constraints that lead to the elimination of the redundant solutions. The method we propose does not involve any assumptions on the symmetry properties of the scattering force; therefore it applies also to problems not covered by previous results.[1-3] In particular, it applies also to the scattering in the presence of external fields, where rotational, parity, and time-reversal invariance may be violated. Our results can be used also for phase determination in the scattering of electromagnetic waves by an arbitrary obstacle, and unlike previous approaches we no longer depend on the assumption that the scatterer is rotationally or parity invariant.

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# Unified Theory of Spectral Line Broadening in Gases

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A quantum-mechanical unified theory of foreign-gas pressure broadening of atomic lines which includes the impact and statistical theories and duration-of-collision effects is developed. The model consists of an absorber atom with two internal states $u$ (upper) and $l$ (lower) interacting with a structureless perturber gas via two spherical pairwise additive potentials $V_u(r)$ and $V_l(r)$, e.g., a simple model of an alkali-atom line perturbed by a rare gas. The dipole-moment correlation function is analyzed in the time domain using Liouville (tetradic) techniques. The correlation function reduces exactly to a two-body form $\phi(t)$ containing the proper thermal weight factors. Detailed balance is obeyed and no $|\hbar(\omega-\omega_0)/kT|<1$ restriction is required. The impact theory follows from a long-time analysis of $\phi(t)$. Sum rules or spectral moments are used to study short-time behavior revealing conventional statistical-theory effects (including satellite bands) and the important duration-of-collision effects which link the statistical and impact regimes. The sum rules are expressed as quadratures involving potential functions and the quantum-mechanical radial distribution function. Unified methods for calculating the total line shapes are suggested: (1) Padé approximants (ratios of polynomials) can be used to interpolate from the known short-time behavior to the known long-time beahvior; this requires the least computational effort; (2) exact results for this model may be obtained numerically from the overlap integrals of radial wave functions (Franck-Condon factors) for the two potentials $V_u$ and $V_l$; (3) classical phase (trajectory) expressions are given which are reasonable approximations in both the impact and statistical limits. A number of related topics are discussed including diabatic effects, collision-induced absorption, non-Lorentzian wings of molecular vibration-rotation bands, and the Condon approximation for the dipole-moment transition strength vs $r$. The use of line shapes to probe atomic interactions, especially in excited states, is emphasized and the suggestion made that experiments be done over as wide a temperature range as possible with the measured line shapes in computer-readable form. The entire line-shape problem is described as the study of the spectrum of an atom-perturber "quasimolecule" (with primarily *unbound* states).

## I. INTRODUCTION

The goal is to present a systematic theory of the absorption line shape for a single atomic line (electronic transition) broadened by foreign-gas perturbers.[1] Some discussion will be given of how the theory can be extended to more complex cases, including overlapping atomic line shapes and molecular lines and bands. The motivation behind such work is that we would like to be able, in a deductive fashion, to pass from a knowledge of detailed interatomic interactions to the line shape and vice versa.

At low perturber-gas densities single lines appear Lorentzian in shape with a width and shift proportional to the perturber-gas density. At higher gas densities anomalous peaks or "satellite lines" often appear, which at high densities may dominate the line. Even if satellites as such are absent, significant deviations from the Lorentzian shape are found in the far wings. A similar situation occurs from molecular bands: When the far-wing absorption can be isolated, it does not follow a sum of Lorentzian shapes of the lines in the band.

The explanation of the Lorentzian shape as because of the interruption of the radiative or absorptive process by perturber collisions was given by Michelson[2] and Lorentz[3] at the turn of the century. This impact theory was given its first definitive statement by Baranger.[4–6] Some of the non-Lorentzian features of lines were originally explained by the statistical theories of Holtzmark,[7] Kuhn,[8] and Margenau.[9] In the statistical theory the motion of the perturbers is assumed to be slow so that an atom emits or absorbs with a frequency dependent only on the positions of the perturbers. The line shape is obtained by suitable averaging over the perturber positions. Molecular bands have been studied in the context of the impact theory but there have been few attempts to explain the anomalous behavior observed in the far wings.

There is one important physical effect that is missing from both the impact and statistical theories—the finite duration of a collision. In the impact theory this time is neglected, it is set to zero. In the statistical theory it is assumed infinite; the perturbers are clamped, without motion, for each configuration in the averaging process.

There has been no quantum-mechanical theory that attempts to combine the impact and statistical theories and duration-of-collision effects in a way that allows practical computations. It is the aim of this paper to develop such a quantum-mechanical unified theory. Of the routes open we have chosen to fashion the theory in terms of quantities that can be calculated with modest effort: Fourier transforms of interatomic potential energy functions, sum rules involving the potentials and the atom-perturber pair distribution function, and impact-theory width and shift parameters which may be taken from fits of experimental data or calculated.

One of the major differences between this paper and others is in its systematic use of sum rules or spectral moment relations, primarily due to Kubo.[10–14] These are used to investigate the statistical theory, duration-of-collision effects, and in the synthesis of the expression for the total line shape.

The strong ties between atomic line broadening and other topics, especially molecular electronic spectra, are examined. It is felt that the lack of interplay between these fields in the past has unduly retarded the development of line-shape theory.

The model and the theory emphasized in this paper have been deliberately chosen as a compromise between the accuracy of the results expected and the computational complexity involved. Extensions are discussed which should give more accurate results with a concomitant increase in effort. All of these theories ultimately demand more refined experimental measurements of line shapes at low to moderate perturber-gas densities—measurements extending further into the line wings and taken over a wide range of temperatures.

Section II presents the model and shows that the calculation can be reduced to the study of a two-body expression including initial atom-pertuber correlations. Sections III–V show how the three effects, impact, duration-of-collision, and the statistical theory, arise from the basic expression. Section VI demonstrates the synthesis of the three features into a single dipole-moment correlation function and hence, through the Fourier transform, to a single line-shape expression. Discussion is kept to a minimum in Secs. II–VI to avoid interrupting the flow of the derivation. The full discussion appears in Sec. VII A. Section VII B examines a series of other topics, pointing out the useful connections that can be established between line-shape theory and these other areas, especially between atomic and molecular spectroscopy.

## II. BASIC FORMULATION

### A. Model and Absorption Coefficient

The physical system envisioned is a very dilute gas of $N_A$ atoms ($A$) emitting and absorbing radiation, mixed with a denser gas of $N$ distinct (foreign) perturber atoms ($P$) which are assumed structureless. The model is simple but we shall see that it retains the most important features of the real problem. Extensions to treat more general cases are discussed in Sec. VII.

Each atom is assumed to be stationary (infinitely massive) and the perturbers assumed independent of one another. This model is, in effect,[15] the one that has been used successfully in past studies of both the impact and statistical theories. The density of atoms is assumed low enough that the absorption of each atom can be treated independently.

The expression for the absorption coefficient[16] (in units of fractional absorption/cm) is then $N_A$ times that for a single atom in the volume $\mathcal{V}$, viz.,

$$A(\omega)=\tfrac{4}{3}\pi[1-e^{-\beta\hbar\omega}]\,\frac{N_A}{\mathcal{V}}\,\frac{\omega}{\hbar c}\int_{-\infty}^{\infty}e^{-i\omega t}\langle\vec{\mu}(0)\cdot\vec{\mu}(t)\rangle\,dt\quad. \tag{2.1}$$

The absorption coefficient is essentially the Fourier transform of the autocorrelation function $\Phi(t)$ of the dipole-moment (Heisenberg) operator $\vec{\mu}$ of the atom,

$$\Phi(t)\equiv\langle\vec{\mu}(0)\cdot\vec{\mu}(t)\rangle\quad, \tag{2.2}$$

with spectrum $S(\omega)$,

$$S(\omega)\equiv\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}\,\Phi(t)\,dt\quad. \tag{2.3}$$

In the above expressions $\mathcal{V}$ is the volume and $\beta\equiv 1/(kT)$. The thermal average for an arbitrary operator $\mathcal{O}$ is

$$\begin{aligned}\langle\mathcal{O}\rangle&\equiv\mathrm{Tr}(e^{-\beta H}\mathcal{O})/\mathrm{Tr}(e^{-\beta H})\\&\equiv Z^{-1}(\beta)\mathrm{Tr}(e^{-\beta H}\mathcal{O})\quad,\end{aligned} \tag{2.4}$$

where $H$ is the total Hamiltonian of the system $A$ and bath $P$, excluding the interaction with the radiation field. $Z(\beta)$ is the partition function.

The theory will be developed for a line corresponding to a transition between two nondegenerate levels of the atom, $l$ (lower) and $u$ (upper). The transition is assumed to be a "high-energy" one, i.e.,

$$\beta(E_u-E_l)\gg 1, \tag{2.5}$$

so that inelastic collisions coupling $l$ and $u$ are neglected. This approximation also applies to widely spaced vibrational levels in molecules. The Hamiltonian $H$ includes three types of terms: the free-atom term

$$H_A=E_u|u\rangle\langle u|+E_l|l\rangle\langle l|\quad, \tag{2.6}$$

which uses the projection operators $|\alpha\rangle\langle\alpha|$ for the atomic states, the free-perturber terms

$$H_{\mathrm{FP}}(n)=(-\hbar^2/2m)\nabla_n^{\,2}\,, \tag{2.7}$$

and the interaction terms

$$H_{\mathrm{AP}}(n)=V_u(r_n)|u\rangle\langle u|+V_l(r_n)|l\rangle\langle l|\quad, \tag{2.8}$$

where the potentials are assumed spherical, and $r_n$ measures the distance from the $n$th perturber to the center of the stationary atom. Other terms in $H$ are omitted according to previous assumptions: The fixed atom yields no atomic kinetic energy term, the high-energy transition leads to the omission of any off-diagonal inelastic terms involving $|u\rangle\langle l|$, and independent perturbers means the omission of perturber-perturber interactions $V_{\mathrm{PP}}$. Assuming the interactions $H_{\mathrm{AP}}$ are additive, the total Hamiltonian can be written using $H_P\equiv H_{\mathrm{FP}}+H_{\mathrm{AP}}$,

$$\begin{aligned}H&=H_A+H_P\\&=\sum_{\alpha=u,l}E_\alpha|\alpha\rangle\langle\alpha|+\left[\sum_{n=1}^{N}\left(\frac{-\hbar^2}{2m}\right)\nabla_n^{\,2}\right.\\&\quad\left.+\sum_{n=1}^{N}\sum_{\alpha=u,l}V_\alpha(r_n)|\alpha\rangle\langle\alpha|\right]\quad.\end{aligned} \tag{2.9}$$

Every term in $H$ is diagonal in the atomic-state subspace so that its eigenstates $|\Psi\rangle$ are products of atomic states $|\alpha\rangle$ and perturber states $|\psi_k;\alpha\rangle$ satisfying

$$[(-\hbar^2/2m)\nabla^2+V_\alpha(r)]|\psi_k;\alpha\rangle=E_{k;\alpha}|\psi_k;\alpha\rangle\quad. \tag{2.10}$$

The Boltzmann operator from Eq. (2.9) is

$$e^{-\beta H}=e^{-\beta H_A}\prod_{n=1}^{N}e^{-\beta H_{\mathrm{P}}(n)}\quad. \tag{2.11}$$

Although the Boltzmann operator is written as a product of Boltzmann factors for the atom and perturbers, the atom-perturber correlations induced by the interaction $V_\alpha(r)$ are included. This point is important because many past treatments have assumed that the factorization[17,18] meant an absence of all (initial time) correlations. The factorization in the presence of correlation persists in this theory because the atom's position, fixed at the origin, is not a dynamical variable. The final assumption made for the model is that the dipole-moment matrix element $\mu_{ul}$ is a scalar constant.[19]

### B. Time-Dependence, Sum Rules

The Liouville operator formalism[20,21] is used to handle time dependence, i.e.,

$$\mu(t)=e^{iLt}\,\mu(0)\quad. \tag{2.12}$$

The Liouville operator $L$ is defined by its action on an arbitrary operator $\mathcal{O}$ by the commutator relation

$$L\mathcal{O}\equiv[H,\mathcal{O}]\quad, \tag{2.13}$$

or equivalently by its action on the "basis vectors" $|a\rangle\langle b|$ of the Liouville space

$$L|a\rangle\langle b|=(E_a-E_b)|a\rangle\langle b|\quad. \tag{2.14}$$

(In this section and throughout the remainder of the paper we use frequency units $\hbar=1$.) In the usual notation in which $H$ is a matrix (two subscripts) $L$ is a tetradic (with four). Thus, $L$ is distributive but not associative over products of ordinary quantum-mechanical operators.

The autocorrelation function and its spectrum can now be written

$$\Phi(t)=\langle\mu(0)\,e^{iLt}\,\mu(0)\rangle \tag{2.15}$$

and

$$S(\omega)=\langle\mu\delta(L-\omega)\mu\rangle\quad. \tag{2.16}$$

A notable property of $S(\omega)$ is the set of sum rules or moment relations it generates. The $n$th moment is

$$M_n \equiv \int_{-\infty}^{\infty} d\omega\, \omega^n S(\omega) \tag{2.17}$$

or equivalently, from Eq. (2.16),

$$M_n = \langle \mu L^n \mu \rangle \quad . \tag{2.18}$$

These expressions for the $M_n$ are the quantum-mechanical sum rules[10-14] which, in this case, relate the spectral moments of the transverse electromagnetic susceptibility, Eq. (2.17), to time-independent thermal averages involving the dipole-moment operator and powers of the Liouville operator, Eq. (2.18).

In the time domain differentiation of $\Phi(t)$ in Eq. (2.15) yields

$$\frac{d^n}{dt^n}\Phi(t)\Big|_{t=0} = (i)^n M_n , \tag{2.19}$$

and hence the power-series expression

$$\Phi(t) = \sum_{n=1}^{\infty} \frac{(i)^n}{n!} M_n t^n \quad . \tag{2.20}$$

This relation is of critical importance to the theory developed in this paper. It expresses the time-dependent function $\Phi(t)$ in terms of the time-independent equilibrium averages $M_n$. These relations are discussed in detail in Sec. IV. One other formal relation which an approximate theory should attempt to satisfy should be noted, the principle of detailed balance[22] relating $S(\omega)$ to $S(-\omega)$.

### C. Reduction to Two-Body Form

The goal of this section is to show that the $N$-body expression for the autocorrelation function

$$\Phi(t) = \langle \mu\, e^{iLt}\, \mu \rangle \tag{2.21}$$

reduces exactly to a two-body expression in the thermodynamic limit:

$$\lim N, \mathcal{V} \to \infty, \quad \rho = N/\mathcal{V} = \text{const} \quad . \tag{2.22}$$

The autocorrelation function will be cast in the form

$$\Phi(t) \propto e^{i\omega_0 t} \exp\left(\rho \langle e^{iL_l t} - 1\rangle_l\right) \tag{2.23}$$

plus a similar term for $-\omega_0$. The utility of this result lies in the fact that $L_l$ is a two-body operator only (one perturber and the atom) and that the thermal average $\langle\cdots\rangle_l$ is taken over the two-body subspace.

The detailed form of $L$ from Eq. (2.9) is

$$L\mathcal{O} = [H_A, \mathcal{O}] + \sum_{n=1}^{N} [H_{\text{FP}}(n) + H_{\text{AP}}(n), \mathcal{O}] \quad . \tag{2.24}$$

The general eigenstate $|\Psi\rangle$ of $H$ has the product form

$$|\Psi_a\rangle = |\psi; a\rangle\, |a\rangle \quad , \tag{2.25}$$

where $|\psi; a\rangle$ is a product state over all perturbers, with the atomic state $a = u$ or $l$ as a parameter and $|a\rangle$ is the atomic state.

The action of $L$ on an arbitrary operator gives one of two results of interest for our case,

$$L|\Psi_a\rangle\langle\Psi_b| = (E_a - E_b + L_b)|\Psi_a\rangle\langle\Psi_b| \quad , \tag{2.26}$$

where

$$L_a\mathcal{O} = \sum_{n=1}^{N} [H_b(n)\mathcal{O} - \mathcal{O}H_a(n)] \quad , \tag{2.27}$$

and the single-perturber Hamiltonian is

$$H_a(n) = -(\nabla_n^2/2m) + V_a(r_n) \quad , \tag{2.28}$$

where the index sets above are $\{a, b\} = \{u, l\}$ or $\{l, u\}$.

The correlation function from Eq. (2.21) is

$$\Phi(t) = Z^{-1}(\beta) \sum_{\Psi_a, \Psi'_{a'}} [\langle\Psi_a| e^{-\beta H} |\Psi_a\rangle \times \langle\Psi_a|\mu|\Psi'_{a'}\rangle\langle\Psi'_{a'}| e^{iLt}\mu|\Psi_a\rangle] \quad . \tag{2.29}$$

The dipole-moment operator $\mu$ has only one matrix element $\mu_{ul} = \mu^*_{lu}$ which is assumed independent of $r$. With this assumption made $\Phi(t)$ can be written in the following form (see the Appendix):

$$\Phi(t) = [1 + e^{-\beta\omega_0}]^{-1} |\mu_{ul}|^2 e^{i\omega_0 t} \exp[\rho\langle e^{iL_l t} - 1\rangle_l] + e^{-\beta\omega_0}[1 + e^{-\beta\omega_0}]^{-1} |\mu_{ul}|^2 \times e^{-i\omega_0 t} \exp[\rho\langle e^{iL_u t} - 1\rangle_u] \quad . \tag{2.30}$$

*Equation* (2.30) *is the basic result of this section.* In this expression the operators $L_a$ and the thermal averages $\langle\cdots\rangle_a$, $a = u$, $l$ contain only the interaction of the atom with a single perturber.

The primary difference between our expression and similar ones that have been derived in the past[23] is the explicit inclusion of the proper thermal factors in the averages. These include the initial-state correlations which will be important throughout the analysis. Many further differences from past treatments will arise because of the manner in which Eq. (2.30) is evaluated.

## III. IMPACT APPROXIMATION

The impact approximation arises when the long-time behavior of $\Phi(t)$ is considered. We will see that "long time" means long compared to the duration of a typical collision. The impact approximation has been derived numerous times[4-6,17,18] so it will not be fully rederived here. A derivation in the time-dependent Liouville formulation[24,25] will be sketched and some conclusions drawn.

The nontrivial part of the basic expression for the correlation function from Eq. (2.30) is

$$\langle e^{iL_l t} - 1\rangle_l = i\int_0^t \langle L_l\, e^{iL_l s}\rangle_l\, ds \quad . \tag{3.1}$$

For simplicity, imagine the case in which the lower-state potential $V_l$ vanishes.[4] A typical matrix element of Eq. (3.1) neglecting the Boltzmann factor is

$$\langle \vec{k}|H_u e^{iH_u s} e^{-iH_l s}|\vec{k}\rangle - \langle \vec{k}|e^{iH_u s} e^{-iH_l s} H_l|\vec{k}\rangle \ . \tag{3.2}$$

Since $V_l$ vanishes this reduces to

$$\langle \vec{k}|V_u e^{iH_u s} e^{-iH_l s}|\vec{k}\rangle \ . \tag{3.3}$$

For large $s$ and noting $V_l = 0$, scattering theory gives[26,27]

$$\lim_{s\to\infty} e^{iH_u s} e^{-iH_l s} = \Omega^{(-)} \ , \tag{3.4}$$

where $\Omega^{(-)}$ is the wave operator for scattering by $V_u$. The result is

$$\langle \vec{k}|V_u \Omega^{(-)}|\vec{k}\rangle = \langle \vec{k}|T|\vec{k}\rangle^* \ , \tag{3.5}$$

where we have introduced the $T$ matrix. From Eq. (3.5) we conclude that the integrand of Eq. (3.1) approaches a constant for large $s$; the integral becomes proportional to $t$.

With thermal averaging and the transition frequency $\omega_0$ reinserted we get

$$\Phi(t) = \exp(i\omega_0 t + i\rho\,\mathrm{Re}\langle T\rangle_l t + \rho\,\mathrm{Im}\langle T\rangle_l |t|) \ . \tag{3.6}$$

The imaginary part of $T$ and the total cross section $\sigma_u$ are related by the optical theorem[26]

$$\mathrm{Im}\langle T\rangle_l = -\tfrac{1}{2}\langle v\sigma_u\rangle_l \ , \tag{3.7}$$

where $v$ is the velocity. The correlation function in Eq. (3.6) gives a Lorentzian line shape with width $w$ and shift $d$,

$$w = \rho\,\mathrm{Im}\langle T\rangle_l \ , \tag{3.8}$$

$$d = \rho\,\mathrm{Re}\langle T\rangle_l \ . \tag{3.9}$$

In the more general case when $V_l$ is not assumed to vanish, $\langle T\rangle_l$ is replaced by

$$i\langle 1 - S_l S_u^{-1}\rangle_l \ , \tag{3.10}$$

containing the $S$ matrices for elastic scattering in both the upper *and* lower states.

The validity conditions for the impact approximation have been frequently discussed. The correlation function in Eq. (3.6) is valid only for times substantially longer than $\tau_c$, the duration of collision. The spectrum given by the impact approximation will then certainly fail at distances $\Delta\omega$ from the line position $\omega_0$ greater than

$$|\Delta\omega| = O(\tau_c^{-1}) \approx v/D \ , \tag{3.11}$$

where $v$ is a typical velocity and $D$ an atomic size. A lower limit for $D$ is the de Broglie wavelength $\lambda$ which gives

$$\hbar|\Delta\omega| = O(kT) \ . \tag{3.12}$$

A typical numerical value, e.g., for Cs-Ar is $|\Delta\omega| = O(100\ \mathrm{cm}^{-1})$. The conditions above show that the impact theory breaks down at any density far enough in the wings. There is another obvious restriction: $w$ in Eq. (3.8) cannot violate the condition of Eq. (3.11). This gives a restriction on the perturber-gas density,

$$\rho = N/\mathcal{V} < O(D^{-3}) \ . \tag{3.13}$$

We conclude that the impact theory is restricted to a certain interval $\Delta\omega$ around the unperturbed line and is useful only when the perturber-gas density is low. In the time domain, the key to going beyond the impact approximation lies in a careful study of the short-time behavior of $\Phi(t)$. This is taken up in Sec. IV.

## IV. SUM RULES: DURATION-OF-COLLISION EFFECTS

In dealing with a high-energy transition, the interest is in the spectrum in the vicinity of the line at $+\omega_0$ so the negative-frequency term in Eq. (2.30) will be neglected. The nontrivial part of the positive-frequency term is extracted from Eq. (2.30) and written as

$$\phi_+(t) \equiv \exp[\rho\langle e^{iL_l t} - 1\rangle_l] \ , \tag{4.1}$$

with spectrum

$$s_+(\omega) \equiv \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\phi_+(t) \ . \tag{4.2}$$

The information missing from the impact approximation is the detailed behavior of $\phi_+(t)$ for short times. In Sec. II, we saw that the short-time behavior of a correlation function, its power-series expansion, can be studied in terms of sum rules. These will be developed below.

We will work with $\phi(t)$ defined by

$$\phi(t) \equiv \langle e^{iL_l t} - 1\rangle_l \ . \tag{4.3}$$

Since the thermal average in Eq. (4.3) involves $e^{-\beta H_l}$, it is useful to write $L_l$ in terms of $H_l$ itself from Eq. (2.27),

$$L_l\mathcal{O} = H_u\mathcal{O} - \mathcal{O}H_l = [H_l, \mathcal{O}] + \Delta V\mathcal{O} \ . \tag{4.4}$$

The difference potential $\Delta V$ is

$$\Delta V(r) \equiv V_u(r) - V_l(r) \ . \tag{4.5}$$

There is a straightforward set of relations between the derivatives of $\phi_+(t)$, which are the moments of interest, and the derivatives of $\phi(t)$, which are directly computable. The two sets of moments $\mu_{n+}$ and $\mu_n$ are defined as

$$\mu_{n+} \equiv (-i)^n \frac{d^n}{dt^n}\phi_+(t)\Big|_{t=0} \tag{4.6}$$

and

$$\mu_n = (-i)^n \frac{d^n}{dt^n}\phi(t)\Big|_{t=0} \ . \tag{4.7}$$

The relations for the first few moments are

$$\mu_{0+}=1 \quad , \tag{4.8a}$$

$$\mu_{1+}=\rho\mu_1 \quad , \tag{4.8b}$$

$$\mu_{2+}=\rho^2\mu_1^2+\rho\mu_2 \quad , \tag{4.8c}$$

$$\mu_{3+}=\rho^3\mu_1^3+3\rho^2\mu_2\mu_1+\rho\mu_3 \quad . \tag{4.8d}$$

The general relation of the $\mu_{n+}$ to the $\mu_n$ is exactly that between the moments of a distribution and the Thiele semi-invariants[12,28] of the distribution.

The problem is now reduced to calculating the moments $\mu_n$ of the function $\phi(t)$. To use $L_l$ efficiently, note the simple relation

$$\langle[H_l,\mathcal{O}]\rangle_l=0 \tag{4.9}$$

for $\mathcal{O}$ arbitrary. This follows from

$$\langle[H_l,\mathcal{O}]\rangle_l \propto \mathrm{Tr}\{e^{-\beta H_l}[H_l,\mathcal{O}]\}=\mathrm{Tr}\{[e^{-\beta H_l},H_l]\mathcal{O}\}=0 \quad . \tag{4.10}$$

The first few moments are

$$\mu_0=0 \quad , \tag{4.11a}$$

$$\mu_1=\langle\Delta V\rangle_l \quad , \tag{4.11b}$$

$$\mu_2=\langle(\Delta V)^2\rangle_l \quad , \tag{4.11c}$$

$$\mu_3=\langle(\Delta V)^3\rangle_l+\langle\Delta V[H_l,\Delta V]\rangle_l \quad . \tag{4.11d}$$

The moments $\mu_{n+}$ are

$$\mu_{0+}=1 \quad , \tag{4.12a}$$

$$\mu_{1+}=\rho\langle\Delta V\rangle_l \quad , \tag{4.12b}$$

$$\mu_{2+}=\rho^2(\langle\Delta V\rangle_l)^2+\rho\langle(\Delta V)^2\rangle_l \quad , \tag{4.12c}$$

$$\mu_{3+}=\rho^3(\langle\Delta V\rangle_l)^3+3\rho^2\langle(\Delta V)^2\rangle_l\langle\Delta V\rangle_l +\rho\{\langle(\Delta V)^3\rangle_l+\langle\Delta V[H_l,\Delta V]\rangle_l\} \quad . \tag{4.12d}$$

One of the salient features of these expressions is that the Hamiltonian $H_l$ does not appear until the third-order term $\mu_{3+}$ or $\mu_3$. The first and second moments contain *only* the difference potential $\Delta V$.

Each of the $\mu_n$ expressions can be further reduced to a form involving the quantum-mechanical radial distribution function $g_l(r)$ defined such that[29,30]

$$\langle\mathcal{O}(r)\rangle \equiv 4\pi\int_0^\infty dr\, r^2 g_l(r)\mathcal{O}(r) \quad . \tag{4.13}$$

In the classical limit $g_l(r)$ has the simple form

$$g_l(r)\rightarrow e^{-\beta V_l(r)} \quad . \tag{4.14}$$

The first and second moments in terms of $g_l(r)$ are

$$\mu_1=4\pi\int_0^\infty dr\, r^2 g_l(r)\Delta V(r) \quad , \tag{4.15}$$

$$\mu_2=4\pi\int_0^\infty dr\, r^2 g_l(r)[\Delta V(r)]^2 \quad . \tag{4.16}$$

The third moment involves $H_l$ and reduces to

$$\mu_3=4\pi\int_0^\infty dr\, r^2 g_l(r)[\Delta V(r)]^3+(2\pi/m)\int_0^\infty dr\, r^2 g_l(r) \times\{(2/r)\Delta V(r)\Delta V'(r)-[\Delta V'(r)]^2\} \quad , \tag{4.17}$$

where the prime denotes differentiation with respect to the scalar $r$. *The second integral in Eq.* (4.17) *represents in explicit calculable form the duration-of-collision contribution to the line shape through the spectral moments of order three.* To explain the role of the duration of collision $\tau_c$ the magnitudes of the two terms in Eq. (4.17) can be estimated. The two terms can be written in a manner which exhibits the duration of collision explicitly. The first term, the "pure potential term," in Eq. (4.17) is written as

$$4\pi v(\Delta E/\hbar)^3 \quad , \tag{4.18}$$

where $v$ is a characteristic atomic volume and $\Delta E$ a characteristic interaction energy ($\hbar$ explicitly included). The second term in Eq. (4.17) is written

$$(2\pi v/m)(\Delta E^2/\hbar D^2) \, , \tag{4.19}$$

where $D$ is a characteristic length associated with the potentials $V_l$ and $\Delta V$. This second term can be rewritten

$$2\pi v(\Delta E/\hbar)(\beta\Delta E/\tau_c^2) \, , \tag{4.20}$$

where $\tau_c$ is the duration of collision.

There are thus two contirubtions to $\mu_3$, the first related to $\Delta V$ alone, and the second depending on the duration of collision $\tau_c$, or equivalently, on the mass $m$. The $\tau_c$-dependent term becomes small as the collisions become slow ($\tau_c\rightarrow\infty$) or as the mass becomes large. Intuitively, the $\tau_c$-dependent term represents a *dynamical modulation effect* in which the motion of the perturber alters the contribution of $\Delta V$ to the line shape. For the higher-order moments, similar conclusions follow. There will be terms dependent on $\Delta V$ alone and terms depending on various powers of $m^{-1}$ or $\tau_c^{-2}$ which represent dynamical or duration-of-collision effects.

## V. STATISTICAL APPROXIMATION

At the end of Sec. IV, we saw that if the perturber motion was eliminated by letting $\tau_c\rightarrow\infty$, or better, $m\rightarrow\infty$, then terms containing *only* $\Delta V$ and no others remained in the spectral moments. This we call the statistical limit or, loosely, the statistical approximation.[31]

In the statistical approximation,

$$L_l\mathcal{O}\rightarrow V_u\mathcal{O}-\mathcal{O}V_l \quad , \tag{5.1}$$

and when working in the $r$ representation, $\Delta V$ is simply the scalar function $\Delta V(r)$. The nontrivial part of the correlation function becomes

$$\phi_+(t) = \exp[\rho\langle e^{i\Delta Vt} - 1\rangle_l] \quad . \tag{5.2}$$

Equation (5.2) is an expression of the statistical theory of Holtsmark, Kuhn, and Margenau, but containing the proper statistical weight factors through the average $\langle\cdots\rangle_l$. Omission of these weight factors in the past has caused some difficulties (see Sec. VII).

The $\phi(t)$ function, cf. Eq. (4.3), and its spectrum are particularly simple,

$$\phi(t) = \langle e^{i\Delta Vt} - 1\rangle_l \tag{5.3}$$

and

$$s(\omega) = 2\pi\langle\delta(\omega - \Delta V)\rangle_l \quad . \tag{5.4}$$

Written in terms of the radial distribution function,

$$s(\omega) = 8\pi^2 \int_0^\infty dr\, r^2 g_l(r)\delta[\omega - \Delta V(r)] \quad . \tag{5.5}$$

This spectrum is strictly related to the statistical or static distribution of the perturber around the atom, hence the name. The functions $\phi(t)$ and $s(\omega)$ describe the spectrum that arises from a single perturber. Subsequent exponentiation of $\phi(t)$ to give $\phi_+(t)$ merely combines the contributions of the $N$ perturbers independently.

From Eq. (5.5) it is apparent that the spectrum at frequency $\omega$ produced by a single perturber arises from points at which $\Delta V(r) = \omega$ with an additional weighting factor $r^2 g_l(r)$ giving the (initial state $l$) probability that the perturber is in the unit spherical shell at $r$. The expression of Eq. (5.5) is equivalent to the use of the Franck-Condon principle of molecular spectroscopy, cf. Sec. VII.

A simple nontrivial case for which $\phi(t)$ and $s(\omega)$ can be calculated analytically is the square well with a repulsive core

$$\begin{aligned} &V_l(r) = \Delta V = +\infty \ , && 0 \le r < \sigma \\ &V_l(r) = -\epsilon_l \ , \quad \Delta V(r) = -\epsilon_\Delta \ , && \sigma \le r < a \\ &V_l(r) = \Delta V(r) = 0 \ , && a \le r \quad . \end{aligned} \tag{5.6}$$

The resultant correlation function is

$$\begin{aligned} \phi(t) &= \tfrac{4}{3}\pi(a^3 - \sigma^3)\, e^{\beta\epsilon_l}\,(e^{-i\epsilon_\Delta t} - 1) \\ &= \alpha(e^{-i\epsilon_\Delta t} - 1) \ , \end{aligned} \tag{5.7}$$

where $\alpha$ absorbs the additional factors. In Eq. (5.7) the perturber contributes a factor of $e^{-i\epsilon_\Delta t} - 1$ when it lies between $r = \sigma$ and $r = a$ and contributes nothing otherwise. The correlation function $\phi_+(t)$ can be expanded in a power series in the density,

$$\begin{aligned} \phi_+(t) &= e^{-\rho\alpha} \sum_{k=0}^{\infty} \frac{(\rho\alpha)^k e^{-ik\epsilon_\Delta t}}{k!} \\ &= e^{-\rho\alpha}\left(1 + \rho\alpha\, e^{-i\epsilon_\Delta t} + \frac{\rho^2\alpha^2}{2!}\, e^{-2i\epsilon_\Delta t} + \cdots\right) \quad . \end{aligned} \tag{5.8}$$

The full spectrum with $\omega_0$ included is

$$\begin{aligned} S_+(\omega) = 2\pi\, e^{-\rho\alpha}\{&\delta(\omega - \omega_0) + \rho\alpha\delta[\omega - (\omega_0 - \epsilon_\Delta)] \\ &+ (\rho^2\alpha^2/2!)\delta[\omega - (\omega_0 - 2\epsilon_\Delta)] + \cdots\} \quad . \end{aligned} \tag{5.9}$$

The spectrum $S_+(\omega)$ consists of a central or unshifted component and a series of "red satellites" at frequencies $\omega_0 - \epsilon_\Delta$, $\omega_0 - 2\epsilon_\Delta$, etc. In the dilute-gas case $\rho\alpha \ll 1$, leaving a strong central component and a series of satellites of rapidly decreasing strength.

In the more general case of a finite-range potential such that $\Delta V(r) = 0$ for $r > a$, it is instructive to expand $\phi_+(t)$ in powers of the reduced density $\rho a^3$ which is small in a sufficiently dilute gas. From Eq. (5.3),

$$\begin{aligned} \phi(t) &= 4\pi \int_0^a dr\, r^2 g_l(r)\, e^{i\Delta V(r)t} - 4\pi \int_0^a dr\, r_l^2(r) \\ &\equiv [\phi_a(t) - c] \ , \end{aligned} \tag{5.10}$$

where $\phi_a(t)$ and $c$ are of order $a^3$. The full correlation function is then

$$\phi_+(t) = e^{-\rho c}[1 + \rho\phi_a(t) + (\rho^2/2!)\phi_a^2(t) + \cdots] \quad . \tag{5.11}$$

The spectrum can be obtained by repeated convolution of the spectrum $s_a(\omega)$ of $\phi_a(t)$. This gives

$$\begin{aligned} S_+(\omega) = e^{-\rho c}[&\delta(\omega - \omega_0) + \rho s_a\big|_{\omega-\omega_0} \\ &+ (\rho^2/2!) s_a \star s_a\big|_{\omega-\omega_0} + \cdots] \quad . \end{aligned} \tag{5.12}$$

Here convolution is defined in the conventional manner,

$$F \star G \equiv \int_{-\infty}^{\infty} d\omega'\, F(\omega - \omega')G(\omega') \quad . \tag{5.13}$$

Each term in the expansion in Eq. (5.12) has a simple interpretation. The undisplaced term (with probability $e^{-\rho c}$) arises from all states in the ensemble for which no perturber lies within the sphere $r < a$. The second term (with probability $\rho e^{-\rho c}$) accounts for all states in the ensemble for which exactly one perturber lies within the sphere $r < a$ and gives rise to the one-perturber spectrum $s_a(\omega - \omega_0)$. The third term [with probability $(\rho^2/2!)e^{-\rho c}$] arises from having two perturbers within the sphere. The spectrum for this third term is produced by considering all possible contributions of the pair of perturbers independently and therefore leads to a convolution of the two single-perturber spectra. Higher-order terms can be interpreted similarly.

An important phenomena in the statistical theory arises in the case in which $\Delta V(r)$ has a relative minimum or maximum at some point. We will see that in the region of such a potential extremum, $s(\omega)$ has a singular behavior which will be interpreted as a "satellite."

To understand the phenomenon in a qualitative way, let us restrict attention to low densities and the single-perturber spectrum $s(\omega)$. Let $\Delta V(r)$ as an example have a minimum $-\epsilon_\Delta$ at the radius $r=r_m$. In the neighborhood of $r_m$, $\Delta V(r)$ can be expanded,

$$\Delta V(r)=-\epsilon_\Delta+\tfrac{1}{2}\Delta V''(r_m)(r-r_m)^2+\cdots \quad . \tag{5.14}$$

The spectrum in this region can similarly be approximated, cf. Eq. (5.4),

$$s(\omega)=8\pi^2 r_m^2 g_l(r_m) \times\int_0^\infty dr\, \delta[\omega+\epsilon_\Delta-\tfrac{1}{2}\Delta V''(r_m)(r-r_m)^2+\cdots] \quad . \tag{5.15}$$

Therefore,

$$s(\omega)=0 \quad \text{for} \quad \omega<-\epsilon_\Delta \tag{5.16}$$

and

$$s(\omega)\approx\frac{8\pi^2 r_m^2 g_l(r_m)}{[2\Delta V''(r_m)]^{1/2}}\;\frac{1}{(\omega+\epsilon_\Delta)^{1/2}} \quad \text{for} \quad \omega\geq-\epsilon_\Delta \quad . \tag{5.17}$$

Thus, $s(\omega)$ has a singularity in the "red" wing at $\omega=-\epsilon_\Delta$ and vanishes further out in the red wing. The singularity is integrable, as it must be. This we interpret as a red satellite band. Higher-order convolutions of this singular one-perturber spectrum give "images" of the singular point at frequencies $-2\epsilon_\Delta$, $-3\epsilon_\Delta$, etc. At low densities, the high-order images are quite weak.

Using Eq. (5.4) it is also quite simple to derive the famous "$\omega^{-3/2}$ law" of Kuhn and Margenau when $\Delta V(r)\sim\epsilon_\Delta(\sigma/r)^6$. This law was predicted and measured at the inception of the statistical theory. The relation is the more important in that it contains, in a simple way, the van der Waals coefficient $\epsilon_\Delta$, the difference between the van der Waals coefficients $\epsilon_u$ and $\epsilon_l$ for the two states.

## VI. TOTAL LINE SHAPE

The major ingredients of a unified theory have been discussed earlier in this paper. They allow a mixed development of the theory with a minimum of calculation. If upper- and lower-state potentials are assumed, then the full statistical line shape can be calculated. A limited number of moments involving the duration-of-collision effects can also be calculated rather easily. The shift and width parameters can also be calculated or can be fitted from experimental observations at low densities.

The particular approach employed in this section is a simple one. Many variants can be devised which may ultimately be superior in actual applications. Some are discussed in Sec. VII. One particular technique for constructing a unified theory has been chosen for expository purposes.

### A. Synthesis of the Correlation Function

The absorption spectrum can be calculated from the Fourier transform of the correlation function, viz.,

$$s_+(\omega)=\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\, e^{\rho\Phi(t)} \quad , \tag{6.1}$$

cf. Sec. IV. In Secs. IV and V, we have seen that $\phi(t)$ can be broken down effectively into two parts, which will be called $\phi_S(t)$, the statistical component, and $\phi_D(t)$, the dynamical component,

$$\phi(t)\equiv\phi_S(t)+\phi_D(t) \quad . \tag{6.2}$$

$\phi_S(t)$ contains only the statistical-theory terms; it has been discussed as the statistical approximation of Sec. V. $\phi_D(t)$ is defined to contain all other terms in $\phi(t)$. Thus $\phi_D(t)$ contains the duration-of-collision terms and also includes the long-time effects which give rise to the impact approximation.

The statistical term $\phi_S(t)$ can be calculated quite straightforwardly, given $V_l(r)$ and $V_u(r)$. An efficient method of doing this is to calculate $s(\omega)$ on a discrete mesh $\{\omega_i\}$ from the expression of Eq. (5.5), then Fourier transform the result to obtain $\phi_S(t)$. This approach can be orders of magnitude faster than evaluating Eq. (5.3) directly by $r$ integration.[32]

The dynamical function $\phi_D(t)$ is difficult to calculate directly. Information is available, however, about both the short-time and long-time behavior of $\phi_D(t)$. For short times, a limited number of terms in the power-series expansion of $\phi_D(t)$ can be calculated through the sum-rule relations, with the number limited by the algebraic complexity of the expressions for the high-order sum rules. In Sec. IV, Eq. (4.11) we saw that each sum rule contained both terms with $\Delta V$ alone, and terms involving dynamical effects through $H_l$. Writing $\phi(t)$ as a sum, the derivatives, Eq. (4.7) can be grouped in a parallel way,

$$\begin{aligned}\mu_n&=(-i)^n\frac{d^n}{dt^n}\,\phi(t)\big|_{t=0}\\&=(-i)^n\frac{d^n}{dt^n}\,[\phi_S(t)+\phi_D(t)]\big|_{t=0}\equiv\mu_{nS}+\mu_{nD} \quad .\end{aligned} \tag{6.3}$$

This implies the power-series expansion

$$\phi_S(t)+\phi_D(t)=\sum_{n=1}^{\infty}\frac{(it)^n}{n!}\,(\mu_{nS}+\mu_{nD}) \quad . \tag{6.4}$$

As a practical matter, we will assume that a limited number of the $\mu_{nD}$ in Eq. (6.4) are known. From Eq. (4.11) it follows that $\mu_{1D}=\mu_{2D}=0$. An explicit expression for $\mu_{3D}$ as part of Eq. (4.17) has been given. The long-time behavior of $\phi_D(t)$ has been studied in Sec. III and found to be linear in $t$.

Let us then assume that some knowledge of the short- and long-time behavior of $\phi_D(t)$ is available. The task is then to synthesize an approximation to

$\phi_D(t)$ which has the correct power-series expansion around $t=0$ and has long-time behavior which is linear in $t$. One simple way to do this is to use the (two-point) Padé approximant.[33,34] A function $f(t)$ is approximated in the form

$$f(t)=P_j(t)/Q_k(t) \quad . \tag{6.5}$$

The ratio of the $j$th-order polynomial $P_j(t)$ to the $k$th-order polynomial $Q_k(t)$ is the $(k, j)$ Padé approximant of $f(t)$ when the power-series expansions around $t=0$ of both sides of Eq. (6.5) are identical to terms of order $t^{j+k+1}$. (By convention, the leading term in $Q_k$ is unity.) This is a normal (one-point) Padé, with the point chosen at $t=0$. A two-point form, using $t=0$ and $\infty$, will be utilized to establish the proper behavior of the correlation function. As $t\rightarrow\infty$, the approximant must become linear in $t$. This requires $j=k+1$.

The situation is actually more involved than this. The real and imaginary parts of $\phi_D(t)$ must be even and odd, respectively, because the spectrum is real, and both must be linear in $t$ for large $t$. Therefore set

$$\mathrm{Re}\phi_D(t)=-[P_{m+1}(t^2)/Q_m(t^2)]^{1/2} \tag{6.6}$$

and

$$\mathrm{Im}\phi_D(t)=R_{n+1}(t)/S_n(t) \quad . \tag{6.7}$$

Further, require that $P/Q$ be real and positive for positive arguments, $R$ be real and odd, $S_n(t)$ be real, positive, and even, and the positive square root be taken in Eq. (6.6). As a simple example of the above forms, the approximation

$$\phi_D(t)\approx-\left(\frac{p_8t^8}{1+q_6t^6}\right)^{1/2}+\frac{ir_3t^3}{1+s_2t^2} \tag{6.8}$$

can be chosen. The initial behavior of $\phi_D(t)$ is then

$$\phi_D(t)=ir_3t^3-p_8^{1/2}t^4+O(t^5) \quad , \tag{6.9}$$

and the long-time behavior is

$$\Phi_D(t)\sim-(p_8/q_6)|t|+i(r_3/s_2)t+O(t^{-1}) \quad . \tag{6.10}$$

Fixing the four unknowns in Eq. (6.8) requires values of the sum rules $\mu_{3D}$, $\mu_{4D}$ and the linewidth and shift from the impact approximation (the Lorentzian line-shape parameters).

### B. Unified Line-Shape Expression

The complete expression for the unified line-shape spectrum $S_{\mathrm{ULS}}(\omega)$ can now be written out using the above ingredients,

$$S_{\mathrm{ULS}}(\omega)=1/2\pi\int_{-\infty}^{\infty}dt\, e^{i(\omega_0-\omega)t}\, e^{\rho\phi_S(t)+\rho\phi_D(t)} \quad , \tag{6.11a}$$

where

$$\phi_D(t)=-[P_{m+1}(t^2)/Q_m(t^2)]^{1/2}+iR_{n+1}(t)/S_n(t) \quad . \tag{6.11b}$$

The major feature which distinguishes this general line-shape expression from the many others that have been written down from time to time is that detailed prescriptions have been presented throughout the paper to numerically calculate or otherwise estimate the various functions involved, $\phi_S$, $P$, $Q$, $R$, and $S_n(t)$ with only a modest amount of effort. This has been the goal: to construct a theory that is rather general but also allows easy calculations.

Although the spectra corresponding to the approximate correlation functions cannot be evaluated in closed form, there are a number of general conclusions that can be drawn. First, note that the total spectrum can be obtained as a convolution of two separate spectra called $s_{+S}$ and $s_{+D}$, in the following way:

$$s_+(\omega)=s_{+S}\star s_{+D} \quad , \tag{6.12}$$

where

$$s_{+A}\equiv\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\, e^{\rho\phi_A(t)}, \quad A=S, D \quad . \tag{6.13}$$

The moments $\mu_{n,+}$ of $s_+(\omega)$ are related to the moments $\mu_{n,+S}$ of $s_{+S}$ and $\mu_{n,+D}$ of $s_{+D}$ in a simple way,

$$\mu_{n+}=\sum_{l=0}^{n}\binom{n}{l}\mu_{n-l,+D}\,\mu_{l,+S} \quad . \tag{6.14}$$

The higher-order moments are determined, intuitively, by the far wings of the line, although this is by no means a rigorous relationship. If the statistical moments are generally much larger than the dynamical moments of the same order, then one can say, approximately, that the line wings are determined by the statistical terms. This would imply the "wing theorem"[35] discussed in the past, which says that the far wings of the line are given correctly by the statistical theory alone, by the spectrum $s_{+S}(\omega)$. A comparison of Eqs. (4.18) and (4.20) indicates, for example, that the ratio of the dynamical to the statistical moments of order 3 is of order of magnitude $(\lambda/D)^2$, where $\lambda$ is the de Broglie wavelength and $D$ a characteristic length associated with the potential. For most atomic cases, high-energy transitions, the ratio will be small, of the order of a few percent for heavy atoms and heavy perturbers.

One might be tempted to devise simpler theories which merely attempt to convolute a Lorentzian with the statistical spectrum. This could lead to gross errors in the wings, since the wings might be dominated by the Lorentzian line shape. (This can be appreciated by noting that all of the moments, excluding only the zeroth, diverge for the Lorentzian shape and cause the moments of the line to diverge.) A refinement of such a simple idea might attempt to convolute the statistical shape with a spectrum which is Lorentzian near the center but falls off rapidly in the wings due to the construction of its correlation function which possesses finite derivatives at $t=0$. This would still be in conflict with the rigorous results by the following argument: The dynamical correlation function developed in this paper is of the form

$$\phi_{+D}(t) = e^{\rho\Phi_D(t)} \quad , \tag{6.15}$$

with

$$\phi_{+D}(t) = 1 + iat^3 + bt^4 + O(t^5) \quad . \tag{6.16}$$

It follows that the zeroth, third, fourth, and higher moments of $s_{+D}(\omega)$ exist, while the first and second moments vanish. This implies that the dynamical spectrum $s_{+D}(\omega)$ cannot be everywhere positive. To obtain the proper total line shape, the statistical spectrum must be convoluted with a dynamical spectrum which is not everywhere positive! This is not what intuition would have suggested.

The total correlation function in Eq. (6.11) will approach, at sufficiently low densities, a form

$$e^{iat-b|t|} \quad , \tag{6.17}$$

in the sense that, for most $t$,

$$|e^{iat-b|t|} - \phi_+(t)| / |\phi_+(t)| \to 0 \quad . \tag{6.18}$$

The Fourier transform of the unified-theory correlation function should therefore approach the Lorentzian shape. Of course at any density, sufficiently far in the wings, the Lorentzian shape will not be valid, as was pointed out in Sec. III. This can be seen as well from the fact that all of the moments of the true line shape exist at any density; in fact, the moments of the line decrease with decreasing density. The higher moments of the Lorentzian line shape diverge at any density, as already mentioned. That all the moments exist for the true line shape can be seen by considering their general form (cf. Sec. IV). The integrals giving rise to the moments converge at small $r$ due to the Boltzmann factor cutoff in $g(r)$. At large $r$ the integrals converge because the potentials generally behave like $r^{-n}$ in that region, and products and derivatives of the potentials will fall off even more rapidly.

The unified line-shape expression has been constructed, Eq. (6.11), and some of its features examined. A general discussion of the entire derivation and related topics is given in Sec. VII.

## VII. DISCUSSION

### A. Derivation of the Theory

The history of line-shape theory and experiment is extensive but will not be reviewed here.[36–40] The development of sum-rule techniques is more recent.[10–14,41]

In Sec. II the basic expression [Eq. (2.1)] for the absorption coefficient was stated in terms of the autocorrelation function of the dipole-moment operator $\vec{\mu}$. This relation expresses the dissipative property (absorption) in terms of the fluctuations of a corresponding microscopic variable.[11,13] The absorption is related by simple factors to the imaginary part of the frequency and wavenumber-dependent susceptibility tensor $\overleftrightarrow{\chi}(\vec{k},\omega)$. We have omitted the $k$ dependence and tensorial character of $\overleftrightarrow{\chi}$ for simplicity. Neither of these omissions are important or particularly relevant to our model problem.[42,43]

By assuming that the absorbing atom is stationary, consideration of two other effects is circumvented, viz., Doppler effects and recoil effects. Both of these effects can be estimated by studying two limiting cases and we will see that they only affect seriously a narrow region around the center of the line.

In the first limiting case we assume that the atom's mass is large compared to the perturber mass. To a good approximation the atoms translate uniformly with a Boltzmann distribution of velocity, and each perturber collision with the atom is essentially an independent event. This gives a Doppler broadening $\Delta\nu$ of the lines, e.g., for Cs at room temperature,[44] $\Delta\nu \approx 0.02$ cm$^{-1}$, a negligible effect. This heavy-atom case is essentially the one we have considered.

The other limiting case is when the atom mass is small compared to the perturber mass, and a "recoil" effect occurs. At each collision the atom exchanges very little energy with the perturber so it undergoes long "chains" of collisions, each with essentially the same energy. The momentum vector is reoriented at each collision but its magnitude is little changed. Each atom in the ensemble gives its own contribution to the line shape $S(\omega;E)$ which is a function of its (essentially constant) energy.

The total line shape is obtained by averaging

$$S(\omega) = \int_0^\infty dE\, \rho(E)\, e^{-\beta E} S(\omega;E) \quad , \tag{7.1}$$

where $\rho(E)$ is the density of states. The theory appropriate to this limiting case would be a "semimicrocanonical" version of the theory presented in this paper with the final line shape obtained through averaging as in Eq. (7.1).

The situation in reality lies between the two limiting cases. An estimate of the effects can be made in this case also. Viewing the process in the time domain, the difference between the two cases will become noticeable in the correlation function at a time equal to the mean free time between collisions $\tau_f$. The spectra for the two cases would then deviate for frequencies $|\Delta\omega| < \tau_f^{-1}$. Since $\tau_f \gg \tau_c$ in a dilute gas, the deviations will occur primarily in the region of validity of the impact theory.[45–50]

The next important assumptions, Eqs. (2.5)–

(2.9), involve the structure of the Hamiltonian, particularly the atom-perturber and perturber-perturber interactions. These assumptions imply that the theory will be most accurate at low-gas densities (where measurements are available[51]). Interaction potentials are not generally pairwise additive.[52–54] Only the induction or van der Waals forces are. For excited states which contribute heavily to optical cross sections, the van der Waals contribution is large, and the additivity results in the proper treatment of overlapping collisions as long as all impact parameters are large. The collisions need not be "weak"; they are only required to act *independently*. Due to the large energy difference between states $u$ and $l$ as compared to $kT$ as has been assumed in the model, it is perfectly legitimate to neglect inelastic transitions between these states due to the breakdown of the Born-Oppenheimer approximation.[55,56] There are cases when inelastic transitions may be important. Electronic transitions in a free atom always involve at least one state with angular momentum $J$ greater than zero. It follows that the state must be $(2J+1)$-fold degenerate. The degeneracy is destroyed by the atom-perturber interaction and inelastic transitions can occur between these closely spaced states during collisions.[57] See Sec. VII B6. The problem of rotational degeneracy (vectorial nature of $\mu$) has also been studied within the impact theory.[6,18,58–60] Any complete treatment of the line-shape problem must eventually include the inelastic processes.

The Liouville formalism was introduced, Eqs. (2.12), etc., to allow generalizations to be made. Liouville techniques have proved useful in multiline broadening problems in the impact approximation.[17,41,60–62]

The reduction to the two-body form (one atom, one perturber) of Eq. (2.30) given in the Appendix was straightforward and *exact* for the model considered, in the thermodynamic limit. Only the partition function was approximated; this changes a normalization factor and can easily be corrected, a minor point withal. Since the reduction is exact, the resulting line-shape expression at this point will be valid even at distances from the line $|\Delta\omega| > kT/\hbar$. The impact approximation[63–68] was briefly derived in Sec. III to point out its form and limitations in the time domain.

The sum rules[10–14] are introduced in Sec. II and used in Sec. IV. Since the sum rules involve thermal averages of various combinations of $\Delta V$ and $H_l$ it is imperative that the atom-perturber interactions be included in the Boltzmann factor as we have done. Thus a product of the free-particle density matrices (Boltzmann operators) for the atom and the perturber may *not* be used in calculating the sum rules. The correlations (at $t=0$) must be included. In the impact approximation the correlations in the initial state can properly be ignored. Sum rules have been used in many applications but few discussions have attempted to treat atomic line broadening.[69]

By successive integration by parts, the moments of any order can be reduced to averages over the quantum-mechanical radial distribution functions $g_l(r)$. For most systems at room temperature or above, $g_l(r)$ can be expressed accurately as its classical limit times a correction series[70–73] in powers of $\hbar^2$.

The statistical approximation[7–9,35] is studied in Sec. V. There is a slight distinction between the statistical limit and the approximation.[74] The statistical approximation has been generally successful in limited applications to date.[75] The first calculations of the statistical spectrum for a nontrivial potential were done by Bergeon *et al.*[76,77] for the Lennard-Jones (6-12) potential $\Delta V \propto ar^{-12} - br^{-6}$. The major simplification used in that work was to set the radial distribution function $g(r)=1$. This is not a bad assumption for large $r$ but is a totally untenable one for small $r$ where $g(r)$ is expected to cut off extremely rapidly. The net result is that the strength of the "blue" wing (high-frequency side of the line) can be greatly overestimated. Similar calculations have been done for lower perturber gas-densities,[32,78,79] revealing the satellite structure described in Eq. (5.17). It is gradually becoming recognized that the satellite bands arise from extrema in $\Delta V(r)$. This has been exploited to estimate excited-state potential parameters from the satellite positions.[80,81]

Attempts have been made to identify the shift of the peak with the first moment and the half-width of the absorption line with the second moment. Only in rare cases will there be a correspondence between the peak position (mode) and the first moment (mean).[82]

It is not difficult to estimate the line shape that the theory predicts at very high densities. From Eqs. (4.3), (4.7), and (4.11), expanding $\phi(t)$ in a power series, we have

$$\phi_+(t) = \exp\left[-i\rho\langle\Delta V\rangle_l t - \tfrac{1}{2}\rho\langle(\Delta V)^2\rangle_l t^2 + O(t^3)\right] \quad . \tag{7.2}$$

If the density is sufficiently high the $O(t^3)$ term can be neglected. The spectrum at high densities is therefore, approximately, a shifted Gaussian,

$$S_+(\omega) \propto \exp\{[\omega - \omega_0 - \rho\langle\Delta V\rangle_l]^2/[\rho\langle(\Delta V)^2\rangle_l]^2\} \quad . \tag{7.3}$$

The Gaussian result in Eq. (7.3) is the general high-pressure result for independent perturber models and is not confined to the statistical approximation. This is because the first two moments of the line are given exactly by the statistical result; no dynamical effects occur until the third-order term as explained in Sec. V. The Gaussian approximation does not depend on the interaction being weak. It depends on the density being high enough so that a large number of perturbers act independently and simultaneously on the atom. The Gaussian is then essentially a consequence of the central-limit theorem. This has been discussed by Kubo[12] as slow modulation in stochastic theories of line shape.

A unified theory for the line shape is developed in Sec. VI. Past attempts divide into: (a) formal theories which give no method for practical calculations or are simplified until some line features can be calculated, (b) simple and essentially classical theories for which calculations can be done for the entire line shape. In the first category are theories by Ohno,[83] Ross,[15] Bezzerides,[84,85] Mead[43] and others.[86–98] Some of these involve many-body effects occurring in resonance broadening. The work of Fiutak[95] occupies an intermediate position. In the second category the first significant work was by Anderson and Talman.[99] Independent perturbers were assumed to move on straight-line paths at a single speed, producing a frequency shift $\Delta\nu\propto r^{-n}$. The theory was shown capable of giving impact, statistical, and intermediate line shapes. Takeo[100] has done a similar analysis for square-well and Lennard-Jones potentials, showing how they give rise to satellite bands. [A discontinuous potential such as the square well cannot be used in a sum-rule approach because the higher moments will diverge, cf. Eq. (4.17).]

The most noteworthy unified theory to date with calculations is the work of Fox and Jacobson.[101] Again the theory is classical, assuming independent perturbers moving in the lower-state potential $V_l(r)$. Frequency perturbations arise from the difference potential $\Delta V(r)$. The theory appears reasonably successful in predicting line shifts and half-widths. The approach appears difficult to generalize to more complex cases, especially molecular bands. The theory offered in this paper on the other hand, is fully quantum mechanical and should not be difficult to generalize to include multiline and diabatic effects (*vide infra*). The particular decomposition into statistical and dynamical terms we have chosen is not unique. A more general decomposition could be written

$$\phi(t)\approx[\alpha\,\phi_s(t)]_{\text{exact}}+[(1-\alpha)\phi_s(t)+\phi_D(t)]_{\text{approx},k}\ , \qquad (7.4)$$

where $0\leq\alpha\leq1$ and "approx, $k$" corresponds to fitting $k$ terms in the power series with Padé or other forms. We have used $\alpha=1$. There are still other ways to construct an approximate unified theory. One might work entirely in the frequency domain as many of the Liouville approaches have, particularly for plasma line broadening.[102,103] Another method is the continued-fraction development in the frequency domain[104,105] (close to the Padé formulation).[106] In the continued-fraction approach one can ensure that to each order of approximation the resulting spectrum is positive definite.[104] More ambitious schemes are even easier to devise in principle, up to and including a complete numerical computation of the two-body correlation function $\phi(t)$ or its spectrum $s(\omega)$.

One point should always be kept in mind: No one has yet discovered a dynamical principle (in ordinary wave mechanics) that allows a conscientious calculation of a cross section without calculating the wave functions themselves as an intermediate step. Therefore, anyone who calculates rigorous cross sections also calculates wave functions, and it is the details of these wave functions (or their appropriate matrix elements) which give the "spectra of collisions" and ultimately the spectral line shape.

One very interesting point about our theory can be traced back to Eq. (2.29) which (for the positive frequency component) has the basic form

$$S_+(\omega-\omega_0;\rho)\propto\mathfrak{F}[e^{\rho f(t)}]\ , \qquad (7.5)$$

where $\mathfrak{F}$ indicates the Fourier transform. This implies that line-shape measurements at various densities should be related to the single complex function $f(t)$, i.e.,

$$f(t)=\rho^{-1}\ln\{\mathfrak{F}^{-1}[S(\omega-\omega_0;\rho)]\}\ , \qquad (7.6)$$

where $\mathfrak{F}^{-1}$ is the inverse transform. Therefore, if the experimental line-shape data at a number of densities are reduced by Eq. (7.6) a single function $f(t)$ should result, independent of density. This conclusion is independent of any approximate schemes involving moments, Padé approximants, etc., it is a prediction based on the form of the theory. The practical difficulties of Fourier transforming experimentally obtained data are not trivial but surely the game is worth the prize. The question then would be, over what range of densities will Eq. (7.6) turn out to be valid?

### B. Connections with Other Problems

The problem studied in this paper and the techniques suggested to solve it can hardly be viewed in isolation. There are links between our problem and a number of others that have barely been explored.[107–109] We hope the discussions below will help to stimulate even more interest in these research areas.

#### 1. *Stochastic Theories*

Much of line-shape theory can be discussed using stochastic models. Kubo[11,12,14] has done this in an admirable way, showing how the impact and statistical theories arise, and how dynamical modulation effects can be included. He has also pointed out connections with kinetic theory, NMR, Mössbauer spectra, etc.

### *2. Experiments*

Experiments have not been discussed because numerical calculations are not presented in this paper. Excellent data are available, however.[39,110–119] There are extensive studies of alkali-atom lines (especially Cs) broadened by noble gases. Suggestions about future experiments are given below and in Sec. VIII.

### *3. Interatomic Potentials*

One of our goals is to relate spectral line shapes to interatomic potentials. There are numerous ways to study interatomic forces,[30,53,54,81,120,121] and spectroscopy,[79,122,123] especially molecular spectroscopy,[124,125] has been one of the best techniques. The development of a reliable unified theory can extend the usefulness of spectroscopy in this regard. The study of line shapes is essentially the *only* way to study the details of interatomic interactions involving excited states which can decay by optically allowed transitions.

### *4. Bound and Unbound States*

The formulation used in this paper treats bound and unbound (scattering) states of the atom-perturber pair in consistent but somewhat different manners. In the statistical approximation both types of states are included with their proper weighting through the radial distribution function $g_l(r)$. This is to be contrasted with explanations in the literature which tend to ascribe satellite structure to *either* bound *or* unbound states.[126] The impact-theory portion includes only scattering states, as these alone lead to the simple long-time behavior characteristic of the impact theory. It is possible to study separately the contributions from bound states, quasibound states, and scattering states. This has been pursued in spectroscopic[127,128] and other contexts.[129,130]

### *5. Molecular Electronic Spectroscopy*

Most diatomic molecules studied spectroscopically have binding energies of 1 to 10 eV.[124,131,132] Atom-perturber systems such as Cs/Ar are estimated to have binding energies of order $10^{-2}$ eV $\approx kT_{\text{room}}$. Diatomic analyses in the main begin by assuming the harmonic oscillator-rigid rotator model, and include other effects as corrections to these simple assumptions.[131,132] For the atom-perturber case the unbound states are dominant. The molecular vibrational levels pass over into unbound relative translational states with a continuous spectrum defined by the appropriate radial Schrödinger equations (nonharmonic!). The diatomic rotational levels similarly pass over into the various angular momentum states in the decomposition of the atom-atom-scattering wave function (nonrigid rotators!).

The decomposition of the molecular wave function into a product of electronic ($e$), vibrational [or translational ($t$)], and rotational [or angular momentum ($l$)] factors is an important simplification in spectroscopy, one that has been used in this paper.[133] It follows that the strength $S(\alpha', \alpha'')$ of an electronic transition at a particular frequency is[134]

$$S(\alpha', \alpha'') \propto \left| \int \Psi^*_{\alpha'} \vec{\mu} \Psi_{\alpha''}\, d\vec{x} \right|^2$$

$$= \left| \int \Psi^*_{e'} \vec{\mu} \psi_{e''}\, d\vec{x}_e \int \psi^*_{t'} \psi_{t''}\, d\vec{x}_t \int \psi^*_{l'} \psi_{l''}\, d\vec{x}_l \right|^2 . \tag{7.7}$$

The only nontrivial factor in Eq. (7.7) is the translational (or vibrational) overlap integral[135] whose squared modulus is called the Franck-Condon factor[131,132,135] $q_{t't''}$,

$$q_{t't''} \equiv \left| \int \psi^*_{t'} \psi_{t''}\, d\vec{x}_t \right|^2 . \tag{7.8}$$

Knowledge of the transition strength as a function of energy *a la* the molecular theory should lead to the full two-body spectrum $s(\omega)$ studied earlier. $s(\omega)$ is the Fourier transform of $\phi(t)$, Eq. (4.3), which can be written out in matrix-element form using eigenstates of $H_l$ and $H_u$,

$$\phi(t) \propto \sum_{l,u} e^{-\beta E_l} \langle l | e^{i(E_u - E_l)t} | u \rangle \langle u | l \rangle$$

$$= \sum_{l,u} e^{-\beta E_l} e^{i\omega_{ul} t} |\langle l | u \rangle|^2 , \tag{7.9}$$

where $\omega_{ul} = E_u - E_l$. The two-body correlation function can therefore be written in terms of the squared modulus of the overlap factor, $|\langle l | u \rangle|^2$, which is exactly the Franck-Condon factor. Within the wide limits of validity of the Born-Oppenheimer approximation this shows the equivalence of the standard molecular approach and our techniques for our model. Baranger was one of the first to show that complete knowledge of the overlap integrals is sufficient to calculate the shape of a collision-broadened line.[136]

In the calculation of Franck-Condon factors the strongest transitions normally occur when the positions $r$ and $r'$ for equal momenta in the upper and lower states are the same ("vertical transitions"). In the statistical limit the perturber mass becomes infinite and only the vertical transitions remain. There is a sum rule (of the conventional oscillator-strength variety) due to Jablonski, developed for molecular spectroscopy,[137] that says that the sum of the transition strengths from a single vibrational state to all other states (of the other electronic level) is a constant, independent of the single state chosen. Therefore, in the statistical limit the transitions collapse to pure vertical transitions, each with the same constant weight. This is the reason behind the particularly simple expression for the statistical spectrum, Eq. (5.4). For finite perturber mass the Franck-Condon factors have a "spread" of a certain amount around the vertical transitions. This can be observed by looking at the distribution of Franck-Condon factors around the locus of their maxima (the Condon parabola) in any tabulation.[138–140] This spread, apart from the pure quantum effects that give discrete states, is a measure of the motional or nonstatistical-limit effects in molecular spectra. In the atom-perturber model the spread corresponds to the duration-of-collision effect that has been discussed. Jablonski has studied the "spread" using WKB techniques for application to the line-broadening theory.[141,142]

Molecular spectroscopy is not confined to bound-state phenomena. A diatomic molecule can absorb a photon and undergo a transition to an upper unbound state (photodissociation). The Schumann-Runge bands of $O_2$ in the uv are notable examples of this.[143] Herzberg[143] has pointed out the strong connections between such molecular continuum absorption and atomic line broadening but more studies of these relations are needed.

### 6. *Diabatic and Adiabatic Processes*

A realistic atom-perturber model must take into account the degeneracy of the electronic states, e.g., the components of the alkali-atom doublets are twofold ($^2P_{1/2}$) and fourfold ($^2P_{3/2}$) degenerate. During a collision these degeneracies are lifted and inelastic transitions can occur between the various sublevels.

As the perturber passes by the atom at moderate distances the atomic angular momentum $\vec{J}$ will be coupled to the internuclear axis in an adiabatic manner. This is Hund's case (c) coupling for angular momenta in diatomic spectroscopy.[144] At even closer separations there will be mixing of the doublet components with a change to Hund's case (b) coupling. When the perturber is far away, $\vec{J}$ will become uncoupled and remain fixed in space. This is the diabatic limit.[145,146]

From the point of view of scattering theory, the inelastic (diabatic) processes can be described by a many-channel set $\{\alpha\}$ of coupled equations containing both the energy levels $V_{\alpha\alpha}(\vec{r},\vec{\Omega})$ and the coupling terms $V_{\alpha\alpha'}(\vec{r},\vec{\Omega})$.[147,148] Here $\vec{\Omega}$ refers to the angle angular momentum variables. For the atom-perturber case, within a given $J$ manifold there are only $2J+1$ open channels. If Hund's case (b) is considered, transitions can occur between different $J$ manifolds. Efficient numerical methods for solving the coupled equations in many-channel processes have been developed recently.[149]

The primary difficulty in these calculations is the choice of proper potentials $V_{\alpha\alpha}$ and $V_{\alpha\alpha'}$. Some evidence of the difficulties involved comes from the appearance of violet satellites in Cs at distances as much as 400 $\text{cm}^{-1}$ from the line for the $^2P_{3/2}$ component.[112,118] This indicates some unusual behavior of the $^2P_{3/2}$ excited-state interaction potential which might result from incipient crossings[150] of split terms within the $J=\frac{3}{2}$ manifold. Sum rules[151] should continue to be of value even in these multichannel problems.

### 7. *Classical and SemiClassical Methods*

In collisions of heavy atoms, classical and semiclassical methods[152,153] can often be used successfully for dynamical calculations. The work of Fox and Jacobson cited earlier[101] is an example. In particular, the width $w$ in the impact theory can often be obtained rather reliably by classical-path methods because long-range (weak) forces give substantial contributions. In the past there have been many efforts to find classical approximations for quantum problems because classical calculations are generally thought to be easier. However, Gordon states[149]: "... for less than about 50 channels, it is now actually easier to solve the rigorous equations for quantum scattering than to solve the classical equations of motion."

### 8. *Collision-Induced Phenomena*

There are a number of spectral processes that *only* occur during collisions, and analyses of these have much in common with the duration-of-collision effects discussed earlier.

A mixture of He and Ar gas, for example shows a broad nonresonant absorption band in the far infrared.[154–156] This is due to the transient dipole moment of the He-Ar pair which only exists during collision (when the pair is a "transient" heteronuclear molecule). The first analysis of this collision-induced translational absorption was done by Poll and Van Kranendonk[157] using moment methods. Calculations of the entire spectrum have been done by Tanimoto,[158] Trafton,[159] and McQuarrie and Bernstein[160] for realistic models. The relation of the absorption measurements to the determination of interaction-potential parameters has been pointed out by the author.[161] From the molecular point of view, translational absorption is a vibration-rotation band with the "vibrational" levels in the continuum.[162] A similar analog of molecular Raman scattering occurs in collision-induced light scattering.[163] Another related phenomena is collision-induced vibrational relaxation.[164,165]

Each of these phenomena: absorption, light scattering, or vibrational relaxation probes the corresponding "spectrum of the collision" in detail just as the unified theory does.

### *9. Molecular Infrared and Microwave Spectra*

In the broadening of molecular absorption bands in the infrared there are unexplained deviations from the impact theory in the far wings which can be understood using the techniques of this paper. The impact theory is valid for molecular line broadening at low gas densities and not too far from the individual lines, throughout the infrared and microwave regions.[48] The impact theory must be generalized to allow "line coupling" when sets of lines are involved. Gordon[166,167] was the first to study such processes systematically. The line coupling manifests itself in off-diagonal terms in the "Liouville matrix" which couples one dipole-matrix element (corresponding to a spectral line) to another (spectral line). The ordinary scalar impact theory for an isolated line gives the correlation function

$$\phi_+(t) \propto e^{(i\omega_0 + id - w)t}, \quad t > 0 \quad . \tag{7.10}$$

We have shown how this must be modified at short times to include the statistical and duration-of-collision effects. The many-line formulation of the impact theory is a matrix generalization of Eq. (7.10),[166,168]

$$\phi_+(t) \propto \vec{\mathrm{d}} \cdot e^{i(\overleftrightarrow{\omega}_0 + i\overleftrightarrow{\pi})t} \cdot \overleftrightarrow{\mathrm{P}} \cdot \vec{\mathrm{d}} \;, \quad t > 0 \tag{7.11}$$

where $\vec{\mathrm{d}}$ is a vector corresponding to the set of line strengths, $\overleftrightarrow{\omega}_0$ is the diagonal matrix giving the unbroadened line positions, $\overleftrightarrow{\pi}$ is the transition matrix with diagonal elements for shifts and broadening and nondiagonal elements for line coupling, and $\overleftrightarrow{\mathrm{P}}$ is the diagonal matrix of thermal weight factors.

It is clear that an error is made in assuming the validity of Eq. (7.11) for short times, just as in the isolated line case. A remedy for this difficulty could be

$$\vec{\mathrm{d}} \cdot \exp[i\,\overleftrightarrow{\omega}_0 t + i\,\mathrm{Re}(\overleftrightarrow{\pi})f(t) - \mathrm{Im}(\overleftrightarrow{\pi})g(t)] \cdot \overleftrightarrow{\mathrm{P}} \cdot \vec{\mathrm{d}} \quad . \tag{7.12}$$

Here only two functions have been used so that all collisional effects are corrected by the same factors $f(t)$ and $g(t)$. These must both possess power-series expansions around $t = 0$ and become equal to $t$ when $t$ is large, as do the Padé forms suggested in Sec. VI. No statistical-theory corrections have been included in Eq. (7.12) other than what are included in $f(t)$ and $g(t)$, since we expect the statistical-theory contributions to be small (duration-of-collision effects are most important). Most of any detailed "statistical" structure is already included in the set of $\overleftrightarrow{\omega}_0$ line frequencies (*vide infra*). Both moment analyses and impact studies[168] have been carried out in the past for molecular spectra but no attempt has been made to combine the two types of analysis as in Eq. (7.12).

The most graphic examples of the breakdown of the impact approximation in the molecular case are the observations of Benedict *et al.*[169] and Burch *et al.*[170] on $\mathrm{CO_2}$. In the free molecule there is no absorption due to a given vibrational transition $\nu_n$ beyond the rotational-band head position $\nu_{nh}$. For the broadened band, Lorentzian forms were assumed[169] and summed over the lines in the band. The observed absorption in the region 200 $\mathrm{cm^{-1}}$ beyond the band head was nearly 3 orders of magnitude less than the predicted Lorentz absorption. The band shape in the wings appeared empirically to fit a sum of shapes of the form[169]

$$A(\omega) \propto \exp[-a(|\omega - \omega_0| - \omega_m)^b] \quad \text{for} \quad |\omega - \omega_0| > \omega_m \quad , \tag{7.13}$$

with $b \approx 0.8$. Note that this line shape possesses all frequency moments as it should. These measurements extend so far into the wings ($\hbar\,\Delta\omega \geq kT$) that a quantum-mechanical analysis may be necessary. Equation (7.12) should be capable of giving results such as Eq. (7.13).

The formation of rotational-band heads accompanying vibrational (or electronic) transitions is closely related to the formation of satellite bands, but this seems never to have been pointed out before. The relation suggests even closer contact between atomic and molecular line-broadening problems. In the atomic case, for satellite formation in the statistical limit, one is concerned with the different forms of the translational states or potential energy vs $r$ for two different electronic states. In addition a selection rule operates. In the statistical limit of vertical transitions, the selection rule is $\Delta r = 0$ (and $\Delta E = \Delta V$) (Sec. V). In the molecular case there is, analogously, a different dependence of the rotational levels on $J$ for two different vibrational states and a corresponding selection rule, $\Delta J = \pm 1$.

The rotational energy dependence is

$$E_R = BJ(J+1) + E_V \quad , \tag{7.14}$$

where the constant $B$ depends on the particular vibrational state, and $E_V$ is the vibrational energy. To be specific consider the $R$ branch defined by $J'$ (upper state) $= J'' + 1$ (lower state). One can plot $E_R$ as a function of $J'$ and $E_{R''}$ as a function of $J''$ with the points $J'$ and $J'' + 1$ corresponding. The difference curve, giving the transition energies or line frequencies, is parabolic with a maximum as a function of $J$ (for the usual case of $B'' > B'$). Such parabolic difference plots (Fortrat diagrams) are common in molecular spectroscopy. The band head, the maximum of the Fortrat parabola where the density of absorption lines per unit frequency is high, is thus analogous to the satellite singularity which arises when the interatomic potential energy difference curve has an extremum leading to an anomalously large amount of absorption near a single frequency.

### *10. Applications*

There are numerous applications for unified line-shape theories in astrophysics and planetary-atmosphere studies that we can touch upon. The far wings of lines are often important because radiant energy can be transported over large distances in the weakly absorbing wing regions. For example the terrestrial atmospheric "window"[171–174] in the 8- to 12-$\mu$ region is controlled by the far wings of certain $H_2O$ bands which are hundreds of $cm^{-1}$ from the window.[175] The impact theory is totally invalid at these frequency separations. The redistribution problem in radiative-transfer theory in astrophysical problems can also be studied using a unified theory.[176,177] Measurements of other planetary atmospheres also depend on a knowledge of line-wing behavior.[178] The major applications of electronic line-shape studies, as we see them, are to develop the theoretical techniques and study the fundamental problems of atomic interactions in ground and excited states.

### *11. Resonant Broadening, Plasmas, and High-Density Systems*

There are three major areas of line broadening which have not been discussed: resonant (or self-) broadening,[179] line broadening in plasmas,[180] and high-density systems.[181] Sum-rule techniques should be useful in studying all of these problems.

## VIII. CONCLUSIONS

The unified theory of line shapes developed in this paper has several distinguishing features: It is fully quantum mechanical; it includes atom-perturber statistical correlations in the initial state; it is couched in an approximate form designed for reasonably simple numerical calculations; a major part of the analysis has been done using sum-rule or spectral-moment techniques. It is a unified theory because it includes the impact and statistical theories. In addition it offers a methodical analysis of the duration-of-collision effects which are then used to link the impact and statistical contributions together in the final syneresis.

The particular line-shape expression developed in this paper, Eq. (6.11), (including Padé approximants for interpolation in time), should not be taken as representing any ultimate theory of line shapes. The more important purpose of the time-domain analysis of this paper has been to elucidate many features omitted or not thoroughly treated in past work, particularly the sum rules and the short-time behavior. For actual computational purposes the Padé form may be successful. On the other hand, essentially classical prescriptions may also be computationally convenient, in the form

$$\phi(t) = \langle \exp\{(i/\hbar) \int_0^t [A_u(s) - A_l(s)]ds\} - 1 \rangle \quad . \tag{8.1}$$

The $A$'s in the expression might be chosen as the potentials or as the Lagrangians for the separate motions in the two potentials $V_u$ and $V_l$.[182] It is only a matter of time before $\phi(t)$ will be computed using a fully quantum-mechanical (though numerical) procedure. These more elaborate calculations can then serve as testing grounds for simpler, but approximate theories.

The ultimate goal of any unified theory of line shapes is a detailed understanding of the relation between line shapes and the underlying atomic and molecular properties that give rise to them, e.g., excited-state potentials in atomic systems and the complex anisotropic intermolecular potentials. Furthermore, a detailed understanding of spectral absorption phenomena is essential in studying radiative transfer in the atmospheres of the Earth, other planets, and stars.

The ties between pressure broadening of atomic lines and molecular electronic spectra are quite strong. The two-body correlation function $\phi(t)$ which played a major role in this paper can be considered the Fourier transform of the absorption spectrum $\tilde{\phi}(\omega)$ of the diatomic quasimolecule atom perturber (AP). The designation quasimolecule is used because in any pressure-broadening situation the overwhelming majority of the states of this pair of atoms in the volume $\mathcal{V}$ will be unbound. The resulting quasimolecular spectrum, therefore, has a very singular character in the neighborhood of $\omega_0$. From the experimental point of view it would be quite interesting to find an AP pair amenable to study over such a wide temperature range that both the conventional molecular electronic spectrum of AP (low temperatures) and the pressure-broadened quasimolecular spectrum of $A$ perturber by the $P$ gas (high temperatures) could be studied.

A number of further studies flow naturally from this one, e.g., numerical calculations, extension to include rotational degeneracies and diabatic effects, and a detailed unified theory of molecular band shapes.[183–185]

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## APPENDIX

Equation (2.30) is derived from Eq. (2.29) which is

$$\Phi(t)=Z^{-1}(\beta)\sum_{\Psi_a,\Psi'_{a'}}\langle\Psi_a|e^{-\beta H}|\Psi_a\rangle$$

$$\times\langle\Psi_a|\mu|\Psi'_{a'}\rangle\langle\Psi'_{a'}|e^{iLt}\mu|\Psi_a\rangle\ . \tag{A1}$$

The first term in the summation is simple. The second term is

$$\mu_{ul}\langle\psi;u|\psi';l\rangle+\mu_{lu}\langle\psi;l|\psi';u\rangle\ . \tag{A2}$$

The third term also decomposes,

$$\sum_{\Psi''_u,\Psi'''_l}(\mu_{ul}\langle\Psi'_{a'}|e^{iLt}|\Psi''_u\rangle\langle\Psi'''_l|\Psi_a\rangle$$

$$+\mu_{lu}\langle\Psi'_{a'}|e^{iLt}|\Psi'''_l\rangle\langle\Psi''_u|\Psi_a\rangle)\ . \tag{A3}$$

The time-development operator $e^{iLt}$ then gives

$$\sum_{\Psi''_a,\Psi'''_b}e^{i(E_a-E_b)t}e^{iL_bt}|\Psi''_a\rangle\langle\Psi'''_b| \tag{A4}$$

for $\{a,b\}=\{u,l\}$ and $\{l,u\}$.

Reassembling $\Phi(t)$ in Eq. (A1) now gives

$$Z^{-1}(\beta)\textstyle\sum_\psi(e^{-\beta E_l}e^{i\omega_0t}|\mu_{ul}|^2\langle\psi;l|e^{-\beta H_l}e^{iL_lt}|\psi;l\rangle$$

$$+e^{-\beta E_u}e^{-i\omega_0t}|\mu_{ul}|^2\langle\psi;u|e^{-\beta H_u}\ {}^{iL_ut}|\psi;u\rangle)\ , \tag{A5}$$

where

$$H_a=\sum_{n=1}^{N}H_a(n)\ ,\quad a=u,l \tag{A6}$$

and

$$\omega_0=E_u-E_l\ . \tag{A7}$$

The product-state forms reduce further, giving

$$\sum_\psi\langle\psi;l|e^{-\beta H_l}e^{iL_lt}|\psi;l\rangle$$

$$=\prod_{n=1}^{N}\sum_{\psi_n}\langle\psi_n;l|e^{-\beta H_l(n)}e^{iL_l(n)t}|\psi_n;l\rangle$$

$$=[\sum_{\psi_1}\langle\psi_1;l|e^{-\beta H_l(1)}e^{iL_l(1)t}|\psi_1;l\rangle]^N\ , \tag{A8}$$

and similarly for the $H_u$, $L_u$ term.

The partition function reduces in a similar way. The "two-body" (AP interaction) partition functions are

$$Z_{1a}(\beta)=\mathrm{Tr}_1\,e^{-\beta H_a(1)}\ ,\quad a=u,l\ . \tag{A9}$$

These functions differ by $O(\mathcal{V}^{-1})$ for $a=u$ and $l$, and the corrections can easily be estimated. We will ignore these differences, which are important only at rather high densities, and write

$$Z(\beta)\approx[Z_l(\beta)]^N(e^{-\beta E_l}+e^{-\beta E_u})\ . \tag{A10}$$

Defining the two-body thermal average as

$$\mathcal{V}^{-1}\langle\cdots\rangle_a\equiv Z_l(\beta)^{-1}\,\mathrm{Tr}[\cdots e^{-\beta H_a(1)}]\ , \tag{A11}$$

so that the expression for $\Phi(t)$ is now reasonably simple, we have

$$\Phi(t)=(1+e^{-\beta\omega_0})^{-1}|\mu_{ul}|^2e^{i\omega_0t}[\mathcal{V}^{-1}\langle e^{iL_l(1)t}\rangle_l]^N$$

$$+e^{-\beta\omega_0}(1+e^{-\beta\omega_0})^{-1}|\mu_{ul}|^2$$

$$\times e^{-i\omega_0t}[\mathcal{V}^{-1}\langle e^{iL_u(1)t}\rangle_u]^N\ . \tag{A12}$$

For $\Phi(t)$ to exist in the thermodynamic limit, it will be assumed (and later verified) that for times $t$ of interest, the expressions

$$\mathcal{V}^{-1}\langle e^{iL_a(1)t}\rangle_a\ ,\quad a=u,l \tag{A13}$$

differ from unity by a term of order $\mathcal{V}^{-1}$. To demonstrate the limit schematically, let $g(t)$ represent $\mathcal{V}^{-1}\langle e^{iL_a(1)t}\rangle_a$,

$$g(t)=1+\mathcal{V}^{-1}f(t)\ . \tag{A14}$$

Then the limit is

$$\lim N,\ \mathcal{V}\to\infty,\quad N/\mathcal{V}=\rho,\quad [g(t)]^N\to e^{\rho f(t)}\ . \tag{A15}$$

Specifically this limit converts terms of the form

$$[\mathcal{V}^{-1}\langle e^{iL_a(1)t}\rangle_a]^N \tag{A16}$$

to

$$\exp[\rho\langle e^{iL_a(1)t}-1\rangle_a]\ . \tag{A17}$$

This leads to Eq. (2.30) of the paper.

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