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Theory of Resonance Absorption Line Shapes in Monatomic Gases*

GENE P. RECK,† HISAO TAKEBE,‡ AND C. ALDEN MEAD§
School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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It is pointed out that the usual theories of pressure broadening disagree with direct experimental measurements of the widths of resonance-broadened alkali doublet lines, although the theories are at least qualitatively confirmed for the wings of resonance lines and for foreign-gas broadening. There are also two conflicting sets of experimental data (both in strong disagreement with theory). Some qualitative arguments are given for doubting the validity, near the center of a resonance line, of the "two-body" approximation generally used in theoretical treatments, and some formal objections to the usual procedure are also presented. The basic equation relating the susceptibility to a resolvent operator matrix element is derived from a more fundamental point of view than usual; the result contains in principle all effects due to translational motion, to the quantized nature of the radiation field, and to "spatial dispersion." In the limit of large absorber mass it is proved rigorously that the two-body approximation can never be valid near the center of a line, even for very low densities. By using different approximations for the wings and the line center, we obtain satisfactory agreement with experiments in both regions for the alkali doublet lines. We are also able to decide between the two conflicting experiments, favoring the square-root density dependence of the linewidth observed by Lauriston and Welsh.

I. INTRODUCTION

THE problem of the pressure broadening of spectral lines in gases has been studied for a long time and by a variety of methods,[1] whose culmination is best represented by a recent article by Fano.[2] These theories concentrate (either implicitly or explicitly) mainly on broadening due to foreign gases, electrons, and/or ions with considerable success, although there is no lack of unsolved problems.

In the case of "self-"or "resonance" broadening, however, we find the situation less satisfactory. The clearest illustration of the phenomenon is the broadening of an absorption line in a monatomic gas by the pressure of the gas itself; in the case of molecular lines, the situation is complicated by the rotational-vibrational structure in the band, and by the presence of permanent moments which influence the shape. For these reasons, with their attendant difficulties, we shall confine ourselves to the monatomic case, especially the alkali doublets, for which experimental data are available. For this case, both the "impact" and "quasistatic"[3] theories predict (with the necessary approximations) that the line should be Lorentzian, with half-width given to within factors of the order of unity, by

$$\delta\omega_{1/2}\sim\mathfrak{N}\mu^2/\hbar.$$

Here $\delta\omega_{1/2}$ is the half-width in frequency units, $\mathfrak{N}$ is the number of atoms per cubic centimeter, and μ is the dipole moment matrix element for the transition involved. The experiments[4] which seemed to confirm these theoretical treatments (at least qualitatively) did so by measuring the wings of the line and inferring the width from the assumption that the lines are in fact Lorentzian. This procedure was used because the resultant widths were less than the expected Doppler widths, and hence could not be determined from a

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† Present address: Chemistry Department, Brown University, Providence, Rhode Island.

‡ Present address: Seikei University, Department of Electrical Engineering, Musashino, Tokyo, Japan.

§ Address, September 1964 to September 1965: Physics Department, Birkbeck College, London, England.

[1] R. Breene, Jr., *The Shift and Shape of Spectral Lines* (Pergamon Press, Inc., New York, 1961).

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

[3] Also called the "collision" and "statistical," respectively, but we have adopted the terminology of M. Baranger, *Atomic and Molecular Processes*, edited by D. Bates (Academic Press Inc., New York, 1962), p. 502.

[4] S-Y Chen, Phys. Rev. **58**, 884 (1940); K. Wananabe, Phys. Rev. **59**, 151 (1941); C. Gregory, Phys. Rev. **61**, 465 (1942).

direct profile measurement. We may conclude from this then, only that the usual theory is essentially correct for the wings of the line. It is to the line center that we must direct our attention.

More recent experimental results involving the center of the line seem to contradict both the existing theories and each other. The direct profile measurements of the absorption of the alkali metal vapors by Tomiser,[5] and Moser and Schultz,[6] give widths that are larger by a factor of 10^3 than the theoretical value, although appearing to confirm the predicted linear dependence on the density. Reflection measurements at much higher pressures by Lauriston and Welsh,[7] on the other hand, give widths proportional to the *square root* of the density, but with magnitudes such as to contradict the other results. For example, in the case of the $^2P_{1/2}$ line of sodium, Tomiser[5] reports a linewidth of 1.075 Å at a density of 7.07×10^{15} atoms/cc while Lauriston and Welsh[7] find a width of only 0.553 Å at a much higher density of 2.3×10^{18} atoms/cc. Hence, unless the lines are actually *narrowed* by increasing pressure in the intermediate region (which seems extremely unlikely), one set of measurements or the other must be badly in error, but, in any case, both sets are in strong disagreement with the usual theories.

As a result of these experimental discrepancies, we feel that a re-examination of the usual theories should be made in order to see how various approximations might account for them. To this end, we will discuss below several of the objections and doubts regarding the older theories that make an alternative formulation seem desirable despite its complexity. In particular, a perturbation expansion in powers of the density (in the limit of large absorber mass) is developed which leads us to conclude that any such expansion will only be good for the wings of the line, but not the center, where many body interactions become important. The results of this examination indicate that the usual theories are quite doubtful in the case of resonance, and that an alternative formulation is of value.

The purpose of the present paper is to develop such a formalism in a way which allows for a clearer understanding of the approximations that may be necessary for greater agreement between theory and experiment, and also to try to decide between the two conflicting sets of data. One of us (C.A.M.) has developed previously a formalism for calculating the complex refractive index of a monatomic gas in the region of an absorption. The treatment begins from the quite fundamental point of view of actually studying the properties of the stationary states of the quantum-mechanical system composed of the radiation field and matter, and therefore avoids the difficulties of the more usual theories to be discussed below. The original theory[8] considered each absorber to occupy a fixed position in space, so that effects due to the motion of the atoms were left out, and depended quite heavily upon the use of "damping operators."[9] More recently the results have been rederived by means of a simpler formalism[10] and at the same time brought into rough agreement with Tomiser's work. We now feel that one of the approximations used in this earlier work [mentioned briefly just before Eq. (29) of Ref. 10] is inappropriate under experimental conditions, for reasons to be discussed in the Appendix to this paper. The basic approach, however, is still valid.

The plan of the article is as follows: In Sec. II, some remarks are made concerning earlier theories. In particular, it is indicated that the practice of treating the line shape as due to independent two-body encounters is highly doubtful near the center of a resonance line even at low densities, though it should be valid for foreign gas broadening and in the wings of the resonance line. Some formal objections are also listed, which make a different derivation of the basic equations desirable. Section III introduces the notation and discusses some preliminary approximations. In Sec. IV, the basic formula relating the observable frequency-dependent susceptibility to the resolvent operator is derived in a way which is free of the formal difficulties discussed in Sec. II. The result is essentially equivalent to the starting equations of most earlier work,[1,2] but is more general in that it includes all effects due to the translational motion of absorbers, to the quantized nature of the radiation field, and to "spatial dispersion."[11] In Sec. V, we specialize to the limit of large absorber mass, so that kinetic effects can be neglected and each absorber may be considered to occupy a fixed position in space. In this limit, the expansion in powers of the density usually employed (most explicitly by Fano[2]) is discussed with the aid of a simple diagrammatic notation. It is shown that if one cuts off this expansion after any finite number of terms, there will always be a region near the center of the line for which the result is badly wrong, and it is concluded that one must study the entire series in order to have any hope of describing the line center. Section VI considers the "two-body" approximation, which should be valid on the wings of the absorption line. Although all previous workers have used the two-body treatment, we believe this is the first time that the spin-orbit interaction has been correctly handled. The results are compared with the experiments of Ref. 4 on the wings of alkali doublet lines and satisfactory agreement is obtained. In Sec. VII, the "extended two-body" approximation is introduced, which permits a qualitative treatment of the center of the line, and order-of-magnitude agreement is obtained with the work of Lauriston and Welsh.[7] In particular, the dependence of the linewidth

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[5] J. Tomiser, Acta Phys. Austriaca **8**, 198 (1953); **8**, 276 (1954); **9**, 18 (1954); **8**, 323 (1954).

[6] H. Moser and H. Schultz, Ann. Physik **4**, 243 (1959).

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

[8] C. A. Mead, Phys. Rev. **120**, 854, 860 (1960).

[9] C. A. Mead, Phys. Rev. **112**, 1844 (1958).

[10] C. A. Mead, Phys. Rev. **128**, 1753 (1962).

[11] J. Neufeld, Phys. Rev. **123**, 1 (1961).

on the square root of the density, observed by them is explained. It is concluded that the experiments of Lauriston and Welsh are to be preferred over those of Tomiser.

An Appendix contains a brief discussion of the "strong linear" approximation used in Refs. 8–10, generalized to include effects of translational motion.

II. REMARKS ON PREVIOUS THEORIES

Inasmuch as generalization is possible, previous workers have taken as their starting point an expression for the spectral distribution [e.g., Fano's Eq. (3)] or alternately its Fourier transform, the autocorrelation function of the position (or light amplitude). This expression is for *one* of the absorbers or emitters which has been singled out for study, and the effect of all the others upon it is calculated. Since the excitation in the resonance case is really a property of the gas as a whole this procedure could lead to difficulty.

In the "impact" approximation, the time of a collision is considered short enough so that the perturbation may be treated as being due to many independent collisions. With this approximation, one assumes the interaction can be represented by that due to a single perturber, and the result multiplied by the total number of perturbers. This is equivalent to the assumption of independent two-body collisions ("two-body approximation") which is not obviously correct in the case of resonance. For, suppose absorber A is initially excited, and it then has a collision with an identical absorber B. At the end of the collision, it is quite possible for the excitation to be transferred to B, and for it to be subsequently transferred to C in a much later collision, etc. In this way, the excitation may well be carried by a large number of other absorbers before it returns to A (if it ever does), even though three or more absorbers are never in close proximity at any one time. In other words, many body processes may be of great importance even at low pressures, making an expansion in powers of the density dubious. For foreign gas broadening (where B is different from A) this problem does not arise because the excitation can only remain on B for a time the order of $(\Delta\nu)^{-1}$, where $\Delta\nu$ is the difference between the frequency of the line in question and a resonant frequency of B. Therefore, it can only be transferred to C if C is close by (a real three-body collision). The wings of the resonance-broadened line also avoid this problem, since here the difference between the driving frequency and the resonant frequency plays the same role as $\Delta\nu$. These considerations, while admittedly rather naive, indicate that the usual impact theory should be very good in the wings, but not necessarily so near the line center—a situation that is apparently verified by experiment.

In the case of the "quasistatic" theories, the time required to complete a single collision is very long so that the motion of the perturbers can be disregarded in the calculation of the Fourier transform of the line shape.[3] The perturbers are assumed to occupy fixed positions, and then a statistical average over positions is performed. To complete the calculation requires the further assumption of the additivity of the perturbations due to different perturbers, an assumption that is not even qualitatively correct in the case of resonance. For both foreign gas broadening and the wings of the resonance case, it is very good, however. It is a peculiar property of the resonance case with dipole-dipole interactions that these two types of theory give essentially the same result.

Both these methods treat the perturbation as due to independent two-body processes. As has been brought out clearly by Fano,[2] this corresponds to expanding in powers of the gas density and keeping only the first term. We now present a dimensional argument which indicates that this is not permissible for the case of resonance in the static limit (large absorber mass). This will be made more explicit and rigorous in Sec. V.

In this limit, the only parameters characterizing the system are the density $\mathfrak{N}$ (cm^{-3}), the square of the dipole moment matrix element of the transition in question, μ^2 (erg cm^3), Planck's constant, $\hbar$ (erg sec), and ω (sec^{-1}), the difference between driving frequency and resonant frequency. The susceptibility may be written as

$$\chi(\omega) = -4\pi\mathfrak{N}\mu^2/\hbar[\omega-\Delta(\omega)].$$

If $\Delta(\omega)$ is constant, the line is Lorentzian with shift and width determined by the real and imaginary parts, respectively, of Δ. For this reason, Δ is the quantity which one normally expands. We write

$$\Delta(\omega) = a_1(\omega)\mathfrak{N} + a_2(\omega)\mathfrak{N}^2 + a_3(\omega)\mathfrak{N}^3 + \cdots.$$

Now Δ has dimensions sec^{-1}, and the only quantity proportional to $\mathfrak{N}$ with these dimensions is $(\mathfrak{N}\mu^2)/\hbar$. Accordingly, the first term in the series must be a dimensionless constant b_1 (independent of the parameters) times $\mathfrak{N}\mu^2/\hbar$. The second term must be proportional to $\mathfrak{N}^2$, and have dimensions sec^{-1}, and it can easily be seen that it must be another dimensionless constant b_2 times $(\mathfrak{N}\mu^2/\hbar)(\mathfrak{N}\mu^2/\hbar\omega)$. Continuing this reasoning, we find

$$\Delta(\omega) = \frac{\mathfrak{N}\mu^2}{\hbar}\left\{b_1 + b_2\left(\frac{\mathfrak{N}\mu^2}{\hbar\omega}\right) + b_3\left(\frac{\mathfrak{N}\mu^2}{\hbar\omega}\right)^2 + \cdots\right\}.$$

Near the center of the line (small ω), the second term becomes larger than the first, the third larger than the second, etc. The conclusion again is that the practice of keeping only the first term is not valid near the center of a resonance line, though it is all right in the wings (large ω), and in the treatment of foreign gas broadening.

In addition, there are some formal objections that one can make to most treatments of the usual theories which will have only a minor practical effect since, in all cases either the effect involved is quite small, or it is easily corrected for, or both. Nevertheless, a theory which automatically includes all these effects would be more satisfying. These objections are:

(1) In practice it is usually the emission rather than the absorption which is calculated. Inasmuch as the two are not rigorously identical, the calculation of the absorption is to be preferred. In fact, the emission spectrum is not even a uniquely defined quantity, since it depends on the conditions of excitation.[12]

(2) The properties of the radiation emitted play no role in the usual theories. Thus all effects due to the quantized nature of the radiation field (e.g., recoil shift) are left out. Also omitted are effects due to the finite velocity of light, such as Doppler broadening.

(3) It is difficult in the usual theories to include magnetic and retardation effects in the interaction between different absorbers, except in lowest order in perturbation theory.

We now proceed to formulate the theory in a way which is free of these difficulties.

III. NOTATION AND HAMILTONIAN

Our system consists of N identical absorbers, each with mechanical mass m, distributed in a volume V, within which the radiation field is required formally to obey periodic boundary conditions. In the "initial" state $|0\rangle$, each atom A has a momentum $\hbar\mathbf{q}_A$ assigned to it, and the number of atoms with momentum in a given region of wave-number space is described by a Boltzmann distribution at some temperature T. For the sake of definiteness, the ground electronic state of each atom is considered to be a nondegenerate s state, and the only excited level (or at least the only one of interest to us) is assumed to be a triply degenerate p level. The effect of spin-orbit coupling will be considered later. The energy difference between the two levels is $\hbar\nu_0$. A given state of the system of radiation field plus matter may differ from the state $|0\rangle$ in one or more of three ways: (1) There may be a photon present; this is denoted by a greek letter, e.g., λ denotes the presence of a bare photon of wave number $\boldsymbol{\kappa}_\lambda$ and polarization $\boldsymbol{\varepsilon}_\lambda$. (2) One or more of the atoms may be excited; this is indicated by a capital Latin letter denoting which atom is excited, with a subscript giving the direction of "polarization" (electric dipole moment matrix element between excited state and ground state). Thus, A_i represents the excitation of atom A, with dipole moment matrix element in the i direction ($i=x, y, z$). (3) One or more of the atoms may have acquired a momentum different from that assigned to it in the state $|0\rangle$. $\boldsymbol{\kappa}(A)$ indicates that atom A has an excess momentum $\hbar\boldsymbol{\kappa}$, so that its total momentum is $\hbar(\mathbf{q}_A+\boldsymbol{\kappa})$. The way in which these symbols are combined in specifying a state is best explained by means of a few examples of states represented in our notation and with their properties also written out in words:

$|\eta,\boldsymbol{\kappa}(A)\rangle$: Photon present with wave number $\boldsymbol{\kappa}_\eta$ and polarization $\boldsymbol{\varepsilon}_\eta$; atom A has excess momentum $\boldsymbol{\kappa}$; all other atoms as in state $|0\rangle$.

$|A_i,\boldsymbol{\kappa}_1(A),\boldsymbol{\kappa}_2(B)\rangle$: Atom A excited, with "polarization" in i direction; atom A has excess momentum $\hbar\boldsymbol{\kappa}_1$; atom B has excess of $\hbar\boldsymbol{\kappa}_2$; all other atoms as in state $|0\rangle$; no photons present.

We are interested in constructing the "dressed" photon state $|\bar{\lambda}\rangle$, which is an eigenstate of the complete Hamiltonian with energy $\hbar\nu_\lambda(\nu_\lambda=c\kappa_\lambda)$, and which in some sense approaches the bare photon state $|\lambda\rangle$ in the limit of zero interaction. In most of what follows, we shall assume that $|\bar{\lambda}\rangle$ can be built up entirely out of two kinds of states: (1) States with one photon present, and no electronic excitation. (2) States with one and only one atom excited, and no photons present. States coming under categories (1) and (2) may still, of course, include any combination of excess translational momenta for the various atoms. Other states, such as two-photon states and states with several atoms excited, may be included later by means of perturbation theory, if desired. The approximation of limiting ourselves to the states of types (1) and (2) should hold in the frequency region $\nu_\lambda\cong\nu_0$, which is the region we are interested in here. It could be made more formally precise by means of the Arnous-Bleuler transformation,[8,13,14] but this would make some of the subsequent manipulations more complicated so it was decided not to use it in this article. The general result of Sec. IV is totally independent of this assumption.

The refractive index can be thought of as describing the propagation of the electric field matrix element

$$\langle 0|\mathbf{E}_0(\mathbf{R})|\bar{\lambda}\rangle=\sum\nolimits_\eta\langle 0|\mathbf{E}_0(\mathbf{R})|\eta\rangle\langle\eta|\bar{\lambda}\rangle.$$

This immediately leads to a difficulty: It would appear that because of momentum conservation $\langle\eta|\bar{\lambda}\rangle=0$ unless $\boldsymbol{\kappa}_\eta=\boldsymbol{\kappa}_\lambda$. This would mean that

$$\langle 0|\mathbf{E}_0(\mathbf{R})|\bar{\lambda}\rangle=\mathbf{E}_{00}\exp(i\boldsymbol{\kappa}_\lambda\cdot\mathbf{R}),$$

corresponding to a refractive index of unity. This problem does not arise in the situation treated in Refs. 7 and 9, since there the momentum conservation is spoiled by holding the atoms fixed. This apparently hopeless difficulty really is the result of a rather trivial effect. Momentum is indeed conserved when an electromagnetic wave propagates through a medium with altered wave number, but the excess momentum is taken up either by the medium as a whole or by the walls containing the medium. Since explicit inclusion of the effects of the walls in a calculation is not feasible, we will treat the excess momentum as belonging to the medium as a whole. From this point of view, the

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[12] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed., pp. 196–204.

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

[14] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed., pp. 348–353.

propagation of the field should be considered relative to the center of mass of the medium. Therefore, instead of

$$\mathbf{E}_0(\mathbf{R})=\sum_\eta \boldsymbol{\varepsilon}_\eta\{s_\eta \exp(i\boldsymbol{\kappa}_\eta\cdot\mathbf{R})+s_\eta{}^\dagger \exp(-i\boldsymbol{\kappa}_\eta\cdot\mathbf{R})\}$$

(where s_η and $s_\eta{}^\dagger$ are, respectively, destruction and creation operators, apart from constants), we use

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_0\left(\frac{1}{N}\sum_A \mathbf{r}_A+\mathbf{r}\right)$$

$$=\sum_\eta \boldsymbol{\varepsilon}_\eta\left\{s_\eta \exp(i\boldsymbol{\kappa}_\eta\cdot\mathbf{r})\prod_A \exp\left(i\frac{\boldsymbol{\kappa}_\eta}{N}\cdot\mathbf{r}_A\right)\right.$$

$$\left.+s_\eta{}^\dagger \exp(-i\boldsymbol{\kappa}_\eta\cdot\mathbf{r})\prod_A \exp\left(-i\frac{\boldsymbol{\kappa}_\eta}{N}\cdot\mathbf{r}_A\right)\right\}.$$

When $\mathbf{E}(\mathbf{R})$ is applied to a state, it not only creates (destroys) a photon, but also alters the momenta of all the atoms by a small and equal amount in such a way that total momentum is conserved. From now on, therefore, when we write down a state it is to be understood that, in addition to the photons, excitations, etc., specifically noted, the state also includes an additional superimposed momentum of the entire medium (equally divided between the N atoms) such that the total momentum of the state is zero. With this understanding all the states we are talking about have the same momentum, and we can study the propagation of

$$\langle 0|\mathbf{E}(\mathbf{r})|\bar{\lambda}\rangle=\sum_\eta\langle 0|\mathbf{E}(\mathbf{r})|\eta\rangle\langle\eta|\bar{\lambda}\rangle.$$

There will be no need to mention this explicitly again. Indeed, most of the subsequent manipulations could be gone through formally without performing this trick at all, the only trouble being that they would be meaningless because of both sides of the various equations being zero. The energy associated with this superimposed motion is, of course, negligible in the limit $N\to\infty$.

We now give some typical Hamiltonian matrix elements. All the ones we will need will differ from these at most by the presence of an excess momentum on an atom appearing on both sides of the matrix element and having no effect except to shift the energy in the case of a diagonal matrix element. The energy of the state $|0\rangle$ is taken as zero. We obtain the following matrix elements for the total Hamiltonian operator $\mathcal{H}_{\text{tot}}$ (includes the dipole-dipole interaction between atoms):

$$\langle A_i,\boldsymbol{\kappa}(A)|\mathcal{H}_{\text{tot}}|A_i,\boldsymbol{\kappa}(A)\rangle=\hbar[\nu_0+K(\mathbf{q}_A,\boldsymbol{\kappa})], \tag{1}$$

where

$$K(\mathbf{q},\boldsymbol{\kappa})=\frac{\hbar}{2m}[2\mathbf{q}\cdot\boldsymbol{\kappa}+\kappa^2], \tag{2}$$

$$\langle\lambda|\mathcal{H}_{\text{tot}}|\eta\rangle=\hbar\nu_\lambda\delta_{\lambda\eta}, \tag{3}$$

$$\langle A_i,\boldsymbol{\kappa}_\eta(A)|\mathcal{H}_{\text{tot}}|\eta\rangle=-\frac{2i\pi^{1/2}}{V^{1/2}}\nu_0\mu\epsilon_{\eta_i}i\left(\frac{\hbar}{2\nu_\eta}\right)^{1/2}, \tag{4}$$

$$\langle A_i,\boldsymbol{\kappa}_1(A)|\mathcal{H}_{\text{tot}}|B_j,\boldsymbol{\kappa}(B),(\boldsymbol{\kappa}_1-\boldsymbol{\kappa})(A)\rangle=\frac{4\pi}{V}\mu^2\left(\frac{\kappa_i\kappa_j}{\kappa^2}\right). \tag{5}$$

In Eqs. (4) and (5), μ is the absolute value of the dipole moment matrix element for the transition. We omit interactions between atoms in the ground state, i.e., we consider the gas in the absence of electronic excitation to be ideal.

For clarity, we consider the Hamiltonian to be representable as

$$\mathcal{H}_{\text{tot}}=E+\mathcal{H},$$

where E is a diagonal matrix corresponding to the unperturbed energy and $\mathcal{H}$ has no diagonal elements. With this, Eqs. (4) and (5) can be written in terms of the $\mathcal{H}$ only.

It will be convenient at this point to dispose of one more preliminary matter. Later on we will have occasion to evaluate the quantity

$$\mathcal{W}=\lim_{\xi\to 0+}\sum_\eta\frac{|\langle A_i,\boldsymbol{\kappa}(A)|\mathcal{H}|\eta,(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\eta)(A)\rangle|^2}{\hbar[\nu_\lambda-\nu_\eta-K(\mathbf{q}_A,\,\boldsymbol{\kappa}-\boldsymbol{\kappa}_\eta)+i\xi]}. \tag{6}$$

In situations of interest to us here,

$$|\nu_\lambda-\nu_0|\ll\nu_0.$$

Thus, we can estimate $\mathcal{W}$ by replacing ν_λ by ν_0. With this replacement, however, $\mathrm{Re}\mathcal{W}$ is just the second-order transverse self-energy of the state $|A_i,\boldsymbol{\kappa}(A)\rangle$, and may therefore be absorbed into ν_0 by renormalization. If we also assume

$$K(\mathbf{q}_A,\,\boldsymbol{\kappa}-\boldsymbol{\kappa}_\eta)\ll\nu_0,$$

then we get (replacing the sum over η by integration)

$$\mathcal{W}=-i\hbar\sigma=-\tfrac{2}{3}i(\nu_0{}^3/c^3)\mu^2, \tag{7}$$

where σ is the natural linewidth. In what follows, we will always use (7). The approximations involved are: (1) Neglect of recoil corrections to the natural linewidth, which are small and can be corrected for if desired; (2) Neglect of the dependence of $\mathrm{Im}\mathcal{W}$ on ν_λ, which is also very small in the frequency region of interest; (3) Neglect of the cutoff-dependent $\mathrm{Re}\mathcal{W}$ when $\nu_\lambda\neq\nu_0$. The formal justification of this requires the Arnous-Bleuler transformation.[7,11 12] If the reader will accept this one result, he will be spared the complications that this transformation would introduce in the subsequent manipulations.

We now present the basic assumptions that are inherent in our view of the problem. Classically, one may expand the electric field $\mathbf{E}$ and polarization $\mathbf{P}$ in Fourier series as follows:

$$\mathbf{E}(\mathbf{r},t)=\int_{-\infty}^{\infty}d\nu\sum_\alpha E_\alpha(\nu)\boldsymbol{\varepsilon}_\alpha \exp i[\boldsymbol{\kappa}_\alpha\cdot\mathbf{r}-\nu t];$$

$$\mathbf{P}(\mathbf{r},t)=\int_{-\infty}^{\infty}d\nu\sum_\alpha P_\alpha(\nu)\boldsymbol{\varepsilon}_\alpha \exp i[\boldsymbol{\kappa}_\alpha\cdot\mathbf{r}-\nu t].$$

Here the notation α represents a wave number $\boldsymbol{\kappa}_\alpha$ and a polarization unit vector $\boldsymbol{\varepsilon}_\alpha$; for each wave number there are three polarizations, two transverse and one longitudinal. The allowed wave numbers are those compatible with the periodic boundary conditions.

The requirements that the medium be isotropic and describable by a refractive index (but with the possibility of "spatial dispersion") may be expressed by

$$4\pi P_\alpha(\nu)=F(\nu,\kappa_\alpha,\boldsymbol{\kappa}_\alpha\cdot\boldsymbol{\varepsilon}_\alpha)E_\alpha(\nu)\,, \tag{8}$$

where F is a function depending only on the frequency ν, the absolute value κ of the wave number, and whether the mode α is longitudinal or transverse. We will also use the notations $F_t(\nu,\kappa)$, $F_l(\nu,\kappa)$ to indicate the transverse and longitudinal susceptibilities, respectively.

The observable refractive index ρ, a function of ν only, is determined by the transverse susceptibility and by the requirement that $\kappa=\rho\nu/c$. Thus we find

$$\rho^2(\nu)-1=F_t[\nu,\rho(\nu)\nu/c]. \tag{8a}$$

In general, the solution of (8a) may require analytic extension to complex values of κ, corresponding to absorption.

Quantum mechanically, $\mathbf{E}$ and $\mathbf{P}$ become operators, but otherwise the situation is unchanged. In the Schrödinger picture, the frequencies are to be replaced by energy differences divided by $\hbar$, and we have different equations for the various matrix elements of the operators. A quantum analog of Eq. (8) is

$$\langle 0|4\pi P_\alpha|\bar{\lambda}\rangle=F(\nu_\lambda,\kappa_\alpha,\boldsymbol{\kappa}_\alpha\cdot\boldsymbol{\varepsilon}_\alpha)\langle 0|E_\alpha|\bar{\lambda}\rangle. \tag{9}$$

It will be convenient to rearrange (9) slightly before using it. We note that

$$\mathbf{E}=\mathbf{E}_{\text{coul}}-c^{-1}(\partial/\partial t)\mathbf{A}\,,$$

where $\mathbf{E}_{\text{coul}}$ is the electrostatic longitudinal Coulomb field, and $\mathbf{A}$ is the transverse vector potential (we use Coulomb gauge throughout). We also have

$$\langle 0|-\frac{1}{c}\frac{\partial}{\partial t}\mathbf{A}|\bar{\lambda}\rangle=\frac{i\nu_\lambda}{c}\langle 0|\mathbf{A}|\bar{\lambda}\rangle. \tag{10}$$

Hence, if we define

$$\boldsymbol{\mathcal{E}}=\mathbf{E}_{\text{coul}}+(i\nu_\lambda/c)\mathbf{A}\,, \tag{11}$$

then we can combine (9), (10), and (11) to obtain

$$\langle 0|4\pi P_\alpha|\bar{\lambda}\rangle=F(\nu_\lambda,\kappa_\alpha,\boldsymbol{\kappa}_\alpha\cdot\boldsymbol{\varepsilon}_\alpha)\langle 0|\mathcal{E}_\alpha|\bar{\lambda}\rangle. \tag{12}$$

Equation (12) is the expression we will use for the requirement that the medium be describable by a refractive index.

It is also useful to notice that the electrostatic dipole-dipole interaction, whose matrix element is given by (5) may be written as

$$\mathcal{H}_{AB}=-\boldsymbol{\mu}_A\cdot\mathbf{E}_{\text{coul}}(B,A)\,, \tag{13}$$

where μ_A is the electric dipole moment operator of atom A and $\mathbf{E}_{\text{coul}}(B,A)$ is the electrostatic field produced by atom B at the position of A. We can therefore write

$$\langle A_i,\boldsymbol{\kappa}(A)|\mathcal{H}|B_j,\boldsymbol{\kappa}_\alpha(B),(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)\rangle$$
$$=-\mu\frac{\kappa_{\alpha i}}{\kappa_\alpha}\langle 0|\mathcal{E}_\alpha|B_j,\boldsymbol{\kappa}_\alpha(B)\rangle. \tag{14}$$

We also note that Eq. (4) can be rearranged as follows:

$$\langle A_j,\boldsymbol{\kappa}_\eta(A)|\mathcal{H}|\eta\rangle=-i\frac{\nu_0}{c}\mu\epsilon_{\eta j}\langle 0|A_\eta|\eta\rangle$$
$$=-\mu\epsilon_{\eta j}\frac{\nu_0}{\nu_\lambda}\langle 0|\mathcal{E}_\eta|\eta\rangle$$
$$\cong-\mu\epsilon_{\eta j}\langle 0|\mathcal{E}_\eta|\eta\rangle\,, \tag{15}$$

since we are interested only in the situation where

$$|\nu_\lambda-\nu_0|\ll\nu_0. \tag{16}$$

IV. CALCULATION OF THE REFRACTIVE INDEX

In order to find expressions for the various matrix elements appearing in Eq. (12), we must know something about the dressed photon state $|\bar{\lambda}\rangle$. As the reader will remember, $|\bar{\lambda}\rangle$ was defined by

$$\mathcal{H}_{\text{tot}}|\bar{\lambda}\rangle=\hbar\nu_\lambda|\bar{\lambda}\rangle$$

with the expansion in terms of the zero-order states

$$|\bar{\lambda}\rangle=|\lambda\rangle+\sum\nolimits_b|b\rangle\langle b|\bar{\lambda}\rangle.$$

Denoting a general zero-order state by a, b, etc., we have by taking the inner product

$$\hbar(\nu_\lambda-\nu_a)\langle a|\bar{\lambda}\rangle=\sum\nolimits_{b\neq a\backslash}a|\mathcal{H}|b\rangle\langle b|\bar{\lambda}\rangle\,, \tag{17}$$

where $\hbar\nu_a$ is the energy of the zero-order state $|a\rangle$. The appropriate "retarded" solution of (17) is

$$\langle a|\bar{\lambda}\rangle=\hbar^{-1}(\nu_\lambda-\nu_a+i\xi)^{-1}\sum\nolimits_{b\neq a}\langle a|\mathcal{H}|b\rangle\langle b|\bar{\lambda}\rangle\,, \tag{18}$$

in which the limit $\xi\rightarrow 0^+$ is always understood.

Now let us examine some field and polarization matrix elements. If η is a transverse mode, so that there are photons of type η, we have

$$\langle 0|\mathcal{E}_\eta|\bar{\lambda}\rangle=\langle 0|\mathcal{E}_\eta|\eta\rangle\langle\eta|\lambda\rangle. \tag{19}$$

For the polarization we have

$$\mathbf{P}(\mathbf{r})=\sum\nolimits_A\boldsymbol{\mu}_A\delta(\mathbf{r}-\mathbf{r}_A)\,,$$
$$P_\eta=\frac{1}{V}\int\boldsymbol{\varepsilon}_\eta\cdot\mathbf{P}(\mathbf{r})\exp(-i\boldsymbol{\kappa}_\eta\cdot\mathbf{r})d^3r\,,$$
$$=\frac{1}{V}\sum\nolimits_A\boldsymbol{\varepsilon}_\eta\cdot\boldsymbol{\mu}_A\exp(-i\boldsymbol{\kappa}_\eta\cdot\mathbf{r}_A)\,,$$

so that

$$\langle 0|4\pi P_\eta|\bar\lambda\rangle=\sum\nolimits_A\langle 0|4\pi P_\eta|A_j,\boldsymbol{\kappa}_\eta(A)\rangle\langle A_j,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle$$
$$=\frac{4\pi\mu}{V}\sum\nolimits_A \epsilon_{\eta j}\langle A_j,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle. \tag{20}$$

Here and henceforth a summation over repeated coordinate indices j, k, etc., is understood. We will now apply (17) to $|a\rangle=|A_j\boldsymbol{\kappa}_\eta(A)\rangle$, and also use (15). The result is

$$\begin{aligned}\hbar[\omega-K(\mathbf{q}_A,\boldsymbol{\kappa}_\eta)]\langle A_j,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle\\ =-\mu\epsilon_{\eta j}\langle 0|\mathcal{E}_\eta|\eta\rangle\langle\eta|\bar\lambda\rangle\\ +\sum\nolimits_{\zeta\neq\eta}\langle A_j,\boldsymbol{\kappa}_\eta(A)|\mathcal{H}|\zeta,(\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\zeta)(A)\rangle\\ \times\langle\zeta,(\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\zeta)(A)|\bar\lambda\rangle\\ +\sum_{B\neq A,\alpha}^{(l)}\langle A_j,\boldsymbol{\kappa}_\eta(A)|\mathcal{H}|B_k,(\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\alpha)(A),\boldsymbol{\kappa}_\alpha(B)\rangle\\ \times\langle B_k,(\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\alpha)(A),\boldsymbol{\kappa}_\alpha(B)|\bar\lambda\rangle.\end{aligned} \tag{20a}$$

Here the last summation goes over all longitudinal modes α, and we have defined

$$\omega\equiv\nu_\lambda-\nu_0.$$

We now apply (18) to the state $|a\rangle=|\zeta,\ (\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\zeta)(A)\rangle$, and also use Eqs. (6), (7), and (19). The result is

$$\begin{aligned}\hbar[\omega-K(\mathbf{q}_A,\boldsymbol{\kappa}_\eta)]\langle A_j,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle\\ =-\mu\boldsymbol{\varepsilon}_{\eta j}\langle 0|\mathcal{E}_\eta|\bar\lambda\rangle-i\sigma\hbar\langle A_j\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle\\ +\sum\nolimits_{B\neq A,\alpha}\langle A_j,\boldsymbol{\kappa}_\eta(A)|\mathcal{K}|B_k,(\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\alpha)(A),\boldsymbol{\kappa}_\alpha(B)\rangle\\ \times\langle B_k,(\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\alpha)(A),\boldsymbol{\kappa}_\alpha(B)|\bar\lambda\rangle.\end{aligned} \tag{21}$$

The last summation now goes over all modes, transverse and longitudinal. In arriving at (21), we have assumed that the omission of the one photon mode η from the summation in (6) does not affect the result. The matrix elements of $\mathcal{K}$ are defined by

$$\begin{aligned}\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{K}|B_k,\boldsymbol{\kappa}_\alpha(B),(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)\rangle=\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|B_k,\boldsymbol{\kappa}_\alpha(B),(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)\rangle\\ +\frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|\alpha,(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)\rangle\langle\alpha,(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)|\mathcal{H}|B_k,\boldsymbol{\kappa}_\alpha(B),(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)\rangle}{\hbar\{\nu_\lambda-\nu_\alpha-K[\mathbf{q}_A,(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)]+i\xi\}}.\end{aligned} \tag{22}$$

The first term on the right-hand side of (22) is nonzero only for longitudinal modes, the second only for transverse modes.

We now make the following definition:

$$\begin{aligned}-i\hbar\sigma\langle A_j,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle\\ +\sum\nolimits_{B\neq A,\alpha}\langle A_j,\boldsymbol{\kappa}_\eta(A)|\mathcal{K}|B_k,(\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\alpha)(A),\boldsymbol{\kappa}_\alpha(B)\rangle\\ \times\langle B_k,(\boldsymbol{\kappa}_\eta-\boldsymbol{\kappa}_\alpha)(A),\boldsymbol{\kappa}_\alpha(B)|\bar\lambda\rangle\\ \equiv\hbar\Delta_{jk}(\omega,\boldsymbol{\kappa}_\eta,\mathbf{q}_A)\langle A_k,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle.\end{aligned} \tag{23}$$

Now Eq. (23) can be inserted into (21) and the result solved for $\langle A_j,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle$. The result is

$$\langle A_j,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle$$
$$=-\frac{\mu}{\hbar}\langle 0|\mathcal{E}_\eta|\bar\lambda\rangle[\omega-K(\mathbf{q}_A,\boldsymbol{\kappa}_\eta)-\Delta]_{jk}^{-1}\epsilon_{\eta k}. \tag{24}$$

The matrix $U=(\omega-K-\Delta)^{-1}$ is, of course, the inverse of the matrix whose elements are $(\omega-K)\delta_{jk}-\Delta_{jk}$. It is now a simple matter to substitute (24) into (20), sum over A using the Boltzmann distribution, and solve Eq. (12) for F_t with the aid of the result. This gives the solution

$$F_t(\omega,\kappa_\eta)=-\frac{4\pi\mu^2}{\hbar}\frac{\mathcal{N}}{V}\left(\frac{\beta}{\pi}\right)^{3/2}\int\exp(-\beta q^2)\epsilon_{\eta j}$$
$$\times[\omega-K(\mathbf{q},\boldsymbol{\kappa}_\eta)-\Delta(\omega,\boldsymbol{\kappa}_\eta,\mathbf{q})]_{jk}^{-1}\epsilon_{\eta k}d^3q, \tag{25}$$

where $\beta=\hbar^2/2mkT$, and k is Boltzmann's constant. We could have replaced the matrix product under the integral sign by

$$\epsilon_{\eta j}U_{jk}\epsilon_{\eta k}=\tfrac{1}{2}\left[U_{kk}-\frac{1}{\kappa^2}\kappa_jU_{jk}\kappa_k\right].$$

It is a straightforward matter to derive an expression analogous to (25) for F_l. The result is

$$F_l(\omega,\boldsymbol{\kappa})=-\frac{4\pi\mu^2}{\hbar}\frac{\mathcal{N}}{V}\left(\frac{\beta}{\pi}\right)^{3/2}\int\exp(-\beta q^2)$$
$$\times\frac{\kappa_j}{\kappa}[\omega-K(\mathbf{q},\boldsymbol{\kappa})-\Delta(\omega,\boldsymbol{\kappa},\mathbf{q})]_{jk}^{-1}\frac{\kappa_k}{\kappa}d^3q. \tag{26}$$

The two susceptibility functions F are determined by Eqs. (25) and (26), if Δ_{jk} can itself be determined; and $\rho(\nu_\lambda)$ is then fixed by Eq. (8a). In the remainder of this section we find a formal series expansion for Δ and show its connection with the resolvent operator.

We can find a formal expansion in the following way: by comparing Eqs. (20a), (21), and (23), it is easy to see that

$$\hbar\Delta_{jk}(\omega,\boldsymbol{\kappa}_\eta,\mathbf{q}_A)\langle A_k,\boldsymbol{\kappa}_\eta(A)|\bar\lambda\rangle$$
$$=\sum\nolimits_\alpha\langle A_j,\boldsymbol{\kappa}_\eta(A)|\mathcal{H}|\alpha\rangle\langle\alpha|\bar\lambda\rangle, \tag{27}$$

where the summation goes over all states except $|\alpha\rangle=|\eta\rangle$. Since there is no singular contribution of $|\eta\rangle$, it may be considered to go over all states.

The next step is to substitute (18) into the right hand side of (27). Then use (18) again to replace all the terms $\langle b|\bar\lambda\rangle$ on the right-hand side of the result, except for

$|b\rangle = |A_k,\boldsymbol{\kappa}(A)\rangle$, and repeat this indefinitely. This gives

$$\begin{aligned}
\hbar\Delta_{jk}(\omega,\boldsymbol{\kappa},\mathbf{q})\langle A_k,\boldsymbol{\kappa}(A)|\bar{\lambda}\rangle
&= \sum\nolimits_a{}' \sum\nolimits_b \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|b\rangle\langle b|\bar{\lambda}\rangle}{\hbar(\nu_\lambda-\nu_a+i\xi)} \\
&= \sum\nolimits_a{}' \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|A_k,\boldsymbol{\kappa}(A)\rangle}{\hbar(\nu_\lambda-\nu_a+i\xi)}\langle A_k,\kappa(A)|\bar{\lambda}\rangle + \sum\nolimits_a{}' \sum\nolimits_b{}' \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|b\rangle\langle b|\bar{\lambda}\rangle}{\hbar(\nu_\lambda-\nu_a+i\xi)} \\
&= \sum\nolimits_a{}' \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|A_k,\boldsymbol{\kappa}(A)\rangle\langle A_k,\boldsymbol{\kappa}(A)|\bar{\lambda}\rangle}{\hbar(\nu_\lambda-\nu_a+i\xi)} \\
&\quad + \sum\nolimits_{a,b}{}' \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|b\rangle\langle b|\mathcal{H}|A_k,\boldsymbol{\kappa}(A)\rangle\langle A_k,\boldsymbol{\kappa}(A)|\bar{\lambda}\rangle}{\hbar^2(\nu_\lambda-\nu_a+i\xi)(\nu_\lambda-\nu_b+i\xi)} + \cdots, \qquad (28)
\end{aligned}$$

where a prime on a summation means that the three states $|A_k,\boldsymbol{\kappa}(A)\rangle$ are to be omitted ($k=x$, y, z). By inspection of this series, we see that Δ_{jk} can be expressed formally as

$$\hbar\Delta_{jk}(\omega,\boldsymbol{\kappa},\mathbf{q}_A) = \sum\nolimits_a{}' \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|A_k,\boldsymbol{\kappa}(A)\rangle}{\hbar(\nu_\lambda-\nu_a+i\xi)} + \sum\nolimits_{a,b}{}' \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|b\rangle\langle b|\mathcal{H}|A_k,\boldsymbol{\kappa}(A)\rangle}{\hbar^2(\nu_\lambda-\nu_a+i\xi)(\nu_\lambda-\nu_b+i\xi)} + \cdots. \qquad (29)$$

Those familiar with the earlier work[8–10] will recognize the connection between Δ_{jk} and the "damping operator." We now wish to demonstrate its connection with the more familiar resolvent operator, defined by $R(z)=(z-\mathcal{H}_{\text{tot}})^{-1}$, where z is a complex number with the dimensions of energy. To this end, consider the following series expansion for a resolvent operator matrix element:

$$\begin{aligned}
\langle A_j,\boldsymbol{\kappa}(A)|R(\hbar\nu)|A_k,\boldsymbol{\kappa}(A)\rangle &= (\hbar\nu-E_{A\kappa})^{-1}\delta_{jk} + (\hbar\nu-E_{A\kappa})^{-2}\Bigg\{\sum\nolimits_a \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|A_k,\boldsymbol{\kappa}(A)\rangle}{\hbar\nu-E_a} \\
&\quad + \sum\nolimits_{a,b} \frac{\langle A_j,\boldsymbol{\kappa}(A)|\mathcal{H}|a\rangle\langle a|\mathcal{H}|b\rangle\langle b|\mathcal{H}|A_k,\boldsymbol{\kappa}(A)\rangle}{(\hbar\nu-E_a)(\hbar\nu-E_b)} + \cdots\Bigg\}, \qquad (30)
\end{aligned}$$

where

$$E_{A\kappa} = \hbar[\nu_0 + K(\mathbf{q}_A,\boldsymbol{\kappa})]. \qquad (31)$$

The terms in the series in curly brackets may be classified according to the number of intermediate states they contain of the form $|A_i,\boldsymbol{\kappa}(A)\rangle$. The total contribution of terms with no such states is easily seen to be just $\hbar\Delta_{jk}(\omega,\boldsymbol{\kappa},\mathbf{q}_A)$, since singling out these terms is equivalent to putting a prime on all the summations, giving the same series as (29). Similarly, each term with *one* such intermediate state can be written as the product of two primed sums times the energy denominator for the intermediate state, so that the contribution of all these terms is seen to be

$$\frac{(\hbar\Delta_{ji})(\hbar\Delta_{ik})}{\hbar\nu-E_{A\kappa}} = \frac{(\hbar\Delta)^2 jk}{\hbar\nu-E_{A\kappa}}.$$

Applying similar reasoning to the terms with two, three, etc., of these intermediate states, one easily finds

$$\langle A_j,\boldsymbol{\kappa}(A)|R(\hbar\nu)|A_k,\boldsymbol{\kappa}(A)\rangle = \frac{\delta_{jk}}{\hbar\nu-E_{A\kappa}} + \frac{\hbar\Delta_{jk}}{(\hbar\nu-E_{A\kappa})^2} + \frac{(\hbar\Delta)^2 jk}{(\hbar\nu-E_{A\kappa})^3} + \cdots = [\hbar\nu-E_{A\kappa}-\hbar\Delta(\omega,\boldsymbol{\kappa},\mathbf{q}_A)]_{jk}^{-1}. \qquad (32)$$

Comparing (32) with (25), we see that the susceptibility can be expressed as

$$F_t(\omega,\boldsymbol{\kappa}_\eta) = -4\pi\mu^2\frac{\mathfrak{N}}{V}\left(\frac{\beta}{\pi}\right)^{3/2}\int \exp(-\beta q_A{}^2)\epsilon_{\eta j}\langle A_j,\boldsymbol{\kappa}_\eta(A)|R(\hbar\nu)|A_k,\boldsymbol{\kappa}_\eta(A)\rangle\epsilon_{\eta k}d^3q_A \qquad (33)$$

(note that $\omega=\nu-\nu_0$). It is understood that ν should always be given a small positive imaginary part.

It might be objected that the series expansions and the rearrangements of them used in deriving (33) are not valid for all values of ν. However, it is sufficient if they are valid for some range of ν values. For then, Eq. (33) holds for a finite range of ν, and hence by analytic extension for all values, since both the susceptibility and the resolvent are analytic functions of ν in the upper half-plane, and the process of analytic extension is unique.

Expressions similar to (33) have, of course, been used by other authors. For example, if one carries out the indicated Fourier transform in Fano's[2] Eq. (3), one finds the following rather minor differences: (1) There are differences in multiplicative constants; (2) Fano's trace over the density matrix is replaced by our integration over q; (3) Our expression includes spatial dispersion and must be combined with (8a) in order to get the observable refractive index.

It is clear, then, that (33) is closely related to the results of other authors, but its derivation is not subject to the formal objections listed in Sec. II. It should be noted also that the resolvent is to be taken with respect to the *total* Hamiltonian, including that of the quantized radiation field. The practice of using only the Hamiltonian for the gas itself should be clearly recognized as an approximation, though it is no doubt a good approximation and will be used by us in the following sections.

V. STATIC LIMIT: DENSITY EXPANSION

Equation (33), or alternatively (25), in principle determines the susceptibility, but evaluating the necessary resolvent matrix elements is of course an impossibly difficult task. The problem can be more easily studied if we make the "static" approximation of allowing m to become infinite; this permits us to assign to each absorber a fixed position in space instead of an initial momentum. It will be recalled that the simple impact theory (which retains only the linear term in the density) gives a result independent of m for our problem, so it appears that the use of the static limit is particularly appropriate for this case.

In this limit, it is easy to see that Δ becomes a scalar, and that F_t is independent of the wave number. Equations (8a), (33), and (25) may therefore be replaced by

$$F_t(\omega)=\rho^2(\omega)-1=-\frac{4\pi\mu^2}{\hbar}\mathfrak{N}(\omega-\Delta)^{-1}$$

$$=-4\pi\mu^2\mathfrak{N}\langle A_i|R(\hbar\nu)|A_i\rangle \quad (34)$$

(no sum over i), where $\mathfrak{N}=N/V$.

We will also make the approximation of replacing $\mathfrak{H}$ (which includes the transverse field Hamiltonian) with the simple dipole-dipole Hamiltonian in taking the resolvent. This means that we are omitting magnetic and retardation effects. The only matrix elements of $\mathfrak{H}$ now are

$$\langle A_i|\mathfrak{H}|B_j\rangle=\frac{\mu^2}{{r_{AB}}^3}\left\{\delta_{ij}-3\frac{r_{ABi}r_{ABj}}{r^2{}_{AB}}\right\}=\frac{\mu^2}{{r_{AB}}^3}Y(\Omega), \quad (35)$$

where $Y(\Omega)$ is a function of angles only.

The perturbation series expansion for the resolvent can be expressed as

$$\langle A_i|R(\hbar\nu)|A_i\rangle=(\hbar\omega)^{-1}$$

$$+(\hbar\omega)^{-2}\left\{\sum_B\frac{\langle A_i|\mathfrak{H}|B_j\rangle\langle B_j|\mathfrak{H}|A_i\rangle}{\hbar\omega}\right.$$

$$\left.+\sum_{B,C}\frac{\langle A_i|\mathfrak{H}|B_j\rangle\langle B_j|\mathfrak{H}|C_k\rangle\langle C_k|\mathfrak{H}|A_i\rangle}{(\hbar\omega)^2}+\cdots\right\}. \quad (36)$$

In (36), there is no sum over i, but we do sum over all other repeated indices. Note that in the approximation we are considering all energy denominators are simply $\hbar\omega$.

It will be convenient to represent the terms in curly brackets in (36) by means of a simple diagrammatic notation. We use labeled circles to represent different absorbers and directed lines to represent Hamiltonian matrix elements connecting two absorbers. The continuity and direction of the lines gives the order of factors for each term. This is best made clear by giving some examples of diagrams together with the terms which they represent. This is done in Fig. 1.

Now consider the expansion of the resolvent in powers of the density:

$$\langle A_i|R(\hbar\nu)|A_i\rangle\equiv R(\omega)=(\hbar\omega)^{-1}+\sum_{n=1}^{\infty}\mathfrak{R}_n(\omega)\mathfrak{N}^n. \quad (37)$$

The corresponding expansion for Δ is:

$$\hbar\Delta(\omega)=\sum_{n=1}^{\infty}\mathfrak{A}_n(\omega)\mathfrak{N}^n. \quad (38)$$

Comparison of (36) and (37) shows that $\mathfrak{R}_n(\omega)\mathfrak{N}^n$ is simply $(\hbar\omega)^{-2}$ times the sum of all diagrams involving n atoms other than atom A. Alternatively, instead of summing all the diagrams one may sum those for a particular set of n absorbers, getting a function of the positions of the n absorbers, multiply this by $\mathfrak{N}^n$ and integrate over the positions of the absorbers. (Some of these integrals may diverge, but the sum of all of them is well behaved, as will be verified explicitly for $n=1$ in the next section.) In order for (34), (37), and (38) to be consistent, it is clear that $\mathfrak{A}_n(\omega)\mathfrak{N}^n$ must be just the sum of all diagrams involving n absorbers other than A, except those which are simply products of two or more diagrams of lower n. Since Δ is closely related to the width and shift of the line, it is the quantity usually expanded. We now prove that if the expansion (38) is

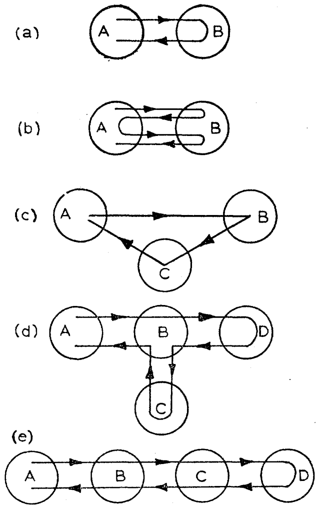

FIG. 1. Examples of diagrams: (a) Lowest order two-body diagram; $\langle A_i|\mathcal{H}|B_j\rangle\langle B_j|\mathcal{H}|A_i\rangle(\hbar\omega)^{-1}$; (b) Second-order two-body diagrams, $\langle A_i|\mathcal{H}|B_j\rangle\langle B_j|\mathcal{H}|A_k\rangle\langle A_k|\mathcal{H}|B_l\rangle\langle B_l|\mathcal{H}|A_i\rangle(\hbar\omega)^{-3}$; (c) Three-body diagrams, $\langle A_i|\mathcal{H}|B_j\rangle\langle B_j|\mathcal{H}|C_k\rangle\langle C_k|\mathcal{H}|A_i\rangle(\hbar\omega)^{-2}$; (d) and (e) Branched two-body diagrams, $\langle A_i|\mathcal{H}|B_j\rangle\langle B_j|\mathcal{H}|D_k\rangle\langle D_k|\times\mathcal{H}|B_l\rangle\langle B_l|\mathcal{H}|C_n\rangle\langle C_n|\mathcal{H}|B_{n'}\rangle\langle B_{n'}|\mathcal{H}|A_i\rangle(\hbar\omega)^{-5}$ and $\langle A_i|\mathcal{H}|B_j\rangle\times\langle B_j|\mathcal{H}|C_k\rangle\langle C_k|\mathcal{H}|D_l\rangle\langle D_l|\mathcal{H}|C_n\rangle\langle C_n|\mathcal{H}|B_{n'}\rangle\langle B_{n'}|\mathcal{H}|A_i\rangle(\hbar\omega)^{-5}$. Sum over repeated indices except i.

cut off after any finite number of terms, the result will always be meaningless sufficiently close to the center of the line.

If we consider a typical diagram with n atoms besides atom A, it is seen that its contribution to $\hbar\Delta$ is given by:

$$\mathfrak{N}^n(\mu^2)^p(\hbar\omega)^{-p+1}\int\cdots\int(R^3)^{-p}Y_{AB}\cdot Y_{BC}\cdots dR^{3n}. \quad (39)$$

Here p is the number of lines (or matrix elements) occurring in the diagram, $(R^3)^p$ is actually the product $R_{AB}{}^3R_{BC}{}^3\cdots$, and the required integration over the n atoms has been performed. From this form of the interaction, each matrix element is seen to contribute a factor $(\mu^2/r_{CD}{}^3)Y_{CD}(\Omega)$. With the simple change of coordinates,

$$\xi=[\hbar|\omega|/\mu^2]^{1/3}\mathbf{r}, \quad d^{3n}r=(\mu^2/\hbar(\omega))^n d^{3n}\xi,$$

(39) becomes

$$\mathfrak{N}^n\hbar\omega\left(\frac{\mu^2}{\hbar|\omega|}\right)^n\left(\frac{\omega}{|\omega|}\right)^p\int\cdots\int\frac{1}{\xi_{AB}{}^3\xi_{BC}{}^3}\cdots \times(Y_{AB}Y_{BC}\cdots)d^{3n}\xi, \quad (40)$$

where the integrated part is independent of the system parameters and depends only upon n. As an immediate consequence of this, we can write

$$\hbar\Delta(\omega)=\sum_{n=1}^{\infty}\left(\frac{\mathfrak{N}\mu^2}{\hbar\omega}\right)^n\hbar\omega\Lambda_n, \quad (41)$$

where Λ_n is an infinite sum of dimensionless integrals such as the one appearing in (40). It should be emphasized that it depends *only* on n (and on the sign of ω). Now it is easy to see that for any n, if

$$\omega<\frac{\mathfrak{N}\mu^2}{\hbar}\frac{\Lambda_{n+1}}{\Lambda_n},$$

then the $n+1$ term of the series (41) is larger than the nth. Thus, if one cuts off the series after any finite number of terms, there will always be a finite region about the center of the line for which the result is not even approximately valid (barring the extremely unlikely possibility that all but a finite number of the Λ_n are exactly zero). It is true that this region becomes narrow as $\mathfrak{N}$ becomes small, but so does the region of absorption. The conclusion is, then, that a finite number of terms of (41) will give a result which is quite accurate in the wings of the line, but totally meaningless in the region of appreciable absorption. Note that this result could not have been proved for broadening by foreign gases, since in that case ω would be replaced by $\omega+(\nu_0-\nu_g)$, where ν_g is a resonance frequency of the broadening gas, and this quantity remains large when ω becomes small.

It appears, then, that one must study the entire series (41) in order to have any hope of describing the absorption near the center. If we introduce the dimensionless variable $y=(\hbar\omega/\mathfrak{N}\mu^2)$, we see that Δ is equal to ω times a function of y. Combining this with (34), it is clear that the susceptibility is a function only of y:

$$F_t(\omega)=F_t(y). \quad (42)$$

There are now two possibilities:

(1) $F_t(y)$ is well behaved everywhere. This would mean either that the series (41) converges for all y or that it converges for sufficiently large y and that its analytic continuation is well behaved for all y. In this case, it is clear that the half-width would be simply proportional to $\mathfrak{N}$, even for very high densities:

$$\omega_{1/2}=(\mathfrak{N}\mu^2/\hbar)y_{1/2}, \quad (43)$$

with a similar relation for the shift, if any. However, one would have to sum the series (41) in order to evaluate the coefficient $y_{1/2}$. Since we don't know how to do this, we have no way at present of estimating the value of the coefficient, or the shape of the line. In particular, it is conceivable that summing (41) might lead to a value of $y_{1/2}$ in agreement with Tomiser's results.

(2) $F_t(y)$ has one or more singularities, most likely at $y=0$. We feel that this is the more likely possibility. In this case, the singularity would have to be smoothed out by taking into account one or more of the effects neglected in this section, such as the translational kinetic energy (noninfinite mass) or the finite atomic radius. The height of the maximum, and hence the half-width, would then depend on the parameters used in the

smoothing-out process (mass, temperature, atomic radius), as well as on the density.

In Sec. VII, we sum a restricted class of diagrams and arrive at a result in accordance with the second of the above possibilities. When the resulting singular susceptibility is averaged over the Doppler line shape, results are obtained which are in qualitative agreement with the experiments of Lauriston and Welsh.

VI. TWO-BODY APPROXIMATION

The "two-body" approximation, to be considered in this section, consists in taking just the first term in the series (41). According to the result of the last section, this is not an appropriate approximation for the center of the line, but should be very good in the far wings, for which experimental data do exist.[4] As we shall see in the next section, moreover, it can serve as a starting point for a qualitative theory of the line center.

While all previous workers on this problem have used the two-body approximation in one guise or another, none to our knowledge has systematically and correctly taken the spin-orbit interaction into account. Since the experimental data apply to the alkali doublets, it is necessary to do this before comparing the results with experiment.

The transition under consideration, then, is from a ${}^2S_{1/2}$ ground state to two different excited levels, ${}^2P_{3/2}$ and ${}^2P_{1/2}$. We will treat these lines as completely resolved; that is, we ignore the effect of each one on the other just as we ignored the effect of excited states other than the one under consideration in the previous sections.

In the case of the $\frac{3}{2}$ component, Eq. (34) is to be replaced by

$$\rho^2(\omega)-1=-\frac{8\pi\mu^2}{3\hbar}\mathfrak{N}(\omega-\Delta_{3/2})^{-1}$$
$$=-\frac{8\pi\mu^2}{3}\mathfrak{N}\langle An|R(\hbar\nu)|An\rangle; \quad (44)$$

while for the $\frac{1}{2}$ component we have

$$\rho^2(\omega)-1=-\frac{4\pi\mu^2}{3\hbar}\mathfrak{N}(\omega-\Delta_{1/2})^{-1}$$
$$=-\frac{4\pi\mu^2}{3}\mathfrak{N}\langle An|R(\hbar\nu)|An\rangle. \quad (45)$$

In Eqs. (44) and (45), μ is still the dipole moment matrix element with spin neglected, ω is calculated relative to the doublet component line under consideration in each equation, and n denotes quantum numbers required to specify a state, given that atom A is excited (e.g., magnetic quantum number of the excited atom and all unexcited ones, relative to some axis). It is clear that we can still use the diagram notation without confusion for this situation.

To find Δ in this approximation, we must sum all the diagrams containing only one atom B besides A, multiply the result by $\mathfrak{N}$, and integrate over the position of atom B.

Consider first the atoms A, B, with only the $\frac{3}{2}$ excitation permitted. A state of the system may be specified as follows: state which atom is excited (A or B); give the magnetic quantum number m_J of the excited atom ($\pm\frac{3}{2}$, $\pm\frac{1}{2}$); and give the spin quantum number of the unexcited atom ($\pm\frac{1}{2}$). Thus, there are sixteen states in all. If the zero of energy is taken as $\hbar\nu_0$, the Hamiltonian breaks up into 8×8 submatrices as follows:

$$\mathcal{H}=\frac{\mu^2}{r^3}\begin{pmatrix}0 & \mathfrak{U}\\ \mathfrak{U} & 0\end{pmatrix}, \quad (45a)$$

where $\mathfrak{U}$ is a matrix referring only to m_J and s (which we collectively call n). We can write a series form for $\Delta_{3/2}$ starting with the obvious analog of (36) as follows (it should be remembered that all diagrams involving only these two atoms are to be included, since none can be written as products of diagrams involving fewer than two atoms):

$$\hbar\Delta_{3/2}=\mathfrak{N}\int\langle An|\sum_{p=1}^{\infty}\frac{\mathcal{H}^{2p}}{(\hbar\omega)^{2p-1}}|An\rangle d^3r_B,$$
$$=\hbar\omega\mathfrak{N}\int\langle n|\sum_{p=1}^{\infty}\left(\frac{\mu^2}{r^3\hbar\omega}\mathfrak{U}\right)^{2p}|n\rangle d^3r_B,$$
$$=\frac{\hbar\omega\mathfrak{N}}{8}\int\mathrm{Tr}\left\{\frac{[(\mu^2/r^3\hbar\omega)\mathfrak{U}]^2}{1-[(\mu^2/r^3\hbar\omega)\mathfrak{U}]^2}\right\}d^3r_B, \quad (46)$$

where the last expression comes from summing the series and noting that because of symmetry all the diagonal elements will become equal after integration over the angles. It is understood that the series is summed for those values of ω for which it converges and the resulting function analytically continued to other values. In terms of the eigenvalues u_l of $\mathfrak{U}$, Eq. (46) takes the form

$$\hbar\Delta_{3/2}=\frac{\pi\hbar\omega\mathfrak{N}}{2}\sum_{l=1}^{8}\int_0^{\infty}\frac{[(\mu^2/r^3\hbar\omega)u_l]^2r^2dr}{1-[(\mu^2/r^3\hbar\omega)u_l]^2}$$
$$=-\frac{i\pi^2\mathfrak{N}\mu^2}{12}\sum_{l=1}^{8}|u_l|. \quad (47)$$

The integral is evaluated most easily by introducing the variable

$$y=\mu^2|u_l|/r^3\hbar$$

and remembering that ω is understood to have a small positive imaginary part.

The eigenvalues u_l are found most easily in a representation in which M_T, the total angular momentum

TABLE I. Comparison of theory with experiments on wings of alkali metal doublet lines.

Quantity:	$i\hbar\Delta_{3/2}/\mathcal{N}\mu^2$	$i\hbar\Delta_{1/2}/\mathcal{N}\mu^2$	$\Delta_{3/2}/\Delta_{1/2}$	Author
Theory:	6.73	4.48	1.59	Present work
	3.87	3.87	1.00	Houston (Ref. 16)
Exptl: Na	6.8±0.9	6.2±0.8	1.16±0.09	Watanabe (Ref. 4)
Rb	7.3±2.0	4.5±1.5	1.66±0.14	Chen (Ref. 4)
Cs	7.9±1.0	4.4±0.7	1.79±0.33	Gregory (Ref. 4)

along the line of centers, and J_T, the total angular momentum quantum number are diagonal. M_T is obviously conserved because of symmetry, so we only have matrix elements of $\mathcal{U}$ connecting states with the same M_T, though perhaps different J_T. Since the only values of J_T are 2 and 1, $\mathcal{U}$ breaks up into parts no larger than 2×2. The needed matrix elements can easily be worked out by the usual angular momentum theory[15] and give the following results:

$$M_T=2 \text{ or } -2;\quad J_T=2;\quad u=1.$$

$$M_T=1 \text{ or } -1;\quad J_T=2,\,1:$$

$$\mathcal{U}=\begin{array}{c|cc} & 2 & 1 \\ \hline 2 & -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ 1 & -\frac{1}{2}\sqrt{3} & -\frac{5}{6} \end{array},\quad u=\tfrac{1}{3}(-2\mp\sqrt{7})$$

$$M_T=0;\quad J_T=2,\,1:$$

$$\mathcal{U}=\begin{array}{c|cc} & 2 & 1 \\ \hline 2 & -1 & 0 \\ 1 & 0 & 5/3 \end{array},\quad u=-1,\ 5/3.$$

The eight eigenvalues u are therefore 1 (twice), $\frac{1}{3}(-2\mp\sqrt{7})$ (twice each), 5/3, and -1. Substituting these into (47) we find

$$\hbar\Delta_{3/2}=\frac{-i\pi^2\mathcal{N}\mu^2}{12}\{3+\tfrac{4}{3}\sqrt{7}+5/3\}=-6.73i\mathcal{N}\mu^2. \tag{48}$$

The procedure for the $\frac{1}{2}$ case is entirely similar. This time $\mathcal{U}$ is a 4×4 matrix with eigenvalues $-\frac{2}{3}$ (twice), $\frac{4}{3}$, and zero. This leads to the result:

$$\hbar\Delta_{1/2}=-i\pi^2\mathcal{N}\mu^2(4/9)=-4.48i\mathcal{N}\mu^2. \tag{49}$$

In this approximation, therefore, both Δ's are purely imaginary, and are to be identified with the half-width at half-height (in angular frequency units) of Lorentzian lines. If finite atomic radius is included, it leads to a cutoff of the absorption far out in the wings. As the work of the last section showed, this should be applied to the actual line only in the wings, but that is precisely the region in which the data of Ref. 4 was taken. A comparison is therefore permissible, and is given in Table I. In compiling Table I, the total oscillator strength of each doublet was taken as unity. The errors given are mean absolute deviations calculated by us from the data. For comparison the earlier theoretical results of Houston[16] are also listed. The agreement seems reasonably satisfactory (and definitely better than those of Houston) though more accurate measurements might be desirable.

Besides kinetic effects, we have also neglected interaction of the two doublet components with one another in the above, and this is not obviously negligible under all the experimental conditions. It is possible to generalize formally the above treatment to this case (still taking advantage of the conservation of M_T), and to show that the interaction introduces asymmetry and shifts in the lines. The details of this are rather formidable, and will not be presented here.

In the next section we use the results of this one as a starting point for a simple qualitative treatment of the line center.

VII. EXTENDED TWO-BODY APPROXIMATION

The work of the previous section allows one to describe the behavior in the wings of the line; in order to study the center, however, one must include diagrams involving arbitrarily large numbers of absorbers. The task of summing *all* diagrams is a formidable one indeed, and we are very far from knowing how to do it. In this section, we develop a very simple method, starting with the two-body result, for summing a restricted class of diagrams. Included in this class are diagrams with any number of absorbers. Many diagrams are omitted, however, and the reason for their omission is not that we can show their contribution to be negligible, but simply that we do not know how to evaluate it. Similarly, some diagrams are included which should not be, since they can be expressed as products of lower n diagrams. Despite these difficulties, we still hope that the results of this treatment are at least qualitatively correct; and the comparison with experiment will reinforce this hope.

Consider a typical two-body (AB) diagram involving atoms A and B, such as that of Fig. 2(a). If we momentarily consider the positions of A and B to be fixed, the diagram may be represented by a product $L_1L_2L_3\cdots$ of contributions from the different lines. We can turn this into a three-body (ABC) diagram by inserting a BC or AC diagram between any two adjacent lines of the original diagram, or after the last one. Examples are shown in Fig. 2 (b,c,d).

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[15] J. L. Powell and B. Crasemann, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1961), pp. 364–374.

[16] W. V. Houston, Phys. Rev. **54**, 884 (1938).

Let us now fix our attention on a particular point of insertion, say after the first line. If we sum over all the BC diagrams that can be inserted, and integrate over the position of C, the result is obviously a factor of (Δ_0/ω), where Δ_0 is now the two-body value of Δ. Hence, the sum of all diagrams consisting of the original AB diagram with a BC diagram inserted after the first line is just the original diagram with L_1 replaced by $L_1(\Delta_0/\omega)$. One can include more diagrams by allowing the inserted BC diagram to be followed immediately by BD diagram, as in Fig. 3. Diagrams of this type clearly give a factor $(\Delta_0/\omega)^2$. Similarly, we may insert any number of successive diagrams BD, BF, etc. (all different atoms, of course), getting successively higher powers of (Δ_0/ω). Hence, the original diagram plus all such insertions after the first line can be gotten by replacing L_1 by

$$L_1\{1+\Delta_0/\omega+(\Delta_0/\omega)^2+\cdots\}=L_1[\omega/(\omega-\Delta_0)].$$

As before, the series is summed in the region where it converges and the result analytically continued to other values of ω. Since insertions can take place after any line in the diagram (having several different lines all followed by insertions is permissible, of course), all insertions of this type may be included by multiplying the contribution of each line by the factor $[\omega/(\omega-\Delta_0)]$. Since each line contributes a factor μ^2 (among other things) we conclude that the effect of all insertions of this type will be included if we simply replace μ^2 in the two-body calculation of Δ by

$$\mu^2[\omega/(\omega-\Delta_0)].$$

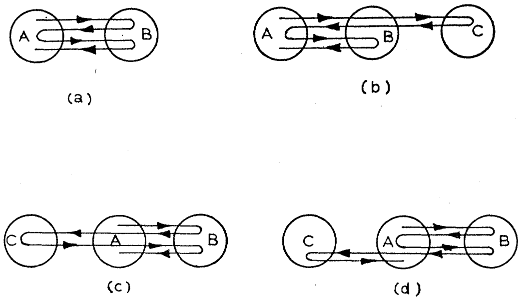

FIG. 2. (a) A typical two-body diagram; (b,c,d) Various ways of inserting a diagram involving a third body into (a).

Since Δ_0 depends linearly on μ^2, this leads to the following new value of Δ

$$\Delta_1=\Delta_0[\omega/(\omega-\Delta_0)]. \qquad (50)$$

It should be emphasized that the only diagrams included here are those that consist of a number of *independent* insertions of two-body diagrams into the original two-body diagram. In other words, all the inserted absorbers must be different, since otherwise the effect on different lines would not be independent. Figure 4 shows some diagrams which are omitted in the derivation of (50), and in the extensions to follow, but which should be included in an exact treatment. In addition, some of the diagrams included are simply products of lower n diagrams, and therefore should be omitted. Part of the contribution of Fig. 2(d) is of this type.

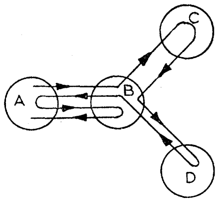

FIG. 3. A BC followed by a BD diagram inserted into Fig. 1(a).

We can include a wider class of diagrams by allowing a wider class of insertions. For example, we could insert any of the diagrams of the type included in Δ_1, leading, for example, to inclusion of diagrams such as that of Fig. 5. This leads to a further approximation for Δ.

$$\Delta_2=\Delta_0[\omega/(\omega-\Delta_1)]. \qquad (51)$$

Continuing this process of extension indefinitely, we finally obtain

$$\Delta=\Delta_0[\omega/(\omega-\Delta)]. \qquad (52)$$

We will use (52) in what follows without claiming to have fully justified it. We indicate the negative imaginary character of Δ_0 by writing $\Delta_0=-i\eta$ and solve (52) for Δ:

$$\Delta=\tfrac{1}{2}\omega\pm\tfrac{1}{2}(\omega^2+4i\eta\omega)^{1/2}\approx-(i\eta\omega)^{1/2}, \qquad (53)$$

with the root chosen to give Δ a negative imaginary part. The last approximate equality gives the leading term for small ω. The pertinent diagonal matrix element of the resolvent $R(\hbar\nu_\lambda)$ is then given from Eq. (44):

$$R=\langle A_n|R|A_n\rangle=[\hbar(\omega-\Delta)]^{-1}\approx\hbar^{-1}(i\eta\omega)^{-1/2}, \qquad (54)$$

with the approximate equality again applying at low frequency. Were the line in fact Lorentzian, as assumed by Laurston and Welsh, the corresponding resolvent

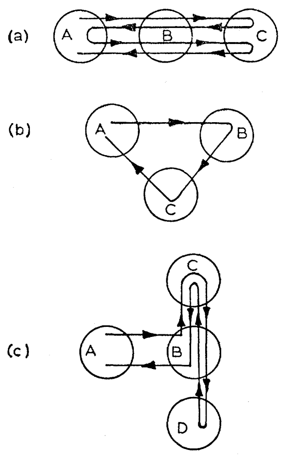

FIG. 4. Some diagrams omitted in the extended two-body treatment.

TABLE II. Comparison of results of Lauriston and Welsh (Ref. 7) with theoretical results.

Element	$\mathfrak{N}$ (atoms/cc) $\times 10^{-18}$	T (°K)	γ_1, 10^{-11} sec^{-1} obs	γ_1, 10^{-11} sec^{-1} calc	γ_2, 10^{-11} sec^{-1} obs	γ_2, 10^{-11} sec^{-1} calc	γ_2/γ_1 obs	γ_2/γ_1 calc
Na	0.34	891	2.3	1.24	3.0	1.53	1.30	1.26
	0.57	929	3.0	1.62	3.8	2.00	1.27	1.26
	0.93	968	3.8	2.09	4.9	2.57	1.29	1.26
	1.25	992	4.5	2.44	5.7	3.02	1.27	1.26
	2.4	1072	6.0	3.45	7.9	4.26	1.32	1.26
	3.1	1076	6.8	3.93	...	4.83	...	1.26
K	0.86	835	4.9	1.71	6.8	2.10	1.39	1.26
	1.31	867	6.0	2.12	8.3	2.61	1.38	1.26
	2.1	906	7.6	2.72	10.2	3.35	1.34	1.26
	3.5	955	9.8	3.55	13.5	4.37	1.38	1.26
	4.2	973	10.9	3.92	...	4.82	...	1.26
Rb	0.55	734	3.8	1.08	4.5	1.34	1.18	1.26
	0.84	763	4.9	1.35	5.7	1.67	1.16	1.26
	1.34	797	6.4	1.73	6.8	2.12	1.06	1.26
	1.8	811	6.8	2.01	9.4	2.48	1.38	1.26

element would be given by

$$R=\hbar^{-1}/(\omega+i\gamma/2)\,,\quad R(0)=-2i/\hbar\gamma\,, \tag{55}$$

where γ is their width at half the maximum intensity. Lauriston and Welsh's procedure was to adjust γ so as to give the best fit to their reflection data, which could not be fit perfectly by any Lorentzian line shape. Hence, it would be difficult to calculate a value for γ from (53) which could be compared directly with theirs. Moreover, since Eq. (52) is at most qualitatively correct anyway, such a calculation would not be worth the trouble. For purposes of qualitative comparison, however, we can simply define an "effective" γ by means of (55).

$$\gamma_{\text{eff}}=-2/\hbar\,\text{Im}R(0)\,. \tag{56}$$

We still have the problem that $R(0)$ is not defined according to (54) because of the singularity. Clearly, this must be smoothed out because of some effect omitted in the derivation of (52). The procedure we use is simply to smooth out our expression for Im(R) for small ω by integrating over all frequencies weighted by the Doppler distribution. That is, we write

$$\text{Im}[R(0)]=-\hbar^{-1}(2\eta)^{-1/2}(\sigma_d\pi^{1/2})^{-1}$$
$$\times\int_{-\infty}^{\infty}\exp(-\omega^2/\sigma_d^2)(|\omega|)^{-1/2}d\omega\,,$$
$$\sigma_d^2=2\nu_0^2kT/mc^2\,.$$

Integrating by means of the change of variables $y=(\omega/\sigma_d)^2$, we get

$$\text{Im}\{R(0)\}=-\hbar^{-1}\eta^{-1/2}(2\pi\sigma_d)^{-1/2}\Gamma(\tfrac{1}{4})\,. \tag{57}$$

It is now a simple matter to combine (56), (57), (48), and (49) to get a theoretical effective γ for each component of the doublet. These results can be compared with the γ's measured by Lauriston and Welsh. In order to find the proper temperature for their density, we have used the recent work of Hicks[17] on the vapor pressure of Na and K to find the temperature from the given density. In the case of Rb, we used the ideal gas law and crude vapor pressure data.[18] The comparison is presented in Table II. γ_1 and γ_2 refer to the $\frac{1}{2}$ and $\frac{3}{2}$ components respectively. In view of the approximations employed, this agreement is quite satisfactory. More than order-of-magnitude agreement could not be expected. The most noteworthy feature, however, is the dependence of the width on the square root of the density (except for the small variation in the temperature) in complete accord with their observations.

The fact that our simple theory gives qualitative agreement with the experiments of Lauriston and Welsh[7] reinforces the hope that the theory is qualitatively correct. It also tends to support Lauriston and Welsh's experimental results over those of Tomiser[5] and Moser and Schultz.[6] We have not been able to discover any approximate theory which agrees well with these latter results. Hence, at present, we must cast our vote in favor of Lauriston and Welsh. However, it would be desirable to have more experimental work done since the question is far from closed.[19]

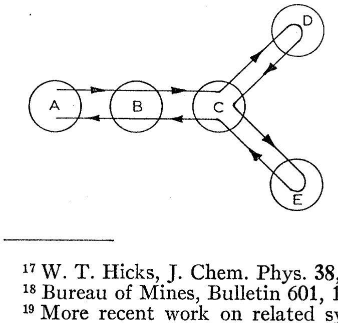

FIG. 5. A diagram included in Δ_2 but not in Δ_1.

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[17] W. T. Hicks, J. Chem. Phys. **38**, 1873 (1963).

[18] Bureau of Mines, Bulletin 601, 1962 (unpublished).

[19] More recent work on related systems has been brought to our attention; T. M. Bieniewski, *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 1055.

APPENDIX: STRONG LINEAR APPROXIMATION

The approximation to be considered here is a generalization of that used in earlier work by one of us.[8–10] We now feel that it is inappropriate under the conditions of the available experiments, but it may be useful under other circumstances. It starts with an assumption which is a generalization of (12):

$$\langle \boldsymbol{\kappa}(A) | 4\pi P_\alpha{}^{(A)} | \bar{\lambda} \rangle = F[\nu_\lambda - K(\mathbf{q}_A, \boldsymbol{\kappa}), \kappa_\alpha, \boldsymbol{\kappa}_\alpha \cdot \boldsymbol{\varepsilon}_\alpha] \langle \boldsymbol{\kappa}(A) | \mathcal{E}_\alpha | \bar{\lambda} \rangle, \quad \text{(A1)}$$

where $P^{(A)}$ is the polarization of the medium due to all atoms except atom A. To understand the meaning of (A1), suppose that the initial state of atom A is not known with certainty, so that the "initial" state of the medium is not simply $|0\rangle$, but

$$|0'\rangle = |0\rangle + u | \boldsymbol{\kappa}(A) \rangle .$$

Now the matrix element $\langle 0' | \mathcal{E}_\alpha | \bar{\lambda} \rangle$ will have a term of frequency

$$\nu_\lambda - K(\mathbf{q}_A, \boldsymbol{\kappa})$$

equal to $u^* \langle \boldsymbol{\kappa}(A) | \mathcal{E}_\alpha | \bar{\lambda} \rangle$, and a similar situation will hold for $P^{(A)}$. Equation (A1) expresses the assumption that the polarization of the rest of the medium is still related to the field (which now includes contributions from the virtual excitations of atom A) by the same susceptibility function. Equation (A1) does represent an approximation beyond (12). Classically, we can always limit our considerations to a linear susceptibility simply by making our fields arbitrarily small; but in quantum mechanics we cannot make the matrix elements appearing in (12) become small. Their values are fixed by the solution of the eigenvalue problem. Nevertheless, we can define a function F by means of (12), and this will lead to no contradictions as long as we restrict ourselves to those matrix elements in (12). Moreover, this is the obvious quantum-mechanical analog to the classical procedure of allowing the fields to approach zero; the one-photon state is as close to zero as we can get and still have any field at all. Strict linearity would be expressed by requiring that equations such as (12) hold for all matrix elements of the operators involved, and in particular for those of (A1). Hence, (A1) is a stronger linearity assumption than (12) and is designated the "strong linear" approximation. In order for (A1) to be quantitatively correct, it is necessary that the medium respond linearly to the field of A right up to the atomic radius [cf. also the remark just before Eq. (29) of Ref. 10]. Since this is obviously not the case, we do not now feel that the approximation is a good one. In terms of diagrams, it is clear that the diagrams omitted in this approximation are those that contain μ_A in higher than the lowest order, i.e., those that have A excited in one or more intermediate states. Hence, it might be expected to work at very high densities, where there are large numbers of atoms besides A within a short distance to carry the excitation in intermediate states. Alternatively, since the results will presently be seen to depend on the atomic radius r_0, it might be useful to use this approximation as a semiempirical model, with r_0 an adjustable parameter representing the radius at which the medium ceases to respond linearly.

In order to avoid divergence later, we introduce a cutoff factor $G(\kappa)$ into Eqs. (4) and (5); multiply (4) by $G^{1/2}(\kappa_\eta)$ and (5) by $G(\kappa)$. Our state $|0\rangle$ has each atom in a definite momentum state, and does not include any interactions in which two atoms can exchange momentum with both remaining in the ground state (direct interactions between atoms in the ground electronic state are neglected). If these were included, their main effect would be to introduce a correlation in the positions of the atoms such that the distance between the centers of mass of two atoms can never be less than an atomic diameter. We take this into account by altering the interaction so that, while atoms are formally permitted to approach each other arbitrarily closely, they are not permitted to exchange electronic excitation except at distances greater than the atomic diameter r_0. In this way, the transfer of excitation should proceed just as if there were no pairs of atoms closer than r_0. In momentum space, the momentum transfer accompanying the exchange of excitation should not be greater than the order of magnitude of $\hbar(1/r_0)$, and this is embodied in the factor $G(\kappa)$ which is a function that is nearly unity when $\kappa \ll 1/r_0$ and becomes very small or zero when $\kappa \gg 1/r_0$. It is a property of the strong linear approximation that the cutoff, not needed in the rest of the paper, is required here to avoid divergence.

Returning now to Eq. (29), we first consider the contribution of the longitudinal Coulomb part of κ to Δ_{jk}. Denoting this by a superscript l, and using Eqs. (5), (22), and (23), we can express this term as

$$\hbar \Delta_{jk}{}^l(\omega, \boldsymbol{\kappa}, \mathbf{q}_A) \langle A_k, \boldsymbol{\kappa}(A) | \bar{\lambda} \rangle \equiv \sum_{B \neq A, \alpha} \langle A_j, \boldsymbol{\kappa}(A) | \mathcal{H} | B_k, \boldsymbol{\kappa}_\alpha(B), (\boldsymbol{\kappa} - \boldsymbol{\kappa}_\alpha)(A) \rangle \langle B_k, \boldsymbol{\kappa}_\alpha(B), (\boldsymbol{\kappa} - \boldsymbol{\kappa}_\alpha)(A) | \bar{\lambda} \rangle$$

$$= \frac{4\pi}{V} \mu^2 \sum_\alpha G(\kappa_\alpha) \frac{\kappa_{\alpha j}}{\kappa_\alpha} \Gamma_\alpha{}^{l(A)}, \quad \text{(A2)}$$

where

$$\Gamma_\alpha{}^{l(A)} = \sum_{B \neq A} \frac{\kappa_{\alpha k}}{\kappa_\alpha} \langle B_k, \boldsymbol{\kappa}_\alpha(B), (\boldsymbol{\kappa} - \boldsymbol{\kappa}_\alpha)(A) | \bar{\lambda} \rangle ,$$

and the sum over α, of course, includes only longitudinal modes. Using (5), (13), and (A2), we can now obtain

$$\begin{aligned}\langle(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)|\mathcal{E}_\alpha|\lambda\rangle&=\langle(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)|\mathcal{E}_\alpha|A_k,\boldsymbol{\kappa}(A)\rangle\langle A_k,\boldsymbol{\kappa}(A)|\bar{\lambda}\rangle\\&\quad+\textstyle\sum_{B\neq A}\langle(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)|\mathcal{E}_\alpha|B_k,\boldsymbol{\kappa}_\alpha(B),(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)\rangle\langle B_k,\boldsymbol{\kappa}_\alpha(B),(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)|\bar{\lambda}\rangle\\&=\frac{4\pi}{V}\mu G(\kappa_\alpha)\frac{\kappa_{\alpha k}}{\kappa_\alpha}\langle A_k,\boldsymbol{\kappa}_\alpha(A)|\bar{\lambda}\rangle-\frac{4\pi}{V}\mu G(\kappa_\alpha)\Gamma_\alpha{}^{l(A)}.\end{aligned}\tag{A3}$$

It is also evident that

$$\langle(\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha)(A)|4\pi P_\alpha{}^{(A)}|\bar{\lambda}\rangle=\frac{4\pi\mu}{V}\Gamma_\alpha{}^{l(A)}.\tag{A4}$$

It is now a simple matter to insert (A3) and (A4) into (A1) and solve for $\Gamma_\alpha{}^{l(A)}$

$$\Gamma_\alpha{}^{l(A)}=-\frac{G(\kappa_\alpha)F_l[\omega-K(\mathbf{q}_A,\,\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha),\,\boldsymbol{\kappa}_\alpha](\kappa_{\alpha k}/\kappa_\alpha)\langle A_k,\boldsymbol{\kappa}(A)|\bar{\lambda}\rangle}{1+G(\kappa_\alpha)F_l[\omega-K(\mathbf{q}_A,\,\boldsymbol{\kappa}-\boldsymbol{\kappa}_\alpha),\,\kappa_\alpha]}.\tag{A5}$$

The next step is to substitute (A5) into (A2), replace the sum over α by integration, and extract the value of Δ_{jk}. The result is

$$\hbar\Delta_{jk}{}^l(\omega,\kappa,q)=-\frac{\mu^2}{2\pi^2}\int\frac{G^2(\kappa')F_l[\omega-K(\mathbf{q},\,\boldsymbol{\kappa}-\boldsymbol{\kappa}'),\,\kappa'](\kappa_j'\kappa_k'/\kappa'^2)d^3\kappa'}{1+G(\kappa')F_l[\omega-K(\mathbf{q},\,\boldsymbol{\kappa}-\boldsymbol{\kappa}'),\,\kappa']}.\tag{A6}$$

There is one more contribution to Δ_{jk}, namely that due to the transverse part of κ. By an entirely similar calculation it turns out to be:

$$\begin{aligned}\hbar\Delta_{jk}{}^t(\omega,\boldsymbol{\kappa},\mathbf{q})=-\frac{\nu_0{}^4\mu^2}{8\pi^2}\int\left[\delta_{jk}-\frac{\kappa_j'\kappa_k'}{\kappa'^2}\right]G^2(\kappa')F_t[\omega-K(\mathbf{q},\,\boldsymbol{\kappa}-\boldsymbol{\kappa}'),\,\kappa']d^3\kappa'\{+\nu_0{}^2G(\kappa')c\kappa'F_t[\omega-K(\mathbf{q},\,\boldsymbol{\kappa}-\boldsymbol{\kappa}'),\,\kappa']\\\times[\nu_\lambda-c\kappa'-K(\mathbf{q},\,\boldsymbol{\kappa}-\boldsymbol{\kappa}')+i\xi]+c^2\kappa'^2[\nu_\lambda-c\kappa'-K(\mathbf{q},\,\boldsymbol{\kappa}-\boldsymbol{\kappa}')+i\xi]^2\}^{-1}.\end{aligned}\tag{A7}$$

The matrix elements of Δ are now given by

$$\Delta_{jk}=-i\sigma_{jk}+\Delta_{jk}{}^l+\Delta_{jk}{}^t.\tag{A8}$$

One can also make the static approximation here, leading to the results of Refs. 8 and 10, to which the reader is referred for details. It is further possible to systematically bring in the kinetic effects by expanding in powers of $(1/m)$. We have done this and found that the first nonvanishing correction has negligible effect under the conditions of Tomiser's experiments on sodium.[5]

The predicted width is of the order of

$$(\mu^2/\hbar)(\mathfrak{N}/r_0{}^3)^{1/2},\tag{A9}$$

while the effective width out on the wings is just the natural linewidth. This last fact means that the strong linear approximation has far too little of the total intensity in the wings, since we know that the two-body approximation should work well there. On theoretical grounds, therefore, we must conclude that the actual line should be considerably narrower than (A9).

The square root density dependence predicted by (A9) is in agreement with Lauriston and Welsh, but the coefficient is much too large unless r_0 is treated as an adjustable parameter. If r_0 is taken as the atomic radius, the resulting very large widths are of the same order of magnitude as those reported by Tomiser over the density range in which he worked; but he observed a linear density dependence, not the square-root dependence of (A9).