AN IMPACT THEORY FOR DOPPLER AND
PRESSURE BROADENING—I
GENERAL THEORY

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Abstract—A quantum-mechanical impact theory for the combined effects of Doppler and pressure broadening is developed from quantum radiation theory. The results are compared with other semiclassical theories and certain simplifying approximations relevant to cases of experimental and theoretical interest are discussed.

1. INTRODUCTION

In most calculations of spectral line shapes, it is assumed that the translational motion of the radiator is unperturbed during the time of interest. The total line profile is then given by the familiar Doppler convolution integral(1)

\[ I(\omega) = \int I_D(\omega') I_P(\omega - \omega') d\omega', \]  

(1.1)

where \( I_P \) is the pressure broadened line profile and \( I_D \) is the unperturbed Doppler profile,

\[ I_D(\omega) = \left( \frac{M c^2}{2 \pi k T \omega_0^2} \right)^{1/2} \exp \left\{ -\frac{\Delta \omega(\omega - \omega_0)}{2(M c^2/2kT)} \right\}, \]  

(1.2)

for radiators of mass \( M \) at a temperature \( T \); \( \Delta \omega = (\omega - \omega_0) \) denotes the frequency separation from the center of the natural line at \( \omega_0 \). If \( I_P \) is a simple Lorentz profile

\[ I_P(\omega) = \frac{2\gamma/\pi}{(\Delta \omega^2 + \gamma^2)} \]  

(1.3)

then \( I(\omega) \) as given by equation (1.1) is referred to as a Voigt profile.

Since recent experimental results(2) have shown an appreciable deviation from these simple calculations, there has been some interest in improving the theoretical description of combined Doppler and pressure broadening. To date, most calculations have used GALATRY'S(3) collisional narrowing results in which the Doppler profile \( I_D(\omega) \) is modified in order to account for the effect of collisions on the radiator motion. Assuming that Doppler and pressure broadening mechanisms are statistically independent, the modified

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Doppler profile is then folded into the pressure broadened line as in equation (1.1). Attempts to describe the statistical correlation between Doppler and pressure broadening mechanisms have employed a classical phase shift treatment of the pressure broadening. A very clear and comprehensive review of this work is given by RAUTIAN and SOBEL’MAN.

In the present paper we derive a quantum mechanical line shape expression which describes the combined effect of Doppler and collisional broadening including their statistical correlation. This derivation is based on a dipole transition probability obtained from quantum radiation theory. The only approximations employed in the formal development are familiar from conventional pressure broadening theories and their regions of validity are well known. The value of the results thus obtained lies in their consistent development from quantum radiation theory.

2. THE MATHEMATICAL MODEL

(A) The particles

We wish to consider the spectral distribution of radiation emitted (or absorbed) by a particular species of atom or molecule when these radiators (or absorbers) are immersed in a gas of perturbing particles of some other species. We will assume that the number of radiators is a small fraction of the total number of particles in the gas so that we may neglect any interaction between radiators. We will therefore regard the gas as being divided into a large number of cells in such a way that each cell contains one radiator and a large number of perturbing particles.

The perturbers will be regarded as a gas of statistically independent particles in equilibrium at a temperature $T$. This approximation is useful because the perturbers can influence the spectral emission from the radiator only through collisions with the radiator. For a gas of neutral atoms or molecules interacting via short range forces, a given radiator-perturber collision is not appreciably affected by the remaining perturbers. Since shielding accounts for the long range forces between charged perturbers, this approximation is also applicable to plasmas if the perturbers are regarded as shielded quasi-particles.

We have now represented the gas by a collection of noninteracting cells. Each cell may be described by a Hamiltonian of the form

$$H = H_r + K_r + V_r + \sum_j [H_p(j) + K_p(j)]$$

where $H_r$ is the Hamiltonian for an unperturbed radiator which is at rest with respect to some observer (i.e. $H_r$ describes the discrete spectrum), $K_r$ is a kinetic energy operator which describes the translational motion of the radiator relative to the observer, $H_p(j)$ describes the internal states (discrete spectrum) of the $j$th perturber and $K_p(j)$ gives its kinetic energy relative to the observer. The interaction $V_r$ between the radiator and perturbers will be regarded as a sum of binary interactions $V(j)$ between the radiator and the $j$th perturber:

$$V_r = \sum_j V(j).$$

The eigenstates and eigenvalues of $H$ will be denoted by $|A\rangle, |B\rangle$, etc. and $E_A, E_B$, etc.
The eigenstates and eigenvalues of $H$, will be denoted by $|a\rangle$, $|b\rangle$, etc. and $E_a$, $E_b$, etc. The mass and translational momentum operator for the radiator will be denoted by $M$ and $P$ so that $K^2 = P^2/2M$. We neglect resonance broadening processes by assuming that the perturbers do not have any natural frequencies near the radiation frequency of the radiator (i.e. we ignore resonant exchange of excitation).

(B) The radiation field

The radiation field in any given cell will be described by a Hamiltonian $H_{\text{rad}}$. This radiation will be quantized in the usual manner (Sect. 7 of Ref. 8) so that

$$H_{\text{rad}} = \sum_{x^4} H_{x^4}$$

where $x$ is the propagation vector for a photon moving in the direction $\hat{x} = \hat{x}/c$ having a frequency $\omega_x = \omega c$ and a polarization $\hat{\ell}(\hat{x})$. The eigenstates of $H_{x^4}$ are denoted by $|n_{x^4}\rangle$ where $n_{x^4}$ denotes the number of photons having a wave vector $x$ and a polarization $\hat{\ell}(x)$. The eigenstates of $H_{\text{rad}}$ are therefore given by products of the states $|n_{x^4}\rangle$.

The field variables are written in terms of the familiar creation and annihilation operators $q_{x^4}$ and $q_{x^4}^\dagger$:

$$q_{x^4} |n_{x^4}\rangle = \sqrt{(n/2\omega_x)} \sqrt{|n_{x^4}-1\rangle}$$

$$q_{x^4}^\dagger |n_{x^4}\rangle = \sqrt{(n/2\omega_x)} \sqrt{|n_{x^4}+1\rangle}$$

In terms of these operators the Hamiltonian $H_{x^4}$ is just $2\omega_x^2 q_{x^4} q_{x^4}^\dagger$ and its eigenvalues are $n_{x^4} \hbar \omega_x$. In the Coulomb gauge, the transverse electric field at some point $R$ may be given by (see p. 58 of Ref. 8)

$$\mathcal{E}(R) = \sqrt{(4\pi)} \sum_{x^4} \omega_x \delta(x^4 - i\omega_x) - q_{x^4}^\dagger q_{x^4} e^{-i\hat{x} \cdot \hat{R}}$$

This electric field describes the free radiation; the longitudinal field, which results from the electrostatic interactions $V_{ep}$, has already been included in the particle Hamiltonian $H$.

(C) The dipole transition probability

The total Hamiltonian for any given cell, $H_{\text{tot}}$, is given by

$$H_{\text{tot}} = H + H_{\text{rad}} + H_{\text{int}}$$

where $H_{\text{int}}$ describes the interaction between the radiation field and the particles. To lowest order in $H_{\text{int}}$, the probability per unit time for emission of a photon with wave vector $x$ and polarization $\hat{\ell}(x)$ into a solid angle $d\Omega$ during a transition from $|A\rangle$ to $|B\rangle$, where $\omega_{AB} = (E_A - E_B)/\hbar = \omega_x$, is given by (Sect. 17 of Ref. 8)

$$w_{AB}(x, \ell) d\Omega = [2\pi \omega_x^2 \rho_A d\Omega/(2\pi c)^3 \hbar^2] \langle B; n_{x^4}+1 | H_{\text{rad}} | A; n_{x^4}\rangle^2$$

where $\rho_A$ denotes the probability of finding the particles in the state $|A\rangle$.

In general, $H_{\text{int}}$ should describe the interaction between the radiation field and each of the particles in the system; however, we will ignore any background radiation from the perturbers by neglecting their interaction with the field. We therefore regard $H_{\text{int}}$ as the interaction between the field and the constituents of the radiator.
It can be shown that (see Appendix), in the dipole approximation, the interaction is given by
\[ H_{\text{int}} = -\mathbf{d} \cdot \mathbf{\sigma}(\mathbf{R}) \]
(2.9)
where \( \mathbf{d} \) denotes the dipole moment of the radiator located at the point \( \mathbf{R} \). Using equations (2.4)-(2.6), we evaluate the \( H_{\text{int}} \) matrix elements required by equation (2.8) and we obtain
\[ w_{AB}(\mathbf{R}, \omega) \, d\Omega = (\omega_{AB}^3 \rho_A \, d\Omega / 2\pi \hbar c^3)(\varepsilon_{AB} + 1) \langle B|\mathbf{d} \cdot \mathbf{\sigma} e^{-i\mathbf{R} \cdot \mathbf{\sigma}}|A\rangle^2. \]
(2.10)

The result differs from the usual result for dipole radiation by the presence of the term \( \exp(-i\mathbf{R} \cdot \mathbf{\sigma}) \). Most pressure broadening theories ignore radiator motion by deleting the radiators translational kinetic energy, \( K_{\text{r}} \), from the particle Hamiltonian, equation (2.1). In such a case, \( \mathbf{R} \) does not operate on the \( H \) eigenstates hence the term \( \exp(-i\mathbf{R} \cdot \mathbf{\sigma}) \) is an unimportant phase shift which factors out of the absolute value as unity. Since we are interested in radiator motion we must retain the kinetic energy operator \( K_{\text{r}} \), in which case \( \mathbf{R} \) is an operator on the states \( |A\rangle, |B\rangle, \ldots \) and it may not be factored out of equation (2.10).

We note finally that equation (2.10) gives the probability for induced and spontaneous dipole transitions. The spontaneous transition probability is obtained simply by setting \( n_{AB} \) to zero in equation (2.10).

(D) The line shape

To obtain \( P(\omega) \), the total spontaneous dipole power per unit frequency interval, we set \( n_{\mathbf{R},AB} \) to zero in equation (2.10), multiply by \( h\omega_{AB} \delta(\omega - \omega_{AB}) \), sum over all possible states \( |A\rangle \) and \( |B\rangle \), sum over polarizations, and integrate over \( d\Omega \) the direction of \( \mathbf{\sigma} \):
\[ P(\omega) = (\omega^4 / 2\pi c^3) \sum_{AB} \rho_A \delta(\omega - \omega_{AB}) \int d\Omega \langle B|\mathbf{d} \cdot \mathbf{\sigma} e^{-i\mathbf{R} \cdot \mathbf{\sigma}}|A\rangle^2. \]
(2.11)

By integrating over \( d\Omega \) we have implicitly assumed that the system is spherically symmetric so that the emission intensity is the same in all directions. For most experimental situations this will be the case; however, if there is some preferred direction in space (e.g. an external magnetic field), the distribution of radiation will not in general be spherically symmetric and one would not want to average over \( d\Omega \). Since the mathematics for the spherically symmetric case are slightly simpler, and since the extension to the more general case is rather obvious, we will consider only spherically symmetric systems in this paper.

The sum of the two polarizations \( \delta(\mathbf{\sigma}) \) which are orthogonal to \( \mathbf{x} \), gives
\[ \sum_{\mathbf{\sigma}} |\langle B|\mathbf{d} \cdot \mathbf{\sigma} e^{-i\mathbf{R} \cdot \mathbf{\sigma}}|A\rangle|^2 = |\langle B|\mathbf{d} \cdot \mathbf{x} e^{-i\mathbf{R} \cdot \mathbf{x}}|A\rangle|^2 - |\langle B|\mathbf{d} \cdot \mathbf{\sigma} e^{-i\mathbf{R} \cdot \mathbf{\sigma}}|A\rangle|^2. \]
(2.12)

When the average over the states \( |A\rangle \) and \( |B\rangle \) is performed explicitly, in the spherically symmetric case, the direction of \( \mathbf{R} \) will not depend on the angle between \( \mathbf{d} \) and \( \mathbf{x} \). This means that the first integral on the right side of equation (2.12) is independent of \( d\Omega \) and the other integral is proportional to \( \cos^2 \varphi \) where \( \varphi \) denotes the angle between \( \mathbf{d} \) and \( \mathbf{x} \). Integrating over \( d\Omega \) and substituting the result back in equation (2.11) we obtain
\[ P(\omega) = (4\omega^4 / 3c^3) I(\omega). \]
(2.13)
\[ I(\omega) = \sum_{AB} \delta(\omega - \omega_{AB}) \rho_A |\langle B|\mathbf{d} e^{-i\mathbf{R} \cdot \mathbf{x}}|A\rangle|^2. \]
(2.14)
Using an integral representation for the delta function, the line shape function \( I(\omega) \) is written in the form

\[
I(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} e^{i\omega t} C(t) \, dt;
\]  

(2.15)

the correlation function \( C(t) \) is given by

\[
C(t) = \sum_{ab} \langle B| e^{iH_0 t} d e^{-i\mathbf{x} \cdot \mathbf{R}} e^{-iH_0 t}|A\rangle 
\cdot \langle A| \rho \ e^{i\mathbf{R} \cdot \mathbf{n}} |B\rangle
\]

\[
= Tr\{ e^{iH_0 t} (d e^{-i\mathbf{x} \cdot \mathbf{R}}) e^{-iH_0 t} \rho (e^{i\mathbf{R} \cdot \mathbf{n}} d) \}
\]  

(2.16)

where \( \rho \) is an equilibrium density matrix for the particles (i.e. it is diagonal in \( H \) eigenstates) and the trace is taken over all particle states. Using the notion

\[
d(t) = e^{iH_0 t} d e^{-iH_0 t}
\]

(2.17)

\[
R(t) = e^{iH_0 t} \mathbf{R} e^{-iH_0 t},
\]

(2.18)

the correlation function may be given by

\[
C(t) = Tr\{ d e^{i\mathbf{x} \cdot \mathbf{R}} d(t) e^{-i\mathbf{x} \cdot \mathbf{R} t} \rho \}
\]

(2.19)

and, since \( C(t) = C^*(-t) \), the line shape becomes

\[
I(\omega) = \frac{1}{\pi} Re \int_{-\infty}^{\infty} e^{i\omega t} C(t) \, dt.
\]  

(2.20)

These equations provide the starting point for our calculation of the line shape. Comparing with earlier pressure broadening theories,\(^{(5–7)}\) we see that this correlation function differs from the usual pressure broadening correlation function by the presence of the \( \mathbf{x} \cdot \mathbf{R} \) exponentials. Our correlation function will also be the same as the one proposed by Rautian and Sobelman if the position operators \( \mathbf{R} \) are replaced by classical vectors and the product of dipole operators \( d \cdot d(t) \) is replaced by the classical phase factor \( \exp \{-i\mathbf{p}(t)\} \) (cf. equation (1.14) of Ref. 1).

3. THE THERMAL AVERAGE

(A) An interaction representation

Using the \( H \), eigenstates \( |a\rangle, |b\rangle, \ldots \), the correlation function \( C(t) \) can be written

\[
C(t) = \sum_{ab} \langle b|d|a\rangle \cdot \langle a|D(t)|b\rangle
\]

(3.1)

where

\[
D(t) = Tr_{n,r} \{ e^{-i\mathbf{x} \cdot \mathbf{R}} e^{-iH_0 t} \rho (e^{i\mathbf{R} \cdot \mathbf{n}} d) e^{iH_0 t} \}
\]

(3.2)

and \( Tr_{n,r} \) denotes a trace over perturber states and translational radiator momentum states.
The time development operator \( \exp(-itH/\hbar) \) can be written in an interaction representation as follows:

\[
\exp(-itH/\hbar) = \exp(-iH_0/\hbar)U_{rp}(t, 0)
\]

(3.3)

\[
H_0 = H_r + K_r + \sum_j [H_p(j) + K_p(j)] = H - V_p
\]

(3.4)

\[
U_{rp}(t) = \mathcal{O} \exp \left\{ -(i/\hbar) \int_0^t \mathcal{P}_p(s) \, ds \right\}
\]

(3.5)

\[
\mathcal{P}_p(s) = e^{iuH_0/\hbar} \mathcal{P}_p e^{-iuH_0/\hbar}
\]

(3.6)

where \( \mathcal{O} \) denotes the time ordering operator and we have used \( U_{rp}(t) \) as an abbreviated notation of the more familiar form \( U_{rp}(t, 0) \). Noting the form of \( V_p \) stated in equation (2.2) we see that \( \mathcal{P}_p(s) \) may be written in the form

\[
\mathcal{P}_p(s) = \sum_j \mathcal{P}(j; s)
\]

(3.7)

\[
\mathcal{P}(j; s) = \exp\{it[H_r + K_r + H_p(j) + K_p(j)]/\hbar\}
\]

(3.8)

hence \( U_{rp}(t) \) may be given by

\[
U_{rp}(t) = \mathcal{O} \Pi_j U(j; t)
\]

(3.9)

\[
U(j; t) = \mathcal{O} \exp \left\{ -(i/\hbar) \int_0^t \mathcal{P}(j; s) \, ds \right\}
\]

(3.10)

where \( U(j; t) \) describes the binary collision between the radiator and the \( j \)th perturber. It should be noted that \( U \) is defined by an ordered series expansion; \( U_{rp} \), as given by equation (3.9), is obtained by taking the product of all \( U \) expansions and applying the time ordering operator once again to all of the various product terms which occur.

In this interaction representation, \( D(t) \) is given by

\[
D(t) = Tr_p,_{\text{r}} \{ \exp\{(-i\mathbf{R} - itH/\hbar)U_{rp}(t, 0) e^{-i\mathbf{R} d} U_{rp}^*(t) e^{i\mathbf{R} d}\} \}
\]

(3.11)

where \( Tr_p,_{\text{r}} \) denotes a trace over all perturber states as well as all translational radiator states.

(B) Tetradic notation

To simplify the formal mathematics, we define tetradic operators \( L_r, L_p(j), \mathcal{P}(j) \) and \( \mathcal{P}(j; s) \) by their operation on an arbitrary matrix \( M_{arb} \) as follows:

\[
L_r M_{arb} = [H_r + K_r, M_{arb}]
\]

(3.12)

\[
L_p(j) M_{arb} = [H_p(j) + K_p(j), M_{arb}]
\]

(3.13)

\[
\mathcal{P}(j) M_{arb} = [V(j), M_{arb}]
\]

(3.14)

\[
\mathcal{P}(j; s) M_{arb} = \mathcal{P}(j; s) M_{arb}.
\]

(3.15)
From these we further define the following

\[ L_\omega = L_r + \sum_j L_p(j) \]  
(3.16)

\[ \gamma_{rp}(s) = \sum_j \gamma(j; s) \]  
(3.17)

\[ \mathcal{U}_{rp}(t) = \mathcal{O} \exp \left\{ -\frac{i}{\hbar} \int_0^t \gamma_{rp}(s) \, ds \right\} \]  
(3.18)

\[ \mathcal{U}(j; t) = \mathcal{O} \exp \left\{ -\frac{i}{\hbar} \int_0^t \gamma(j; s) \, ds \right\} \]  
(3.19)

We next note the identities

\[ e^{-i\omega_0 t} M_{arb} e^{i\omega_0 t} = e^{-i\omega_0 t} M_{arb} \]  
(3.20)

\[ U_{rp}(t) M_{arb} U_{rp}^*(t) = U_{rp}(t) M_{arb} \]  
(3.21)

which may be verified by differentiating with respect to \( t \) and noting that both sides of the equation satisfy the same differential equation. Finally we note the identities which will be used later,

\[ \gamma(j; t) = e^{i\omega_0 t} \gamma(j) e^{-i\omega_0 t} \]  
(3.22)

\[ \mathcal{U}_{rp}(t) = \mathcal{O} \Pi_j \mathcal{U}(j; t) \]  
(3.23)

which may be verified by operating on \( M_{arb} \) and using the definitions stated in equations (3.12) through (3.19).

Using equations (3.11), (3.20) and (3.21), \( D(t) \) is given in tetradic notation as

\[ D(t) = \text{Tr}_{\rho_{\text{int}}} \left\{ e^{-ix\mathbf{R}} e^{-i\omega_0 t} \mathcal{U}_{rp}(t) \rho e^{ix\mathbf{R}} \mathcal{U}_{rp}^*(t) \right\} \]  
(3.24)

(C) Approximate treatment of statistics

We will make the weak coupling approximation on the density matrix by assuming that it can be written in the direct product form (see p. 399 of Ref. 7)

\[ \rho = \rho^{(r)} W \rho^{(pert)} \]  
(3.25)

where \( \rho^{(r)} \) is an equilibrium density matrix for the internal states of the radiator, \( W \) is a Maxwellian momentum distribution for the radiators translational states, and \( \rho^{(pert)} \) is an equilibrium density matrix for the perturbers.

The weak coupling approximation is made by neglecting the influence of \( V_{rp} \) on the initial distribution of states. This approximation has been shown to break down only when the frequency separation \( \Delta \omega \) from the center of the natural line is on the order of the thermal energy \( kT \) or larger (see Sect. 7B of Ref. 7). With this approximation, \( D(t) \) becomes

\[ D(t) = \text{Tr}_{\rho} \left\{ e^{-ix\mathbf{R}} e^{-i\omega_0 t} \mathcal{U}_{rp}(t) \rho W e^{ix\mathbf{R}} \mathcal{U}_{rp}^*(t) \rho^{(pert)} \right\} \]  
(3.26)

where we have noted that

\[ \text{Tr}_{\rho} \left\{ e^{-i\omega_0 t} M_{arb} \right\} = e^{-i\omega_0 t} \text{Tr}_{\rho} \left\{ M_{arb} \right\} \]  
(3.27)
and defined a quantity $\langle U_p(t) \rangle$ by

$$\langle U_p(t) \rangle = Tr_p[U_p(t)\rho^{(px)}]. \quad (3.28)$$

This quantity denotes the thermal average (i.e. average over perturber states of $U_p(t)$); it should be noted that $\langle U_p(t) \rangle$ is still a tetradic operator in the radiator subspace.

Noting the form of $U_p(t)$ given in equation (3.23), we define an operator $\varphi(j; t)$ by

$$\varphi(j; t) = U(j; t) - 1 \quad (3.29)$$

so that

$$U_p(t) = \mathcal{O} \prod_j [1 + \varphi(j; t)]. \quad (3.30)$$

Having assumed that the perturbers are statistically independent, each interaction $\mathcal{I}(j; s)$ will be statistically independent of all the others so that the $U(j; t)$ operators, and therefore the $\varphi$ operators, may be averaged separately. Since all perturbers are the same under the average, the index $j$ becomes redundant and, assuming that the number of perturbers $N$ is large, equation (3.30) gives

$$\langle U_p(t) \rangle = \mathcal{O} [1 + \langle \varphi(t) \rangle]^N = \mathcal{O} \exp\{N\langle \varphi(t) \rangle\} = \mathcal{O} \exp\{N\langle U(t) - 1 \rangle\}. \quad (3.31)$$

Equation (3.31) gives the thermal average of $U_p(t)$ in terms of an average over the binary collision operator $\mathcal{I}(t)$. This average therefore requires only the one-body distribution function $n/N$, where $n$ denotes the perturber density (Eq. (29.17) of Ref. (9)). Equation (3.31) thus becomes

$$\langle U_p(t) \rangle = \mathcal{O} \exp[\mathcal{I}(t) - 1]_{av}. \quad (3.32)$$

where the subscript $av$ refers to the single particle average. This average is given by

$$[\mathcal{I}(t) - 1]_{av} = n \sum_{px} \langle px \rangle \langle [\mathcal{I}(t) - 1]\rho^{(0)f} \rangle [px] \quad (3.33)$$

where $|x\rangle$ and $|p\rangle$ refer to the internal state and the translational momentum of a single perturber; that is, $|x\rangle$ and $|p\rangle$ are eigenstates of $\mathcal{H}_p$ and $K_p$ where we have dropped the index $j$ to denote the fact that $\mathcal{H}_p$ and $K_p$ refer to any perturber. The matrices $\rho^{(0)}$ and $f$ are diagonal in $|px\rangle$ states and $\rho^{(0)}_{x}$ gives the probability of finding a perturber in the state $|x\rangle$ while $f(p)$ is a Maxwellian momentum distribution function for the perturbers.

4. THE IMPACT THEORY

The form of equation (3.32) may be altered slightly by noting from the definition of $U$, equation (3.19), that

$$\mathcal{I}(t) - 1 = -(i/\hbar) \int_0^t \mathcal{F}(s)\mathcal{I}(s) ds. \quad (4.1)$$
One can also show that
\[ U(\tau, 0) = e^{itL_v/h}U(0, -\tau) e^{-itL_v/h} \] (4.2)
hence
\[ [U(\tau) - 1]_{av} = -(i/h) \int_0^\tau e^{isL_v/h} [y'(0)U(0, -s)]_{av} e^{-isL_v/h} ds \] (4.3)

where we have used equation (3.27) and noted that \( L_v \) commutes with \( \rho^{(ij)} \).

At this point it is convenient to make the impact approximation and the completed collision approximation. These two approximations constitute the essence of the impact theory and our results will be shown to be identical in form with the impact theory results.

We make the completed collision or Markov approximation (cf. Sect. 4B of Ref. 10) by assuming that there is some relaxation time or average collision time \( \tau_{av} \) such that, for \( s > \tau_{av} \),
\[ [y'(0)U(0, -s)]_{av} = [y'(0)U(0, -\tau_{av})]_{av} = [y'(0)U(0, -\infty)]_{av} \] (4.4)

and we assume that all times of interest \( t \) in \( \langle U_{ref}(t) \rangle \) are greater than \( \tau_{av} \). This essentially makes the collisions instantaneous so that temporal overlap effects are neglected. Defining an operator \( \Phi \) by
\[ \Phi = -(i/h) [y'(0)U(0, -\infty)]_{av} \] (4.5)
the quantity \( [U(\tau) - 1]_{av} \) given in equation (4.3) becomes
\[ [U(\tau) - 1]_{av} = \int_0^\tau e^{isL_v/h}\Phi e^{-isL_v/h} ds \] (4.6)

plus a correction term whose magnitude is on the order of
\[ \int_0^{\tau_{av}} \{ (i/h) [y'(0)U(0, -s)]_{av} - \Phi \} ds \] (4.7)
or smaller. At \( s = 0 \) the integrand is just \( -\Phi \); at \( s = \tau_{av} \), the integrand is zero; between these limits we expect the integrand to be slowly increasing, hence we estimate the magnitude of this integral by \( \tau_{av} \Phi \). The impact approximation assumes \( \tau_{av} \Phi \ll 1 \langle U_{ref}(t) \rangle \) is therefore given by equations (3.32) and (4.6) as
\[ \langle U_{ref}(t) \rangle = e^{itL_v/h} \exp \left\{ \int_0^t e^{isL_v/h}\Phi e^{-isL_v/h} ds \right\} = e^{itL_v/h} \exp \{ t\Phi - itL_v/h \} \] (4.8)
where we have also used \(\exp(t\omega, \Phi) \approx 1\). Substituting this result into equation (3.26) we have

\[
D(t) = T_{t, x} [\exp \{ t\Phi - itL_{x} \hbar \} (\rho^{\mu} W e^{i\Phi} d) ;
\]

(4.9)

which is identical in form with the usual result of an impact theory (cf. equations (4.5) and (4.9) with equations (39) and (42) of Ref. 6 and equations (55) and (56) in Ref. 10). Note that in the above equation the real part of \(\Phi\) provides the damping of \(D(t)\) and thereby essentially becomes the half-width of the line. In the Lorentz theory the half-width is just the collision frequency and, as will be seen later, this is essentially the same in this case: the condition \(r\Phi \ll 1\) is therefore a statement that the collision duration time is much less than the time between collisions and this is the essence of the impact approximation.

We have now represented the effect of the perturbers by means of the familiar thermal average. At this point in a pressure broadening theory one would take the Fourier transform of \(D(t)\) and invert the resulting atomic matrix. However, since we have included radiator motion, the operator \(\Phi\) is not diagonal in translational radiator states; this operator is therefore represented by an infinite dimensional matrix whose inversion would be intractable. We will therefore follow the differential equation approach used by RAUTIAN and SOBEL'MAN in calculating the effect of radiator motion.

5. THE EFFECT OF RADIATOR MOTION

(A) The kinetic equation

The operator \(D(t)\) given by equation (4.9) involves a trace over translational radiator states. This trace will be written out explicitly in terms of the eigenstates \(|P\rangle\) of the translational radiator momentum operator \(P\). Noting that \(K_{r} = P^{2}/2M\) and

\[
e^{i\Phi/\hbar} = |P + \hbar X\rangle,
\]

(5.1)

we obtain the identity

\[
e^{-i\Phi/\hbar} L_{P} e^{i\Phi/\hbar} = L_{P} + \hbar X \cdot P/M + \hbar^{2} X^{2}/2M.
\]

(5.2)

The matrix elements \(\langle a | D(t) | b \rangle\) required by equation (3.1) may be obtained from

\[
\langle a | D(t) | b \rangle = \sum_{P} F_{ab}(P, t)
\]

(5.3)

\[
F_{ab}(P, t) = \langle a | F(t) | b \rangle
\]

(5.4)

\[
F(t) = e^{-i\Phi/\hbar} \exp \{ t\Phi - itL_{P} \hbar \} (\rho^{\mu} W e^{i\Phi} d).
\]

(5.5)

Taking the derivative with respect to \(t\) and using equation (5.2) we obtain the differential equation

\[
\left[ \frac{\partial}{\partial t} + i \left( \frac{L_{P} \cdot P}{\hbar} - \frac{\hbar X^{2}}{2M} \right) \right] F(t) = \Lambda \{ F(t) \}
\]

(5.6)

\[
\Lambda \{ F(t) \} = (e^{-i\Phi/\hbar} \Phi e^{i\Phi/\hbar}) F(t).
\]

(5.7)

Taking matrix elements of equation (5.6) we have

\[
\left[ \frac{\partial}{\partial t} + i \left( \omega_{ab} \cdot \frac{X}{M} \right) \right] F_{ab}(P, t) = \langle a \rho^{\mu} W e^{i\Phi} d | b \rangle.
\]

(5.8)
where we have neglected the term $\hbar x^2/2M$ since it provides only a negligible frequency shift. To verify this we note that the magnitude of this term is given by $(\hbar \omega^2/2Mc^2)$ where $\omega$ is the frequency of the emitted radiation; since $\hbar \omega \ll 2Mc^2$ this term shifts the unperturbed frequency $\omega_{ab}$ by a negligible amount.

Equation (5.8) has the general form of a kinetic equation. The natural or unperturbed oscillation frequency of $F_{ab}(P, t)$ is given by the unperturbed radiator frequency $\omega_{ab}$ plus a Doppler shift $x \cdot P/Mc$ (recall that $x = \hat{x}(\omega/c)$). The 'collision integral' $\Lambda(F(t))$ represents changes in $F$ caused by collisions between the radiator and perturbers. This collision term will be discussed in detail in the following sections.

(B) The collision integral

To write out the collision term $\Lambda$ given in equation (5.7) we use equations (3.15), (3.19), (3.33), (4.5) and we use the Møller operator $\Omega^{(+)}$ for a binary collision, (See equations (1.25) and (3.31) in Chap. 8 of Ref. 12)

$$\Omega^{(+)} = \mathcal{U}(0, -\infty) = \mathcal{O} \exp\left\{ -\left(\frac{i}{\hbar}\right) \int_{-\infty}^{0} \hat{P}(s) \, ds \right\}. \quad (5.9)$$

The matrix elements $\langle aP|\Lambda|bP \rangle$ are thus given by

$$\langle aP|\Lambda(F(t))|bP \rangle = -(in/h) \sum_{\rho} \langle aP|e^{-ix\cdot R\hat{\Omega}^{(+)}}, e^{ix\cdot R} \rho(0)/F(t)\Omega^{(+)}\rangle \hat{P}(s) \right|_{bP}$$

where $\rho(0)$ and $\hat{P}$ denote operators pertaining to the distribution of internal and translational perturber states as defined in Sect. 3(C) and the states $|a\rangle, |x\rangle, |p\rangle$, and $|P\rangle$ are eigenvectors of $H_r, H_p, K_r$ and $K_r$ respectively.

We next note that since $V$ depends only on radiator and perturber coordinate operators, it will commute with the $x \cdot R$ factors. Thus both terms in equation (5.10) involve the operator

$$e^{-ix\cdot \hat{R}\hat{\Omega}^{(+)}}e^{ix\cdot R} = \mathcal{O} \exp\left\{ -\left(\frac{i}{\hbar}\right) \int_{-\infty}^{0} e^{-ix\cdot \hat{P}(s)} e^{ix\cdot \hat{P}(s/M)} \, ds \right\} = \mathcal{O} \exp\left\{ -\left(\frac{i}{\hbar}\right) \int_{-\infty}^{0} \hat{P}(s) \, ds \right\} \quad (5.11)$$

where we have used equations (4.4), (5.2) (5.9) and noted that $(x \cdot P/M) \lesssim (\omega r)(v_{rad}/c) \ll 1$ where $v_{rad}$ denotes the speed of the radiator and $\omega$ is the frequency of the observed radiation. Noting equation (5.1), we may interpret equation (5.11) as a statement that the translational dynamics of the radiator are not appreciably altered by the recoil momentum $\hbar K$ which should be added to $r$ in order to conserve momentum when a photon is emitted.
The $T$-matrix for a binary collision is given by equation (2.66) on p. 182 of Ref. (12) as

$$ T = \mathcal{V}\Omega^{+} $$

(5.12)

hence the collision integral is given by

$$ \langle aP | A | bP' \rangle = -\frac{\langle aXpbp' | T \rho^{\dagger}f F(t) \Omega^{+} | bXpbp' \rangle}{\langle aXpbp' | T \rho^{\dagger}f F(t) \Omega^{+} | bXpbp' \rangle}.

(5.13)

The momentum of the center of mass, $(p + P)$, will be conserved during a collision hence both $\langle pP | T | p'P' \rangle$ and $\langle pP | \Omega^{+} | p'P' \rangle$ will vanish unless $(p + P) = (p' + P)$. Equations (5.13) thus becomes

$$ \langle aP | A | bP' \rangle = -\frac{\langle aXpbp' | T \rho^{\dagger}f F(t) \Omega^{+} | bXpbp' \rangle}{\langle aXpbp' | T \rho^{\dagger}f F(t) \Omega^{+} | bXpbp' \rangle}.

(5.14)

where momentum conservation was used to eliminate the $F(t)$ matrix elements which are off-diagonal in $|P\rangle$. The equation of motion for $F(P, t)$, obtained by combining equations (5.8) and (5.14), thus requires only diagonal matrix elements of $F(t)$ in $|P\rangle$ states. In a similar manner one finds that the equation of motion for the off-diagonal elements of $F(t)$ depends only on other off-diagonal elements. Since $F(0)$ is diagonal in $|P\rangle$ states (see equation (5.5), the above considerations imply that $F(t)$ remains diagonal in $|P\rangle$ states for any time $t$.

6. DOPPLER BROADENING ONLY

In order to illustrate the similarity between our approach and the one used by Rautian and Sobel'man, we next consider the collisional narrowing of a pure Doppler profile. That is, we assume that the internal state of the radiator is not influenced by collisions so that the only effect of collisions on the line shape is through their alteration of the radiator's trajectory. The results obtained for this case will be just a quantum mechanical generalization of the results obtained by Rautian and Sobel'man.

We remove the influence of collisions on the internal state of the radiator by assuming that $V$, and therefore $T$ and $\Omega^{+}$, is diagonal in the $H_e$ eigenstates $|a\rangle$, $|b\rangle$, ... and all non-zero matrix elements are the same. For convenience we also ignore the internal states of the perturbers. These conditions give

$$ \langle aP | T | a'p'P' \rangle = \delta_{aa} \langle aP | T | p'P' \rangle $$$$ \langle aP | \Omega^{+} | a'p'P' \rangle = \delta_{aa} \langle aP | \Omega^{+} | p'P' \rangle. $$

(6.1)

Using these relations and the identity (13) (See equations (2.38) and (2.54) of Chap. 6 in Ref. 12)

$$ \langle pP | \Omega^{+} | p'P' \rangle = \delta_{pp} \delta_{pp'} + \langle pP | T | p'P' \rangle $$

$$ \cdot [\mathcal{F}^{-1} 1/E_{pp} - E_{pp}] - \frac{\delta_{pp}}{E_{pp} + E_{pp'}}. $$

(6.2)
where $\delta$ denotes a principle part, equation (5.14) becomes
\[
\langle aP|A|bP \rangle = (2n/h)F_{ab}(P, t) \sum_p f(p) \text{Im}
\langle p|T|pP \rangle 
\]
\[
+ (2n\pi/h) \sum_{pp'} f(p') \langle pP|T|p'P \rangle^2 \delta(E_{pp'} + E_{pp})F_{ab}(P', t).
\]
(6.3)

The transition rate $w(p', P'; p, P)$ for $(p', P') \rightarrow (p, P)$ transitions where $p \neq p'$ and $P \neq P'$ is given by
\[
w(p, P'; p, P) = (2n/h)\delta(E_{pp'} + E_{pp}) \langle p|T|pP \rangle^2
\]
and the optical theorem (equation (3.9) on p. 184 of Ref. 12) gives
\[
\text{Im} \langle pP|T|pP \rangle = -\pi \sum_{p'P'} \langle pP|T|p'P' \rangle^2 \delta(E_{pp'} + E_{pp}).
\]
(6.5)

Equation (6.3) may thus be written in the form
\[
\langle aP|A|bP \rangle = \sum_{P} A(P', P) F_{ab}(P', t) - \nu(P) F_{ab}(P, t)
\]
(6.6)

where
\[
A(P', P) = \sum_{pp'} w(p', P'; p, P) f(p')
\]
(6.7)
\[
\nu(P) = \sum_{P'} A(P, P').
\]
(6.8)

The quantity $A(P', P)$ gives the $P' \rightarrow P$ transition rate for the radiators and $\nu(P)$ is the collision frequency for radiators which have a momentum $P$.

Noting that the coefficients $A$ and $\nu$ do not depend on internal radiator states, we define a quantity $F(P, t)$ by
\[
F_{ab}(P, t) = \rho_{pp'} d_{ab} F(P', t);
\]
(6.9)
combining equations (5.8) and (6.6) we obtain
\[
\left[ \frac{\partial}{\partial t} + \nu(P) + i \left( \omega_{ab} + \frac{x \cdot P}{M} \right) \right] F(P, t) = \sum_{P'} A(P', P) F(P', t).
\]
(6.10)

The boundary condition for $F(P, t)$ is obtained from equations (5.5) in the form
\[
F(P, 0) = \langle P + h\mathbf{x}|W|P + h\mathbf{x} \rangle
\]
\[
= (2\pi M kT)^{-3/2} \exp\left(-P^2/2MkT\right)
\]
(6.11)

where we have used a Maxwell–Boltzmann distribution $W(P)$ for the radiator momenta and used $(h\mathbf{x} \cdot P/M) \ll kT$ to neglect the $h\mathbf{x}$ factors; this is valid for $h\Delta \omega \ll kT$.

Taking the Fourier transform of equation (6.10) we obtain
\[
\left[ \nu(P) + i \left( \frac{x \cdot P}{M} - \Delta \omega \right) \right] F(P, \omega) = W(P) + \sum_{P'} A(P', P) F(P', \omega)
\]
(6.12)
where \( \Delta \omega = (\omega - \omega_{ab}) \) and

\[
F(P, \omega) = \int_0^\infty e^{i\omega t} F(P, t) \, dt.
\]

From equations (2.20), (3.1), (5.3), (6.9) and (6.13), we see that the line shape is given by

\[
I(\omega) = \left(1/\pi \right) \sum_{ab} \rho_a^0|d_{ab}|^2 \text{Re} \sum_P F(P, \omega).
\]

Comparing equations (6.12) and (6.14) with Rautian and Sobel'man's equations (2.11) and (3.1) we see that, apart from the fact that their oscillator strength is unity, our results are identical with theirs.

To get numerical results for \( F(P, \omega) \) it is still necessary to solve the rather difficult Fredholm integral equation given by equation (6.12). Rautian and Sobel'man discuss approximate solutions obtained making a strong collision approximation or a diffusion approximation; the latter produces Galatry's results.\textsuperscript{13}

7. FURTHER SIMPLIFICATIONS

(A) Center of mass coordinates

The problem of obtaining solutions \( \text{F}_{\text{ab}}(P, t) \) which account for both Doppler and pressure broadening is essentially centered in the evaluation of the collision integral \( \langle aP|A|bP \rangle \). In this section we will simplify the form of \( A \) in order that the approximate solutions, discussed in the following sections, may be pursued with a minimum of mathematical complication.

We first note that the internal states of the perturbers constitute an unnecessary complication of the formalism (but not the numerical calculations). We will therefore suppress the states \( |z \rangle \), remembering that we must average \( A \) over internal perturber states when calculations are performed (note equation 5.14).

We next express \( A \) in terms of the center of mass momenta \( q \) and \( Q \) by means of the canonical transformation:

\[
Q = p + P
\]

\[
q = \mu(p/m - P/M)
\]

\[
p = \mu Q/M + q
\]

\[
P = \mu Q/m - q
\]

\[
\mu = mM/(m + M).
\]

In this transformation, \( \mu \) is the reduced mass, \( q \) is the momentum in the center of mass and \( Q \) is the momentum of the center of mass. We may transform from \( |pP \rangle \) to \( |qQ \rangle \) using\textsuperscript{13}

\[
|pP\rangle = \sum_{qQ} |qQ\rangle \langle qQ|pP\rangle
\]

\[
= \sum_{qQ} |qQ\rangle \delta(q, \mu p/m - \mu P/M) \delta(Q, P + P).
\]
In terms of these coordinates, equation (5.13) becomes

\[
\langle aP|AlbP \rangle = -(\sin/h) \sum_{qQ} \delta(q, \mu Q, M - P) \times \langle aqQ|T/\mathcal{F}(t)\mathcal{O}_Q^+T'/\mathcal{F}(t)'|bqQ \rangle.
\]

(7.7)

Since the momentum of the center of mass, \(Q\), is not altered by collisions, we have

\[
\langle aqQ|T|a'q'Q' \rangle = \langle aqQ|T|a'q'Q' \rangle \delta_{QQ'}
\]

(7.8)

\[
\langle aqQ|\mathcal{O}^+_Q|a'q'Q' \rangle = \langle aqQ|\mathcal{O}^+_Q|a'q'Q' \rangle \delta_{QQ'}
\]

(7.9)

Noting that \(f\) and \(F(t)\) are diagonal in \(|q\rangle\) and \(|P\rangle\) respectively, we obtain

\[
\sum_{qQ} \delta(q, \mu Q/M - P) \langle aqQ|TF(t)|bqQ \rangle = (m/\mu)^3 \sum_{qQ} \langle aqT|a'q' \rangle \langle b'q'|\mathcal{O}^+_Q|bq \rangle
\]

using \(\Delta q = (q - q')\) equation (7.7) becomes

\[
\langle aP|AlbP \rangle = -(\sin/h)(m/\mu)^3 \sum_{qQ} \left\{ \frac{m}{\mu} \mathcal{F}_{a'b'}(P + \Delta q, t) \right\} \times \langle aqT|a'q' \rangle \langle b'q'|\mathcal{O}^+_Q|bq \rangle - \langle aq|\mathcal{O}^+_Q|a'q' \rangle \langle b'q'|T'|bq \rangle.
\]

(7.11)

While this result is still rather complicated, it is nonetheless considerably simpler than equation (5.14) which it replaces.

(B) The no-quenching approximation

From scattering theory, we know that the probability for an inelastic transfer of an amount of energy \(\Delta E\), during a collision of duration \(\tau\), will be small unless (See equation 137 of Ref. 14)

\[
(\tau \Delta E/h) < 1.
\]

(7.12)

We also know that the natural oscillation frequency for \(\mathcal{F}_{a}(P, t)\), obtained by setting \(\Lambda\) to zero in equation (5.8), is just \((\omega_{ab} + \mathbf{x} \cdot \mathbf{P}/M)\). Thus, for an emission line, we regard \(|a\rangle\) and \(|b\rangle\) as initial and final states respectively. Using equation (7.12) we note that collision induced transitions from \(|a\rangle\) to \(|a'\rangle\) or \(|b\rangle\) to \(|b'\rangle\) are negligible unless \((\tau E_{ab}/h) < 1\) or \((\tau E_{ba}/h) < 1\) respectively. We therefore define an average collision time \(\tau_{av}\) and we restrict the sum over \(|a\rangle\) and \(|b\rangle\) in equation (7.11) to include only those states which satisfy \(E_{aa} < (h/\tau_{av})\) and \(E_{ab} < (h/\tau_{av})\); the states \(|a\rangle\) and \(|b\rangle\) which satisfy this criterion are also referred to as initial and final states (even though some \(|a\rangle\rightarrow|b\rangle\) may not correspond to allowed radiative transitions). The above restriction on the type of matrix elements to be considered is referred to as the no-quenching approximation.
8. SMALL PERTURBER LIMIT

At this point it is perhaps useful to show how the usual Voigt profile may be recovered from the present results. For this purpose, we consider an example where \( m \ll M \) (e.g., electron perturbers). In this case the recoil of the radiator will be negligible \( \Delta P \ll P \). Since the momentum of the center of mass, \( Q \), is not changed by a collision, equation (7.4) indicates that \( \Delta q = \Delta P \ll P \). For simplicity we also assume that all initial and final states are quasi-degenerate so that \( E_{aa'} \approx E_{bb'} \approx 0 \) and \( \omega_{aa'} = \omega_{bb'} \). With these assumptions, the matrix elements of \( \Omega^{\pm} \) may be given by (See equations 2.38 and 2.54 in Chap. 6 of Ref. 12)

\[
\langle a|Q^\pm|a' \rangle = \delta_{aa'} \delta_{qq'} + \langle a|T|a' \rangle \left[ \mathcal{A}(1/E_{aa'}) - i\pi \delta(E_{qq'}) \right]
\]  

(8.1)

and equation (7.11) becomes

\[
\langle aP|\Phi|bP \rangle = \sum_{a'b'} \langle ab|\Phi|a'b' \rangle F_{ab}(P, t)
\]  

(8.2)

where \( \Phi \) is a matrix in the 'double atom' or tetradic notation

\[
\Phi = -(in/\hbar) \sum_q q \left[ \langle \Phi q \rangle \langle q \Phi \rangle - \langle q \Phi \rangle \langle \Phi q \rangle \right] + 2\pi i \sum_q \langle \Phi q \rangle \langle q \Phi \rangle \delta(E_{qq'}) \langle q \Phi \rangle \langle q \Phi \rangle \}
\]  

(8.3)

In this notation, \( T_l \) and \( T_r \) operate only on initial and final states,

\[
\langle ab|T_l|a'b' \rangle = \langle a|T|a' \rangle \delta_{ab}
\]

\[
\langle ab|T_r|a'b' \rangle = \langle b|T|b' \rangle \delta_{aa'}
\]

(8.4)

The operator \( \Phi \) is identically the same as the 'effective interaction' operator which appears in the impact theory for pressure broadening (cf. equations (62) and (67) of Ref. 15 noting that \( \Phi = -i\mathcal{H} \) in the notation of that paper).

Combining equation (8.2) with (5.8), and noting equation (6.11), we obtain

\[
\left[ \frac{\partial}{\partial t} + i \left( \omega_0 + \frac{\mathbf{x} \cdot \mathbf{P}}{M} \right) \right] F_{ab}(P, t) = \sum_{a'b'} \langle ab|\Phi|a'b' \rangle F_{a'b'}(P, t)
\]  

(8.5)

\[
F_{ab}(P, 0) = d_{ab} \rho_{ab} W(P)
\]  

(8.6)

hence

\[
F_{aa}(P, t) = W(P) \sum_{a'b'} \langle ab| \exp \left\{ -i(t(\omega_0 + \mathbf{x} \cdot \mathbf{P}/M + i\Phi)|a'b' \rangle \rho_{ab} d_{a'b'} \right.  
\]

(8.7)

Using \( \Delta \omega = \omega - \omega_0 \), the line shape obtained from equations (2.20), (3.1), (5.3), and (8.7) is

\[
I(\omega) = \frac{1}{(2\pi M kT)^{3/2}} \sum_{a'b'} \rho_{a'b'} d_{a'b'} \cdot d_{a'b'}
\]

\[
\cdot \Im \left\langle ab \left| \int d^3P \exp\left( -P^2/2MkT \right) \left( \Delta \omega - \mathbf{x} \cdot \mathbf{P}/M - i\Phi \right) \right| a'b' \right\rangle
\]

(8.8)

We perform the integrals over the two \( P \) components normal to \( \mathbf{x} \) and, for the component \( P_x \) which is parallel to \( \mathbf{x} \), we change variables to

\[
\omega' = xP_x/M \approx \omega_0 P_x/Mc
\]
In this manner, \( I(\omega) \) reduces to the convolution form stated in equations (1.1) and (1.2) with \( I_r \) given by

\[
I_r(\omega) = -(1/\pi) \sum_{ab} \rho_{ab}^\prime \mathbf{d}_{ab} \cdot \mathbf{d}_{a'b'} \text{Im} \langle ab | [\Delta \omega - i \Phi]^{-1} | a'b' \rangle. \tag{8.9}
\]

From these results we see that when collisions have no influence on the radiators trajectory, we obtain the familiar Voigt profile.

9. NO LOWER STATE INTERACTION

In many problems of interest, the final states \(|b\rangle, |b'\rangle\), etc. are more tightly bound and less polarizable than the upper states \(|a\rangle, |a'\rangle\), etc. In such case one frequently finds that the matrix elements of \( V \) between the lower states are negligible in comparison with the upper state matrix elements. The lower state interaction may then be neglected by using \( \langle b | V | b' \rangle = 0 \) for all final states. This approximation results in \( \langle b | \Omega | b' \rangle = \delta_{bb'} \) and \( \langle b | T | b' \rangle = 0 \). With this approximation, equations (5.8) and (7.1) provide

\[
\left[ \frac{\partial}{\partial t} + i \left( \omega_{ab} + \frac{\mathbf{x} \cdot \mathbf{P}}{M} \right) \right] F_{ab}(\mathbf{P}, t) = \sum_q \langle a | \Phi(\mathbf{P}) | a' \rangle F_{a'b'}(\mathbf{P}, t) \tag{9.1}
\]

where \( \Phi(\mathbf{P}) \) is a matrix defined by

\[
\langle a | \Phi(\mathbf{P}) | a' \rangle = -(i \hbar/h)(m/\mu)^3 \sum_q \langle aq | T | a'q \rangle f \left\{ \frac{m(q/\mu + P)}{M} \right\}. \tag{9.2}
\]

Equation (9.1) can be solved, with the aid of equation (8.6), giving

\[
F_{ab}(\mathbf{P}, t) = \sum_q \langle a | \exp \left\{ -i t \left[ \omega_0 + \frac{\mathbf{x} \cdot \mathbf{P}}{M} + i \Phi(\mathbf{P}) \right] \right\} | a' \rangle W(P) \rho_{ab}^\prime \mathbf{d}_{ab} \tag{9.3}
\]

where we have again used \( \omega_0 \) to denote the emission frequency. Comparing with equation (8.7) we see that the only significant difference is in the momentum dependence of the \( \Phi \)-matrix. This momentum dependence is responsible for a statistical coupling of Doppler and pressure broadening mechanisms.

A line shape can readily be obtained using equations (2.20), (3.1), (5.3) and (9.3) and this line shape expression should be calculable without too much difficulty. In fact, the great advantage in neglecting lower state interaction is that this approximation results in a calculable line shape expression. When lower state interactions cannot be neglected, the kinetic equation in \( P \) (e.g. equation 6.12) presents an additional complication for which additional approximations must be introduced.

10. SUMMARY AND DISCUSSION

In the previous sections we have derived an expression for the line shape due to both Doppler and pressure broadening. This result may be summarized by the following equations:

\[
I(\omega) = (1/\pi) \text{Re} \sum_{ab} \langle b | d | a \rangle \int e^{i\omega t} F_{ab}(\mathbf{P}, t) \, dt \tag{10.1}
\]

\[
\left[ \frac{\partial}{\partial t} + i \left( \omega_{ab} + \frac{\mathbf{x} \cdot \mathbf{P}}{M} \right) \right] F_{ab}(\mathbf{P}, t) = \langle a | \Lambda | F(t) | b \rangle. \tag{10.2}
\]
The collision integral $A$ is a function of $F_{ab}(P, t)$ where $a, a', \ldots$ denote initial states and $b, b', \ldots$ denote final states. The general form for $A$ is given by equation (5.14) in terms of $|p, P\rangle$ states and by equation (7.11) in terms of center of mass states $|q, Q\rangle$.

The approximations used in deriving these general results are the impact approximation, the completed collision assumption, the weak coupling density matrix, and the no quenching assumption. The first two assumptions concern the dynamics of the system: these approximations should be valid for neutral gases with short range forces and they are also valid if the initial and final states are not mixed over part of the line profile for Stark broadened lines. The weak coupling density matrix has been shown to be valid for $h\Delta\omega < kT$. The no-quenching assumption is useful if the initial and final states are not mixed by the perturbation of the radiator; if such a mixing does occur, the no-quenching approximation is easily removed by simply summing over both initial and final states.

REFERENCES

13. All delta functions which appear in this paper are Kronecker delta functions because we are using discrete momentum states. In order to perform calculations, one may pass to the continuum limit in which case $\delta_{\omega} \rightarrow (2\pi\hbar)^{-1} \delta(\omega - \omega^\prime)$ and $\Sigma \rightarrow (2\pi\hbar)^{-1} |d\omega|$ cf. equations 1.12 and 1.13 in Chap. 6 of Ref. 12.

APPENDIX

To prove the result stated in equation (2.9), we consider a radiating atom having only one ‘orbital’ electron. The mass, position and momentum are denoted by $m$, $r$, and $p$, for the electron and by $M$, $R$ and $P$ for the nucleus ($r$, $p$, $R$ and $P$ are vector operators whose eigenvalues are referenced to some fixed observer). We will assume, for convenience, that $M \gg m$, so that $M$, $R$ and $P$ also describe the center of mass of the atom. The dipole moment is thus given by

$$d = e(R - r).$$

(A.1)

The fundamental interaction between the radiation field and the particles is given by (p. 176 of ref. 8)

$$H_{int} = \frac{e^2}{c} [ (p/m) \cdot \nabla (r) ] - (P/M) \cdot \nabla (R)$$

(A.2)

where $\nabla (R)$ denotes the vector potential at the point $R$.

$$\nabla (R) = \sqrt{(4\pi)} \sum_q [ q_q \delta_3^q e^{i \mathbf{q} \cdot \mathbf{R}} + q_{q}^* \delta_3^{-q} e^{-i \mathbf{q} \cdot \mathbf{R}}]$$

(A.3)

and we have neglected terms of order $\alpha^2$ (two-photon transitions).
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We next assume that the wavelength of the emitted radiation is much greater than the dimensions of the radiator so that \((\mathbf{x} \cdot \mathbf{d} \cdot \mathbf{e}) \ll 1\) or, using equation (A.1),

\[
\exp(\mathbf{x} \cdot \mathbf{r}_e) = \exp(\mathbf{x} \cdot \mathbf{R})[1 - (\mathbf{x} \cdot \mathbf{d} \cdot \mathbf{e}) + \cdots].
\]  

(A.4)

Neglecting the \((\mathbf{x} \cdot \mathbf{d} \cdot \mathbf{e})\) correction terms gives the dipole approximation \(\mathcal{A}(\mathbf{r}_e) \approx \mathcal{A}(\mathbf{R})\) or

\[
H_{\text{int}} = \frac{\mathbf{e}}{c}(\mathbf{p}_I + \mathbf{p}_M) \cdot \mathcal{A}(\mathbf{R}).
\]  

(A.5)

Using \([\mathbf{P} - (\mathbf{e} \cdot \mathbf{c})\mathcal{A}(\mathbf{R})] = (i/\hbar)[H_{\text{int}}, \mathbf{R}]\) with equation (A.1) and neglecting terms of order \(\mathcal{O}\) we obtain

\[
H_{\text{int}} = -(i/\hbar c)[H_{\text{int}}, \mathbf{d}] \mathcal{A}(\mathbf{R})
\]

\[
= -(i/\hbar c)[[H_{\text{int}}, \mathbf{d} \cdot \mathcal{A}(\mathbf{R})] - \mathbf{d} \cdot [H_{\text{int}}, \mathcal{A}(\mathbf{R})]]
\]

\[
= -(i/\hbar c)[[H + H_{\text{int}}, \mathbf{d} \cdot \mathcal{A}(\mathbf{R})] - \mathbf{d} \cdot [H + H_{\text{int}}, \mathcal{A}(\mathbf{R})]].
\]  

(A.6)

From the matrix elements for emission (see equation 2.8)

\[
\langle B; n_a + 1| [H + H_{\text{int}}, \mathbf{d} \cdot \mathcal{A}(\mathbf{R})]|A; n_a \rangle
\]

\[
= \hbar (\omega_a - \omega_{ab}) \langle B; n_a + 1|\mathcal{A}(\mathbf{R})|A; n_a \rangle
\]

\[
= 0
\]  

(A.7)

since \(\omega_a = \omega_{ab}\). Using the expression for \(H_{\text{int}}\) given in Sect. 2(B) and the commutation relations (p. 57 of Ref. 8),

\[
[q_{ax}, q_{ax}^*] = (\hbar/2\omega_a)\hbar \delta_{aa}, \delta_{kk},
\]  

(A.8)

one can show that

\[
(i/\hbar c)[H_{\text{int}}, \mathcal{A}(\mathbf{R})] = -\mathcal{A}(\mathbf{R})
\]  

(A.9)

where \(\mathcal{A}(\mathbf{R})\) is given by equation (2.6). The remaining term in equation (A.6) is

\[
(i/\hbar c)[H, \mathcal{A}(\mathbf{R})] = (i/2\hbar Mc)[\mathbf{P} \cdot \mathbf{V}, \mathcal{A}(\mathbf{R})]
\]

\[
= \frac{\mathbf{P} \cdot \mathbf{V}}{Mc} \mathcal{A}(\mathbf{R}).
\]  

(A.10)

Taking the gradient of \(\mathcal{A}(\mathbf{R})\) (see equation A.3) we obtain the components of \(\mathcal{A}(\mathbf{R})\) (see equation 2.6) multiplied by \((\mathbf{P} \cdot \mathbf{V}/Mc) \leq (\mathbf{V}_{\text{rad}}/c)\) where \(\mathbf{V}_{\text{rad}}\) denotes the radiator velocity; this term thus adds a negligible relativistic correction to equation (A.9). Substituting these results back into equation (A.6) we obtain

\[
H_{\text{int}} = -\mathbf{d} \cdot \mathcal{A}(\mathbf{R}).
\]  

(A.11)