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Technical Report

A STUDY OF LINE SHAPE WITH HEITLER'S DAMPING THEORY

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I. INTRODUCTION

Spectral lines of an atom are shifted and broadened when the atom interacts with its surroundings. The structure of the perturbed lines can be studied in the first approximation in terms of (a) the motion of the emitting atom (Doppler effect), (b) the finite life-time of the atomic excited states due to the light emission (natural broadening), and (c) the perturbation in the internal states of the radiating atom by the other particles of the medium (pressure effect). The physical properties of the medium are reflected in the line structure because of (a) and (c). Thus, the study of the photon line shape of a radiating atom can convey significant information about some of the physical properties of the surrounding medium. The success of this method as a noninterfering diagnostic tool certainly depends on one's theoretical understanding of the line broadening and the line shift phenomena. Line shape theory has received increasing attention in recent years with the start of high temperature plasma experiments. The optical line shape is regarded as a probe for measuring temperatures and ion concentrations within a plasma, where the use of material probes is ruled out because of the high temperature involved. Consequently, the line shape theory has enjoyed rapid progress in the past 15 years. Accuracies better than 20% in determining the ion density with the line width technique have been reported.[1]

No attempt will be made in this work to review the present state of line shape theory and calculations, because several review articles are available

in the literature. The most recent one, by M. Baranger,[1] contains the latest theoretical and experimental advances and will be the main reference for this work.

The present work proposes a new approach to the line broadening and line shift phenomena. It was motivated by a need for a more systematic and comprehensive theory of line shape, which could be applied to neutron scattering experiments as well as to photon experiments. Furthermore, the existing theory of line shape, in spite of its numerical success as noted above, contains some intuitive arguments, such as the folding of Doppler and pressure effects, as well as some gaps. It treats the effect of ions in the quasi-static limit by assuming the ions to be at rest, whereas it treats the electron effects with the impact approximation. It does not offer any good treatment for the intermediate region, where neither of these two limiting approximations is valid (see p. 504 of Ref. 1).

The line shape theory presented in this study is based on an entirely different approach and involves approximations of a different nature. This approach was chosen because it illuminates the manner in which the various simultaneous contributions to a line shape arise and are combined, and because it provides a calculational framework within which one may improve upon existing approximations. This framework, which is damping theory as discussed by Heitler,[2,3] appears to provide a more systematic and interpretable method than any employed previously. When applied to the line shape of an atom in a plasma, it provides a unified treatment of electrons and ions. In the quasi-static limit, it gives the Holtsmark theory. The dominant features of the

electron impact theory can be obtained from the present approach with use of the ergodic theorem.

The present theory of line shape has been developed in the case of a neutral atom to the point where numerical calculations are imperative for further progress. Extension of the theory to the case of an emitting ion appears to be straightforward.

It is hoped that the present work will contribute to a better understanding of the mechanism of line broadening and line shift.

II. DAMPING THEORY

A. INTRODUCTION

The present study of line shape is based* on Heitler's damping theory.[2-4] Therefore this chapter will be devoted to a brief discussion of the fundamental aspects of the damping theory from the standpoint of its present application. Section II.B follows essentially Heitler's presentation, and certain details are elaborated in Sections II.C and II.D.

B. BASIC THEORY

The temporal development of a quantum-mechanical system is determined by the "time-evolution" operator $U(t)$:

$$|t> = U(t)|0>, \tag{2.1}$$

where $|0>$ and $|t>$ are the state vectors at $t = 0$ and at time t. When the Hamiltonian H of the system is not an explicit function of t, $U(t)$ is given by

$$U(t) = e^{-itH/\hbar}. \tag{2.2}$$

Assume that H can be split into two parts as

$$H = H^{o} + V$$

*The use of the damping theory in line shape calculations has been also suggested by O. Rourke (cf. Ref. 4).

in such a way that the eigenvalue problem

$$H^{o}|n> = E_n|n>$$

can be solved. The eigenvectors $|n>$ are assumed to be complete and orthonormal, and thus to provide a basis for the physical problem under consideration. To avoid complications associated with the continuous spectrum, the calculations will be performed first in a large box of volume Ω, and then in the limit as $\Omega \to \infty$.

It is desired to compute the probability of finding the system in an eigenstate $|m>$ at time t, knowing that it was in the eigenstate $|n>$ at $t = 0$. This probability is equal to $|U_{mn}(t)|^2$, where U_{mn} is the matrix element of the time-evolution operator. Damping theory provides a method for computing $|U_{mn}(t)|^2$.

Let $G(z)$ denote the resolvent* of H, which is defined by

$$G(z) \equiv \frac{1}{z-H} , \qquad (2.3)$$

where z is a complex number. The evolution operator is the inverse Laplace transform of $G(z)$, i.e.,

$$U(t) = \frac{1}{2\pi i} \int_{-\infty+i\epsilon}^{+\infty+i\epsilon} dz\, G(z)\, e^{-itz/\hbar}, \qquad \epsilon > 0 . \qquad (2.4)$$

One can verify that

*See for example Ref. 5, p. 609, vol. II (French edition).

$$G(z) \equiv \sum_{\mu,\nu} \frac{|\mu\nu><\mu\nu|}{z-\mathcal{E}_\mu} \tag{2.5}$$

where $|\mu\nu>$ are the eigenvectors of H corresponding to the energy $\mathcal{E}_\mu$, i.e., $(H-\mathcal{E}_\mu)|\mu\nu> = 0$. The quantum number ν indicates the degeneracy of the energy eigenvalues. The $<\mu\nu|$ is the Hermitian conjugate of $|\mu\nu>$, and $\sum_\nu |\mu\nu><\mu\nu|$ is the projection operator on the subspace spanned by the eigenvectors $|\mu 1>$, $|\mu 2> \cdots |\mu\nu> \cdots$. Since the energy eigenvalues are real and positive, the singularities of $G(z)$ all lie on the positive real axis. In fact, $G(z)$ has branch cuts on the positive real axis corresponding to the continuous portion of the spectrum $\mathcal{E}_\mu$ in the limit as $\Omega \to \infty$. The foregoing argument indicates that the path of integration in (2.4) can be shifted towards the real axis by letting $\epsilon > 0$ tend to zero in performing the inversion integral.

The problem thus reduces to finding the matrix elements of $G(z)$ in the representation $\{H^o\}$. For this, one introduces two new operators, N and Q, such that

$$G = N + NQN \quad . \tag{2.6}$$

To determine N and Q uniquely, one imposes the condition that in the representation $\{H^o\}$, they be diagonal and nondiagonal respectively. Thus, N and NQN are the diagonal and nondiagonal parts of G in $\{H^o\}$. The reason for introducing these two operators becomes apparent if one considers the expansion of G in powers V, viz.,

$$G \equiv \frac{1}{z-H^{o}-V} \equiv \frac{1}{1-G_{o}V} G_{o} \equiv \sum_{n=0} (G_{o}V)^{n} G_{o} = \sum_{n=0} G_{o}(VG_{o})^{n} ,$$

where

$$G_{o} \equiv \frac{1}{z-H^{o}} .$$

The conventional perturbation theory is obtained by truncating this series after a finite number of terms. The validity of this approximation is restricted to the small values of t such that the decay of the initial state is negligible. This can be seen by considering the probability of finding the system in the initial state $|n>$ at time t, viz., $|U_{nn}(t)|^{2}$. The latter can be obtained as the magnitude square of the inverse Laplace transform of $G_{nn}(z) \equiv N_{nn}(z)$. Retaining the first two terms in the foregoing expansion, one finds that

$$|U_{nn}(t)|^{2} = 1 + |V_{nn}|^{2} t^{2} ,$$

which exceeds unity. This result is not correct even qualitatively. Similar unrealistic results are obtained even if one retains more than two terms in the expansion of G. It follows that the power series expansion is not adequate to investigate the variation of $|U_{nn}(t)|^{2}$ with time, which plays a fundamental role in the theory of line shape. In the damping theory, one tries to sum the infinite series representing N and NQN, viz.,

$$N \equiv \sum_{n=0} G_{o}[(VG_{o})^{n}]_{d} \qquad (2.7)$$

and

$$NQN \equiv \sum_{n=0} G_o[(VG_o)^n]_{nd} , \tag{2.8}$$

by solving certain integral equations by iteration. This procedure yields an approximation which is sufficiently accurate to take into account the variations of $|U_{nn}(t)|^2$.

An integral equation for N and Q can be obtained by rewriting (2.3) as

$$(z-H^o-V)G = 1 ,$$

substituting G from (2.6), and equating the diagonal and nondiagonal operators on both sides. The result is

$$Q = V_{nd} + [V_{nd}NQ]_{nd} - [(VNQ)_d NQ]_{nd} , \tag{2.9}$$

where

$$N \equiv [z-H^o-(\hbar/2)\Gamma(z)]^{-1} , \tag{2.10}$$

where

$$(\hbar/2)\Gamma(z) \equiv (V+VNQ)_d . \tag{2.11}$$

The subscripts d and nd indicate respectively the diagonal and nondiagonal parts of the operators they qualify. Treating N in (2.9) as independent of Q, one obtains by iteration an expansion of Q in powers of V:

$$Q = V_{nd} + V_{nd}NV_{nd} + \cdots . \tag{2.12}$$

Only the first term in (2.12) need be kept in order to discuss the dominant features of the line shape. Thus, the off-diagonal matrix elements of G(z)

will be approximated by

$$G_{mn}(z) = \frac{V_{mn}}{[z-E_m-(\hbar/2)\Gamma_{mm}][z-E_n-(\hbar/2)\Gamma_{nn}]} . \qquad (2.13)$$

The diagonal elements are of course given by N_{nn}, i.e.,

$$G_{nn}(z) = [z-E_n-(\hbar/2)\Gamma_{nn}]^{-1} . \qquad (2.14)$$

The expansion for $\Gamma(z)$ can be obtained by inserting (2.12) into (2.11) and replacing N by $(z-H^o)^{-1}$. The result is

$$(\hbar/2)\Gamma = V_d + \left[V \frac{1}{z-H^o} V_{nd}\right]_d + \ldots . \qquad (2.15)$$

The first two terms will be retained in the present treatment of the line shape theory.

One is now in a position to write an approximate expression for the matrix elements of the time-evolution operator U(t) by combining (2.15), (2.13), and (2.4). The off-diagonal elements read as follows:

$$U_{mn}(t) = \frac{1}{2\pi i} \int_{-\infty+i\epsilon}^{+\infty+i\epsilon} dz\, e^{-itz/\hbar} \frac{V_{mn}}{[z-E_m-(\hbar/2)\Gamma_{mm}][z-E_n-(\hbar/2)\Gamma_{nn}]} , \qquad (2.16)$$

where

$$(\hbar/2)\Gamma_{nn}(z) = V_{nn} + \sum_{n' \neq n}' \frac{|V_{n'n}|^2}{z-E_{n'}} . \qquad (2.17)$$

The diagonal elements follow from (2.14) as

$$U_{nn}(t) \equiv F_n(t) = \frac{1}{2\pi i} \int_{-\infty+i\epsilon}^{\infty+i\epsilon} dz \frac{e^{-itz/\hbar}}{z-E_n-(\hbar/2)\Gamma_{nn}(z)} . \qquad (2.18)$$

where the symbol $F_n(t)$ is introduced for future use.

The quantity $(\hbar/2)\Gamma_{nn}(z)$, which thus far has served merely as a mathematical symbol, has a physical significance. It will be seen later that the real and imaginary parts of $\Gamma_{nn}(z)$ at $z = E_n$ yield an approximation to the energy shift and the life-time of the state $|n>$.

C. EVALUATION OF THE INVERSION INTEGRAL

The inversion integral in (2.16) can be expressed as the convolution of $F_n(t)$ and $F_m(t)$, which are defined according to (2.18). Thus one has

$$U_{mn}(t) = \int_0^t F_m(t-\tau)\, F_n(\tau)\, d\tau = \int_0^t F_m(\tau)\, F_n(t-\tau)\, d\tau . \tag{2.19}$$

To evaluate $F_n(t)$ and hence $U_{mn}(t)$, one has first to investigate the analyticity of the integrand in (2.18), and in particular the analyticity of $\Gamma_{nn}(z)$. One can verify from (2.17) that the singularities of the latter are all located on the portion of the real axis defined by $x > E_o$, where E_o is the lowest eigenvalue of H^o. These singularities are all simple poles when the spectrum E_n is discrete. In the limit $\Omega \to \infty$, $\Gamma_{nn}(z)$ has cuts on the portions of the real axis that correspond to the continuous portion of the spectrum. As will be apparent presently, it is convenient to take the limit $\Omega \to \infty$ at this stage and to assume that $\Gamma_{nn}(z)$ has a cut on the real axis for $x > E_o$. It is noted that the following procedure is valid also in the case of a discrete spectrum. Moreover, it can be verified that $\mathrm{Im}\Gamma_{nn}(z)$ and $\mathrm{Im}\, z$ are always of opposite signs. Hence, the denominator in (2.18), i.e.,

$$D_n(z) \equiv z - E_n - (\hbar/2)\Gamma_{nn}(z) ,$$

can vanish only on the real axis. Thus, D_n^{-1} is analytic everywhere except on the real axis. The path of integration in (2.18) can therefore be shifted towards the real axis by letting $\epsilon \to 0^+$. The behavior of $\Gamma_{nn}(x+i\epsilon)$ in this limit can be obtained using the following relation:

$$\lim_{\epsilon\to 0} \frac{1}{x\pm i\epsilon} = PP \frac{1}{x} \mp i\pi\delta(x) ,$$

where PP indicates the Cauchy principal part whenever $(1/x)$ is integrand over a region containing $x = 0$. Equation (2.17) yields

$$\lim_{\epsilon\to 0} (\hbar/2)\Gamma_{nn}(x+i\epsilon) = S_n(x) - i(\hbar/2)\gamma_n(x) , \tag{2.20}$$

where

$$\gamma_n(x) \equiv (2\pi/\hbar) \sum_{n'\neq n} |V_{n'n}|^2 \delta(x-E_{n'}) \tag{2.21}$$

and

$$S_n(x) \equiv V_{nn} + PP \sum_{n'\neq n} \frac{|V_{n'n}|^2}{x-E_{n'}} . \tag{2.22}$$

Note that $\gamma_n(x)$ is a sequence of Dirac delta functions located at $x = E_{n'}$, and is zero elsewhere when the spectrum $E_{n'}$ is discrete. In the case of a continuous spectrum, or more explicitly when E_n is a continuous function of one of the quantum numbers contained in the set of indices (n), $\gamma_n(x)$ is finite and satisfies the following conditions:

$$\begin{aligned} \gamma_n(x) &= 0 \quad \text{for} \quad x < E_o , \\ \gamma_n(x) &> 0 \quad \text{for} \quad x > E_o . \end{aligned} \tag{2.23}$$

Now consider the behavior of $D_n(x+i\epsilon)$ as $\epsilon \to 0$. Let the limit of $D_n(x+i\epsilon)$ be denoted by $d_n(x)$, i.e.,

$$d_n(x) \equiv \lim_{\epsilon \to 0} D(x+i\epsilon) = x - E_n - S_n(x) + i(\hbar/2)\gamma_n(x) . \qquad (2.24)$$

In view of (2.23), one finds that $d_n(x)$ is nonvanishing for $x > E_o$. Furthermore, if the perturbation energy V is sufficiently small, it is nonvanishing also for $x < E_o$ [cf. (2.22)]. It will be assumed in the subsequent analysis that $d_n(x)$ is nonvanishing for all x. This assumption leads to

$$\lim_{\epsilon \to 0} D_n^{-1}(x+i\epsilon) = d_n^{-1}(x) \qquad (2.25)$$

and to

$$\lim_{\epsilon \to 0} D_n^{-1}(x-i\epsilon) = d_n^{-1}(x)^* , \qquad (2.26)$$

where the asterisk denotes complex conjugation.

The conclusion drawn from the foregoing discussion is that the integrand in (2.18) is analytic in the complex plane cut by Im z = 0 and Re $z > E_o$. Thus, the complex integration can be expressed as a real integral by shifting the path as indicated in Fig. 1. The result is

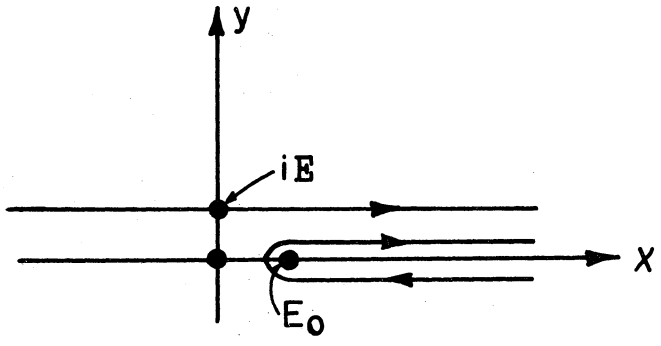

Fig. 1. Path of integration.

$$F_n(t) = \frac{1}{\pi}\int_{E_o}^{\infty} dx\, e^{-ixt/\hbar}\, \frac{(\hbar/2)\,\gamma_n(x)}{[x-E_n-S_n(x)]^2+(\hbar/2)^2\gamma_n^2(x)} \quad . \qquad (2.27)$$

It might perhaps be interesting to note, as a digression, that the integral in (2.27) can be performed rigorously when the spectrum is discrete. In the latter case $\gamma_n(x)$ is a sequence of delta functions, as mentioned previously. Since the integrand vanishes when $\gamma_n(x) \to \infty$, one may delete the points at which $\gamma_n(x) \neq 0$ without affecting the integral. On the other hand, the integrand reduces to a delta function when $\gamma_n(x) \to 0$, as can be seen from the following relation:

$$\lim_{\epsilon\to 0} \frac{\epsilon}{x^2+\epsilon^2} = \pi\delta(x) \quad .$$

Hence, $F_n(t)$ can be written as

$$F_n(t) = \int_{E_o}^{\infty} dx\, e^{-ixt/\hbar}\, \delta[x-E_n-S_n(x)] \quad .$$

One notes furthermore that

$$\delta[\phi(x)] = \sum_j \frac{\delta(x-x_j)}{|\phi'(x_j)|}$$

where x_j are the roots of $\phi(x) = 0$, which are assumed to be single, and $\phi'(x)$ is the derivative of $\phi(x)$. With the aid of this formula, $F_n(t)$ can be written as follows:

$$F_n(t) = \sum_j e^{-ix_jt/\hbar}\, \frac{1}{|1-S_n'(x_j)|} \quad .$$

One can verify easily that the roots of $x-E_n-S_n(x) = 0$ are all single. This result can be obtained directly from (2.18) by using the residue theorem. Thus, by taking the limit $\Omega \to \infty$ at an earlier stage and hence by using a branch cut rather than working with the poles, one actually obtains a method for evaluating the limit of the infinite sum involved in the last expression as $\Omega \to \infty$.

We now turn to the task of evaluating the integral in (2.27) in the case of a continuous spectrum. Since $S_n(x)$ and $\gamma_n(x)$ are small quantities, the integrand attains its maximum in the vicinity of the point $x \doteq E_n$, and the dominant contribution to the integral comes from this region. Furthermore, the functions $S_n(x)$ and $\gamma_n(x)$ are slowly varying functions of x, as will be discussed in Section II.D and thus can be treated as constants in a narrow region about the point $x = E_n$. Their constant value can be taken as $S_n(E_n)$ and $\gamma_n(E_n)$. Finally, one can replace the lower limit of the integral by $-\infty$ when $E_n \gg E_o$. With the foregoing assumptions, $F_n(t)$ can be expressed approximately as follows:

$$F_n(t) \approx e^{-\gamma_n t/2} e^{-i\bar{E}_n t/\hbar}, \tag{2.28}$$

where

$$\bar{E}_n = E_n + S_n(E_n) . \tag{2.29}$$

Henceforth, γ_n and S_n will denote $\gamma_n(E_n)$ and $S_n(E_n)$. The magnitude of the error involved in (2.28) can be estimated by

$$\frac{\hbar}{2\pi} \int_{-\infty}^{+\infty} dx \left| \frac{\gamma_n(x)}{[x-E_n-S_n(x)]^2+(\hbar/2)^2\gamma_n^2(x)} - \frac{\gamma_n}{(x-\bar{E}_n)^2+(\hbar/2)^2\gamma_n^2} \right| .$$

Since this is independent of time, the relative error on $F_n(t)$ will be appreciable for large values of t, i.e., $\gamma_n t \gg 1$, where $F_n(t)$ is small.*

The matrix element $U_{mn}(t)$ can now be evaluated approximately, by substituting $F_n(t)$ and $F_m(t)$ from (2.28) into (2.19). Since one is interested in the probabilities rather than in the matrix elements, only $|U_{mn}(t)|^2$ will be considered:

$$|U_{mn}(t)|^2 \cong \frac{|V_{mn}|^2}{(\bar{E}_m-\bar{E}_n)^2+(\hbar/2)^2(\gamma_m-\gamma_n)^2} \left| e^{-\frac{1}{2}\gamma_m t} - e^{-\frac{1}{2}\gamma_n t} e^{-i(\bar{E}_n-\bar{E}_m)t/\hbar} \right|^2 . \tag{2.30}$$

The validity of this result is limited by the approximations made in deriving (2.28). Considering the fact that $U_{mn}(t)$ involves the convolution of two approximate functions, one can convince himself that (2.30) is valid when either $\gamma_n t \ll 1$ or $\gamma_m t \ll 1$ holds. When both $\gamma_m t$ and $\gamma_n t$ are large as compared to unity, the validity of the equation becomes questionable.

The behavior of $|U_{mn}(t)|^2$ in different time intervals can be discussed with the aid of (2.30).

(i) $\gamma_n t \ll 1$, $\gamma_m t \ll 1$, $t > \hbar/|\bar{E}_n-\bar{E}_m|$

For such an interval of time to exist, $|\bar{E}_n-\bar{E}_m|$ must be much greater than both $\hbar\gamma_n$ and $\hbar\gamma_m$. The behavior of $|U_{mn}(t)|^2$ in this interval can be obtained by setting $\gamma_n = \gamma_m = 0$ and taking the limit $t \to \infty$ in (2.30). Noting also that

$$\lim_{t\to\infty} \frac{|1-e^{-ixt}|^2}{x^2 t} = 2\pi\delta(x) ,$$

*See p. 860 of Ref. 5.

one obtains the well-known first order perturbation result, i.e.,

$$|U_{mn}(t)|^2 = \frac{2\pi}{\hbar} t|V_{mn}|^2 \delta(\bar{E}_n - \bar{E}_m) . \qquad (2.31)$$

It is noted that, in this time interval, the meaningful concept appears to be the transition probability per unit time, i.e., $|U_{mn}(t)|^2/t$, rather than the probability of finding the system in the state $|m>$ at time t.

(ii) $\gamma_n t \gg 1$, $\gamma_m t \ll 1$ (or vice versa)

This time interval exists when $\gamma_n \gg \gamma_m$ or vice versa. In this interval, (2.30) reduces to

$$|U_{mn}|^2 = \frac{|V_{mn}|^2}{(E_m - E_n - S_{nm})^2 + (\hbar/2)^2 \gamma_n^2} , \qquad (2.32)$$

where S_{nm} is defined by

$$S_{nm} \equiv S_n - S_m . \qquad (2.33)$$

Note that in obtaining (2.32), γ_m has been neglected as compared to γ_n in the denominator of (2.30) so that the equation will be consistent with the condition $\gamma_n \gg \gamma_m$. It will be seen later (cf. Section IV.G) that γ_m and S_m represent the effect on the line shape of the interaction of the emitter with its surroundings, when the emitter is in its lower state. That γ_m does not appear in (2.32) indicates that the lower state interaction affects the line shape mainly through the shift in the energy of the lower state. The effect of finite life-time of the lower state seems to be a secondary effect. It is tempting to retain γ_m in (2.32) as a correction, and to replace (2.32) by

$$|U_{mn}|^2 = \frac{|V_{mn}|^2}{(E_m - E_n - S_{nm})^2 + (\hbar/2)^2 \gamma_{nm}^2} , \qquad (2.32a)$$

where

$$\gamma_{nm} \equiv \gamma_n - \gamma_m . \qquad (2.33a)$$

Although (2.32a) has the attractive feature of containing the shift and the width of both the initial and final states in a symmetric way, (2.32) will be used in the present study for the sake of a consistent and systematic theory.

It may be pointed out here that (2.32) rigorously follows[4] from (2.16) or from (2.19) if $\Gamma_{mm}(z) = 0$. This can be seen as follows: When $\Gamma_{mm}(z) = 0$, $F_m(t)$ can be evaluated rigorously [cf. (2.18)] as

$$F_m(t) = e^{-iE_m t/\hbar} .$$

Substituting this into (2.19) gives

$$|U_{mn}(t)|^2 = \left| \int_0^t d\tau \, e^{iE_m \tau/\hbar} \, F_n(\tau) \right|^2 . \qquad (2.34)$$

To obtain the behavior of $|U_{mn}(t)|^2$ for large times, i.e., $\gamma_n t \gg 1$, one has to consider the limit of (2.34) as $t \to \infty$. In this limit, the integral involved in (2.34) defines the Laplace transform of $F_n(\tau)$, which is given by (2.14). Thus, replacing z by E_m in (2.14) immediately gives (2.32). However there is a slight difference between (2.32) and the result obtained with the rigorous derivation. The S_n and γ_n are evaluated at $x = E_n$ in (2.32), whereas they are evaluated at $x = E_m$ in the latter case. But since the difference between E_n and E_m is of the order of a line width, and furthermore

since $S_n(x)$ and $\gamma_n(x)$ are slowly varying functions of x, no distinction will be made between $\gamma_n(E_n)$ and $\gamma_n(E_m)$ or between $S_n(E_n)$ and $S_n(E_m)$.

In conclusion, one may state that when the widths of both initial and final states are much smaller than the transition frequency $(E_n-E_m)/\hbar$, the transition probability per unit time appears to be a meaningful concept. On the other hand, when $\gamma_n \gg \gamma_m$, the meaninful concept is the conditional probability of finding the system in the state $|m>$ after it is certain that a transition from the initial state $|n>$ to any other state has taken place ($\gamma_n t \gg 1$). The only requirement for this concept to be meaningful is that the life-time of the final state be much longer than that of the initial state. It is important to note that the widths of the initial and final states need not be small as compared to $|E_n-E_m|/\hbar$, as was required in the previous case. It is this feature of the damping theory, i.e., the case (ii), which makes it suitable to the treatment of the line shift and line broadening phenomena. Moreover, the conditional probability of finding the system in a given state after a transition has occurred enables one to write the frequency distribution of a photon emitted in this transition.

D. WIDTH AND SHIFT FUNCTIONS

In this section, the width and shift functions, i.e., $\gamma_n(x)$ and $S_n(x)$, will be discussed in some detail. It will be seen later that the basic set $\{|n>\}$ could be written as

$$|n> = |\alpha M>|\beta\nu> , \qquad (2.35)$$

where the eigenvectors $|\alpha M>$ span a finite dimensional space and $|\beta\nu>$ span a continuous space. The energy E_n of a state $|n>$ now has the following form: $E_n = E_\alpha + E_\beta$, where β is a continuous index. The symbols M and ν describe degenerate states corresponding to the energies E_α and E_β respectively. One recalls that the eigenvectors $|n>$ are generated by H^o; they are not specified otherwise. In dealing with the degenerate levels E_α, it proves to be convenient to choose the base vectors to diagonalize the operator $P_\alpha V P_\alpha$ as well as H^o. Here, P_α denotes the projection operator on the subspace spanned by the vectors $|\alpha M>$ belonging to the energy eigenvalue E_α, i.e.,

$$P_\alpha = \sum_M |\alpha M><M\alpha| \ .$$

More explicitly, one has

$$<\alpha M|V|\alpha M'> = <\alpha M|V|\alpha M>\delta_{M,M'} \ . \tag{2.36}$$

To convert a summation over a continuous index to an integral, one defines a density function as follows:

$$\rho(\beta,\nu)\,d\beta\,d\nu = \sum_{(\beta,\nu)\in d\beta d\nu} \ .$$

With the foregoing definition in mind, one writes $\gamma_n(x)$ from (2.21) as follows:

$$\gamma_n(x) = \frac{2\pi}{\hbar}\Bigg[\sum_{\alpha'\neq\alpha}\int d\beta'\delta(x-E_{\alpha'}-E_{\beta'})\sum_{M'}\int d\nu'\rho(\beta',\nu')\,|<n'|V|n>|^2$$

$$+\int d\beta'\delta(x-E_\alpha-E_{\beta'})\sum_{\nu'_\beta\neq\nu_\beta}\int d\nu'\rho(\beta',\nu')\,|<n'|V|n>|^2\Bigg] . \tag{2.37}$$

It is noted that the restriction $n' \neq n$ in (2.21) now reduces to $\nu'_\beta \neq \nu_\beta$ in the integration on ν' in (2.37). Since the latter restriction corresponds to deleting a point in an integration, one can drop it out without affecting the value of the integral. A remark of caution is due here. The foregoing conclusion does not hold when the eigenvectors $|\beta\nu>$ diagonalize V as well as H^o, i.e., when

$$< \beta'\nu' |V| \beta\nu > \equiv < \beta\nu |V| \beta\nu > \delta_{\beta',\beta} \delta_{\nu',\nu} .$$

In this case, $\gamma_n(x)$ takes the following form:

$$\gamma_n(x) = \frac{2\pi}{\hbar} \sum_{\substack{M' \\ \alpha' \neq \alpha}} |< \beta\nu\alpha' M' |V| \beta\nu\alpha M >|^2 \delta(x - E_{\alpha'}) .$$

This equation indicates that $\gamma_n(x) = 0$ in the neighborhood of the point $x = E_\alpha$ even in the limit as $\Omega \to \infty$. This special case will be encountered when the quasi-static approximation is made (cf. Section V.B).

When the restriction $\nu'_\beta \neq \nu_\beta$ is omitted in (2.37), $\gamma_n(x)$ can be written as follows:

$$\gamma_n(x) = \frac{2\pi}{\hbar} \sum_{\alpha'} \int d\beta' \delta(x - E_{\alpha'} - E_{\beta'}) \sum_{M'} \int d\nu' \rho(\beta', \nu') | < n' |V| n >|^2 . \tag{2.38}$$

Similarly, the shift function can be obtained from (2.22) as

$$S_n(x) = < n|V|n > + \sum_{\alpha'} PP \int d\nu' \frac{\sum_{M'} \int d\nu' \rho(\beta', \nu') | < n' |V| n >|^2}{x - E_{\alpha'} - E_{\beta'}} . \tag{2.39}$$

The variation of $\gamma_n(x)$ and $S_n(x)$ with x in the neighborhood of the point $x = E_n$ can now be seen more clearly. Equation (2.38) indicates that $\gamma_n(x)$ is proportional to

$$\sum_{M'\alpha'} \int d\nu' \rho(\beta', \nu') \frac{d\beta'}{dE_{\beta'}} \; | < n' | V | n > |^2 \; , \qquad (2.40)$$

which is evaluated at $E_{\beta'} = x - E_{\alpha'}$. One may argue on physical grounds that (2.40) is a smooth and slowly varying function of $E_{\beta'}$, and thus of x. Similar arguments can also be given for $S_n(x)$.

III. EMISSION SPECTRUM

A. INTRODUCTION

In this section, we attempt to obtain an expression for the spectrum of energy radiated by a finite aggregate of particles. The system is assumed to be optically thin so that the emitted photons escape the system without interacting with the particles. This assumption simplifies the analysis by eliminating the problems connected with photon transport in the system.[6] The temperature of the system is kept constant by heating the container walls externally. Thus the energy carried away by emitted photons is made up through the collisions of the particles with the heated walls.

The following derivation differs from the standard derivation of the emission spectrum[3,6] in the treatment of $|U_{mn}(t)|^2/t$.

B. BASIC THEORY

The Hamiltonian of the system can be written as

$$H = H^s + H^r + V^r , \tag{3.1}$$

where H^s and H^r are the Hamiltonians of the particle system and of the radiation field respectively, and V^r is the interaction energy between the two. We split H as $H = H^o + V$ where the unperturbed Hamiltonian H^o and the perturbation energy V are given by

$$\begin{aligned} H^o &= H^s + H^r , \\ V &= V^r . \end{aligned} \tag{3.2}$$

The set of base vectors generated by H^o are labelled as $|n\eta> = |n>|\eta>$, where $|n>$ are the eigenvectors of the particle system, i.e.,

$$(H^s - E_n)\,|n> \;=\; 0\,, \tag{3.3}$$

and $|\eta>$ are the eigenvectors appropriate to the radiation field, i.e.,

$$(H^r - E_\eta)\,|\eta> \;=\; 0\,. \tag{3.4}$$

We shall assume that in the representation (3.4) the photon number operator $\rho_\lambda(\underline{k})$ for photons of momentum $\hbar\underline{k}$ and polarization $\underline{\epsilon}_\lambda(\underline{k})$ is diagonal, i.e.,

$$<\eta'|\rho_\lambda(\underline{k})\,|\eta> \;=\; \eta_\lambda(\underline{k})\,\delta_{\eta,\eta'}\,, \tag{3.5}$$

where $\eta_\lambda(\underline{k})$ is the number of photons of the specified type when the system is in the state $|\eta>$.

The expected number of photons of a given kind is known to be[6]

$$\chi_\lambda(\underline{k}) \;=\; \mathrm{Tr}[\rho_\lambda(k)\;D] \tag{3.6}$$

where D is the density matrix which is governed by

$$i\hbar\dot{D} \;=\; [H,D]\,, \tag{3.7}$$

where the dot indicates differentiation with respect to time. Since H is not an explicit function of time, the solution of (3.7) can be expressed in terms of the time-evolution operator [cf. (2.2)] as

$$D(t+s) \;=\; U(s)\;D(t)\;U^{+}(s)\,. \tag{3.8}$$

The rate of change in the photon number is obtained from (3.6) as

$$\dot{\chi}_\lambda(\underline{k}) \;=\; \mathrm{Tr}[\rho_\lambda(\underline{k})\ \dot{D}] \quad .$$

Expressing $\dot{D}(t)$ as

$$\dot{D}(t) \;=\; \frac{1}{s}\,[D(t+s) \;-\; D(t)\,] \;,$$

one obtains

$$\dot{\chi}_\lambda(k) \;=\; \frac{1}{s}\,\mathrm{Tr}\left\{\rho_\lambda(\underline{k})\,[D(t+s) \;-\; D(t)\,]\right\} \quad . \tag{3.9}$$

Substituting $D(t+s)$ from (3.8) gives

$$\dot{\chi}_\lambda(\underline{k}) \;=\; \frac{1}{s}\,\mathrm{Tr}\left\{\rho_\lambda(\underline{k})\ [U(s)\ D(t)\ U^{+}(s) \;-\; D(t)\,]\right\} \quad . \tag{3.10}$$

Expressing the trace in the representation $\{|n\eta>\}$ which diagonalizes the photon number operator, and neglecting the off-diagonal matrix elements of D, one obtains

$$\dot{\chi}_\lambda(\underline{k}) \;=\; \frac{1}{s}\left\{\sum_{n\eta,\,n'\eta'} \eta\,|U_{n\eta,\,n'\eta'}|^2\ D_{n'\eta',\,n'\eta'} \;-\; \sum_{n'\eta'} \eta'\ D_{n'\eta',\,n'\eta'}\right\} , \tag{3.11}$$

where U and D are to be evaluated at s and t respectively. Since U is a unitary matrix, one has

$$\sum_{n\eta} |U_{n\eta,\,n'\eta'}|^2 \;=\; 1 \quad . \tag{3.12}$$

Multiplying the last term in (3.11) by (3.12), which is unity, one finds for (3.11):

$$\dot{\chi}_\lambda(\underline{k}) = \sum_{n'\eta',n\eta} (\eta'-\eta) W_{n'\eta',n\eta} D_{n\eta,n\eta} , \qquad (3.13)$$

where

$$W_{n'\eta',n\eta}(s) \equiv \frac{|U_{n'\eta',n\eta}(s)|^2}{s} . \qquad (3.14)$$

The difference $J = (\eta'-\eta)$ in (3.13) is an integer, and denotes the change in the number of photons in the transition $|\eta> \rightarrow |\eta'>$. The summation over η' in (3.13) can be replaced by a summation over j:

$$\dot{\chi}_\lambda(\underline{k}) = \sum_{n\eta,n'j} j\, W_{n'(\eta+j),n\eta} D_{n\eta,n\eta} ,$$

where $j = \pm 1, \pm 2, \ldots$. The negative and positive terms correspond to absorption and emission respectively. Since the system is assumed to be optically thin, the absorption terms can be disregarded. Furthermore, the contribution of the transitions involving more than one photon, i.e., $j > 1$, can be ignored as a first approximation. Then, the last equation takes the following form:

$$\dot{\chi}_\lambda(\underline{k}) = \sum_{nn'\eta} W_{n'(\eta+1),n\eta} D_{n\eta,n\eta} ,$$

where $\eta = 0,1,2,\ldots$. Henceforth, we shall confine ourselves to the spontaneous emission by assuming that the radiation is not present in the initial state, i.e., $\eta = 0$. This simplifying assumption is realistic for emission experiments involving an optically thin system where the emitted photons can be assumed to leave the system instantaneously. However, the effect of

the induced emission can also be included in the present analysis if the experimental conditions (e.g., those for laser experiments) so require. The foregoing assumptions imply that the state vector of the whole system remains, during its evolution with time, in the subspace spanned by the eigenvectors with $\eta = 1$ (one-photon states) and $\eta = 0$ (zero-photon states). Henceforth we shall denote one-photon states by

$$|m> \equiv |n'\underline{k}_\lambda> = |n'>|\underline{k}_\lambda> , \tag{3.15}$$

and zero-photon states by

$$|n> = |n>|0> . \tag{3.16}$$

The total power radiated in all directions in the frequency interval dw about w can be obtained from (3.13) as

$$I(w)\,dw = \sum_{\hat{\underline{k}}_\lambda,\, w \in dw} \hbar w\, \dot{\chi}_\lambda(\underline{k}) , \tag{3.17}$$

where $\hat{\underline{k}} = (\underline{k}/k)$ and $w = ck$. Recalling that

$$\sum_{\underline{k}} \to \frac{\Omega}{(2\pi c)^3}\, w^2 dw\, d\Omega_{\hat{\underline{k}}} ,$$

one obtains the intensity distribution I(w) as

$$I(w) = \frac{\Omega w^3 \hbar}{(2\pi c)^3} \sum_{\lambda, n, n'} \int d\Omega_{\hat{\underline{k}}}\, W_{mn}\, P_n , \tag{3.18}$$

where

$$P_n = D_{n,n} \tag{3.19}$$

is introduced to emphasize the physical significance of $D_{n,n}$ as being the probability of finding the particle system in $|n>$ and the photon system in $|0>$. It is taken here to be

$$P_n = <n|e^{-\beta H}|n>/Tr[e^{-\beta H}] \quad . \tag{3.20}$$

If one neglects the interaction energy V^r in H, (3.20) can be approximated by

$$P_n = Z^{-1} e^{-\beta E_n} \tag{3.21}$$

where $Z = Tr \exp[-\beta H]$. Furthermore, in (3.20) and (3.21), $\beta = (1/KT)$, where K is the Boltzman constant and T is the temperature.

Now we consider W_{mn}, which can be written alternatively [cf. (3.14)] as

$$W_{mn}(s) = \frac{|U_{mn}(s)|^2}{s} = \frac{|U_{mn}(s)|^2}{\sum_{m\neq n} |U_{mn}(s)|^2} \sum_{m\neq n} \frac{|U_{mn}(s)|^2}{s} \quad . \tag{3.22}$$

Instead of interpreting $W_{mn}(s)$ as the transition probability per unit time and thus using (2.31)—which is valid when s satisfies $\gamma_n s \ll 1$, $\gamma_m s \ll 1$, and $s \gg \hbar/|E_n - E_m|$ [case (i)]—we proceed as follows: We evaluate the first factor in (3.22) for $\gamma_n s \gg 1$ and $\gamma_m s \ll 1$ [case (ii)], and the second factor for the values of s in case (i). Since U is unitary, one can write the denominator of the first term as $1-|U_{nn}(s)|^2$ [cf. (3.12)]. One finds from (2.28) that

$$|U_{nn}(s)|^2 = e^{-\gamma_n s} \quad . \tag{3.23}$$

Hence, one can neglect $|U_{nn}(s)|^2$ as compared to unity for $\gamma_n s \gg 1$, and can

replace the denominator in (3.22) by one. The numerator is given by (2.32) for the values of s in case (ii).

As to the second factor, we combine (2.31) and (2.21), and obtain

$$\sum_{m\neq n} |U_{mn}(s)|^2/s = \gamma_n \quad . \tag{3.24}$$

In conclusion, we approximate $W_{mn}(s)$ by

$$W_{mn}(s) = |U_{mn}|^2 \gamma_n \quad . \tag{3.25}$$

Substituting (3.25) into (3.18), and using (2.32) for $|U_{mn}|^2$, one obtains the following formula for the emission spectrum:

$$I(w) = \frac{\Omega w^3 \hbar}{(2\pi c)^3} \sum_{n,n',\lambda} \int d\Omega_{\hat{k}} P_n \frac{\gamma_n |V^r_{mn}|^2}{(E_m - E_n - S_{nm})^2 + (\hbar/2)^2 \gamma_n^2} \quad , \tag{3.26}$$

which will serve as the starting point in the present treatment of line shape theory.

C. AUTOCORRELATION FORMALISM

Before proceeding further, we shall briefly discuss the autocorrelation formalism which has been the starting point in almost all previous treatments of line shape theory. In autocorrelation analysis, $W_{mn}(s)$ is interpreted as the transition probability per unit time, and is thus approximated by (2.31). The same result can be obtained directly from (3.26) by letting γ_n and S_{nm} tend to zero. Recalling that

$$\lim_{\epsilon\to 0} \frac{\epsilon}{x^2+\epsilon^2} = \pi\delta(x) \quad ,$$

one obtains

$$I(w) = \Omega \frac{w^3}{4\pi^2 c^3 \hbar} \sum_{n',n,\lambda} \int d\Omega_{\hat{k}} |V^r_{mn}|^2 P_n \delta(w-w_{n'n}) . \qquad (3.27)$$

The matrix element of V^r_{mn} can be expressed as

$$V^r_{mn} = \sqrt{\frac{2\pi h}{\Omega w}} R_{n'n} \qquad (3.28)$$

where R is an operator defined by

$$R(\underline{k}_\lambda) = \sum_j e^{-i\underline{k}\cdot\underline{r}_j} (e_j/m_j) \underline{p}_j \cdot \underline{\epsilon}_\lambda(\underline{k}) . \qquad (3.29)$$

The summation in (3.29) is extended over the particles. The charge, mass, momentum, and position of the jth particle are denoted by e_j, m_j, $\underline{p}_j$ and $\underline{r}_j$ respectively. The $W_{n'n}$ in (3.27) is given by

$$W_{n'n} = (E_n - E_{n'})/\hbar .$$

Inserting (3.28) into (3.27) yields

$$I(w) = \frac{w^3}{2\pi c^3} \sum_{n',n,\lambda} \int d\Omega_{\hat{k}} P_n |R_{n'n}|^2 \delta(w-w_{n'n}) . \qquad (3.30)$$

Using the Fourier representation of the delta function, i.e.,

$$\delta(x) = \int_{-\infty}^{+\infty} e^{ixt/\hbar} dt/2\pi\hbar ,$$

one can write (3.30) as follows:

$$I(w) = \frac{w^2}{4\pi^2 c^3} \int_{-\infty}^{+\infty} e^{iwt} \phi(t) dt , \qquad (3.31)$$

where

$$\phi(t) = \mathrm{Tr}\left[D^S \sum_{\lambda} \int d\Omega_{\underline{k}} \, R^+(0) \, R(t) \right] . \qquad (3.32)$$

The time-dependent operator R(t) is defined by

$$R(t) = e^{itH^S/\hbar} \, R(0) \, R^{-itH^S/\hbar} . \qquad (3.33)$$

In (3.32), D^S denotes the density matrix for the particle system.

The function $\phi(t)$ is known as the autocorrelation function of the light amplitude (see p. 498 of Ref. 1). In the usual dipole approximation, $\phi(t)$ reduces to

$$\phi(t) = \frac{8\pi}{3} w^2 \, \mathrm{Tr}[D^S \, \underline{d}^+(0) \cdot \underline{d}(t)] . \qquad (3.34)$$

It is observed that the autocorrelation formalism follows from the emission spectrum formula (3.26) when the width and the shift of the particle states are ignored. Since the transitions between these states are caused by the electromagnetic interaction, the approximation involved in obtaining (3.31) from (3.26) is equivalent essentially to neglecting the natural width. Equation (3.26) expresses the spectrum as the weighted superpositions of a sequence of Lorentzian distributions which represent the spectrum of the individual photons emitted in transitions $|n> \rightarrow |n'>$. In (3.27), these Lorentzian curves are replaced by a sequence of delta functions. When the width of the observed spectral lines is much greater than the natural width, as is the case in most applications, the use of delta functions instead of Lorentzian distributions is a valid approximation. Therefore, the emission

spectrum formulas (3.26) and (3.31) can be regarded as two starting points which are equivalent as far as exact calculations are concerned. For approximate calculations, however, one approach may be preferable to the other. This can be found out by comparing the number and the nature of approximations that have to be made in both approaches to obtain a practical line shape formula. The autocorrelation approach has been fully investigated in the literature.[1] The subsequent sections will explore the possibilities of the present formalism so that it can be compared with the autocorrelation approach.

IV. LINE SHAPE

A. INTRODUCTION

Line shape is defined as the frequency distribution of those photons that are emitted in transitions between two bound states. Photons which are due to transitions involving one or two free states (continuum radiation) can be disregarded in discussing the shape of a spectral line whose intensity is sufficiently greater than the continuum radiation.

It is convenient to think of the particle system as composed of two interacting quantum-mechanical systems; these will be referred to henceforth as the emitter and the perturber. It is assumed that only the emitter has discrete energy levels. The perturber can be visualized as an aggregate of interacting, structureless particles. The interaction of the radiation field with the perturber can be ignored, because it gives rise to Bremsstrahlung.

The Hamiltonian H^s of the particle system [cf. (3.1)] can now be written as

$$H^s = H^e + H^p + V^p \tag{4.1}$$

where H^e and H^p are the Hamiltonians of the emitter and the perturber respectively, and V^p is the interaction energy between the emitter and the perturber. The Hamiltonian of the system, including the particles and photons, is

$$H = H^r + H^e + H^p + V^r + V^p \tag{4.2}$$

where V^r represents the interaction between the emitter and the radiation.

The individual spectral lines corresponding to transitions between the internal energy levels of the emitter are not recognizable in the emission spectrum formula (3.26). By a proper choice of the base vectors $|n>$, one can express the intensity $I(w)$ as the superposition of the spectral lines. This will be task of the present section.

B. LINE SHAPE FORMULA IN THE REPRESENTATION $\{|\alpha M>|\beta>\}$

It is desired to split the Hamilton H as H^o+V in such a way that the base vectors $|n>$ for the particle system will be of the following form:

$$|n> = |\alpha M>|\beta> , \tag{4.3}$$

where $|\alpha M>$ are the internal energy eigenstates of the emitter with energy E_α. The quantum number M indicates the degeneracy of the levels. Thus, if H_I^e is the Hamiltonian for the internal motion of the emitter, one has

$$(H_I^e - E_\alpha)|\alpha M> = 0 . \tag{4.4}$$

The eigenstates $|\beta>$ will be defined presently. The requirement that $|n>$ be factorizable as in (4.3) restricts the choice of H^o to the following form:

$$H^o = H_I^e + H^\beta , \tag{4.5}$$

where H^β is the part of H which does not depend upon the internal coordinates of the emitter. To express H^β explicitly, let it be assumed that V^p can be split as

$$V^p = \mathcal{O}^p + \bar{V}^p \tag{4.6}$$

where $\bar{V}^p$ is not a function of the internal coordinates of the emitter. Then, H^β can be written as follows:

$$H^\beta = H^e_{ex} + H^p + \bar{V}^p \ , \tag{4.7}$$

where H^e_{ex} is the Hamiltonian which describes the center of mass motion of the emitter. The eigenstates $|\beta>$ can now be defined as the solutions of the following eigenvalue problem:

$$(H^\beta - E_\beta)\,|\beta> = 0 \ . \tag{4.8}$$

The manner in which V^p is broken up into $\mathcal{O}^p$ and $\bar{V}^p$ depends on the nature of the emitter and the perturber as well as on our ability to solve the eigenvalue problem (4.8). Since the perturbation potential V which enters the damping theory is now given by

$$V = V^r + \mathcal{O}^p \ , \tag{4.9}$$

the choice of $\mathcal{O}^p$ and $\bar{V}^p$ affects the approximation inherent in the line shape formula obtained in this representation. In the case of a neutral emitter, as will be assumed in the subsequent sections, the natural choice is $\bar{V}^p = 0$. Then, $|\beta>$ can be further factorized as

$$|\beta> = |K>|p> \ , \tag{4.10}$$

where $|K>$ denotes the external eigenstates of the emitter and $|p>$ denotes the eigenstates of the perturber, i.e.,

$$(H^e_{ex}-E_K)\,|K> \;=\; 0\;, \tag{4.11}$$

$$(H^p-E_p)\,|p> \;=\; 0\;. \tag{4.12}$$

In the case of an ionic emitter, $\overline{V}^p$ may be chosen as the interaction between a point charge located at the center of mass of the emitter and the perturber.

The spectrum I(w) can be expressed in the representation $\{|\alpha M>|\beta>|\eta>\}$ by replacing V^r in (3.26) by $\mathcal{V}^p+\overline{V}^p$, and computing the matrix elements in this new representation. To compress writing we denote the initial and final states of the emitter by $|i> \equiv |\alpha_i M_i>$ and $|f> = |\alpha_f M_f>$, and any arbitrary state by $|\mu> = |\alpha M>$. Similarly, $|\beta_i>$ and $|\beta_f>$ will denote the initial and final states of the perturber plus the external motion of the emitter. Thus, $|n>$ and $|m>$, which have been defined as the initial and final states of the whole system [cf. (3.15) and (3.16)] become

$$|n> \;\equiv\; |i>|\beta_i> \;\equiv\; |\alpha_i M_i>|\beta_i>\,, \tag{4.13}$$

$$|m> \;\equiv\; |f>|\beta_f>|\underline{k}_\lambda> \;\equiv\; |\alpha_f M_f>|\beta_f>|\underline{k}_\lambda>\;. \tag{4.14}$$

Consider now the matrix element V_{mn}. Since the number of photons changes by one in the transition $|n> \to |m>$, the matrix element of $\mathcal{V}^p$, which depends only particle coordinates, vanishes. Thus,

$$V_{mn} \;=\; V^r_{mn}\;.$$

The matrix element of the electromagnetic interaction, i.e., V^r_{mn}, can be calculated by using (3.28) and (3.29). Putting the center of mass coordinate $\underline{r}_o$

of the emitter in evidence in (3.29), ignoring the radiative effects due to the center of mass motion, and making the usual dipole approximation for the sake of simplicity, one obtains

$$V^r_{mn} = \sqrt{\frac{2\pi\hbar}{\Omega w}}\; w_{if} \; < f|\underline{d}\cdot\underline{\epsilon}_\lambda(\underline{k})\,|i> < \beta_f|e^{i\underline{k}\cdot\underline{r}_o}|\beta_i> , \qquad (4.15)$$

where

$$w_{if} = (E_{\alpha_i} - E_{\alpha_f})/\hbar \quad . \qquad (4.16)$$

After V^r_{mn} is substituted into (3.26), one can perform the integration over the direction of propagation as well as the summation over the direction of polarization, with the assumption that the emission is isotropic:

$$\sum_\lambda \int d\Omega_{\hat{\underline{k}}} |\, < f|\underline{d}\cdot\underline{\epsilon}_\lambda(\underline{k})\,|i> \,|^2 = \frac{8\pi}{3}\,|\underline{d}_{fi}|^2 , \qquad (4.17)$$

where $|\underline{d}_{fi}|^2$ denotes the sum over the three components of $\underline{d}$.

The probability P_n which appears in (3.26) can be approximated in this representation by

$$P_n = P_{\alpha_i}\, P_{\beta_i} , \qquad (4.18)$$

where the definition of P_{α_i} and P_{β_i} can be obtained from (3.20).

With the foregoing remarks, one finds the spectrum as follows:

$$I(w) = \sum_{i,f} A_{if} \sum_{\beta_i,\beta_f} P_{\beta_i} \frac{\gamma_n |< \beta_f|e^{i\underline{k}\cdot\underline{r}_o}|\beta_i>|^2}{(\hbar\Delta w_{if} - S_{nm} + E_{\beta_f} - E_{\beta_i})^2 + (\hbar/2)^2\gamma_n^2} , \qquad (4.19)$$

where

$$A_{if} \equiv \frac{2}{3\pi}\frac{(\hbar w)^2}{c^3}\; w_{if}^2\, P_{\alpha_i}\,|\underline{d}_{fi}|^2 , \qquad (4.20)$$

$$\Delta w_{if} \equiv w - w_{if} \quad . \tag{4.21}$$

The matrix element $< \beta_f | \exp(i\underline{k}\cdot\underline{r}_o) | \beta_i >$ in (4.19) represents the recoil of the emitter and the perturber as a whole in the emission of a photon, and the term $(E_{\beta_f} - E_{\beta_i})$ is the recoil energy. It is observed that (4.19) gives the spectrum as the superposition of the spectral lines as indicated by the summation over the quantum numbers i and f. In the following sections, we shall confine ourselves to a neutral emitter and take $\overline{V}^p = 0$, as mentioned previously. Therefore the expressions for γ_n and S_{nm} need not be given in this representation.

C. LINE SHAPE FORMULA IN THE REPRESENTATION $\{ |\alpha M > |K > |p > \}$

In this representation, the last factor in (4.15) takes the following form:

$$|< \beta_f | e^{i\underline{k}\cdot\underline{r}_o} | \beta_i >|^2 = \delta(\underline{K}_f + \underline{k} - \underline{K}_i)\delta_{p_i, p_f} \, , \tag{4.22}$$

where the δ's are Kronecker deltas. In view of (4.22), the recoil energy $(E_{\beta_f} - E_{\beta_i})$ in (4.19) can be written as

$$E_{\beta_f} - E_{\beta_i} = E_{K_f} - E_{K_i} = \frac{(\hbar w)^2}{Mc^2} - S_d \, , \tag{4.23}$$

where S_d is defined by

$$S_d \equiv (\underline{K}_i \cdot \underline{k})/Mc^2 \quad . \tag{4.24}$$

As will be seen later, S_d represents the Doppler effect. The quantity M is the mass of the emitter. Substituting (4.22) and (4.23) into (4.19), one

obtains the line shape formula in the representation $\{|\alpha M>|K>|p>\}$ as follows:

$$I(w) = \sum_{i,f} A_{if} \sum_{p,K} P_{Kp} \frac{\gamma_n}{(\hbar\Delta w_{if}-S_{nm}-S_d)^2+(\hbar/2)^2\gamma_n^2} , \qquad (4.25)$$

where $(\hbar w/Mc^2)$ is ignored as compared to unity, and the subscript i on K_i and p_i is dropped to compress writing. Henceforth, $|K>$ will denote the initial external state of the emitter, and $|p>$ will denote the initial state of the perturber. In (4.25) we have dropped also the summation over K_f by approximating it by K_i everywhere except in the Doppler term S_d, because the dominant effect of the recoil of the emitter on the line shape is included through the term S_d. In view of the foregoing remarks, the base vectors $|n>$ and $|m>$ in (4.25) take the following form [cf. (4.13) and (4.14)]:

$$|n> \equiv |i>|K>|p> \equiv |\alpha_i M_i>|K>|p> , \qquad (4.26)$$

$$|m> \equiv |f>|K>|p>|\underline{k}_\lambda> \equiv |\alpha_f M_f>|K>|p>|\underline{k}_\lambda> . \qquad (4.27)$$

Equation (4.25) is the basic line shape formula of the present study. It contains all the dominant features of the line shift and line width phenomena. The rest of this work will be devoted to the discussion of (4.25).

D. STATISTICAL APPROXIMATION

In this section, we shall discuss an approximation which is made by replacing the average of a ratio of two functions by the ratio of the averaged functions. This approximation, which is referred to here as the statistical approximation, will be used to simplify the basic line shape formula (4.25).

First we propose to discuss the implications of this approximation in a qualitative and general manner.

Consider a function $z = f(X,Y)$, where X and Y are themselves functions of some set of stochastic variables $\tau = (t_1, t_2 .. t_n)$. The joint distribution function for τ is denoted by $P(\tau)$. The mean value of z is defined by

$$\bar{z} = \int f(X,Y)\ P(\tau) d\tau \ . \tag{4.28}$$

The mean values of X and Y, which are also defined according to (4.28), are denoted by $\bar{X}$ and $\bar{Y}$. Let x,y be the deviations of X and Y from their mean values, $X = \bar{X}+x$, $Y = \bar{Y}+y$. Substituting these into f(X,Y) and expanding into Taylor series, one obtains

$$\bar{z} = f(\bar{X},\bar{Y}) + \frac{1}{2}\left[\underline{x^2}\ f''_{x^2} + 2\underline{xy}\ f''_{xy} + \underline{y^2}\ f''_{y^2}\right] + \ldots \ , \tag{4.29}$$

where the linear terms in $\bar{x}$ and $\bar{y}$ vanish by definition. Note that the mean values of x^2 and y^2 are denoted by $\underline{x^2}$ and $\underline{y^2}$. If x and y depend on different sets of stochastic variables, then $\underline{xy}$ vanishes. In this qualitative argument we shall neglect the cross term in (4.29) even if $\underline{xy}$ is not zero.

It follows from (4.25) that in the present problem, f(X,Y) has the following form:

$$z = \frac{X}{Y^2+X^2} \ , \tag{4.30}$$

where

$$\begin{aligned} X &= \gamma_n \ , \\ Y &= \hbar\Delta w_{if} - S_{nm} - S_d \ . \end{aligned} \tag{4.31}$$

The stochastic variables upon which X and Y depend are the quantum numbers describing the states of the system. They are denoted by K and p respectively. The corresponding distribution function is P_{Kp}.

Combining (4.30) and (4.29) yields

$$\bar{z} = \frac{\bar{X}}{\bar{X}^2+\bar{Y}^2}\left[1 - (\underline{y}^2-\underline{x}^2)\frac{\bar{X}^2-3\bar{Y}^2}{(\bar{X}^2+\bar{Y}^2)^2}\right] .$$

Treating the second term in the parenthesis as a small quantity and using $(1-x) \approx (1+x)^{-1}$, one obtains

$$\bar{z} = \frac{\bar{X}}{\bar{Y}^2\left[1 - \frac{3(\underline{y}^2-\underline{x}^2)}{\bar{Y}^2+\bar{X}^2}\right] + \bar{X}^2\left[1 + \frac{\underline{y}^2-\underline{x}^2}{\bar{Y}^2+\bar{X}^2}\right]} . \qquad (4.32)$$

The mean value of Y is a function of frequency, as can be seen from (4.31), viz.,

$$\bar{Y} = \hbar\Delta w_{if} - \bar{S}_{nm} ,$$

since the mean value of the Doppler term S_d is zero. It follows that $\bar{Y}^2$ in (4.32) can assume all the values from zero to infinity. However, the variance $\underline{y}^2$ is independent of frequency. At the center of a line where $\bar{Y} = 0$, (4.32) reduces to

$$\bar{z} = \frac{\bar{X}}{\bar{X}^2+\underline{y}^2-\underline{x}^2} , \qquad (4.33)$$

whereas at the wings of a line it becomes

$$\bar{z} = \frac{\bar{X}}{\bar{Y}^2} .$$

The following qualitative conclusions can be drawn from the foregoing remarks:

(i) When the correction terms in (4.32) are neglected, one obtains

$$\overline{z} = \frac{\overline{X}}{\overline{Y}^2+\overline{X}^2} , \tag{4.35}$$

which is a Lorentzian distribution. This result corresponds to the approximation of replacing the average of a function by the function of the average. Comparing (4.35) to (4.33) and (3.34), one finds that this approximation is good at the wings of the line, but may not be good at the center if $(\underline{y}^2-\underline{x}^2)$ is not small compared to $\overline{X}^2$. Since X is a positive quantity, one may assume as a first approximation that its variance $\underline{x}^2$ is small compared to $\overline{X}^2$. But one can not assume, even as a first approximation, that $\underline{y}^2 \ll \overline{X}^2$, because $\underline{y}^2$ is the variance of a different quantity. As will be shown later, (4.35) corresponds to the impact limit (cf. V.C).

(ii) Consider now the approximation of replacing the average of the ratio of two functions by the ratio of the average of the functions. When applied to (4.30), this approximation yields the following Lorentzian distribution:

$$\overline{z} = \frac{\overline{X}}{\overline{Y}^2+\overline{X}^2+\underline{y}^2} , \tag{4.36}$$

where we have ignored $\underline{x}^2$ as compared to $\overline{X}^2$. A comparison of (4.36) to (4.33) and (4.34) indicates that (4.36) is a better approximation than (4.35) both at the wings and at the center of the line, provided $\underline{x}^2 \ll \overline{X}^2$ holds.

(iii) Both of the previous approximations replace the actual line shape by a pure Lorentzian distribution. Deviations from the Lorentzian distribution can be investigated by (4.32). By differentiating the denominator of

of (4.32) with respect to $\overline{Y}$, one finds that (4.32) has two peaks on both sides of the line center if $(\underline{y}^2-\underline{x}^2) > (\overline{X}^2/4)$. When these peaks are not present, the top of (4.32) is more flat than the top of a pure Lorentzian shape.

(iv) When the variance of X is negligible as compared to its mean, one can write (4.30) as follows:

$$\overline{z} = \int d\tau\, P \frac{\overline{X}}{Y^2+\overline{X}^2} \quad . \tag{4.37}$$

In quasi-static limit, where the emitter and the perturber are assumed to be infinitely heavy, $\overline{X}$ is equal to the natural width [cf. (5.10)]. Then, one may replace (4.37) by

$$\overline{z} = \pi \int d\tau\, P\, \delta(Y) \quad , \tag{4.38}$$

which is the basis of the Holtsmark theory [cf. (5.11)].

The four cases listed above represent the statistical approximations in order of increasing accuracy; these approximations will be encountered in the subsequent sections. We shall use the case (ii), i.e., (4.36), for our discussions of the line shape because it appears to be a compromise between the impact and quasi-static limits, and because it leads to a line shape formula where various mechanisms contributing to the structure of a line can be sorted out.

E. LINE SHAPE FORMULA IN THE STATISTICAL APPROXIMATION

Combining (4.36) and (4.25), one obtains the line shape formula in the statistical approximation:

$$I(w) = \sum_{i,f} A_{if} \frac{\bar{\gamma}_n}{(\hbar\Delta w_{if} - S_{nm})^2 + (\hbar/2)^2 \gamma_t^2} , \qquad (4.39)$$

where we define

$$\gamma_t^2 = \gamma_d^2 + \bar{\gamma}_n^2 + \gamma_s^2 . \qquad (4.40)$$

The quantity γ_d in (4.40) is defined by

$$\frac{\hbar^2}{4} \gamma_d^2 \equiv \sum_K P_K S_d = \frac{2\Theta}{Mc^2} (\hbar w)^2 , \qquad (4.41)$$

and can be identified as the Doppler broadening. The averaged width $\bar{\gamma}_n$ is defined by

$$\bar{\gamma}_n \equiv \sum_{K,p} P_{Kp} \gamma_n . \qquad (4.42)$$

The quantity γ_s is a broadening which is statistical in nature, like the Doppler broadening, and is due to the spread of the individual lines corresponding to the states $|Kp>$. We shall refer to γ_s as the statistical broadening, although the name should include the Doppler broadening as well. It is defined by

$$\frac{\hbar^2}{4} \gamma_s^2 = \sum_{K,p} P_{Kp} [S_{nm}^2 - (\overline{S_{nm}})^2] . \qquad (4.43)$$

Our next task will be to investigate the averaged width $\bar{\gamma}_n$, which is the width due to the finite life-time of the states.

F. AVERAGED WIDTH $\bar{\gamma}_n$

In this section, we shall first express γ_n in the representation $\{|\alpha M>|K>|p>\}$ and then consider its average. An arbitrary eigenvector in

this representation will be labelled as follows:

$$\begin{aligned} |m'> &\equiv |n'>|\underline{k}'_\lambda> , \\ |n'> &\equiv |\mu'>|K'>|p'> , \\ |\mu'> &\equiv |\alpha' M'> . \end{aligned} \tag{4.44}$$

The initial state $|n>$ and the final state $|m>$ have been defined by (4.26) and (4.27). In interpreting the matrix elements appearing in the following formulas, the foregoing definitions should be kept in mind.

The γ_n can be obtained from its definition (2.21) by substituting $V = V^r+V^p$ and $x = E_n$:

$$\gamma_n \equiv \frac{2\pi}{\hbar} \sum_{m'} |< n|V^r + V^p|m'>|^2 \, \delta(E_n - E_{n'} - \hbar w') , \tag{4.45}$$

where $w' = ck'$. The following can be readily verified:

$$|< n|V^r + V^p|m'>|^2 = |V^r_{nm'}|^2 \, \delta_{p,p'} + |V^p_{nm'}|^2 \, \delta_{\underline{k}'_\lambda, 0} . \tag{4.46}$$

Inserting (4.46) into (4.45), one finds that γ_n can be split up into two parts:

$$\gamma_n \equiv \gamma^r_n + \gamma^p_n ,$$

where

$$\gamma^r_n \equiv \frac{2\pi}{\hbar} \sum_{\mu', \underline{k}'_\lambda} |< i|V^r|\mu' \underline{k}'>|^2 \, \delta\left(E_{\alpha_i} - E_{\alpha'} - \hbar w' - \frac{\underline{K}\cdot\underline{k}'}{Mc^2}\right) , \tag{4.47}$$

and

$$\gamma^p_n \equiv \frac{2\pi}{\hbar} \sum_{n'} |V^p_{n'n}|^2 \, \delta(E_{\alpha_i} - E_{\alpha'} + E_p - E_{p'} + E_K - E_{K'}) . \tag{4.48}$$

The quantity γ_n^r is the natural width corresponding to the radiative transitions of the emitter. Combining (4.15), (4.17), and (4.22) with (4.47), and ignoring the recoil term in the argument of the delta function, one obtains for γ_n^r:

$$\gamma_i^r = \frac{4}{3\hbar c^3} \sum_{\substack{\mu' \\ (E_{\alpha'} < E_{\alpha_i})}} w_{\alpha_i\alpha'}^3 |\underline{d}_{i,\mu'}|^2 \quad . \tag{4.49}$$

Note that we have changed the subscript n into i, to indicate that the natural width depends only on the initial state of the emitter. When the internal energy levels of the emitter do not have accidental degeneracies, one can choose the internal states as the definite orbital angular momentum states. Then, M in $|\alpha M>$ will be the magnetic quantum number. In this case, one can further simplify (4.49) by using the Wigner-Eckart theorem,[5] and noting that

$$\sum_{M'} |<i|\underline{d}|\mu'>|^2 = \frac{1}{2\ell_i+1} |<\alpha_i\|\underline{d}\|\alpha'>|^2 \ , \tag{4.50}$$

where ℓ_i is the orbital angular momentum quantum number of the initial state, and $<\alpha_i\|\underline{d}\|\alpha'>$ is the reduced matrix element of the dipole moment operator appropriate to the emitter. Inserting (4.50) into (4.49) gives:

$$\gamma_{\alpha_i}^r = \frac{4}{3\hbar c^3} \frac{1}{2\ell_i+1} \sum_{\substack{\alpha' \\ (E_{\alpha'} < E_{\alpha_i})}} w_{\alpha_i\alpha'}^3 |<\alpha_i\|\underline{d}\|\alpha'>|^2 \ . \tag{4.51}$$

The number of terms in the summation on α' in this expression is limited by the usual selection rules. It is noted that the natural width is independent of the initial magnetic quantum number M_i, as implied by the subscript α_i in (4.51).

Now we consider γ_n^p in (4.48), which is the width due to the interaction of the emitter with the perturber. Since this is equal to the transition probability per unit time from the initial state $|n>$ to other states, its average with respect to the perturber states can be expressed in terms of a scattering cross-section for the emitter:

$$\gamma_{iK}^p \equiv \sum_p P_p \gamma_n^p = \frac{\hbar K}{M} n_p \sigma_i(K) . \qquad (4.52)$$

The first term on the right hand side is the speed of the emitter, n_p is the number density of the perturber, and $\sigma_i(K)$ is the total scattering cross-section for the emitter. The latter is defined as follows: $n_p \sigma_i(K)$ is the probability per unit path that the emitter will make a transition from the state $|i>|K>$ to any other state. Note that $\sigma_i(K)$ includes the collective behavior of the perturber, although it is defined per particle. The average of γ_{iK}^p with respect to the external motion of the emitter can be formally written, assuming a Maxwellian distribution for the momenta, as follows:

$$\gamma_i^p \equiv \frac{\hbar}{M} n_p \sum_K P_K K \sigma_i(K) ,$$

or

$$\gamma_i^p = \frac{\hbar^4}{M(2\pi M\Theta)^{3/2}} n_p \int d^3K \, K \sigma_i(K) \, e^{-(\hbar K)^2/2M\Theta} , \qquad (4.53)$$

where Θ is the mean energy. We note that γ_i^p may depend on the magnetic quantum number M_i of the initial state. But if the perturber as a whole is spherically symmetric, then γ_i^p depends only on α_i.

The averaged width $\bar{\gamma}_n$ defined by (4.42) can now be written as

$$\overline{\gamma}_n = \gamma_i^r + \gamma_i^p \,. \tag{4.54}$$

The first term is the natural width mentioned earlier. The second term is known as the pressure broadening. The physical conditions of the medium (or the perturber) are reflected on the line shape partly through the pressure broadening. Therefore, it might be illuminating to investigate how the pressure broadening can be related to the dynamic properties of the medium. The following analysis is nothing but a calculation of an effective scattering cross-section in the first Born approximation.

Assume that the interaction between the emitter and the perturber can be expressed as

$$V^p = \sum_{i,j} e_i \, e_j \, V(|\underline{r}_i - \underline{R}_j|) \,, \tag{4.55}$$

where $\underline{r}_i$ and $\underline{R}_j$ denote the positions of the constituent particles of the emitter and the perturber respectively. The charges of the particles are e_i and e_j. One can also write V^p as follows:

$$V^p = \frac{1}{(2\pi)^3} \int d^3X \, \mathcal{J}(X) \, P(\underline{X}) \, E(\underline{X}) \,, \tag{4.56}$$

where

$$\mathcal{J}(X) = \frac{4\pi}{X} \int_0^\infty R \, V(R) \, \sin XR \, dR \,, \tag{4.57}$$

$$P(\underline{X}) = \sum_j e_j \, e^{i\underline{R}_j \cdot \underline{X}} \,, \tag{4.58}$$

$$E(\underline{X}) = \sum_s e_s \, e^{-i\underline{r}_s \cdot \underline{X}} \,.$$

Separating the center of mass coordinate $\underline{r}_o$, one can write $E(\underline{X})$ as

$$E(\underline{X}) = e^{-i\underline{r}_o \cdot \underline{X}} \Lambda(\underline{X}) , \tag{4.59}$$

where

$$\Lambda(\underline{X}) \equiv \sum_s e_s \, e^{-i\underline{r}'_s \cdot \underline{X}} . \tag{4.60}$$

The vectors $\underline{r}'_s$ denote the positions of the particles in the emitter with respect to the center of mass. The summation on s includes nuclei as well as electrons.

To assure the convergence, and to justify the interchange of certain improper integrals which will be encountered below, we assume that V(R) decays exponentially for large values of R. For example, the Coulomb interaction will be assumed to be given by

$$V(R) = e^{-\lambda R}/R , \tag{4.61}$$

where λ is a small positive number. It will be taken to zero in the final results.

The matrix element of V^p in the representation (4.44) can be obtained as

$$V^p_{nn'} = \frac{1}{\Omega} \mathcal{O}(X) < p|P(\underline{X})|p'> < i|\Lambda(\underline{X})|\mu'> , \tag{4.62}$$

where

$$\underline{X} = \underline{K} - \underline{K}' .$$

Inserting (4.62) into (4.48) gives

$$\gamma^p_n = \frac{2\pi}{\hbar} \frac{1}{\Omega^2} \sum_{n'} |\mathcal{O}(X)|^2 F_{i\mu'}(\underline{X}) |< p|P(\underline{X})|p'>|^2 \delta[E_{\alpha i} + E_p - E_{\alpha'} - E_{p'} + \frac{\hbar^2}{2M} \cdot (K^2 - K'^2)] , \tag{4.63}$$

where

$$F_{i\mu'}(X) \equiv |< i|\Lambda(\underline{X})|\mu'>|^2 \quad . \tag{4.64}$$

The average of γ_n^p with respect to P_{Kp} can be expressed in a compact way by using the Fourier representation for the delta function in (4.63). After some lengthy manipulations, one finds:

$$\gamma_i^p = \frac{\Omega^{-1}}{(2\pi)^3} \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \int d^3X \, e^{-\frac{X^2}{2M}(t^2\Theta - it\hbar)} f_i(\underline{X},t) \, S_p(\underline{X},t) \, |\mathcal{G}(X)|^2 \, , \tag{4.65}$$

where

$$S_p(\underline{X},t) = \sum_p P_p < p|P(\underline{X},t)P^+(\underline{X},0)|p> \, , \tag{4.66}$$

$$f_i(\underline{X},t) = < i|\Lambda(\underline{X},t)\Lambda^+(\underline{X},0)|i> \quad . \tag{4.67}$$

The time-dependent operators $P(\underline{X},t)$ and $\Lambda(\underline{X},t)$ are defined by

$$P(\underline{X},t) = \sum_j e_j \, e^{i\underline{R}_j(t)\cdot\underline{X}} \, , \tag{4.68}$$

$$\Lambda(\underline{X},t) = \sum_s e_s \, e^{-i\underline{r}'_s(t)\cdot\underline{X}} \tag{5.69}$$

and

$$\underline{R}_j(t) = e^{iH^p t/\hbar} \, \underline{R}_j(0) \, e^{-iH^p t/\hbar} \, , \tag{4.70}$$

$$\underline{r}'_s(t) = e^{iH_I^e t/\hbar} \, \underline{r}'_s(0) \, e^{-iH_I^e t/\hbar} \, . \tag{4.71}$$

Equation (4.65) reveals that the pressure broadening depends on the medium through the function $S_p(\underline{X},t)$, which is the Fourier transform of the

$G(\underline{r},t)$ function with respect to $\underline{r}$. Since the latter is discussed by Van Hove in some detail for a number of systems,[7] we shall not dwell upon this point any further. In Section VI we shall actually evaluate (4.65) for a plasma, assuming that the perturber which consists of electrons and ions can be treated as a perfect gas.

G. THE SHIFT S^p_{nm}

In this section we shall discuss the shift S_{nm} in the representation $\{|\alpha M>|K>|p>\}$. This shift has been defined by (2.33) and (2.22). Substituting $V = V^r+V^p$ into (2.22) and using (4.46), one finds that S_{nm}, like γ_n, splits into two parts:

$$S_{nm} = S^r_{nm} + S^p_{nm} ,$$

where S^r_{nm} is the shift caused by electromagnetic interaction and S^p_{nm} is the shift caused by the perturber. One can also show that S^r_{nm} depends only on the initial and final states of the emitter, i.e., $S^r_{nm} = S^r_{if}$. Therefore, S^r_{if} is present also in the measured spectrum of a free atom. If the spectrum of the perturbed atom is compared to that of the free atom, the observed shifts will be given by S^p_{nm}. Hence, for our purpose it is sufficient to compute only S^p_{nm}.

The expressions of S^p_n and S^p_m can be found from (2.22), with $x = E_n$ and $x = E_m$. The result is:

$$S^p_n = V^p_{nn} + \sum_{n'} PP \frac{|V^p_{nn'}|^2}{E_{\alpha_i}+E_p+E_K-E_{\alpha'}-E_{p'}-E_{K'}} \qquad (4.72)$$

and

$$S^p_m = V^p_{n_f n_f} + \sum_{n'}{}' \, PP \, \frac{|V^p_{n_f n'}|^2}{E_{\alpha_i}+E_p+E_K-E_{\alpha'}-E_{p'}-E_{K'}} , \qquad (4.73)$$

where we have introduced

$$|n_f> \equiv |\alpha_f M_f> |K> |p>$$

in addition to (4.26), (4.27), and (4.44). Furthermore, in (4.73) we have ignored the recoil of the emitter and replaced $E_{\alpha_f}+\hbar w$ by E_{α_i}.

It is to be noted that S^p_n and S^p_m are, respectively, the shifts in the energy of the upper state and the lower state of the atom. It is often true that the interaction of the atom with the perturber in the lower state is much weaker than its interaction in the upper state, because the atom is more tightly bound in the lower state. Therefore, S^p_n is often larger than S^p_m, and it may be a good approximation to neglect S^p_m as compared to S^p_n (see p. 505, Ref. 1). But to be all-inclusive, we shall keep S^p_m in the general theory.

We shall now discuss the diagonal matrix element of V^p in (4.72) and (4.73). It is obtained from (4.62) as

$$V^p_{nn} = \lim_{X\to 0} \frac{1}{\Omega} \, \mathscr{P}(X) < p|P(\underline{X})|p> < i|\Lambda(\underline{X})|i> . \qquad (4.74)$$

The last factor in (4.74) behaves like $\underline{X}\cdot < i|\underline{d}|i>$ as $X\to 0$ when the emitter is neutral, which we are assuming in the present study, and when the upper state $|i>$ is degenerate. In the case of nondegenerate levels, it vanishes as X^2. The factor $< p|P(\underline{X})|p>/\Omega$ in (4.74) approaches the average charge density of the perturber as $X\to 0$, and hence also vanishes. Finally, the first

factor follows from (4.61) and (4.57) as

$$\mathcal{G}(X) = \frac{4\pi}{X^2+\lambda^2} \quad . \tag{4.75}$$

It follows from the above observations that V^p_{nn} vanishes irrespective of the degeneracy of the states. In the case of nondegenerate states, this conclusion holds even if one sets $\lambda = 0$ in (4.75) before the limit $X \to 0$ is taken. When the states have accidental degeneracy, the order of limits $\lambda \to 0$ and $X \to 0$ becomes important, indicating that the order of integrations involved in the matrix element $V^p_{nn'}$ [cf. (4.62) and (4.56)] can not be interchanged if the unshielded Coulomb potential ($\lambda = 0$) is used. By taking the limit $X \to 0$ first and then letting λ tend to zero, we avoided this difficulty.

The foregoing discussions indicate that the shift S^p_{nm} depends on V^p quadratically in the representation $\{|\alpha M\rangle|K\rangle|p\rangle\}$, since the linear term in (4.72) and (4.73) vanishes. The S^p_{nm} can be expressed by inserting (4.62) into (4.72) and (4.73), and converting the summation over K' into an integral as follows:

$$S^p_{nm} = \frac{1}{(2\pi)^3\Omega} \sum_{n'} PP \int d^3X |\mathcal{G}(X)|^2 \frac{[F_{i\mu'}(\underline{X}) - F_{f\mu'}(\underline{X})] |\langle p|P(\underline{X})|p'\rangle|^2}{E_{\alpha_i} - E_{\alpha'} + E_p - E_{p'} - \frac{\hbar^2}{2M}(X^2 - 2\underline{X}\cdot\underline{K})} \quad . \tag{4.76}$$

which is valid both in the degenerate and nondegenerate cases.

The average of S^p_{nm} with respect to P_{Kp}, i.e.,

$$S^p_{if} = \sum_{p,K} P_{Kp} S^p_{nm} \quad , \tag{4.77}$$

does not lend itself to a simple interpretation as the averaged width γ_i^p does. Therefore we shall not discuss it here in general terms, but in Section VI shall actually compute it for the case of a plasma.

Before proceeding further, we want to obtain a formula for the shift in the approximation in which the emitter is assumed to be infinitely heavy and at rest. This formula will be needed in Section V.B when we discuss the quasi-static limit. First we consider the diagonal term in (4.72) and (4.73). When the motion of the emitter is ignored, V_{nn}^p takes the following form:

$$V_{nn}^p \equiv \langle ip|V^p|ip\rangle = \frac{1}{(2\pi)^3}\int d^3X\, \mathscr{N}(X) \langle p|P(\underline{X})|p\rangle\langle i|\Lambda(\underline{X})|i\rangle . \tag{4.78}$$

In the dipole approximation which corresponds to retaining the first term in the expansion of $\Lambda(\underline{X})$ [cf. (4.60)], (4.78) takes the following, more familiar form:

$$V_{nn}^p = -\langle i|\underline{d}|i\rangle \cdot \langle p|\underline{\mathscr{E}}|p\rangle , \tag{4.79}$$

where $\underline{\mathscr{E}}$ is the electric field operator acting on the perturber coordinates, i.e.,

$$\underline{\mathscr{E}} = \sum_j \frac{e_j \underline{R}_j}{R_j^3} , \tag{4.80}$$

at the point where the emitter is located. One finds from (4.79) that V_{nn}^p is zero when the states are nondegenerate, because then that states $|i\rangle = |\alpha_i M_i\rangle$ have a definite parity. In the case of accidental degeneracy, one chooses the base vectors $|\alpha M\rangle$ in such a way that the component of the dipole operator along a specified direction $\underline{\Omega}$ will be diagonal [cf. (2.36)]. The diagonalization process can be automatically carried out if one makes use of the par-

abolic coordinates.* In this case, the internal states of the emitter are labelled as $|\alpha sM>$ where α is the principal quantum number, s is the "electric" quantum number ($s = 0,1,\ldots\alpha-M-1$), and M is the usual magnetic quantum number [$M = 0,\pm1,\ldots\pm(\alpha-1)$]. Equation (4.79) then becomes:

$$V^p_{nn} = -\frac{3}{2}\frac{\hbar^2}{me}\,[\alpha_i(\alpha_i-2s_i-|M_i|-1)]\,<p|\mathcal{E}_z|p>\,, \qquad (4.81)$$

where $\mathcal{E}_z$ is the component of the electric field operator along the direction of quantization which is taken as the z-axis. One finds that V^p_{nn} is not zero when the states are degenerate and when the emitter is assumed to be infinitely heavy. It must be pointed out that all the matrix elements appearing in the line shape formula (4.39) should be computed in the representation $\{|\alpha sM>|p>\}$ when the states have accidental degeneracy. Since the second term in (4.72) and (4.73) is of second order in powers of V^p, the shift S^p_{nm} can be written as $V^p_{nn}-V^p_{n_fn_f}$ when both the upper and lower levels are degenerate. Using (4.81), one finds

$$S^p_{nm} = -\frac{3}{2}\frac{\hbar^2}{me}\,[\alpha_i(\alpha_i-2s_i-|M_i|-1)-\alpha_f(\alpha_f-2s_f-|M_f|-1)]\,<p|\mathcal{E}_z|p>\,. \qquad (4.82)$$

We now consider the second term in (4.72) and (4.73), which is the first nonvanishing term in the expansion of S^p_n or S^p_m when the states are nondegenerate and the emitter is assumed to be at rest, and when the interaction V^p is approximated by (4.79). In this case, S^p_{nm} can be obtained as

*See p. 1676 of Ref. 8 or p. 229 of Ref. 9.

$$S^{p}_{nm} = \sum_{\alpha' p' \nu} PP \frac{|< p|\mathcal{E}_{\nu}|p'>|^2}{E_{\alpha_i}+E_p-E_{\alpha'}-E_{p'}} \left[\frac{|<\ell' 1 M_i-\nu,\nu|\ell_i M_i>|^2 |< \alpha_i||\underline{d}||\alpha'>|^2}{2\ell_i+1} \right.$$

$$\left. - \frac{|<\ell' 1 M_f-\nu,\nu|\ell_f M_f>|^2 |< \alpha_f||\underline{d}||\alpha'>|^2}{2\ell_f+1} \right] , \qquad (4.83)$$

where $< \ell' 1, M-\nu, \nu|\ell_i M_i >$ is the Clebsch-Gordon coefficient,[5] $< \alpha_i||\underline{d}||\alpha' >$ is the reduced matrix element, ℓ_i and ℓ_f are the orbital angular momentum quantum numbers of the upper and lower states, and $\mathcal{E}_{\nu}$ are the spherical components of the electric field operator ($\nu = 0, \pm 1$).

V. COMPARISON WITH OTHER LINE SHAPE THEORIES

A. INTRODUCTION

This section is devoted to establishing a connection between the present theory of line shape and the other theories. In the other theories, ions and electrons are treated in the quasi-static and the impact approximations respectively. The quasi-static approximation ignores the motion of the particles of the perturber as well as the motion of the emitter. The procedure for computing the line shape is as follows: One first assumes that the perturber particles are located at fixed positions, and then calculates the spectrum of sharp lines which are split by the constant electric field of the perturber. Finally, one performs a statistical average over positions of the perturber particles to obtain the broadened spectrum. This approximation, which is also known as the statistical approximation, was the basis of the Holtsmark[10] theory developed for the treatment of ions.

In the impact approximation, the collisions are assumed to be instantaneous. In each collision, the radiation from the emitter suffers a certain phase change which depends on the distance of closest approach. In the early impact theories, the radiative process is assumed to be interrupted when the phase change is greater than a certain value. The effect of the collision on the radiating atom is ignored completely when the phase shift is smaller than the threshold value. This simple model is the basis of the Lorentz theory, which treats the radiative process as a train of light waves of finite durations. The duration of each train is determined by the free time T between

collisions. The intensity of distribution of this radiative process is obtained by computing the Fourier components of a finite wave train of duration T. This distribution is averaged over the probability that the free time between collisions is T. The latter probability is $\nu \exp(-\nu T)$, where ν is the collision frequency. This procedure leads to a line shape proportional to

$$\frac{1}{(w-w_o)^2+\nu^2} ,$$

which is the Lorentzian distribution.

The modified impact theories are more complicated and include the effect of the small as well as the large phase shifts. Since a detailed presentation of the modern impact theory can be found in Ref. 1 and in the excellent review articles listed there, no attempt will be made in this work to reproduce either the impact or the statistical theory.

B. QUASI-STATIC LIMIT

This section is devoted to the derivation of the Holtsmark (or statistical) theory from the line shape formula (4.25). The following assumptions are made about the physical system:

(i) The emitter is at rest;

(ii) $V^p = -\underline{d}\cdot\underline{\mathcal{E}}$;

(iii) The motion of the perturber is small.

In view of the first assumption, the summation over K in (4.25) as well as the Doppler term S_d drop out. The second assumption implies that the electric field produced by the perturber is uniform within the emitter. The third assumption implies that the kinetic energy of the perturber particles is neg-

ligible. Hence, the Hamiltonian of the perturber can be approximated by the Coulomb energy between the particles, i.e.,

$$H^p = Q(\underline{R}_1, \ldots \underline{R}_N) ,$$

where $\underline{R}_j$ are the positions of the particles. In view of this approximation, one finds that H^p and V^p commute, i.e., $[H^p, V^p] = 0$. Hence, the base vectors $|p>$ can be chosen to diagonalize both H^p and V^p. In this representation, γ_n^p takes the following form [cf. (4.48) and Section II.D]:

$$\gamma_n^p = \frac{2\pi}{\hbar} \sum_{\substack{\alpha' M' \\ \neq \alpha_i M_i}} |<\alpha_i M_i|\underline{d}|\alpha M'> \cdot <p|\underline{\mathcal{E}}|p>|^2 \, \delta(E_{\alpha_i} - E_{\alpha'}) = 0 . \quad (5.1)$$

The reason why γ_n^p vanishes is that the terms for which $E_{\alpha_i} = E_{\alpha'}$ are excluded in the summation. When the states are nondegenerate, the matrix element of the dipole operator between the states belonging to the same energy is zero. In the case of accidental degeneracy, d_z is assumed to be diagonalized in the subspace belonging to each energy level. Since the diagonal element is excluded in the summation, again there is no term with $E_{\alpha_i} = E_{\alpha'}$. The fact that γ_n^p vanishes when the perturber is at rest could be expected on physical grounds.

In the representation where both H^p and V^p are diagonal, S_{nm}^p is obtained from (4.83) as follows:

$$S^p_{nm} = \sum_{\nu} |< p|\underline{\mathcal{E}}_\nu|p >|^2 \sum_{\alpha' \neq \alpha_i} \frac{1}{E_{\alpha_i} - E_{\alpha'}} \left[\frac{|<\ell' 1 M_i - \nu, \nu | \ell_i M_i>|^2 |< \alpha_i \| \underline{d} \| \alpha' >|^2}{2\ell_i + 1} \right.$$

$$\left. - \frac{|< \ell' 1 M_f - \nu, \nu | \ell_f M_f>|^2 |< \alpha_f \| \underline{d} \| \alpha' >|^2}{2\ell_f + 1} \right] . \qquad (5.2)$$

When the states are degenerate, S^p_{nm} is given by (4.82). In either case, S^p_{nm} is a function of $\underline{E}_p$, which is an eigenvalue of the electric field operator, i.e.,

$$S^p_{nm} = S^p_{if}(\underline{E}_p) . \qquad (5.3)$$

With the foregoing remarks, the line shape formula (4.25) can be written as follows:

$$I(w) = \sum_{i,f} A_{if} \sum_{p} P_p \frac{\gamma^r_{\alpha_i}}{[\hbar \Delta w_{if} - S^p_{if}(\underline{E}_p)]^2 + (\hbar/2)^2 (\gamma^r_{\alpha_i})^2} . \qquad (5.4)$$

Let the last factor in (5.4) be denoted by $\mathcal{J}(\underline{E}_p)$. Then, (5.4) involves the expected value of $\mathcal{J}(\underline{E}_p)$, i.e.,

$$\sum_{p} P_p \mathcal{J}(\underline{E}_p) = Tr[D^p \mathcal{J}(\underline{\mathcal{E}})]/Tr[D^p] , \qquad (5.5)$$

where D^p is the density matrix appropriate to the perturber. Equation (5.5) can also be expressed in terms of the distribution function $W(\underline{E})$ of the electric field as

$$\int d^3E \, W(\underline{E}) \mathcal{J}(\underline{E}) . \qquad (5.6)$$

The latter can be obtained as the Fourier transform of the characteristic function* which is the expected value of the quantity $\exp(i\underline{X} \cdot \underline{\mathcal{E}})$, i.e.,

*See p. 176, Vol. I (English translation) of Ref. 5.

$$W(\underline{E}) = \frac{1}{(2\pi)^3}\int d^3X\, e^{-i\underline{X}\cdot\underline{E}}\, \mathrm{Tr}[D^p\, e^{i\underline{X}\cdot\underline{\mathcal{E}}}]/\mathrm{Tr}[D^p]\ , \qquad (5.7)$$

where the electric field operator is as defined by (4.80). Substituting (4.80) into (5.7), and expressing the trace in either momentum or coordinate representation, one writes (5.7) as follows:

$$W(\underline{E}) = \frac{1}{(2\pi)^3}\left\{\int d^3X\, e^{i\underline{X}\cdot\underline{E}}\iint d^3R_1..d^3R_{N_p}\, e^{-\beta Q(\underline{R}_1..\underline{R}_{N_p})}\exp\left[i\underline{X}\cdot\sum\nolimits_j e_j\underline{R}_j/R_j^3\right]\right\}$$
$$\left[\iint d^3R_1..d^3R_{N_p}\, e^{-\beta Q(\underline{R}_1..\underline{R}_{N_p})}\right]^{-1} . \qquad (5.8)$$

If the Boltzman factor $\exp(-\beta Q)$ is ignored, one obtains

$$W(\underline{E}) = \frac{1}{(2\pi)^3}\int d^3X\, e^{-i\underline{X}\cdot\underline{E}}\left[\frac{1}{\Omega}\int d^3R\, e^{i\underline{X}\cdot\underline{R}/R^3}\right]^{N_p}\ , \qquad (5.9)$$

which is the Holtsmark distribution function. The line shape formula now becomes:

$$I(w) = \sum_{i,f} A_{if}\int W(\underline{E})\, d^3E\, \frac{\gamma^r_{\alpha_i}}{[\hbar\Delta w_{if}-S^p_{if}(\underline{E})]^2+(\hbar/2)^2(\gamma^r_{\alpha_i})^2}\ , \qquad (5.10)$$

or, if the natural width is ignored,

$$I(w) = \sum_{i,f} A_{if}\int W(\underline{E})\, d^3E\, \delta[\hbar\Delta w_{if}-S^p_{if}(\underline{E})]\ . \qquad (5.11)$$

The last formula expresses the line shape as the statistical average of the sharp lines split by the constant electric field $\underline{E}$. Equation (5.10) includes the finite natural width of these lines. The remaining task in completion of the Holtsmark theory is to evaluate the integrals in (5.9). We need not go into these details, however, since they can be found in the literature.[10]

We shall now compare the line shape formula (4.39), which was obtained with the statistical approximation, to (5.10) or (5.11) to check the statistical approximation in the quasi-static limit. To simplify the comparison, the lower state interaction will be ignored and the initial state will be assumed to be an s-state. Then, (5.2) reduces to $S^p_{if} = C_i E^2$, where C_i depends only on the initial state. Let $H(E^2)$ be defined by

$$2EH(E^2) = \int W(\underline{E})\, d\Omega_{\hat{\underline{E}}} \quad . \tag{5.12}$$

The reason for introducing $H(E^2)$ to characterize the distribution of the electric field will be soon evident. Inserting $S^p_{if} = C_i E^2$ and (5.12) into (5.11), one finds that the line shape is proportional to $H(x)$ where $x = (\hbar \Delta w_{if}/C_i)$. On the other hand, the line shape formula (4.39) reduces in the quasi-static limit to

$$I(w) \sim \frac{1}{(x-x_o)^2 + x_w^2} \quad , \tag{5.13}$$

where

$$x_o = \int_o^\infty H(y)\, y\, dy \quad ,$$

$$x_w^2 = \int_o^\infty H(y)(y-x_o)^2\, dy \quad .$$

Hence, the statistical approximation is equivalent in this case to replacing the distribution function $H(x)$ by a Lorentzian shape with a center frequency which is equal to the mean value of $H(x)$, and with a width which is equal to the standard deviation of $H(x)$. The validity of the statistical approxima-

tion in the quasi-static limit depends on the shape of the distribution of $H(x)$. For example, the approximation yields the correct half-width in the case of a gaussian distribution about the mean. The actual shape of $H(x)$ and its first and second moments, which are needed for a more definite conclusion as to the validity of the statistical approximation in this limiting case, calls for numerical study since no analytical form of the Holtsmark distribution function is available at present. We shall not pursue this comparison any further, because checking the validity of an approximation, i.e., the statistical approximation, is not justified in a limiting case which itself may not describe the actual physical system adequately. This point will be clarified in Section VI.B, where we actually compute the width for ions, which is ignored completely in the quasi-static limit. We shall see that even in the zero temperature limit, where the quasi-static approximation may be expected to be valid, the width due to ions is not zero.

C. IMPACT APPROXIMATION

In this section an attempt is made to establish the connection between the impact theory and the line shape formula (4.39). The impact approximation corresponds to the statistical approximation introduced by (4.35), namely by replacing the average of a function by the function of the average. The latter approximation is equivalent to ignoring the statistical width γ_s [cf. (4.40)] in the line shape formula (4.39). To facilitate the comparison, we shall also ignore the natural width $\gamma^r_{\alpha_i}$, the Doppler effect S_d and γ_d, and the shift S^p_f of the final state. Then, (4.39) reduces to

$$I(w) = \sum_{i,f} A_{if} \frac{\gamma_i^p}{(\hbar\Delta w_{if} - S_i^p)^2 + (\hbar\gamma_i^p/2)^2} \quad . \tag{5.14}$$

This formula of line shape is identical in form to Eq. (47) of Ref. 1. The next task is therefore to show the connection between the shifts and the widths in these two formulas. By using (2.20) one can write S_i^p and γ_i^p in a compact form as

$$S_i^p \equiv \mathrm{Re} < i|\mathcal{H}|i >$$

and

$$\gamma_i^p \equiv \mathrm{Im} < i|\mathcal{H}|i > ,$$

where $< i|\mathcal{H}|i >$ is

$$< i|\mathcal{H}|i > \equiv \lim_{\epsilon\to 0} \sum_p P_p \left\{ < ip|V^p|ip > + \sum_{\mu'p'} \frac{|< ip|V^p|\mu'p'>|^2}{i\epsilon + (E_{\alpha_i} + E_p - E_{\alpha'} - E_{p'})} \right\} . \tag{5.15}$$

The last term in (5.15), which contains the summation on the intermediate states $|\mu'p'>$, can be written as follows:

$$< ip|V^p[i\epsilon + E_{\alpha_i} + E_p - (H^e + H^p)]^{-1} V^p|ip > , \tag{5.16}$$

where H^e denotes the internal Hamiltonian of the emitter, i.e., $H^e = H_I^e$, since the emitter is assumed to be at rest. The following operator identity can be easily proven by recalling the definition of the time-dependence of an operator, i.e.,

$$V(t) = e^{itH/\hbar} V(0) e^{-itH/\hbar} ,$$

and performing the indicated integration:*

$$\frac{1}{a-H} V \equiv \frac{1}{i\hbar} \int_0^\infty dt\, V(-t)\, e^{it(a-H)/\hbar} , \tag{5.17}$$

where a is a complex number with a positive real part, and H and V are two operators. Using (5.17) in (5.16) with $a = i\epsilon+(E_{\alpha_i}+E_p)$, $H = H^e+H^p$, and $V = V^p$, one obtains

$$\frac{1}{i\hbar} \int_0^\infty dt\, e^{-\epsilon t} < ip|V^p(0)\, V^p(t)\,|ip > \quad . \tag{5.18}$$

Inserting (5.18) into (5.15) and lettin $\epsilon \to 0$ yields

$$< i|\mathcal{H}|i > = < i\left|\sum_p P_p \; < p\right| V^p + \frac{1}{i\hbar} \int_0^\infty dt\; V^p(0)\, U(t)\, V^p(-t) U^+(t) \left|p >\right| i > , \tag{5.19}$$

where $U(t) \equiv \exp[-itH^e/\hbar]$, indicating the time-evolution of the emitter, and where the time-dependence of $V^p(t)$ is due to the time-evolution of the perturber alone. At this stage, we make use of the assumed equality of the ensemble average and the time average, i.e.,

$$\sum_p P_p < p|V^p|p > \; = \; \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{+T} dx < \psi(x)\,|V^p|\psi(x) > , \tag{5.20}$$

where $\psi(t)$ is the state of the perturber at time t. Following the notations of Ref. 1, we define

$$\overline{\mathcal{V}}(t) \equiv < \psi(t)\,|V^p|\psi(t) > \tag{5.21}$$

and

$$\widetilde{\mathcal{V}}(t) \equiv U(t)\, \overline{\mathcal{V}}(t) U^+(t) \quad . \tag{5.22}$$

*An alternative but lengthier proof of this identity has been given by O. von Roos (Ref. 11).

The first term in (5.19) can be written as follows:

$$\sum_p P_p < ip|V^p|ip > = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{+T} dx \, \mathcal{V}(x) \quad . \tag{5.23}$$

The second term in (5.19) becomes:

$$< i \left| \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{+T} dx \int_0^\infty dt < \psi(x) \left| V^p(0) U(t) V^p(-t) U^+(t) \right| \psi(x) > \right| i > . \tag{5.24}$$

It should be pointed out that in obtaining (5.23) and (5.24) no assumption has been made except for replacing the ensemble average by the time average. We now approximate the matrix element $< \psi(x) | \ldots | \psi(x) >$ by

$$< \psi(x) | V^p(0) | \psi(x) > U(t) < \psi(x) | V^p(-t) | \psi(x) > U^+(t) \quad , \tag{5.25}$$

which is essentially equivalent to replacing the expected value of a product by the product of the expected values. Noting that

$$< \psi(x) | V^p(-t) | \psi(x) > = < \psi(x-t) | V^p(0) | \psi(x-t) > \, , \tag{5.26}$$

one can write (5.25) as follows:

$$\bar{\mathcal{V}}(x) U(t) \bar{\mathcal{V}}(x-t) U^+(t) \quad . \tag{5.27}$$

Inserting (5.27) into (5.24), and then combining (5.23) and (5.24) with (5.19), one obtains

$$< i|\mathcal{H}|i > = < i \left| \lim_{T\to\infty} \frac{1}{2T} \left\{ \int_{-T}^{+T} dx \, \mathcal{V}(x) + \frac{1}{i\hbar} \int_{-T}^{+T} dx \int_{-\infty}^{x} dy \, \tilde{\mathcal{V}}(x) \tilde{\mathcal{V}}(y) \right\} \right| i > . \tag{5.28}$$

This expression, which yields the shift and the width according to (5.15), is essentially equivalent to the formula (42) of Ref. 1. [See also Eqs. (48)

and (49) of Ref. 1.] However, the latter is derived with the assumption that the perturber consists of noninteracting particles (electrons). Furthermore, the calculations are made by first assuming a single perturber to be present, and then multiplying the results by the number of perturbers. These assumptions can be introduced in (5.28) by writing the wave function $\psi(t)$ as a product of the wave functions of each electron, expressing $\tilde{\mathcal{V}}(x)$ as the sum of interactions with each electron, and finally ignoring the cross terms due to the quadratic form of $\tilde{\mathcal{V}}(x)\,\tilde{\mathcal{V}}(y)$. In evaluating the time average for a single electron, one must choose a time interval 2T which is much greater than the average collision time to achieve good statistics. From this point on, one may use arguments almost identical to those used in obtaining Eqs. (40), (41), (42), and (43) of Ref. 1.

The foregoing remarks should be sufficient to demonstrate how the present formulation reduces to the impact theory with certain approximations. Since the two approaches are based on entirely different approximations, a one-to-one correspondence between the final line shape formulas cannot be expected. However, the dominant features of the impact theory follow from the present theory of line shape through the foregoing analysis.

D. TWO NONINTERACTING PERTURBERS

In this section, we consider a case where the perturber consists of two noninteracting parts. Then, the wave function $|p>$ of the perturber can be written as

$$|p> = |q>|Q>,$$

where $|q>$ and $|Q>$ are the eigenfunctions of each part. In dealing with the spectral line shape from a plasma, one usually treats the electrons and the ions as two noninteracting systems of particles. Therefore, the present analysis has a direct application and will indicate how to combine the effects of ions and electrons on the line shape.

An inspection of (4.58) reveals that the matrix element $|<p|P(\underline{X})|p'>|^2$ appearing in (4.63) and (4.76) can be written as follows:

$$|P_{pp'}|^2 = |P^i_{QQ'}|^2 \delta_{qq'} + |P_{qq'}|^2 \delta_{QQ'} + [P^i_{QQ} P^e_{qq} + P^i_{QQ} P^e_{qq}] \delta_{QQ'} \delta_{qq'} , \tag{5.29}$$

where we have omitted the argument of $P(\underline{X})$ to compress writing. The superscripts i and e distinguish between two parts of the perturber. When (5.29) is inserted into (4.63) and (4.76), one can recognize three different terms for the width and the shift: γ^i_n, γ^e_n, γ^{ei}_n and S^i_{nm}, S^e_{nm}, S^{ei}_{nm} respectively. The terms labelled by i and e represent the width and shift due to ions and electrons alone. The occurrence of the cross term labelled by ei indicates that the effects of ions and electrons on the line shape are not strictly additive. Inserting (5.29) into (4.63), one obtains for γ^e_n and γ^{ei}_n:

$$\gamma^e_n = \frac{2\pi}{\hbar} \frac{1}{\Omega^2} \sum_{K'\mu'q'} |\mathcal{J}(X)|^2 F_{i\mu'}(\underline{X}) |<q|P^e(\underline{X})|q'>|^2$$

$$\cdot \delta\left[E_{\alpha_i} - E_{\alpha'} + E_q - E_{q'} + \frac{\hbar^2}{2M}(K^2 - K'^2)\right] , \tag{5.30}$$

and

$$\gamma^{ei}_n = \frac{2\pi}{\hbar} \frac{1}{\Omega^2} \sum_{K'\mu'} |\mathcal{J}(X)|^2 F_{i\mu'}(\underline{X}) 2\mathrm{Re}\left[<q|P^e(\underline{X})|q><Q|P^i(-\underline{X})|Q>\right]$$

$$\cdot \delta\left[E_{\alpha_i} - E_{\alpha'} + \frac{\hbar^2}{2M}(K^2 - K'^2)\right] , \tag{5.31}$$

where $\underline{X} = \underline{K}-\underline{K}'$, and E_q, E_Q represent the energy of electrons and ions respectively. The ion width γ_n^i can be obtained by replacing q by Q in (5.30).

In the subsequent analysis, the cross terms γ_n^{ei} and S_n^{ei} will be ignored as an approximation. Under some circumstances, the cross terms may vanish as a consequence of certain assumptions made about the system. For example, we shall see in Section VI that the diagonal matrix elements $< q|P^e(\underline{X})|q >$ and $< Q|P^i(\underline{X})|Q >$ vanish unless $\underline{X} = 0$, if one treats the electrons and ions as an ideal gas by neglecting the interaction between electrons and between ions. Then, γ_n^{ei} vanishes because $F_{i\mu'}(0) = 0$. The same holds for S_n^{ei}. Thus, if one makes the ideal gas approximation in a plasma, the cross terms disappear automatically. Another example is the case where the emitter is assumed to be at rest. In this case, (5.31) involves only a discrete summation on α' and thus vanishes, as explained in Section II.D [see also (5.1)]. However, S_n^{ei} does not necessarily vanish if the motion of the emitter is ignored. It follows that the approximation of ignoring the cross terms may be justified in some circumstances.

The expression for S_{nm}^e and S_{nm}^i are obtained by replacing $|p >$ in (4.76) by $|q >$ and $|Q >$ respectively.

With the foregoing remarks, the line shape formula (4.39) takes on the following form:

$$I(w) = \sum_{i,f} A_{if} \sum_{qQK} P_{KQq} \frac{\gamma_{\alpha_i}^r + \gamma_n^e + \gamma_n^i}{(\hbar\Delta w_{if} - S_{nm}^e - S_{nm}^i - S_d)^2 + \frac{\hbar^2}{4}(\gamma_{\alpha_i}^r + \gamma_n^e + \gamma_n^i)^2} . \tag{5.32}$$

The assumption that the perturber consists of two noninteracting parts enables

one to treat each part by a different approximation. Suppose that the electrons are treated by the impact approximation, and ions by the quasi-static approximation. Furthermore suppose that the emitter is at rest. To simplify writing, neglect the natural width. Impact approximation implies that γ_n^e and S_{nm}^e are replaced by their mean values γ_i^e and S_{if}^e. In the quasi-static limit $\gamma_n^i = 0$ and $S_{nm}^i = S_{if}^i(\underline{E})$, where $\underline{E}$ is the electric field produced by ions. With the foregoing assumptions, (5.32) becomes

$$I(w) = \sum_{i,f} A_{if} \int d^3E\, W(\underline{E}) \frac{\gamma_i^e}{[\hbar\Delta w_{if} - S_{if}^i(\underline{E}) - S_{if}^e]^2 + (\hbar\gamma_i^e/2)^2} \quad . \quad (5.33)$$

This formula expresses the line shape as a weighted superposition of Lorentzian distributions whose center frequencies are shifted by the ionic field and by a constant averaged shift due to electrons. The widths of these Lorentzian distributions are identical and are determined by electrons. Equation (5.33) represents the present status of line shape calculations, which is summarized by Baranger[1] as follows: "First, the atom is assumed to lie in a fixed electric field created by the ions, with attending Stark splitting. The effect of electrons on the corresponding sharp lines is computed with the impact approximation. Then one averages the electron broadened spectrum with the probability distribution of the ionic field. Finally, one investigates the possible corrections due to the motion of the ions." It should be noted, however, that in the present theory of line shape, calculation of the electron width and shift is based on different formulas, as explained in the previous section.

We shall now investigate the case of two noninteracting perturbers with the aid of the line shape formula (4.39) based on the statistical approximation. With minor modifications, (4.39) is reproduced here as (5.34) to facilitate reference:

$$I(w) = \sum_{i,f} A_{if} \frac{\overline{\gamma}_n}{(\hbar\Delta w_{if} - S^p_{if})^2 + \frac{\hbar^2}{4}\gamma_t^2} , \tag{5.34}$$

where

$$\overline{\gamma}_n = \gamma^r_{\alpha_i} + \gamma^p_i , \tag{5.35}$$

$$\gamma_t = \gamma_d^2 + \gamma_s^2 + \overline{\gamma}_n^2 , \tag{5.36}$$

$$\gamma_s^2 = \frac{4}{\hbar^2} \sum_{K,p} P_{Kp} [(S^p_{nm})^2 - (S^i_{if})^2] . \tag{5.37}$$

In this formalism, the calculation of line shape is reduced to the determination of three quantities, i.e., γ^p_i, S^i_{if}, and γ_s, for a given perturber. In the case of two noninteracting perturbers, γ^p_i and S^i_{if} can be written as follows [cf. (5.29)]:

$$\gamma^p_i = \gamma^e_i + \gamma^i_i + \gamma^{ei}_i , \tag{5.38}$$

$$S^p_{if} = S^e_{if} + S^i_{if} + S^{ei}_{if} . \tag{5.39}$$

Once again, we shall ignore the cross terms without further comment. The statistical width γ_s then becomes:

$$\gamma_s^2 = (\gamma^e_s)^2 + (\gamma^i_s)^2 + \frac{8}{\hbar^2} \sum_{KqQ} P_{KqQ} [S^e_{nm} S^i_{nm} - S^e_{if} S^i_{if}] . \tag{5.40}$$

Since S^e_{nm} and S^i_{nm} involve only electron and ion states, respectively, the last term vanishes if the center of mass motion of the emitter is neglected. Then, the average of the produce $S^e_{nm}S^i_{nm}$ is equal to the product of averages. We shall ignore this term even in the case where the motion of the emitter is taken into account, because this term is probably of the same order of magnitude as the cross terms, which have been ignored in the preceding discussion. It is emphasized that these simplifications are introduced for a qualitative discussion of line shape. In numerical calculations, one may retain these terms if they are not found to be negligible.

With the above simplifications, the following line shape formula is obtained:

$$I(w) = \sum_{i,f} A_{if} \frac{\gamma^e_i+\gamma^i_i+\gamma^r_{\alpha_i}}{(\hbar\Delta w_{if}-S^i_{if}-S^e_{if})^2 + \frac{\hbar^2}{4}\left[\gamma_d^2+(\gamma^e_s)^2+(\gamma^i_s)^2+(\gamma^e_i+\gamma^i_i+\gamma^r_{\alpha_i})^2\right]} . \tag{5.41}$$

This formula includes all the dominant effects which influence the line shape. It treats the ions and electrons in the same manner. The relative magnitude of the various terms in the total width depends on the physical conditions and on the nature of the perturber, e.g., temperature and mass. For example, γ^i_i vanishes if the mass of ions is infinite (quasi-static approximation), and the terms corresponding to the pressure broadening become dominant if the temperature is sufficiently high (impact limit). It is important to realize that the approximations involved in (5.41) are all operational rather than physical, and therefore can be tested in principle by estimating the magnitude of the terms which are thrown away.

VI. APPLICATION TO PLASMAS

A. INTRODUCTION

In this section the line shape theory developed in the previous sections will be applied to the emission spectrum from a plasma. In a plasma, the perturber consists of electrons and ions. It is assumed that ions can be treated as structureless particles. Furthermore, the interaction between electrons, ions, and electron-ion pairs is ignored. Thus, the perturber is treated as an ideal gas. The emitter is assumed to be a neutral atom.

The purpose of this section is to compute analytically the pressure width and shift due to electrons and ions, so that some aspects of the line shape theory may be better understood. This computation will also reduce the number of numerical calculations necessary to obtain the line shape. We shall not attempt to evaluate the statistical width [cf. (5.37)], the third quantity which must be calculated to determine the line shape, because that would involve numerical calculations. Therefore, this section should be regarded as a guide in applying the general theory of line shape to a given physical system, rather than a complete treatment of line shape in plasmas.

B. THE WIDTH DUE TO ELECTRONS AND IONS

We shall use (5.30) to compute the width γ_i^e due to electrons. The ionic width γ_i^i can be obtained by replacing the electron mass by the ion mass in the final result.

The wave function $|q>$ for electrons which are treated as an ideal gas

will be labelled by the occupation numbers of the single-electron wave functions, i.e.,

$$|q> \;=\; |n_1,\ldots n_j..> \;,$$

where n_j denotes the number of electrons in the eigenstate

$$\frac{1}{\sqrt{\Omega}}\; e^{i\underline{r}\cdot\underline{q}_j} \;,$$

where $\hbar\underline{q}_j$ is the momentum of the electron. The operator $P^e(\underline{X})$ appearing in (5.30) is explicitly given by

$$P^e(\underline{X}) \;=\; e\sum_j\; e^{i\underline{r}_j\cdot\underline{X}} \;, \tag{6.1}$$

where $\underline{r}_j$ is the position of the jth electron. The matrix elements $<q'|P^e(\underline{X})|q>$ can be computed easily* by expressing $P^e(\underline{X})$ in terms of creation (A^+) and destruction (A) operators, viz.,

$$P^e(\underline{X}) \;=\; e\sum_{j,k}\; \delta(\underline{X}+\underline{q}_k-\underline{q}_j)\; A_j^+A_k \;. \tag{6.2}$$

The result is found to be

$$|<n_1,..n_j,..n_k-1..|P^e(\underline{X})|n_1,..n_j..n_k..>|^2 \;=\; e^2\, n_k(1\pm n_j)\,\delta(\underline{X}+\underline{q}_k-\underline{q}_j) \;. \tag{6.3}$$

The factor $(1\pm n_j)$ is a quantum-mechanical effect and can be replaced by unity in the present problem since the number of states available for an electron is much greater than the number of electrons. The diagonal matrix element $<q|P^e(\underline{X})|q>$ can be computed as

*See p. 215 of Ref. 12.

$$< n_1,..n_j..|P^e(\underline{X})|n_1,..n_j...> \;=\; e\,N_e\,\delta(\underline{X})\;, \qquad (6.4)$$

where N_e is the number of electrons. It is important to note that the δ,s appearing in (6.3) and (6.4) are Kronecker deltas. It is observed from (6.4) that the diagonal element is zero unless $\underline{X} = 0$; this conclusion has been referred to in Section V.D.

Inserting (6.3) into (5.30), converting the summation on K' into an integral, and performing the summation on j with the help of the Kronecker delta, one obtains

$$\gamma_n^e \;=\; \frac{e^2}{4\pi^2\Omega\hbar}\sum_{\mu'}\int d^3X|\mathcal{G}(X)|^2\,F_{i\mu'}(\underline{X})\sum_k n_k$$
$$\cdot\,\delta\left[E_{\alpha_i}-E_{\alpha'}-\frac{\hbar^2}{2m}(X^2+2\underline{X}\cdot\underline{q}_k)-\frac{\hbar^2}{2M}(X^2-2\underline{X}\cdot\underline{K})\right]\;. \qquad (6.5)$$

Using

$$\sum_{\underline{q}_k\in d^3q_k} n_k \;=\; d^3q_k\,n(\underline{q}_k)\;,$$

which defines the number density $n(\underline{q})$ in the momentum space, one can write (6.5) as follows:

$$\gamma_n^e \;=\; \frac{e^2}{4\pi^2\Omega\hbar}\sum_{\mu'}\int d^3X\,|\mathcal{G}(X)|^2\,F_{i\mu'}(\underline{X})\int d^3q\,n(\underline{q})$$
$$\cdot\,\delta\left[E_{\alpha_i}-E_{\alpha'}-\frac{(\hbar X)^2}{2m_r}-\hbar\underline{X}\cdot(\underline{v}-\underline{V})\right]\;, \qquad (6.6)$$

where m_r is the reduced mass

$$m_r \;=\; \frac{mM}{m+M}\;,$$

and where $\underline{v}$ and $\underline{V}$ are the velocities of the electron and the emitter respectively.

The mean value of γ_n^e can now be computed by assuming a Maxwellian distribution of momenta $\hbar\underline{K}$ and $\hbar\underline{q}$. Thus,

$$\gamma_i^e \equiv \sum_{qK} P_q P_K \gamma_n^e = \frac{e^2}{4\pi^2\hbar} n_e \sum_{\alpha'} \int dX\, X^2 |\mathcal{O}(X)|^2 f_{i\alpha'}(X)$$

$$\cdot \int d^3v \mathcal{M}(v,m) \int d^3V \mathcal{M}(M,V)\, \delta\left[E_{\alpha_i} - E_{\alpha'} - \frac{(\hbar X)^2}{2m_r} - \hbar\underline{X}\cdot(\underline{v}-\underline{V})\right] , \quad (6.7)$$

where $\mathcal{M}(v,m)$ is the normalized Maxwellian distribution, i.e.,

$$\mathcal{M}(v,m) \equiv \left(\frac{m}{2\pi\Theta}\right)^{3/2} e^{-(mv^2/2\Theta)} , \quad (6.8)$$

n_e is the number of electrons per unit volume, and $f_{i\alpha'}(X)$ is defined by

$$f_{i\alpha'}(X) \equiv \sum_{M'} \int d\Omega_{\hat{\underline{X}}}\, F_{i\mu'}(\underline{X}) . \quad (6.9)$$

When the states are nondegenerate, one may simplify (6.9) by expanding the exponential function in the definition of $F_{i\mu'}(\underline{X})$ given by (4.64) and (4.60) into spherical harmonics, and employing the Wigner-Eckart theorem. One finds that

$$f_{i\alpha'}(X) = \sum_{L=1} |\langle \alpha' \| T_L(X) \| \alpha_i \rangle|^2 , \quad (6.10)$$

where the irreducible tensor operators T_{LM} are defined by

$$T_{LM}(X) \equiv 4\pi e \sum_{j=1}^{Z} Y_{LM}(\hat{\underline{r}}_j')\, j_L(Xr_j') . \quad (6.11)$$

In the last expression, Y_{LM} and j_L are spherical harmonics and spherical

Bessel functions. It is noted that $f_{i\alpha'}$ is independent of the magnetic quantum number M_i of the initial state. In the dipole approximation,

$$f_{i\alpha'}(X) \equiv \frac{4\pi}{3} X^2 |< \alpha' \| \underline{d} \| \alpha_i >|^2 , \tag{6.12}$$

where $\underline{d}$ is the dipole operator for the emitter. The case of degenerate states will be discussed later.

Substituting $\mathcal{J}(X)$ from (4.75) into (6.7), and performing the indicated integrations (see Appendix A), one obtains

$$\gamma_i^e = \frac{8e^2}{\hbar} n_e \sum_{\alpha'}' \int_0^\infty dX \frac{X^2}{(\lambda^2+X^2)^2} f_{i\alpha'}(X) \; I(X) , \tag{6.13}$$

where $I(X)$ is defined by

$$I(X) \equiv \frac{1}{\hbar X} \sqrt{\frac{m_r}{2\pi\Theta}} \exp\left[- \frac{m_r}{2\Theta} \left(\frac{E_{\alpha_i} - E_{\alpha'}}{\hbar X} - \frac{\hbar X}{2m_r} \right)^2 \right] . \tag{6.14}$$

We shall now attempt to draw some conclusions from (6.13) about the pressure width. First we consider the zero temperature limit. From the definition of $I(X)$ given by (6.14), it follows that $I(X)$ reduces to a delta function as $\Theta \to 0$, i.e.,

$$I(X) \to \delta\left[E_{\alpha_i} - E_{\alpha'} - \frac{(\hbar X)^2}{2m_r} \right] . \tag{6.15}$$

Inserting (6.15) into (6.13) yields

$$\gamma_i^e = \frac{4e^2}{\hbar} n_e \sum_{\substack{\alpha' \\ (E_{\alpha'} < E_{\alpha_i})}} \frac{\eta^3}{(\lambda^2+\eta^2)^2} \frac{f_{i\alpha'}(\eta)}{E_{\alpha_i} - E_{\alpha'}} , \tag{6.16}$$

where

$$\eta \equiv \left[\frac{2m_r}{\hbar^2}\ (E_{\alpha_i}-E_{\alpha'})\right]^{1/2} . \qquad (6.17)$$

It is observed that the pressure broadening does not approach zero in the zero temperature limit. There is a finite width due to the transitions to the lower states ($E_{\alpha'} < E_{\alpha_i}$). This result indicates that ions can cause transitions even if their motion is negligible before the interaction. Therefore, to ignore the width due to ions on the ground of their relatively slow motion, as is done in the quasi-static limit, may not be justified. However, the width approaches zero as m_r tends to infinity, as can be verified by noting that

$$f_{i\alpha'}(\eta) \to (1/\eta^2) \quad \text{as } \eta \to \infty .$$

Hence, the quasi-static limit actually corresponds to assuming that the masses of both the emitter and the perturber are infinite.

It is now in order to discuss the role of the parameter λ in (6.13) and (6.16) as well as in the subsequent formulas. This parameter was introduced as a convergence factor [cf. (4.61)] to allow interchange of integrations. Therefore, it is to be set equal to zero in the final results, e.g., in (6.16). However, one may improve the theory numerically by interpreting λ as the inverse of the Debye shielding distance. The reason for this is that the theory developed in this section ignores the interaction between electrons and ions, and it is not realistic to do so. This approximation may be improved by introducing a shielded Coulomb potential between charged particles.[1] The improvement may be expected to be appreciable particularly in the case of

closely adjacent levels, and also in the case of electrons. This is because λ enters the formula (6.16) as $(\lambda^2+\eta^2)$, and its effect is appreciable only when $\lambda > \eta$ [cf. (6.17)].

The computation of γ_i^e can be simplified by making the dipole approximation in (6.16). Substituting (6.12) into (6.16) gives

$$\gamma_i^e = \frac{16\pi e^2}{3\hbar} n_e \sum_{\substack{\alpha' \\ (E_{\alpha'} < E_{\alpha_i})}} |<\alpha'\|\underline{d}\|\alpha_i>|^2 \frac{\eta^5}{(\eta^2+\lambda^2)^2(E_{\alpha_i}-E_{\alpha'})} . \qquad (6.18)$$

A note of caution is due here. The dipole approximation is valid when the argument of $f_{i\alpha'}$ in (6.16) is sufficiently small [cf. (6.10) and (6.11)]. If r_o is the radius of the emitter, an approximate criterion for the validity of the dipole approximation may be given as $\eta r_o < 1$. Taking $r_o \approx 10^{-8}$ cm, one finds that in the case of electrons, the dipole approximation holds for transitions for which $E_{\alpha_i}-E_{\alpha'} \leq 8$ ev, whereas in the case of ions, e.g., He, the dipole approximation holds only for transitions for which $E_{\alpha_i}-E_{\alpha'} \leq .002$ ev. Therefore, (6.18) may be a better approximation for electrons than for ions. In the case of ions, one may use the asymptotic value of $f_{i\alpha'}$ for large arguments. The latter decreases as $1/\eta^2$ for $\eta r_o > 1$, as can be verified from (6.10) and (6.11). From these discussions one may expect the width due to ions to be smaller than the width due to electrons at low temperatures, although a definite conclusion requires a careful numerical evaluation.

We now turn to the task of evaluating (6.13) at any temperature. We first consider the case of $E_{\alpha_i} \neq E_{\alpha'}$, which corresponds to the contribution of the inelastic collisions to the width. The integral in (6.13) can be performed numerically as it stands, and can be worked out analytically if

one makes the dipole approximation and sets $\lambda = 0$. The result can be shown to be (see Appendix A):

$$\gamma_i^e = \frac{16e^2}{3\hbar^2} n_e \sqrt{\frac{2\pi m_r}{\Theta}} \sum_{\substack{\alpha' \\ (E_{\alpha_i} \neq E_{\alpha'})}} |\langle \alpha_i \| \underline{d} \| \alpha' \rangle|^2 \, e^{(E_{\alpha_i} - E_{\alpha'})/2\Theta} K_o(|E_{\alpha_i} - E_{\alpha'}|/2\Theta) , \tag{6.19}$$

where K_o is the modified Bessel function of the second kind. The summation on α' includes transitions both to upper and lower energy levels. Equation (6.19) reduces to (6.18) as $\Theta \to 0$. That (6.19) diverges as $m_r \to \infty$ is a consequence of the dipole approximation. The temperature dependence as well as the dependence of the width on the mass of the perturber can be studied with the aid of (6.19). We shall not go into details of these calculations, which are of numerical nature. It is emphasized that the validity of (6.19) is restricted by the dipole approximation. When the latter is not justified in a given temperature range, or for a given perturber mass, the original Eq. (6.13) should be used.

The contribution of the elastic collisions, i.e., $E_{\alpha_i} = E_{\alpha'}$, can be obtained from (6.13) as follows:

$$\gamma_i^e = \frac{8e^2}{\hbar^2} n_e \sqrt{\frac{m_r}{2\pi\Theta}} \int_o^\infty dx \, \frac{X}{(\lambda^2 + X^2)^2} \, f_{i\alpha_i}(X) \, e^{-(\hbar^2 X^2 / 8\Theta m_r)} , \tag{6.20}$$

where the symbol $f_{i\alpha_i}(X)$ means [cf. (6.9)] explicitly

$$f_{i\alpha_i}(X) \equiv \sum_{M'} \int d\Omega_{\hat{\underline{X}}} \, |\langle i | \Lambda(\underline{X}) | \alpha \, M' \rangle|^2 . \tag{6.21}$$

When the initial state is nondegenerate, the parity selection rule excludes the dipole moment and all the other odd moments in the expansion of $f_{i\alpha_i}$.

Since γ_i^e due to the elastic collisions involves higher moments, it can be neglected as compared to the width caused by the inelastic collisions given by (6.19).

When the initial state has accidental degeneracy, the contribution of the elastic collisions is not negligible, because the matrix element of the dipole operator between two states with the same energy does not vanish. We shall treat this case only in the dipole approximation, and assume that the degenerate eigenstates of the upper level diagonalize the z-component of the dipole operator [cf. (4.81)]. The internal states can be labelled as $|\alpha sM>$ in parabolic coordinates. To compress writing we denote the quantum numbers (sM) by ν. The case of degenerate states differs from that of nondegenerate states only in the choice of the representation in the subspaces corresponding to a given energy. The results of the previous case can be used directly by modifying (6.9) slightly. In dipole approximation, (6.9) reads

$$f_{i\alpha'}(X) = \sum_{\nu'} \int d\Omega_{\underline{\hat{X}}} \, |< i|\underline{d}\cdot\underline{X}|\alpha'\nu'>|^2 \, . \tag{6.22}$$

Noting that

$$\int d\Omega_{\underline{\hat{X}}} \, X_i X_j = \frac{4\pi}{3} X^2 \delta_{ij} \, , \tag{6.23}$$

one writes (6.22) as follows:

$$f_{i\alpha'}(X) = \frac{4\pi}{3} X^2 \sum_{\nu'} |< i|\underline{d}|\alpha'\nu'>|^2 \, . \tag{6.24}$$

The matrix element on the right hand side now denotes the sum of the squares of the matrix elements of the components. The difference between (6.24) and

(6.12) lies in the summation over ν'. Equations (6.18) and (6.19) can be used with the foregoing modification. For example, (6.19) reads

$$\gamma_i^e = \frac{16e^2}{3\hbar^2} n_e \sqrt{\frac{2\pi m_r}{\Theta}} \sum_{\alpha'\nu'} |< i|\underline{d}|\alpha'\nu'>|^2 \, e^{(E_{\alpha_i}-E_{\alpha'})/2\Theta} K_o(|E_{\alpha_i}-E_{\alpha'}|/2\Theta) \, . \tag{6.25}$$

The contribution of the elastic collisions can be obtained from (6.20) as follows:

$$\gamma_i^e = \frac{8\sqrt{2\pi}}{3\hbar^2} e^2 n_e \sqrt{\frac{m_r}{\Theta}} \, F\left(\frac{\hbar^2}{8\Theta m_r R_D}\right) |< i|d_z|i>|^2 \, , \tag{6.26}$$

where $F(z)$ is defined by

$$F(z) = \int_0^\infty dx \, \frac{x}{(1+x)^2} \, e^{-zx} \, . \tag{6.27}$$

In (6.26), R_D is the Debye shielding distance. It is important to note that in the case of degenerate levels, the width due to the elastic collisions diverges if the quantity λ in (6.20) is taken to zero. This indicates that the use of a shielded Coulomb potential or any other appropriate cut-off procedure is imperative in the present case.

C. THE SHIFT DUE TO ELECTRONS AND IONS

We shall use (4.76) to compute the shift due to electrons and ions. The shift of the upper state takes on the following form in the case of a plasma:

$$S_n^e = \frac{e^2}{(2\pi)^2\Omega} \sum_{\mu'} \int d^3X \, |\mathcal{G}(X)|^2 \, F_{i\mu'}(X) \, PP \int d^3q \, n(\underline{q}) \cdot \left[E_{\alpha_i}-E_{\alpha'} - \frac{(\hbar X)^2}{2m_r} - \hbar\underline{X}\cdot(\underline{v}-\underline{V})\right]^{-1} \, . \tag{6.28}$$

The shift of the lower state can be obtained by replacing $|i>$ by $|f>$. The mean value of S_n^e can be written as

$$S_i^e = \frac{e^2}{(2\pi)^3} n_e \sum_{\alpha'} \int_0^\infty dX\, X^2 |\mathcal{O}(X)|^2 f_{i\alpha'}(X) \int d^3v\, \mathcal{M}(v,m)$$

$$\cdot \int d^3V\, \mathcal{M}(V,M) \left[E_{\alpha_i} - E_{\alpha'} - \frac{(\hbar X)^2}{2m_r} - \hbar \underline{X} \cdot (\underline{v} - \underline{V}) \right]^{-1} . \qquad (6.29)$$

Following the procedure described in Appendix A, one finds the analogous formula to (6.13):

$$S_i^e = \frac{e^2}{\pi} n_e \sum_{\alpha'} \int_0^\infty dX \frac{X^2}{(\lambda^2+X^2)^2} f_{i\alpha'}(X)\, I(X) , \qquad (6.30)$$

where

$$I(X) = \frac{1}{\hbar X} \frac{4}{\sqrt{\pi}} \xi^{3/2} \int_0^\infty du\, u\, e^{-\xi u^2} \ln \left| \frac{E_{\alpha_i} - E_{\alpha'} - \frac{(\hbar X)^2}{2m_r} + \hbar X u}{E_{\alpha_i} - E_{\alpha'} - \frac{(\hbar X)^2}{2m_r} - \hbar X u} \right| , \qquad (6.31)$$

where

$$\xi \equiv \frac{m_r}{2\Theta} .$$

The zero temperature limit is obtained by using

$$\lim_{\xi \to \infty} \frac{4}{\sqrt{\pi}} \xi^{3/2} e^{-\xi u^2} = \frac{\delta(u)}{u^2} ,$$

and noting that

$$\lim_{\xi \to \infty} I(X) = PP \frac{1}{E_{\alpha_i} - E_{\alpha'} - \frac{(\hbar X)^2}{2m_r}} , \qquad (6.32)$$

as follows:

$$S_i^e = -\frac{e^2}{\pi} n_e \sum_{\substack{\alpha' \\ (E_{\alpha'} > E_{\alpha_i})}} \int_0^\infty dX \frac{X^2}{(\lambda^2+X^2)^2} f_{i\alpha'}(X) \frac{1}{(E_{\alpha'}-E_{\alpha_i}) + \frac{(\hbar X)^2}{2m_r}} . \qquad (6.33)$$

It is observed that in (6.33), transitions only to upper energy levels contribute to the shift in the zero temperature limit. This is in contrast to the zero temperature limit of the width, i.e., (6.16). Furthermore, the shift does not vanish as $m_r \to \infty$ (quasi-static limit), whereas the width does vanish. In the dipole approximation, (6.33) reduces to

$$S_i^e = -\frac{4\pi e^2}{3\hbar} n_e \sqrt{2m_r} \sum_{\substack{\alpha' \\ (E_{\alpha'} > E_{\alpha_i})}} \frac{|<\alpha'\|\underline{d}\|\alpha_i>|^2}{\sqrt{E_{\alpha'}-E_{\alpha_i}}} . \qquad (6.34)$$

The discussions about the validity of the dipole approximation as well as the choice of λ apply also to the shift.

The shift at any temperature can be obtained in the dipole approximation and with $\lambda = 0$. Performing the integrations in (6.31) and (6.30) (see Appendix B), one obtains

$$S_i^e = -\frac{4\pi}{3\hbar} n_e \sqrt{\frac{2m_r}{\Theta}} \sum_{\substack{\alpha' \\ (E_{\alpha'} > E_{\alpha_i})}} |<\alpha'\|\underline{d}\|\alpha_i>|^2 e^{-(E_{\alpha'}-E_{\alpha_i})/2\Theta} I_o\left(\frac{E_{\alpha'}-E_{\alpha_i}}{2\Theta}\right) , \qquad (6.35)$$

where I_o is the modified Bessel function of the first kind.

We shall give the shift formula for the case of degenerate levels without any further comment:

$$S_i^e = -\frac{4\pi e^2}{3\hbar} n_e \left[\sqrt{\frac{2\pi m_r}{\Theta}} \sum_{\substack{\alpha'\nu' \\ (E_{\alpha'} > E_{\alpha_i})}} |< i|\underline{d}|\alpha'\nu'>|^2 \, e^{-(E_{\alpha'} - E_{\alpha_i})/2\Theta} \right.$$

$$\left. \cdot \, I_o\left(\frac{E_{\alpha'} - E_{\alpha_i}}{2\Theta}\right) + \frac{2m_r R_D}{\pi\hbar} |< i|d_z|i>|^2 \, G\left(\frac{\hbar^2}{8\Theta m_r R_D}\right) \right] , \qquad (6.36)$$

where

$$G(z) \equiv \frac{4}{\sqrt{\pi}} z^{3/2} \int_0^\infty dx \, x \, e^{-zx^2} \int_0^\infty dy \, \frac{y^3}{(1+y^2)^2} \ln\left|\frac{y+x}{y-x}\right| . \qquad (6.37)$$

VII. CONCLUSIONS

The present theory of line shape has, as its starting point, the emission spectrum formula (3.26), which is based on Heitler's damping theory. The starting point of the existing theories, i.e., the quantum mechanical Fourier integral formula which expresses the spectrum as the Fourier transform of the autocorrelation function of the time-dependent dipole operator [cf. (3.34)], follows from (3.26) when the natural width is neglected. These two starting formulas are therefore equivalent in all practical applications where the width of the lines is greater than the natural width. However, the form of (3.26) lends itself to a more systematic treatment of the line shape. When the interaction between the emitting and perturbing systems is treated as part of the perturbation energy, (3.26) reduces to (4.25), which is the basic line shape formula of the present study. Equation (4.25) expresses the spectrum as the superposition of the perturbed lines of the emitter. The structure of each line in turn is expressed as the weighted superposition of a sequence of Lorentzian distributions. Equation (4.25) contains the limiting approximations, advanced in the existing theories, as special cases. The Holtsmark theory follows from (4.25) when the emitting and perturbing systems are treated in the quasi-static limit. The impact theory is obtained by making the assumption of replacing the average of a function by the function of the average, and by using the ergodic theorem.

When applied to plasmas, the present theory treats the ions and electrons on the same basis. It also indicates that the pressure width due to ions or

electrons does not vanish in the zero temperature limit. This result implies that neglect of the ion width on the ground of the slow motion of ions, as assumed in the quasi-static limit, is not justified even at very low temperatures. In other words, the zero temperature limit does not correspond to the limit of infinite mass.

It is concluded that the present theory of line shape is more systematic and more interpretable than the existing theories. There is reason to expect that the computational framework provided by this theory will improve the accuracy of the line shape calculations particularly in the intermediate region, where neither impact nor the quasi-static approximation is valid.

APPENDIX A

DERIVATION OF THE WIDTH FORMULA

We start with (6.7) and substitute $\underline{u} = \underline{v}-\underline{V}$ to perform the integration on $\underline{V}$. The latter yields

$$\int d^3V \mathcal{M}(V,M)\, \mathcal{M}(|\underline{V}+\underline{u}|,m) = \mathcal{M}(u,m_r) , \qquad (A.1)$$

where m_r is the reduced mass, and where $\mathcal{M}(v,m)$ is the normalized Maxwellian distribution. The Eq. (A.1) can be verified easily by using the following tabulated integral:[13]

$$\int_0^\infty dx\, e^{-sx} \sinh a\sqrt{x} = \frac{a}{2s}\sqrt{\pi/s}\, e^{a^2/2s} .$$

We then carry out the integration over u, i.e.,

$$I(x) = 2\pi \int u^2 \mathcal{M}(u)\, du \int_{-1}^{+1} d\mu\, \delta\left[\mathcal{E} - \frac{(\hbar X)^2}{2m_r} - \hbar X u\, \mu\right] , \qquad (A.2)$$

where the z-axis is chosen parallel to $\underline{X}$. Integration over u yields

$$I(X) = \frac{2\pi}{\hbar X} \int_0^\infty u\, \mathcal{M}(u)\, D(u)\, du , \qquad (A.3)$$

where D(u) is defined by

$$\begin{aligned} D(u) &= 1 \quad \text{for} \quad u_o < u \\ &= (1/2) \quad \text{for} \quad u_o = u \\ &= 0 \quad \text{for} \quad u_o > u , \end{aligned}$$

where

$$u_o = \left| \mathcal{E} - \frac{(\hbar X)^2}{2m_r} \right| \frac{1}{\hbar X} \quad . \tag{A.4}$$

Using the definition of D(u) in (A.3) and inserting $\mathcal{M}(u)$ from (6.8), one obtains (6.14).

In obtaining (6.19) from (6.13) in dipole approximation, one encounters the following integral:

$$M \equiv \int_0^\infty \frac{dx}{x} \exp\left[-a\left(\frac{b}{x} - cx\right)^2\right] ,$$

which can be written as

$$M = e^{2abc} \int_0^\infty \frac{dx}{x} \exp\left[-\left(\frac{b^2 a}{x^2} + ac^2x^2\right)\right] .$$

The last integral is tabulated:[13]

$$M = e^{2abc} K_o(2|abc|) .$$

This result leads to (6.19).

APPENDIX B

DERIVATION OF THE SHIFT FORMULA

To obtain (6.35) from (6.30) in the dipole approximation, we substitute (6.31) into (6.30) and perform the integration on X. The following integral is encountered:

$$I^{+} = \int_{0}^{\infty} \frac{dx}{x} \ln \left| \frac{x^2+2ax-1}{x^2-2ax-1} \right| , \quad \text{for} \quad \mathcal{E} \equiv E_{\alpha_i} - E_{\alpha'} > 0 , \quad \text{(B.1)}$$

and

$$I^{-} = \int_{0}^{\infty} \frac{dx}{x} \ln \left| \frac{x^2+2ax+1}{x^2-2ax+1} \right| , \quad \text{for} \quad \mathcal{E} < 0 , \quad \text{(B.2)}$$

where

$$a^2 = \frac{u^2 m_r}{2|\mathcal{E}|} .$$

Substituting

$$x^2 + 2ax - 1 = (x+x_1)(x-x_2),$$

$$x^2 - 2ax - 1 = (x-x_1)(x+x_2)$$

in (B.1), one can verify that I^{+} vanishes. The roots x_1 and x_2 are, of course, given by

$$x_1 = \sqrt{1+a^2} + a ,$$

$$x_2 = \sqrt{1+a^2} - a .$$

Now consider I^{-}. When $a > 1$, one again substitutes

$$x^2 + 2ax + 1 = (x+x_1)(x+x_2) ,$$

$$x^2 - 2ax + 1 = (x-x_1)(x+x_2)$$

in (B.2), and finds that

$$I^- \equiv \pi^2 \quad \text{for} \quad a > 1 .$$

When $a < 1$, the argument of the logarithim is always positive, and one can therefore drop the absolute sign. Thus,

$$I^- = \int_0^\infty \frac{dx}{x} \ln \frac{x^2+2ax+1}{x^2-2ax+1} = \int_{-\infty}^{+\infty} \frac{dx}{x} \ln(x^2+2ax+1) . \qquad (B.3)$$

To evaluate the last integral, one may proceed as follows:

$$\frac{dI^-}{da} = 2\int_{-\infty}^{+\infty} \frac{dx}{x^2+2ax+1} = 2\pi/\sqrt{1-a^2} . \qquad (B.4)$$

Hence,

$$I^- = 2\pi \sin^{-1}a + C ,$$

where C is the constant of integration. Since (B.3) vanishes for $a = 0$ (odd function), C is zero. Thus,

$$I^- = 2\pi \sin^{-1}a, \quad \text{for} \quad a < 1 . \qquad (B.5)$$

In computing the remaining integration on u with the foregoing value of I^-, the following integral is encountered:

$$I \equiv \int_0^1 dx\, e^{-sx} \sin^{-1}\sqrt{x} .$$

By integrating by parts, and using

$$\int_0^1 dx \quad e^{-sx} / \sqrt{x(x-1)} \quad = \quad \pi \, e^{-s/2} \, I_0(s/2) \ ,$$

one proves that

$$I \quad = \quad - \frac{1}{2s} \quad e^{-s} + \frac{\pi}{2s} \, e^{-(s/2)} \quad I_0(s/2) \ .$$

The last formula leads to (6.35).

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