) we have introduced a set of boson field operators which satisfy $[a_{\mu\vec{k}}, a^{\dagger}_{\mu'\vec{k}'}] = \delta_{\mu,\mu'} \delta_{\vec{k},\vec{k}'}$ and $[b_{\gamma\vec{k}}, b^{\dagger}_{\gamma'\vec{k}'}] = \delta_{\gamma,\gamma'} \delta_{\vec{k},\vec{k}'}$. We are ultimately interested in the dilute-gas limit, where the choice of particle statistics is irrelevant.

For the noninteracting system the gas pressure is given by $P = P_a + P_b$, where the partial pressures are

$$P_a = \bar{N}_a / \beta V \quad \text{and} \quad P_b = \bar{N}_b / \beta V , \tag{2.11}$$

with

$$\bar{N}_a = \sum_{\mu\vec{k}} n(\epsilon^a_{\mu\vec{k}}) , \quad \bar{N}_b = \sum_{\gamma\vec{k}} n(\epsilon^b_{\gamma\vec{k}}) . \tag{2.12}$$

Here

$$n(\epsilon^a_{\mu\vec{k}}) = \{\exp[\beta(\epsilon^a_{\mu\vec{k}} - \mu_a)] - 1\}^{-1} , \tag{2.13}$$

or $n(\epsilon^a_{\mu\vec{k}}) \simeq \exp[-\beta(\epsilon^a_{\mu\vec{k}} - \mu_a)]$ in the dilute-gas limit.

In second-quantized notation we can now write Eq. (2.2) in the form

$$W_{\text{abs}} = 4\pi^2 \omega \sum_{\mu\gamma} \sum_{\mu'\gamma'} \langle \mu' | d^z_a | \mu \rangle \langle \gamma' | d^z_a | \gamma \rangle \frac{1}{V} \sum_{\vec{k}\vec{k}'} \sum_{IF} \rho(E_I) \langle I | a^{\dagger}_{\mu'\vec{k}'} a_{\mu\vec{k}} | F \rangle \langle F | a^{\dagger}_{\gamma\vec{k}'}, a_{\gamma\vec{k}'} | I \rangle \delta(E_F - E_I - \hbar\omega) . \tag{2.14}$$

We must now specify the internal states of the molecules.[25,47] We write these as $|\mu\rangle = |j_{\mu} m_{\mu}\rangle$, where j_{μ} stands for the total angular momentum quantum number J_{μ} and other quantum numbers necessary to specify the internal state. We take the z axis (the direction of polarization of the incident radiation) as the common axis of quantization. Then m_{μ} is the quantum number for the z component of the angular momentum. With the above choice, the dipole moment operator is diagonal in the m_{μ} indices. Applying the Wigner-Eckart theorem,[48] we have

$$\langle j_{\mu} m_{\mu'} | d^z_a | j_{\mu} m_{\mu} \rangle = \langle j_{\mu'} \| d_a \| j_{\mu} \rangle \langle J_{\mu}\, 1 - m_{\mu}\, 0 | J_{\mu}\, 1 J_{\mu'} - m_{\mu} \rangle \delta_{m_{\mu}, m_{\mu'}} . \tag{2.15}$$

In the above equation, the first factor is a reduced matrix element[48] and the second factor is a Clebsch-Gordan coefficient. Since d^z_a is diagonal in the magnetic quantum numbers, we have

$$W_{\text{abs}} = 4\pi^2 \omega \sum_{\substack{j_{\mu} j_{\gamma} \\ j_{\mu'} j_{\gamma'}}} \sum_{m_{\mu} m_{\mu'}} \langle j_{\mu} m_{\mu} | d^z_a | j_{\mu} m_{\mu} \rangle \langle j_{\gamma} m_{\mu'} | d^z_a | j_{\gamma} m_{\mu'} \rangle \times \frac{1}{V} \sum_{\vec{k}\vec{k}'} \sum_{IF} \rho(E_I) \langle I | a^{\dagger}_{j_{\mu'} m_{\mu} \vec{k}} a_{j_{\mu} m_{\mu} \vec{k}} | F \rangle \langle F | a^{\dagger}_{j_{\gamma} m_{\mu}, \vec{k}'} a_{j_{\gamma} m_{\mu}, \vec{k}'} | I \rangle \delta(E_F - E_I - \hbar\omega) . \tag{2.16}$$

We now assume that the transitions of interest are all well resolved, i.e., we do not attempt to treat the case of overlapping lines. In this case it seems rather clear physically that it should be a good approximation to set $j_{\gamma'}=j_\mu$ and $j_\gamma=j_{\mu'}$ in Eq. (2.16). Note, however, that it is not justified to set $m_{\mu'}=m_\mu$ for the degeneracy indices. We next wish to compress the notation somewhat. We define the following four states which will have the same meaning throughout the paper,

$$|\mu\rangle=|j_\mu m_\mu\rangle,\quad |\tilde{\mu}\rangle=|j_\mu m_{\mu'}\rangle,\qquad |\mu'\rangle=|j_{\mu'}m_{\mu'}\rangle,\quad |\tilde{\mu}'\rangle=|j_{\mu'}m_\mu\rangle. \tag{2.17}$$

We also define the quantity

$$\sigma(m_\mu,m_{\mu'})=(-1)^{J_\mu-J_{\mu'}}(J_\mu\,1-m_\mu\,0\,|J_\mu\,1J_{\mu'}-m_\mu)\times(J_{\mu'}1-m_{\mu'}\,0\,|J_{\mu'}\,1\,J_\mu-m_{\mu'}), \tag{2.18}$$

where the dependence on the J's is suppressed in the notation. Using Eq. (2.15) we then write $W_{\rm abs}$ in the following form:

$$W_{\rm abs}=4\pi^2\omega\sum_{j_\mu j_{\mu'}}(-1)^{J_\mu-J_{\mu'}}\langle j_{\mu'}\|d_a\|j_\mu\rangle\langle j_\mu\|d_a\|j_{\mu'}\rangle\times f_{\mu'\mu}(\hbar\omega). \tag{2.19}$$

Here we shall call $f_{\mu'\mu}(\hbar\omega)$ the total line-shape function for the transition $\mu'\to\mu$, i.e., it is the line-shape function summed over the degeneracy indices (m_μ) of the transition. The expression for this function is

$$f_{\mu'\mu}(\hbar\omega)=\sum_{m_\mu m_{\mu'}}\sigma(m_\mu,m_{\mu'})Q_{\mu'\mu}(\hbar\omega), \tag{2.20}$$

with

$$Q_{\mu'\mu}(\hbar\omega)=\frac{1}{V}\sum_{\vec{k}\vec{k}'}\sum_{F}\rho(E_I)\langle I|a^\dagger_{\tilde{\mu}'\vec{k}'}a_{\mu\vec{k}}|F\rangle\langle F|a^\dagger_{\tilde{\mu}\vec{k}}a_{\mu'\vec{k}'}|I\rangle\times\delta(E_F-E_I-\hbar\omega), \tag{2.21}$$

and where the four internal states which appear in Eq. (2.21) are defined explicitly by Eq. (2.17). For the unperturbed ($\mathcal{V}=0$) system $f_{\mu'\mu}(\hbar\omega)$ evaluates to give

$$f_{\mu'\mu}(\hbar\omega)=\Big(\sum_{m_\mu}\sigma(m_\mu,m_\mu)\Big)\delta(\epsilon^a_\mu-\epsilon^a_{\mu'}-\hbar\omega)\times\frac{1}{V}\sum_{\vec{k}}n(\epsilon^a_{\mu'\vec{k}})[n(\epsilon^a_{\mu\vec{k}})+1], \tag{2.22}$$

with $\epsilon^a_\mu>\epsilon^a_{\mu'}$ for absorption of radiation, and where $n(\epsilon^a_{\mu\vec{k}})$ is given by Eq. (2.13).

We must now consider the interaction term $\mathcal{V}$ as given by Eq. (2.6). It is, of course, difficult to treat the problem of extremely close collisions, where the center-of-mass separation $|\vec{R}_a-\vec{R}_b|$ is small. In Anderson's theory this difficulty is treated by introducing a minimum impact parameter b_0 and assuming $S_2(b)=1$ for $b<b_0$. This is then joined to the result for $S_2(b>b_0)$, obtained from a multipole expansion, using an extrapolation scheme involving Anderson's "approximation numbers." This scheme is not unique, but if the contribution from collisions with $b>b_0$ is dominant, the theory should give meaningful results. In the present approach we have the same difficulty with close collisions, but we will attempt to treat it in a somewhat different fashion.

Making the usual multipole expansion of Eq. (2.6) and using the electrical neutrality condition (2.4), we obtain

$$\mathcal{V}=\sum_{ab}[\mathcal{V}^{(1)}(\vec{R}_{ab})+\mathcal{V}^{(2)}(\vec{R}_{ab})+\mathcal{V}^{(3)}(\vec{R}_{ab})+\cdots], \tag{2.23}$$

where $\mathcal{V}^{(1)}$, $\mathcal{V}^{(2)}$, $\mathcal{V}^{(3)}$ are, respectively, the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions given by

$$\mathcal{V}^{(1)}(\vec{R}_{ab})=(1/|\vec{R}_{ab}|^3)(\vec{d}_a\cdot\vec{d}_b-3\hat{R}_{ab}\cdot\vec{d}_a\hat{R}_{ab}\cdot\vec{d}_b), \tag{2.24}$$

$$\mathcal{V}^{(2)}(\vec{R}_{ab})=(\tfrac{3}{2}/|\vec{R}_{ab}|^4)\{[2\hat{R}_{ab}\cdot\vec{Q}^t_b\cdot\vec{d}_a-5\hat{R}_{ab}\cdot\vec{d}_a(\hat{R}_{ab}\cdot\vec{Q}^t_b\cdot\hat{R}_{ab})]-[2\hat{R}_{ab}\cdot\vec{Q}^t_a\cdot\vec{d}_b-5\hat{R}_{ab}\cdot\vec{d}_b(\hat{R}_{ab}\cdot\vec{Q}^t_a\cdot\hat{R}_{ab})]\}, \tag{2.25}$$

$$\mathcal{V}^{(3)}(\vec{R}_{ab})=\tfrac{3}{4}(1/|\vec{R}_{ab}|^5)[2\,\mathrm{Tr}(\vec{Q}^t_a\cdot\vec{Q}^t_b)-20\hat{R}_{ab}\cdot\vec{Q}^t_a\cdot\vec{Q}^t_b\cdot\hat{R}_{ab}+35(\hat{R}_{ab}\cdot\vec{Q}^t_a\cdot\hat{R}_{ab})(\hat{R}_{ab}\cdot\vec{Q}^t_b\cdot\hat{R}_{ab})]. \tag{2.26}$$

Here $\vec{R}_{ab}=-\vec{R}_{ba}=\vec{R}_a-\vec{R}_b$ in terms of the center-of-mass coordinates. Also in these equations, the dipole moment operator is given by Eqs. (2.3), (2.4), (2.7) and the traceless quadrupole-moment tensor $\vec{Q}^t_a$ is given by

$$\vec{Q}^t_a=\sum_\alpha e_{a\alpha}[\vec{f}_\alpha(a)\vec{f}_\alpha(a)-\tfrac{1}{3}|\vec{f}_\alpha(a)|^2\vec{1}], \tag{2.27}$$

where $\vec{1}$ is the unit tensor. For simplicity in the treatment which follows, in considering the dipole-quadrupole term, we will consider the case where

either the matrix elements of $\vec{Q}_a^t$ or those of $\vec{d}_b$ are negligible, so that we henceforth keep only the first term in Eq. (2.25).

We next introduce the Fourier transform of the potentials according to

$$v^{(i)}(\vec{q}) = \int d^3r\, v^{(i)}(\vec{r}) e^{-i\vec{q}\cdot\vec{r}}, \tag{2.28}$$

so that

$$v^{(i)}(\vec{R}_{ab}) = \frac{1}{V}\sum_{\vec{q}} v^{(i)}(\vec{q}) e^{i\vec{q}\cdot(\vec{R}_a - \vec{R}_b)}. \tag{2.29}$$

The Fourier transforms are then given by

$$v^{(1)}(\vec{q}) = -g_c(\vec{q})(\tfrac{1}{3}q^2\vec{d}_a\cdot\vec{d}_b - \vec{q}\cdot\vec{d}_a\vec{q}\cdot\vec{d}_b), \tag{2.30}$$

$$v^{(2)}(\vec{q}) = g_c(\vec{q})\tfrac{1}{2}i[\tfrac{2}{5}q^2(\vec{q}\cdot\vec{Q}_b^t\cdot\vec{d}_a) - (\vec{q}\cdot\vec{d}_a)(\vec{q}\cdot\vec{Q}_b^t\cdot\vec{q})], \tag{2.31}$$

$$v^{(3)}(\vec{q}) = g_c(\vec{q})\tfrac{1}{4}[\tfrac{2}{35}q^4\,\mathrm{Tr}(\vec{Q}_a^t\cdot\vec{Q}_b^t) - \tfrac{4}{7}q^2(\vec{q}\cdot\vec{Q}_a^t\cdot\vec{Q}_b^t\cdot\vec{q}) + (\vec{q}\cdot\vec{Q}_a^t\cdot\vec{q})(\vec{q}\cdot\vec{Q}_b^t\cdot\vec{q})]. \tag{2.32}$$

where $g_c(\vec{q}) = 4\pi/q^2$ is the Fourier transform of the Coulomb potential $1/r$.

The difficulty, of course, is that the series (2.23) does not converge for small $\vec{R}_{ab}$. Equivalently, in Fourier-transform space, the series (2.30)–(2.32) does not converge for large $\vec{q}$. In order to make the multipole expansion meaningful, it is therefore necessary to somehow cut off the high-frequency ($\vec{q}$) components of the interaction. One simple method is given in the following. As in Anderson's treatment, it is certainly not unique, and other possibilities could be considered without altering the general structure of the theory which follows. Suppose we replace $g_c(\vec{q}) = 4\pi/q^2$ by the exponentially cut-off potential

$$g(\vec{q}) = (4\pi/q^2)e^{-qr_c}, \tag{2.33}$$

where the cut-off length r_c is to be chosen from physical considerations similar to those which determine b_0 in Anderson's theory. The Fourier transform of $g(\vec{q})$ is given by

$$g(\vec{r}) = \frac{1}{V}\sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} g(\vec{q}) = \frac{2}{\pi}\frac{1}{|\vec{r}|}\arctan\left(\frac{|\vec{r}|}{r_c}\right). \tag{2.34}$$

It is seen that $g(\vec{r})$ approaches the pure Coulomb potential $1/|\vec{r}|$ for $|\vec{r}|/r_c \gg 1$, but approaches the finite constant $g(0) = 2/\pi r_c$ for $|\vec{r}|/r_c \ll 1$.

The final step in the treatment of v is to put it into second-quantized notation. This procedure is straightforward and gives

$$v = \frac{1}{V}\sum_{\vec{q}\vec{k}_1\vec{k}_1'} g(\vec{q}) \sum_{\mu_1\mu_1'}\sum_{\gamma_1\gamma_1'} K_{\mu_1\mu_1',\gamma_1\gamma_1'}(\vec{q}) a^+_{\mu_1\vec{k}_1} a_{\mu_1'\vec{k}_1'+\vec{q}} \times b^+_{\gamma_1\vec{k}_1'} b_{\gamma_1'\vec{k}_1'-\vec{q}}. \tag{2.35}$$

Here

$$K_{\mu_1\mu_1',\gamma_1\gamma_1'}(\vec{q}) = K^{(1)}_{\mu_1\mu_1',\gamma_1\gamma_1'}(\vec{q}) + K^{(2)}_{\mu_1\mu_1',\gamma_1\gamma_1'}(\vec{q}) + K^{(3)}_{\mu_1\mu_1',\gamma_1\gamma_1'}(\vec{q}) + \cdots, \tag{2.36}$$

with

$$K^{(1)}_{\mu_1\mu_1',\gamma_1\gamma_1'}(\vec{q}) = (-\tfrac{1}{3}q^2\langle\mu_1|\vec{d}_a|\mu_1'\rangle\cdot\langle\gamma_1|\vec{d}_b|\gamma_1'\rangle + \vec{q}\cdot\langle\mu_1|\vec{d}_a|\mu_1'\rangle\vec{q}\cdot\langle\gamma_1|\vec{d}_b|\gamma_1'\rangle), \tag{2.37}$$

$$K^{(2)}_{\mu_1\mu_1',\gamma_1\gamma_1'}(\vec{q}) = \tfrac{1}{2}i(\tfrac{2}{5}q^2\langle\mu_1|\vec{d}_a|\mu_1'\rangle\cdot\langle\gamma_1|\vec{Q}_b^t|\gamma_1'\rangle\cdot\vec{q} - \vec{q}\cdot\langle\mu_1|\vec{d}_a|\mu_1'\rangle\vec{q}\cdot\langle\gamma_1|\vec{Q}_b^t|\gamma_1'\rangle\cdot\vec{q}), \tag{2.38}$$

$$K^{(3)}_{\mu_1\mu_1',\gamma_1\gamma_1'}(\vec{q}) = \tfrac{1}{4}[\tfrac{2}{35}q^4\,\mathrm{Tr}(\langle\mu_1|\vec{Q}_a^t|\mu_1'\rangle\cdot\langle\gamma_1|\vec{Q}_b^t|\gamma_1'\rangle) - \tfrac{4}{7}q^2\vec{q}\cdot\langle\mu_1|\vec{Q}_a^t|\mu_1'\rangle\cdot\langle\gamma_1|\vec{Q}_b^t|\gamma_1'\rangle\cdot\vec{q} + \vec{q}\cdot\langle\mu_1|\vec{Q}_a^t|\mu_1'\rangle\cdot\vec{q}\,\vec{q}\cdot\langle\gamma_1|\vec{Q}_b^t|\gamma_1'\rangle\cdot\vec{q}]. \tag{2.39}$$

III. METHOD OF MOMENTS

We define a set of averages of the line-shape function $f_{\mu'\mu}(\hbar\omega)$ by

$$\langle(\hbar\omega)^n\rangle = \frac{\int_{-\infty}^{\infty} d(\hbar\omega) f_{\mu'\mu}(\hbar\omega)(\hbar\omega)^n}{\int_{-\infty}^{\infty} d(\hbar\omega) f_{\mu'\mu}(\hbar\omega)}. \tag{3.1}$$

We define the moments of $f_{\mu'\mu}(\hbar\omega)$ as

$$M^{(n)}_{\mu'\mu} = \int_{-\infty}^{\infty} d(\hbar\omega) f_{\mu'\mu}(\hbar\omega)(\hbar\omega)^n, \tag{3.2}$$

then

$$\langle(\hbar\omega)^n\rangle = M^{(n)}_{\mu'\mu}/M^{(0)}_{\mu'\mu}. \tag{3.3}$$

In particular, we have

$$\langle\hbar\omega\rangle = M^{(1)}_{\mu'\mu}/M^{(0)}_{\mu'\mu}. \tag{3.4}$$

For a single line which is symmetric about its peak, it is then easy to show that $\langle\hbar\omega\rangle = \hbar\omega_{\mathrm{peak}}$, and the moment analysis can be used to locate the line center.

From Eqs. (2.20) and (2.21) and using closure we immediately obtain

$$M^{(0)}_{\mu'\mu} = \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'}) \frac{1}{V} \sum_{\vec{k}\vec{k}'} \mathrm{Tr}\{\rho(\mathcal{H}) a^\dagger_{\mu'\vec{k}'} a_{\mu\vec{k}} a^\dagger_{\mu\vec{k}} a_{\mu'\vec{k}'}\} , \tag{3.5}$$

$$M^{(1)}_{\mu'\mu} = \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'}) \frac{1}{V} \sum_{\vec{k}\vec{k}'} \mathrm{Tr}\{\rho(\mathcal{H}) a^\dagger_{\mu'\vec{k}'} a_{\mu\vec{k}} [\mathcal{H}, a^\dagger_{\mu\vec{k}} a_{\mu'\vec{k}'}]\} . \tag{3.6}$$

The above commutator is easy to calculate. Using Eqs. (2.9) and (2.35) we find

$$[\mathcal{H}, a^\dagger_{\tilde{\mu}\vec{k}} a_{\mu'\vec{k}'}] = (\epsilon^a_{\tilde{\mu}\vec{k}} - \epsilon^a_{\mu'\vec{k}'}) a^\dagger_{\tilde{\mu}\vec{k}} a_{\mu'\vec{k}'} + \frac{1}{V} \sum_{\vec{q}\vec{k}'_1} g(\vec{q}) \sum_{\mu_1\gamma_1\gamma'_1} [K_{\mu_1\tilde{\mu},\gamma_1\gamma'_1}(\vec{q}) a^\dagger_{\mu_1\vec{k}'-\vec{q}} a_{\mu'\vec{k}'} - K_{\mu'\mu_1,\gamma_1\gamma'_1}(\vec{q}) a^\dagger_{\tilde{\mu}\vec{k}} a_{\mu_1\vec{k}'+\vec{q}}] \cdot b^\dagger_{\gamma_1\vec{k}_1} b_{\gamma'_1\vec{k}'_1-\vec{q}} . \tag{3.7}$$

Using the separable property [Eq. (2.10)] of the unperturbed energies, $\epsilon^a_{\tilde{\mu}\vec{k}'} - \epsilon^a_{\mu'\vec{k}'} = \epsilon^a_{\tilde{\mu}} - \epsilon^a_{\mu'} = \epsilon^a_{\tilde{\mu}} - \epsilon^a_{\mu'}$, where in the last step we have used the fact that the states $|\tilde{\mu}\rangle$ and $|\mu\rangle$ have the same energy, as do the states $|\tilde{\mu}'\rangle$ and $|\mu'\rangle$. This gives

$$\begin{aligned} M^{(1)}_{\mu'\mu} &= (\epsilon^a_{\tilde{\mu}} - \epsilon^a_{\mu'}) M^{(0)}_{\mu'\mu} \\ &+ \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'}) \frac{1}{V} \sum_{\vec{k}\vec{k}'} \frac{1}{V} \sum_{\vec{q}\vec{k}'_1} g(\vec{q}) \sum_{\mu_1\gamma_1\gamma'_1} \{K_{\mu_1\tilde{\mu},\gamma_1\gamma'_1}(\vec{q}) \mathrm{Tr}[\rho(\mathcal{H}) a^\dagger_{\tilde{\mu}\vec{k}} a_{\mu\vec{k}} a^\dagger_{\mu_1\vec{k}'-\vec{q}} a_{\mu'\vec{k}'} b^\dagger_{\gamma_1\vec{k}'_1} b_{\gamma'_1\vec{k}'_1-\vec{q}}] \\ &\quad - K_{\mu'\mu_1,\gamma_1\gamma'_1}(\vec{q}) \mathrm{Tr}[\rho(\mathcal{H}) a^\dagger_{\mu'\vec{k}} a_{\mu\vec{k}} a^\dagger_{\tilde{\mu}\vec{k}'} a_{\mu_1\vec{k}'+\vec{q}} b^\dagger_{\gamma_1\vec{k}'_1} b_{\gamma'_1\vec{k}'_1-\vec{q}}]\} . \end{aligned} \tag{3.8}$$

The above expression is exact, and in the absence of interactions yields the expected result $\langle\hbar\omega\rangle = \epsilon^a_{\tilde{\mu}} - \epsilon^a_{\mu'}$. Let us now consider the first-order correction to the result. The second term in Eq. (3.8) is already of first order in the interaction (i.e., is of first order in the K's). Thus, the first-order correction is simply obtained by setting $\rho(\mathcal{H}) = \rho(\mathcal{H}_0)$ in this term. Furthermore, $\rho(\mathcal{H}_0)$ clearly factors into $\rho(\mathcal{H}_0) = \rho(\mathcal{H}^a_0)\rho(\mathcal{H}^b_0)$ so that the a, b traces can be done separately. The result of this calculation gives

$$\langle\hbar\omega\rangle = E^a_{\tilde{\mu}} - E^a_{\mu'} , \tag{3.9}$$

where

$$E^a_{\tilde{\mu}} = \epsilon^a_{\tilde{\mu}} - G^a_{\tilde{\mu}} , \tag{3.10}$$

and where $G^a_{\tilde{\mu}}$ is the first-order (Hartree) self-energy given by

$$G^a_{\tilde{\mu}} = G^a_{\tilde{\mu}\vec{k}} = -\frac{1}{V} \sum_{\vec{k}'_1\gamma_1} g_{\tilde{\mu}\mu,\gamma_1\gamma_1} n(\epsilon^b_{\gamma_1\vec{k}'_1}) . \tag{3.11}$$

Note that this is independent of the center-of-mass index $\vec{k}$. Also in Eq. (3.11)

$$g_{\tilde{\mu}\mu,\gamma_1\gamma_1} = [g(\vec{q}) K_{\tilde{\mu}\mu,\gamma_1\gamma_1}(\vec{q})]_{\vec{q}=0} . \tag{3.12}$$

From Eqs. (2.35)–(2.39) we note that for any multipole interaction higher than the dipole-dipole case $g_{\tilde{\mu}\mu,\gamma_1\gamma_1}$ vanishes.[49] Moreover, even if this were not the case, we note that Eq. (3.11) involves the diagonal matrix element $\langle\gamma_1|\,\mathcal{O}\,|\gamma_1\rangle$, where $\mathcal{O}$ stands for the b molecule's dipole or quadrupole-moment operator. Using the argument presented in the Introduction, when this is summed over the degeneracy index m_{γ_1}, the result will vanish.

Thus, as expected, we have to go to second order to obtain a shift. To do this one has to expand $\rho(\mathcal{H})$ in the second term of Eq. (3.8). One does this by writing

$$\exp[-\beta(\mathcal{H} - \mu_a N_a - \mu_b N_b)] = \exp[-\beta(\mathcal{H}_0 - \mu_a N_a - \mu_b N_b)] U(\beta) \tag{3.13}$$

and $U(\beta)$ satisfies the Bloch equation

$$U(\beta) = 1 - \int_0^\beta \mathcal{V}(\beta') U(\beta')\, d\beta' , \tag{3.14}$$

with

$$\mathcal{V}(\beta') = e^{\beta'\mathcal{H}_0} \mathcal{V} e^{-\beta'\mathcal{H}_0} .$$

To obtain the second-order correction, we need only the first iteration of Eq. (3.14). The traces can then be evaluated using Wick's theorem for thermal averages. We shall not give the details of this calculation as it is straightforward but lengthy. In performing this calculation one may again ignore pairings of operators which lead to $[g(\vec{q})K(\vec{q})]_{\vec{q}=0}$ factors. Some of these correspond to the Hartree corrections which we have already discussed in the first-order calculation. Others correspond to improper polarization graphs which also vanish except for the dipole-dipole case.[49] Similarly, one can ignore pairings which lead to $\delta_{\tilde{\mu}',\mu}$ or $\delta_{\tilde{\mu},\mu'}$ since $j_{\mu'} \neq j_\mu$ by assumption.

The result of the second-order calculation can be written

$$M^{(1)}_{\mu'\mu} = (\epsilon^a_\mu - \epsilon^a_{\mu'})M^{(0)}_{\mu'\mu} - \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'})\delta_{m_\mu, m_{\mu'}} \frac{1}{V}\sum_{\vec{k}} \{n(\epsilon^a_{\mu',\vec{k}})\Sigma(\mu\vec{k}) - [n(\epsilon^a_{\mu\vec{k}})+1]\Sigma(\mu'\vec{k})\}$$

$$+ \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'}) \frac{1}{V}\sum_{\vec{k}} \{n(\epsilon^a_{\mu',\vec{k}})\psi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}) - [n(\epsilon^a_{\mu\vec{k}})+1]\psi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu'\vec{k})\}. \tag{3.15}$$

Here $\Sigma(\mu\vec{k})$ is a quantity that can be expressed in terms of the self-energy for state $|\mu\vec{k}\rangle$, while the ψ's are contributions from vertex corrections (see Sec. IV for further discussion of these two types of corrections). The explicit expressions[50] for the above quantities are presented in Appendix A along with an alternative derivation based on an expression for the line-shape function obtained from the graphical analysis of Sec. IV. To obtain $\langle\hbar\omega\rangle$ one has only to divide Eq. (3.15) by $M^{(0)}_{\mu'\mu}$. Since the correction terms in Eq. (3.15) are already of second order in the interaction, $M^{(0)}_{\mu'\mu}$ can be evaluated to zeroth order and gives

$$M^{(0)}_{\mu'\mu} = \left(\sum_{m_\mu} \sigma(m_\mu, m_\mu)\right)\frac{1}{V}\sum_{\vec{k}} n(\epsilon^a_{\mu',\vec{k}})[n(\epsilon^a_{\mu\vec{k}})+1]$$

$$= \tfrac{1}{3}[(2J_\mu+1)(2J_{\mu'}+1)]^{1/2}\frac{1}{V}\sum_{\vec{k}} n(\epsilon^a_{\mu',\vec{k}})[n(\epsilon^a_{\mu\vec{k}})+1]. \tag{3.16}$$

The above method of obtaining the spectral shift is simple and direct. Unfortunately, the result appears to be quite unphysical. For simplicity, we drop the vertex contributions (they suffer from exactly the same malady). Then, in the dilute-gas limit where the factors $n(\epsilon^a_{\mu\vec{k}}) \ll 1$, the result of Eq. (3.15) states that only the self-energy corrections in the initial state (μ') are important. What we expect physically is a result similar to that which we obtained in first order [Eqs. (3.9) and (3.10)], i.e., something involving the *differences* of the self-energy corrections in the initial and final states. The exact source[51] of the previous difficulty is not completely obvious, but it appears to be due to a rather general asymmetry associated with the thermal population factors of the initial and final states.

Our main purpose in considering the moment method was to obtain a formula [Eq. (3.15)] which includes both self-energy and vertex corrections. In Sec. IV we show for the self-energy terms that, if one makes certain "quasiparticle" approximations (similar to the assumptions invoked in impact approximation theories) before calculating the spectral moments, a sensible result for the first moment can be obtained. In Appendix A this analysis is generalized to include also the vertex corrections.

IV. GRAPHICAL ANALYSIS OF THE LINE-SHAPE FUNCTION

We begin by defining the quantity

$$\overline{Q}_{\mu'\mu}(\beta', 0) = \frac{1}{V}\sum_{\vec{k}\vec{k}'} \mathrm{Tr}\{\rho(\mathcal{H})T[a^\dagger_{\tilde{\mu}',\vec{k}}(\beta')a_{\tilde{\mu}\vec{k}}(\beta')a^\dagger_{\tilde{\mu}\vec{k}'}a_{\tilde{\mu}',\vec{k}'}]\}, \tag{4.1}$$

where $\beta > \beta' > 0$, $\mathcal{O}(\beta') = e^{\beta'\mathcal{H}}\mathcal{O}e^{-\beta'\mathcal{H}}$, and where T is the β-ordering operator. The function $\overline{Q}_{\mu'\mu}(\beta', 0)$ will have a Fourier expansion of the form

$$\overline{Q}_{\mu'\mu}(\beta', 0) = \frac{1}{\beta}\sum_{\xi_{l_0}} e^{-\beta'\xi_{l_0}}\overline{Q}_{\mu'\mu}(\xi_{l_0}), \tag{4.2}$$

with $\xi_{l_0} = 2\pi i l_0/\beta$ and $l_0 =$ integer. The function $Q_{\mu'\mu}(\hbar\omega)$, as defined by Eq. (2.21), is then given by

$$Q_{\mu'\mu}(\hbar\omega) = (1 - e^{-\beta\hbar\omega})^{-1}(1/2\pi i) \times [\overline{Q}_{\mu'\mu}(\hbar\omega + i0^+) - \overline{Q}_{\mu'\mu}(\hbar\omega - i0^+)], \tag{4.3}$$

where the analytic continuation $\xi_{l_0} \to \hbar\omega \pm i0^+$ is to be carried out at the last stage in the calculation.

We introduce the basic unperturbed propagators according to

$$D^a_{\mu\vec{k}}(\beta_i, \beta_j) = \mathrm{Tr}\{\rho(\mathcal{H}_0)T[a^\dagger_{\mu\vec{k}}(\beta_i)a_{\mu\vec{k}}(\beta_j)]\}, \tag{4.4}$$

$$D^b_{\gamma\vec{k}}(\beta_i, \beta_j) = \mathrm{Tr}\{\rho(\mathcal{H}_0)T[b^\dagger_{\gamma\vec{k}}(\beta_i)b_{\gamma\vec{k}}(\beta_j)]\}, \tag{4.5}$$

where $\mathcal{O}(\beta_i) = e^{\beta_i\mathcal{H}_0}\mathcal{O}e^{-\beta_i\mathcal{H}_0}$. We denote $D^a_{\mu\vec{k}}(\beta_i, \beta_j)$ by a solid line with a single arrow going from β_i to β_j, and similarly for $D^b_{\gamma\vec{k}}(\beta_i, \beta_j)$ except that it will carry a double arrow. The propagators have the Fourier representation

$$D^a_{\mu\vec{k}}(\beta_i, \beta_j) = \frac{1}{\beta}\sum_{\xi^a_l} e^{\xi^a_l(\beta_i - \beta_j)}D^a_{\mu\vec{k}}(\xi^a_l), \tag{4.6}$$

$$D^b_{\gamma\vec{k}}(\beta_i, \beta_j) = \frac{1}{\beta}\sum_{\xi^b_l} e^{\xi^b_l(\beta_i - \beta_j)}D^b_{\gamma\vec{k}}(\xi^b_l), \tag{4.7}$$

with $\xi^a_l = 2\pi i l/\beta + \mu_a$, $\xi^b_l = 2\pi i l/\beta + \mu_b$, and where μ_a, μ_b are the chemical potentials. The Fourier coefficients are

$$D^a_{\mu\vec{k}}(\xi^a_l) = (\epsilon^a_{\mu\vec{k}} - \xi^a_l)^{-1},$$
$$D^b_{\gamma\vec{k}}(\xi^b_l) = (\epsilon^b_{\gamma\vec{k}} - \xi^b_l)^{-1}. \tag{4.8}$$

The graph giving the zeroth-order contribution to $\overline{Q}_{\mu'\mu}(\xi_{l_0})$ is shown in Fig. 1. Explicitly, its contribution is given by

$$\overline{Q}_{\mu'\mu}(\xi_{l_0}) = \delta_{m_\mu, m_{\mu'}} \frac{1}{V} \sum_{\vec{k}} \frac{1}{\beta} \sum_{\xi^a_{l_1}} D^a_{\mu'\vec{k}}(\xi^a_{l_1}) D^a_{\mu\vec{k}}(\xi^a_{l_1} + \xi_{l_0}) . \tag{4.9}$$

The Fourier sum over $\xi^a_{l_1}$ is carried out using the standard formula

$$\frac{1}{\beta} \sum_{\xi^a_{l_1}} F(\xi^a_{l_1}) = -[\text{sum of the residues of } F(\xi) n^a(\xi) \text{ at the poles of } F(\xi)], \tag{4.10}$$

where $F(\xi)$ has simple poles, and where $n^a(\xi)$ denotes the Bose function [Eq. (2.13)] for chemical potential μ_a. This yields

$$\overline{Q}_{\mu'\mu}(\xi_{l_0}) = \delta_{m_\mu, m_{\mu'}} \frac{1}{V} \sum_{\vec{k}} \frac{n(\epsilon^a_{\mu'\vec{k}}) - n(\epsilon^a_{\mu\vec{k}})}{\epsilon^a_{\mu\vec{k}} - \epsilon^a_{\mu'\vec{k}} - \xi_{l_0}} . \tag{4.11}$$

Performing the analytic continuation of Eq. (4.3) immediately yields the result of Eq. (2.22) for $f_{\mu'\mu}(\hbar\omega)$.

Going to first-order perturbation theory there are only the Hartree self-energy contributions shown in Fig. 2(a). We have previously shown that these can be ignored. In second-order perturbation theory we can also ignore such Hartree insertions, and in addition, we ignore improper polarization graphs having the structure shown in Fig. 2(b). The remaining second-order graphs are the two self-energy graphs shown in Fig. 3, and the vertex correction graph shown in Fig. 4. We have explicitly inserted the labels of the states in these graphs in order to make some connection with the ATC theory of pressure broadening. In particular, one need only examine the structure of the matrix elements to see that the self-energy contributions correspond to the quantity $S_2(b)_{\text{outer}}$

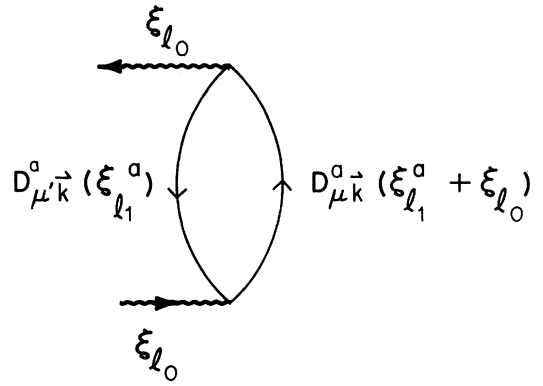

FIG. 1. Zeroth-order contribution to $\overline{Q}_{\mu'\mu}(\xi_{l_0})$.

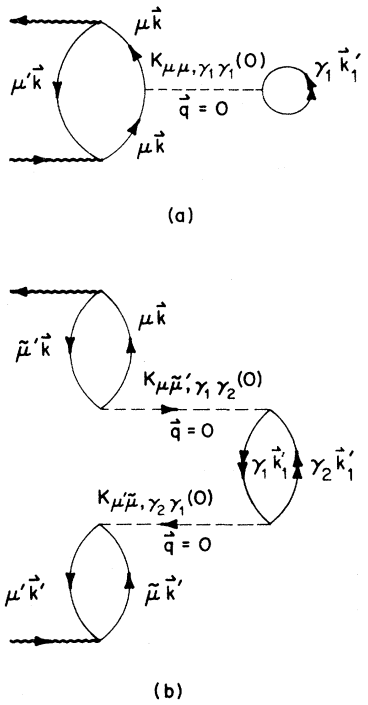

FIG. 2. Two graphs with $\vec{q}=0$ matrix elements. (a) A first-order Hartree self-energy graph. (b) A second-order improper polarization graph.

of ATC theory, while the vertex corrections correspond to $S_2(b)_{\text{middle}}$ in their treatment.

To go further, we can define the exact propagators by replacing $\mathcal{H}_0$ by $\mathcal{H}$ everywhere in Eqs. (4.4) and (4.5). While the self-energy function is diagonal in the center-of-mass indices ($\vec{k}$) due to momentum conservation, it is not diagonal in the internal indices. However, in the present problem we will ignore off-diagonal elements of the self-energy function, since this is sufficient for obtaining a second-order approximation equivalent to that resulting from the moment analysis of Sec. III. This approximation is often made anyway,[9,10] in order to yield a formalism which is tractable. With this approximation, Dyson's equation can be solved to give

$$\overline{D}_{\mu\vec{k}}(\xi^a_l) = [\epsilon^a_{\mu\vec{k}} - G^a_{\mu\vec{k}}(\xi^a_l) - \xi^a_l]^{-1} , \tag{4.12}$$

where $\overline{D}$ denotes the renormalized propagator, and where G is the proper self-energy function. The general expression for $\overline{Q}_{\mu'\mu}(\xi_{l_0})$ can then be written

$$\overline{Q}_{\mu'\mu}(\xi_{l_0}) = \frac{1}{V} \sum_{\vec{k}} \frac{1}{\beta} \sum_{\xi^a_{l_1}} \overline{D}^a_{\mu'\vec{k}}(\xi^a_{l_1}) \overline{D}^a_{\mu\vec{k}}(\xi^a_{l_1} + \xi_{l_0}) \times \Lambda_{\mu'\tilde{\mu}', \mu\tilde{\mu}}(\vec{k}, \xi^a_{l_1}, \xi_{l_0}) . \tag{4.13}$$

Here Λ is the vertex function which satisfies a Bethe-Salpeter equation of the form

$$\Lambda_{\mu'\tilde{\mu}'\,,\,\mu\tilde{\mu}}(\vec{k},\xi^a_{l_1},\xi_{l_0}) = \delta_{\mu',\tilde{\mu}'}\delta_{\mu,\tilde{\mu}} + \frac{1}{V}\sum_{\vec{k}_1}\sum_{\mu_1\mu_1'}\frac{1}{\beta}\sum_{\xi^a_{l_2}} I_{\mu_1'\tilde{\mu}',\mu\mu_1}(\vec{k}-\vec{k}_1,\xi^a_{l_1}-\xi^a_{l_2})\bar{D}^a_{\mu_1'\vec{k}_1}(\xi^a_{l_2})\bar{D}^a_{\mu_1\vec{k}_1}(\xi^a_{l_2}+\xi_{l_0})\Lambda_{\mu'\mu_1',\mu_1\tilde{\mu}}(\vec{k}_1,\xi^a_{l_2},\xi_{l_0}), \tag{4.14}$$

where I is the irreducible scattering function.

Unfortunately, Eq. (4.14) is very difficult to solve. This, of course, was the basic point of the moment analysis, because it avoided the problem of having to solve a complicated transport equation. Let us, however, consider for the present the case where vertex corrections are ignored. In this case we will show that if certain "quasiparticle" approximations are made *before* computing the moments of the spectral function, physically sensible results can be obtained. This procedure suggests a modification which can also be applied to the vertex corrections.

For the case where vertex corrections are ignored, $\bar{Q}_{\mu'\mu}(\xi_{l_0})$ is given by Eq. (4.9) with the unperturbed propagators D replaced by the renormalized propagators $\bar{D}$. One can carry out the Fourier sum over $\xi^a_{l_1}$ in the same fashion as before by introducing the spectral representation of the corrected propagators,

$$\bar{D}^a_{\mu\vec{k}}(\xi^a_{l_1}) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{dE\,A_{\mu\vec{k}}(E)}{E-\xi^a_{l_1}}, \tag{4.15}$$

with $A_{\mu\vec{k}}(E) = \mathrm{Im}\bar{D}^a_{\mu\vec{k}}(E+i0^+)$, the spectral density function. The function $A_{\mu\vec{k}}(E)$ may be shown to have the following spectral representation in terms of exact eigenstates of the system,

$$A_{\mu\vec{k}}(E) = \pi(e^{\beta(E-\mu_a)}-1)\sum_{IF}\rho(E_I)\langle I|\,a^\dagger_{\mu\vec{k}}\,|F\rangle\langle F|\,a_{\mu\vec{k}}\,|I\rangle \times\delta(E_F-E_I+E). \tag{4.16}$$

From this expression one immediately has the following two sum rules

$$\frac{1}{\pi}\int_{-\infty}^{\infty}A_{\mu\vec{k}}(E)\,dE = 1, \tag{4.17}$$

$$\frac{1}{\pi}\int_{-\infty}^{\infty}A_{\mu\vec{k}}(E)n^a(E)\,dE = \mathrm{Tr}[\rho(\mathcal{H})a^\dagger_{\mu\vec{k}}a_{\mu\vec{k}}] \equiv n^a_{\mu\vec{k}}, \tag{4.18}$$

where again $n^a(E)$ denotes the Bose function for chemical potential μ_a and $n^a_{\mu\vec{k}}$ is the number of molecules in state $|\mu\vec{k}\rangle$. For the noninteracting system $n^a_{\mu\vec{k}} = n(\epsilon^a_{\mu\vec{k}})$.

Performing the Fourier sum in Eq. (4.13) using Eq. (4.15) gives

$$Q_{\mu'\mu}(\xi_{l_0}) = \delta_{m_{\mu'},m_\mu}\frac{1}{V}\sum_{\vec{k}}\frac{1}{\pi^2}\int_{-\infty}^{\infty}dE\,dE'\,A_{\mu'\vec{k}}(E')A_{\mu\vec{k}}(E) \times\frac{n^a(E')-n^a(E)}{E-E'-\xi_{l_0}}.$$

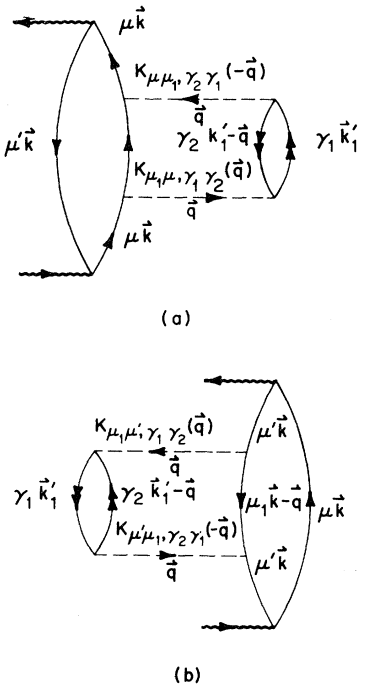

FIG. 3. Two second-order proper self-energy graphs.

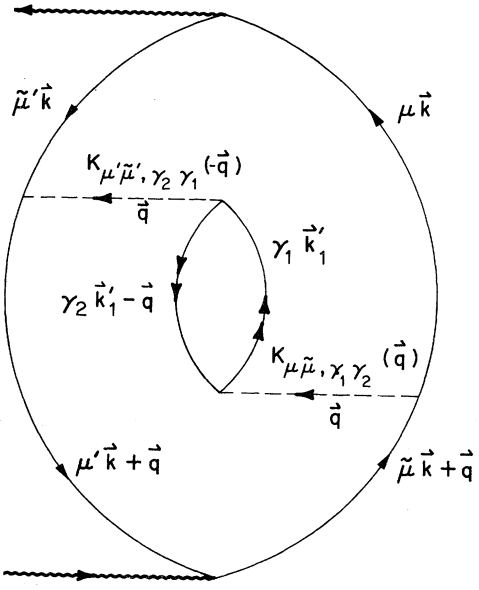

FIG. 4. Second-order vertex correction.

Carrying out the analytic continuation indicated by Eq. (4.3), and using Eq. (2.20), we obtain the following result for the line-shape function (for the case where vertex corrections are ignored),

$$f_{\mu'\mu}(\hbar\omega)=\left(\sum_{m_\mu}\sigma(m_\mu,m_\mu)\right)\frac{1}{V}\sum_{\vec{k}}\frac{1}{\pi^2}\int_{-\infty}^{\infty}dE\,dE'\,A_{\mu'\vec{k}}(E')A_{\mu\vec{k}}(E)n^a(E')[n^a(E)+1]\delta(E-E'-\hbar\omega)\,. \tag{4.19}$$

For the noninteracting system where $A_{\mu\vec{k}}(E)=\pi\delta(E-\epsilon^a_{\mu\vec{k}})$, we immediately recover the result of Eq. (2.22).

In Appendix A we demonstrate that calculating the first spectral moment from Eq. (4.19) without introducing further approximations yields exactly the (unphysical) result of the moment analysis. We now want to introduce a number of approximations before attempting to compute the first moment of the line-shape function. Although we shall refer to these approximations as "quasiparticle" approximations, they appear to be essentially equivalent to assumptions invoked in impact approximation theories of line shapes. Two features of the usual impact theories are (i) the assumption that the widths of the perturbed states are in some sense small and (ii) a further approximation such that the analysis is valid only near the line center, and may be expected to break down in the far wings.

Before proceeding further, it is convenient to introduce the spectral representation of the self-energy function. Because the first-order (Hartree) self-energy vanishes in the present problem, we can write

$$G^a_{\mu\vec{k}}(\xi^a_{i_1})=\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{dE'\,\Gamma_{\mu\vec{k}}(E')}{E'-\xi^a_{i_1}}\,, \tag{4.20}$$

where $\Gamma_{\mu\vec{k}}(E')=\mathrm{Im}G^a_{\mu\vec{k}}(E'+i0^+)$ is the imaginary part of the self-energy. From Eq. (4.20) one also obtains the Kramers-Kronig relation

$$\Delta_{\mu\vec{k}}(E)=\frac{\mathrm{Pr}}{\pi}\int_{-\infty}^{\infty}\frac{dE'\,\Gamma_{\mu\vec{k}}(E')}{E'-E}\,, \tag{4.21}$$

where $\Delta_{\mu\vec{k}}(E)=\mathrm{Re}\,G^a_{\mu\vec{k}}(E+i0^+)$ is the real part of the self-energy. The imaginary part of the self-energy as given by the graphs of Fig. 3 is readily found to be

$$\Gamma_{\mu\vec{k}}(E)=(1-e^{-\beta(E-\mu_a)})\frac{\pi}{V^2}\sum_{\vec{q}\vec{k}'_1}\sum_{\mu_1\gamma_1\gamma_2}g(\vec{q})^2\,|K_{\mu_1\mu,\gamma_1\gamma_2}(\vec{q})|^2\,n(\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}})[n(\epsilon^b_{\gamma_1\vec{k}'_1})+1][n(\epsilon^a_{\mu_1\vec{k}-\vec{q}})+1]$$
$$\times\delta(\epsilon^b_{\gamma_1\vec{k}'_1}-\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}}+\epsilon^a_{\mu_1\vec{k}-\vec{q}}-E)\,. \tag{4.22}$$

We now return to Eq. (4.19) and make some quasiparticle approximations before computing the spectral moments. We first assume that $A_{\mu'\vec{k}}(E')$ and $A_{\mu\vec{k}}(E)$ will be sharply peaked near the two quasiparticle energies $E^a_{\mu'\vec{k}}$ and $E^a_{\mu\vec{k}}$, respectively, which will be defined below. Hence we approximate the factor $n^a(E')[n^a(E)+1]$ by $n(E^a_{\mu'\vec{k}})[n(E^a_{\mu\vec{k}})+1]$. We then approximate the spectral density functions by simple Lorentzians with the self-energy evaluated at the unperturbed energies, i.e., take

$$A_{\mu'\vec{k}}(E')\simeq\frac{\Gamma_{\mu'\vec{k}}}{(E'-E^a_{\mu'\vec{k}})^2+\Gamma^2_{\mu'\vec{k}}}\,, \tag{4.23}$$

with $\Gamma_{\mu'\vec{k}}=\Gamma_{\mu'\vec{k}}(\epsilon^a_{\mu'\vec{k}})$ and where $E^a_{\mu'\vec{k}}=\epsilon^a_{\mu'\vec{k}}-\Delta_{\mu'\vec{k}}(\epsilon^a_{\mu'\vec{k}})$ is the quasiparticle energy. Performing the integration on dE in Eq. (4.19) then gives

$$f_{\mu'\mu}(\hbar\omega)\simeq\sum_{m_\mu}\sigma(m_\mu,m_\mu)\frac{1}{V}\sum_{\vec{k}}n(E^a_{\mu'\vec{k}})[n(E^a_{\mu\vec{k}})+1]$$
$$\times\frac{1}{\pi^2}\int_{-\infty}^{\infty}dE'\,A_{\mu'\vec{k}}(E')A_{\mu\vec{k}}(E'+\hbar\omega)\,.$$

Consider now the function

$$g(E')=(1/\pi^2)A_{\mu'\vec{k}}(E')A_{\mu\vec{k}}(E'+\hbar\omega)$$
$$\simeq\frac{1}{\pi^2}\frac{\Gamma_{\mu'\vec{k}}}{(E'-E^a_{\mu'\vec{k}})^2+\Gamma^2_{\mu'\vec{k}}}\frac{\Gamma_{\mu\vec{k}}}{(E'+\hbar\omega-E^a_{\mu\vec{k}})^2+\Gamma^2_{\mu\vec{k}}}\,. \tag{4.24}$$

Under the resonance condition

$$\hbar\omega\simeq\epsilon^a_{\mu\vec{k}}-\epsilon^a_{\mu'\vec{k}}\simeq E^a_{\mu\vec{k}}-E^a_{\mu'\vec{k}}\,,$$

the above function is seen to be sharply peaked near $E' = E^a_{\mu'\vec{k}}$. We turn it into a δ function by writing

$$g(E') = C_{\vec{k}}(\hbar\omega)\delta(E' - E^a_{\mu'\vec{k}}), \tag{4.25}$$

where $C_{\vec{k}}(\hbar\omega)$ is to be determined such that the normalization is correct, i.e.,

$$\int_{-\infty}^{\infty} g(E')\,dE' = C_{\vec{k}}(\hbar\omega). \tag{4.26}$$

This calculation is straightforward and gives

$$C_{\vec{k}}(\hbar\omega) = \frac{1}{\pi}\frac{\Gamma_{\mu\vec{k}} + \Gamma_{\mu'\vec{k}}}{(E^a_{\mu\vec{k}} - E^a_{\mu'\vec{k}} - \hbar\omega)^2 + (\Gamma_{\mu\vec{k}} + \Gamma_{\mu'\vec{k}})^2}. \tag{4.27}$$

With these approximations the line-shape function becomes simply the sum of Lorentzians

$$f_{\mu'\mu}(\hbar\omega) \simeq \sum_{m_\mu} \sigma(m_\mu, m_\mu)\frac{1}{V}\sum_{\vec{k}} n(E^a_{\mu'\vec{k}})[n(E^a_{\mu\vec{k}}) + 1]\frac{1}{\pi}\frac{\Gamma_{\mu\vec{k}} + \Gamma_{\mu'\vec{k}}}{(E^a_{\mu\vec{k}} - E^a_{\mu'\vec{k}} - \hbar\omega)^2 + (\Gamma_{\mu\vec{k}} + \Gamma_{\mu'\vec{k}})^2}. \tag{4.28}$$

The moments of this function are readily computed, and we obtain

$$M^{(1)}_{\mu'\mu} = (\epsilon^a_\mu - \epsilon^a_{\mu'})M^{(0)}_{\mu'\mu} - \sum_{m_\mu} \sigma(m_\mu, m_\mu)\frac{1}{V}\sum_{\vec{k}} n(E^a_{\mu'\vec{k}})[n(E^a_{\mu\vec{k}}) + 1][\Delta_{\mu\vec{k}}(\epsilon^a_{\mu\vec{k}}) - \Delta_{\mu'\vec{k}}(\epsilon^a_{\mu'\vec{k}})], \tag{4.29}$$

with

$$M^{(0)}_{\mu'\mu} = \sum_{m_\mu} \sigma(m_\mu, m_\mu)\frac{1}{V}\sum_{\vec{k}} n(E^a_{\mu'\vec{k}})[n(E^a_{\mu\vec{k}}) + 1]. \tag{4.30}$$

Again one obtains $\langle\hbar\omega\rangle$ by dividing (4.29) by $M^{(0)}_{\mu'\mu}$, and because the Δ's are already of second order in the interaction, the correction term can be evaluated setting $n(E^a_{\mu'\vec{k}}) \simeq n(\epsilon^a_{\mu'\vec{k}})$, $n(E^a_{\mu\vec{k}}) \simeq n(\epsilon^a_{\mu\vec{k}})$.

The result (4.29) now makes good sense physically. In Appendix A we demonstrate that this same result can be derived by making a simple modification in the formula obtained from the moment method calculation of Sec. III. When a similar modification is applied to the vertex corrections (see Appendix A) we find that the modified first moment can be written

$$M^{(1)}_{\mu'\mu} = (\epsilon^a_\mu - \epsilon^a_{\mu'})M^{(0)}_{\mu'\mu} - \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'})\delta_{m_\mu, m_{\mu'}}\frac{1}{V}\sum_{\vec{k}} n(\epsilon^a_{\mu'\vec{k}})[n(\epsilon^a_{\mu\vec{k}}) + 1][\Delta_{\mu\vec{k}}(\epsilon^a_{\mu\vec{k}}) - \Delta_{\mu'\vec{k}}(\epsilon^a_{\mu'\vec{k}})]$$
$$+ \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'})\frac{1}{V}\sum_{\vec{k}} n(\epsilon^a_{\mu'\vec{k}})[n(\epsilon^a_{\mu\vec{k}}) + 1][\chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}) - \chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu'\vec{k})], \tag{4.31}$$

with

$$\chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}) = \frac{\mathrm{Pr}}{\pi}\int_{-\infty}^{\infty}\frac{dE\,\phi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}, E)}{E - \epsilon^a_{\mu\vec{k}}}, \tag{4.32}$$

and where $\phi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}, E)$ is given by

$$\phi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}, E) = (e^{\beta(E-\mu_a)} - 1)\frac{\pi}{V^2}\sum_{\vec{q}\vec{k}_1'}\sum_{\gamma_1\gamma_2} g(\vec{q})^2 K_{\mu\tilde{\mu},\gamma_1\gamma_2}(\vec{q})K_{\mu'\tilde{\mu}',\gamma_2\gamma_1}(-\vec{q})$$
$$\times n(\epsilon^b_{\gamma_2\vec{k}_1'-\vec{q}})[n(\epsilon^b_{\gamma_1\vec{k}_1'}) + 1]n(\epsilon^a_{\mu\vec{k}+\vec{q}})\delta(\epsilon^b_{\gamma_2\vec{k}_1'-\vec{q}} - \epsilon^b_{\gamma_1\vec{k}_1'} + \epsilon^a_{\mu\vec{k}+\vec{q}} - E). \tag{4.33}$$

From Eqs. (4.21), (4.22), (4.32), and (4.33) explicit expressions for $\Delta_{\mu\vec{k}}(\epsilon^a_{\mu\vec{k}})$ and $\chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k})$ can readily be obtained. Finally one obtains $\langle\hbar\omega\rangle$ by dividing Eq. (4.31) by $M^{(0)}_{\mu'\mu}$ as given by Eq. (3.16).

In Sec. V we will find that all of this considerably simplifies in the dilute-gas limit. We find in this limit that the vertex corrections cancel out, because $\chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}) = \chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu'\vec{k})$ for the dilute gas.

V. REDUCTION OF FORMULAS

In the dilute-gas limit we have $n(\epsilon^a_{\mu\vec{k}}) \simeq e^{-\beta(\epsilon^a_{\mu\vec{k}} - \mu_a)} \ll 1$ and similarly for $n(\epsilon^b_{\gamma\vec{k}})$. From the formulas given in Sec. IV one readily finds that μ_a cancels out of the expression for $\langle\hbar\omega\rangle$. The chemical po-

tential μ_b can be eliminated in terms of the partial pressure P_b using Eqs. (2.11)–(2.13), i.e., using

$$\beta P_b = e^{\beta\mu_b}\frac{1}{V}\sum_{\vec{k}\gamma} e^{-\epsilon^b_{\gamma\vec{k}}} = e^{\beta\mu_b}\sum_{\gamma} e^{-\beta\epsilon^b_\gamma}\frac{1}{V}\sum_{\vec{k}} e^{-\beta\epsilon^b_{\vec{k}}}. \tag{5.1}$$

It is convenient to introduce the normalized Boltzmann distribution functions

$$\rho(\epsilon^{a,b}_{\vec{k}}) = \frac{(1/V)e^{-\beta\epsilon^{a,b}_{\vec{k}}}}{(1/V)\sum_{\vec{k}} e^{-\beta\epsilon^{a,b}_{\vec{k}}}}, \tag{5.2}$$

$$\rho(\epsilon^{a,b}_{\mu,\gamma}) = \frac{e^{-\beta\epsilon^{a,b}_{\mu,\gamma}}}{\sum_{(\mu \text{ or } \gamma)} e^{-\beta\epsilon^{a,b}_{\mu,\gamma}}}, \tag{5.3}$$

where $\epsilon^{a,b}_{\mu,\gamma}$ stands for ϵ^a_μ or ϵ^b_γ and similarly for $\epsilon^{a,b}_{\vec{k}}$. We then find

$$\langle\hbar\omega\rangle = (\epsilon^a_\mu - \epsilon^a_{\mu'}) - [(\Delta\omega)_{SE} - (\Delta\omega)_{VX}], \tag{5.4}$$

where the self-energy contribution is

$$(\Delta\omega)_{SE} = \left(\sum_{m_\mu}\sigma(m_\mu, m_\mu)\right)^{-1}\sum_{m_\mu m_{\mu'}}\sigma(m_\mu, m_{\mu'})\delta_{m_\mu, m_{\mu'}}\sum_{\vec{k}}\rho(\epsilon^a_{\vec{k}})[\Delta_{\mu\vec{k}}(\epsilon^a_{\mu\vec{k}}) - \Delta_{\mu'\vec{k}}(\epsilon^a_{\mu'\vec{k}})] \tag{5.5}$$

and the vertex contribution is

$$(\Delta\omega)_{VX} = \left(\sum_{m_\mu}\sigma(m_\mu, m_\mu)\right)^{-1}\sum_{m_\mu m_{\mu'}}\sigma(m_\mu, m_{\mu'})\sum_{\vec{k}}\rho(\epsilon^a_{\vec{k}})[\chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}) - \chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu'\vec{k})]. \tag{5.6}$$

In the dilute-gas limit we also find

$$\Delta_{\mu\vec{k}}(\epsilon^a_{\mu\vec{k}}) = \frac{P_b\beta}{V}\sum_{\vec{q}\vec{k}'_1}\sum_{\mu_1\gamma_1\gamma_2} g(\vec{q})^2\left|K_{\mu_1\mu,\gamma_1\gamma_2}(\vec{q})\right|^2 \Pr\frac{\rho(\epsilon^b_{\gamma_2})\rho(\epsilon^b_{\vec{k}'_1-\vec{q}})}{\epsilon^a_{\mu_1\vec{k}-\vec{q}} - \epsilon^a_{\mu\vec{k}} + \epsilon^b_{\gamma_1\vec{k}'_1} - \epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}}}, \tag{5.7}$$

$$\chi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}) = \frac{P_b\beta}{V}\sum_{\vec{q}\vec{k}'_1}\sum_{\gamma_1\gamma_2} g(\vec{q})^2 K_{\mu\tilde{\mu},\gamma_1\gamma_2}(\vec{q})K_{\mu'\tilde{\mu}',\gamma_2\gamma_1}(-\vec{q})\Pr\frac{\rho(\epsilon^b_{\gamma_1})\rho(\epsilon^b_{\vec{k}'_1})}{\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}} - \epsilon^b_{\gamma_1\vec{k}'_1} + \epsilon^a_{\mu\vec{k}+\vec{q}} - \epsilon^a_{\mu\vec{k}}}. \tag{5.8}$$

We now note that the vertex contributions in Eq. (5.6) cancel out because the energy denominator in Eq. (5.8) is seen to be independent of the internal energy ϵ^a_μ. Thus, although the vertex corrections must contribute to the linewidth, we find that they cancel out of the expression for the line shift. We mention in passing that there are also simple cases where the χ's themselves vanish due to the vanishing of the matrix elements $K_{\mu\tilde{\mu},\gamma_1\gamma_2}$ and $K_{\mu'\tilde{\mu}',\gamma_2\gamma_1}$. This has been noted previously by ATC for the case of a rigid linear a molecule whose interaction with the perturbers is through its dipole moment, i.e., they find that $S_2(b)_{\text{middle}}$ vanishes in this case.

We next put $(\Delta\omega)_{SE}$ in a form where the summations over the degeneracy indices can be easily carried out. We can write

$$(\Delta\omega)_{SE} = P_b\beta\left(\sum_{m_\mu}\sigma(m_\mu, m_\mu)\right)^{-1}\sum_{m_\mu m_{\mu'}}\sigma(m_\mu, m_{\mu'})\delta_{m_\mu, m_{\mu'}}\frac{1}{V}\sum_{\vec{q}}\sum_{\mu_1\gamma_1\gamma_2}\rho(\epsilon^b_{\gamma_2})g(\vec{q})^2$$
$$\times[\left|K_{\mu_1\mu,\gamma_1\gamma_2}(\vec{q})\right|^2\gamma_{\vec{q}}(\epsilon^a_\mu, \epsilon^a_{\mu_1}, \epsilon^b_{\gamma_2}, \epsilon^b_{\gamma_1}) - \left|K_{\mu_1\mu',\gamma_1\gamma_2}(\vec{q})\right|^2\gamma_{\vec{q}}(\epsilon^a_{\mu'}, \epsilon^a_{\mu_1}, \epsilon^b_{\gamma_2}, \epsilon^b_{\gamma_1})], \tag{5.9}$$

with

$$\gamma_{\vec{q}}(\epsilon^a_\mu, \epsilon^a_{\mu_1}, \epsilon^b_{\gamma_2}, \epsilon^b_{\gamma_1}) = \sum_{\vec{k}\vec{k}'_1}\rho(\epsilon^a_{\vec{k}})\rho(\epsilon^b_{\vec{k}'_1-\vec{q}})\Pr\frac{1}{\epsilon^a_{\mu_1\vec{k}-\vec{q}} - \epsilon^a_{\mu\vec{k}} + \epsilon^b_{\gamma_1\vec{k}'_1} - \epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}}}. \tag{5.10}$$

The important point, in reducing the results further, is to note that when the sums over $\vec{k}$ and $\vec{k}'_1$ in Eq. (5.10) are carried out, $\gamma_{\vec{q}}$ can only be a function of $|\vec{q}|$. Thus, $g(\vec{q})^2\gamma_{\vec{q}}$ is spherically symmetric. One can then perform the angular integration over $\vec{q}$, after which it is relatively easy to perform the summations over the degeneracy indices.

We now give the results of this calculation for the case of dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. First define

$$L^{(n)}(\epsilon^a_\mu, \epsilon^a_{\mu_1}, \epsilon^b_{\gamma_2}, \epsilon^b_{\gamma_1}) = \frac{1}{V}\sum_{\vec{q}} q^n g(\vec{q})^2\gamma_{\vec{q}}(\epsilon^a_\mu, \epsilon^a_{\mu_1}, \epsilon^b_{\gamma_2}, \epsilon^b_{\gamma_1}). \tag{5.11}$$

We consider first the dipole-dipole case. When the angular integration over $\vec{q}$ is performed in Eq. (5.9) we find

$$(\Delta\omega)_{SE}=\frac{P_b\beta}{15}\Big(\sum_{m_\mu}\sigma(m_\mu,m_\mu)\Big)^{-1}\sum_{m_\mu m'_\mu}\sigma(m_\mu,m_{\mu'})\delta_{m_\mu,m_{\mu'}}\sum_{\mu_1\gamma_1\gamma_2}\rho(\epsilon^b_{\gamma_2})$$
$$\times\{L^{(4)}(\epsilon^a_\mu,\epsilon^a_{\mu_1},\epsilon^b_{\gamma_2},\epsilon^b_{\gamma_1})[|\langle\mu_1|\vec{d}_a|\mu\rangle|^2|\langle\gamma_1|\vec{d}_b|\gamma_2\rangle|^2-\tfrac{2}{3}|\langle\mu_1|\vec{d}_a|\mu\rangle\cdot\langle\gamma_1|\vec{d}_b|\gamma_2\rangle|^2+|\langle\mu_1|\vec{d}_a|\mu\rangle\cdot\langle\gamma_1|\vec{d}_b|\gamma_2\rangle^*|^2]$$
$$-(\text{same with }\mu\to\mu')\}. \tag{5.12}$$

Using the Wigner-Eckart theorem, we can write

$$\langle\mu_1|\vec{d}_a|\mu\rangle=\langle j_{\mu_1}\|d_a\|j_\mu\rangle\{(J_\mu 1-m_\mu 0|J_\mu 1J_{\mu_1}-m_\mu)\hat{z}\,\delta_{m_{\mu_1},m_\mu}$$
$$-(J_\mu 1-m_\mu-1|J_\mu 1J_{\mu_1}(-m_\mu-1))[(\hat{x}-i\hat{y})/\sqrt{2}]\delta_{m_{\mu_1},m_\mu+1}$$
$$+(J_\mu 1-m_\mu 1|J_\mu 1J_{\mu_1}(-m_\mu+1))[(\hat{x}+i\hat{y})/\sqrt{2}]\delta_{m_{\mu_1},m_\mu-1}\}. \tag{5.13}$$

Here the reduced matrix element $\langle j_{\mu_1}\|d_a\|j_\mu\rangle$ is to be calculated in the usual way.[48] For the special case of rigid symmetric-top molecules with $|j_\mu m_\mu\rangle=|J_\mu K_\mu m_\mu\rangle$, where K_μ denotes the projection of J_μ along the symmetry axis ($K_\mu=0$ for linear molecules), it evaluates to give

$$\langle j_{\mu_1}\|d_a\|j_\mu\rangle=|\vec{d}_a|\,\delta_{K_{\mu_1},K_\mu}\Big(\frac{2J_\mu+1}{2J_{\mu_1}+1}\Big)^{1/2}(J_\mu 1-K_\mu 0|J_\mu 1J_{\mu_1}-K_\mu). \tag{5.14}$$

The reader may consult the appendix of TC for the details of this calculation. Using Eq. (5.13), the sums over the degeneracy indices in Eq. (5.12) can be carried out using various well-known theorems concerning Clebsch-Gordan coefficients. When the sums over m_{μ_1}, m_{γ_1}, m_{γ_2} are carried out in Eq. (5.12), the result is found to be independent of $m_\mu=m_{\mu'}$. Hence the factor of $[\sum_{m_\mu}\sigma(m_\mu,m_\mu)]^{-1}$ cancels out of Eq. (5.12). The final result for the dipole-dipole case is

$$(\Delta\omega)_{SE}=\tfrac{2}{27}(P_b\beta)\sum_{j_{\gamma_1}j_{\gamma_2}}\rho(\epsilon^b_{\gamma_2})(2J_{\gamma_1}+1)|\langle j_{\gamma_1}\|d_b\|j_{\gamma_2}\rangle|^2\sum_{j_{\mu_1}}\Big(\frac{2J_{\mu_1}+1}{2J_\mu+1}|\langle j_{\mu_1}\|d_a\|j_\mu\rangle|^2L^{(4)}(\epsilon^a_\mu,\epsilon^a_{\mu_1},\epsilon^b_{\gamma_2},\epsilon^b_{\gamma_1})$$
$$-\frac{2J_{\mu_1}+1}{2J_{\mu'}+1}|\langle j_{\mu_1}\|d_a\|j_{\mu'}\rangle|^2L^{(4)}(\epsilon^a_{\mu'},\epsilon^a_{\mu_1},\epsilon^b_{\gamma_2},\epsilon^b_{\gamma_1})\Big). \tag{5.15}$$

Next we consider the case of dipole-quadrupole interactions. Applying the Wigner-Eckart theorem, the matrix elements of the traceless quadrupole moment can be written

$$\langle\gamma_1|\vec{Q}^t_b|\gamma_2\rangle=\langle j_{\gamma_1}\|Q^t_b\|j_{\gamma_2}\rangle\{\delta_{m_{\gamma_1},m_{\gamma_2}}(J_{\gamma_2}2-m_{\gamma_2}0|J_{\gamma_2}2J_{\gamma_1}-m_{\gamma_2})\tfrac{2}{3}[\hat{z}\hat{z}-\tfrac{1}{2}\hat{x}\hat{x}-\tfrac{1}{2}\hat{y}\hat{y}]$$
$$+\delta_{m_{\gamma_1},m_{\gamma_2}+2}(J_{\gamma_2}2-m_{\gamma_2}-2|J_{\gamma_2}2J_{\gamma_1}(-m_{\gamma_2}-2))\tfrac{1}{2}\sqrt{\tfrac{2}{3}}[(\hat{x}\hat{x}-\hat{y}\hat{y})-i(\hat{x}\hat{y}+\hat{y}\hat{x})]$$
$$+\delta_{m_{\gamma_1},m_{\gamma_2}-2}(J_{\gamma_2}2-m_{\gamma_2}2|J_{\gamma_2}2J_{\gamma_1}(-m_{\gamma_2}+2))\tfrac{1}{2}\sqrt{\tfrac{2}{3}}[(\hat{x}\hat{x}-\hat{y}\hat{y})+i(\hat{x}\hat{y}+\hat{y}\hat{x})]$$
$$-\delta_{m_{\gamma_1},m_{\gamma_2}+1}(J_{\gamma_2}2-m_{\gamma_2}-1|J_{\gamma_2}2J_{\gamma_1}(-m_{\gamma_2}-1))\tfrac{1}{2}\sqrt{\tfrac{2}{3}}[(\hat{z}\hat{x}+\hat{x}\hat{z})-i(\hat{z}\hat{y}+\hat{y}\hat{z})]$$
$$+\delta_{m_{\gamma_1},m_{\gamma_2}-1}(J_{\gamma_2}2-m_{\gamma_2}1|J_{\gamma_2}2J_{\gamma_1}(-m_{\gamma_2}+1))\tfrac{1}{2}\sqrt{\tfrac{2}{3}}[(\hat{z}\hat{x}+\hat{x}\hat{z})+i(\hat{z}\hat{y}+\hat{y}\hat{z})]\}. \tag{5.16}$$

For the case of a rigid symmetric-top molecule the reduced matrix element is

$$\langle j_{\gamma_1}\|Q^t_b\|j_{\gamma_2}\rangle=|\vec{Q}_b|\,\delta_{K_{\gamma_1},K_{\gamma_2}}\Big(\frac{2J_{\gamma_2}+1}{2J_{\gamma_1}+1}\Big)^{1/2}(J_{\gamma_2}2-K_{\gamma_2}0|J_{\gamma_2}2J_{\gamma_1}-K_{\gamma_2}), \tag{5.17}$$

where $|\vec{Q}_b|=\sum_\beta e_{b\beta}f_\beta(b)^2_{z'z'}$ is one-half the definition given by TC, and where z' denotes the symmetry axis. The remainder of the calculation proceeds in the same fashion as for the dipole-dipole case. The final result for the case of dipole-quadrupole interactions can be written

$$(\Delta\omega)_{SE}=\frac{P_b\beta}{225}\sum_{j_{\gamma_1}j_{\gamma_2}}\rho(\epsilon^b_{\gamma_2})(2J_{\gamma_1}+1)\left|\langle j_{\gamma_1}\|Q^t_b\|j_{\gamma_2}\rangle\right|^2\sum_{j_{\mu_1}}\left(\frac{2J_{\mu_1}+1}{2J_\mu+1}\left|\langle j_{\mu_1}\|d_a\|j_\mu\rangle\right|^2L^{(6)}(\epsilon^a_\mu,\epsilon^a_{\mu_1},\epsilon^b_{\gamma_2},\epsilon^b_{\gamma_1})\right.$$
$$\left.-\frac{2J_{\mu_1}+1}{2J_{\mu'}+1}\left|\langle j_{\mu_1}\|d_a\|j_{\mu'}\rangle\right|^2L^{(6)}(\epsilon^a_{\mu'},\epsilon^a_{\mu_1},\epsilon^b_{\gamma_2},\epsilon^b_{\gamma_1})\right). \tag{5.18a}$$

In the case that the dipole-quadrupole interaction arising from matrix elements of Q^t_a and d_b is also important, the total shift is given by Eq. (5.18a), plus an additional term which simply replaces $Q^t_b\to d_b$, $d_a\to Q^t_a$. A similar, rather tedious, calculation yields the following result for the case of quadrupole-quadrupole interactions:

$$(\Delta\omega)_{SE}=\tfrac{2}{7875}P_b\beta\sum_{j_{\gamma_1}j_{\gamma_2}}\rho(\epsilon^b_{\gamma_2})(2J_{\gamma_1}+1)\left|\langle j_{\gamma_1}\|Q^t_b\|j_{\gamma_2}\rangle\right|^2\sum_{j_{\mu_1}}\left(\frac{2J_{\mu_1}+1}{2J_\mu+1}\left|\langle j_{\mu_1}\|Q^t_a\|j_\mu\rangle\right|^2L^{(8)}(\epsilon^a_\mu,\epsilon^a_{\mu_1},\epsilon^b_{\gamma_2},\epsilon^b_{\gamma_1})\right.$$
$$\left.-\frac{2J_{\mu_1}+1}{2J_{\mu'}+1}\left|\langle j_{\mu_1}\|Q^t_a\|j_{\mu'}\rangle\right|^2L^{(8)}(\epsilon^a_{\mu'},\epsilon^a_{\mu_1},\epsilon^b_{\gamma_2},\epsilon^b_{\gamma_1})\right). \tag{5.18b}$$

It may also be shown that when all three interactions discussed above are simultaneously present and important, the contribution to the shift is just the sum of the shifts given by Eqs. (5.15), (5.18a), (5.18b), i.e., there are no interference terms between the various multipole interactions. This conclusion is in agreement with a similar result obtained from ATC theory for second-order broadening due to multipole interactions.

We turn next to the function $\gamma^-_{\tilde q}(\epsilon^a_\mu,\epsilon^a_{\mu_1},\epsilon^b_{\gamma_2},\epsilon^b_{\gamma_1})$ as given by Eq. (5.10). Using the separable property of the energies, this can be written as $\gamma^-_{\tilde q}(\Delta E_\mu)$, where $\Delta E_\mu=(\epsilon^a_{\mu_1}-\epsilon^a_\mu)+(\epsilon^b_{\gamma_1}-\epsilon^b_{\gamma_2})$. Although the integrations over d^3k and $d^3k'_1$ in Eq. (5.10) appear to be rather complicated, we show in Appendix B that $\gamma^-_{\tilde q}(\Delta E_\mu)$ can be put in the remarkably simple form

$$\gamma^-_{\tilde q}(\Delta E_\mu)=\frac{1}{\sqrt{2\pi}}\left(\frac{\beta m}{\hbar^2q^2}\right)^{1/2}\Pr\int_{-\infty}^{\infty}\frac{dE'\exp(-\beta mE'^2/2\hbar^2q^2)}{\Delta E_\mu+\hbar^2q^2/2m-E'}, \tag{5.19}$$

where $m=M_aM_b/(M_a+M_b)$ is the reduced mass of the colliding molecules. Equation (5.19) expresses $\gamma^-_{\tilde q}(\Delta E_\mu)$ as the Hilbert transform of a simple Gaussian. This transform is known[52] and can be expressed in terms of the error function of imaginary argument.[53] The result can be written

$$\gamma^-_{\tilde q}(\Delta E_\mu)=(2\beta m/\hbar^2q^2)^{1/2}f(y), \tag{5.20}$$

with

$$f(y)=e^{-y^2}\int_0^y e^{t^2}\,dt=e^{-y^2}\,\mathrm{erfi}(y), \tag{5.21}$$

and with

$$y=(\beta m/2\hbar^2q^2)^{1/2}(\hbar^2q^2/2m+\Delta E_\mu). \tag{5.22}$$

The properties of the function $f(y)$ are easily deduced.[54] The function is an odd function of y (positive for $y>0$), with the asymptotic behavior

$$f(y)\simeq 1/2y \quad \text{as} \quad |y|\to\infty, \tag{5.23}$$

and with a maximum and minimum occurring near $y_{max}\simeq 0.92$, $y_{min}\simeq -0.92$.

From the above result one sees if $\hbar^2q^2/2m\gg\Delta E_\mu$ that y and $f(y)$ are positive and that the maximum value of $f(y)$ occurs for $\hbar^2q^2/2m\simeq 3.38k_BT$, i.e., the maximum occurs for $\hbar^2q^2/2m$ of order thermal kinetic energies. This might suggest that the inelasticity ΔE_μ plays a minor role if $\Delta E_\mu\ll k_BT$. This conclusion turns out to be misleading because the minimum cut-off length (r_c) leads to a convergence factor e^{-2qr_c} in Eq. (5.11) which constrains the important values of q to be $q\lesssim 1/2r_c$. With r_c of order angstroms, a rough calculation shows that $\hbar^2/8mr_c^2$ can be substantially smaller than thermal kinetic energies for typical molecular constituents. This point is important because if one could make the elastic collision approximation $\Delta E_\mu\simeq\Delta E_{\mu'}\simeq 0$, then it is possible to show from Eqs. (5.14), (5.15), and (5.18) that the self-energy shifts would cancel for rigid symmetric-top molecules.

Next we insert Eq. (5.20) into Eq. (5.11), perform the angular integration over $\tilde{\mathbf{q}}$ (which simply gives a factor of 4π), and obtain

$$L^{(n)}(\Delta E_\mu)=8\left(\frac{2\beta m}{\hbar^2}\right)^{1/2}\int_0^\infty dq\,q^{n-3}e^{-2qr_c}f(y), \tag{5.24}$$

where $f(y)$ is given by Eq. (5.21). The integral over dq is the *only* remaining integration in the present theory. Here we simply wish to study the

sensitivity of Eq. (5.24) to the cut-off parameter r_c, which should typically be of the order of a few angstroms, but whose proper choice is always somewhat uncertain.

For every multipole interaction of interest $n = 4, 6, \ldots$, the integral (5.24) is surely divergent at large q if r_c is allowed to approach zero. This follows from the asymptotic behavior [Eq. (5.23)] of $f(y)$, which gives $f(y) \propto q^{-1}$ as $q \to \infty$. Hence if $r_c \to 0$, Eq. (5.24) diverges like $1/r_c$ for the dipole-dipole case ($n = 4$), diverges like $1/r_c^3$ for the dipole-quadrupole case ($n = 6$), etc. This means that the results will indeed be sensitive to the choice of r_c. At first sight it appears that this dependence is reduced in the present theory as compared to the second-order results of ATC theory for broadening which diverge as one higher power of $1/b_0$, where b_0 is the minimum impact parameter, for each order of multipole interaction. This again turns out to be misleading because, from physical considerations, the limit $r_c \to 0$ is not appropriate. Whether one identifies r_c with the kinetic diameter, effective hard-sphere radius, etc., typical values of r_c correspond to a few angstroms. With this sort of estimate for r_c, and for typical reduced molecular masses m, we have found from rough calculations that the dependence of the function $L^{(n)}(\Delta E_\mu)$ [as given by Eq. (5.24)] on the cut-off parameter r_c is approximately the same as what one would expect from the ATC classical path approach. This is a reflection of the fact that the classical path approximation is reasonably well justified for intermolecular collisions.

To perform detailed numerical calculations from these formulas, one must evaluate the integral (5.24) and carry out the sums over states in Eqs. (5.15), (5.18a), and (5.18b). This should be amenable to high-speed computer calculation provided that the various matrix elements and energies are known.

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APPENDIX A

The explicit expressions[50] for the quantities $\Sigma(\mu\vec{k})$ and $\psi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k})$ which appear in Eq. (3.15) (derived from the moment method) are

$$\Sigma(\mu\vec{k}) = \frac{n(\epsilon^a_{\mu\vec{k}})}{V^2} \sum_{\vec{q}\vec{k}'_1} \sum_{\mu_1\gamma_1\gamma_2} g(\vec{q})^2 \left| K_{\mu_1\mu,\gamma_1\gamma_2}(\vec{q}) \right|^2 [n(\epsilon^a_{\mu_1\vec{k}-\vec{q}}) + 1] n(\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}}) [n(\epsilon^b_{\gamma_1\vec{k}'_1}) + 1]$$
$$\times \frac{\exp[\beta(\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}} - \epsilon^b_{\gamma_1\vec{k}'_1} + \epsilon^a_{\mu\vec{k}} - \epsilon^a_{\mu_1\vec{k}-\vec{q}})] - 1}{\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}} - \epsilon^b_{\gamma_1\vec{k}'_1} + \epsilon^a_{\mu\vec{k}} - \epsilon^a_{\mu_1\vec{k}-\vec{q}}} , \tag{A1}$$

$$\psi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}) = [n(\epsilon^a_{\mu\vec{k}}) + 1] \frac{1}{V^2} \sum_{\vec{q}\vec{k}'_1} \sum_{\gamma_1\gamma_2} g(\vec{q})^2 K_{\mu\tilde{\mu},\gamma_1\gamma_2}(\vec{q}) K_{\mu'\tilde{\mu}',\gamma_2\gamma_1}(-\vec{q}) n(\epsilon^a_{\mu\vec{k}+\vec{q}}) n(\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}}) [n(\epsilon^b_{\gamma_1\vec{k}'_1}) + 1]$$
$$\times \frac{\exp[\beta(\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}} - \epsilon^b_{\gamma_1\vec{k}'_1} + \epsilon^a_{\mu\vec{k}+\vec{q}} - \epsilon^a_{\mu\vec{k}})] - 1}{\epsilon^b_{\gamma_2\vec{k}'_1-\vec{q}} - \epsilon^b_{\gamma_1\vec{k}'_1} + \epsilon^a_{\mu\vec{k}+\vec{q}} - \epsilon^a_{\mu\vec{k}}} . \tag{A2}$$

Note that there is no singularity in these expressions when the energy denominators vanish.

Next, for the case where vertex corrections are ignored, we show how to derive the moment calculation result [Eq. (3.15)] using the graphical line-shape formula given in Eq. (4.19). We begin by observing from Eq. (A1) and Eq. (4.22) that $\Sigma(\mu\vec{k})$ can be expressed in terms of the imaginary part of the self-energy according to

$$\Sigma(\mu\vec{k}) = \frac{1}{\pi} \int_{-\infty}^{\infty} dE\, \Gamma_{\mu\vec{k}}(E) \frac{n(\epsilon^a_{\mu\vec{k}}) - n^a(E)}{E - \epsilon^a_{\mu\vec{k}}} . \tag{A3}$$

Notice also, from the Kramers-Kronig relation (4.21), that one term in this expression is just $n(\epsilon^a_{\mu\vec{k}}) \Delta_{\mu\vec{k}}(\epsilon^a_{\mu\vec{k}})$.

Now we compute the zeroth and first moments of the line-shape function using Eq. (4.19) and find

$$M^{(0)}_{\mu',\mu} = \sum_{m_\mu} \sigma(m_\mu, m_\mu) \frac{1}{V} \sum_{\vec{k}} n^a_{\mu',\vec{k}} (n_{\mu\vec{k}} + 1) , \tag{A4}$$

$$M^{(1)}_{\mu',\mu} = \sum_{m_\mu} \sigma(m_\mu, m_\mu) \frac{1}{V} \sum_{\vec{k}} \left(n^a_{\mu',\vec{k}} \frac{1}{\pi} \int_{-\infty}^{\infty} dE\, E A_{\mu\vec{k}}(E)[n^a(E)+1] - (n^a_{\mu\vec{k}}+1) \frac{1}{\pi} \int_{-\infty}^{\infty} dE\, E A_{\mu',\vec{k}}(E) n^a(E) \right) . \tag{A5}$$

In obtaining these results we have used the sum rules (4.17) and (4.18). Consider next the integral

$$I = \frac{1}{\pi} \int_{-\infty}^{\infty} dE\, E A_{\mu\vec{k}}(E)[n^a(E)+1]$$

$$= \frac{1}{\pi} \int_{-\infty}^{\infty} dE\, \mathrm{Im}\{E \bar{D}^a_{\mu\vec{k}}(E+i0^+)[n^a(E)+1]\} . \tag{A6}$$

We write $E = \epsilon^a_{\mu\vec{k}} - G^a_{\mu\vec{k}}(E+i0^+) - \bar{D}^a_{\mu\vec{k}}(E+i0^+)^{-1}$, insert this into Eq. (A6), and note that one term vanishes because

$$\mathrm{Im}\{\bar{D}^a_{\mu\vec{k}}(E+i0^+)^{-1} \bar{D}^a_{\mu\vec{k}}(E+i0^+)[n^a(E)+1]\} = \mathrm{Im}[n^a(E)+1] = 0 .$$

This gives

$$I = \epsilon^a_{\mu\vec{k}}(n^a_{\mu\vec{k}}+1) - \frac{1}{\pi} \int_{-\infty}^{\infty} dE\, [n^a(E)+1]\, \mathrm{Im}[G^a_{\mu\vec{k}}(E+i0^+) \bar{D}^a_{\mu\vec{k}}(E+i0^+)] , \tag{A7}$$

where we have again used the sum rules (4.17) and (4.18). From this calculation we obtain

$$M^{(1)}_{\mu',\mu} = (\epsilon^a_\mu - \epsilon^a_{\mu'}) M^{(0)}_{\mu',\mu} - \sum_{m_\mu} \sigma(m_\mu, m_\mu) \frac{1}{V} \sum_{\vec{k}} \left(n^a_{\mu',\vec{k}} \frac{1}{\pi} \int_{-\infty}^{\infty} dE [n^a(E)+1]\, \mathrm{Im}[G^a_{\mu\vec{k}}(E+i0^+) \bar{D}^a_{\mu\vec{k}}(E+i0^+)] \right.$$

$$\left. - (n^a_{\mu\vec{k}}+1) \frac{1}{\pi} \int_{-\infty}^{\infty} dE\, n^a(E)\, \mathrm{Im}[G^a_{\mu',\vec{k}}(E+i0^+) \bar{D}^a_{\mu',\vec{k}}(E+i0^+)] \right) . \tag{A8}$$

Since the G's in the correction term are already of second order in the interaction, we can evaluate the rest of the expression to zeroth order. Thus, we can set $n^a_{\mu',\vec{k}} = n(\epsilon^a_{\mu',\vec{k}})$, $n^a_{\mu\vec{k}} = n(\epsilon^a_{\mu\vec{k}})$, and replace the $\bar{D}$'s by unperturbed propagators, which gives

$$\mathrm{Im}\{G^a_{\mu\vec{k}}(E+i0^+) D^a_{\mu\vec{k}}(E+i0^+)] = \Gamma_{\mu\vec{k}}(E) \frac{\mathrm{Pr}}{\epsilon^a_{\mu\vec{k}} - E} + \pi \delta(\epsilon^a_{\mu\vec{k}} - E) \Delta_{\mu\vec{k}}(E) . \tag{A9}$$

From this last relation we note that

$$\int_{-\infty}^{\infty} dE\, \mathrm{Im}[G^a_{\mu\vec{k}}(E+i0^+) D^a_{\mu\vec{k}}(E+i0^+)] = \pi \Delta_{\mu\vec{k}}(\epsilon^a_{\mu\vec{k}}) + \mathrm{Pr} \int_{-\infty}^{\infty} \frac{dE\, \Gamma_{\mu\vec{k}}(E)}{\epsilon^a_{\mu\vec{k}} - E} = 0 , \tag{A10}$$

because of the Kramers-Kronig relation (4.21). This result tells us that we can replace the factor $[n^a(E)+1]$ in Eq. (A8) by $n^a(E)$. Using Eqs. (A8), (A9), and the Kramers-Kronig relation (4.21) we then obtain precisely the (self-energy part) result (3.15) of the moment analysis, with $\Sigma(\mu\vec{k})$ given by either of the equivalent expressions (A1) or (A3). This verifies that the graphical formalism and moment method agree when the graphical formula is treated "exactly."

Finally we show how to modify the result (3.15) of the moment method to give a generalization (which includes vertex corrections) of the "quasi-particle" approximation result obtained in Eq. (4.29). To do this we note from Eqs. (A1)–(A3) and (4.32)–(4.33) that Eq. (3.15) can be written as

$$M^{(1)}_{\mu',\mu} = (\epsilon^a_\mu - \epsilon^a_{\mu'}) M^{(0)}_{\mu',\mu} - \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'}) \delta_{m_\mu, m_{\mu'}} \frac{1}{V} \sum_{\vec{k}} \left(n(\epsilon^a_{\mu',\vec{k}}) \frac{\mathrm{Pr}}{\pi} \int_{-\infty}^{\infty} \frac{dE\, \Gamma_{\mu\vec{k}}(E)}{E - \epsilon^a_{\mu\vec{k}}} \{[n(\epsilon^a_{\mu\vec{k}})+1] - [n^a(E)+1]\} \right.$$

$$\left. - [n(\epsilon^a_{\mu\vec{k}})+1] \frac{\mathrm{Pr}}{\pi} \int_{-\infty}^{\infty} \frac{dE\, \Gamma_{\mu',\vec{k}}(E)}{E - \epsilon^a_{\mu',\vec{k}}} [n(\epsilon^a_{\mu',\vec{k}}) - n^a(E)] \right)$$

$$+ \sum_{m_\mu m_{\mu'}} \sigma(m_\mu, m_{\mu'}) \frac{1}{V} \sum_{\vec{k}} \left(n(\epsilon^a_{\mu',\vec{k}}) \frac{\mathrm{Pr}}{\pi} \int_{-\infty}^{\infty} \frac{dE\, \phi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k}, E)}{E - \epsilon^a_{\mu\vec{k}}} \{[n(\epsilon^a_{\mu\vec{k}})+1] - [n^a(E)+1]\} \right.$$

$$\left. - [n(\epsilon^a_{\mu\vec{k}})+1] \frac{\mathrm{Pr}}{\pi} \int_{-\infty}^{\infty} \frac{dE\, \phi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu'\vec{k}, E)}{E - \epsilon^a_{\mu',\vec{k}}} [n(\epsilon^a_{\mu',\vec{k}}) - n^a(E)] \right) , \tag{A11}$$

where $\Gamma_{\mu\vec{k}}(E)$ and $\phi_{\mu\vec{\mu},\mu'\vec{\mu}'}(\mu\vec{k},E)$ are given by Eqs. (4.22) and (4.33). The principal value symbols in Eq. (A11) are unnecessary, but will be needed in the step which follows. Note also that we have added and subtracted the same term inside two of the integrands in Eq. (A11).

Our procedure now is simply to drop the terms proportional to $n^a(E)$ and $[n^a(E)+1]$ in Eq. (A11). This leads immediately to Eq. (4.31), and while the above procedure is rather *ad hoc*, we see that it agrees exactly with the result obtained from the quasiparticle approximation (for the case where the vertex contributions are ignored).

APPENDIX B

We present a few details of the reduction of the function $\gamma_{\vec{q}}$ as given by Eq. (5.10). We define $\Delta E_\mu = (\epsilon^a_{\mu_1} - \epsilon^a_\mu) + (\epsilon^b_{\gamma_1} - \epsilon^b_{\gamma_2})$, and make the change of variables $\vec{k} \to \vec{k}' + \vec{q}$. Equation (5.10) can then be written

$$\gamma_{\vec{q}}(\Delta E_\mu) = \Pr \int_{-\infty}^{\infty} \frac{dE}{\Delta E_\mu - E} \times \frac{1}{Z} \int d^3k\, d^3k'\, e^{-\beta\epsilon^a_{\vec{k}}} e^{-\beta\epsilon^b_{\vec{k}'}} \times \delta[E + (\epsilon^a_{\vec{k}-\vec{q}} - \epsilon^a_{\vec{k}}) + (\epsilon^b_{\vec{k}'+\vec{q}} - \epsilon^b_{\vec{k}'})], \tag{B1}$$

where

$$Z = \int d^3k\, d^3k'\, e^{-\beta\epsilon^a_{\vec{k}}} e^{-\beta\epsilon^b_{\vec{k}'}} = \left(\frac{2\pi(M_a M_b)^{1/2}}{\beta\hbar^2}\right)^3. \tag{B2}$$

The integration over one of the $\vec{k}$ vectors (say d^3k) in Eq. (B1) is precisely the same integration which occurs in the problem of Doppler broadening, where in that problem $\vec{q}$ is the wave vector of the absorbed radiation. This integration is easily done and leads to the familiar Gaussian form characteristic of Doppler broadening. We find

$$\gamma_{\vec{q}}(\Delta E_\mu) = \frac{1}{2\pi}\left(\frac{\beta\hbar^2}{(M_b M_a)^{1/2}}\right)^3 \frac{M_a}{\hbar^2 q}\frac{M_a}{\beta\hbar^2} \Pr \int_{-\infty}^{\infty} \frac{dE}{\Delta E_\mu - E} \int_0^\infty k'^2\, dk'\, e^{-\beta(\hbar^2 k'^2/2M_b)} \times \int_{-1}^{1} dt' \exp\left\{-\frac{\beta M_a}{2\hbar^2 q^2}\left[E + \frac{\hbar^2 q^2}{2}\left(\frac{1}{M_a}+\frac{1}{M_b}\right) + \frac{\hbar^2 q k' t'}{M_b}\right]^2\right\}, \tag{B3}$$

where it remains to perform the integration over $k' = |\vec{k}'|$ and over t', the cosine of the angle between $\vec{k}'$ and $\vec{q}$. The integration $\int_0^\infty dk' \int_{-1}^{1} dt'$ can be manipulated into the more convenient form $\int_0^1 dt' \int_{-\infty}^{\infty} dk'$, and the integral over dk' can then be performed by completing the square in the argument of the exponential. Making the change of variables $E' = E + \hbar^2 q^2/2m$, where $m = M_a M_b/(M_a + M_b)$ is the reduced mass, we obtain

$$\gamma_{\vec{q}}(\Delta E_\mu) = \frac{1}{\sqrt{2\pi}}\left(\frac{\beta m}{\hbar^2 q^2}\right)^{1/2} \Pr \int_{-\infty}^{\infty} \frac{dE'}{\Delta E_\mu + \hbar^2 q^2/2m - E'} \left(1 + \frac{M_a}{M_b}\right)^{1/2} \int_0^1 \frac{dt'}{f(t')^{3/2}} \exp\left(-\frac{\beta m E'^2}{2\hbar^2 q^2}\frac{(1+M_a/M_b)}{f(t')}\right) \times \left(1 + \frac{\beta m E'^2}{\hbar^2 q^2}\frac{M_a}{M_b}\frac{t'^2(1+M_a/M_b)}{f(t')}\right), \tag{B4}$$

where

$$f(t') = 1 + (M_a/M_b)t'^2. \tag{B5}$$

We next make the change of variables

$$z = \frac{(1+M_a/M_b)^{1/2} t'}{[1+(M_a/M_b)t'^2]^{1/2}}, \tag{B6}$$

and find

$$\gamma_{\vec{q}}(\Delta E_\mu) = \frac{1}{\sqrt{2\pi}}\left(\frac{\beta m}{\hbar^2 q^2}\right)^{1/2} \Pr \int_{-\infty}^{\infty} \frac{dE'}{\Delta E_\mu + \hbar^2 q^2/2m - E'} \exp\left[-\frac{\beta m E'^2}{2\hbar^2 q^2}\left(1 + \frac{M_a}{M_b}\right)\right] J(\sigma), \tag{B7}$$

where

$$J(\sigma) = \int_0^1 dz\, e^{\sigma z^2}(1 + 2\sigma z^2), \tag{B8}$$

with

$$\sigma = \frac{\beta m E'^2}{2\hbar^2 q^2}\frac{M_a}{M_b}. \tag{B9}$$

We can rewrite Eq. (B8) as

$$J(x) = \frac{1}{x}\int_0^x dt\, e^{t^2}(1 + 2t^2), \tag{B10}$$

where we have let $t=\sqrt{\sigma}z=xz$. From (B10) we note that

$$J(0)=1\,. \tag{B11}$$

We then differentiate Eq. (B10) with respect to x and obtain

$$\frac{dJ(x)}{dx}=-\frac{1}{x}J(x)+\frac{1}{x}e^{x^2}(1+2x^2)\,,$$

or

$$x\frac{dJ(x)}{dx}+J(x)=e^{x^2}(2x^2+1)\,. \tag{B12}$$

It is easily verified that the solution of this equation which satisfies the boundary condition (B11) is

$$J(x)=e^{x^2}=\exp\left(\frac{\beta m E'^2}{2\hbar^2q^2}\frac{M_a}{M_b}\right). \tag{B13}$$

Inserting into Eq. (B7) yields the final result

$$\gamma_{\vec{q}}''(\Delta E_\mu)=\frac{1}{\sqrt{2\pi}}\left(\frac{\beta m}{\hbar^2q^2}\right)^{1/2}\times\mathrm{Pr}\int_{-\infty}^{\infty}\frac{dE'\exp(-\beta mE'^2/2\hbar^2q^2)}{\Delta E_\mu+\hbar^2q^2/2m-E'}\,. \tag{B14}$$

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[50]In Eq. (3.15) for $\psi_{\mu\tilde{\mu},\mu'\tilde{\mu}'}(\mu\vec{k})$, the subscripts $\mu\tilde{\mu},\mu'\tilde{\mu}'$ denote the dependence on the K matrix elements while the argument $(\mu\vec{k})$ denotes the dependence on the energy variables.
[51]In microwave spectroscopy, at sufficiently high pressures, there typically exists a distinct asymmetry in the line-shape function (see, e.g., Ref. 25, pp. 343–345). If $\beta\hbar\omega \ll 1$, then the factor of $(1-e^{-\beta\hbar\omega})$ in Eq. (2.1) and the factor of ω in Eq. (2.2) combine to give an asymmetry factor of ω^2. However, our function $f_{\mu'\mu}(\hbar\omega)$ does not include this factor, and simple theories predict $f_{\mu'\mu}(\hbar\omega)$ to be a symmetric Lorentzian. Also, for the case of infrared transitions (which may be the more interesting regime to observe shifts), the above source of asymmetry should be reduced since typically $\beta\hbar\omega \gg 1$ and the asymmetry is reduced to a factor of ω.
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