RICE UNIVERSITY

STATIC LINE BROADENING THEORY AND THE
SPECTRA OF ELECTRON-BOMBARDED LIQUID HELIUM

by

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF ARTS IN PHYSICS

Thesis Director's signature:

[Signature]

Houston, Texas
December, 1971
Abstract

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Recent observations of the absorption and emission spectra of electron-bombarded liquid helium and the development of a detailed model describing the state of an excited atomic species in liquid helium have made it desirable to have a method of computing spectral line properties from the model. In this work we have investigated the application of static line broadening theory when a nonspherical, numerical potential and a nonspherical distribution are required and the theory is to be employed at high densities. Techniques for the application of the intensity expression and analysis of computed spectral lines are performed for several model distributions and potentials. The results of computations using the Hickman model are compared with the observed spectra.
ACKNOWLEDGEMENTS

I wish to thank Dr. Neal Lane for his understanding and encouragement during this work. I wish also to thank Mr. Albert Hickman. Without his model and calculations, this thesis would not have been possible. A large debt of gratitude is owed Dr. Neal Carron. His patient criticism was a great help in surmounting several of the mathematical obstacles which arose in this work. Finally, I am especially grateful to Miss Lillie Frank for her aid with the production of this thesis.
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I. INTRODUCTION

When a radiation field interacts with matter, the field is changed in a manner characteristic of the constituents of that material and certain properties of those constituents are available by measuring these changes in the field. In particular, if the radiation field can interact at a frequency corresponding to the resonant frequency of a transition between two atomic quantum states, then the field provides a sensitive probe of the energies of these states. The energy of these states will depend upon the atom's environment so that the structure of the environment is reflected in the measured radiation. It is frequently not immediately clear, however, how to interpret the radiation. In this work, we will consider the case of the optical absorption and emission spectra of electron-bombarded liquid helium. We will analyze the effects of certain model distributions of liquid atoms about the excited atomic or molecular species on the observed spectra.

Interest in the optical spectra of liquid helium began in 1964 when Jortner, Meyer, Rice and Wilson studied the spectra produced by implanting an alpha particle source in a dewar of liquid helium. The observed radiation was identified with electronic transitions of $\text{N}_2$ and $\text{O}_2$ impurities
in the liquid. Since this spectra persisted when the impurity concentration was made very small, this group postulated the existence of a preferential energy transfer mechanism in which the liquid helium absorbed the energy of the alpha particles and then transferred some of it to the oxygen and nitrogen.

In 1968 Surko and Rief\textsuperscript{2} immersed an alpha particle source in liquid helium and measured the electric current produced. By varying the potentials on grids placed above and below the surface of the liquid, they determined the existence of an "anomalous current" which is not affected by the grids placed in the liquid. They concluded that the carriers of this current must be produced at the liquid surface by an energetic neutral excitation. By magnetic deflection measurements, positive charge current carriers above the surface were found to be $\text{He}_2^+$ ions and the negative charge carriers were electrons. On the basis of these and other measurements, they suggested that the neutral excitation may be either the metastable atomic or molecular species of helium.

In order to more fully understand the nature of these neutral excitations, a program of spectroscopic investigation of electron-bombarded liquid helium was undertaken by the Rice
Atomic Physics Laboratory. A method of injecting 160 keV. electrons in a dewar of liquid helium at 1.7°K was perfected. Dennis et al. observed the emission spectra of the liquid and identified transitions between the ground state and the first few excited states of molecular helium and between the lowest excited states of atomic helium. By passing light from a scanning monochromator through the excited liquid helium, Hill et al. were able to detect the absorption spectra. They identified transitions originating from the lowest triplet atomic and molecular states to the first few excited states.

These experiments confirmed the existence of excited atomic and molecular species in liquid helium which has been excited by energetic charged particles, but they immediately raised questions concerning the structure of the liquid atoms about these excited states. The observed spectral lines were shifted from their dilute gas values by less than 100 cm\(^{-1}\) indicating that the electronic energy levels were not greatly perturbed. The charge cloud of an excited state could extend as much as 10 a₀ from the nucleus while the charge cloud from a ground state nucleus extends out 3 a₀, but the inter-nuclear separation in liquid helium in only 7 a₀. If
the excited species were only 7.a. from the liquid atoms, the charge clouds would greatly overlap and the energy levels would be significantly perturbed. Since this was not seen, Dennis suggested that the excited species exists in a cavity in the liquid where the size of the cavity is somewhat greater than the average internuclear separation between atoms. The fact that the rotational levels of spherically symmetric molecular states are not thermalized also suggests that such a cavity must exist.

A related phenomena is observed when low energy electrons are injected into liquid helium. There is evidence that these electrons form a cavity about themselves due to the strongly repulsive interaction between the electron and the ground state helium atoms. Dennis first suggested this model and calculated perturbations of energy levels using it. A more sophisticated model was developed by Hickman and is described later in this thesis.

Hickman's model includes an intermolecular potential and a distribution function which describes the configuration of liquid atoms about the excited atoms. To test this model against experiment, we should calculate spectral line shapes using this potential and distribution and this requires a theory of spectral line broadening. The development and
application of a line broadening theory to this problem is the object of this thesis.

Due to the Doppler effect and the finite lifetime of an excited atomic state, the spectral line from an isolated atom would not be infinitely sharp. However, when the excited atom is surrounded by other atoms, the effect of a finite lifetime will be small compared to the perturbing effects of the adjacent atoms. The development of a line broadening theory begins with the time-dependent Hamiltonian describing the excited atom and the interactions of the surrounding atoms and the radiation field on this state. The excited state is not a stationary state due to the perturbations of the adjacent atoms, but, for the case of an atomic transition, the time dependence of this state may be given by the adiabatic approximation. The transition probability due to the interaction of the excited state with the radiation field is calculated to first order in the electric dipole approximation using the variation of constants method and treating the radiation field classically. One obtains the expression for the spectral line intensity as a function of frequency as the Fourier transform of the transition dipole correlation function. If the time variation of the perturbations of the surrounding atoms is slow compared to
the correlation time of this dipole, then one may use the static line broadening approximation to find the intensity expression.

Because static line broadening theory had not been applied at these densities, we investigated the behavior of calculated spectral lines using various model potentials and distributions. Various techniques involving series expansions are developed to evaluate the intensity expression and the results of these computations are analyzed. Non-spherical distributions and numerical, non-spherical potentials are also not discussed in the literature and new techniques for evaluating the intensity expression for these cases are developed. The theory is applied to the $^2S-^2P$ transition in helium using Hickman's potentials and distributions and the results compared with experiment. Certain molecular transitions are qualitatively considered using the analysis developed here. The question of the validity of the application of the static theory is considered. Finally improvements in the model and the accuracy of the calculations are suggested.
II. LINE-BROADENING THEORY:

A. **The Width of a Spectral Line from an Isolated Atom**

Bohr's theory of atomic structure provides the simplest model for a description of atomic line spectra. There the radiation emitted or absorbed by an atom at rest with respect to the observer is monochromatic and its frequency \( \nu_{nm} \) is determined by the relation

\[
\nu_{nm} = \frac{E_n - E_m}{h}
\]

where \( E_n \) and \( E_m \) are the energies of the atom for the nth and mth states respectively.\(^7\) Observed spectral lines, however, have a non-vanishing width which depends in general on the environment about the optically active atom. Moreover, the peak of the line profile frequently does not coincide exactly with \( \nu_{nm} \). To explain these deviations, we must use a more precise quantum mechanical description of the radiation process and consider the effects of atomic motion and perturbations due to surrounding atoms. Heitler\(^8\) lists four causes of spectral line broadening and shifting. In this section we briefly consider two causes which depend only on the isolated atom. In the next section we shall discuss the other two which depend on interaction with surrounding atoms.

One of the smallest effects is that associated with the natural line breadth. An excited atomic state is not a pure
eigenstate due to the interaction of the atom with the radiation field. This is called radiation damping. Thus there is, in general, a probability of finding the atom and radiation field in one of several states. This may be thought of as limiting the lifetime of the excited atomic state and thus introducing an uncertainty in the value of the energy of that state since the uncertainty relation for time and energy is

\[ \Delta E \Delta t = \hbar \]

where \( \Delta E \) is the uncertainty in the energy of the atomic state. Letting \( \tau \) be the lifetime of the atomic state due to the radiation transition probability, then \( \Delta E = \hbar / \tau \). This should be a measure of the line width. Heitler shows that a more complete analysis gives an expression for the emission line shape as

\[ I(\nu) d\nu = \frac{\nu}{2\pi} \frac{\hbar \nu d\nu}{(\nu - \nu_b)^2 + \gamma^2} \]

where \( \nu \) is the observed frequency, \( \nu_b \) is the Bohr frequency, and \( \gamma = 1/\tau \). This is called a Lorentzian line shape. It is easily seen that this is symmetric about \( \nu_b \) and that when \( \nu - \nu_b = \gamma / 2 \), the intensity is reduced to half its value at \( \nu_b \). Thus the width given by the uncertainty relation corresponds to the width of the line at half maximum.
A case of interest is the $^3P \rightarrow ^3S$ transition in helium where the lifetime $\tau = 10^{-7}$ sec. Thus the natural line breadth is $3 \times 10^{-4}$ cm$^{-1}$. We shall see that this is much smaller than the observed line width so that natural line broadening is not of further interest to us. There is also a shift of the peak of the line profile associated with the interaction of the radiation field but it is of approximately the same order of magnitude as the width and so does not concern us.

From special relativity one knows that the frequency of a radiation source that is moving with respect to an observer appears to be shifted with respect to the frequency seen in the rest frame of the source. This is known as the Doppler effect. For non-relativistic velocities, the magnitude of the shift is

$$\Delta \nu = \nu_0 \frac{\nu}{c}$$

where $\nu_0$ is the frequency in the rest frame, $\nu$ is the relative velocity of the source with respect to the observer, and $c$ is the velocity of light. In a gas, for example, the atoms would have Maxwellian velocity distribution which would produce a spectral line with a Gaussian shape

$$I(\nu)d\nu = \alpha d\nu \exp[-(\Delta \nu / \gamma)^2]$$

where $\alpha$ and $\gamma$ are constants.
We obtain an estimate for the magnitude of this effect in liquid helium by using the values given by Gibbs and Harling for the average atomic kinetic energy in liquid helium. At a temperature of 1.7°K, the average kinetic energy is 17.6°K which corresponds to an average velocity of $2.7 \times 10^4$ cm/sec so that the Doppler shift is about $10^{-2}$ cm. Effects of this magnitude are completely negligible relative to the observed width and shifts.
B. **Adiabatic Pressure Broadening Theory**

If an atom emits or absorbs radiation in the presence of other atoms, the surrounding atoms will affect the radiation process and will generally broaden and shift the spectral lines. The general term for this effect is pressure broadening. One traditionally pictures two distinct sorts of perturbing processes which are called impact broadening and static broadening. In early pressure broadening work there was no clear connection between these two theories. Subsequently a more general quantum mechanical theory was developed which exhibits one or the other of these two theories under certain limiting conditions. In the calculations of the following sections, we shall be interested in the static broadening theory. However, to better understand static broadening theory and what it neglects, in this section we shall first describe a simple impact broadening theory, then give an intuitive derivation of static broadening, and finally derive the static theory as a special case of the general quantum mechanical theory.

A number of authors have discussed impact broadening of spectral lines. As we shall not be especially interested in this particular theory in the work that follows, we refer
the reader to the reviews by Ch'en and Takeo \textsuperscript{12}, Margenau and Lewis \textsuperscript{13} and Breene \textsuperscript{14} for more thorough discussions. We describe here only a simple impact theory originally due to Lorentz which is contained in the review of Margenau and Lewis.

Consider an atom in an excited state. We saw above that the finite lifetime of that state gave rise to a certain width in the spectral line. Suppose that atom is surrounded by a few other atoms which are moving very rapidly. Most of the time the atom is free to radiate as if it were isolated from all other atoms. But eventually the excited atom will suffer a collision of relatively short duration with one of these fast atoms. Under the assumption of the Lorentz impact theory, this collision terminates the radiation process, thus shortening the lifetime and broadening the line. To compute the line profile for such a process, we describe the emitting atom as a classical oscillating dipole of frequency $\omega_0$. We suppose that the atom began radiating at $t = 0$ and continued until $t = T$ when it collided with a fast atom and the emission process ended. The emitting atom's oscillating dipole has the form
\[ M(t) = \begin{cases} \mu_0 e^{-i\omega_0 t} & 0 < t < T \\ 0 & \text{otherwise} \end{cases} \]

The total energy emitted by a radiating dipole is

\[ U \propto \int_{-\infty}^{\infty} dt |\dot{\mu}(t)|^2 \]

By a formula from Fourier analysis,

\[ \int_{-\infty}^{\infty} dt |f(t)|^2 = 4\pi \int_{0}^{\infty} |F(\omega)|^2 d\omega \]

where \( F(\omega) \) is the Fourier transform of \( f(t) \).

Then

\[ F(\omega) = \frac{i}{\lambda} \int_{-\infty}^{\infty} e^{i\omega t} \mu(t) dt \]
\[ = \frac{\mu_0}{2\pi} \int_{0}^{T} e^{i\omega t} e^{-i\omega_0 t} dt \]
\[ = \frac{\mu_0}{2\pi} \frac{e^{i(\omega-\omega_0)T} - 1}{i(\omega-\omega_0)} \]

The frequency distribution for the power radiated by an atom with a radiative lifetime \( T \) is then given by \( |F(\omega)|^2 \).

But we have an ensemble of atoms. Let the mean time between collisions be \( \tau \). Then the probability that an atom will radiate until a time \( T \) and then suffer a radiation terminating collision between \( T \) and \( T + dT \) is \( \frac{1}{\tau} \exp\left(-\frac{T}{\tau}\right) dT \).

Thus the frequency distribution of radiation from the ensemble will be

\[ I(\omega) = \frac{1}{\tau} \int_{0}^{\infty} |F(\omega)|^2 \exp\left(-\frac{T}{\tau}\right) dT \]
\[ \propto \frac{1}{(\omega-\omega_0)^2 + \gamma^2} \]
where $\nu_c = 1/\tau$ is the collision frequency. Thus impact broadening is characterized by a Lorentzian line shape as is natural lifetime broadening. The collision frequency can be expressed as

$$\nu_c = n \sigma v$$

where $n$ is the number density of atoms, $v$ is the velocity, and $\sigma$ is the "optical" collision cross-section. When this distribution was compared with experimental results, it was usually found necessary to use a cross-section several times larger than the gas kinetic cross-section.

In later developments of impact broadening theory, the idea of short duration collisions was kept but the effect of the collisions was modified. The collisions were now pictured as changing the frequency of the emitting atom for some short period of time. The total change was called a phase change. Some theories were developed in which a phase change of some arbitrary magnitude (e.g. unity) corresponded to a termination of the radiation process. Smaller changes were ignored. The impact parameter corresponding to phase changes of this size could then be used to compute the "optical" collision cross-section mentioned above. Still later theories were able to consider collisions resulting in phase changes of all magnitudes.
These were the first to predict line shapes which include a shift as well as a width. However, as long as the assumption of very short collision duration is kept, one obtains the Lorentz line shape. To go beyond this assumption takes us to the general theory which is discussed later. One might expect that this assumption of very short collision duration would recommend this type of live broadening theory for situations in which one had a low density, high temperature gas and in fact this is what is found. Breene suggests that impact theories are not applicable at pressures over one atmosphere. Since in liquid He we have densities which are several hundred times that of the gas at room temperature and one atmosphere, we should not expect impact broadening to give us a very good description of the line profile in liquid He. Rather we should look for a theory which considers a continuous interaction of the emitting atom with a number of perturbers. The static broadening theory is based on such an assumption.

In order to develop a broadening theory based on the static interaction of the radiating atom with the surrounding atoms, we need an expression for this interaction. We shall describe this interaction by the intermolecular potential energy function, which, for our purposes, gives
the total electronic energy of a polyatomic system as a function of the internuclear separations. Of course, this approach depends upon being able to specify internuclear separations between the atoms. The average velocity of a helium atom at 1.7°K as given by Gibbs and Harling\textsuperscript{11} corresponds to a de Broglie wavelength of 7. a\textsubscript{o} so that there is some question about the validity of this approach especially at small separations where the potential changes rapidly. The alternative, however, a solution of the polyatomic Schrodinger equation, is essentially impossible so that we will employ the intermolecular potential.

Suppose that we have a diatomic system, the optically active atom and the perturbing atom. Suppose further that the optically active atom has two electronic states with the corresponding intermolecular potentials $E_2(R)$ for the upper state and $E_1(R)$ for the lower and that the perturbing atom is in its ground state. If the distance between the two atoms were fixed at $R_0$, then we would see a single sharp emission line at the frequency

$$\omega = \left[ E_2(R_0) - E_1(R_0) \right] / \hbar = V(R_0) + \left[ E_2(\infty) - E_1(\infty) \right] / \hbar$$

$V(R)$ is the difference potential. The difference potential specifies the deviation of the radiation frequency from the
unperturbed atomic transition frequency as a function of the spatial configuration of the two atoms. However the two atoms are free to assume different positions with respect to each other. We can specify the probability of different configurations by a distribution function \( g(R) \) which gives the relative probability of finding a value \( R \) for the vector between the two atoms. It seems plausible that the spectral line intensity at a particular frequency will be related to the probability that the two atoms will be found in a configuration corresponding to that frequency difference between the two states. This is the fundamental hypothesis of static or statistical line broadening theory.

Two assumptions are necessary to describe the influence of \( N \) perturbing atoms on an optically active atom. The first is that the effects of all the perturbing atoms on the radiating atom are additive. Thus the electronic energy for a state is the sum of two body potentials. Similarly the frequency associated with a given configuration is

\[
\omega = \omega_o + V(R_1, R_2, \ldots, R_N) = \omega_o + \sum_{i=1}^{N} V_i(R_i)
\]

For long-range interactions of the dispersion or van der Waals type, this is probably a reasonable
approximation. Other types of interactions, such as the resonant dipole-dipole interaction, require more careful specification.

The second assumption is that the positions of the perturbers are not correlated. If \( P(R_1, R_2, \ldots, R_n) \) is the probability of finding \( N \) perturbers in a configuration specified by \( R_1, R_2, \ldots, R_n \), then from the assumption of uncorrelated motions

\[
P(R_1, R_2, \ldots, R_N) = \frac{1}{V_N} \prod_{i=1}^{N} g(R_i)
\]

where \( g(R) \) is the distribution function described above and \( \frac{1}{V_N} \) is a normalizing factor.

Static line broadening theory develops from the notion that the intensity of a particular frequency in a spectral line will be proportional to the probability for the existence of that spatial configuration of perturbers whose distorting effects correspond to radiation of that particular frequency. Thus

\[
I(\omega) \, d\omega \propto \frac{1}{V_N} \int \cdots \int g(R_1) \cdots g(R_N) \, d^3R_1 \cdots d^3R_N \, d\omega
\]

where \( I(\omega) \, d\omega \) is the intensity in a frequency interval \( \omega \) to \( \omega + d\omega \) and the integration is over a domain such that

\[
\omega \leq \omega_0 + V(R_1, \ldots, R_n) \leq \omega + d\omega
\]

We employ a delta function to allow the extension of the integration domain over all space. Using the
integral representation of the delta function we have

\[ I(\omega) d\omega \propto \frac{d\omega}{\sqrt{\pi}} \int d\tau \int \cdots \int d^3R \, g(R) \, d^3R \, \exp \left[ i \tau (\omega - (\omega_i + \sum_{j=1}^N V_j)) \right] \]

We change the frequency variable to \( \nu = \omega - \omega_0 \), the frequency measured from the unperturbed frequency and notice that the spatial integrations reduce to the product of \( N \) identical integrals so that

\[ I(\nu) d\nu = \int_{-\infty}^{\infty} \exp (i \nu \tau) \left[ \frac{1}{\sqrt{\nu}} \int d^3R \, g(R) \, \exp (-i \nu V(R)) \right]^N d\nu \]

Now consider the term in square brackets

\[ \frac{1}{\sqrt{\nu}} \int d^3R \, g(R) \exp (-i \nu V(R)) = \frac{1}{\sqrt{\nu}} \int d^3R \left[ 1 - (1 - \exp [-i \nu V(R)]) \right] g(R) \]

\[ = \frac{1}{\sqrt{\nu}} \int d^3R \, g(R) \frac{1}{\sqrt{\nu}} \int d^3R \left[ 1 - \exp [-i \nu V(R)] \right] g(R) \]

\[ = 1 - \frac{A(\tau)}{\nu} \]

since

\[ \frac{1}{\sqrt{\nu}} \int d^3R \, g(R) = 1 \]

We now have

\[ \left\{ \frac{1}{\sqrt{\nu}} \int d^3R \, g(R) \exp (-i \nu V(R)) \right\}^N = \left[ 1 - \frac{A(\tau)}{\nu} \right]^N \]

\[ = 1 - \frac{N}{\nu} A(\tau) + \frac{N(N-1)}{2!} A^2(\tau) \cdots \]

which is the limit that \( \nu \to \infty \) and \( N \to \infty \) such that \( \rho = \frac{N}{\nu} \) is a constant becomes

\[ \left\{ \frac{1}{\sqrt{\nu}} \int d^3R \, g(R) \exp (-i \nu V(R)) \right\}^N = \exp (-\rho A(\tau)) \]

and the intensity expression becomes

\[ I(\nu) d\nu \propto \int_{-\infty}^{\infty} d\tau \exp (i \nu \tau) \exp (-\rho A(\tau)) d\nu \]

where

\[ A(\tau) = \int_{\text{space}} d^3R \left[ 1 - \exp (-i \nu V(R)) \right] g(R) \]
Since we assumed that the perturbers were static and were constantly interacting with the radiating atom, we should expect the static line broadening intensity expression to describe the line shape in high density, low temperature situations. It has been applied to such situations with some success but we will postpone until the following section a more detailed discussion of its applicability.

We have seen two line broadening theories which started from different intuitive concepts of how a radiating atom is perturbed in various circumstances. With these ideas as a guide, we now will develop a more general line broadening theory based on the time dependent Schrödinger equation and its solution using perturbation theory. Our development will closely parallel that of Tsao and Curnutte.\textsuperscript{16}

We consider the case of absorption. The system includes the absorbing atom, the perturbing atoms, and the radiation field. The motion of the perturbers will be described by classical straight-line trajectories. The Hamiltonian for such a system is

\[ H = H_a + H_p + H_c + H_{ar} \]

where

- \( H_a \) is the Hamiltonian of the absorbing atom,
- \( H_p \) that of the perturbing atom,
- \( H_c \) that of the interaction of the
perturbers with the absorbing atom, $H_{ar}$ that of the interaction of the radiation field with the absorbing atom. The unperturbed part of the Hamiltonian is

$$H_0 = H_a + H_p$$

which determines a complete, orthonormal, time-independent set of eigenfunctions of the form

$$\phi_b \psi_i \cdots \psi_n$$

where $\phi_b$ is an eigenfunction of the bth state of $H_a$, and $\psi_i$ is an eigenfunction of the ground state of the ith perturber. Since the internal state of the perturber does not change, we will denote the product of $\phi_b$ and the N perturber eigenfunction simply as $\phi_b$.

To describe the time evolution of this system, we consider first the time development of the entire atomic system and then the interaction of the radiation field with the atomic system. The Hamiltonian of the atomic system is

$$H_i = H_a + H_p + H_c.$$ We solve the Schrodinger equation for this Hamiltonian in the adiabatic approximation. At $t = 0$, the atomic system is in the state $a$. At a later time $t$, according to the adiabatic assumption, the system is still in state $a$. The wavefunction at this time is

$$\Phi_a(t) = \phi_a(t) \exp \left[ \frac{i}{\hbar} \left( i \hbar \right)^{-1} \int_0^t E_a(t') dt' \right]$$

where

$$H_i(t) \phi_a(t) = E_a(t) \phi_a(t).$$
The adiabatic approximation is good only when the time-dependent part of the Hamiltonian varies in time with frequencies far from any resonant transition frequencies of the system. This condition is not met in the case of molecular spectra where one would expect collisions to induce transitions between rotational and perhaps even vibrational levels of the radiating molecule. For this reason, we consider only atomic transitions in this work.

In order to calculate the absorption intensity, we consider the effect of the radiation on the adiabatic atomic states. Using the method of variation of constants to compute the transitions induced by the radiation field, employing the semiclassical treatment of radiation, and using the adiabatic approximation to describe the time evolution of the atomic states, we obtain for the first order electric dipole transition amplitude

\[ a_k(T) = \frac{e}{\hbar c} | A \rangle \langle k_n | r_n \rangle \int_0^T dt e^{i \omega t} e^{i \xi} \int_0^T dt [E_k(T) - E_n(T)] \]

This result is derived in detail in Appendix 1. Then the average energy absorbed per second per unit intensity by a single atom is

\[ \frac{\hbar \omega_{kn}}{|a_k(T)|^2} \frac{1}{T} = \frac{1}{T} \frac{2\pi e^2}{\hbar c} \omega_{kn} | \langle k_n | r_n \rangle |^2 \int_0^T dt e^{i \omega t} e^{i \xi} \int_0^T dt [E_k(T) - E_n(T)]^2 \]
which agrees with Tsao and Curnutte's equation (41). Hence the absorption line is

\[ I(\omega) \propto \frac{1}{T} \left| \int_0^T dt \exp \left[ i(\omega t - \int_0^t dt' V(t')) \right] \right|^2 \]

where \( V(t) = V(R_i, t), \ldots, R_N(t) \) is the difference potential described earlier and the frequency \( \omega \) is now measured from the unperturbed resonant frequency.

Following the work of Anderson, we now show that this result reduces to the expression given by static line broadening. Express \( I(\omega) \) as

\[ I(\omega) \propto \frac{1}{T} \left| \int_0^T dt \exp (i \omega t) \varphi(t) \right|^2 \]

where

\[ \varphi(t) = \exp \left[ -i \int_0^t dt'' V(t'') \right] \]

Then

\[ I(\omega) \propto \frac{1}{T} \int_0^T dt \int_0^T dt' \exp \left[ i \omega (t-t') \right] \varphi(t) \varphi^*(t') \]

We make the change of variable

\[ \tau = t - t' \]
\[ d \tau = dt \]
\[ t_o = \tau' \]
\[ dt_o = dt' \]

The transformation of the domain of integration is shown in Figure 1. \( I(\omega) \) becomes

\[ I(\omega) \propto \frac{1}{T} \left\{ \int_0^T d \tau \exp (i \omega \tau) \int_{t_o}^{T-\tau} dt_o \varphi(\tau + t_o) \varphi^*(t_o) \right\} \]

\[ + \int_0^T d \tau \exp (i \omega \tau) \int_{t_o}^{T-\tau} dt_o \varphi(\tau + t_o) \varphi^*(t_o) \]

Consider the first integral and let

\[ (T-\tau) C(\tau) = \int_{t_o}^{T-\tau} dt_o \varphi(\tau + t_o) \varphi^*(t_o) \]

\( T \) is large. We use the ergodic hypothesis to replace
Figure 1 The change of variables used in the integration of the correlation function.
the time integrations with a configuration space average.

Thus

\[(T - \tau) C(\tau) = (T - \tau) \langle \varphi(\tau) \varphi^*(0) \rangle\]

where \(\langle \rangle\) brackets denotes the configuration space average which will be more precisely described later.

An identical result is obtained in the same way for the second integral. Then

\[I(\omega) = \frac{1}{T} \int_T^T (T - \tau) \langle \varphi(\tau) \varphi^*(0) \rangle \exp(i\omega \tau)\]

We take the limit as \(T \to \infty\) to obtain

\[I(\omega) = \int_{-\infty}^\infty \exp(i\omega \tau) \langle \varphi(\tau) \varphi^*(0) \rangle\]

The function \(C(\tau) = \langle \varphi(\tau) \varphi^*(0) \rangle\) is called the correlation function so that the intensity is given as the Fourier transform of the correlation function. Thus it is clear that the correlation function contains all the information that the intensity function does. When we discuss techniques for evaluating the intensity expression in the following sections, we shall find it convenient to work with the correlation function. Here we shall briefly describe some of its properties.

Suppose that the perturbing atoms occupied fixed positions in a perfect lattice. Then the difference potential
\( \psi(t) \) would be a constant, \( v_o \), and we would have

\[
\psi(t) = \exp\left[-i v_o t \right]
\]

and

\[
(T - \tau) C(\tau) = \int_0^{T - \tau} \exp\left[-i v_o (\tau + t_o) + i v_o t_o \right]
\]

\[
= (T - \tau) \exp\left[-i v_o \tau \right]
\]

so that

\[
C(\tau) = \exp\left[-i v_o \tau \right]
\]

The expression for the intensity becomes

\[
I(\omega) = \int \omega e^{i \omega \tau} e^{-i v_o \tau} d \tau
\]

\[
= \delta(\omega - v_o)
\]

so that the spectra would show a sharp peak at a frequency corresponding to the resonant frequency plus the perturbed frequency as we would expect.

Next we consider the case in which the perturbation may take different values. We represent the difference potential of these different perturbations by a set of functions \( V_i(t) \). Then the correlation function may be expressed as an average over these functions

\[
C(\tau) = \frac{1}{N} \sum_{j=1}^{N} e^{i \int_0^\tau V_j(t) dt}
\]

since each \( V_j(t) \) will represent a particular perturber configuration. We are interested in the cases for which \( \tau = 0 \), \( \tau \) is small and \( \tau \) is large.

If \( \tau = 0 \), then \( \int_0^\tau V_j(t) dt = 0 \) and \( C(0) = 1 \). For small \( \tau \), the arguments of the exponentials will be small so that
each of the terms in the above series will be slightly less than 1. Then $C(\tau) < 1$ for $\tau$ small. Finally when becomes large, the arguments of the exponentials will take essentially random values with respect to each other so that the terms will assume random values between 0 and 1 and the correlation function will vanish.

We may understand this behavior in terms of the electric dipoles induced in an atomic transition. The expectation value of the transition dipole for our system is

$$\mu(t) = e \langle \psi|\lambda|\eta\rangle \exp\left\{ (i \hbar)^{-1} \int_{0}^{t} d\tau [E_k(\tau)-E_n(\tau)] \right\} 
\propto \psi(t)$$

where $\psi(t)$ has been defined above. Then the correlation function for the transition dipole is

$$\langle \mu(\tau)\mu(0) \rangle \propto \langle \psi(\tau)\psi(0) \rangle = C(\tau)$$

The set of possible $V_i(t)$ correspond to a set of different time developments for the transition dipole. At $\tau = 0$, all of these are in phase so that $C(0) = 1$. As time progresses, each $V_i(t)$ causes the associated transition dipole to evolve with a slightly different time evolution than any other so that after a sufficiently long time all correlation is lost and the correlation function vanishes. We note that this effect depends on the existence of different possible perturbations of the atomic system and not on the explicit
time variation of the perturbations. In particular, the
effect will exist in the case in which all of the $V_i(t)$ are
different but constant in time. This explains why one may
speak of a correlation time in static line broadening
theory. These points will be discussed in more detail for
the case of a continuum of perturbed energies when we con-
sider the validity of the static approximation. We now
continue our development of the expression for the line in-
tensity.

As before, we assume that the total perturbation of
the radiating atom may be represented as the sum of the
interactions of the radiating atom with each perturber.
Again the difference potential for $N$ perturbers is
$$V(R_1(t), \ldots, R_N(t)) = \sum_{i=1}^{N} \nu(R_i(t))$$
and the correlation function becomes
$$C(t) = \left(\frac{1}{N}\right)^N \int d^3R_1 \ldots \int d^3R_N \ e^{-i \int_0^T \sum_{i=1}^{N} \nu(R_i(t)) dt} g(R_1) \ldots g(R_N)$$
where $g(R_1)$ is the distribution function discussed above.
This defines the configuration space average. Since all
the distribution functions and two-body intermolecular poten-
tials are identical, we have
\[ C(\tau) = \left[ \frac{1}{N} \int d^3R \ e^{-i \int_0^\tau \nu(R(t)) dt} g(R) \right]^N \]

\[ = \left[ 1 - \frac{1}{N} \int d^3R \ (1 - \exp(-i \int_0^\tau \nu(R(t)) dt)) g(R) \right]^N \]

\[ \exp(-\rho U(\tau)) \]

where \( U(\tau) = \int \left[ 1 - \exp(-i \int_0^\tau \nu(R(t)) dt) \right] g(R) d^3R \)

in the limit that \( N \to \infty \) and \( V \to \infty \) such that \( \rho = \frac{N}{V} \) = constant.

If the perturbers are static so that \( R \) is time independent, then

\[ U(\tau) = \int \left[ 1 - \exp(-i \nu(R) \tau) \right] g(R) d^3R \]

which agrees with the result of the intuitive static broadening theory.

In this section we have described a simple impact broadening theory, the static broadening theory, and the general adiabatic quantum mechanical theory. The general theory has been shown to reduce to the static theory in the limit of zero perturber velocity. These theories are restricted to cases in which there is no resonant interaction between perturbers and the radiating atom. For the case of resonant interaction, one must redefine the stationary states of the atomic system. The perturbation energies will then depend on these states and will not be well represented by simple sums of two-body potentials.

We have qualitatively suggested that the static broadening theory is the one to use for the case of liquid
helium but we have not shown this in any detail. In the next section we shall develop methods for evaluating the intensity expression which appears in these theories. In doing this, we shall give more formal justification for the use of static theory for this case.
C. The Application of Static Pressure Broadening Theory: Numerical and Analytic Techniques for Various Models

The choice of static pressure broadening theory does not finish the problem since one must still specify a two-body potential and distribution, and one must have some way of evaluating the intensity expression for a particular potential and distribution. We choose to present calculations for various potentials and distributions, both those contained in the literature and our own work, as an evolutionary process. It is thought to be valuable for both doing calculations and understanding the physical situation to present computations involving several different models.

Margenau around 1935 was the first to develop the static theory and apply it to spectra. He considered the case of a uniform distribution \( g(R) = 1 \) and represented the potential as a pure van der Waals' interaction where

\[
V(r) = -\frac{C}{R^6}
\]

Under these conditions, the intensity equation given above may be integrated in closed form to yield

\[
I(\Delta \nu) = \frac{2}{3} \pi \beta^{1/2} N (\Delta \nu)^{-3/2} e^{\chi \phi} \left[ -\frac{4}{9} \frac{\pi^3 \beta N^2}{\Delta \nu} \right]
\]

where \( \beta \) is the difference between the van der Waals coefficients for the upper and lower states and \( N \) is the number density. The shift corresponding to the maximum intensity is

\[
\Delta \nu_m = \left( \frac{2}{3} \pi \right)^3 \beta N^2
\]
The half-width is
\[ \delta = 82 \pi^3 \left( \frac{2}{3} \right)^2 \beta N^2 \]

Breene\textsuperscript{20} develops a rough measure of the validity of these results. He points out that the intensity of the shift corresponding to small separations of the perturber from the radiating atom should be negligible since the approximation of an attractive potential becomes invalid at small separations where the actual potential becomes strongly repulsive. Also, this repulsive force affects the perturbers so that the distribution function should vanish at small separations. Thus we take the ratio of the shift at a small separation to the shift at maximum intensity. For the case of liquid helium, we find that these shifts are comparable. Thus we should not expect the static theory using these simple potentials and distributions to provide very good results when applied to the case of liquid helium.

The next development of the static pressure broadening theory toward higher densities was a series of three papers by Bergeon, Robin and Vodar\textsuperscript{21} which appeared between 1952 and 1955. These authors recognized that repulsive forces must play an important role in determining line shifts and shapes at high densities. However they considered only a uniform distribution of perturbers.
We recall that the static theory provided the intensity expression

\[ I(A^\nu) = \int_{-\infty}^{\infty} d\tau \exp(i\tau \nu) \exp(-\rho A(\tau)) \]

where

\[ A(\tau) = \int_{\text{sph}} d^3R \left[ 1 - \exp(-i\tau V(R)) \right] q(R) \]

\( A(\tau) = J T V(h) q(B) \)

Bergeon, et al., used the spherically symmetric potential of the Lennard-Jones form.

\[ V(R) = -\frac{\alpha}{R^6} + \frac{\beta}{R^{12}} \]

and let \( g(R) = 1 \).

After changing to a set of reduced variables

\[ \delta = \frac{\pi \rho}{\sqrt{\alpha}} \]

\[ \eta = \left| \frac{\beta}{\alpha^2} \right| \nu \]

and

\[ z = \frac{\rho}{\beta} \tau \]

they found they could express the intensity as

\[ I(\eta) = \int_{0}^{\infty} e^{-\delta A'(\bar{x})} \cos(\delta B'(\bar{x}) + \eta \bar{x}^2) \bar{x} \, d\bar{x} \]

where

\[ A'(z) + i B'(z) = -e^{i\frac{\pi}{8}} \Gamma\left(\frac{1}{4}\right) F\left(\frac{1}{4}, \frac{1}{2}, -\frac{z}{4}\right) Z^{1/4} \]

\[ -e^{i\frac{3\pi}{8}} \Gamma\left(\frac{1}{4}\right) F\left(\frac{1}{4}, \frac{3}{2}, -i\frac{z}{4}\right) Z^{3/4} \]

and

\[ Z = \bar{x}^2 \]

\( \Gamma'(a) \) and \( F(a,b,u) \) are the gamma and confluent hypergeometric functions respectively. Bergeon, et al., numerically integrated the equation for \( I(\eta) \).

They compared these results and Margenau’s results with their experimental data of Na spectra broadened by A at relative densities up to 300. The Margenau theory began to fail
badly at a relative density of about 50. The results of Bergeon, et al., however, agreed very well with experimental values for the shift throughout the entire density range investigated. Their agreement with the observed half-widths was not quite as favorable since, while their theoretical curve for half-width as a function of density displayed the same shape as the graph of experimental values, the theoretical values lay below the experimental ones at the higher pressures.

We decided to apply this version of the static broadening theory to the liquid helium spectra. Approximate values for the parameters for the helium $^3\text{P} \leftrightarrow ^3\text{S}$ transition which appear in the Lennard-Jones potential were chosen based on the calculations of Kodaira and Watanabe. A computer program was written which evaluated the confluent hypergeometric function by a truncated infinite series

$$F(a, b, z) = 1 + \frac{a}{b} \frac{z}{1!} + \frac{a(a+1)}{b(b+1)} \frac{z^2}{2!} + \frac{a(a+1)(a+2)}{b(b+1)(b+2)} \frac{z^3}{3!} + ...$$

which is given in Gradshteyn and Ryzhik and the remaining integral by Simpson's Rule integration. The program was tested by reproducing the results of Bergeon, et al.

Potential parameters corresponding to the case of the $^2\text{S} - ^2\text{P}$ transition in liquid helium were used to com-
pute line shapes and the results compared with experiment. The asymmetric, very wide, and greatly blue-shifted lines computed did not agree with the almost symmetric, narrower, more moderately shifted lines observed. The principle cause of the disparity was the use of a uniform distribution of perturbing atoms which allows a non-vanishing probability for a perturber to be very close to the optically active atom. Because the intermolecular potentials are very large and repulsive in these regions, the perturbers should be excluded from this small volume lying about the optically active atom. By employing a model which places perturbers in this region, we are including the effects of these unphysical, large perturbations on the computed lines. It seemed that these effects could explain the greater part of the disparity between experiment and calculation and that the model distribution should be modified to exclude these effects.

The first change was to introduce a step function distribution and a program was written which integrated the intensity equation for such a distribution. One must now specify six parameters: the van der Waals coefficients and the position of the null value of the potential for both the initial and final states and the position of the distribution discontinuity for the upper and lower states. One can obtain
approximate values for the van der Waals coefficients, but four parameters will remain undetermined. Moreover, one is no longer able to represent the integral for the correlation function in terms of confluent hypergeometric functions so that the entire integration must be done numerically. This is difficult to do accurately because of the rapidly oscillating integrand for small R values. Since there are four unknown parameters, one would need to make a number of long computer runs to determine whether a set of parameters could be found to reproduce the observed spectra. This was not done. A few runs were made using different sets of parameters to determine whether the gross discrepancies of the previous model could be removed. This model predicted relatively small shifts and narrow lines at liquid helium densities. Thus we verified that the major problem with the previous model was the uniform distribution of perturbers which allowed unphysically large blue shifts.

Knowing that the static broadening theory could give sensible results at high densities, we needed a convenient model distribution which could be used in a more detailed study of the theory at these high densities. Somewhat arbitrarily we chose a Boltzmann distribution of the form

$$g(R) = \exp\left(-\frac{V_c(R)}{kT}\right)$$
where \( V_i(R) \) is the intermolecular potential for the initial state, \( k \) is Boltzmann's constant and \( T \) is the temperature. We do not suggest that this is correct or that \( T \) represents the physical temperature. \( T \) should be considered to some extent a free parameter but \( T \) should be fixed for both absorption and emission. We chose this distribution for the following reasons. First, it simply relates the potential to the distribution so that we eliminate two free parameters. Second, one would expect a density gradient about the radiating atom as opposed to a density discontinuity as in the step function distribution. Third, recent calculations by Pollock and Hansen \(^{24} \) of the distribution function for the \( 2^3S \) state of helium are of approximately this form. And fourth, with this distribution, the integral over configuration space may be represented by an infinite series.

Not including \( T \), we must know four parameters before we can begin our calculations. Two of these, the van der Waals' coefficients for the initial and final states, may be obtained from approximate calculations. The remaining two, however, are not known as accurately as is necessary for these calculations. If we have both the absorption and the emission spectra for a given transition, these coefficients
may be obtained by fitting the potentials to the observed shifts. An approximate expression for the shift is

$$\Delta \nu_{\text{max}} \approx \rho \int_{\text{space}} V_0(R) g(R) \, d^3R$$

where $\rho$ is the perturber density, $V_0(R)$ is the difference potential, $g(R)$ is the distribution function, and $\Delta \nu_{\text{max}}$ is the approximate position of the intensity maximum. This may be understood intuitively as the shift of the most probable distribution of perturbers. We shall see later that it is the mean value of the shift and so corresponds to the peak only if the line is sufficiently symmetric. A fitting procedure similar to this has been discussed by Margenau and Jacobson.¹⁵

A program was written to search for the positions of the null values of the potentials for given van der Waals' coefficients and empirical shifts. First subroutines were written to evaluate the integral for given values of the four parameters. The search routine involved successive applications of the half-interval method. A trial set of null positions were used to compute an emission shift. This was compared with the experimental shift and the lower state null position varied until agreement with the emission shift was obtained. The null position of the upper state
was then varied until agreement with the absorption shift was reached. A new value of the upper state null position was chosen, the shifts calculated to see if agreement with the experimental values had been found and, if not, the entire process repeated until agreement was reached. The integrals were calculated using Simpson's rule integration. For a typical set of initial positions and upper and lower bounds on the positions, the program required about 2 minutes of B5500 time to find values which reproduced the experimental shifts.

We are primarily interested in the \( ^3S-^3P \) transition in liquid helium. Most of our model calculations were done at a relative density of 750, which corresponds to a particle density of 2.99 atoms \( a_0^{-3} \). A value for the van der Waals coefficients of the \( ^3S \) state was obtained from the calculation of Victor, Dalgarno, and Taylor\(^26\) and for the \( ^3P \) from Hickman and Lane.\(^6\) These values are \( C_{2p} = 10.973 \times 10^6 \text{ cm}^{-1} a_0^6 \) and \( C_{2S} = 6.3413 \times 10^6 \text{ cm}^{-1} a_0^6 \).

The first attempt at integrating the intensity equation used a straightforward application of Simpson's Rule to compute both the correlation function and the Fourier transform. This approach was not successful since one must use a very small step size to accurately integrate the oscillating part of the
correlation function integrand and a very large upper bound to integrate the slowly decreasing difference potential at large internuclear separations. The computer code was modified to integrate the oscillating part and long range part of the correlation function integrand separately. The ratio of the long range region step size to the oscillating region step size was typically between thirty and fifty to one. An accurate integration of the intensity integral could then be done in one or two minutes of B5500 time. A more sophisticated version of this approach was used by Kieffer who developed a program which divided each oscillation of the oscillatory region into an equal number of intervals and then integrated each of these individually. He too integrated the long range part separately. This method was not tried for our problem as faster methods involving series expansions were found.

We recall that these difficulties with the oscillating part of the integrand of $A(t)$ did not arise in the calculation of Bergeon et al. because they were able to find an analytic expression for this integral. In the case we are considering now, an analytic expression for $A(t)$ also exists. We show in appendix 2 that $A(t)$ may be expressed in terms of parabolic cylinder functions. Using this technique, a line profile
involving computation of the intensity for two hundred frequencies could be obtained in about 25 seconds. This represents a factor of 6 or 7 faster than by the previous method.

The relative speed of these calculations enabled us to study the variation of the computed line profile as the values of the parameters of the model were changed. In the next chapter we shall discuss the dependence of the line shift and width on the temperature and density parameters. These results will illustrate the relation between the difference potential, the distribution function, and the line shape for the case of spherically symmetric distributions and potentials. The model developed by Hickman for the helium atomic transition makes use of non-spherical potentials and distributions, but the concepts we use to understand the simpler spherically symmetric case will be useful in understanding the Hickman model.

This approach to the calculation of line profiles may be simplified if we note that the parabolic cylinder functions involve confluent hypergeometric functions and gamma functions. The possibility that the configuration space integral could be expressed directly in an expansion involving gamma functions was investigated. Appendix 3 shows that such an expansion is possible and produces a simpler result. An intensity profile,
however, took about the same amount of computer in each case because the program written to evaluate the configuration space integral using the gamma function expansion had the capability of treating non-spherical potentials and distributions and was not optimized for the spherical case.

The expression for the approximate shift may also be evaluated using a similar expansion. A program was written to do this. This technique has in fact been used by Margenau and Jacobson\textsuperscript{25} to evaluate this expression for spherical potentials and distributions although they did not apply it to the intensity expression.

The next modification of the model involves the addition of an angle dependent part to one of the intermolecular potentials. We recall that we are interested in the $2^3P - 2^3S$ transition. The P state is not spherically symmetric so that we would not expect that the potential between an excited helium atom in a P state and a ground state helium atom to be spherically symmetric. Calculations by Hickman\textsuperscript{6} have shown that a term proportional to the second Legendre polynomial $P_2(\theta)$ should be added to both the attractive and repulsive parts of the potential. Thus for the $2^3P$ state, we choose a modified Lennard-Jones potential of the form
\[ V_p(R, \theta) = C_p \frac{R_p^6}{R^6} \left( 1 + a_1 P_2(\theta) \right) - C_p \frac{1}{R^6} \left( 1 + a_2 P_2(\theta) \right) \]

where \( a_1 \) and \( a_2 \) are the asymmetry parameters. Hickman's calculations show that \( a_2 = 0.4 \). We have fit Hickman's numerical repulsive potential to a \( 1/R^{12} \) repulsive term and found that \( a_1 = 1.80 \) although this becomes a poor approximation for small \( R \). The nonspherical difference potential becomes

\[ V_d(R, \theta) = V_{D_0}(R) + V_{D_2}(R) P_2(\theta) \]

where \( V_{D_0}(r) \) is identical to the spherical difference potential and

\[ V_{D_2}(R) = C_A \left( R_A^6 \frac{1}{R^{12}} - \frac{1}{R^6} \right) \]

where \( C_A = C_p \alpha_2 \)

and \( R_A^6 = R_p^6 \alpha_1 / \alpha_2 \)

The distribution for the emission case becomes

\[ g(R, \theta) = \exp \left( -\frac{1}{kT} V_p(R, \theta) \right) \]

as an extension of our previous model. The distribution for the absorption case is as before. The nonspherical distribution can be characterized by the dimensions of the equi-density contour at its largest and smallest points. For \( V_p(R, \theta) = 0 \), the largest radial value is \( 1.1R_p \) at \( \theta = 0 \) and the smallest is at \( 0.65R_p \) for \( \theta = \pi/2 \). This gives a cavity shape which is not too different from Hickman's.
The same procedure which had been used for the case of spherical potentials was planned for the nonspherical case. The correlation function and the expression for the approximate shift may be found by using an expression in gamma functions. The derivation is quite similar to that contained in appendix 3 and will not be given. The codes described above were written using these more general expressions. There is an additional integration over the angular coordinate which must be performed. Two different approaches were tried. The first computed the angular integral by Simpson's rule. The second employed a Gauss-Legendre quadrature procedure. The Gauss-Legendre method was 50-100% faster than the Simpson's rule method for comparable results. Appendix 3 contains the expressions for the intensity and approximate shift for this nonspherical case.
D. Arbitrary Potentials and Distributions and Moment Analysis

We might at this point recall the objective of our research. We want to describe the broadening of the atomic transition lines seen by Dennis $^3$ and Hill $^4$. We would like to be able to use the previous work done on this problem by Hickman $^6$ who computed numerical potential curves for the interaction of helium atoms in various excited states with helium atoms in the ground state and found parameters for a model distribution using a variational calculation. The existence of the Hickman potential in tabular form, however, precludes the use of the analytic techniques so far discussed. Moreover, the comments made earlier regarding the difficulty of a direct numerical integration of the equations involved apply here with the additional complication that the difference potential is not spherically symmetric but is cylindrically symmetric so that the integral involving the potential becomes a double integral and the direct calculation would thus be even more difficult and consume much more computer time. Thus the direct approach was judged not feasible and a different model sought.

Some effort was devoted to investigating various schemes for calculating the line profiles. The primary criteria for such
a scheme were, first, that it give accurate estimates of the line widths from the broadening theory, and, second, that computations of these widths could be complete within a reasonable amount of computer time. The following method seemed to best fulfill these criteria.

We recall that the line profile as a function of frequency $f$ is given by

$$I(f) = \int_{-\infty}^{\infty} d\tau e^{i2\pi f \tau} C(\tau)$$

where

$$C(\tau) = \exp \left( -\rho \int_{\text{space}} d^3 R \left[ 1 - \exp \left( -i2\pi \epsilon E(R)/\hbar \right) \right] g(R) \right)$$

The line shape is the Fourier transform of the correlation function. The problems arise when one wishes to evaluate the correlation function. The expression we shall derive can best be understood when expressed in dimensionless form. To do this, we shall need a characteristic energy for the system. Here we shall develop an expression for this energy. We begin by changing from energy units to inverse wavelength units.

$$V(R) = \frac{E(R)}{\hbar C}$$

and

$$t = 2\pi c \tau$$

where

$$I(v) = \int_{-\infty}^{\infty} dt e^{itv} C(t)$$

$$C(t) = \exp \left( -\rho \int_{\text{space}} d^3 R \left[ 1 - \exp \left( -i t V(R) \right) \right] g(R) \right)$$
It is the integral in the argument of the exponent of the correlation function which creates the problem, so it is this which we must express in an alternative form. Thus we use that

\[-\rho \left[ 1 - \exp(-itV(R)) \right] = \rho \sum_{k=1}^{\infty} \frac{1}{k!} (-i)^k V^k(R) t^k\]

to write

\[C(t) = \exp \left\{ \rho \sum_{k=1}^{\infty} \frac{1}{k!} (-i)^k \mathcal{M}(k) t^k \right\}\]

where

\[\mathcal{M}(k) = \int_{\text{space}} d^3 R \ V^k(R) \ g(R)\]

To examine the convergence properties of this integral, it will be convenient to work in dimensionless quantities. To do this we need to define the characteristic value of the energy for the problem. We shall now show that such a value is the second moment about the mean of the line profile. This analysis is also of value as it demonstrates that a certain amount of observable information about the line profile is, in principle, easily accessible from the theory.

We begin with some definitions. The mean value of the frequency measured from the unperturbed line is

\[m = \frac{\int_{-\infty}^{\infty} d\nu \ \nu I(\nu)}{\int_{-\infty}^{\infty} d\nu \ I(\nu)}\]

The \(n\)th moment about this mean is

\[M(n) = \frac{\int_{-\infty}^{\infty} d\nu \ (\nu - m)^n I(\nu)}{\int_{-\infty}^{\infty} d\nu \ I(\nu)}\]

We shall show that these quantities may be directly computed
the correlation function.

Consider the inverse Fourier transform of the intensity expression.

\[ F(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\nu s} I(\nu) d\nu \]

Then

\[ i \frac{d}{ds} F(s) \big|_{s=0} = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{-i\nu s} I(\nu) d\nu \big|_{s=0} \]

\[ = \frac{i}{2\pi} \int_{-\infty}^{\infty} \nu I(\nu) d\nu \]

\[ = \frac{i}{2\pi} m \int_{-\infty}^{\infty} d\nu I(\nu) \]

Likewise for the second moment about the mean

\[ G(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(\nu-m)s} I(\nu) d\nu \]

and

\[ i \frac{d}{ds} G(s) \big|_{s=0} = \frac{i}{2\pi} \int_{-\infty}^{\infty} (\nu-m) I(\nu) d\nu \]

\[ - \frac{d^2}{ds^2} G(s) \big|_{s=0} = \frac{i}{2\pi} \int_{-\infty}^{\infty} (\nu-m)^2 I(\nu) d\nu \]

\[ = \frac{i}{2\pi} M(2) \int_{-\infty}^{\infty} I(\nu) d\nu \]

and, in general,

\[ (i)^n \frac{d^n}{ds^n} G(s) \big|_{s=0} = \frac{i}{2\pi} \int_{-\infty}^{\infty} (\nu-m)^n I(\nu) d\nu \]

\[ = \frac{i}{2\pi} M(n) \int_{-\infty}^{\infty} I(\nu) d\nu \]

but

\[ F(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\nu s} d\nu \int_{-\infty}^{\infty} dt \ e^{i\nu t} C(t) \]

\[ = \int_{-\infty}^{\infty} dt \ C(t) \left( \frac{1}{2\pi} \right) \int_{-\infty}^{\infty} e^{i\nu (t-s)} d\nu \]

\[ = \int_{-\infty}^{\infty} dt \ C(t) \ \delta(t-s) \]

\[ = C(s) \]

so that \[ F(t) = C(t) \]

Note that

\[ F(0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I(\nu) d\nu = C(0) \]
but \[ C(t)\bigg|_{t=0} = \exp \left[ -\rho \sum_{\text{space}} d^2 R [1 - \exp(-i t V(R))] g(R) \right] \bigg|_{t=0} \]
so that
\[ \int_{-\infty}^{\infty} I(\nu) d\nu = 2\pi \]
and
\[ i \frac{d}{dt} C(t)\bigg|_{t=0} = \frac{1}{2\pi} m \int_{-\infty}^{\infty} d\nu I(\nu) \]
\[ = m \]
So that we have the result that the derivative of the correlation function at \( t=0 \) times \( i \) is the mean.

Likewise
\[ G(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\nu e^{-i(\nu-m)s} \int_{-\infty}^{\infty} dt e^{i\nu t} C(t) \]
\[ = \int_{-\infty}^{\infty} dt C(t) e^{im(s)(\frac{1}{2\pi})} \int_{-\infty}^{\infty} d\nu e^{i\nu(t-s)} \]
\[ = \int_{-\infty}^{\infty} dt C(t) e^{im\nu} \delta(t-s) \]
so that
\[ G(t) = C(t) e^{imt} \]
and
\[ (i)^n \frac{d^n}{dt^n} \left[ C(t) e^{imt} \right] \bigg|_{t=0} = M(n) \]
This gives the result that the \( n \)th derivative of the correlation function modified by the additional phase factor \( mt \) is proportional to the \( n \)th moment about the mean. We now calculate the mean and the second moment about the mean. Using the form of the correlation function with the series expansion in the argument of the exponential, we have
\[ m = i \frac{d}{dt} C(t) \bigg|_{t=0} \]
\[ = \left. i \frac{d}{dt} \left\{ \exp \left[ \rho \sum_{K=1}^{\infty} \frac{1}{K!} (-i)^K \mu(K) t^K \right] \right\} \right|_{t=0} \]
\[ = \left. \rho \sum_{K=1}^{\infty} \frac{K}{K!} (-i)^K \mu(K) t^{K-1} \right\} \exp \left[ \rho \sum_{K=1}^{\infty} \frac{1}{K!} (-i)^K \mu(K) t^K \right] \right|_{t=0} \]
\[ = \rho (-i)^1 \]
\[ = \rho \mu(1) \]

so that

\[ m = \rho \mu(1) \]

Likewise
\[ M(2) = (i)^2 \frac{d^2}{dt^2} \left\{ C(t) e^{imt} \right\} \bigg|_{t=0} \]
\[ = (i)^2 \frac{d}{dt} \left\{ \exp \left[ i (m - \rho \mu(1)) t + \rho \sum_{K=2}^{\infty} \frac{K (K-1)}{K!} (-i)^K \mu(K) t^K \right] \right\} \bigg|_{t=0} \]
\[ = (i)^2 \left\{ \rho \sum_{K=2}^{\infty} \frac{K (K-1)}{K!} (-i)^K \mu(K) t^{K-2} + \rho [i (m - \rho \mu(1))] \right. \]
\[ \left. + \sum_{K=2}^{\infty} \frac{K}{K!} (-i)^K \mu(K) t^{K-1} \right\} \exp \left[ \rho \sum_{K=1}^{\infty} \frac{1}{K!} (-i)^K \mu(K) t^K \right] \bigg|_{t=0} \]

but \[ m = \rho \mu(1) \]

\[ M(2) = \rho \mu(2) \]

If we continued these calculations we would find that

\[ M(3) \] had the same form as \[ M(2) \]. Beginning with \[ M(4) \], however, the expression for \[ M(n) \] would become more complicated as they consist of the sums of products of, in general, several \[ \mu \]-factors. We list the first six such moments in Table 1.

These moments clearly provide us with some qualitative information about the shape of the spectral line. First the existence of non-vanishing odd moments can occur only in
TABLE 1
SPECTRAL LINE MOMENTS FROM THE STATIC THEORY

<table>
<thead>
<tr>
<th>n</th>
<th>M(n) for line profile</th>
<th>M(n) for Gaussian distribution*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>( \rho \mu(2) )</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>3</td>
<td>( \rho \mu(3) )</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>( \rho \mu(4) + 3\rho^2[\mu(2)]^2 )</td>
<td>( 3\sigma^2 )</td>
</tr>
<tr>
<td>5</td>
<td>( \rho \mu(5) + 10\rho^2\mu(3)\mu(2) )</td>
<td>0</td>
</tr>
</tbody>
</table>
| 6  | \( \rho \mu(6) + 5\rho^2[3\mu(4)\mu(2) + 2(\mu(3))^2] \)  
                  \quad + 15\rho^3(\mu(2))^3 \) | \( 15\sigma^3 \)              |

* Gaussian distribution = \( \exp(-\nu^2/(2\sigma)) \)
the case of asymmetric profiles. For all of the calculations considered in this work, the odd factors did not vanish and the corresponding line shapes did exhibit some asymmetry. Indeed, the sign of the third moment tells us on which side of the mean we should expect to see the line fall off more slowly, positive third moments corresponding to long tails on the blue side of the mean and negative values the opposite. Moreover, the existence of the asymmetry prevents us from identifying the mean, with the position of the intensity maximum (the shift) a fact which has been stressed by Gordon. Nevertheless, if the line is not too asymmetric, then the mean should be an approximate value for the shift. This fact has been used by Margenau and Jacobson, by Hickman and by us in this work. For our model calculations, we found that the shifts did in fact differ from the means by as much as 30 cm$^{-1}$. We note that Hickman calculated quantities which were the means of the spectral lines and compared them with observed shifts. Part of the discrepancies between his theoretical and experimental shifts can be explained by small asymmetries in the spectral lines. We shall return to this point when we discuss the results of our calculations.

Second, an examination of Table 1 shows that, besides the existence of non-vanishing odd moments, there are further
differences between the line profiles and a simple Gaussian form. Thus we should not, a priori, expect that the line intensities should be given by a Gaussian distribution, a form which has been occasionally used to represent such lines.

Third, we should mention that similar results have been obtained by others. Rebane has computed the same first three moments using the Franck-Condon approximation which is equivalent to our assumptions. Recently Jacobson has examined the moments calculated from more general line broadening theories. He found expressions for the first and second moments which are equal to ours but that the expression for the third moment contains terms equivalent to ours plus a term which depends on the time variation of the potentials. This arises from an adiabatic theory which does not neglect perturber motion. Thus we should expect the mean and second moment about the mean to be given by our expressions in all cases and for our expression for the higher moments to be valid whenever the potentials change slowly in time. Clearly this condition will be met when the perturber motion may be neglected which is the essential assumption of the static theory.

Recall that we are interested in finding a characteristic energy of the perturbation. The square root of the second
moment should provide some measure of the line width. But the
line width should depend on the size of the deviations of the
perturbation from the average perturbation. We notice that
the square root of the second moment is just the root mean
square value of the perturbation which confirms these ob-
servations. Thus we take
\[ \alpha = \left[ \rho \mu(2) \right]^{1/2} \]
as the characteristic energy of the system. We then define
the reduced difference potential as
\[ U(r) = \frac{1}{\alpha} V(r) \]
and a reduced time
\[ S = \alpha t = 2\pi c \alpha \tau \]
The expression for the correlation function becomes
\[ C(s) = \exp \left\{ \rho \sum_{k=1}^{\infty} \frac{1}{k!} (-i)^k \eta(k) S^k \right\} \]
where
\[ \eta(k) = \int_{\text{space}} d^3R \, U^k(R) \, q(R) \]
There is little more which may be said at this point.
The question of the convergence of this series depends on the
set of coefficients \( \{ \eta(k) \} \) and these depend on the details
of the potentials and distributions. They shall be discussed
when we consider line profiles calculated using these expressions.
The final line profiles are calculated by numerically computing
the set \( \{ \eta(k) \} \) and using these in numerically taking the
Fourier transform.
E. A Criteria for the Validity of the Application of Static Line Broadening Theory

As the name implies, static line broadening theory may be used to describe perturber broadening of spectral lines for those cases in which the perturbed potential may be taken to be slowly varying. It is, however, not immediately clear what the time variation in the perturbation is to be compared with. In our development of the theory, we have stressed the role of the correlation function which describes the time correlation of the transition dipoles of the atomic system. One can define a correlation time as the time at which the correlation function has decayed to some fraction of its original value but the physical meaning of the time requires some discussion.

We recall that the expression for the correlation function as a time integral was essentially

\[ C(t) = \frac{1}{T} \int_0^T dt \, \psi^*(t + t_0) \psi(t_0) \]

where \( \psi(t) \) expresses the time dependence of the transition dipole. For the static case, the form of \( \psi(t) \) is

\[ \psi(t + t_0) = e^{i V(t_0) t} \]

\( V(t_0) \) represents the difference between the intermolecular potentials for the two states involved in the transition.
However, due to the movement of the perturbing atoms, these are not stationary states of the excited atom and we cannot know the precise energies of these states. Hence, we cannot know the time dependence of the wavefunction describing the states. To a zeroth approximation, the time dependence is the same as in the unperturbed case so that the observed spectral line falls near the dilute gas line. If we use a better approximation, we consider the range of possible energies available to these states at the beginning of an absorption or emission event. Then even if we neglect further changes in the energy during the optical process, we find we have a spread of possible frequencies which describe the time evolution of the states. In particular in the theory, as we do not know when a photon is absorbed or emitted, we integrate over all times and assign some energy $V(t)$ to each time. When we go to compute the transition probability we then find that the different phases of the different possible energies cause destructive interference and give the correlation function its characteristic behavior. The details of this destructive interference may be more clearly presented by measuring energies from the mean value of the spectral line and considering a certain spread of possible energies about that mean. Then
from the form of the correlation function, it is clear that we can expect destructive interference after a length of time corresponding to the reciprocal of this energy spread. The range of possible energies depends upon the magnitude and shape of the two potentials, the shape of the initial distribution function and its relation to the difference potential, and the density which partly determines the total magnitude of the perturbation. These are precisely the quantities which we should have expected to be reflected in the width of the spectral line. Mathematically they are connected through the relation between the width of the correlation function and the width of the intensity distribution, its Fourier transform. It is well known that the greater the mean extent of a function, the smaller the mean extent of its transform. The famous uncertainty principle of quantum mechanics is an example of this. Thus the greater the spread of possible perturbed energies, the smaller will be the time corresponding to constructive interference of the time development of the wavefunction and non-negligible values of the correlation function and so the narrower the correlation function. But a narrow correlation function corresponds to a broad intensity distribution as its Fourier transform as we expected.
This analysis provides a criteria for the validity of static broadening theory. Suppose we define a correlation time as the time at which the correlation function has decayed to some fraction of its original value. Then if this time is less than the time necessary for the perturbing atom to have moved a sufficiently great distance to change the value of the potential, then we may say that the static broadening theory is applicable. We shall see when we consider the results of calculations using Hickman's potentials, that the correlation time is of the same order of magnitude as the time for the perturbing atoms to move a significant distance so that we should expect static broadening theory to give a good, though not excellent, description of line breadths.
III. THE SPECTRA OF ELECTRON-BOMBARRED LIQUID HELIUM

In the development of the previous chapter, we have seen that when a quantum mechanical system makes an electromagnetic transition between two states in the presence of a perturbing field, the spectrum of the emitted or absorbed photons is modified by the perturbation. In some cases, the perturbing field may be described as assuming random values and as static in time. For this case, static line broadening theory provides an expression for the line profile. Let be the frequency as measured from the unperturbed value.

Then

\[ I(\nu) = \int_{-\infty}^{\infty} e^{i\nu \tau} C(t) \]

where

\[ C(t) = \exp \left\{ -\rho \sum_{\text{space}} d^3R \left[ 1 - \exp(-iTV(R)) \right] g(R) \right\} \]

and C(t) is the correlation function.

\( V(R) \) is the difference between the perturbing potentials of the two states, and

\( g(R) \) is the distribution of perturbers.

We have applied this theory to the \( ^2S - ^2P \) transition of helium in liquid helium (both absorption and emission).

The object of the study was to allow us to use a numerical
potential and a particular distribution developed by Hickman in calculations of the line shape. In the process of doing this, preliminary studies were made using various analytic potentials and distributions in order to more fully understand the theory and to provide a check on the approximations which were eventually employed. All together, six different combinations of potentials and distributions were considered. These are:

a. van der Waals potential, uniform distribution
\[ g(R) = 1 \]
\[ V(R) = \frac{-c}{R^6} \]

b. Lennard-Jones potential, uniform distribution
\[ g(R) = 1 \]
\[ V(R) = \frac{b}{R^{12}} - \frac{c}{R^6} \]

c. Lennard-Jones potential, step-function distribution
\[ g(R) = \begin{cases} 
0 & R < R_c \\
1 & R \geq R_c 
\end{cases} \]
\[ V(R) = \frac{b}{R^{12}} - \frac{c}{R^6} \]

d. Lennard-Jones potential, Boltzmann distribution
\[ g(R) = \exp[-\beta V_i(R)] \]
\[ V(R) = \frac{b}{R^{12}} - \frac{c}{R^6} \]
e. Nonspherical potential, nonspherical distribution

\[ g(R) = \exp[-\beta V_i(R, \Theta)] \]

\[ V(R, \Theta) = \frac{b(\Theta)}{R^2} - \frac{c(\Theta)}{R^6} \]

f. Hickman model

\[ g(R) = 1 - [1 + \alpha(R-R_0(\Theta))] \exp[-\alpha(R-R_0(\Theta))] \]

Numerical potential

The results of these studies are described below.
A. van der Waals Potential, Uniform Distribution

For this case, the intensity equation may be integrated in closed form. Wiley Dennis considered this case in his thesis and shows a graph of the type of line shape one contains. It is characterized by marked asymmetry and goes to zero at the unperturbed line position. For these reasons, Dennis rejected this theory. In fact, these features are peculiar to this case and indicate that one must use a more realistic potential and distribution but not that static broadening theory is not applicable.
B. Lennard-Jones Potential, Uniform Distribution

This case is characterized by a uniform distribution of perturbing atoms at all points in space. As one might expect, this leads to difficulties at high densities as very large perturbations arising from atoms lying close to the center of the potential begin to dominate the line shape. The calculations described earlier for this case were performed using reasonable values for the parameters of the difference potential at several densities. One finds at low densities that the calculations predict a red shift. As the density is increased to a relative density of 300, the red shift remained but the line became severely asymmetrical rising sharply on the red side and falling very slowly on the blue. As the density was further increased, the red-shifted maximum disappears and the intensity rises toward larger blue shifts until a blue shift of 200 cm.\(^{-1}\) is reached at which point most of the calculations were terminated. We show a graph of these results in figure 2.

This behavior is completely at odds with the observed spectra. First, the observed lines are only slightly asymmetrical. Second, in neither emission nor absorption spectra are very large blue shifts observed. And third, this model
Figure 2 Line shapes computed with a Lennard-Jones potential and a uniform distribution.
is not able to predict the differences between absorption lines and emission lines. As mentioned above, these problems seem to reflect the uniform distribution of perturbers which allows unphysically large perturbations. Clearly we must modify the distribution. The first modified distribution is the step-function distribution.
C. Lennard-Jones Potential, Step-function Distribution

Calculations were done using the step-function distribution of perturbers suggested by Dennis in his thesis. Here all integrations are performed numerically. Typical results showed smaller shifts and narrower lines and thus suggested that static line broadening theory could be applied and give reasonable results. However, including van der Waals coefficients, one has to specify six parameters for each calculation and these all-numerical integrations are time consuming so that an extensive investigation of width and shift dependence on various parameters was not undertaken.
D. **Lennard-Jones Potential, Boltzmann Distribution**

In this case the configuration space integration may be represented by a series and the computation time is thus substantially reduced. We recall that for this case there are the five parameters $T, C_p, C_s, R_p, R_s$. $T$ is a temperature-like variable which determines the height and width of the perturber distribution immediately outside the excited atom's cavity. $C_p$ and $C_s$ are the van der Waals coefficients for the upper and lower states, and $R_p$ and $R_s$ are the positions of the zeroes of the upper and lower state potentials. The van der Waals coefficients are known from prior calculation and are not varied. $R_p$ and $R_s$ are found by using the approximation which equates the observed shift with the mean value of the perturbed spectrum. A code was written which varies these two parameters until agreement between the mean value and the observed shift is found. $T$ is not determined and a range of values for $T$ should be considered. It is also interesting to vary the perturber density for fixed values of $C_p, C_s, R_p, R_s$ and $T$.

Figures 3 and 4 show the dependence of the calculated shift and half-width on the temperature parameter both in absorption and emission at liquid helium density. The
Figure 3 Absorption half-width and shift for a spherical potential and Boltzmann distribution.
Figure 4 Emission half-width and shift for a spherical potential and Boltzmann distribution.
behavior of these quantities and the ones to follow reflects the relation between the distribution and the difference potential. We show the upper and lower state potentials and distributions and the difference potential in figure 5 for the case of $T = 3$. As $T$ increases, the distribution maxima become small and wider. Now consider figure 3. For the smallest values of $T$, the distribution is quite sharply peaked over some positive value of the difference potential. However, the distribution does not extend very far onto the difference potential. Thus the range of possible perturbations is small. This results in a relatively narrow line showing a large blue shift. As $T$ increases, more of the distribution begins to overlap negative regions of the difference potential so that some of the blue shift is cancelled. The range of different perturbations available has not changed a great deal, however, so that the line remains of about the same width. As $T$ increases still more, the distribution begins to overlap the more positive parts of the difference potential. Since the difference potential increases rapidly, a relatively small amount of overlap here may produce large effects and we see the shift swing back to become more blue. However, this time we have a large range of shifts available so that the width is also large.
The Lennard-Jones potentials and Boltzmann distributions.
The case of the emission profile is very similar. We see the same increase of width and shift as $T$ increases for the large values of $T$. The different behavior of the emission shift for small values of $T$ simply reflects the fact that here the distribution is sharply peaked over a negative value of the difference potential.

Based on this analysis, we can qualitatively predict what one should see if the temperature of the helium were raised. Since we are in the region of larger values of $T$, one should expect the absorption lines to become wider and more blue shifted, and the emission lines to also become wider, although not as much as in the absorption case, and the shift to move a little toward the blue. Finally we point out that these studies have been done in a region in which the thermal energies are comparable to the potential energies. For higher temperatures, the distribution should not be so sensitive to small changes in the temperature so that we should not see such pronounced effects.

The usual line broadening problem involves a study of shift and width as a function of perturber density. Some studies of this sort were done for this case and are shown in figures 6, 7, 8, and 9. This analysis is also based on the relation between the difference potential and the distribution.
Figure 6 shows the calculations for the shift as a function of density for three different temperatures. For the smaller temperatures, the distribution is sharply peaked over negative values of the difference potential. Thus the main effect of an increase in density is to proportionally increase the number of perturbers in this region which causes a linear increase of shift with density. For the higher temperatures, the distribution is spread over a greater range of the difference potential so that contributions from positive regions of the difference potential become more important. One should realize that this is not a linear theory in density. Thus as density increases, the effect of configurations of perturbers involving several perturbers in positive valued regions of the difference potential become more important non-linearly. This is why the shift at higher temperatures shows deviations from linearity.

Figure 7 shows the absorption shift for the same temperature and density regions. Here the departures from linearity are even more pronounced. One sees that for smaller densities, the contributions from perturbers in the shallow negative difference potential region dominate,
Figure 6 The dependence of computed emission line shift on density for three temperatures.
Figure 7 The dependence of computed absorption line shift on density for three temperatures.
but, as the density increases, the effect of the perturbers lying closer to the atom become more important. Again these effects are more pronounced for the larger temperatures whose distributions have a greater spread along the difference potential. This reversal of the direction of the shift has been seen in systems similar to ours. In their review paper, Chen and Takeo report such behavior for the $^{2}P_{3/2} - ^{2}S_{1/2}$ transition of Rb perturbed by argon and for Rb perturbed by N$_2$ in absorption at high density. They offer no theoretical explanation but suggest on the basis of the experiments that when the pressure is sufficiently high the shift will be toward the violet for all gases. Our calculations and analyses would support this conclusion for all cases in which the positive part of the upper state potential is greater than the positive part of the lower state potential. This still allows two possibilities for the negative parts of these potentials. If the van der Waals coefficient for the upper state is greater than the van der Waals coefficient for the lower state, one would expect to see the shifts depend on the density as described above. However, if the situation is reversed, one would expect to see no red shifts at any density but rather increasing blue shifts. Takeo and Chen
report that this situation is seen in the absorption spectra of several of the alkali atoms perturbed by helium so that we could infer this relation between the van der Waals coefficients.

Figure 8 shows the width at half maximum as a function of density for the emission case at several temperatures. Here the width increases essentially linearly with density since the possible values of the perturbation will increase in this way for these values of difference potential and distribution. The greater temperatures show greater widths at high densities for the same reason.

The absorption case shown in figure 9, is more interesting. Here the widths increase more rapidly than the density for lower densities then begin to increase less rapidly. The point at which this increase begins to change corresponds approximately to the density at which the shifts begin to reverse the direction of their change with density. This supports the idea that at about this density the effects of the perturbations produced by the positive region of the difference potential begin to dominate so that a smaller range of the distribution is causing the increases in the width. Thus the width does not increase so quickly. Again the effect is more noticeable in the higher temperature cases.
Figure 8 The dependence of computed emission line width on density for three temperatures.
Figure 9 The dependence of computed absorption line width on density for three temperatures.
Takeo and Chen do not report the widths for the cases mentioned earlier for the shifts so that we cannot make comparisons with experiments.

This completes our discussions of the behavior of the intensities calculated from spherical potentials as a function of temperature and density. Additional studies were done on the dependence of the positions of the zeroes of the potentials as a function of temperature and we show these in Table 2. We recall that in this model the zeroes of the potentials determine the position of the distributions. Thus it is interesting to compare these values with Hickman's although Hickman used a distribution of a different form. The values for $T = 3$ compare well with Hickman's values while the values at the other two temperatures are somewhat too small.
TABLE 2

ZEROES OF THE SPHERICAL LENNARD-JONES POTENTIAL AS A FUNCTION OF TEMPERATURE

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>$R_p(a_o)$</th>
<th>$R_s(a_o)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>9.63</td>
<td>8.92</td>
</tr>
<tr>
<td>10.0</td>
<td>8.51</td>
<td>7.88</td>
</tr>
<tr>
<td>15.0</td>
<td>8.21</td>
<td>7.60</td>
</tr>
</tbody>
</table>
E. Nonspherical Potential, Nonspherical Distribution

For this case one must decide upon some simple form to represent the nonspherical part of the upper state potential. As described before, we took this to be proportional to the second Legendre polynomial where the proportionality constant was found by a comparison to Hickman's potentials in the region of interest. In the initial attempts at fitting potentials of this form to the observed shifts, no solutions to the fitting equations could be found for any value of the temperature. When the asymmetry of the repulsive part of the potentials was reduced, however, fits could be obtained. Intensities were calculated using these positions of the zero values of the potentials but very little analysis has been done since there are a number of parameters and it is not clear how the results for different parameter sets should be compared.
F. Hickman Model for the $2^3S-2^3P$ Transition

Wiley S. Dennis, J. Clifton Hill and others have studied the optical spectra of electron-bombarded liquid helium. They observed atomic and molecular spectra in both emission and absorption. The following section discusses the molecular spectra. In this section, we describe the $2^3S-2^3P$ transition of atomic helium. This particular transition is best known experimentally and offers the greatest possibility of quantitative description from a priori calculations.

The analysis described in this thesis and in this section especially complements that of A. P. Hickman. Hickman calculated approximate atomic wavefunctions for this transition by a variational method. He then used a pseudo-potential developed by Kestner et al. to describe this interaction between a zero energy electron and a ground state helium atom. This electron was placed in a particular excited atomic orbit and its contribution to the intermolecular potential was calculated using the approximate wavefunction. The complete intermolecular potential is given by adding this potential to the potential between the helium ion core and a ground state helium atom and the long-range attractive
potential associated with the van der Waals interaction.
To compute properties of the spectral line shape, the equilibrium configuration of the liquid atoms about the excited atom must be known. In Hickman's model, the total energy of a liquid configuration is given as the sum of the intermolecular potential integrated over a model distribution function, the energy associated with the surface tension due to the perturbers forming a cavity or bubble about the excited atom, the pressure-volume work necessary to create such a cavity, and a term associated with the change in kinetic energy of the liquid atoms forming the edge of the cavity. The total energy will then depend upon parameters related to the radius of the cavity $R_o$, its shape $\beta$, and the length of the interval over which the perturber distribution increases from zero to the average liquid density. These three parameters were varied in the distribution function and a minimum found for the total energy. The values of these parameters at this energy minimum specified the equilibrium perturber configuration. Finally Hickman calculated the mean value of the shift of the spectral line and compared that with the maximum of the observed spectral line.
The experiments which produced the spectral data described here involved the bombardment of superfluid helium by a beam of 160 keV. electrons. Windows in the liquid helium dewar allowed the absorption and emission spectra of the excited species to be studied. The details of the experiments are well described in the theses of Dennis and Hill and will not be repeated here.

The $^3S-^3P$ transition was chosen for detailed investigation for four reasons. First, it is an atomic transition so that the perturbations caused by the liquid atoms on the electronic states may be studied without the complication of closely spaced rotational levels. Second, simple approximate wavefunctions for the atomic states should be more accurate than similar wavefunctions for the molecular states. Third, this is a triplet state so that the complications involving the dipole-dipole resonance interaction peculiar to the singlet atomic spectra need not be considered. And fourth, this is the only atomic state for which both absorption and emission spectra were observed. The analysis above should make clear the intimate relation between the two spectra which makes knowledge of both very desirable. However, Hill mentions a major problem in interpreting the
absorption data for this transition. There is a spectral feature at 9232. cm\(^{-1}\) which Hill interprets as the atomic absorption line. His reasons for this assignment include the fact that the position of the unperturbed transition is 9234. cm\(^{-1}\) and, in absorption, the molecular lines generally lie quite close to their unperturbed positions. The (0 -1) \(\ce{ca}\) molecular transition is expected near 9271. cm\(^{-1}\) although its intensity should be only about one-seventh of the intensity of the observed feature. This position lies within the envelope of the feature at 9232. cm\(^{-1}\) which has a half-width of approximately 100. cm\(^{-1}\). The observed line is somewhat asymmetric, decreasing more rapidly for long-wavelengths than for short-wavelengths. Finally the (1-2) \(\ce{ca}\) transition appears with a maximum at 9108. cm\(^{-1}\) so that this line overlaps the long-wavelength end of the atomic transition. These overlapping lines will prevent us from making detailed comparisons between computed and observed line profiles.

The emission line, however, does not suffer from any of these problems. In the emission spectra, a feature is observed with a peak at 9165. cm\(^{-1}\) and a half-width of approximately 30. cm\(^{-1}\) The profile of this line is only
very slightly asymmetric, decreasing only a little more slowly on the long-wavelength side than the short-wavelength side.

The analysis of these observations begins with the line broadening theory in the static perturbation approximation. The potential and distribution produced by Hickman are used. The calculation of the line profiles make use of the expansion for the configuration space integral discussed in the last section of the second chapter. This approximation of the configuration space integral by a sum with a finite number of terms implies that the correlation function will be accurately represented by this approximation for only a finite time interval. For times longer than this the integration in the Fourier transform of the correlation function is truncated. The error introduced by this truncation is discussed in appendix 4. In principle, we can make this error as small as we please but only at the cost of very long running times on the computer now employed for this calculation, a Burroughs B5500. We hope to develop a code based on this approximation scheme in which the desired accuracy of the result in the only factor determining the number of terms in the series expansion. This program would
then be run on a faster machine. However, this has not yet been done. The available results seem sufficiently accurate for our purposes.

The results of this calculation are shown in figure 10 as a function of the cavity size $R_0$ and the asymmetric $\beta$. The absorption shift and width correspond to $\beta = 0$ since the initial state is the spherically symmetric $S$ state. The emission case corresponds to a non-zero value for the asymmetry since the initial state is the cylindrically symmetric $P$ state. In particular, Hickman found that the total energy of the excited atom and cavity was minimized by choosing $\beta = .3$ or .4 depending on the value specified for the surface tension constant. These results are presented as a function of $R_0$ since the shift and width are clearly sensitive to this parameter. The errors arising from approximations made in the calculation are discussed in appendix 4.

Hickman gives the radius of the equilibrium cavity configuration as 9.5 or 10. $a_0$ in the case of absorption. The graph shows that cavities of this size yield shifts close to the observed value of 2. cm$^{-1}$ blue. The agreement with the observed width is 100. cm$^{-1}$ and the computed widths are 50.-75. cm$^{-1}$ for cavities of this size. However, as there is
Figure 10  Half-widths and shifts computed with the Hickman model.
some uncertainty in the experimental value since adjacent spectral lines overlap and because the width depends strongly on the cavity size in this region, the observed and calculated widths are not in strong disagreement. Finally, the calculated line is asymmetric in the same sense that the observed line is asymmetric.

The agreement between the observed and calculated quantities in the emission spectra, however, is not quite as favorable. Hickman's cavity size for emission is 9.5 $a_0$. The largest calculated shift is for $\beta = .4$ and that value is 20. cm$^{-1}$ less than the observed value of 69. cm$^{-1}$ red. Moreover, the calculated widths are three times larger than the observed widths of 30. cm$^{-1}$. These quantities also depend on the cavity size but adjusting $R_c$ to provide better agreement with the observed widths would cause greater disparity between observed and calculated shifts. The observed emission line has slight asymmetry. The calculated lines are asymmetric in the same sense as the observed lines but show greater amount of asymmetry. To more accurately describe the experimental results, either the line broadening theory, the potentials, or the distributions will require some modification if we are to have agreement between theory and experiment. The validity of the line broadening theory will be described in a subsequent section. The potentials
could be modified but we should not expect the form and behavior of the potentials to change much. An alternate form which should significantly modify the computed line shapes is possible for the distribution function. To understand the effect of the distribution on the line shapes, the relation between the distribution and the difference potential must be considered.

Figure 11 shows a cross-section of the cavity for $R_0 = 9.5$, $\beta = 0.4$. It also shows the equipotential line for which the difference potential vanishes. The effect of the nonspherical cavity compared to a spherical one is to exclude a region of positive-valued difference potential and to include a region of negative-valued potential. This is also seen in the figures 12 and 13. These show liquid atom distributions and difference potentials for $R_0 = 9.5$, $\beta = 0.0$, 0.3, and 0.4 for the two directions $\theta = 0$ and $\theta = \pi/2$. One should notice that as the cavity is made more asymmetric, the distribution overlaps larger negative-valued regions of the difference potential and smaller positive-valued regions. This explains why the computed shift becomes more negative as the asymmetry of the cavity is increased. Also as the cavity size is increased, regions
Figure 11 Cross-section of the difference potential null surface and the cavity boundary.
Figure 12. Distribution functions and difference potentials for three values of $\beta$ in the $\theta = \pi/2$ direction. $R_0 = 9.5$. 
Figure 13. Distribution functions and difference potentials for three values of $\beta$ in the $\theta = 0$ direction. $R_0 = 9.5$. 
in which the difference potential is smaller in absolute size dominate and the computed spectra shows evidence of less perturbation.

These figures may be used to understand the behavior of the computed line width. It has been explained earlier that the width depends on the spread of possible perturbed energies for the system. If one picks a particular value of the distribution function and compares the spread of the values of the difference potentials for various values of for that value of the distribution, one may see that these spreads are approximately of the same size. This explains why the computed widths vary so little as a function of $\beta$. The widths do of course depend strongly on the cavity radius since the difference potential decreases in absolute size very quickly as a function of the radial distance from the atom.

This analysis suggests how the distribution function may be modified to achieve greater agreement with observed emission spectra. The distribution function must produce larger shifts but smaller widths. Consider a distribution function that rises sharply from the cavity edge to a maximum and then decays to unity. This places a larger number
of perturbers over the large negative-valued region of the
difference potential which should produce an additional red
shift in the observed spectra. If we allow the cavity to
expand, the distribution peak will overlap smaller, more
slowly varying regions of the difference potential so that
the width could also be adjusted. Another reason for con-
sidering this form for the distribution function is that such
a form has been calculated for the distribution of liquid
atoms surrounding a $^2S$ helium atom by Hansen and Pollock$^{24}$. The calculation of line shapes using this form of the dis-
tribution function is planned once the codes have been modi-
fied for the faster computer.
G. The Molecular Spectra

The molecular spectra of electron-bombarded liquid helium has been well described in the theses of Dennis and Hill. In this work, we do not calculate line profiles for molecular transitions. It is possible, however, to obtain a qualitative explanation of certain features of the molecular spectra by applying ideas developed in the preceding sections. In this section, we consider several of the observed electronic transitions of He₂.

Hill has begun this sort of analysis with a discussion of the \( \frac{3}{2} \Sigma^+ \rightarrow \frac{1}{2} \Sigma^+ \) transition. This molecular transition is an analog of the \( 2^3S-2^3P \) atomic transition since the excited electron undergoes a transition between a \( 3p\sigma \) orbital and a \( 2s\sigma \) orbital. The \( 3p\sigma \) orbital is large compared to the \( 2s\sigma \). In emission the cavity boundary will lie in the region where the difference potential is small in absolute size. But for absorption, the small \( 2s\sigma \) orbital will determine that the intermolecular potential for this state is small for some rather large values of the difference potential. Thus the cavity boundary will lie in regions in which the difference potential is large, and, as in the atomic case, in emission we should expect to see small shifts and relatively narrow
lines. The absorption spectra should display large blue shifts and fairly wide lines. The observed emission line is shifted 15. cm\(^{-1}\) blue and has a width of 38. cm\(^{-1}\) while the absorption line is shifted 105. cm\(^{-1}\) blue and has a width of 73. cm\(^{-1}\).

When a transition is observed in emission and absorption, it may be analyzed in terms of one difference potential and two different distributions, as we have just seen. A different situation arises in the case of two absorption lines which originate from the same state. Here it is the distributions which are the same and the difference potentials which are different.

The absorption transition \(a^3\Sigma_u^+ \rightarrow b^3\Pi_g\) is observed. The excited electron in this state occupies a 2p\(\Pi\) orbital with an energy between that of the a and c states. We should expect this orbital to be less extended than the 3p\(\sigma\) orbital so that, for a particular value of \(R\), the difference potential should be smaller in absolute value than that of the previous case. Since the distribution functions are originally the same in both cases, we should expect to see the \(a^3\Sigma_u^+ \rightarrow b^3\Pi_g\) transition less blue shifted and narrower than the \(a^3\Sigma_u^+ \rightarrow c^3\Sigma_g^+\) transition. It is observed to be only
3. cm$^{-1}$ blue shifted and 22. cm$^{-1}$ wide. Thus the 2p$\pi$ orbital in the liquid is probably of about the same size relative to the 2s$\sigma$ as are the atomic 2s and 2p orbits for which calculations were performed. The 3p$\sigma$ orbital, however, must be quite large compared to the 2s$\sigma$.

A more quantitative discussion of the molecular spectra awaits better molecular wavefunctions and liquid distribution functions. Moreover, an adiabatic line broadening theory has been used throughout this work. For some molecular states, one must consider collision-induced transitions between rotational states. The rotational levels of c states are in thermal equilibrium with the liquid so that a more general line broadening theory should be used to rigorously treat these states.
H. Evaluation of the Criteria for the Use of the Static Line Broadening Theory

The validity of the static theory depends upon the time variations of the perturbations. The fundamental idea of the static theory is that this variation is slow. In particular, we have discussed a correlation function. We may define a correlation time as the time at which the correlation function has fallen to some small fraction of its original value. Thus if this time is small compared to the time necessary for the perturbing atoms to move an appreciable distance, then we may say that the use of static line broadening theory is justified.

Suppose we let the correlation time be defined as the time at which the real part of the correlation function has fallen to half of its original value. Then the average correlation times are about $2.5 \times 10^{-13}$ sec. Recent experiments report kinetic energies for helium atoms at $1.7^\circ K$ corresponding to velocities of about $2.7 \times 10^4$ cm./sec. Thus the helium atoms have moved a distance of about $0.75 \times 10^{-8}$ cm. or $1.5a_0$ in this time. There are regions of the potential where changes of this size will have only small effects and others where the changes will be somewhat larger. One
could conclude that velocity effects could contribute small changes to the observed line width.

Another characteristic velocity in the system is the velocity of sound. In liquid helium at 1.7°K, sound travels at a velocity of $2.34 \times 10^4$ cm./sec.\(^3\) Thus during the correlation time, a sound wave will not have moved a great distance. Moreover, a weak sound wave will not greatly affect the movement of the liquid atoms near the excited atom so that the effects of static line broadening theory would still be evident.
IV. SUMMARY AND CONCLUSIONS

The study of the optical spectra of electron-bombarded dense helium has been of major interest to the Atomic Physics Group at Rice University. Edgar Durbin investigated the emission spectra of the dense helium gas excited by electron impact. The emission and absorption spectra have been described by W.S. Dennis and J.C. Hill respectively. These studies indicated that the excited atomic and molecular species existed in a cavity in the liquid similar to the cavity known to exist about a slow free electron in liquid helium. The first model of this phenomena was proposed by Dennis. A more sophisticated model was developed by Hickman who calculated intermolecular potentials between excited and ground state helium atoms and described the distribution of liquid atoms about the excited atom by minimizing the energy of this distribution. Both of these models produced values which were to be compared with the shift of the observed spectral lines from the dilute gas values.

An experiment which measures a spectral line provides more information than the shift. The whole line between
intensity limits determined by the sensitivity of the apparatus is generally available. In order to use this information to evaluate a particular model distribution or potential, one must have a theory of line shapes. Because of the relatively weak interactions between helium atoms, we have chosen to view liquid helium as a dense gas. General line broadening theory provides an approximate theory, static line broadening, which is applicable to certain atomic transitions in dense gases.

The potentials and distributions used in static broadening theory in previous work have always been spherically symmetric and been given by analytic expressions. Indeed, in the usual application, one uses spectral data at some densities to obtain potential and distribution parameters and then uses the theory to extrapolate to higher densities. In this work, we have used nonspherical numerical potentials and nonspherical distributions. Both potential and distribution are given so that we have no adjustable parameters. Finally we are interested in higher densities than have been considered before.

The results of the work may be divided into two categories, those involving analysis and those of application.
By considering spectral lines calculated by static line broadening theory for different model potentials and distributions, we have tried to show how a particular potential and distribution interact at high densities to produce the observed spectral lines. For the case of spherical potentials and distributions, we saw that when the distribution overlaps a large, positive-valued, rapidly changing region of the difference potential, we should expect to see broad, blue-shifted spectral lines. If the distribution lies over a weak, negative, slowly-changing region of the difference potential, the lines will be narrow and red-shifted. The first case is characteristic of absorption and the second of emission. We went on to consider how the spectral lines changed as a function of density and of the size and shape of the distribution. We showed how this analysis must be generalized for the case of nonspherical potentials and distributions.

In the area of application of static line broadening theory, we showed how the line shapes may be computed from expansions in parabolic cylinder functions for the spherical case with particular analytic expressions for the potentials and distributions. We next developed an expansion in gamma
functions for the nonspherical case with similar analytic expressions for the potentials and distributions. A general method, applicable to any potential and distribution, was also developed to treat the case of Hickman's potential. An error analysis of the last method was provided and results calculated by two different methods were compared and found in good agreement. Spectral line shapes were computed for the potentials and distributions developed by Hickman and properties of these lines were compared with the observed absorption and emission lines of the $2^3S-2^3P$ transition. The computed absorption line was found to be in reasonable agreement with the experimental results but there were noticeable discrepancies between theory and experiment for the emission spectrum. An alternative form of the distribution function was proposed although calculations using this distribution were not performed. Comments were made on the implications of the observed molecular spectra in terms of the analysis developed here. Finally the validity of the application of the static line broadening theory was assessed in terms of the correlation time.

Results of this investigation suggest future work which involves calculations using the alternative distribution
function which has only recently become available and more accurate calculation of line shape properties which must be performed on a faster computer than the one employed for these computations. We plan to proceed in these directions.
APPENDIX 1:
DERIVATION OF THE TRANSITION AMPLITUDE
IN THE ADIABATIC APPROXIMATION

The derivation of the transition amplitude for an atom in a radiation field is well known. We include this derivation because we have used the adiabatic approximation to describe the time development of the polyatomic system isolated from the radiation field. This results in an expression which differs from the usual one for the transition amplitude. Our derivation closely follows Schiff.

We begin with the time-dependent Schrödinger equation

\[ i\hbar \frac{\psi}{\psi} = \mathcal{H} \psi = \left( \mathcal{H}_i + \mathcal{H}_{\text{R}} \right) \psi \]

the wavefunction \( \psi(t) \) shall be expressed as a linear combination of eigenfunctions of the polyatomic Hamiltonian \( \mathcal{H}_i \). We recall that these are of the form

\[ \Phi_j(t) = \psi_j(t) \exp \left[ -i \int_0^t \mathcal{E}_j(t') \, dt' \right] \]

where

\[ \mathcal{H}_i(t) \psi_j(t) = \mathcal{E}_j(t) \psi_j(t) \]

Thus

\[ \psi(t) = \sum_n a_n(t) \psi_n(t) \exp \left[ -i \int_0^t \mathcal{E}_n(t') \, dt' \right] \]
Substitution of this into the Schrödinger equation gives

\[ i\hbar \sum m \dot{a}_m(t) \varphi_m(t) \exp \left[ -\left( \frac{i\hbar}{\mu^2} \right) \int_0^t E_m(t') dt' \right] + i\hbar \sum m a_m(t) \dot{\varphi}_m(t) \exp \left[ -\left( \frac{i\hbar}{\mu^2} \right) \int_0^t E_m(t') dt' \right] + \sum_m a_m(t) \varphi_m(t) E_m(t) \exp \left[ -\left( \frac{i\hbar}{\mu^2} \right) \int_0^t E_m(t') dt' \right] = \sum_m a_m(t) \left( H_i(t) + H_{ar}(t) \right) \varphi_m(t) \exp \left[ -\left( \frac{i\hbar}{\mu^2} \right) \int_0^t E_m(t') dt' \right] \]

We let \( H_i(t) \) operate on \( \varphi_n(t) \) and note that the time variation of \( \varphi_n(t) \) is assumed to be very small compared to the time variation of the remaining functions of time so that

\[ i\hbar \sum m \dot{a}_m(t) \varphi_m(t) \exp \left[ -\left( \frac{i\hbar}{\mu^2} \right) \int_0^t E_m(t') dt' \right] = \sum_m a_m(t) H_{ar}(t) \varphi_m(t) \exp \left[ -\left( \frac{i\hbar}{\mu^2} \right) \int_0^t E_m(t') dt' \right] \]

If we multiply through by some \( \varphi_k^*(t) \) and integrate over space recalling that the \( \varphi_n(t) \) form an orthogonal set, at any point in time, we have that

\[ i\hbar \dot{a}_k(t) \exp \left[ -\left( \frac{i\hbar}{\mu^2} \right) \int_0^t E_k(t') dt' \right] = \sum_m a_m(t) \exp \left[ -\left( \frac{i\hbar}{\mu^2} \right) \int_0^t E_m(t') dt' \right] \langle K(t) | H_{ar}(t) | m(t) \rangle \]

or

\[ \dot{a}_k(t) = \left( \frac{i\hbar}{\mu^2} \right) \sum_m a_m(t) \exp \left[ \left( \frac{i\hbar}{\mu^2} \right) \int_0^t (E_k(t') - E_m(t')) dt' \right] \langle K(t) | H_{ar}(t) | m(t) \rangle \]

The perturbation \( H_{ar}(t) \) may be written as \( \lambda H_{zR}(t) \) and the transition amplitudes may be expressed as a power
series in \( \lambda \),

\[
a_n = a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \ldots
\]

Substitution of this expansion into the expression for \( \dot{a}_k(t) \) gives the two lowest order equations as

\[
\dot{a}_k^{(0)}(t) = 0
\]

\[
\dot{a}_k^{(1)}(t) = (i\hbar)^{-1} \sum_m a_m(t) \exp \left[ \left( i\hbar \right)^{-1} \int_0^t \left( E_k(t') - E_m(t') \right) d t' \right] \langle h(t) | H_{aR}(t) | n(t) \rangle
\]

From the first of these equations, we see that the zeroth order terms in the expansion of the \( a_n(t) \) are constants. Their values are the initial conditions of the problem and specify the state of the system before the perturbation is applied. We suppose that the system is in the state \( n \) at time \( t \). \( a_k^{(0)} = \delta_{kn} \) and we obtain the equations for the \( a_k^{(1)}(t) \)

\[
\dot{a}_k^{(1)}(t) = (i\hbar)^{-1} \exp \left[ \left( i\hbar \right)^{-1} \int_0^t \left( E_k(t') - E_n(t') \right) d t' \right] \langle h(t) | H_{aR}(t) | n(t) \rangle
\]

The radiation field is described by the vector potential \( \mathbf{A} \) where, for plane waves in free space,

\[
\mathbf{A} = A_0 \exp \left[ i \left( \mathbf{k} \cdot \mathbf{r} - \omega t \right) \right] + c.c.
\]

The interaction between the field and the atom is

\[
H_{aR} = \frac{i e \hbar}{m c} \mathbf{A} \cdot \mathbf{v}
\]

\[
= \frac{i e \hbar}{m c} \exp \left[ i \left( \mathbf{k} \cdot \mathbf{r} - \omega t \right) \right] A_0 \cdot \mathbf{v}
\]

\[
= \frac{i e \hbar}{m c} |A| \exp \left[ i \left( \mathbf{k} \cdot \mathbf{r} - \omega t \right) \right] \nabla A
\]
We note that $\mathbf{V}_A$ does not act on $\exp [i \mathbf{k} \mathbf{r}]$ since $A$ is orthogonal to $\mathbf{k}$.

The matrix element becomes

$$\langle K(t) | H_{aR} (t) | n(t) \rangle = \frac{i e \hbar}{m c} |A| \langle K(t) | \exp (-i \omega t) \exp (i \mathbf{k} \cdot \mathbf{r}) \mathbf{V}_A | n(t) \rangle$$

For visible light, the wavelength of the radiation is much greater than the size of the atom. Thus we make the electric dipole approximation

$$\exp(i \mathbf{k} \cdot \mathbf{r}) = 1$$

We further assume that the time variation of the wavefunctions is very slow compared to the oscillations of the exponential so that we may neglect this time dependence.

The matrix element may now be written

$$\langle K(t) | H_{aR} (t) | n(t) \rangle = \frac{i e \hbar}{m c} |A| e^{i \omega t} \langle K | \mathbf{V}_A | n \rangle$$

but

$$\langle K | \mathbf{V}_A | n \rangle = \frac{e}{\hbar} \langle K | \mathbf{p}_A | n \rangle = \frac{i m}{\hbar} \frac{d}{dt} \langle K | r_A | n \rangle$$

$$= - \frac{m \omega_{kn}}{\hbar} \langle K | r_A | n \rangle$$

so that

$$\langle K(t) | H_{aR} (t) | n(t) \rangle = - \frac{i e}{c} \omega_{kn} |A| e^{i \omega t} \langle K | r_A | n \rangle$$

and

$$a_{k \mu} (t) = \frac{e}{\hbar c} |A| \omega_{kn} \langle K | r_A | n \rangle \exp [i \omega t + (i \hbar) \int_0^t (E_k (t') - E_n (t')) dt']$$
so that the amplitude for a transition to occur from state \( n \) to state \( k \) is to first order

\[
a_{nk}(t) = \frac{e}{\hbar c} |A| \Omega _{kn} \langle k | r \rangle \langle n \rangle \int_0^T \exp \left[ i \omega t + (i \hbar) \int_0^t (E_k(t') - E_n(t')) \, dt' \right] \, dt
\]

which is the expression given in the text.
APPENDIX 2:

EVALUATION OF THE STATIC THEORY INTENSITY EQUATION
FOR A SPHERICALLY SYMMETRIC POTENTIAL AND A BOLTZMANN
DISTRIBUTION BY USE OF PARABOLIC CYLINDER FUNCTIONS

The intensity equation from static theory was found
to be
\[ I(v) dv = \int_{-\infty}^{\infty} dt \exp\left(i \frac{t}{v}\right) \exp\left(-\rho A(t)\right) \]

where
\[ A(t) = \int \frac{d^3 R}{\delta_{sp}} \left[ 1 - \exp\left(-i \frac{t}{v} V_{d}(R)\right) \right] g(R) \]

We consider the case of a spherically symmetric potential and
distribution so that the angular integration in A(t) becomes
trivial. We will use the Boltzmann distribution
\[ g(R) = \exp\left(-\beta V_{i}(R)\right) \]

where \( V_{i}(R) \) is the intermolecular potential of the initial
state. We shall represent these potentials by Lennard-Jones potentials
\[ V_{u}(R) = C_{u} \left[ \left(\frac{R_{u}}{R}\right)^{6} - \frac{1}{R^{12}} \right] \]

and
\[ V_{\ell}(R) = C_{\ell} \left[ \left(\frac{R_{\ell}}{R}\right)^{6} - \frac{1}{R^{12}} \right] \]

from which we obtain the difference potential
\[ V_{d}(R) = V_{u}(R) - V_{\ell}(R) = C_{d} \left[ \left(\frac{R_{d}}{R}\right)^{6} - \frac{1}{R^{12}} \right] \]

where
\[ C_{d} = C_{u} - C_{\ell} \]

and
\[ R_{d} = \left\{ \frac{C_{u} (R_{u})^{6} - C_{\ell} (R_{\ell})^{6}}{C_{u} - C_{\ell}} \right\}^{\frac{1}{6}} \]
Our goal is to form an expression for \( A(z) \).

We write \( A(z) \) with these potentials

\[
A(z) = 4\pi \int_0^\infty dR \left\{1 - \exp\left[-z c_D \left( R_0^2 \frac{1}{R^2} - \frac{1}{R_0^2}\right)\right]\right\} \times \exp\left[-\frac{c_R}{kT} \left( R_0^2 \frac{1}{R^2} - \frac{1}{R_0^2}\right)\right] R^2
\]

Let

\[ s = \frac{c_D}{R_0^2} \]

and

\[ z = \left( \frac{R_0}{R} \right)^6 \Rightarrow -\frac{1}{6} z^{-3/2} R_0^2 dR = R^2 dR \]

so we have

\[
A(s) = \frac{2\pi}{3} R_0^2 \left\{ \int_0^\infty dz \ z^{-3/2} \exp\left[-\beta \left( \alpha z^2 - z\right)\right] - \int_0^\infty dz \ z^{-3/2} \exp\left[-\gamma z^2 + \delta z\right] \right\}
\]

where

\[ \beta = \frac{c_i}{kT R_0^6}; \quad \alpha = \left( \frac{R_0}{R} \right)^6; \quad \gamma = i s + \alpha \beta; \quad \text{and} \quad \delta = i s + \beta \]

After an integration by parts we obtain

\[
A(s) = \frac{2\pi}{3} R_0^3 \left\{ -2 z^{-1/2} \left[ \exp\left(-\alpha \beta z^2 + \beta z\right) - \exp\left(-\gamma z^2 + \delta z\right) \right]\right\}^\infty_0
\]

\[
+ 2 \int_0^\infty \left(-2 \alpha \beta z^{-1/2} + \beta z^{-1/2}\right) \exp\left[-\alpha \beta z^2 + \beta z\right] dz
\]

\[
+ 2 \int_0^\infty \left(-2 \gamma z^{-1/2} + \delta z^{-1/2}\right) \exp\left[-\gamma z^2 + \delta z\right] dz \right\}
\]

Clearly the first term vanishes in the limit that \( Z \to \infty \).

It should also be apparent that the difference of the exponentials is linear in \( Z \) for small \( Z \) so that the first
term also vanishes for \( Z = 0 \). We are left with

\[
A(s) = \frac{4\pi}{3} R_D^3 \left\{ -2\alpha \beta \int_0^\infty \frac{Z^{-\alpha - 1}}{e^Z} e^{-(\alpha \beta Z^2 - (\beta Z)} dZ + \beta \int_0^\infty \frac{Z^{-\alpha - 1}}{e^Z} e^{-(\alpha \beta Z^2 - (\beta Z)} dZ + 2\gamma \gamma \int_0^\infty \frac{Z^{-\alpha - 1}}{e^Z} e^{-(\beta Z^2 - (\gamma Z)} dZ \
- \delta \int_0^\infty \frac{Z^{-\alpha - 1}}{e^Z} e^{-(\gamma Z^2 - (\delta Z)} dZ \right\}
\]

\[
= \frac{4\pi}{3} R_D^3 \Gamma\left(\frac{1}{2}\right) \left\{ \exp\left(\frac{\beta}{2\alpha}\right) \left[ \beta \left(2\alpha \beta - \gamma \right) D_{2\alpha\beta} \left(\frac{-\beta}{2\alpha\beta}\right) - \frac{1}{2} \left(2\alpha \beta\right)^{1/4} \exp\left(\frac{\beta}{2\alpha}\right) D_{2\alpha\beta} \left(\frac{1}{2\alpha\beta}\right) \right] + \exp\left(\frac{s^2}{2\gamma}\right) \left[ \frac{1}{2} \left(2\gamma \right)^{1/4} D_{2\gamma} \left(\frac{-s}{2\gamma}\right) - \delta \left(2\gamma\right)^{1/4} D_{2\gamma} \left(\frac{-s}{2\gamma}\right) \right] \right\}
\]

We have used that

\[
\int_0^\infty x^{-\alpha - 1} e^{-\eta x^\gamma} e^{\gamma x} dx = \left(\frac{\gamma}{\eta}\right)^{-1/2} \Gamma(\gamma) \exp\left(\frac{\gamma^2}{\eta}\right) D_{2\gamma} \left(\frac{1}{2\gamma}\right)
\]

where \( \Re \eta > 0, \Re \gamma > 0 \) which was obtained from Gradshteyn and Ryzhik.\(^{36}\)

\[
D_p(z) = 2^{\frac{3\gamma - 1}{2}} \left\{ \frac{\Gamma\left(\frac{1-p}{2}\right)}{\Gamma\left(\frac{1-p}{2}\right)} F\left(-\frac{p}{2}, \frac{1}{2}, \frac{z}{2}\right) - \frac{2\pi}{\Gamma\left(\frac{p}{2}\right)} F\left(-\frac{1}{2}, \frac{3}{2}, \frac{z}{2}\right) \right\}
\]

is the parabolic cylinder function as given in Gradshteyn and Ryzhik\(^{37}\). \( F \) is the confluent hypergeometric function which has been defined above. Thus we have an expression of \( A(\tau) \).
Let $A(\tau) = R(\tau) + id(\tau)$ where $R(\tau)$ and $I(\tau)$ are real functions. It should be reasonably clear from the definition of $A(\tau)$ that $R(\tau)$ is symmetric in $\tau$ and $I(\tau)$ is anti-symmetric. From this, one can see that the real part of the integrand of the intensity integral is symmetric in $\tau$ and the imaginary part is anti-symmetric. This verifies that the intensity will be real as it must and allows us to simplify the integral for computational purposes.

$$I(\nu) d\nu = \int_0^\infty d\tau \exp (-\rho R(\tau)) \cos (\tau \nu - \rho \ell(\tau))$$

where $R(\tau)$ and $I(\tau)$ are computed in terms of the parabolic cylinder functions as given above.
APPENDIX 3: EVALUATION OF THE STATIC THEORY
INTENSITY EQUATION FOR A SPHERICALLY SYMMETRIC
POTENTIAL AND A BOLTZMANN DISTRIBUTION
BY USE OF AN EXPANSION IN GAMMA FUNCTIONS

We begin with equation (A2.1) of the previous appendix:

\[ A(i) \sim e^{\gamma - (\gamma \gamma) \beta} \]

Let \( S = \frac{C_B}{R_B} \) \( \tau \)

and \( \chi = \left( \frac{R_B}{R} \right)^{1/2} \) so that \( -\frac{R_B^3}{R} \left( \frac{1}{\chi} \right)^{5/4} d\chi = R dR \)

Then

\[ A(s) = \frac{4\pi}{3} R_B^3 \int_0^\infty \left\{ 1 - \exp \left[ -i \tau \left( \gamma - \chi \gamma \right) \right] \right\} \exp \left[ -\beta \left( \chi - \chi \gamma \right) \right] \chi^{-5/4} d\chi \]

where \( \alpha, \beta, \gamma, \) and \( \delta \) are defined as in appendix 2. Each term is integrated by parts.

\[ A(s) = \frac{4\pi}{3} R_B^3 \left\{ -\left( \frac{1}{\chi} \right)^{5/4} \left[ \exp (-\alpha \beta \chi + \beta \chi \gamma) - \exp (-\gamma \chi + \delta \chi \gamma) \right] \right\}_0^\infty \]

\[ + \int_0^\infty \left( -\alpha \beta \chi^{-5/4} + \frac{\beta}{2} \chi^{-3/4} \right) \exp (-\alpha \beta \chi) \exp (\beta \chi \gamma) d\chi \]

\[ - \int_0^\infty \left( -\gamma \chi^{-5/4} + \frac{\delta}{2} \chi^{-3/4} \right) \exp (-\gamma \chi) \exp (\delta \chi \gamma) d\chi \]
The first term vanishes at \( x = 0 \) and \( x \to \infty \). We notice that the integrands of the integrals in the second and third terms become small for large \( x \). We use this to expand the second exponential factors in each of these integrals.

Thus

\[
A(s) = \frac{4\pi}{3} R_0 \left\{ \frac{-\alpha \beta}{s} \int_0^\infty x^{-1/4} \exp(-\alpha \beta x) \sum_{n=0}^\infty \frac{1}{n!} \beta^n x^{n/2} \, dx \\
+ \frac{\beta}{2} \int_0^\infty x^{-1/4} \exp(-\alpha \beta) \sum_{n=0}^\infty \frac{1}{n!} \beta^n x^{n/2} \, dx \\
+ \gamma \int_0^\infty x^{-1/4} \exp(-\gamma x) \sum_{n=0}^\infty \frac{1}{n!} \delta^n x^{n/2} \, dx \\
- \frac{\delta}{2} \int_0^\infty x^{-3/4} \exp(-\gamma x) \sum_{n=0}^\infty \frac{1}{n!} \delta^n x^{n/2} \, dx \right\}
\]

\[
= \frac{4\pi}{3} R_0 \left\{ \frac{-\alpha \beta}{s} \sum_{n=0}^\infty \frac{1}{n!} \beta^n \int_0^\infty x^{(2n+3)/4-1} \exp(-\alpha \beta x) \, dx \\
+ \frac{\beta}{2} \sum_{n=0}^\infty \frac{1}{n!} \beta^n \int_0^\infty x^{(2n+1)/4-1} \exp(-\alpha \beta x) \, dx \\
+ \gamma \sum_{n=0}^\infty \frac{1}{n!} \delta^n \int_0^\infty x^{(2n+3)/4-1} \exp(-\gamma x) \, dx \\
- \frac{\delta}{2} \sum_{n=0}^\infty \frac{1}{n!} \delta^n \int_0^\infty x^{(2n+1)/4-1} \exp(-\gamma x) \, dx \right\}
\]

\[
= \frac{4\pi}{3} R_0 \left\{ -\left(\alpha \beta\right)^{1/4} \sum_{n=0}^\infty \frac{1}{n!} \frac{\beta^n}{(\alpha \beta)^{n/2}} \Gamma \left( \frac{2n+3}{4} \right) \\
+ \frac{1}{2} \beta \left(\alpha \beta\right)^{-1/4} \sum_{n=0}^\infty \frac{1}{n!} \frac{\beta^n}{(\alpha \beta)^{n/2}} \Gamma \left( \frac{2n+1}{4} \right) \\
+ \gamma^{1/4} \sum_{n=0}^\infty \frac{1}{n!} \frac{\delta^n}{\gamma^{n/2}} \Gamma \left( \frac{2n+3}{4} \right) \\
- \frac{1}{2} \delta \gamma^{-1/4} \sum_{n=0}^\infty \frac{1}{n!} \frac{\delta^n}{\gamma^{n/2}} \Gamma \left( \frac{2n+1}{4} \right) \right\}
\]
We note that in coding this expression for a computer, one can specify the values of $\Gamma(1/4)$ and $\Gamma(3/4)$ and then recursively compute a table of gamma and factorial functions which will be used by the calculation with the formulae

$$\Gamma(z + 1) = z \Gamma(z)$$

and

$$(n+1)! = (n+1) n!$$

This scheme is simpler to code than is the previous method but the program running times were comparable for
the reason mentioned in the text. The Fourier transform was taken numerically as before.

The derivation of the analogous results for the case of the nonspherical Lennard-Jones potential and nonspherical Boltzmann distribution will not be given here since it is similar to that for the spherical case. We give equations for the nonspherical case below.

The line intensity is given by

\[ I(\nu) d\nu = \int_{-\infty}^{\infty} d\tau \exp(i \tau \nu) \exp(-\rho A(\tau)) \]

where

\[ A(\tau) = \iiint_{\text{sphere}} d^3 R \left[ 1 - \exp(-i \tau V_0(R)) \right] g(R) \]

\[ = 4\pi \int_0^1 dx \int_0^\infty R^2 dR \left[ 1 - \exp(V_0(R) + V_2(R) P_2(\theta)) \right] \exp\left(\frac{-i}{\hbar R} V_1(R, x)\right) \]

where \( V_{10}(r), V_{21}(r) \) and \( P_2(\theta) \) are defined in the text. \( V_1(r, \theta) \) refers to the initial state.

We make the change of variable \( S = \frac{C_D}{R_D^6} t \) and, using the expansion in gamma functions,

\[ A(s) = -\frac{4}{3} \pi R_D^3 \int d^3 x \left\{ \gamma(x)^{\nu \mu} \left[ \Gamma\left(\frac{3}{4}\right) + \sum_{m=1}^{\infty} \frac{1}{m!} \left( \frac{\delta(x)}{\sqrt{\gamma(x)}} \right)^m \left( \frac{2m-3}{4} \Gamma\left(\frac{2m-1}{4}\right) \right) \right] \right. \]

\[ + \left( \frac{\mu(x)}{\mu(x)} \right)^{\nu \mu} \left[ \Gamma\left(\frac{3}{4}\right) + \sum_{m=1}^{\infty} \frac{1}{m!} \left( \frac{\lambda(x)}{\sqrt{\mu(x)}} \right)^m \left( \frac{2m-3}{4} \Gamma\left(\frac{2m-1}{4}\right) \right) \right] \]
where \( \gamma(x) = \frac{1}{kT R_0^6} c_i \left( \frac{R_i}{R_0} \right)^6 \left[ 1 + a_1 P_2(x) \right] \)
\( \delta(x) = \frac{1}{kT R_0^6} c_i \left[ 1 + a_2 P_2(x) \right] \)
\( \mu(x) = \gamma(x) + i \delta \left[ 1 + a_1 \left( \frac{C_i}{C_0} \right) \left( \frac{R_i}{R_0} \right)^6 P_2(x) \right] \)
\( \chi(x) = \delta(x) + i \delta \left[ 1 + a_2 \left( \frac{C_i}{C_0} \right) P_2(x) \right] \)

\( C_s \) and \( r_s \) are the van der Waals coefficients and null position respectively for the initial state. \( C_D \) and \( r_D \) are the same parameter as in appendix 2 and

\( a_1 \) and \( a_2 \) are the asymmetry parameters. These would vanish in the case of absorption from the \( 2^3S \) state since that state is spherical.

The expression for the approximate shift in the nonspherical case is

\[
\Delta \nu_{\text{max}} \approx \int_{\text{space}} d^3 R \, V_0(R) \, g(R) \\
= 4\pi \rho_0 \int_0^1 d\chi \int_0^\infty dR \left( V_{\xi 0}(R) + V_{\xi 2}(R) P_2(x) \right) \exp \left( \frac{i}{kT} V_s(R, \chi) \right)
\]

We note that in the absorption case, the distribution is spherically symmetric so that the angle dependent term of the
difference potential vanishes due to the orthogonality properties of the Legendre polynomials. The approximate shift in absorption can be shown to be

$$\Delta \nu_2 \approx \frac{\pi}{3} \frac{C_p}{R_p^2} \left( \lambda_a \right)^{-1/4} \rho_a \left\{ \sum_{m=1}^{\infty} \frac{1}{m!} \left( \frac{m}{M_a} - 1 \right) \left[ \Gamma \left( \frac{m}{2} + \frac{1}{4} \right) \left( \frac{M_a}{\sqrt{\lambda_a}} \right)^m - \Gamma \left( \frac{1}{4} \right) \right] \right\}$$

where

$$M_a = \frac{c_s}{k T R_p^6}$$

$$\lambda_a = \mu_a \left( \frac{R_s}{R_p} \right)^6$$

and $c_s$ and $r_s$ are the van der Waals' coefficient and null position of the potential for the spherically symmetric initial state.

In the case of emission, the integration over the angle variable is non-trivial and we have

$$\Delta \nu_e \approx \frac{\pi}{3} \frac{C_p}{R_p^2} \rho_o \int_0^{\pi} d \chi \left( \lambda_e (\chi) \right)^{-1/4} \left\{ \sum_{m=1}^{\infty} \frac{1}{m!} \left[ \frac{M_e(\chi)}{\lambda_e(\chi)} \right]^{1/2} \Gamma \left( \frac{m}{2} + \frac{1}{4} \right) \chi \left[ \frac{m}{M_e(\chi)} \gamma(\chi) - \delta(\chi) \right] - \delta(\chi) \Gamma \left( \frac{1}{4} \right) \right\}$$

where

$$M_e(\chi) = \frac{C_p}{k T R_p^6} \left( 1 + a_1 P_2(\chi) \right)$$

$$\lambda_e(\chi) = \frac{C_p}{k T R_p^6} \left( \frac{R_p}{R_o} \right)^6 \left( 1 + a_1 P_2(\chi) \right)$$

$$\gamma(\chi) = c_b + a_1 C_p \left( \frac{R_p}{R_o} \right)^6 P_2(\chi)$$
\[ \delta(x) = C_D + \alpha_2 C_p P_2(x) \]

c and \( r \) are the van der Waals' coefficient and null position of the potential for the nonspherical initial state. The integration over \( x \) was done using both Simpson's Rule and Gauss-Legendre quadrature. The Gauss-Legendre method using 20 integration points was found to be 50-100% faster than the comparably accurate Simpson's Rule method which required 31 integration points.
APPENDIX 4: ERROR ANALYSIS OF THE CALCULATION OF LINE SHAPE

We recall that the expression for the line profile provided by static line broadening theory was

\[
I(\vec{\xi}) = \int_{-\infty}^{\infty} dt \ e^{i s \vec{\xi} \cdot \vec{C}(s)}
\]

where

\[
\vec{C}(s) = \exp \left[ -\rho \int_{\text{space}} d^3 \vec{R} \left[ 1 - \exp (-i s \vec{U}(\vec{R})) \right] q(\vec{R}) \right]
\]

\(c(s)\) is the correlation function,
\(\vec{\xi}\) is the reduced frequency,
\(s\) is the reduced time, and
\(\vec{U}(\vec{R})\) is the reduced difference potential.

The correlation function was calculated by an expansion

\[
\vec{C}(s) = \exp \left\{ \rho \sum_{k=1}^{\infty} \frac{1}{k!} (-i)^k \eta(k) s^k \right\}
\]

where

\[
\eta(k) = \int_{\text{space}} d^3 \vec{R} \ \vec{U}^k(\vec{R}) q(\vec{R})
\]

It was practical to include only a certain number of terms of the expansion in the calculation. For most cases, this was forty-five terms. This approximation for the correlation function will converge only for \(s \leq s_0\) and a
truncated correlation function must be used to compute the intensity. Here we estimate the error involved in this truncation.

The magnitude of the integrand in the correlation function will be determined by the real part of the correlation function. In order to estimate the error involved in the truncation of this integral, we require an approximate expression for this part of the correlation function in the truncated region. Values of this function were printed in the course of the calculation and various analytic expressions were used to approximate these values in the region of large $t$. The expression which gave the best values was a simple exponential so that

$$\text{Re} \ C(s) \approx e^{-s/\gamma}$$

for large $s$.

If the correlation function has been truncated at value $s_0$, then we have

$$\text{Re} \ C(s_0) = e^{-s_0/\gamma}$$

or

$$\ln \ [\text{Re} \ C(s_0)] = -s_0 / \gamma$$

or

$$\gamma = s_0 / \ln \ [\text{Re} \ C(s_0)]$$

This approximation appears to slightly overestimate the truncated part of the integrand.
For large values of $f$ corresponding to large frequencies, we should expect the integrand to oscillate a great deal so that the neglected part of the correlation function would be averaged out. For smaller frequencies, this will not occur. Our error estimate should reflect this. If we keep the exponential factor in the Fourier transform and measure frequencies from the frequency corresponding to the maximum of the computed intensity expression, our error estimate will approximate the frequency dependence of the error. Hence the approximate error in the intensity at a frequency $f$ is given by

$$E = \int_{-\infty}^{-s_0} \exp \left[ (i (f - f_m) + \frac{i}{\gamma}) s \right] ds + \int_{s_0}^{\infty} \exp \left[ (i (f - f_m) - \frac{i}{\gamma}) s \right] ds$$

$$\approx \frac{2 s_0 |\ln [\Re C(s_0)]|}{s_0^2 (f - f_m)^2 + |\ln [\Re C(s_0)]|^2} \Re C(s_0)$$

Errors in shift and width for several values cavity size and asymmetry and for line shapes computed thirty and forty-five terms in the expansion are given in table 3. The error decreases as the number of terms increases since our approximation for a fixed number of terms is best the larger
### TABLE 3

**ERROR BOUNDS ON RESULTS**

<table>
<thead>
<tr>
<th>NMU</th>
<th>$R_o$</th>
<th>$\beta$</th>
<th>Shift ± Error</th>
<th>Width ± Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>9.0</td>
<td>0.</td>
<td>22. ± 7.</td>
<td>110. ± 2.</td>
</tr>
<tr>
<td>45</td>
<td>10.0</td>
<td>0.</td>
<td>4. ± 3.</td>
<td>52. ± 1.</td>
</tr>
<tr>
<td>30</td>
<td>10.0</td>
<td>0.</td>
<td>6. ± 7.</td>
<td>52. ± 2.</td>
</tr>
<tr>
<td>45</td>
<td>9.5</td>
<td>.3</td>
<td>-30. ± 8.</td>
<td>70. ± 1.</td>
</tr>
<tr>
<td>30</td>
<td>9.5</td>
<td>.3</td>
<td>-34. ± 17.</td>
<td>75. ± 5.</td>
</tr>
<tr>
<td>45</td>
<td>11.0</td>
<td>.3</td>
<td>-23. ± 2.</td>
<td>28. ± 1.</td>
</tr>
<tr>
<td>45</td>
<td>9.5</td>
<td>.4</td>
<td>-47. ± 16.</td>
<td>90. ± 6.</td>
</tr>
<tr>
<td>45</td>
<td>10.0</td>
<td>.4</td>
<td>-40. ± 11.</td>
<td>65. ± 4.</td>
</tr>
<tr>
<td>30</td>
<td>10.0</td>
<td>.4</td>
<td>-46. ± 24.</td>
<td>75. ± 7.</td>
</tr>
<tr>
<td>45</td>
<td>11.0</td>
<td>.4</td>
<td>-29. ± 4.</td>
<td>35. ± 1.</td>
</tr>
</tbody>
</table>
and more spherical the cavity. This reflects the fact that the perturbation is smallest for large spherical cavities and the series converges fastest in these cases. The table shows that the widths are computed to better accuracy than the shifts but that for most cases, this approximation technique yields good results.

As a check on both the calculation and the accuracy of the approximation, we have computed line profiles for the case of a spherical potential and Boltzmann distribution in absorption and emission by this technique and by the method described earlier using an expansion in parabolic cylinder functions. These are shown in figures 14 and 15. The very good agreement between the results of the two methods provides additional confidence in our results.
Figure 14. Comparison of absorption line profiles computed with $\mu$-factors and with parabolic cylinder functions. These calculations use a spherical potential and Boltzmann distribution.
Figure 15. Comparison of emission line profiles computed with $\mu$-factors and with parabolic cylinder functions. These calculations use a spherical potential and Boltzmann distribution.
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