PRESSURE BROADENING AND
COHERENCE TRANSIENTS EFFECTS
- A KINETIC THEORY APPROACH

by

DENNIS ALLAN COOMBE
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Department of Chemistry

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date March 26/1976
ABSTRACT

The response of a polyatomic gas to microwave radiation - including both steady state (pressure broadening) and time dependent (coherence transients) effects - is described theoretically. The treatment is based on solutions of a quantum mechanical Boltzmann equation and employs kinetic theory methods which have previously been used in the explanation of the field dependence of transport phenomena (Senftleben-Beenakker effects).

Much of the recent theoretical work of pressure broadening and coherence transient phenomena is based on a two (energy) state model for the gas molecules. This model, when developed from a density operator point of view, results in a coupled set of three equations which are mathematically equivalent to the Bloch equations of NMR. The present work reexamines this description, and replaces it with a two level model for the gas system. Here, the term "level" implies explicit consideration of the rotational (magnetic) degeneracy associated with each energy state. This model gives a more appropriate representation of the interaction of microwave radiation with a real molecular system. In particular, a more complete set of coupled equations result from this description and involve quantities in addition to the three moments used in a two state approach. The most important of these latter effects are represented by spherical harmonics $\mathcal{Y}_J^l(\hat{\mathbf{r}})$ in the angular momentum $J$ of the relevant energy levels. An analogous
treatment of rotational effects has previously been used in Senftleben-Beenakker studies. Specific molecular types of interest in microwave spectroscopy - diamagnetic diatomics and linear polyatomics, symmetric tops, and inverting symmetric tops - are treated separately by this two level approach. The vector (and tensor) nature of the motions are emphasized throughout.

The number of rotational polarizations that arise in the general two level case is often quite large. The simplest example of a two level system is the \( j=0 \) to \( j=1 \) transition of a diamagnetic diatomic. This is studied in some detail. Here, the scalar component \( Y^{(2)0}_j \) is the only rotational polarization affected by linearly polarized radiation in the usual experiments. The effect of this quantity on both steady state and transient phenomena is described, and a new "combination" experiment is suggested as the best way to detect the presence of this additional polarization.

The Doppler effect is treated by appropriately including the effects of translational motion in the quantum Boltzmann equation. A more general set of coupled moment equations then results, and the manner in which the macroscopic velocity polarizations arise is thereby established. A model method solution of the quantum Boltzmann equation, emphasizing the parity invariance of the collision superoperator, is given for a steady state absorption experiment in the absence of saturation but including Doppler effects.
Throughout this thesis, the relaxation rates are related to kinetic theory collision cross sections by solving the quantum Boltzmann equation. Extensive use is made of rotational invariance to reduce the number of independent collision integrals, and their approximate evaluation is accomplished within the context of the distorted wave Born approximation. All collision integrals for the pure internal state polarizations are found to be expressible in terms of one translational factor, which is itself further approximated by a modified Born approximation. Correspondingly, the translational factor which arises in the relaxation of macroscopic velocity polarizations is completely specified by relating it to the $\Omega^{(L,s)}$ integrals of traditional kinetic theory.
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All quotations are from Lewis Carroll's "Alice's Adventures in Wonderland" and "Through the Looking Glass."
"Mine is a long sad tale" said the Mouse turning to Alice and sighing. "It is a long tail, certainly" said Alice, looking down with wonder at the Mouse's tail, "but why do you call it sad?"
This thesis represents an attempt at a unified formulation of several related microwave experiments - pressure broadening, saturation broadening and Doppler broadening of steady state lineshapes as well as the corresponding time domain transient emission and absorption effects - on a dilute gas of polyatomic molecules. The approach is based on the solution of a quantum mechanical Boltzmann equation and is presented in a manner that is consistent with earlier explanations of the field dependence of transport phenomena (Senftleben-Beenakker effects). It is hoped that this systematic development will provide a framework for the description of most gas phase phenomena in the binary collision regime and thus allow a greater understanding of both experimental and theoretical results.

The thesis is divided into seven chapters. The first provides a qualitative overview of the general field of pressure broadening and related phenomena. The more specific areas of concern are then presented in a quantitative fashion in chapter II, based on a consistent, but somewhat elementary, approach of other workers. Chapter III summarizes the theoretical methods employed in the study of Senftleben-Beenakker effects. These same kinetic theory methods then allow a re-examination, in chapters IV, V, and VI, of the internal state effects described in chapter II. Indeed, Chapter IV discusses the treatment quite generally, with particular emphasis on collisional aspects. The approach is
pursued further in chapter V and connections are made with
the more elementary theory of chapter II, for specific
molecular types. Chapter VI is included as an illustrative
example of the new effects which are predicted from this
kinetic theory treatment. Chapter VII points out that the
methods of chapter III are also useful in discussing the
complications introduced by translational (velocity) effects.
Conceptually then, chapters IV through VII can be viewed as
a synthesis of chapters II and III.
Because the nature of this thesis is that of connection and comparison, and because the huge volume of material already published on pressure broadening and related phenomena demands a certain amount of editing, it was felt that a qualitative overview of the subject should first be presented. This chapter, then, is intended as a general perspective on the "state of affairs" without invoking the detailed mathematical arguments of later chapters. Included are definitions of terms usually employed in the explanation of these effects as well as a description of how these microwave experiments can be viewed in relation to analogous experiments in other regions of the electromagnetic spectrum.

An idealized experimental set up is shown in figure 1. It consists of three components - a source of a disturbance, a system to which the disturbance is applied, and a detector which measures the response of the system to the disturbance. In particular, the source may be continuous wave (c.w.) microwave radiation, the detector a steady state frequency detecting system, and the system a collection of completely isolated, nontranslating atoms (or molecules) each having a number of discrete internal state energy levels. A transition (say absorption) between two of these definite energy states should result in a sharp line in the detected spectrum. Yet experimentally, these lines have a finite width. What factors are involved in creating the observed shape? Succeeding paragraphs will discuss the various contributions, in turn.
Figure 1: A block diagram of the idealized experiment.
The most fundamental (universal) contribution to an observed line shape is the natural line shape\textsuperscript{1,2} which results from an interruption of the radiation process by a totally quantum mechanical phenomena - spontaneous emission - (although classical electromagnetic theory interprets natural broadening in terms of radiation damping). The natural line shape can be shown to have a Lorentzian form

\[ I(\omega) = \frac{I_0 \gamma}{2\pi} \frac{1}{(\omega - \omega_0)^2 + \frac{\gamma^2}{4}} \]

with the half width $\gamma$ correctly identified as the total spontaneous transition probability per unit time.

Spontaneous emission is caused by the interaction of the quantum mechanical system with a photon even when the expectation value of the electric field is strictly zero. That there exists a non-zero probability of having a photon present when there is no electric field is a quantum mechanical aspect of light - namely that $E$, the operator for the electric field, and $n$, the operator for the number of photons, do not commute $[E, n] = E$ and hence obey an uncertainty relation of the form $\Delta E \Delta n \geq \frac{\hbar}{2} |E|$. 

The spontaneous transition probability per unit time, and thus the natural line width $\gamma$, varies as the frequency cubed, $\omega^3$. In the microwave region of the spectrum, this contribution is many orders of magnitude smaller than other broadening mechanisms (to be discussed below) and hence can be safely neglected. However, since the natural width
increases markedly with frequency, a neglect of the spontaneous emission mechanism in optical regions of the spectrum can not be so easily rationalized. From these considerations, it is felt that a classical description of the radiation field is sufficient in regions where the natural line shape can be neglected, but a QM treatment of light is mandatory whenever spontaneous emission is a significant broadening mechanism.

The realization that the individual molecules in a gas are not isolated but in constant, mutual interaction brings one to the much discussed phenomena of pressure broadening. The term "pressure broadening" is derived from the usual experimental observation that an increase in the pressure in the gas cell (i.e. an increase in the number of interacting molecules) leads to an increased broadening of the line under study. Various qualitative aspects of pressure broadening – definitions, natural diversions and sub-classifications – are outlined in the next few paragraphs. The more detailed mathematical descriptions begin in chapter II.
Aspects of Pressure Broadening

There are two limiting cases of pressure broadening—termed the statistical and impact limits. In the former, the perturbers are assumed to move past the radiating molecules infinitely slowly. This creates a static but random perturbation in the energy levels of the radiating molecule. The impact theory, on the other hand, considers sharp, impulsive collisions which create an incoherence in the emitted radiation. The regions of validity of each of these approaches can be stated in terms of three relevant parameters: \( \omega - \omega_0 \), the deviation from line centre, \( \tau_c \), the duration of a collision, and \( \tau_f \) the mean time between collisions. Then, as discussed by Spitzer and Holstein, in the binary collision regime (\( \tau_c < \tau_f \)) the impact theory is valid near the line centre \( \left( (\omega - \omega_0)\tau_c < 1 \right) \) while the statistical theory is valid in the wings \( \left( (\omega - \omega_0)\tau_c > 1 \right) \). As the pressure is increased past the dilute gas region (\( \tau_c > \tau_f \)), the concept of an isolated collision becomes meaningless and a statistical theory must apply. A unified treatment of the two theories has been presented by Anderson and later by Futrelle.

Margenau and Lewis have reviewed the structure of plasma spectral lines starting with the classic work of Holtsmark. Here, in addition to the presence of neutral perturbers, consideration must be given to the effects of ions and electrons. For the fast moving electron effects, a form of the impact theory is usually suitable, while for the heavier (and hence slower moving) ions, a statistical theory is deemed necessary. The effects of charged perturbers is
known generally as **Stark broadening**.

The impact theory of broadening by neutral molecules is now discussed in greater detail. Here, a Lorentzian line shape is generally expected for an isolated line, with a width $\frac{1}{T_2}$. The pioneering work of Anderson ushered in the modern era of impact broadening treatments in that the relationship between the intermolecular forces and collisions was explicitly displayed. Anderson's theory, in one sense, represents a generalization of the work of Foley to include inelastic (diabatic) collisional effects. That is, $\frac{1}{T_2} = \frac{1}{T_2} \text{ elastic} + \frac{1}{T_2} \text{ inelastic}$. This generalization allowed Anderson's treatment to be applicable to lines in the microwave region where inelastic effects are expected to occur quite readily. To see this, consider the quantity $\frac{\hbar \omega_0}{kT}$ where $\omega_0$ is the frequency difference between the two levels under consideration and $kT$ represents an average available kinetic energy. In the optical region at normal temperatures $\frac{\hbar \omega_0}{kT} \gg 1$ and there is not sufficient translational energy available on the average to cause inelastic "optical" transitions. Thus elastic (also called phase-shifting or adiabatic) collisions dominate, $\frac{1}{T_2} = \frac{1}{T_2} \text{ elastic}$. In the microwave region, however, $\frac{\hbar \omega_0}{kT} \ll 1$ and by similar reasoning, inelastic effects must be considered. In his treatment, Anderson employed a semi-classical description wherein the translational degrees of freedom are treated classically. He further assumed that this translational motion could be approximated by straight line trajectories - indicating that distant collisions (large impact parameters) should
be dominant. Anderson's treatment is discussed in detail (and some further simplifications pointed out) in a paper by Tsao and Curnutte.\textsuperscript{15} In summary, then, Anderson's work on isolated lines gives a Lorentzian line shape with an expression for the width $\frac{1}{T_2}$ in terms of detailed (elastic and inelastic) collisional effects and the intermolecular potential.

The ease with which inelastic collisions occur in the microwave region also necessitates consideration of collisional couplings between various lines. Indeed, the overlapping of spectral lines in the microwave portion of the spectrum is almost the rule rather than the exception. Kolb and Griem\textsuperscript{16} and Baranger, in a series of papers,\textsuperscript{17} independently extended Anderson's work to include overlapping lines. In essence, the one relaxation rate $\left(\frac{1}{T_2}\right)$ description of an isolated line is replaced by a matrix of relaxation rates $\left(\frac{1}{T_2}\right)$ - the off diagonal elements of which are usually designated as frequency coupling terms. It was Baranger, with his definition of "line space" (later termed Liouville space) who probably first realized that the problem of pressure broadening was naturally a question of operators (observables) and how they evolve and relax. This basic change in attitude is most elegantly presented in a paper by Fano\textsuperscript{18} and it is this approach which I feel is necessary for the clearest understanding of the variety of effects involved. Needless to say, the "operator" point of view will be emphasized throughout this thesis.

The effects on line shapes of degenerate magnetic states (rotational invariance) and various invariance properties of
collision processes have been discussed in a comprehensive fashion by Ben-Reuven\textsuperscript{19}. He then applied these ideas to a treatment of overlapping lines and the transition from resonant to non-resonant (Debye; zero frequency) line shapes in microwave spectra.\textsuperscript{20} By these considerations, he derived detailed collisional sequences for the phenomenological parameters in the Van Vleck-Weiskopf line shape\textsuperscript{21} and showed how it could be generalized.

In connection with Debye relaxation, some further comments seem appropriate. Birnbaum\textsuperscript{22} treated the problem of non-resonant absorption starting from a quantum mechanical kinetic equation approach. However, the kinetic equation chosen by Birnbaum (Wang-Chang Uhlenbeck equation)\textsuperscript{23} is inappropriate in that it does not treat the degenerate magnetic states properly - yet non-resonant absorption is fundamentally concerned with just these states. An alternate treatment has been given by Tip and McCourt,\textsuperscript{24} which is based on the appropriate equation for these "zero frequency" effects - the Waldmann-Snider equation.\textsuperscript{25,26} This thesis generalizes the work of Tip and McCourt to "non-zero frequency" effects (resonant absorption). As discussed in chapter IV, the appropriate kinetic equation has the Waldmann-Snider form.
(d) Saturation Effects

The descriptions outlined above have implicitly assumed low power input by the source. An additional broadening effect, termed saturation (or power) broadening, occurs when the source of radiation is very strong. This has been treated by Townes and Schawlow and, using a density matrix point of view, by Karplus and Schwinger. Saturation will be described in some detail in the next chapter. The present discussion is limited to a few qualitative remarks.

Basically, first order effects in the source-system coupling $\mathbf{u} \cdot \mathbf{E}_0$ create forced oscillations between the two levels resonant with the radiation, but do not change the equilibrium populations of these two states (i.e. no saturation). It is this saturation that has been discussed in the preceding subsection where it has been pointed out that this forced oscillation decays at a rate $\frac{1}{T_2}$ (assuming an isolated line). However, at higher powers, second order terms in the coupling $\mathbf{u} \cdot \mathbf{E}_0$ became significant as well, and these terms are responsible for creating a non-equilibrium population difference which can relax to its equilibrium value at a relaxation rate $\frac{1}{T_1}$. The recognition that (at least) two distinct relaxation processes are occurring here, means that the two relaxation times are not necessarily equal. Indeed, one recognizes that the relaxation of population differences governed by $\frac{1}{T_1}$, can only occur through inelastic collisions while $\frac{1}{T_2}$ processes include contributions from both elastic and inelastic effects. From these arguments, it is expected that
\[ \frac{1}{T_2} > \frac{1}{T_1}, \] depending on how effective the elastic collision contribution is to \( \frac{1}{T_1} \). If, as has been suggested, the inelastic collisional effects dominate relaxation processes in the microwave region, then \( \frac{1}{T_2} \sim \frac{1}{T_1} \). This is known as the strong collision model. The qualitative discussion just given will be put in quantitative terms in chapter II and developed further in later parts of the thesis. In fact, considerable emphasis will be placed on this aspect of pressure broadening.

Before leaving the general area of pressure broadening, it is felt that some selected contributions of R.G. Gordon should be mentioned. He has developed\(^{29}\) a treatment of line widths and shifts that does not make the approximations of perturbation theory and straight line trajectories, in contrast to Anderson. Because Gordon's approach here is of a more classical nature, it is especially useful in "picturing" various collisional effects. Some comments on how populations relax have been given in another paper\(^{30}\) by Gordon. Additional approaches involving semiclassical\(^{31}\) and completely quantum\(^{32}\) calculations of line shapes, and other relaxation phenomena, have also been described. However, it is Gordon's efforts to correlate widely varying gas phase collision phenomena that has been most appreciated. Two articles\(^{33,34}\) in particular illustrate this philosophy. (The work presented in this thesis has also been motivated by the same underlying idea. Namely, that a fuller understanding of intermolecular forces can be gained by a comparison of results within a unified framework.)
The recent review article by H. Rabitz$^{35}$ provides further references to more detailed aspects of pressure broadening of spectral lines in the microwave region.
(c) Doppler Broadening

The **Doppler contribution to the line shape** is the result of the translational reaction of the molecules. Indeed, if a stationary molecule emits light of frequency $\omega_0$, then this molecule, when moving with velocity $v$, will emit light whose frequency is shifted by an amount $k \cdot v$. Since a velocity $v$ occurs with a probability proportional to $\exp[-mv^2/2k_BT]$, the resultant Doppler line shape can be regarded as an infinite sum (i.e. integral) over the various velocity components, weighted with a Boltzmann distribution: namely

$$I_D(\omega) = \int \int dv (\frac{m}{2\pi k_B T})^{3/2} \exp\left[ -\frac{mv^2}{2k_BT} \right] \delta(k \cdot v - \Delta \omega)$$

$$= \left( \frac{mc^2}{2\pi k_BT \omega_0} \right)^{1/2} \exp\left[ -\frac{mc^2}{2k_BT} \left( \frac{\Delta \omega}{\omega_0} \right)^2 \right] .$$

Consequently the resultant profile is Gaussian. It then follows that the half width at half maximum is

$$\Delta \omega_D = (\frac{2kT}{m} \ln 2)^{1/2} \frac{\omega_0}{c} .$$

From the earlier discussion of pressure broadening, each velocity component should possess a finite width of its own, due to molecule-molecule interactions affecting the interval states. The observed line shape should be due to a composite of pressure broadening and Doppler effects. If the effects were independent, then the line shape would be the convolution of the Doppler profile $I_D(\omega)$ and the Lorentzian profile $I_L(\omega)$, namely

$$I(\omega) = \int d\omega ' I_D(\omega ') I_L(\omega - \omega ') .$$

This resulting lineshape is known as a **Voigt profile** and is a sufficient description for many qualitative features of the line shapes. However,
it does not represent the whole story. The effects of velocity-changing collisions (Dickie narrowing) are not included—this aspect is treated in detail in chapter VII. For the purpose of the present discussion, however, the Doppler half width $\Delta \omega_D$ is small in the microwave region of the spectrum, and thus (except for quite low pressures in the gas cell where pressure broadening is insignificant) the Doppler effect on lineshapes can be neglected.
(f) Related Areas of Spectroscopy

Although this thesis is concerned with line shapes and related phenomena in the microwave region of the spectrum, a great deal of additional understanding can be obtained by comparing relative magnitudes of the effects and various approaches to the general problem in the parts of the electromagnetic spectrum which surround the microwave region. To this end, some comments on analogous gas phase phenomena in the radio frequency and optical frequency regions are now presented.

Despite its relatively late development, nuclear magnetic resonance now ranks as probably the most highly studied, most highly developed form of spectroscopy. A set of three coupled evolution-relaxation equations for a spin $1/2$ system (either in the form of Bloch or Redfield equations) is an ideal way to concisely describe the line shape, saturation, and related phenomena. (In fact, one would be well on the way to understanding the corresponding effects in the microwave region if an analogous set of coupled equations could be derived and their limits of validity established.) In the Bloch equations, the $T_2$ relaxation of $M^+$ and $M^-$ is related to the relaxation of the coherences $|\frac{1}{2}\rangle<\frac{1}{2}|$ and $|\frac{1}{2}\rangle<\frac{1}{2}|$, while the $T_1$ relaxation of $M^+$ is proportional to the relaxation of a population difference. Thus the $T_1, T_2$ nomenclature employed in earlier paragraphs in the discussion of microwave relaxations is seen to be consistent with the NMR definitions. Further, phenomenological line shape expressions involving
$T_1$ and $T_2$ are of the same form\textsuperscript{29} as the microwave case. It should be stressed, however, that the actual mechanism for relaxation in gas phase NMR can differ greatly from the microwave situation. Indeed, as discussed above, collisions are directly responsible for relaxation in the microwave region. This is also true for nuclear spin relaxation in monatomic gases. Here relaxation times are extremely long because direct collisional effects on nuclear spin states are very weak. In polyatomic gases, this same "weakness of collisions" means that other relaxation mechanisms are preferred, when available. Thus, for example, nuclear states in polyatomics are relaxed predominantly by intramolecular coupling (spin-rotation) to rotational states which are in turn relaxed by collisions. Even when this mechanism dominates, however, the relaxation times are found to be much larger than microwave relaxation times. A kinetic theory approach to both the monatomic\textsuperscript{40a} and polyatomic\textsuperscript{40b} cases have been discussed by Chen and Snider.

Doppler effects play a negligible role in NMR spectral line shapes since the wavelengths involved are much larger than the length of the cell and hence no spatial inhomogeneities resulting from the r.f. field occur. (In fact, any spatial dependence is more readily attributable to field inhomogeneities in the magnet and to diffusion effects.\textsuperscript{41}

Finally, it should be pointed out that in NMR no mention is ever made of natural line shape effects and that a classical description of the radiation field is always employed.
The coherent source means that macroscopic oscillations are induced in the system while the coherent detector means that both in-phase and out-of-phase components of these oscillations can be determined. It is this coherent nature of the field-system interaction that allows time-dependent (Fourier transform) studies to be undertaken. Fourier transform techniques give the same information as the steady state experiments but have the marked advantage of improved signal to noise ratio. An additional technical advantage of detection in the NMR region is that one is dealing with low frequency and long lasting signals, so that many coherent data points can easily be measured. This explains why coherent methods have been pioneered in the NMR region.

Spectroscopy in the optical region of the spectrum should be compared and contrasted with the radio frequency (NMR) and microwave results. For an isolated line in this region of the spectrum, Doppler broadening is the dominant effect (remember Δω_D ~ ω_o). The pressure broadening widths are much smaller than in the microwave region since only elastic collisional effects should contribute to 1/T_2. (Thus the Voigt profile has been a traditional description.) Also, the natural line width contribution (γ ~ ω_o^3) has increased to the point where it can become comparable with pressure broadening effects, at least at lower pressures. These considerations, plus the advent of intense, monochromatic coherent (laser) light sources have contributed to a new form of high resolution steady state spectroscopy called Lamb-dip spectroscopy. Here, only a particular velocity group is resonant.
\((\omega = \omega_0 + k \cdot v)\) with the extremely monochromatic laser source and a narrow line is observed. In this way, the Doppler spread has been eliminated and only the homogeneously line broadening effects (natural and/or pressure widths) remain.

The existence of intense coherent laser light sources has opened up the possibility of time dependent (Fourier transform) spectroscopy in the optical region of the spectrum where analogues of NMR nutation and free induction decay experiments are carried out. (The general term coherence transients will be used to denote these effects.) Here, a Stark switching method of creating pulses is employed. A continuous wave laser light source is effectively switched in and out of resonance with the molecular levels by the brief application of a Stark field which causes the energy separation between molecular levels to change momentarily. The method of coherent detection employs, by necessity, a heterodyne technique so that it is the difference frequency which is actually picked up. The basic theory for these optical effects dates back to the work of Feynman and Vernon who were the first to recognize that electric dipole interactions with a two state system could be expressed in the same form (i.e. three coupled equations) as NMR interactions. Indeed, with the addition of relaxation times, this coupled set of equations looks like the Bloch equations - hence the obvious NMR analogies.

Several attempts at obtaining quantum mechanical Boltzmann equations, valid for the optical region, should be
mentioned. Indeed, these provide a molecular basis for the above mentioned "optical Bloch equations." One approach is represented by the work of Berman and Lamb\textsuperscript{47} who also recognize, at least phenomenologically, the existence of spontaneous emission effects (natural line widths) in their equations. A second method has been produced by the JILA group at Boulder, Colorado.\textsuperscript{48} More detailed comparisons between these approaches and the point of view taken in this thesis will be left to later chapters. In fact, many of the remarks made in this thesis, although strictly intended for application in the microwave region, could also be applied to the optical region.
(g) Summary

Chapter I has discussed qualitatively, the various factors affecting a microwave line shape and contrasted this situation with those found in NMR and the optical regions. Further, it has been pointed out that these latter two regions can also be studied by time dependent spectroscopic techniques. Thus it should not be surprising that the microwave region exhibits observable transient phenomena as well. These effects shall be discussed at great length in the next chapter, based on the quantitative approach of Flygare and coworkers. Steady state lineshapes can also be discussed naturally within this framework.) Although various other groups have observed microwave transient behaviour, this author feels that Flygare's papers show the greatest appreciation of the observed effects and his approach will be followed.
"Would you tell me, please, which way I ought to go from here?"
"That depends a good deal on where you want to get to," said the Cat
"I don't much care where -" said Alice
"Then it doesn't matter which way you go," said the Cat.
(a) Introduction

This chapter describes the steady state and transient responses of a system of gaseous molecules to coherent radiation, employing the basic approach of Flygare and his co-workers. As such, it is presented within the context of a two state model for the individual molecules. The term "two state", as employed here, implies two distinct non-degenerate energy eigenstates of the free one molecule internal state Hamiltonian. Implicit in this model is the assumption that the natural resonance frequency between these two states is sufficiently different from any other natural frequency separation between other energy states. This implies that the coherent radiation can interact resonantly with only one pair of states at a time, while it effectively ignores the presence of the remaining energy states.

Generalizations of the two state model can readily be visualized in several directions. Indeed, the consideration of the presence of magnetic quantum numbers (rotational degeneracy) leads to the concept of a two level model which is treated in detail in chapters IV, V and VI. This generalization to correctly include properties of the rotational motion - the distinction between the two state and two level models - is a major emphasis of this thesis. A further extension to describe translational motions and the Doppler effect is given in chapter VII.

By restricting the present discussion to the two state case, however, much of the basic phenomena (both free motion and collisional aspects) appear in a relatively clear and
simple manner. In fact, many of the qualitative remarks outlined in chapter I are put on a quantitative basis in this chapter. In terms of the block diagram of figure 1, the source is a monochromatic, coherent beam of microwave radiation and is specified as $2E_0 \cos(\omega t - ky)$. This source acts on the gas sample and drives it out of equilibrium. Different types of experiments can be performed and are described in some detail. Because the two state model is employed for the system motion, the response portrayed by the system is expected, in each case, to be as simple as possible.
(b) Kinematics

The two states of the "two state" system are the energy eigenstates $|a\rangle$ and $|b\rangle$ of the field free Hamiltonian $\mathcal{H}_o$ with associated eigenvalues $E_a$ and $E_b$ ($E_a < E_b$). This allows $\mathcal{H}_o$ to be written as

\begin{equation}
\mathcal{H}_o = E_a |a\rangle\langle a| + E_b |b\rangle\langle b|.
\end{equation}

The natural resonance frequency of this system is

\begin{equation}
\omega_o = \frac{E_b - E_a}{\hbar},
\end{equation}

while the applied radiation of frequency $\omega$ deviates from resonance by an amount

\begin{equation}
\Delta\omega = \omega_o - \omega.
\end{equation}

The electric dipole moment operator for the two state system is written as

\begin{equation}
\mu = \mu_d + \mu.
\end{equation}

where

\begin{equation}
\mu_d = |a\rangle \mu_{aa} <a| + |b\rangle \mu_{bb} <b|
\end{equation}

\begin{equation}
\mu = |a\rangle \mu_{ab} <b| + |b\rangle \mu_{ba} <a|.
\end{equation}
In many instances, the diagonal part of the dipole moment operator $\mu_d$ is identically zero.

Consideration of equations (2.1) and (2.4) shows that the four operators $|a><a|$, $|b><b|$, $|a><b|$, and $|b><a|$ form an operator basis for the two state system. That is, any operator can be expressed in terms of these four basis operators. Indeed, the state of the system itself, represented by the density operator $\rho$, has a representation in terms of this basis set

\begin{equation}
\rho = \rho_{aa} |a><a| + \rho_{ab} |a><b| + \rho_{ba} |b><a| + \rho_{bb} |b><b| .
\end{equation}

Here $\rho_{aa}$, $\rho_{bb}$ are the populations of states $|a>$ and $|b>$, respectively, while $\rho_{ab}$ and $\rho_{ba}$ are referred to as coherences and measure the amount of superposition between these two states.

Equation (2.5) is not the only possible representation of the state of the system, however. As pointed out by Fano, the density operator may be conveniently expressed in terms of any basis set of operators. For the two state system interacting with radiation via its electric dipole, a description involving the dipole operator itself might be appropriate. Indeed, as shall be seen shortly, a representation in terms of the four operators $1$, $\Delta N_{\text{er}}$, $\mathbf{\mu}$, and $\mathbf{\tilde{\mu}}$ is very useful. These four operators are defined as
Equations (2.6) can be equally viewed as a transformation between basis sets of operators, with the inverse transformation given as

\[
\begin{align*}
|a><a| &= \frac{1}{2} I + \frac{1}{2} \frac{\Delta N_{ep}}{N} \\
|b><b| &= \frac{1}{2} I - \frac{1}{2} \frac{\Delta N_{ep}}{N} \\
|a><b| &= \frac{1}{2\mu_{ab}} (\mu + i\mu^* ) \\
|b><a| &= \frac{1}{2\mu_{ba}} (\mu - i\mu^* ) 
\end{align*}
\]

In the second choice of basis, the density operator \( \rho \) is written as

\[
\rho = \frac{1}{2} I + \Delta N \frac{\Delta N_{ep}}{2N^2} + \rho \frac{\mu}{\mu^2} - \rho \frac{i\mu^*}{\mu^2}
\]

with the coefficients of the two expressions related by

\[
\begin{align*}
\Delta N &= N(\rho_{aa} - \rho_{bb}) \\
\rho_r &= \frac{N}{2}(\mu_{ba}\mu_{ab} + \mu_{ab}\mu_{ba}) \\
\rho_i &= \frac{N}{2i}(\mu_{ba}\mu_{ab} - \mu_{ab}\mu_{ba})
\end{align*}
\]
These relations are easily obtained by applying the transformation (2.7) to equation (2.5). The $\Delta N$, $P_1$, and $P_i$ notation in equation (2.8) is due to Flygare - these numbers are related to the expectation values of $\Delta N^{ref}$ and $\mu$, respectively, see equation (2.23).

Before closing this section, it should be stressed again that the representations in terms of the two basis sets (2.6) and (2.7) are exactly equivalent - they present the same effects from a different point of view but contain the same amount of information.
A system of gas molecules, described by a one-particle density operator $\sigma$, evolves in time due to both free motion and collisional effects. The free motion, in the presence of an oscillating elective field, is governed by the time dependent Hamiltonian

$$\mathcal{H} = \omega_0 - 2\mu_0 \cos(\omega t - ky),$$

while the collisional effects are described by a general relaxation matrix $\mathcal{R}$, which is to be discussed later. The equation of motion that $\sigma$ satisfies is then

$$i \frac{\partial}{\partial t} \sigma = [\mathcal{H}, \sigma] - i \mathcal{R}\sigma.$$

The method of solution of this equation follows the approach taken in the corresponding NMR equations and is described in the succeeding paragraphs. In short, it is based on a transformation to a "rotating frame", in-phase with the applied electric field, and a subsequent "rotating wave approximation" wherein the highly oscillatory parts of the equation are dropped. The resulting equation is governed by an effective time independent Hamiltonian.

The transformation of the density operator to the frame rotating at frequency $\omega$ is accomplished by
(2.12) \[ \rho = \exp\left[\frac{i}{\hbar} S(t-y/c)\right] \sigma \exp\left[-\frac{i}{\hbar} S(t-y/c)\right] \]

where \( S \) is a time independent operator which is defined to satisfy the relations

(2.13) \[ [\mathcal{H}, S] = 0 \quad [S, \mu] = -\omega \mu \quad [S, \dot{\mu}] = \omega \mu \]

Applying the transformation (2.12) to the equation of motion (2.11), the exact result

(2.14) \[ \frac{\partial \rho}{\partial t} = [\mathcal{H} - S - 2\mu S E_0 \cos(\omega t-ky), \rho] - i\mathcal{R}_S(t)\rho \]

is obtained. Here, \( \mathcal{R}_S(t) \) is the transformed collision matrix (being explicitly time dependent), while \( \mu_S \) is the transformed dipole moment operator

(2.15) \[ \mu_S = \exp\left[\frac{i}{\hbar} S(t-y/c)\right] \mu \exp\left[-\frac{i}{\hbar} S(t-y/c)\right] \]

Consideration of (2.13), (2.15) and the identity

(2.16) \[ \cos(\omega t-ky) = \frac{1}{2}\{\exp[i(\omega t-ky)] + \exp[-i(\omega t-ky)]\} \]

implies that the radiation-system coupling in the rotating frame can be split into a time-independent part and a rapidly oscillating part. Indeed,

(2.17) \[ -2\mu_S E_0 \cos(\omega t-ky) = -E_0 \mu + \text{rapidly oscillating terms} \]
The neglect of these rapidly oscillating terms in equation (2.17), as well as the time dependent terms in $R_s(t)$, constitutes the rotating wave approximation and is the method by which the radiation-system coupling will be treated in this chapter (indeed, in this thesis). Corrections to this rotating wave approximation via perturbation theory have been treated elsewhere.³

Within this approximation, equation (2.14) can be written as

$$(2.18) \quad i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H} - S - \mu E_0, \rho] + R_s \rho$$

Equation (2.18) is considered as the fundamental equation governing the evolution of the gas molecules. While the discussion in this section has been quite general so far, the remainder explicitly assumes the two state model for the molecules.

The density operator $\rho$ in equation (2.18) is a function of time. This implies the expansion coefficients in any basis expansion of $\rho$ will be time dependent and satisfy moment equations derivable from equation (2.18). In particular, the expansions (2.5) and (2.8) are now considered.

In the first basis, the coupled set of equations are
Since only those parts $\mathcal{R}_s$ of the collision matrix $\mathcal{R}_s(t)$ have been retained which are time independent, it follows that $\mathcal{R}_s$ only connects elements of $\rho$ having the same frequency. (This property is also consistent with the conservation of energy in the detailed collision processes contributing to $\mathcal{R}_s$, as discussed in the next section.) The fact that $\mathcal{R}_s$ preserves frequency implies that matrix elements of $\mathcal{R}_s$ are most naturally considered in the "frequency" basis (2.5).

Equations of motion in the alternate basis (2.8) are still desirable, however, in view of the macroscopic interpretation that this description yields. The moment equations are then
\[ (2.20) \quad \frac{d}{dt} P_r + \Delta \omega P_i + \frac{P_r}{T_2} = 0 \]

\[ \frac{d}{dt} P_i - \Delta \omega P_r + \kappa^2 E_o \left( \frac{\Delta N}{4} \right) + \frac{P_i}{T_2} = 0 \]

\[ \frac{d}{dt} \left( \frac{\Delta H}{4} \right) = E_o P_i + \frac{1}{T_1} \left( \frac{\Delta N}{4} \right) - \frac{\Delta N}{4} \text{eq} = 0 \]

where \( \kappa^2 = \frac{\mu^2}{4 \hbar^2} \) and the transformation (2.6) has been used.

In equation (2.20) the identification

\[ (2.21) \quad \frac{1}{T_1} = R_{aa;aa} + R_{bb;bb} - R_{aa;bb} - R_{bb;aa} \]

\[ \frac{1}{T_2} = R_{ab;ab} + R_{ba;ba} \]

has been made. Equation (2.20) also assumes that the relaxation matrix is real and that \( \langle \Delta N \rangle \) is collisionally uncoupled from \( \langle 1 \rangle \).

Equations (2.19) and (2.20) are seen to be the microwave analogues (for a two-state system) of the Redfield and Bloch equations of NMR. Alternatively, one might say that equation (2.20) allows a classical mechanical interpretation while (2.19) points out the quantum mechanical motions. However, it is emphasized once more, that (2.19) and (2.20) are completely equivalent descriptions of the same physical phenomena.

The effect of the transformation (2.12) on the dipole moment operator (2.4) can be shown to be
\begin{align*}
\text{(2.22)} \quad P(t) & = N \operatorname{tr}\{\sigma(t)\mu\} \\
& = \{P_r(t) + iP_i(t)\} \exp[i(\omega t - ky)] + \{P_r(t) - iP_i(t)\} \\
& \quad \exp[-i(\omega t - ky)] + N(\mu_{aa} + \mu_{bb}) + \left(\frac{\mu_{aa} - \mu_{bb}}{2}\right) \Delta N(t)
\end{align*}

where

\begin{align*}
\text{(2.23)} \quad P_r(t) & = \frac{N}{2} \operatorname{tr}\{\rho(t)\mu\} \quad P_i(t) = \frac{N}{2} \operatorname{tr}\{\rho(t)\mu\} \quad \Delta N(t) = \operatorname{tr}\{\rho(t)\Delta N\}
\end{align*}

Equations (2.22) and (2.23) point out most clearly the descriptions of the motions in the "lab frame" versus the "rotating frame". Further, for the two state system, these equations show that the time dependence of the diagonal parts of the dipole moment are determined completely by the evolution of the population difference \(\Delta N(t)\).
The purpose of the present discussion is to give a physical picture of those types of detailed collision processes which can contribute to any particular matrix element of $R_s$. This section is produced within the context of a two state system where the complications of rotational degeneracy are not present to distract from the basic effects. These shortcomings are corrected in chapter IV where a rigorous presentation of collisional effects is given.

In essence, one would like to visualize how the microscopic view of collisions between two molecules is related to the overall measured relaxation rate specified in terms of $R_{ij;i'j'}$. The elementary processes are given in terms of well defined directionally averaged cross sections $C$ describing the collision between a molecule of interest and a perturber molecule, with the pair having a definite initial relative translational energy $e_{tr}$. The directionally averaged cross sections are independent of the centre of mass velocities before and after collision. These elementary processes are then averaged over an equilibrium distribution of initial perturber internal states, averaged over an equilibrium distribution of increasing relative translational energy, and summed over final states of the perturber. It is these kinetically averaged results which are identified with the relaxation matrix elements.

Consider $R_{ij;i'j'}$ with $i \neq i'$, $j \neq j'$. This matrix element represents the total rate that the one molecule state $|i'\rangle \langle j'|$
can be converted to the state $|i><j|$ by collisions. In view of the previous remarks, the identification

$$R_{ij;i'j'} = n(\frac{8kT}{\mu})^{1/2} \int d\epsilon_{tr} \int d\epsilon'_{tr} \exp[-\epsilon_{tr}'] \epsilon_{tr}'$$

should be reasonable. Here $\delta(E' - E)$ expresses the fact that the total relative energy is conserved in the collision processes, see chapter IV for some technical aspects of energy conservation. In equation (2.24), because the coherent states $|i><j|$ and $|i'><j'|$ are involved, energy conservation requires two equalities

$$\epsilon_{tr} + \epsilon_{c_2} + \epsilon_i = \epsilon_{tr}' + \epsilon_{c_2}' + \epsilon_{i'}$$

Subtracting one conservation law from the other implies the frequency conservation property.

$$\epsilon_{i} - \epsilon_{j} = \epsilon_{i'} - \epsilon_{j}'$$

The matrix elements $R_{aa;bb}$ and $R_{bb;aa}$ of the last section obviously have the form of equation (2.24), with zero frequency.
The relaxation matrix elements $R_{ij;ij}$ are slightly more complicated in that they represent all possible routes by which the coherence $|i><j|$ can relax. As such, the form of $R_{ij;ij}$ is

$$
(2.27) \quad R_{ij;ij} = \frac{n(\frac{\hbar kT}{\mu})^{1/2}}{\exp[-\frac{\hbar kT}{\mu}] \int d\epsilon_{tr} \int d\epsilon_{tr}, \exp[-\epsilon_{tr},] \epsilon_{tr},}
$$

$$
\sum_{c_2} \sum_{c_2'} \exp[-\epsilon_{c_2'}] \delta(\epsilon_{c_2'') - \epsilon) \left[ C(|i><j|; |c_2'><c_2'|, \epsilon_{tr}, \epsilon_{tr}, + |j><j|, |c_2'><c_2'|, \epsilon_{tr}) + \frac{1}{2} \sum_{k} C(|i><j|; |c_2'><c_2'|, \epsilon_{tr}, + |k><k|, |c_2'><c_2'|, \epsilon_{tr}) \right]
$$

Equation (2.27) includes the matrix elements $R_{aa;aa'}, R_{bb;bb'}, R_{ab;ab'}$ and $R_{ba;ba}$ of the last section as special cases.

Comparing the forms (2.24) and (2.27) with (2.21), expressions for $T_1$ and $T_2$ in terms of the contributing microscopic collision events can be established. Indeed,
\[(2.28)\]
\[
\frac{1}{T_1} = n \left(\frac{8kT}{\mu}\right)^{1/2} \int d\varepsilon_{tr} \int d\varepsilon'_{tr} \exp[-\varepsilon_{tr}] \varepsilon_{tr} \Sigma \Sigma \exp[-\varepsilon_c] c_2^* c_2^\prime + \delta(\varepsilon' - \varepsilon) C(|i><i|, |c_2^*><c_2^\prime|, \varepsilon_{tr} \rightarrow |k><k|, |c_2><c_2^\prime|, \varepsilon_{tr})
\]
\[
+ \delta(\varepsilon' - \varepsilon) C(|j><j|, |c_2^*><c_2^\prime|, \varepsilon_{tr} \rightarrow |k><k|, |c_2><c_2^\prime|, \varepsilon_{tr})
\]
\[
+ \varepsilon \delta(\varepsilon' - \varepsilon) C(|i><i|, |c_2^*><c_2^\prime|, \varepsilon_{tr} \rightarrow |c_2><c_2^\prime|, \varepsilon_{tr})
\]
\[
+ \varepsilon \delta(\varepsilon' - \varepsilon) C(|j><j|, |c_2^*><c_2^\prime|, \varepsilon_{tr} \rightarrow |k><k|, |c_2><c_2^\prime|, \varepsilon_{tr})
\]
and

\[(2.29)\]
\[
\frac{1}{T_2} = n \left(\frac{8kT}{\mu}\right)^{1/2} \int d\varepsilon_{tr} \int d\varepsilon_{tr} \exp[-\varepsilon_{tr}] \varepsilon_{tr} \Sigma \Sigma \exp[-\varepsilon_c] c_2^* c_2^\prime + \delta(\varepsilon' - \varepsilon) C(|i><i|, |c_2^*><c_2^\prime|, \varepsilon_{tr} \rightarrow |i><i|, |c_2><c_2^\prime|, \varepsilon_{tr})
\]
\[
+ \delta(\varepsilon' - \varepsilon) C(|j><j|, |c_2^*><c_2^\prime|, \varepsilon_{tr} \rightarrow |j><j|, |c_2><c_2^\prime|, \varepsilon_{tr})
\]
\[
+ \varepsilon \delta(\varepsilon' - \varepsilon) C(|i><i|, |c_2^*><c_2^\prime|, \varepsilon_{tr} \rightarrow |k><k|, |c_2><c_2^\prime|, \varepsilon_{tr})
\]
\[
+ \varepsilon \delta(\varepsilon' - \varepsilon) C(|j><j|, |c_2^*><c_2^\prime|, \varepsilon_{tr} \rightarrow |k><k|, |c_2><c_2^\prime|, \varepsilon_{tr})
\]
are the results. These equations demonstrate that only inelastic collisions contribute to \((T_1)^{-1}\) while \((T_2)^{-1}\) has both elastic and inelastic effects. Thus, it is expected that

\[(2.30)\]
\[
\frac{1}{T_1} < \frac{1}{T_2},
\]
and that the strong collision model, (equality of $T_1$ and $T_2$), would be valid only when elastic contributions to $(T_2)^{-1}$ are small.

In closing this section, it should be emphasized that the above identifications, especially (2.24) and (2.27), are not presented as derived results. Rather, they represent an attempt to aid in visualising the collisional aspects of the two state problem. A rigorous treatment of collisions is presented in chapter IV.
The simplest experiments which can be carried out are the traditional steady state absorption experiments. Here the gas is initially assumed to be in equilibrium, which implies

\begin{align}
\rho_r(o) &= 0 \\
\rho_i(o) &= 0 \\
\Delta N(o) &= \Delta N_{eq}
\end{align}

and then is subjected to a continuous wave (cw) microwave source. The desired solution is the steady state representing the long time behaviour of the system after all transients have died away. At this stage, the only oscillations are at the frequency of the applied field. This solution is most easily obtained by setting all time derivative equal to zero in the rotating frame. Thus equations (2.20) become

\begin{align}
\Delta \omega \rho_i + \frac{\rho_i}{T_2} &= 0 \\
-\Delta \omega \rho_r + \kappa^2 E_0 \left( \frac{\hbar \Delta N}{4} \right) + \frac{\rho_i}{T_2} &= 0 \\
-E_0 \rho_i + \frac{\kappa}{4} \left( \frac{\Delta N - \Delta N_{eq}}{T_1} \right) &= 0.
\end{align}

The solution to these equations, subject to the initial condition (2.31) are then easily found to be
Equations (2.33) should be viewed within the qualitative comments of chapter I. The expression for $P_i$ gives the line-shape for a microwave line, when both Doppler effects and natural line widths are assumed negligible and when no overlapping with other spectral lines is significant. The above equation does account for saturation broadening, however, and shows how it becomes negligible in the low (input) power case when $\kappa^2 E_o^2 < 1$, that is, when $\Delta N = \Delta N_{eq}$. In this limit, it is seen that $T_1$ plays no role in determining the steady state (2.33). Thus the fundamental line width parameter is $\frac{1}{T_2}$, the relaxation time associated with the relaxation of the coherence between the two states.
A selective discussion of microwave transient experiments based on the work of McGurk et al.\textsuperscript{1} is given in the remainder of this chapter. Additional material, experimental details and results, may be found in a series of papers by this group.\textsuperscript{5,6,7,8} Each experiment is represented by a particular time dependent solution to equations (2.20). As first indicated by Torrey,\textsuperscript{9} for problems of this type, these time dependent solutions take the form

\begin{equation}
(2.34) \quad f(t) = Ae^{-at} + Be^{-bt} \cos \Omega t + \frac{Ce^{-bt}}{\Omega} \sin \Omega t + D,
\end{equation}

where \( f(t) \) represents any of \( P_i(t) \), \( P_x(t) \), and \( \Delta N(t) \). Here the time constants \( a, b+i\Omega, b-i\Omega \) are the three roots of the secular determinant

\begin{equation}
(2.35)
\Delta(u) \equiv (u + \frac{1}{\kappa E_0 T_1})(u + \frac{1}{\kappa E_0 T_2})^2 + \frac{\Delta \omega}{2}^2 (u + \frac{1}{\kappa E_0 T_1})^2 + (u + \frac{1}{\kappa E_0 T_2}) = 0
\end{equation}

which just depend on the properties of the system. The constants \( A, B, C \) and \( D \), on the other hand, depend on the particular experiment. Since the time independent part \( D \) represents the appropriate steady state solution [equations (2.330), equation (2.34) specifies the manner in which the steady state values are approached. The secular equation
(2.35) can only be solved in closed form for certain cases—see sections (g) and (h). The constants $A, B, C$ and $D$ are also evaluated for specific experiments in these sections.
(f) Detection of Radiation

Before proceeding with the detailed discussion of the transient experiments, some general comments on the detected radiation are presented - the third stage that is illustrated in figure 1. These remarks are, for the most part, independent of the particular microwave experiment that is being carried out on the gas sample and are therefore collected in one section. Further, this separation of the detected radiation from the underlying system motion implies that these remarks are also relatively independent of the two state model used in this chapter and so may be reapplied to the modified system models discussed in later chapters.

The resultant electric field is calculated by solving Maxwell's equations in the presence of a dielectric (polarizable) medium. These equations are of the form:

\[ \nabla \cdot E = 4\pi \rho_{\text{pol}}, \quad \nabla \cdot B = 0 \]

\[ \frac{1}{c} \frac{\partial E}{\partial t} + \frac{4\pi}{c} J_{\text{pol}} = \nabla \times B \quad \frac{1}{c} \frac{\partial B}{\partial t} = -\nabla \times E \]

where

\[ \rho_{\text{pol}} = -\nabla \cdot \mathbf{P} \quad \text{and} \quad J_{\text{pol}} = \frac{\partial}{\partial t} \mathbf{P} \]

For a gas in the absence of external static fields

\[ \nabla \cdot \mathbf{P} = 0 \]
and the wave equation

\[ \nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 p}{\partial t^2} \]

is obtained as the equation of motion of the emitted field.

In the experiments that are to be described, the polarization \( P(t) \) arises in response to an applied electric field \( E = E_0 \cos(\omega t - ky) \). By isotropy, the polarization \( P(t) \) is also along the \( E_0 \) direction (where \( \hat{E}_0 \perp \hat{y} \)). Thus equation (2.39) reduces to the one dimensional wave equation.

\[ \frac{\partial^2}{\partial y^2} E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 p}{\partial t^2} \]

where the polarization along the \( E_0 \) direction is expressed as [compare (2.22)]

\[ P(t) = 2P_r(t) \cos(\omega t - ky) - 2P_i(t) \sin(\omega t - ky) \]

\[ + \frac{\mu_{aa} - \mu_{bb}}{2} \Delta N(t) + (\mu_{aa} + \mu_{bb}) N \]

Neglecting the time derivatives of \( P_r(t), P_i(t) \) and \( \Delta N(t) \), the source term in equation (2.40) is evaluated approximately as

\[ \frac{\partial^2 p}{\partial t^2} - \omega^2 \{2P_r(t) \cos(\omega t - ky) - 2P_i(t) \sin(\omega t - ky)\} \]
The wave equation (2.40, with equation (2.42) as the source term can be approximately solved in the form

\[(2.43) \quad E = 2[\epsilon_i \cos(\omega t-ky) + \epsilon_r \sin(\omega t-ky)]\]

where the slowly varying quantities \(\epsilon_i(yt)\) and \(\epsilon_r(yt)\) satisfy

\[(2.44) \quad \frac{\partial \epsilon_i}{\partial y} = \frac{2\pi \omega}{c} p_i, \quad \frac{\partial \epsilon_r}{\partial y} = \frac{2\pi \omega}{c} p_r .\]

This involves neglecting the following quantities:

\[\frac{\partial^2 \epsilon_i}{\partial t^2} , \frac{\partial^2 \epsilon_i}{\partial t^2} , \frac{\partial \epsilon_i}{\partial t} , \frac{\partial \epsilon_i}{\partial t} , \frac{\partial^2 \epsilon_r}{\partial y^2} , \text{and} \frac{\partial^2 \epsilon_i}{\partial y^2} .\]

As shown in figure 1, the incident radiation \(2E_0 \cos(\omega t-ky)\) enters the sample at \(y=0\) and the resulting radiation in the form of equation (2.43) exits at \(y=\lambda\). The appropriate boundary conditions for the differential equations (2.44) are then

\[(2.45) \quad \epsilon_i = E_0 \quad \text{at} \quad z=0\]

\[\epsilon_r = 0,\]

so that the corresponding solutions are given immediately as
\[ (2.46) \quad \varepsilon_i(yt) = E_0 + \frac{2\pi \omega y}{c} P_i(t) \]

\[ \varepsilon_r(yt) = \frac{2\pi \omega y}{c} P_r(t). \]

The field which the detector observes at \( y=l \) is

\[ (2.47) \quad E(\xi t) = 2E_o \cos(\omega t-k\xi) + \frac{4\pi \omega \xi}{c} [P_r(t) \sin(\omega t-k\xi) \]

\[ + P_i(t) \cos(\omega t-k\xi)] \]

which is obtained from a combination of equations (2.43) and (2.46). For a "square law" detector, the measured signal \( S \) is proportional to the time average \( E^2(t) \) of the square of the electric field entering the detector, namely

\[ (2.48) \quad S = \beta E^2(t) \]

\( \beta \) being the proportionality constant for the particular detector. The change in signal \( \Delta S \) due to the presence of the gas molecules is from equations (2.47) and (2.48)

\[ (2.49) \quad \Delta S = S - \beta E^2_o \]

\[ = \frac{4\pi \beta \omega \xi}{c} E_o P_i(t) + \frac{8\pi \omega^2 \xi^2}{c^2} \beta [P_i^2(t) + P_r^2(t)] \]
In this equation, all rapidly oscillating terms have vanished due to the time averaging. When the $E_o$ field is present, absorption of radiation occurs, see section (g). On the other hand, if $E_o$ is absent, emission can occur, see section (h).

Since $\Delta S(=S)$ is in this case quadratic in both $P_r$ and $P_i$, and hence proportional to the square of the number of molecules, it is clear that this is coherent stimulated emission and not spontaneous emission (in spontaneous emission, the power emitted is directly proportional to the number of molecules present).

A modified detection scheme commonly used to detect transient emission employs a reference field $E_r(t)$, given as

$$(2.50) \quad E_r(t) = 2E_r \cos(\omega_r t-k\ell),$$

which oscillates at a fixed frequency $\omega_r$ while the system itself is oscillating at frequency $\omega_o$ and producing an emitted field $E_E(t)$. The two fields interfere to give a signal

$$\Delta S = \beta \frac{E_{ref}(t) E_E(t)}{E_r(t)},$$

at the detector. This involves the beat frequencies $\omega_r+\omega_o$ and $|\omega_r-\omega_o|$. The precise form for $E_E(t)$ in terms of $P_r(t)$ is discussed in section (h).
Equation (2.49) [or (2.51)] gives the expression for the detected signal. Here, $P_x(t)$ and $P_y(t)$ are solutions of the coupled set of equations (2.20) subject to a certain set of initial conditions. Each particular set of initial conditions corresponds to a particular experiment which can be carried out on the two state gas sample. The following sections discuss the two main types of transient experiments — transient absorption (both on-resonance and off-resonance cases) and transient emission (produced by continuous wave or pulse irradiation). These experiments are the microwave analogs of NMR rotation and free induction decay experiments, respectively. Additional discussions and references can be found in the paper by McGurk et al.¹
(h) Transient Absorption

Transient absorption arises when radiation is brought into (or near) resonance with a two state system in a time short relative to the relaxation time. Technically, this is achieved through the method of Stark switching. Here, the two state system, which is originally far off-resonance with a continuous wave source of microwave radiation, is suddenly brought into resonance by the application of a Stark field. There are two cases of special interest where the solutions to the secular equation (2.35), and thus to (2.20), can be written in closed form - the on-resonance case, $\Delta \omega = 0$, which can be used to study the relationship between $T_1$ and $T_2$, and the strong collision model case $T_1 = T_2$, which can be used to study the off-resonant transient signal.

The on-resonance case gives the transient response as

$$P_i(t) = \frac{+\kappa^2 \Delta N_{eq} E_o}{4T_2} \left\{ \frac{e^{-t/T}}{T_2^2 + \frac{T_1}{T_2} \kappa^2 E_o^2} \right\}$$

$$+ \left\{ \frac{\frac{1}{T_2} \left( \frac{1}{T_1} + \frac{1}{T_2} \right)}{\frac{1}{T_2}} - T_2 \right\} e^{-t/T} \sin \Omega t \}$$
when the initial conditions are given by equation (2.31). Here, the oscillation frequency $\Omega$ and the decay time $T$ are given by

$$\Omega = \left[ \kappa^2 E_0^2 - \frac{1}{4} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)^2 \right]^{1/2}$$

$$T = \frac{2}{T_1 + \frac{1}{T_2}}$$

Equation (2.52) is a particular example of the general form (2.34), wherein $a=0$, $b=\frac{1}{T}$ and $\Omega$ is given by (2.53). As can be seen from equations (2.52) and (2.53) studies of this type can be used to determine the relative sizes of $T_1$ and $T_2$. Indeed, as an example, the rotational transition $J=0$ to $J=1$ in OCS was found to obey $T_1 = T_2$ within an accuracy of 15%. This represents an experimental justification of the strong collision model.

Alternatively, with the strong collision model as a working hypothesis, off-resonance transient absorption experiments can be carried out by varying the degree of off-resonance character $\Delta \omega$. The solution to (2.20) in this case (again with the initial conditions (2.31)), is given as

$$P_i = \frac{\kappa^2 \Delta N}{4} \left[ \frac{e^{-t/T} \cos \Omega t - 1}{\frac{1}{T^2} + \Omega^2} \right]^{\frac{1}{T}}$$

$$+ \left[ \frac{1}{T^2 + \Omega^2} - 1 \right] e^{-t/T} \frac{\sin \Omega t}{\Omega}$$
where

\[(2.55) \quad \Omega = \left( \kappa^2 E_o^2 + (\Delta \omega)^2 \right)^{1/2} \]

\[T = T_1 = T_2.\]

Figure 2 illustrates the shape of \(P_i(t)\) for various values of \(\Omega\).
Figure 2: Plots of $P_1(t)$ for various values of $\Omega$, with time in microseconds. A relaxation time of 5 μsec is assumed. (From McGurk et al., Adv. Chem. Phys. XXV, 1, (1975).)
(h) Transient Emission

The phenomenon of transient emission must be considered in two parts. In the first stage, the system is prepared in some nonequilibrium state by interaction with external radiation. The second stage occurs when the external radiation is shut off and the system is allowed to decay back to its equilibrium state. It is in this second stage that the actual emission processes occur. In the description given here, the behaviour of the system in the emitting stage is first considered for an arbitrary nonequilibrium preparation (i.e. arbitrary values of $P_r(t_1)$, $P_i(t_1)$ and $\Delta N(t_1)$ at time $t_1$). Then the three usual methods of preparing the system are discussed - namely, continuous wave irradiation and two pulse techniques.

In the absence of any radiating field ($E_0 = 0$), the system equations (2.20) can be easily solved in terms of the arbitrary initial conditions at time $t_1$ to give, for $t>t_1$,

\begin{align*}
P_r(t) &= \exp[-(t-t_1)/T_2]\{P_r(t_1)\cos[\Delta \omega(t-t_1)] - P_i(t_1)\sin[\Delta \omega(t-t_1)]\} \\
P_i(t) &= \exp[-(t-t_1)/T_2]\{P_i(t_1)\cos[\Delta \omega(t-t_1)] + P_r(t_1)\sin[\Delta \omega(t-t_1)]\} \\
N(t) &= \Delta N_{eq} + \exp[-(t-t_1/T_1](\Delta N(t_1)-\Delta N_{eq})
\end{align*}

The emitted field $E_E(t)$ is then calculated by combining (2.56) with (2.47), when $E_0 = 0$. The result is
This equation states that the system emits light at its natural frequency of oscillation $\omega_0$, while it relaxes at a rate $\frac{1}{T_2}$.

As indicated in section (f), there are two methods used to detect this signal. In the first (direct) method, the field itself is time averaged by the detector. The result is equation (2.49) with $E_0=0$ and $P_r(t)$ and $P_i(t)$ given by equation (2.56). The second, more usual, method of detection involves the beating of the pure emission field (2.57) with some reference field (2.50). The detected signal is then (2.51). An oscillatory decay to a steady value is observed which is similar in appearance to the transient absorption experiment.

Both transient absorption and transient emission can be observed in turn, by employing the method of Stark switching. With the Stark field off, the applied radiation

\[ E_E(t) = \frac{4\pi\omega_l}{c} \exp\left(-\frac{(t-t_1)}{T_2}\right) \left\{ P_i(t_0 \cos[\omega_0(t-t_1)-k\ell+\omega t_1] + P_r(t_1)\sin[\omega_0(t-t_1)-k\ell+\omega t_1] \right\} \]

\[ = \frac{4\pi\omega_l}{c} \exp\left\{ t/T_2 \right\} \left\{ P_i(t_1)\cos(\Delta\omega t_1) - P_r(t_1)\sin(\Delta\omega t_1) \right\} \]

\[ \exp\left\{-t/T_2\right\} \cos(\omega_0 t-k\ell) + \left\{ P_i(t_1)\sin(\Delta\omega t_1) \right\} \exp\left\{-t/T_2\right\} \sin(\omega_0 t-k\ell) \]
of frequency $\omega_r$ is resonant with the molecular levels $(\omega_r = \omega_o)$ and transient absorption can be measured. Then suddenly, the Stark field is turned on, shifting the molecular energy levels to a new frequency difference $\omega_o'$ and the molecules emit at this frequency. The emitted radiation mixes with the applied radiation (of frequency $\omega_r$) to create a beat signal at the detector. The overall scheme is indicated in figure 3.

To complete the discussion of the transient emission experiment, expressions for $P_r(t_1)$ and $P_i(t_1)$ must be obtained to insert into equation (2.56). Three such methods of preparation are outlined. The first method consists of irradiating the system with continuous wave radiation until a steady state has been achieved. The solution for this case has already been discussed (see equation (2.33)) and consequently, the values

$$P_r/\Delta N_{eq} = \frac{\kappa^2 E_o \Delta \omega}{4} \frac{1}{T_2} + (\Delta \omega)^2 + \left(\frac{T_1}{T_2}\right) \kappa^2 E_o^2$$

$$P_i/\Delta N_{eq} = \frac{\kappa^2 E_o}{4} \frac{1}{T_2} \frac{1}{T_2} + (\Delta \omega)^2 + \left(\frac{T_1}{T_2}\right) \kappa^2 E_o^2$$

can be substituted into equation (2.56).
Figure 3: Diagram showing transient absorption (field off) and transient emission (field on) as obtained from Stark switching. (From McGurk et al., Adv. Chem. Phys. XXV, 1, (1975).)
Two other methods of preparation involve pulse techniques where the pulse times are assumed short in comparison to the relaxation times. Thus, during the evolution of the pulse, the system equations (2.20) can be simplified to read

\[
\frac{dP_r}{dt} + \Delta \omega P_i = 0 \quad \frac{d}{dt} \left( \frac{\hbar \Delta N}{4} \right) - E_0 P_i = 0
\]

\[
\frac{dP_i}{dt} - \Delta \omega P_r + \kappa^2 E_0 \left( \frac{\hbar \Delta N}{4} \right) = 0
\]

The solution to these equations (again employing the method of Laplace transforms and the initial conditions (2.31)), can be written as

\[
(2.60) \quad P_r(t_1) = 0 \quad P_i(t_1) = \frac{\kappa}{\Delta N_{eq}} \Delta N_{eq} \sin(\kappa E_0 t_1)
\]

\[
\Delta N(t_1) = \Delta N_{eq} \cos(\kappa E_0 t_1) \quad \text{for } \kappa E_o >> \Delta \omega
\]

The two pulse techniques then can be expressed in analogy to NMR as

\[
(2.61) \quad t_{\pi/2} = \frac{\pi}{2 \kappa E_0} \quad P_i(t_{\pi/2}) = \frac{\hbar \kappa}{4} \Delta N_{eq}
\]

\[
P_r(t_{\pi/2}) = 0 \quad N(t_{\pi/2}) = 0
\]

and
Thus the emitted field is a maximum following a π/2 pulse and is zero following a π pulse.
(i) Summary

In conclusion, it should be mentioned that other experimental situations have also been studied. For example, additional (multiple) pulse experiments have been carried out\textsuperscript{1,12} in analogy with NMR. Further, the treatment employed by Flygare and coworkers has \textit{not} completely neglected the questions of magnetic quantum number (m) dependence or velocity contributions. Rather, we feel that their treatment in these areas is incomplete and it is the aim of this thesis to re-examine these effects.
 CHAPTER III

Senftleben-Beenakker Effects and the Linearized Waldmann-Snider Collision Superoperator

"I could have done it in a much more complicated way" said the Queen, immensely proud.
Introduction

Chapter III makes a seemingly abrupt departure from the spectroscopic discussions of the previous two chapters in that the subject under discussion here is transport phenomena, where non-equilibrium effects are caused by velocity and temperature gradients, instead of applied radiation fields. However, the gaseous system under study is the same and the mechanism by which the system returns to equilibrium (collisions) is consequently the same. This chapter—indeed, this thesis—shows that much can be gained from a closer inspection of both phenomena from a unified point of view.

Over the past decade, improved experimental techniques and more detailed observations have shown that transport phenomena and pressure broadening are more closely associated than originally imagined. Senftleben-Beenakker studies, wherein external static electric and magnetic fields modify transport coefficients, have been particularly well developed in this time span. These show that internal states do affect the translational transport coefficients. Equally well, Doppler effects and velocity relaxations must be taken into account for a complete description of spectroscopic phenomena. Thus, in each instance, there are secondary mechanisms which couple translational and internal degrees of freedom.

Usual kinetic theory approaches to transport phenomena and Senftleben-Beenakker effects are extremely detailed in their treatment of rotational aspects and translational effects. This is in direct contrast to the simplified
treatment of the system motion in the spectroscopic case, described in Chapter II. Chapter III will therefore outline the methods employed in the description of Senftleben-Beenakker effects with an eye to applying these concepts to the microwave phenomena in subsequent chapters. In fact, this chapter serves the dual purpose of introducing notation and defining quantities that will be used again, as well as presenting S-B formulae which can be directly compared with "spectroscopic" results.

The presentation of Senftleben-Beenakker effects given here is admittedly somewhat limited, in that the emphasis will be on mathematical techniques rather than on the complete description of the actual physical phenomena. A fuller account of the theory and experiments can be found in several excellent reviews. 1,2,3,4
(b) The Linearized Waldmann-Snider Equation

An equation of motion, appropriate to the study of Senftleben-Beenakker effects, must first be established. The starting point is the generalized quantum Boltzmann equation of Snider and Sanctuary valid for molecules with internal state structure,

\[
(3.1) \quad \frac{\partial \rho}{\partial t} = \mathcal{L}_\rho + \text{tr}_2 \mathcal{J} \rho \rho_2.
\]

This represents the most general equation obtained within the philosophy of the original Boltzmann approach and its "derivation" is given in appendix A. The superoperator notation employed in equation (3.1) is also discussed in this appendix.

Equation (3.1) is now specialized to obtain the working equation for this chapter - an equation usually known as the Waldmann-Snider equation. To this end, the description of the translational degrees of freedom is clarified by the introduction of the Wigner distribution function

\[
(3.2) \quad f(p_\mathbf{x}) \equiv \frac{1}{\hbar^3} \int dq \exp[i/\hbar \mathbf{q} \cdot \mathbf{r}] \begin{bmatrix} p + \frac{1}{2} \mathbf{q} \mid \rho \mid p + \frac{1}{2} \mathbf{q}^* \end{bmatrix}.
\]

Because of the definition (3.2), \( f(p_\mathbf{x}) \) is still an operator in internal state space. Also, it should be emphasized that the transformation (3.2) is one-to-one (i.e. has a unique inverse) and no information is lost. It is an example of the Weyl correspondence between translational
operators and phase space functions. The representation in
terms of \( f(rpt) \) is preferred to one involving \( p \), in that a
classical interpretation can be associated with \( f \) even
though it is quantal in nature. Indeed, the free motion
superoperator \( \mathcal{L} \), when subjected to this transformation,
gives rise to both a drift term from the translational states
and an internal state Liouville operator \( \mathcal{L}_{\text{int}} \). The trans-
formed collision term is much more complicated. It is
most conveniently expressed using a parametrization due to
Baerwinkle and Grossmann\(^{10}\) according to the form\(^{11}\)

\[
(3.3) \quad \frac{\partial f}{\partial t} + \frac{p}{m} \cdot \frac{\partial f}{\partial x} + \frac{i}{\hbar} \mathcal{L}_{\text{int}} f = J(rpt)
\]

with

\[
(3.4) \quad J(rpt) = -\frac{2\hbar}{\hbar} \left( \frac{2}{\hbar} \right)^3 \text{tr}_2 \int \exp \left[ -\frac{2i}{\hbar} (x \cdot k - q \cdot \gamma) \right] \mathcal{J}(pgkk)
\]

\[
f_1 \left( r + \frac{1}{2}(y-x), p + \beta - k \right) f_2 \left( r + \frac{1}{2}(y+x), p + \beta + k \right) d\beta dq dk dxdy
\]

Here, \( \mathcal{J}(pgkk) \) is a superoperator acting on internal state
operators only, namely

\[
(3.5) \quad \mathcal{J}(pgkk) A = \langle \beta + q | t | k + \kappa \rangle A \langle k - \kappa | \Omega^+ | \beta - q \rangle
\]

\[
-\langle \beta + q | \Omega | k + \kappa \rangle \lambda \langle k - \kappa | t^+ | \beta - q \rangle
\]
This is a momentum representation of $\mathcal{J}$. The collision expression (3.4) is non-local since the colliding molecules are not at the same position, nor at the position $\mathbf{r}$ of the distribution function in the drift terms on the left hand side of (3.3). For the description of dilute gas transport phenomena, it is useful to employ a localization approximation by neglecting the $x$ and $y$ position dependencies in $f_1$ and $f_2$. That is, $f$ is assumed to be a slowly varying function of position. The net result is a local collision operator of the form

$$
(3.6) \quad \mathcal{J}(\mathbf{r}'t) + \mathcal{J}_o(\mathbf{r}'t) = -64\pi^3 i\hbar^2 \text{tr}_2 \int \mathcal{J}(\mathbf{r}_0 k) f_1(\mathbf{r}, \mathbf{p} + \mathbf{k}) f_2(\mathbf{r}, \mathbf{p} + \mathbf{k}) d\mathbf{p} d\mathbf{k}
$$

$$
= -i(2\pi)^4 \hbar^2 \text{tr}_2 \int \mathcal{J}(\frac{\mathbf{p}_2 - \mathbf{p}}{2}), \mathbf{p}, \frac{\mathbf{p} + \mathbf{p}_2}{2} - \mathbf{p}_1', \mathbf{o}) f_1(\mathbf{r}, \mathbf{p}') f_2(\mathbf{r}, \mathbf{p}_2, \mathbf{p}_1') d\mathbf{p}_1 d\mathbf{p}_2 .
$$

Further, it is assumed that the distribution function of interest is diagonal in internal energy. This assumption is based on the concept of "phase randomization"$^{11b}$ which states that all observable internal state effects can be described in terms of a density operator which almost commutes with the internal state hamiltonian. The remaining high frequency portions of the density operator, if produced, vanish so quickly due to their rapidly oscillating
free motion, that they are normally not observed and hence can be disregarded. Diagonality of $f(\mathbf{q}_F)$ in energy also implies that the transition operators in equation (3.5) are on the energy shell. Coupling this statement with the Lippmann-Schwinger integral equation

$$\Omega \left| E \right> = \left\{ 1 + \lim_{\epsilon \to 0^+} \frac{1}{E - \mathcal{A} + i\epsilon} \right\} \left| E \right>, \quad$$

the Waldmann-Snider collision operator

$$J^{WS}_{\mathbf{n}}(\mathbf{q}_F) = (2\pi)^4 \hbar^2 \text{tr} \int \frac{d\mathbf{p}_2}{2 \pi} \frac{d\mathbf{p}_1}{2 \pi} \times \left[ \left\langle \mathbf{p}_2 - \mathbf{p}_1 \right| t \left| \mathbf{p}_2 + \mathbf{p}_1 \right> - \left\langle \mathbf{p}_1 \right| f_1(\mathbf{r}_F) f_2(\mathbf{r}_F') \left| \mathbf{p}_2 + \mathbf{p}_1 \right> \right]$$

$$+ (2\pi i)^{-1} \left\langle \mathbf{p}_2 - \mathbf{p}_1 \right| t \left| \mathbf{p}_2 - \mathbf{p}_1 \right> f_1(\mathbf{r}_F) f_2(\mathbf{r}_F')$$

$$- f_1(\mathbf{r}_F) f_2(\mathbf{r}_F') \left\langle \mathbf{p}_2 - \mathbf{p} \right| t^+ \left| \mathbf{p}_2 - \mathbf{p} \right> \right\rangle$$

is obtained. The $\delta(E)$ factor expresses conservation of energy across the $t$ operator.

Finally, in transport theory, it is usually assumed that the gas is close to local equilibrium, so that the linearization
(3.9) \( f(r pt) = f^{(0)}(1 + \phi) \)

can be performed. Here,

\[
(3.10) \quad \frac{f^{(0)}}{n} = e^{-\frac{W^2}{kT}} \exp\left[\frac{\nu_{\text{int}}}{kT}\right]; \quad W = \left(\frac{m}{2kT}\right)^{1/2}(v - v_0)
\]

are the local equilibrium Wigner distribution function density operator and the reduced peculiar velocity, respectively. The local density \( n \), the mass of the particle \( m \), and the local temperature \( T \) are used in the above definitions. Note that in equation (3.9), there is no worry about commutation problems between \( f^{(0)} \) and \( \phi \) since \( f \) is assumed to be diagonal in internal energy. (A discussion of commutation troubles that can occur upon linearization whenever off diagonalities in internal energy do occur is given by Snider.\textsuperscript{12}) The linearized Waldmann-Snider collision operator is defined as

\[
(3.11) \quad J^{\text{WS}}_{(r pt)} \rightarrow -f^{(0)}(r pt) R \phi
\]

with, in the usual notation,

\[
(3.12) \quad R \phi = -(2\pi)^{4}h^{2} tr_{2} f^{(0)}_{2} d_{2} \{ t^{g}_{g}(\phi_{1} + \phi_{2}) \delta(K) t^{g+}_{g} d(\mu g') \}
\]

\[+ (2\pi i)^{-1} \{ t^{g}_{g}(\phi_{1} + \phi_{2}) - (\phi_{1} + \phi_{2}) t^{g+}_{g} \} \]
Here $g$ and $g'$ are the relative velocities after and before collision while $t^g_\rightarrow$, remains an operator on internal states,

$$(3.13) \quad \langle a | t^g_\rightarrow, | b \rangle = \langle a | g_\nu | t | b \mu g' \rangle .$$

Thus the linearized Waldmann-Snider equation takes the form

$$(3.14) \quad (\mathcal{R} + i/\hbar \mathcal{L}_{\text{int}}) \phi = - \frac{1}{\mathcal{f}(o)} \left\{ \frac{\partial}{\partial t} + \frac{p}{m} \frac{\partial}{\partial x} \right\} \phi(o)$$

Substitution of the conservation laws into (3.14) gives

$$(3.15) \quad (\mathcal{R} + i/\hbar \mathcal{L}_{\text{int}}) \phi = X$$

where $X$ is the source term for the non equilibrium situation. This is calculated to be

$$(3.16) \quad X = 2 [\tilde{\kappa}]^{(2)} : [-\nabla \cdot v_\nu]^{(2)} - \left[ (\frac{2}{3} - \frac{k}{c_v}) (\tilde{\kappa}^{2/3}) - \frac{\mathcal{H}_{\text{int}} - \langle \mathcal{H}_{\text{int}} \rangle}{c_v T} \right] \nabla \cdot v_\nu + \nabla \left[ (\tilde{\kappa}^{2/3}) - \frac{\mathcal{H}_{\text{int}} - \langle \mathcal{H}_{\text{int}} \rangle}{c_v T} \right] \cdot [-\nabla \ln T] .$$

Equation (3.15) represents the equation of motion for the gas under the influence of external gradients and represents the working equation of chapter III. It contains a well defined, though approximate, collision superoperator $\mathcal{R}$, whose properties are discussed further in sections (d) and (e). The
approximations involved in arriving at $R$ - namely linearization, localization, and energy conservation - have been presented in some detail here to facilitate comparisons with the form of the collision superoperator discussed in chapters IV and VII.
A choice of basis for the description of transport and Senftleben-Beenakker phenomena is now discussed. This section is presented not only as a preliminary to the remaining sections of chapter III but also as a summary of the understanding that has developed over the past decade regarding the appropriateness of each type of basis. The "intuition" that has thus been gained from a study of the Senftleben-Beenakker effects, can then be used (beginning in chapter IV) for choosing an appropriate basis for the description of the spectroscopic phenomena.

For computational purposes, it is convenient to use a basis that is orthonormal with respect to the inner product of an appropriate Hilbert space. In this chapter, a Hilbert space of tensor operators $A(W)$ is involved - these operators are both tensor valued functions of the reduced peculiar velocity $W$ and tensor valued operators, diagonal in internal energy, over the space of internal states of one molecule. The inner product between any two such tensor operators $A_1(W)$ and $A_2(W)$ is defined as

$$<A_1 | A_2> = \text{tr} \int dp \left( \frac{f(0)}{n} \right)^{1/2} A_1^\dagger(W) \left( \frac{f(0)}{n} \right)^{1/2} A_2(W)$$

where $^\dagger$ is the operator adjoint and $^t$ is the tensor transpose. Basis sets which are both orthogonal and normalized in this inner product are now defined.
The translational motion is described by a set of tensor valued functions $L^{\text{PS}}(W)$ of $W$ which are defined as

\begin{equation}
L^{\text{PS}}(W) = \left\{ \frac{\Gamma(s+1)(2p+1)(2p+1)}{\Gamma(s+p+3/2)2^{p+1}(p!)} \right\}^{1/2} L_{s}^{p+1/2} (w^2) [w]^{(p)}
\end{equation}

\begin{equation}
= \left\{ \frac{\pi^{1/2}\Gamma(s+1)}{2\pi^{p}(s+p+3/2)} \right\}^{1/2} W_{p} L_{s}^{p+1/2} (w^2) Y^{(p)}(\hat{W})
\end{equation}

\begin{equation}
= \pi^{1/4} \mathcal{R}_{\text{sp}}(W) \exp\left[\frac{w^2}{2}\right] Y^{(p)}(\hat{W}).
\end{equation}

Here the velocity magnitude is expressed in terms of combinations of associated Laguerre polynomials $L_{s}^{p+1/2}(w^2)$ or equivalently in terms of normalized 3-dimensional harmonic oscillator wavefunctions $\mathcal{R}_{\text{sp}}(W)$. The angular description is given in terms of the irreducible Cartisian tensors $Y^{(p)}(\hat{W})$ with components in a spherical basis

\begin{equation}
(3.19) Y^{(p)m}(\hat{W}) = e^{(p)m}\hat{p}Y^{(p)}(\hat{W}) = 4\pi^{1/2} i^{p} Y^{(p)m}(\hat{W}).
\end{equation}

Here $Y^{(p)m}(\hat{W})$ are the spherical harmonics of Edmonds and the $e^{(p)m}$ form the Cartesian basis for spherical tensors, as discussed in appendix B. The $L^{\text{PS}}(W)$ basis is the only one which has been employed in gas kinetic theory for the description of the translational degrees of freedom.

In contrast, three sets of tensor operator basis have proven useful in the description of the internal state motion.
The first such basis recognizes the internal level structure and is the $q$th rank tensor

$$\langle 3.20 \rangle \quad (P_{jv})^{-1/2} \mathcal{J}^{(q)}(j) \rho^j(vv),$$

with $\rho^j(vv)$ being the operator

$$\langle 3.21 \rangle \quad \rho^j(vv) = \sum_m |jm\bar{v}\rangle\langle jmv|,$$

composed of particular ket-bia combinations of eigenstates of the internal state Hamiltonian. Here $j$ gives the total angular momentum magnitude $[j(j+1)]^{1/2} \hbar$, $m$ gives the component $m \hbar$ of angular momentum in the space fixed direction, and $v$ is a comprehensive label for the other internal degrees of freedom. Consistent with the picture of phase randomization given earlier, the operators $|jm\bar{v}\rangle\langle jmv|$ are considered to be diagonal in internal state energy, in particular $\bar{v}$ and $v$ label degenerate states. Also in equation (3.20), the Boltzmann weight

$$\langle 3.22 \rangle \quad p_{jv} = \frac{e^{-E(jmv)/kT}}{Q} (2j+1)$$

and the irreducible Cartesian tensor operators $\mathcal{J}^{(q)}(j)$ have been used. These latter quantities are $q$th rank combinations of the angular momentum vector operator $\mathcal{J}$ which possess the convenient normalization
where \( E(q) \) is the idempotent identity tensor for symmetric traceless tensors of rank \( q \). The identification

\[
(3.24) \quad Y^q(j) P_j^{(v v)} = E^q(\cdot) Y^q(j) P_j^{(v v)}
\]

completes the definition of these tensor operators. Further properties are discussed in appendix B. (A generalization of the tensor operators (3.24) will prove useful in describing the spectroscopic effects as developed in chapter IV.)

A combination of (3.18) and (3.20) gives the composite tensor operator basis

\[
(3.25) \quad A_{pqsjvv} = L^{PS}(j) (p_j^v)^{1/2} Y^q(j) P_j^{(v v)}
\]

which is capable of describing simultaneous translational and internal state effects. These tensors are orthonormal in the inner product (3.17), namely

\[
(3.26) \quad \langle A_{pqsjvv} | A_{p'q'sj'v'v'} \rangle = \delta(pqsjvv \ p'q'sj'v'v') E^q(\cdot) q \langle [ \ ] (q) E(p) (\ ) \rangle (q).
\]
This basis is used in the discussion of collisions given in sections (e) and (f).

A second choice for the internal state description has been found useful in the discussion of the simpler Senftleben-Beenakker effects. This basis is similar in structure to the translational basis given in equation (3.18), having the form

\[
\begin{align*}
(3.27) \quad R_t(q) \frac{\mathcal{K}_{\text{int}}}{kT} [J](q).
\end{align*}
\]

This is seen to consist of irreducible Cartesian tensors \([J](q)\) and normalized Wang-Chang-Uhlenbeck polynomials \(R_t(q)\mathcal{K}_{\text{int}}/kT\). The latter quantities are obtained for each \(q\) by Gram-Schmidt orthonormalization of the series of powers of \(\mathcal{K}_{\text{int}}/kT\) according to

\[
(3.28) \quad (2q+1)^{-1/2} \frac{1}{2} \text{tr} [J](q) \mathcal{K}_{\text{int}}/kT [J](q) e^{-\mathcal{K}_{\text{int}}/kT} R_t(q) \frac{\mathcal{K}_{\text{int}}}{kT} R_{t'}(q) \frac{\mathcal{K}_{\text{int}}}{kT} = \delta_{tt'}
\]

In terms of (3.27), the second composite basis has the form

\[
(3.29) \quad B_{pqst} = \mathcal{L}^{2S}(\mathcal{W}) [J](q) R_t(q) \mathcal{K}_{\text{int}}/kT
\]

\[
= jv (p_jv)^{1/2} \Lambda_{pqsjv} R_t(q) \mathcal{K}_{\text{int}}/kT
\]
and is also orthonormal in the inner product (3.17). Indeed,

\[
\langle \langle B_{pqst} | B_{p'q's't'} \rangle \rangle = \delta(pqst | p'q's't') E(q) E(p) \langle q | \langle q \rangle E(q) E(p) \rangle
\]

is immediately verified. As the second form of (3.29) illustrates, the $B_{pqst}$ basis is essentially a particular average of the $A_{pqstj}$ basis. For this reason, the basis (3.25) is the more fundamental one. The $B_{pqst}$ basis has been used to describe transport phenomena when the internal state effects are not too complicated, see the next section.

While both (3.25) and (3.29) have been employed in the discussions of low static field Senftleben-Beenakker effects, high static field measurements have necessitated the introduction of a third basis set for a satisfactory description of the observed phenomena. In this instance, the operators

\[
(P_{jv})^{-1/2} \langle \rho^j(vv) \rangle | jmv \rangle \langle jmv | -(2j+1)^{-1} \langle vv | jv \rangle \delta_{mm} ,
\]

where the level population $\rho^j(vv)$ has been explicitly considered as one basis element. Note that in contrast to the internal state bases (3.20) and (3.27), this basis set does not possess the property of rotational invariance - one reason why this basis is not employed unless absolutely necessary. Indeed, this basis is not considered further in chapter III, although some comments on the applicability of an analogous basis for the description of spectroscopic
effects are given in chapters IV and V.

In summary, all of the bases (3.20), (3.27) and (3.31) are equivalent in that they are connected by well defined transformations. However, the most appropriate choice—the one requiring the fewest terms to give an adequate representation of the system—depends very much on the situation to be described. Generally, the basis which most closely resembles the free motion eigenoperators is considered the most appropriate, with collisional considerations playing a secondary role.\textsuperscript{15,16,17} Again, note that all three basis sets are diagonal in $j$ quantum numbers, consistent with the concept of phase randomization mentioned earlier.
(d) Moment Equations - the Shear Viscosity Coefficient for $N_2$

The third stage in the treatment of the Senftleben-Beenakker effects is the establishment of the equations of motion for the expectation values of the relevant basis elements, starting from equation (3.15). Since the purpose of this chapter is to introduce a few useful aspects involved in the treatment of S-B effects, one simple example will suffice. To this end, the field dependence of the shear viscosity coefficient for $N_2$ in a small magnetic field is considered. While this problem has been treated before, the present development is slightly different. This part of chapter III is provided for completeness - to stress the parallelism in the treatment of moment equations for transport properties and for spectroscopic phenomena.

The symmetric traceless part of the viscous pressure tensor $\Pi^{(2)}_{\sim}$ is macroscopically related to the symmetric traceless part of the velocity gradient $[\nabla \nabla_0]^{(2)}$ by the phenomenological equation

$$
(3.32) \quad \Pi^{(2)}_{\sim} = -2\eta [\nabla \nabla_0]
$$

where $\eta$ is the phenomenological shear viscosity coefficient tensor. The kinetic theory of gases identifies the pressure tensor as a microscopic or statistical average of the symmetric-traceless part of the one molecule momentum flux $m[W]^{(2)}$, namely
Here, $\phi$ represents the solution to that part of equation (3.15) which is responsible for the momentum flux. The equation to be solved is therefore

\[
(3.34) \quad 2[\mathbb{W}]^{(2)}: [-\nabla v_\omega] = (\mathbb{R} + \frac{i}{\hbar} \mathbb{L}_{\text{int}}) \phi.
\]

A comparison of the phenomenological and statistical definitions of $\Pi^{(2)}_z$ allows a kinetic theory evaluation of the phenomenological $\Pi$ in terms of the solution of equation (3.34).

The solution is obtained by a moment method wherein an adequate description employing the smallest number of moments is desired. For the case of $N_2$ in a small magnetic field, the use of two tensor moments has given good agreement with experiment. In terms of the orthonormal basis set (3.29), a two moment ansatz expands the distribution function $\phi$ in the form

\[
(3.35) \quad \phi = \langle B_{2000} \rangle : B_{2000} + \langle B_{0200} \rangle : B_{0200},
\]

where the expectation values $\langle A \rangle$ are defined as

\[
(3.36) \quad \langle A \rangle \equiv \langle \langle \phi | A \rangle \rangle
\]
for any operator A. In particular, note that equation (3.33) can be rewritten in the form

\[(3.37) \quad \Pi^{(2)}_n = \frac{2nkT}{\sqrt{2}} \langle B_{2000} \rangle \]

Substitution of equation (3.35) into the equation of motion (3.34) and employing the spherical basis tensors \(e^{(2)}\) allows the set of coupled moment equations to be written in component form as

\[(3.38) \]

\[<B_{2000}>^\mu + \psi <B_{0200}>^\mu = -\sqrt{2} \tau [\nabla \nu_\circ]^{(2)}_\mu \]

\[ <B_{0200}>^\mu + \frac{\psi_{\text{int}}}{\tau} <B_{2000}>^\mu - i\mu \omega_{\text{int}} <B_{0200}>^\mu = 0 \]

In equation (3.38), the relaxation parameters

\[(3.39) \quad \langle< B_{2000} | R | B_{2000} >\rangle = \frac{1}{\tau} E^{(2)} \]

\[ <B_{0200} | R | B_{0200} >\rangle = \frac{1}{\tau_{\text{int}}} E^{(2)} \]

\[ <B_{0200} | R | B_{2000} >\rangle = \frac{\psi}{\tau} E^{(2)} \]

have been employed. Further, the particular form of \(\psi_{\text{int}}\) for \(N_2\) in a weak magnetic field has allowed the evaluation
to be performed. The coupled equations (3.38) have the
solution

\[ \langle B_{0200} \rangle = \frac{2\sqrt{2}}{\tau} \tau [\nabla \psi_{\alpha}]^{(2)\mu} \left( \frac{\tau_{\text{int}}}{1 - i\omega \tau_{\text{int}}} \right) \]

\[ = \sqrt{2} \tau [\nabla \psi_{o}]^{(2)\mu} + \frac{\psi^* \psi \tau_{\text{int}}}{1 - i\omega \tau_{\text{int}}} \sqrt{2} [-\nabla \psi_{o}]^{(2)\mu} \text{ for } \psi^* \psi \ll 1 \]

The approximation employed in equation (3.41) seems to be verified by experiment and basically states that the collisional coupling between velocity and internal angular momentum directions is weak.

Substitution of (3.41) into (3.37) gives, for the two moment ansatz, the shear pressure tensor

\[ \Pi^{(2)} = \sum_{\mu} e^{(2)\mu} (-1)^{\mu} \Pi^{(2)\mu} \]

\[ = 2n\kappa T \sum_{\mu} e^{(2)\mu} (-1)^{\mu} e^{(2)\mu} (\cdot) [\nabla \psi_{o}]^{(2)} \]

\[ + \psi^* \psi 2n\kappa T \sum_{\mu} e^{(2)\mu} (-1)^{\mu} \frac{\tau_{\text{int}}}{1 - i\omega \tau_{\text{int}}} e^{(2)\mu} (\cdot) [-\nabla \psi_{o}]^{(2)} \]

Comparison of (3.42) and (3.32) implies that the shear viscosity coefficient tensor for N\textsubscript{2} in the presence of a
weak magnetic field has the form

\begin{align}
(3.43) \quad \bar{\eta} &= \bar{\eta} E^{(2)} + \Delta \eta,
\end{align}

where

\begin{align}
(3.44) \quad \bar{\eta} &= n k T \tau
\end{align}

and

\begin{align}
(3.45) \quad \Delta \eta &= \psi^* \psi n k T \sum_{\mu} e^{(2)} \frac{(-1)^{\mu} \mu \tau_{\text{int}}}{1 - \tau \mu \omega \tau_{\text{int}}} e^{(2)\mu}.
\end{align}

Expressions (3.43), (3.44) and (3.45) show that in the presence of a weak magnetic field, there are five independent viscosity coefficients which are produced by the collisional coupling of velocity and internal angular momentum directions. Further, these complex coefficients \( \Delta \eta_\mu \) can be divided into their real and imaginary parts according to

\begin{align}
(3.46) \quad \frac{\Delta \eta_\mu}{\bar{\eta}} &= \frac{\Delta \eta^+}{\bar{\eta}} + i \frac{\Delta \eta^-}{\bar{\eta}},
\end{align}

where

\begin{align}
(3.47) \quad \frac{\Delta \eta^+}{\bar{\eta}} &= \psi^* \psi \frac{\tau^2}{\tau_{\text{int}}} \left\{ \frac{1}{1 + \mu^2 \omega^2 \tau_{\text{int}}^2} \right\},
\end{align}

\begin{align}
\frac{\Delta \eta^-}{\bar{\eta}} &= \psi^* \psi \frac{\tau^2}{\tau_{\text{int}}} \left\{ \frac{\mu \omega \tau_{\text{int}}}{1 + \mu^2 \omega^2 \tau_{\text{int}}^2} \right\}.
\end{align}
These coefficients are plotted in figure 4 as a function of $\mu \omega T_{\text{int}}$ and are seen to behave as Lorentz absorption and dispersion shapes, respectively. They are in very good agreement with the experimental curves for $N_2$. 
Figure 4: Even and odd viscosity coefficients for $\text{N}_2$. 
(e) Collisional Expressions

In the description of transport phenomena, matrix elements of the linearized Waldmann-Snider collision superoperator arise naturally. In particular, for the evaluation of the viscosity coefficients of $N_2$, the three collisional parameters $T$, $T_{int}$, and $\psi$ are involved. Thus the calculation of collision matrix elements is required and, indeed, represents an important aspect of kinetic theory. This has been the subject of detailed investigations - first for diamagnetic diatomics\(^{13}\) and later extended to general polyatomics.\(^ {19}\) In the last two sections of chapter III, some of these considerations are presented with the idea of reapplying this technical expertise in later chapters to the collision integrals of pressure broadening and related phenomena.

The linearized Waldmann-Snider collision superoperator $\mathcal{R}$ has several general symmetry properties\(^ {6,13,20}\) that reduce the number of independent matrix elements. The usual case where $\mathcal{R}$ can be assumed independent of the external static electric and magnetic fields is treated here.

The parity superoperator $\Pi$ is defined such that

\begin{equation}
(3.48) \quad \Pi A(\omega) \equiv \pi A(-\omega) \nonumber
\end{equation}

where $\pi$ is the parity operator acting on quantum mechanical internal states. It can then be shown\(^ {5}\) that

\begin{equation}
(3.49) \quad \mathcal{R} \Pi = \Pi \mathcal{R} \nonumber
\end{equation}
and hence $\mathcal{R}$ does not mix operators of different parity. The time reversal superoperator $\mathcal{O}$, defined as

$$\mathcal{O} A(W) = O A(-W) \theta^{-1}$$

where $\theta$ is the internal state antilinear time reversal operator, does not commute with $\mathcal{R}$, however. Indeed, similar considerations establish

$$\mathcal{O} \mathcal{R} = \mathcal{R}^\# \mathcal{O}$$

where $\mathcal{R}^\#$ is the superoperator adjoint of $\mathcal{R}$. Equation (3.51) implies that $\mathcal{R}$ can mix operators of different time reversal symmetry. The definition of the rotation superoperator $\mathcal{R}$ is given by

$$\mathcal{R} A(W) = \mathcal{R} A(R-W) \mathcal{R}^{-1}$$

in terms of a 3x3 Cartesian rotation matrix $R$ and the internal state rotation operator $r$. Then the rotational properties of $\mathcal{R}$ are stated succinctly as

$$\mathcal{R} \mathcal{R} = \mathcal{R} R$$

and $\mathcal{R}$ is an isotropic superoperator which can couple only tensor operators of the same rotational symmetry. More detailed aspects of rotational invariance of $\mathcal{R}$ are explored momentarily.
Collision integrals $<<\Lambda|\mathcal{R}|\Lambda'>>$ have the units of inverse time and thus can be considered as collision rates or frequencies. It is traditional to express these matrix elements as kinetic cross sections

\[(3.54) \quad \mathfrak{E}(pqsjv' | p'q's'j'v''v''') \]

\[= n^{-1} \left( \frac{\mu}{8kT} \right)^{1/2} <<\Lambda_{pqsjv'v''v'''} | R_{p'q's'j'v''v'''}>>. \]

Here $\left( \frac{\mu}{8kT} \right)^{1/2}$ is the average relative velocity, $n$ is the density, and the basis chosen is defined in equation (3.25). Matrix elements in the second basis (3.29) are just appropriately averaged versions of (3.54).

The effects of the rotational invariance property of on the kinetic cross sections is now presented in detail. The tensor cross sections of equation (3.54) can be expressed in terms of a set $\mathfrak{E}(\cdot\cdot\cdot\cdot\cdot\cdot\cdot)$ of scalar cross sections by the relation

\[(3.55) \quad \mathfrak{E}(pqsjv'v'' | p'q's'j'v''v''') = \sum_k (-1)^{k+q+q'} \Omega(kqq')^{1/2} V(kpp')^{1/2} V(qkq')(\cdot\cdot\cdot)q'+k [I(q')V(kpp')] (q') \]

\[\mathfrak{E}(pqsjv'v'' | p'q's'j'v''v''')_k \]

where $V(kpp')$ are Cartesian 3-j tensors and $\Omega(kpp')$ are their normalization factors.\textsuperscript{13,14} In equation (3.55) the coupling scheme chosen is one which first couples the velocity tensors
together and likewise for the angular momentum tensors, and then considers the directional correlation between velocity and angular momentum spaces. The choice of coupling scheme is predicated on the idea that the effects of the non-spherical part of the intermolecular potential are weak. Indeed, if the intermolecular potential were isotropic, then only the $k=0$ component would result. Thus $k\neq 0$ contributions measure the collisional coupling between velocity and angular momentum directions and are expected to be smaller than the $k=0$ terms. In fact, the approximation $\psi^*\psi<1$ used in the previous section is a particular example of this type of reasoning.

The scalar coefficients in (3.55) are given by

$$\langle pqsj\bar{v}v|p'q's'j'\bar{v}'v'\rangle_k = (-1)^{k+p+p'}(2k+1)\Omega(kq'|q)\frac{1}{\sqrt{2^k(kq|q)}}$$

$$\Omega(kp'|p)^{1/2}V(q'kq)(\cdot)^{k+q}\left[\left(q\right)_{V(kp'|p)}\right]\left(q\right)$$

$$(-)^{p+p'+q+q'}\langle pqsj\bar{v}v|p'q's'j'\bar{v}'v'\rangle .$$

Substitution of (3.25) into (3.54) and then into (3.56) allows the integral over the centre of mass momentum to be evaluated. The transformations used are

$$\tilde{W}''_1 + \tilde{W}''_2 = \tilde{W}_1 + \tilde{W}_2 = \sqrt{2} \tilde{\gamma}$$

$$\tilde{W}_2 - \tilde{W}_1 = \sqrt{2}\gamma \quad \tilde{W}_2' - \tilde{W}_1' = \sqrt{2}\gamma'$$

$$\gamma = \left(\frac{m}{4kT}\right)^{1/2}$$
and the result (following the methods of Chen, Moraal and Snider\textsuperscript{13}) is

\[
(3.58) \sum_k (pqsj\bar{v}|p'q's'j'\bar{v}'v)_k
\]

\[
= (2k+1) \sum_{\ell n} \left\{ \Omega(kl\ell') \right\}^{1/2} (k) I_{\ell n l' n'; psp's'}
\]

\[
\{ \sum' \left( \ell qn j\bar{v}|\ell' q'n' j'\bar{v}'v' \right)_k \} + (-1)^{\ell'} \sum'' \left( \ell qn j\bar{v}|\ell' q'n' j'\bar{v}'v' \right)_k
\]

\[
= (2k+1) \sum_{\ell n} \left\{ \Omega(kl\ell') \right\}^{1/2} (k) I_{\ell n l' n'; psp's'}
\]

\[
\left\{ \sum_{j_2 v_2 j'_2 v'_2} \left( p_{j_2 v_2} p_{j'_2 v'_2} \right)^{1/2} \left( \ell n j\bar{v} v j_2 v_2 q | \ell' n' j'\bar{v}'v' j'_2 v'_2 q' \right)_k \right. \] + (-1)^{\ell'} \sum_{j_2 v_2 j'_1 v'_1} \left( p_{j_2 v_2} p_{j'_1 v'_1} \right)^{1/2} \left( \ell n j\bar{v} v j_2 v_2 q | \ell' n' j'\bar{v}'v' j'_2 v'_2 q' \right)_k \right\}.
\]

The second form represents the usual presentation while the first form is that preferred by the present author. In equation (3.58), the transformation $I^{(k)}$ connects the description $\sum_k$ in terms of the initial and final moments of one molecule (represented by the indices $psp's'$), with the descriptions $\sum'_{k'} \sum''_{k''}$ in terms of the initial and final relative moments of the colliding pair (represented by the indices $\ell n\ell' n'$). This is a necessary complicating factor due to the presence of velocity polarizations and their rotational properties - it reduces to the identity transformation when
p=s=p'=s'=0. Reference 13, appendix B defines \( I^{(k)} \) and gives a formula for its evaluation.

The two effective scalar cross sections introduced in equation (3.58) are given by

\[
(3.59) \quad \mathcal{E}^{(s')}_{\ell \ell' n' j' \ell \ell' n j} \kappa
\]

\[
= (-1)^{q+q'} (2\pi)^{\frac{3}{2}} \frac{\mu}{8kT} \frac{1}{\pi^{3/2}} \Omega(kq')^{-1/2} \Omega(k\ell'^2)_{-1/2} V(q'\kappa)(\ell') \mathcal{V}(k\ell'\ell)(\ell) \mathcal{L}^{\ell+\ell'+q+q'} \Sigma \left\{ \frac{P_{j_2} v_2}{(2j_2+1)} \times \frac{P_{j_2'} v_2'}{(2j_2'+1)} \right\}^{1/2} j_2 v_2 j_2 v_2
\]

\[
\{ \int \frac{d\gamma}{\gamma} \int \frac{d(\mu q')}{\mu q'} \exp\left[-\frac{1}{2}(\gamma^2+\gamma^2(2))\right] L_{\ell \ell'} n'(\gamma) L_{\ell \ell' n'}(\gamma')
\]

\[
\begin{align*}
\text{tr}_1 \text{tr}_2 \left[ \rho_{j_1}^{j_1}(v_1 v_1) \rho_{j_2}^{j_2}(v_2 v_2) \right] Y^{(q')}_{j_1 j_2} \left( \frac{1}{2} \right) <\psi_1 | t | \psi_2> \\
+ (-1)^{q+q'} (2\pi)^{-\frac{1}{2}} \delta(j_1 j_2 | j_1' j_2') \delta(v_2 | v_2') \int \frac{d\gamma}{\gamma} e^{-\gamma^2} L_{\ell \ell'} n(\gamma) L_{\ell \ell' n'}(\gamma)
\end{align*}
\]

\[
\begin{align*}
\text{tr}_1 \text{tr}_2 \left[ \frac{Y^{(q')}_{j_1}}{(2j_1+1)} \right] \delta(v_1 | v_1') - \rho_{j_1}^{j_1}(v_1 v_1) \rho_{j_2}^{j_2}(v_2 v_2) Y^{(q')}_{j_1 j_2} \left( \frac{1}{2} \right) \\
<\mu q | t^+ | \mu q > \delta(v_1 | v_1')
\end{align*}
\]
\[(3.60) \sum \langle \ell q n j_1 \bar{v}_1 v_1 | \ell' q' n' j_2 \bar{v}'_2 v'_2 \rangle_k \]

\[
= (-1)^{q+q'} (2\pi)^{4} \frac{k^2}{8kT} \frac{1}{\pi^{3/2}} \frac{1}{\pi^{3/2}} \Omega(kqq')^{-1/2} \Omega(k\ell\ell')^{-1/2} \]

\[
\times \sum_{j_2 v_2} \left\{ \frac{p_{j_2 v_2}}{(2j_2+1)} \times \frac{p_{j_1 v'_1}}{(2j_1'+1)} \right\}^{1/2} \]

\[
\left\{ d\gamma \right\} \left\{ d(\mu g') \right\} \exp\left\{ \frac{-1}{2}(\gamma^2 + \gamma'^2) \right\} L L' n(\gamma) L L' n'(\gamma') \]

\[
\sum_{\ell} \left\{ (2j_1 + 1) \right\}^{1/2} \left\{ (2j_2 + 1) \right\}^{1/2} \left\{ (2j_1' + 1) \right\}^{1/2} \left\{ (2j_2' + 1) \right\}^{1/2} \]

\[
\langle \mu g | t | \mu g' \rangle \left\{ \delta(\kappa) t^\dagger | \mu g \rangle \right\} \]

\[+ (-1)^{q+q'} (2\pi)^{-1} \delta(j_1 j_2 | j_1' j_2') \int d\gamma e^{-\gamma^2} L L' n(\gamma) L L' n'(\gamma) \]

\[
\sum_{\ell} \left\{ (2j_1 + 1) \right\}^{1/2} \left\{ (2j_2 + 1) \right\}^{1/2} \left\{ (2j_1' + 1) \right\}^{1/2} \left\{ (2j_2' + 1) \right\}^{1/2} \]

\[
\times \left\{ \delta(v_1 v_2 | v_1' v_2') - \delta(v_1' v_2 | v_1 v_2') \right\} \left\{ \delta(\bar{v}_1 v_2 | \bar{v}_1' v_2') \right\} \left\{ \delta(\bar{v}_1' v_2 | \bar{v}_1 v_2') \right\} \left\{ \delta(\bar{v}_1' v_2 | \bar{v}_1 v_2') \right\} \]

\[
\left\{ \delta(\bar{v}_1 v_2 | \bar{v}_1' v_2') \right\} \left\{ \delta(\bar{v}_1' v_2 | \bar{v}_1 v_2') \right\} \left\{ \delta(\bar{v}_1 v_2 | \bar{v}_1' v_2') \right\} \left\{ \delta(\bar{v}_1' v_2 | \bar{v}_1 v_2') \right\} \]

\[
\langle \mu g | t | \mu g \rangle \delta(\bar{v}_1 v_2 | \bar{v}_1' v_2') \rangle \}
\]
Physically, the cross section $\Sigma_k$ describes effects where the polarizations, both before and after the collision, refer to the same molecule. Collision processes wherein the polarizations are passed from one molecule to the other are accounted for in the "transfer cross sections", $\Sigma_k'$. In particular, resonant processes fall into this latter category. As has been seen, this subdivision of collisional effects is a natural one which follows directly from the linearization of the appropriate quantum mechanical Boltzmann equation.

The evaluation of the angular integrals and the internal state traces in equations (3.59) and (3.60) produces transition operator matrix elements in an angular momentum representation. More particularly, the use of

$$(3.61) \quad |\mu g\rangle = \sum_{\lambda s} |p\lambda s\rangle\langle \lambda s|\hat{p}\rangle = \sum_{\lambda s} |p\lambda s\rangle \cdot i^{-\lambda} Y_{\lambda s}^* (\hat{p})$$

where $Y_{\lambda s} (\hat{p})$ are the spherical harmonics of Edmonds and

$$(3.62) \quad \text{tr}_1 \text{tr}_2 \left( \rho^{j_1}_1 (V_1 \vec{v}_1) \rho^{j_2}_2 (V_2 \vec{v}_2) \right)$$

$$(3.63) \quad \sum_{m_1, m_2} \langle j_1 m_1 \vec{v}_1 j_2 m_2 \vec{v}_2 | \Lambda | j_1 m_1 v_1 j_2 m_2 v_2 \rangle$$

$$(3.64) \quad \langle j_1 m_1 v_1 j_2 m_2 v_2 p\lambda s | t | j_1' m_1' v_1' j_2' m_2' v_2' p' \lambda' s' \rangle$$

$$\langle j_1 m_1 v_1 j_2 m_2 v_2 p\lambda s | t | j_1' m_1' v_1' j_2' m_2' v_2' p' \lambda' s' \rangle$$
But the transition operator itself is also a rotationally invariant quantity. It follows that the matrix elements (3.63) can be expressed in terms of reduced (scalar) quantities. Several coupling schemes have been described for their decomposition. In this chapter, only the translational-internal coupling scheme is used since it is the scheme most suitable for the distorted wave Born approximation (given below). Thus, the matrix element (3.63) in the translational-internal coupling scheme is written as

\[
\langle j_1^m_1 v_1^j_1 m_2^v_2 p^\lambda s | t | j_1^m_1 v_1^j_1 m_2^v_2 p^\lambda' s' \rangle
\]

\[
= (2\pi i \mu)^{-1} (pp')^{-1/2} (-1)^{j_1+j_2+\lambda+j_1'+j_2'+\lambda'} (-1)^{m_1+m_2+s}
\]

\[
[(2j_1+1)(2j_2+1)(2\lambda+1)]^{1/2} \sum_{\lambda_1 \lambda_2 \lambda} [(2\lambda_1+1)(2\lambda_2+1)(2\lambda+1)]^{1/2}
\]

\[
E \left( j_1^v_1j_2^v_2\lambda; \lambda_1 \lambda_2 \lambda; j_1^v_1j_2^v_2\lambda \right)
\]

where \(E\) is the Yutsis, Levinson, and Vanagas type diagram, see figure 5. It should be noted that the indices on the right hand side of equation (3.64) are in the reverse order to those on the left hand side - this should be kept in mind when interpreting formulae involving the reduced \(T\) matrix elements.

Substitution of (3.64) into (3.59) and (3.60) allows all magnetic summations to be performed explicitly, to yield the totally (rotational) invariant expressions.
Figure 5: Coupline diagram $E$
\[
(3.65) \sum \left( \xi_{q} n_{j_{1}} \bar{v}_{1} v_{1} | 2' q' n' j_{1} \bar{v}_{1} v_{1} \right)_{k}
\]

\[
= (-1)^{k+q+q'} \Omega(kq')^{-1/2} \sum_{l+2 l} \left( \frac{(2q+1)(2q'+1)}{1/2} \right)_{k+q+q'}
\]

\[
\left( \frac{(2j_{1}+1)(2j_{1}'+1)}{1/2} \right)_{k+q+q'} \frac{\pi_{k+2}^{2}}{\mu} (8kT)^{1/2}
\]

\[
f d\gamma \frac{d\gamma'}{g} \frac{1}{gg'} \mathcal{A}_{n_{1}} \left( \gamma \right) \mathcal{A}_{n_{2}} \left( \gamma' \right) \delta \left( E_{j_{1}} v_{1} + E_{j_{2}} v_{2} + \frac{\mu g^{2}}{2} \right) - E_{j_{1}} v_{1}
\]

\[
\left. \right\} \Lambda_{1} \Lambda_{2} \left( 2 \Lambda' + 1 \right) \left( 2 \Lambda'' + 1 \right) (-1)^{\Lambda + \Lambda''}
\]

\[
T \left( j_{1} \bar{v}_{1} j_{2} \bar{v}_{2} \lambda' ; l_{1} \bar{c}_{2} \bar{c}_{4} ; j_{1} \bar{v}_{1} j_{2} \bar{v}_{2} \lambda \right) T^{*} \left( j_{1} \bar{v}_{1} j_{2} \bar{v}_{2} \lambda'' ; l_{1} \bar{c}_{2} \bar{c}_{4} ; j_{1} \bar{v}_{1} j_{2} \bar{v}_{2} \lambda'' \right)
\]
\[ + \sum_{\mathbf{p}_{j_2} \cdot \mathbf{v}_2} \frac{p_{j_2} \cdot \mathbf{v}_2}{(2j_2+1)} \delta(j_1 j_2 | j'_1 j'_2) \delta(v_2 | v'_2) \Omega(kqq')^{-1/2} q^q q' \]

\[ \frac{(2q+1)(2q'+1)}{2k+1} \frac{j_1 q_1 j_1 k}{(2j_2+1)(2j_2+1)} \delta(v_1 | v'_1) \]

\[ \frac{\pi \hbar^2}{\mu} \left( \frac{\pi \mu}{8kT} \right)^{1/2} \Omega(kll')^{-1/2} (-i \ell + l') \]

\[ [(2\ell+1)(2\ell'+1)]^{1/2} \begin{pmatrix} 0 & 0 & 0 \end{pmatrix} \]

\[ \int d\gamma \frac{\gamma^2}{\mu g} \mathcal{R}_{n^t} (\gamma) \mathcal{R}_{n} (\gamma) \Sigma_{n, \ell, \ell'} (2\ell+1)^{1/2} (2\ell'+1)(-1)^{\ell''} k \lambda \lambda'' \]

\[ \begin{pmatrix} 0 & 0 & 0 \end{pmatrix} \]

\[ \mathbf{T} (j_1 \tilde{\mathbf{v}}_1 j_2 \mathbf{v}_2 \lambda; \mathbf{k} \mathbf{v}_1 j_1 \mathbf{v}_2 \lambda) + \delta(\tilde{\mathbf{v}}_1 | v'_1)(-1)^{k+q+q'} \]

\[ \frac{\pi \hbar^2}{\mu} \left( \frac{\pi \mu}{8kT} \right)^{1/2} \Omega(kll')^{-1/2} (+i \ell + l') \]

\[ [(2\ell+1)(2\ell'+1)]^{1/2} \begin{pmatrix} 0 & 0 & 0 \end{pmatrix} \]

\[ \int d\gamma \frac{\gamma^2}{\mu g} \mathcal{R}_{n^t} (\gamma) \mathcal{R}_{n} (\gamma) \Sigma_{n, \ell, \ell'} (2\ell+1)^{1/2} (2\ell'+1)(-1)^{\ell''} k \lambda \lambda'' \]

\[ \begin{pmatrix} 0 & 0 & 0 \end{pmatrix} \]

\[ \mathbf{T}^* (j_1 \mathbf{v}'_1 j_2 \mathbf{v}_2 \lambda; \mathbf{k} \mathbf{v}_1 j_1 \mathbf{v}_2 \lambda) \]

and

\[ (3.66) \quad \sum_{\ell q n j_1 \mathbf{v}_1 | \ell' q' n' j'_2 \mathbf{v}'_2} \]

\[ = (-1)(-1)^{q+q'} \Omega(kqq')^{-1/2} \Omega(kq')^{-1/2} \left( \frac{(2q+1)(2q'+1)}{2k+1} \right)^{1/2} \]

\[ [(2j_1+1)(2j_1'+1)]^{1/2} \]

\[ \sum_{\mathbf{\ell}_1 \mathbf{\ell}_2 \mathbf{\ell}'} \left[ \frac{(2\ell_1+1)(2\ell_2'+1)(2\ell'+1)}{(2\ell_2'+1)(2\ell'+1) (2\ell_1'+1)} \right]^{1/2} \]

\[ \frac{(2j_1+1)(2j_2+1)}{2k+1} \frac{j_1 q_1 j_1 k}{(2j_2+1)(2j_2+1)} \delta(v_1 | v'_1) \]

\[ \begin{pmatrix} 0 & 0 & 0 \end{pmatrix} \]
Equations (3.65) and (3.66) are exact and may be viewed as the result of combining the rotational invariance properties of $t$ with the rotational invariance properties of $\rho$ as a whole. They are complicated because they contain both internal state and velocity polarization effects.

While equations (3.65) and (3.66) are the forms for $\Sigma_k'$ and $\Sigma_k''$ that are usually presented, alternate (but completely equivalent) forms can be obtained. One such form whose format is closer to expressions commonly used in pressure broadening studies, is obtained by employing the transformation

\begin{equation}
T(a_{ab} \tilde{v}_a \tilde{v}_b \lambda; \lambda_a \lambda_b | \ell_a \ell_b \lambda)
= \delta(a_{ab} \tilde{v}_a \tilde{v}_b \lambda \mid \lambda_a \lambda_b \lambda) \delta(\lambda_a \lambda_b | 000)
- s(a_{ab} \tilde{v}_a \tilde{v}_b \lambda; \lambda_a \lambda_b | \ell_a \ell_b \lambda)
\end{equation}

along with the identifications
\[
\frac{\pi \hbar^2}{\mu \frac{1}{8kT}} \int_0^2 \frac{\Theta}{\Theta} \, d\gamma \mathcal{R}_{n \ell} (\gamma) \mathcal{R}_{n' \ell'} (\gamma)
\]

(3.68) \[
= \frac{1}{(kT)^2} \int_0^\infty dE \, \frac{\pi \hbar^2}{\mu^2 g} \bar{\mathcal{R}}_{n \ell} (\gamma) \bar{\mathcal{R}}_{n' \ell'} (\gamma)
\]

and

(3.69) \[
\frac{\pi \hbar^2}{\mu \frac{1}{8kT}} \int_0^2 \frac{\Theta}{\Theta} \, d\gamma \frac{(q')^2}{gg'} \, dg' \mathcal{R}_{n \ell} (\gamma) \mathcal{R}_{n' \ell'} (\gamma')
\]

\[
= \frac{1}{(kT)^2} \int_0^\infty dE \, dE' \, \bar{\mathcal{R}}_{n \ell} (\gamma) \bar{\mathcal{R}}_{n' \ell'} (\gamma') \frac{\pi \hbar^2}{\mu^2 g} \exp \left[ -\frac{1}{2} (\gamma^2 + \gamma'^2) \right].
\]

Here

(3.70) \[
\mathcal{R}_{n \ell} (\gamma) = \frac{2}{\pi^{1/4}} \exp \left[ -\frac{\gamma^2}{2} \right] \bar{\mathcal{R}}_{n \ell} (\gamma).
\]

The results are then

(3.71) \[
\sum' (\ell q \nu \gamma \nu_1 | \ell' q' \nu' \gamma' \nu_1) \]

\[
= \frac{-1}{(kT)^2} \int_0^\infty dE \, dE' \, \bar{\mathcal{R}}_{n \ell} (\gamma) \bar{\mathcal{R}}_{n' \ell'} (\gamma') \exp \left[ -\frac{\gamma^2 + \gamma'^2}{2} \right]
\]

\[
\sum \left\{ \frac{P_{j_2 \nu_2}}{(2j_2 + 1)} \frac{P_{j_2' \nu'_2}}{(2j_2' + 1)} \right\} \frac{1}{2} \delta(E_1 \nu_1 + E_2 \nu_2 + E - E_1' \nu_1' - E_2' \nu_2')
\]

\[
\hat{C}' (E; \ell q \nu \gamma \nu_1 | \ell' q' \nu' \gamma' \nu'_1) \]

k
The quantities $\hat{C}'(E)_k$ and $\hat{C}''(E)_k$ are effectively rotationally invariant forms of energy dependent total cross sections. Equations (3.61) and (3.62) demonstrate that the kinetic cross sections $\underline{c}''_k, \underline{c}''_k$ represent particular averages (over translational energy and second molecule internal states) of these total cross sections. The particular kind of averaging employed - equal Boltzmann weights for incoming and outgoing states - has been chosen so as to yield the most symmetric forms possible for $\underline{c}''_k, \underline{c}''_k$ under time reversal. 24

To complete the process which began with equation (3.67), the precise forms for $\hat{C}'(E)_k$ and $\hat{C}''(E)_k$ are given. Namely,
\[ (3.73) \quad \hat{c}'(E; \ell, q j_1 \bar{v}_{1j_2} \bar{v}_2) \bigg| \ell', q j_1 \bar{v}_{1j_2} \bar{v}_2 \bigg)_{k'} = \]

\[
\frac{\pi \hbar^2}{\mu^2 g^2} \frac{[(2q+1)(2q'+1)(3\ell+1)(2\ell'+1)]^{1/2}}{\Omega(k \ell \ell')^{1/2} \Omega(k q q')^{1/2}} \delta_{q-q'+\ell+\ell'}
\]

\[
[(2j_2+1)(2j_2'+1)]^{1/2} \sum_{\ell_1 \ell_2 \ell} (-1)^{\ell_1 + \ell_2 + \ell'} \lambda_1 \lambda_2 \lambda \lambda' \lambda''
\]

\[
[(2j_1+1)(2j_1'+1)(3\ell_1'+1)(2\ell_1'+1)]^{1/2} \xi_{12} \xi_{12'} \xi_{1} \xi_{1'} \xi_{1''}
\]

\[
[(2\lambda_1+1)(2\lambda_1'+1)(2\lambda_2+1)(2\lambda_2'+1)]^{1/2} (-1)^{k+q+q'+\ell+\ell'}
\]

\[
(-1)^{\lambda+\lambda''} [(2\lambda_1+1)(2\lambda_2+1)]^{1/2} \begin{pmatrix}
\lambda & \lambda'' & \lambda' & \lambda' \\
0 & 0 & 0 & 0
\end{pmatrix}
\]

\[
\frac{(2j_1+1)(2j_2+1)(2j_1'+1)(2j_2'+1)}{(2j_1+1)(2j_2+1)}^{1/2} \begin{pmatrix}
j_1 & j_1 & \ell_1 & \ell_1' \\
j_1' & j_1' & \ell_1' & \ell_1
\end{pmatrix} \begin{pmatrix}
\lambda & \lambda'' & \lambda' & \lambda'
\end{pmatrix}
\]

\[
[S(j_1 \bar{v}_{1j_2} \bar{v}_2 \lambda'; \ell_1 \ell_2; j_1 \bar{v}_{1j_2} \bar{v}_2 \lambda)]
\]

\[
S^*(j_1 \bar{v}_{1j_2} \bar{v}_2 \lambda''; \ell_1 \ell_2 \ell'; j_1 \bar{v}_{1j_2} \bar{v}_2 \lambda'')
\]

\[-\delta(\ell_1 \ell_2 \ell_1 \ell_1') \delta_{000000} \delta(j_1 \bar{v}_{1j_2} \bar{v}_2 \lambda'j_1 \bar{v}_{1j_2} \bar{v}_2 \lambda) \delta(\lambda', \lambda'' | \lambda \lambda'') \]

and
\( \hat{c}''(E', \lambda q_1 j_1 \tilde{v}_1 \tilde{v}_1 j_2 \tilde{v}_2 | \ell', q' j_1' \tilde{v}_1 j_2' \tilde{v}_2')_k = \)

\[
\frac{\pi \hbar^2}{\mu^2 g^2} \left\{ \frac{(2q+1)(2q'+1)(2\ell+1)(2\ell'+1)}{\Omega(kq \ell')^{1/2} \Omega(kq' \ell')^{1/2}} \right\}^{1/2} q' - q + \lambda + \ell'
\]

\[
[(2j_2 + 1)(2j_1 + 1)]^{1/2} \sum_j \frac{\lambda + \lambda''}{(2\ell + 1)} (-1)^{\ell + \ell' + 1} \\
[(2\ell_1 + 1)(2\ell_2 + 1)(2\ell + 1)(2\ell' + 1)]^{1/2}
\]

\[
[(2\lambda + 1)(2\lambda_1 + 1)(2\lambda_2 + 1)(2\lambda'' + 1)]^{1/2} (-1)^{q + q' + \lambda + \ell'}
\]

\[
(-1)^{\lambda + \lambda''} [(2\lambda_1 + 1)(2\lambda_2 + 1)]^{1/2} \begin{pmatrix} \lambda & \lambda'' & \lambda & \lambda \\ 0 & 0 & 0 & 0 \end{pmatrix}
\]

\[
\frac{(2j_1 + 1)(2j_2 + 1)(2j_1' + 1)(2j_2' + 1)}{(2j_1 + 1)(2j_2 + 1)} \left\{ \frac{1}{(2j_1' + 1)(2j_2' + 1)} \right\}^{1/2} (-1)^{j_1 + j_2 + j_1' + j_2'}
\]

\[
\{\ell, \ell', \ell''\} \begin{pmatrix} \ell & \ell' & \ell'' \\ \ell & \ell' & \ell'' \end{pmatrix}
\]

\[
[S(j_1 \tilde{v}_1 j_2 \tilde{v}_2 \lambda' \ell_1 \ell_2 | j_1 \tilde{v}_1 j_2 \tilde{v}_2 \lambda')]
\]

\[
S^*(j_1 \tilde{v}_1 j_2 \tilde{v}_2 \lambda'' \ell_1 \ell_2 | j_1 \tilde{v}_1 j_2 \tilde{v}_2 \lambda'')
\]

\[
- \delta(\ell_1 \ell_2 \ell_1 \ell_2 | 000000) \delta(\lambda', \lambda'' | \lambda \lambda') \delta(j_1 j_2 | j_1 j_2)
\]

\[
\delta(v_1 v_1 v_1 v_2 v_2 | v_1 v_1 v_2 v_2)
\]
The $S$ matrix versions (3.73) and (3.74) may appear more familiar to some than the $T$ matrix forms (3.65) and (3.66) given earlier. They are still complicated, however, mainly due to the presence of velocity polarizations. Indeed, the complicated orientational averaging ($6j$ and $9j$ symbols involving $\ell$ and $\ell'$) required to get rotationally invariant cross sections, and the nonequilibrium $(\kappa^2_{n\ell}(\gamma), \kappa^2_{n\ell'}(\gamma'))$ averaging over translational energy in equations (3.71) and (3.72), are a direct consequence of these translational polarizations.

It should be emphasized that equations (3.73) and (3.74) are exact and are completely equivalent to the $T$ matrix expressions. Both represent rotationally invariant expressions in the translational-internal coupling scheme. $S$ and $T$ matrix expressions in other coupling schemes can also be visualized (but will not be presented explicitly). Indeed, a multitude of equivalent exact expressions — $S$ versus $T$, one coupling scheme versus another — can be obtained. Which is preferable? The choice is determined by the approximate scheme to be used in evaluating these matrix elements. Throughout this thesis, the distorted wave Born approximation (DWBA) will be employed. The appropriate starting point is then a $T$ matrix representation in the translational-internal coupling scheme. In chapter III, this is given by equations (3.65) and (3.66).
(f) The Distorted Wave Born Approximation (DWBA)

The kinetic theory collision integrals described in this chapter involve both translational and internal state effects. The distorted wave Born approximation is a method of approximately evaluating these matrix elements, in which both types of motions are considered. It is based on a division of the intermolecular potential $V$ into a spherical (internal state independent part $V_o$) and a remaining non-spherical (anisotropic) part $V_1$. Thus

\begin{equation}
V = V_o + V_1
\end{equation}

where $V_1$ is written as

\begin{equation}
V_1 = \sum_{\lambda_1 \lambda_2 \lambda_1} \left( \mathcal{O}_{\lambda_1}^{(\lambda_1)} \mathcal{O}_{\lambda_2}^{(\lambda_2)} \right) \hat{V}_{\lambda_1 \lambda_2 \lambda_1} \mathcal{Y}_{\lambda_1}(\hat{R})
\end{equation}

with $\hat{R} = R \hat{R}$ as the position of molecule 2 relative to molecule 1 and $\mathcal{O}_{\lambda_1}$, $\mathcal{O}_{\lambda_2}$ as the internal state operators for molecules 1 and 2, respectively. The radial ($R$) dependence is specified by the scalar coefficient $b_{\lambda_1 \lambda_2 \lambda_1}(R)$. The potential (3.75) is quite general, although it does not include momentum dependent potentials such as the spin-rotation type

\begin{equation}
V_{sr} = (\mathcal{J}_1 + \mathcal{J}_2) \cdot R \times p \mathcal{Y}_{sr}(R)
\end{equation}
which can be significant for molecules with spin 1/2 nuclei.

In equation (3.75), the nonspherical part $V_1$ is assumed much "smaller" than $V_0$, so that a perturbation expansion in $V_1$ can be performed. Thus

\[(3.78) \quad t \equiv \Omega \Omega = t_0 + t_1 + t_2 + \ldots,\]

where

\[(3.79) \quad t_0 = V_0 \Omega_0\]

and

\[(3.80) \quad t_1 = V_1 + V_0G(t_1) + V_1G(t_0)\]

\[= \tilde{\Omega} V_1 \Omega_0\]

Here $\tilde{\Omega}_0$ is the transpose (or $\mathcal{A}$ conjugate) of the spherical Møller wave operator $\Omega_0$ mentioned in appendix A. In the notation of (3.13), equation (3.78) is written as

\[(3.81) \quad [tg]_\Omega \equiv \langle \mu_g | t_1 | \mu_{g'} \rangle = \sum_{\lambda_1 \lambda_2} \left( \begin{array}{c} \lambda_1 \\ \lambda_2 \end{array} \right) \left( \begin{array}{c} \lambda_1' \\ \lambda_2' \end{array} \right) \chi_1^{\lambda_1} \chi_2^{\lambda_2} \nu(\lambda_2 \lambda_1') \chi_1^{\lambda_1'} \chi_2^{\lambda_2'},\]

with the translational dependence entirely factored into the quantity
Equation (3.81) states that the transition operator, in first order, is a sum of products of translational and internal state contributions. For transition matrix elements of the form (3.63), one has $t_1$ expressible as,

\begin{equation}
\langle j_1 v_1 j_2 v_2 \lambda s | t_1 | j_1 v_1 j_2 v_2 \lambda' s' \rangle
\end{equation}

\begin{equation}
= \sum_{L_1 L_2 \lambda} \left\langle j_1 v_1 | L_1 \lambda \rangle \left| j_1 v'_1 \right\rangle \left| j_2 v_2 \right\rangle \left\langle j_2 v'_2 | L_2 \lambda' \rangle \right.
\end{equation}

\begin{equation}
\langle \lambda | L \rangle_{L_1 L_2} \langle gg' | \rangle \langle \lambda' | (\lambda - \lambda' - \lambda s) \rangle
\end{equation}

where $<||||>$ is a reduced matrix element according to Edmonds' convention. The inverse relationship to (3.64), when combined with the definition (3.83), implies the relation

\begin{equation}
T_1 (j_1 v_1 j_2 v_2 \lambda \lambda' ; L_1 L_2 ; j_1 v_1 j_2 v_2 \lambda)
\end{equation}

\begin{equation}
= 2 \pi \mu_i (pp')^{1/2} \langle j_2 v_2 | L_2 \lambda' \rangle \left| j_2 v'_2 \right\rangle \left| j_1 v_1 \right\rangle \left\langle j_1 v'_1 | L_1 \lambda \rangle \right.
\end{equation}

\begin{equation}
\langle j_1 v_1 | L_1 \lambda \rangle \langle j_2 v_2 | L_2 \lambda' \rangle \langle j_1 v'_1 | \rangle \left| j_2 v'_2 \right\rangle
\end{equation}

\begin{equation}
\left[ (2j_1^* + 1)(2j_2^* + 1)(2 \lambda'^* + 1)(2 \lambda_1 + 1)(2 \lambda_2 + 1)(2 \lambda + 1) \right]^{-1/2}
\end{equation}
between reduced quantities. The transition operator $t$ can be divided into its real and imaginary parts

$$(3.85) \quad t_g = \frac{1}{2}(t^g + t^g\dagger) + \frac{1}{2}(t^g - t^g\dagger) =$$

$$(t^g)_g - 2\pi i \int g\cdot g\delta(E) g\cdot (tg\dagger (ug'))$$

where the optical theorem has been used in the second line of equation (3.85). The reduced $T$ matrix expression analogous to (3.85) is

$$(3.86) \quad T(j_1j_2\lambda; \bar{j}_1\bar{j}_2\lambda') =$$

$$T_h(j_1j_2\lambda; \bar{j}_1\bar{j}_2\lambda') + \frac{1}{2}[(2j_1+1)(2j_2+1)(2\lambda+1)]^{1/2} \sum \frac{(-1)}{\bar{j}_1j_2\lambda} \frac{\bar{j}_1j_2\lambda + j_1j_2\lambda'}{\bar{j}_1j_2\lambda}$$

$$\sum \frac{(-1)}{L_1L_2L'} \frac{L_1L_2\lambda}{L_1L_2\lambda} \frac{L_1L_2\lambda}{L_1L_2\lambda} \frac{L_1L_2\lambda}{L_1L_2\lambda} \frac{L_1L_2\lambda}{L_1L_2\lambda}$$

$$\frac{1}{2} \int dE_{\text{tr}} T^*(j_1j_2\lambda; \bar{j}_1\bar{j}_2\lambda'; \bar{j}_1\bar{j}_2\lambda)$$

$$T(j_1j_2\lambda; \bar{j}_1\bar{j}_2\lambda')$$
\[ \delta(E_{tr} + E_j - E_j v_1 = E_j v_2 = E_j v_2) \]

with

\[ T_h(j_1 v_1 j_2 v_2 \lambda^\prime; \lambda Z_2 \lambda; j_1 v_1 j_2 v_2 \lambda) = \]

\[ \frac{1}{2} \tilde{T}(j_1 v_1 j_2 v_2 \lambda^\prime; \lambda Z_2 \lambda; j_1 v_1 j_2 v_2 \lambda) \]

\[ - \frac{1}{2} \tilde{T}*(j_1 v_1 j_2 v_2 \lambda; \lambda Z_2 \lambda; j_1 v_1 j_2 v_2 \lambda^\prime) (-1)^{j_1^+ j_1^+} \]

\[ (-1)^{j_2^+ j_2^+} (-1)^{\lambda + \lambda^\prime + \lambda} \frac{(2j_1 + 1)(2j_2 + 1)(2\lambda + 1)}{(2j_1 + 1)(2j_2 + 1)(2\lambda + 1)} \]

Consider now the quadratic in T part of equation (3.65), denoted by \( E_k^\prime(--) \). Insertion of equation (3.84) into this expression yields directly

\[ \tilde{E}_k^\prime (-| \tilde{E}_q^\prime | \tilde{E}_q^\prime \lambda) \]

\[ = \sum \left\{ \frac{p_{j_2 v_2} \lambda^\prime}{(2j_2 + 1)} \frac{p_{j_2^\prime v_2^\prime} \lambda^\prime}{(2j_2^\prime + 1)} \right\} \sum \left\{ \frac{\lambda Z_2 \lambda \tilde{E}_q^\prime}{(2j_1 + 1)} \frac{\lambda Z_2 \lambda \tilde{E}_q^\prime}{(2j_1 + 1)} \right\} \]

\[ (-1)^{i^+ i^+} (-1)^{i^\prime} \frac{\lambda Z_2 \lambda \tilde{E}_q^\prime}{(2j_2 + 1)} \frac{\lambda Z_2 \lambda \tilde{E}_q^\prime}{(2j_2 + 1)} \]

\[ \Omega(kqq^\prime)^{1/2} (2\lambda + 1)^{1/2} \]
The linear in $T$ parts of (3.65), indicated as $\Sigma \langle \cdots \rangle^k$, require more involved manipulations, in that the transformation (3.86) must first be employed. Subsequent use of (3.84) then yields

\[\langle \epsilon q \rangle \langle \cdots \rangle^k \langle \epsilon^* q \rangle \langle n \rangle \langle n' \rangle \langle j' \rangle \langle v_1 \rangle \langle j'' \rangle \langle v_1 \rangle k = \]

\[\Sigma \Sigma \{ \frac{p_{j_2 v_2}}{(2j_2 + 1)} \} \frac{p_{j_2' v_2'}}{(2j_2' + 1)} \}^{1/2} \frac{p_{j_1 v_1}}{(2j_1 + 1)} \frac{p_{j_2 v_2}}{(2j_2 + 1)} \}

\[\langle \epsilon q \rangle \langle \cdots \rangle^k \langle \epsilon^* q \rangle \langle n \rangle \langle n' \rangle \langle j' \rangle \langle v_1 \rangle \langle j'' \rangle \langle v_1 \rangle k = \]

\[\left( \frac{(2j_1 + 1)(2j_2 + 1)}{(2j_1' + 1)(2j_2' + 1)} \right)^{1/2} \delta_{j_1 j_1'} \delta_{j_2 j_2'} \delta_{v_2 v_2'} \frac{1}{2} \Sigma \frac{\epsilon q \epsilon^*}{(2q + 1)(2q' + 1)} \]

\[\langle j_2 v_2 \rangle \langle \epsilon q \rangle \langle \cdots \rangle^k \langle \epsilon^* q \rangle \langle n \rangle \langle n' \rangle \langle j' \rangle \langle v_1 \rangle \langle j'' \rangle \langle v_1 \rangle k = \]

\[\left( \frac{(2j_1 + 1)(2j_2 + 1)}{2j_2 + 1} \right)^{1/2} \delta_{j_1 j_1'} \delta_{j_2 j_2'} \delta_{v_2 v_2'} \frac{1}{2} \Sigma \frac{\epsilon q \epsilon^*}{(2q + 1)(2q' + 1)} \]

\[\langle j_2 v_2 \rangle \langle \epsilon q \rangle \langle \cdots \rangle^k \langle \epsilon^* q \rangle \langle n \rangle \langle n' \rangle \langle j' \rangle \langle v_1 \rangle \langle j'' \rangle \langle v_1 \rangle k = \]

\[\left( \frac{(2j_1 + 1)(2j_2 + 1)}{2j_2 + 1} \right)^{1/2} \delta_{j_1 j_1'} \delta_{j_2 j_2'} \delta_{v_2 v_2'} \frac{1}{2} \Sigma \frac{\epsilon q \epsilon^*}{(2q + 1)(2q' + 1)} \]
Equations (3.88) and (3.89) represent the DWBA for $E_k'$. They consist of products of internal state factors with three translational integrals $\sum_p^{(1)}$, $\sum_v^{(1)}$ and $\sum_h^{(1)}$. Again, it is emphasized that the DWBA allows a separation of internal state and translational motions. This separation is incomplete, however, in that the translational integrals still depend explicitly on the energy inelasticity.

\[ x \equiv E_{j_1'v'_1} + E_{j_2'v'_2} - E_{j_1v_1} - E_{j_2v_2} \]
This is the amount of energy transferred between translational and internal states during a collision. Explicitly, the three translational integrals are given as

\[(3.91) \sum_p \langle \ell'_n \ell'_l \ell'_2 | \ell' n' \ell' l' \ell'_2 | x \rangle_k = \]

\[\frac{(2\pi)^{\frac{1}{2}} \frac{\Pi}{8kT} \Omega(k \ell l')^{-1/2} \pi^{-3/2}}{\int \exp[-\gamma_2^2 + \gamma_1^2] \ell n(\gamma) L^l n'(\gamma) (\cdot) \ell + \ell', \]

\[V(\ell', \ell k)(\cdot)k V(k \ell', \ell')(\cdot) \ell' + \ell' \lambda \lambda' (gg') \lambda \lambda' * (gg')\]

\[\delta \left( \frac{1}{2} \mu g^2 - \frac{1}{2} \mu g'^2 + x \right) d\mu g' d\gamma \]

\[= \frac{1}{(kT)^2} \int_0^\infty dE_{tr} \int_0^\infty dE_{\ell} \exp\left[ -\frac{1}{2} \frac{E_{tr}}{kT} \right] \frac{E_{tr}}{kT} \rightarrow \frac{\pi \hbar^2}{2} \]

\[\delta (E_{tr} - E_{\ell} + x) \Omega(k \ell l')^{-1/2} \Sigma_{\lambda \lambda', \lambda''} [2\pi \mu^2 (gg')^{1/2}] \]

\[\langle \lambda | \lambda'_{\ell \ell'} (gg') | \lambda'' \rangle \rangle_{n'l'} \langle \ell' n' l' | (gg') | \lambda' \rangle \rangle_{n \ell \ell'} \langle \ell n l | (gg') | \lambda \rangle \rangle_{n' \ell' \ell'} \]

\[\{ (2\ell + 1) (2\ell' + 1) (2\lambda + 1) (2\lambda'' + 1) \}^{1/2} \ell + \ell' + \lambda + \lambda'' \]

\[(-1)^{\lambda + \lambda' + \ell'} \ell' \ell' k \quad \lambda \lambda' k \quad \lambda \lambda'' k \]

\[0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad \ell' \ell' \lambda' \lambda' \]
\[(3.92) \quad \left( \ell \ell_1 \ell_2 \right) (n)n \ell_1 \ell_1 \ell_2 | x \right) = \]

\[
(2\pi)^4 \hbar^2 \left( \frac{\pi^2}{8kT} \right)^{1/2} \Omega(k\ell \ell) - \frac{1}{2} - \frac{3}{2} \int \exp \left[ -\frac{\gamma^2 + \gamma'}{2} \right] L \ell n \left( \gamma \right)
\]

\[
L \ell \eta \left( \gamma \right) \left( \ell \right) \ell' + \ell \right) V(n \ell \ell) \left( \ell \right) \epsilon \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \ell' + \ell'
\]

\[
A \left( \ell \ell_1 \ell_2 \right) \left( gg' \right) \left( \ell \ell_1 \ell_2 \right) \left( gg' \right) \delta \left( \frac{1}{2} \mu g' \right) - \frac{1}{2} \mu g^2 + x \right) d \left( \mu g' \right) d \gamma
\]

\[
= + \frac{1}{(kT)^2} \int_0^\infty \frac{dE}{dE} \int_0^\infty \frac{dE'}{dE} \exp \left[ -\frac{1}{2} \left( \frac{E}{kT} + \frac{E'}{kT} \right)^2 \right]
\]

\[
E \left( \ell \right) \left( \ell \ell_1 \ell_2 \right) \left( gg' \right)^{1/2} \delta \left( E - E + x \right) \Omega(k\ell \ell) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right)
\]

\[
\left[ 2\pi \mu^2 \left( gg' \right)^{1/2} \right] \left( 2\ell + 1 \right) \left( 2\ell' + 1 \right) \left( 2\lambda + 1 \right) \left( 2\lambda' + 1 \right) \left( 2\lambda'' + 1 \right) \left( 2\lambda''' + 1 \right) \left( 2\lambda'''' + 1 \right) \left( 2\lambda''''' + 1 \right) \left( 2\lambda''''''' + 1 \right)
\]

\[
\left( -k \right) \left( \ell \ell' + \ell + \lambda + \lambda' + \lambda'' + \lambda''' \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right)
\]

\[
\begin{pmatrix}
\lambda & \ell & \ell' \\
\ell' & k & \ell \\
\ell'' & \ell' & \ell'''
\end{pmatrix}
\]

\[
\left( \ell \right) \left( \ell \right) \left( \ell \right) \left( \ell \right) \left( \ell \right) \left( \ell \right) \left( \ell \right) \left( \ell \right)
\]

\[
\epsilon \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right) \left( \ell \ell \ell \ell \right)
\]

\[
\mathcal{R}_{n \ell} \left( \gamma \right) \mathcal{R}_{n \ell} \left( \gamma \right)
\]
\[
(3.93) \quad \sum_{h}^{(1/2)} (\ell n l', n')_{k_{q}q',} = \\
\frac{(2\pi)^{4}h^{2}}{\Omega(k \ell l',)}^{1/2} \frac{\pi^{1/2}}{(8 \kappa T)^{1/2}} \frac{1}{\pi^{3/2}} \int_{-\infty}^{\infty} d\gamma \int_{0}^{2\pi} \rho_{n}^{L}(\gamma) \rho_{n'}^{L'}(\gamma)(\gamma) e^{-\gamma^2} \\
\mathcal{V}(\ell' l k) (\cdot)^{k} \mathcal{R}_{q q'}(\gamma, g) \\
= \frac{2\pi}{(kT)^2} \int_{0}^{\infty} dE_{r} dE_{r} \frac{\pi^{1/2}}{2g^{2}} \mathcal{R}_{n \ell}(\gamma) \mathcal{R}_{n' \ell'}(\gamma) e^{-\gamma^2} \\
\frac{1}{\Omega(k \ell l',)}^{1/2} \sum_{\lambda \lambda'} \lambda + \lambda' - \lambda - \lambda' \left( \begin{array}{c}
\ell \\
\ell'
\end{array} \right) \left( \begin{array}{c}
\ell \\
\ell'
\end{array} \right) \\
\frac{1}{2} \left\{ \langle \lambda | \hat{h}_{qq'}^{(k)}(gg') | \lambda' \rangle + \langle \lambda | \hat{a}_{qq'}^{(k)}(gg') | \lambda' \rangle^{*} \right\} .
\]

In particular,

\[
(3.94) \quad \sum_{h}^{(1/2)} (\ell n l', n')_{k_{k}0} = \sum_{h}^{(1/2)} (\ell n l', n')_{k,} .
\]

In principle, \( \sum_{h}^{(1)} \) measures velocity changes and \( \sum_{p}^{(1)} \) governs the relaxation rates of internal state polarizations. In the language of chapter I, \( \sum_{v}^{(1)} \) describes "velocity changing" collisions while \( \sum_{p}^{(1)} \) has to do with a kind of "phase changing" collisional effect. \( \sum_{h}^{(1/2)} \) is linear in \( V_{1} \) and contributes to frequency shifts.

A distorted wave Born approximation can also be derived for \( \sum_{k}^{(1)} \). Indeed, substitution of (3.84) and (3.86) into
equation (3.66) yields an expression for $\xi_k^n$ that is analogous to equations (3.88) and (3.89). Explicitly, the results are

(3.94) $\xi_k^n = (\ell q n j_1 \bar{v}_1 v_1 | \ell' q' n' j'_{21} \bar{v}_2 v_2)_k = \sum_{j_1} \sum_{j_2} \frac{P_{j_2 v_2}}{(2j_2 + 1)} \frac{P_{j_1' v_1'}}{(2j_1' + 1)} \frac{1}{\sqrt{2(2j_2 + 1)l_j^2 + 1}} \sum_{j'_{12}} (-1)^{j_2 + j_1} \frac{L_1 L_2}{L_1' L_2'} \frac{q}{q'} \frac{q'}{q'} \frac{k}{k'}$

$\langle j_1 \bar{v}_1 | \Omega_1^{[1]} | j_1 v_1 \rangle \langle j_1 v_1 | \Omega_1^{[1]} | j_1 v_1 \rangle$

$\langle j_2 v_2 | \Omega_2^{[2]} | j_2 v_2 \rangle \langle j_2 v_2 | \Omega_2^{[2]} | j_2 v_2 \rangle$

$\left( \xi_{1}^{(1)} - \xi_{p}^{(1)} \right) (\ell q n \Lambda_1 \Lambda_2 | \ell' q' n' \Lambda_1' \Lambda_2') E_{j_1 v_1} + E_{j_2 v_2} - E_{j_1 v_1}$

and
\[
\ell(n^{\frac{1}{2}} (\ell j n j_1 \bar{v}_1 \bar{v}_1 \ell j' n' j_2 \bar{v}_2 \bar{v}_2))_k = \\
\sum \left\{ \frac{P_{j_2 \bar{v}_2}}{(2j_2+1)} \frac{P_{j_1 \bar{v}_1}}{(2j_1+1)} \right\}^{1/2} \sum \left\{ \frac{P_{j'' \bar{v}''}}{P_{j_1 \bar{v}_1}} \frac{P_{j'' \bar{v}''}}{P_{j_2 \bar{v}_2}} \right\}^{1/2} \\
\delta_{j_1 j_1'} \delta_{j_2 j_2'} \\
\frac{(2j_1+1)(2j_2+1)}{(2j''+1)(2j''+1)}^{1/2} \\
\frac{\delta_{j_1 j_1'} \delta_{j_2 j_2'}}{(-i)^{q+q'}} \\
\frac{(2q+1)(2q'+1)}{\Omega(kqq')^{1/2}} \sum \left\{ \frac{q \ell_1 \ell_1'}{\ell_1 \ell_2 \ell_2'} \right\} \left\{ \frac{q' \ell_2 \ell_2'}{\ell_1 \ell_2 \ell_2'} \right\} \\
\left\{ \ell_2 \ell_1 \ell_2' \right\} \\
\left\{ \ell_2 \ell_1 \ell_1' \right\} \\
\left\{ \ell_2 \ell_1 \ell_1' \right\} \\
\frac{(2j_2+1)(2j_2+1)}{(2j''+1)(2j''+1)}^{1/2} \\
= \frac{1}{2} \left( \delta_{\bar{v}_1 \bar{v}_1} \delta_{\bar{v}_2 \bar{v}_2} + \delta_{\bar{v}_1 \bar{v}_1} \delta_{\bar{v}_2 \bar{v}_2} \right) \\
\ell_P^{(1)}(2n \ell \ell_2 | \ell' n' \ell' \ell_2 | E_{j_1 \bar{v}_1} + E_{j_2 \bar{v}_2} - E_{j_1 \bar{v}_1} - E_{j_2 \bar{v}_2})_k \\
+ \sum \left\{ \frac{P_{j_2 \bar{v}_2}}{(2j_2+1)} \frac{P_{j_1 \bar{v}_1}}{(2j_1+1)} \right\}^{1/2} \delta_{j_1 j_1'} \delta_{j_2 j_2'} \frac{i^{q+q'}}{2\pi i} \\
\frac{(2j_2+1)(2j_2+1)}{(2j''+1)(2j''+1)}^{1/2} \\
\frac{(2q+1)(2q'+1)}{(kqq')^{1/2}} \\
\frac{(2k+1)(2k+1)}{(2q+1)(2q'+1)}^{1/2} \\
\frac{(kqq')^{1/2}}{(2k+1)(2k+1)}^{1/2} \\
\frac{\delta_{j_1 j_1'} \delta_{j_2 j_2'}}{(-i)^{q+q'}} \\
\end{array}
\]

\[ \mathcal{L}_h^{(1/2)}(\ell n^l, n')_{kqq}, \ (\delta_{\nu_1} - \delta_{\nu_1} \delta_{\nu_1} \delta_{\nu_1} \delta_{\nu_1} \delta_{\nu_1} \delta_{\nu_1} \delta_{\nu_1} \delta_{\nu_1}). \]

Again the results are products of explicit internal state factors and the translational integrals \( \mathcal{L}_v \), \( \mathcal{L}_p \) and \( \mathcal{L}_h^{(1/2)} \).

As is discussed in reference (25), it is generally expected that \( \mathcal{L}_k' \gg \mathcal{L}_k'' \), unless resonant processes play a major role. (Hydrogen isotope collisions provide an example of this later effect.26) The neglect of \( \mathcal{L}_k'' \) contributions entirely can therefore provide a further useful approximation in many cases.
Within the distorted wave Born approximation, there still remains the problem of evaluating the translational factors $\mathcal{G}_v^{(1)}$, $\mathcal{G}_p^{(1)}$ and $\mathcal{G}_n^{(1/2)}$. This has been investigated in some detail, see references (13) and (25). The present treatment is limited to a description of the translational integrals which arise in connection the shear viscosity coefficient for $N_2$. This is sufficient to illustrate the salient features of the approach taken by Snider and co-workers. In addition, the remarks presented here are ultimately applicable to the cross sections encountered in spectroscopic studies - see chapters IV and VII for further discussions of this point.

The underlying features to Snider's approach are as follows. First, the energy inelasticity

$$\Delta = \frac{X}{kT}$$

is neglected whenever possible, or if this gives a vanishing result, $\Delta$ is considered to first order only. Second, the transition operator for the spherical part of the potential, $\Lambda^{(0)}_{\infty}(gg')$, is treated exactly whenever it arises. Conversely, for $\Lambda^{(1)}_{1/2}(gg')$, a crude approximation is used which is based on approximating $V_0$ as a rigid spherical potential for molecules of diameter $d$. The effect of the Møller operator $\Omega_0$ (which describes the collision dynamics of the spherical potential) is then approximated as excluding a rigid care of
radius d from the radial integral. From the definition (3.82), the approximate form for \( \mathcal{A}_{1/2}^{(4)} (gg') \) is therefore

\[
(3.97) \quad \mathcal{A}_{1/2}^{(4)} (gg') = h^{-3} \int_{R > d} e^{iK \cdot R} \mathcal{Y}^{(4)}(\hat{R}) b_{1/2}^{(4)}(R) dR
\]

where \( \sim \) is defined as the change in wavenumber during the collision

\[
(3.98) \quad \sim = \mu (g' - g) / h
\]

In obtaining equation (3.97), the translational ket \( |\mu g'\rangle \) has been expressed in position representation. This approximation was first used by Chen and Snider,\(^{27}\) and then subsequently by Moraal\(^{28}\) and Snider.\(^{25}\) Shizgal\(^{29}\) has termed it the "modified Born approximation" to the transition operator since, in effect, equation (3.97) is just a modified Fourier transform of the nonspherical potential.

By rotational invariance, \( \mathcal{A}_{1/2}^{(4)} (gg') \) must be proportional to \( \mathcal{Y}^{(4)}(\hat{K}) \) in this approximation, and its explicit form is given as

\[
(3.99) \quad \mathcal{A}_{1/2}^{(4)} (gg') = 4\pi \hbar^{-3} \int_{R > d}^\infty j(KR) b_{1/2}^{(4)}(R) R^2 dR \mathcal{Y}^{(4)}(\hat{K}),
\]

where \( j_4(KR) \) is the spherical Bessel function. For the spherical case of a multipole-type potential, \( b_{1/2}^{(4)}(R) = b_{1/2}^{(4)} R^{-4} \), and the radial integral can be evaluated in closed form with the result
\[(3.100) \Lambda_{L_1 L_2}^{(2)} (gg') = 4\pi l_{L_1} l_{L_2} l_{L_2} (\frac{K \hbar^3 d}{d - 1}) - 1 j_{L - 1}(Kd) j^{(L)}(K) \]

\[= (2\pi \hbar u)^{-1} \Lambda_{L_1 L_2} j^{(L)}(K).\]

(The scalar \(A_{L_1 L_2}\) has the dimensions of length and its square can be interpreted as a kind of differential cross section.) The essence of the modified Born approximation is seen from equations (3.99) or (3.100) - the transition operator \(A_{L_1 L_2}^{(L)} (gg')\) does not depend separately on the direction of \(g\) and \(g'\) but only on the momentum transfer \(K\). With these comments as a background, the three collision parameters \(\tau\), \(\tau_{\text{int}}\) and \(\psi\) are now discussed.

The first collision parameter to be considered is \(\tau\). From equation (3.39), it is seen that this describes the relaxation of a pure velocity polarization. Since the spherical part of the potential \(\lambda_0 = \lambda_1 = \lambda_2 = 0\) can contribute to velocity relaxation and, within the context of the DWBA, it is assumed to dominate, the relaxation of a pure velocity polarization is approximated by employing the effect of the spherical potential only. This implies that the translational factors to be considered are of the form

\[\mathcal{E}_p^{(1)}(\lambda_0 0 0 0 / l n 0 0 0 / 0), \mathcal{E}_p^{(1)}(\lambda n 0 0 0 / l n 0 0 0 / 0), \] and

\[\mathcal{E}_n^{(1/2)}(\lambda n n'), \text{ where } \lambda = \lambda' = 2 \text{ and } n = n' = 0 \text{ for the particular velocity polarization treated in } \tau.\] Further, as discussed in reference (13), the internal state factors are such that the contributions of \(\mathcal{E}_p^{(1)}\) and \(\mathcal{E}_n^{(1/2)}\) separately vanish, with the result that the relaxation of a pure velocity
polarization, in the spherical potential approximation, is described in terms of the one translational integral
\[ \sum_{\nu}^{(1)} \langle \ell n 0 0 0 | \ell' n' 0 0 0 | 0 \rangle. \]

From equation (3.91) and (3.92), the explicit form for this translational integral is

\[ (3.101) \sum_{\nu}^{(1)} \langle \ell n 0 0 0 | \ell' n' 0 0 0 | 0 \rangle \delta_{\ell \ell'} (2 \ell + 1)^{-1} (2\pi)^{-1} \int_{-\infty}^{\infty} e^{-\gamma^2 L_{\ell n}(\gamma) \gamma} \left[ L_{\ell n'}(\gamma) - L_{\ell n'}(\gamma') \right] \]

\[ = \delta_{\ell \ell'} (2 \ell + 1)^{-1} (2\pi)^{-1} \int_{-\infty}^{\infty} e^{-\gamma^2 L_{\ell n}(\gamma) \gamma} \left[ L_{\ell n'}(\gamma) - L_{\ell n'}(\gamma') \right] \]

\[ \gamma (2\pi)^{\frac{1}{2}} \mu^2 \lambda_{oo} (gg') \lambda_{oo}^{(o)*} \delta \delta' \mathrm{d} \gamma \]

This can be expressed in terms of the \( \Omega \) integrals of Chapman and Cowling,

\[ (3.102) \Omega(\ell, s) \equiv (\frac{2\pi kT}{\mu})^{1/2} \int_{-\infty}^{\infty} e^{-\gamma^2} \gamma^{2s+3} (1 - \cos \chi) \sigma(g\chi) \mathrm{d} \cos \chi \mathrm{d} \gamma \]

where

\[ (3.103) \chi = \hat{\gamma} \cdot \hat{\gamma}' \]

\[ \sigma(g\chi) = (2\pi)^{\frac{1}{2}} \mu^2 \lambda_{oo} (gg') \lambda_{oo}^{(o)*} \]

In general, the identification is somewhat complicated, involving several weighted sums over \( \Omega \) integrals. The general formulae are given in reference (13). For the particular
translational integral used in the evaluation of $\tau$, the simple result

\[(3.104) \sum_v (2000|2000|0)_o = \frac{4}{5} \left(\frac{2\pi}{kT}\right)^{1/2} \Omega(2,2)\]

is obtained. The resulting expression for $\tau$ is also derived in reference (13) and is given as

\[(3.105) \frac{1}{\tau} = n \left(\frac{8kT}{\pi\hbar}\right)^{1/2} \sum_v (0) \begin{pmatrix} 2 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 \end{pmatrix} = \frac{8}{5} n \Omega(2,2)\]

In summary, the relaxation of a pure translational polarization can ultimately be expressed, in approximate form, in terms of the $\Omega$ integrals of Chapman and Cowling. Equation (3.105) is a particular example of this result.

The $\tau_{int}$ parameter, obtained in section (d), is an example of the relaxation of a pure internal state polarization - see equation (3.39) for the definition of $\tau_{int}$. As such, the translational factors which are involved in its collisional description are of the form $\sum_p^{(1)} (00\angle_1 \angle_2 |00\angle_1' \angle_2'|0)_o$, $\sum_v^{(1)} (00\angle_1 \angle_2 |00\angle_1' \angle_2'|0)_o$, and $\sum_h^{(1/2)} (0000)_o$. In a manner similar to the pure velocity polarization care, the contribution from $\sum_h^{(1/2)}$ cancels.

At the same time, the $\sum_v^{(1)}$ term vanishes identically since the spherical potential cannot affect internal state changes. Thus, the relaxation of a pure internal state
polarization involves only the translational factor
\[ \sum_{p}^{(1)} (00\ell' \ell_2 | 00\ell \ell_2 | 0) \]. This integral, which involves
the nonspherical part of the intermolecular potential, is
estimated by means of the modified Born approximation.

Indeed, the substitution of equation (3.100) into (3.91) for
the particular case when \( \ell = \ell' = n = n' = 0 \) leads directly to

\[ (3.106) \sum_{p}^{(1)} (00\ell \ell_2 | 00\ell \ell_2 | 0) \]

\[ = \frac{1}{\pi \mu (8\mu kT)^{1/2}} \iint \exp \left\{ -\frac{1}{2} (\gamma^2 + \gamma'^2) \right\} \delta \left( \frac{\mu g^2}{2} - \frac{1}{2} \mu g'^2 \right) \]

\[ a_{\ell \ell_2}^* a_{\ell \ell_2} \exp \left\{ -\frac{1}{2} (\gamma^2 + \gamma'^2) \right\} v(0, \ell) v(\ell) y^{(\ell)}(K) y^{(\ell)}(K) \]

Employing the relation

\[ (3.107) v(0, \ell) v(\ell) y^{(\ell)}(K) y^{(\ell)}(K) = (2\ell + 1)^{1/2} \]

and the transformations

\[ (3.108) \iint \delta \left( \frac{\mu g^2}{2} - \frac{1}{2} \mu g'^2 \right) d(\mu g') d\gamma = 8\pi^2 \mu (2\mu kT)^{1/2} \]

\[ \int_{0}^{\infty} d\Gamma d\gamma \]

\[ \gamma = (8\mu kT)^{-1/2} K^2 \]

\[ \Gamma = \frac{1}{2} (\gamma^2 + \gamma'^2) \]
allows equation (3.106) to be rewritten in the form

\[
(3.109) \quad \sum_p^{(1)} (00|\ell_1 \ell_2|00|\ell_1 \ell_2|0) = 4\pi(2\ell+1)^{1/2} \int_0^\infty d\gamma \int_0^\infty \frac{d\gamma}{\gamma} e^{-\gamma} \mathcal{A}_{\ell_1 \ell_2} \mathcal{A}^*_{\ell_1 \ell_2} \approx (2\ell+1)^{1/2} \frac{2\pi^3 \mu \ell_1 \ell_2}{h^2 kT} \frac{b_{\ell_1 \ell_2} \ell_1 \ell_2}{d^{2\ell-2} \ell (\ell-1)}
\]

where the asymptotic form of the spherical Bessel function used in definition (3.100) has been used in approximating the \( J \) integral. The manipulations involved in equations (3.106) through (3.109) have been presented more generally in reference (25). Equation (3.109) represents the "modified Born approximation" for the translational integral

\[
\sum_p^{(1)} (00|\ell_1 \ell_2|00|\ell_1 \ell_2|0).
\]

An expression for \( \tau_{\text{int}} \) in terms of \( \sum_p^{(1)} \), which is quite analogous to the expression for \( \tau \) in terms of \( \sum_v^{(1)} \), can then be obtained, although this has not been done explicitly.

The final relaxation parameter \( \psi \) which occurs in the study of the shear viscosity of \( N_2 \) is an example of a production collision integral. Here, an internal state polarization is produced from a translational polarization by collision. Generally, these production integrals are one or more orders of magnitude smaller than the relaxation collision integrals. Further, in many cases, the previously employed approximation of neglecting the energy inelasticity
in the translational factors leads to a vanishing result.

The parameter $\Psi_{ij}$, defined by equation (3.39), is a particular example of this. Here, the only translational integral which contributes is $\sum_{v}^{(1)} (00\langle l_{1} l_{2} | 20 \langle l'_{1} l'_{2} | x \rangle)_{2}$ and an approximation which is first order in $\Delta = x/kT$

\[ (3.110) \sum_{v}^{(1)} (00\langle l_{1} l_{2} | 20 \langle l'_{1} l'_{2} | x \rangle)_{2} \]

\[ \approx \Delta \sum_{v}^{(1)} (00\langle l_{1} l_{2} | 20 \langle l'_{1} l'_{2} | 0 \rangle)_{2} \]

where the prime here denotes the derivative with respect to $\Delta$. The evaluation of $\Psi_{ij}$ is discussed in some detail in reference (18).

The remarks of this section are not intended as a complete account of the treatment of collision integrals but rather are presented as a perspective in which to view the collisional calculations employed in the succeeding chapters. Chapters IV through VI deal completely with internal state polarizations and so it should not be surprising that the only translational integral which arises is $\sum_{p}^{(1)} (00\langle l_{1} l_{2} | 00 \langle l'_{1} l'_{2} | x \rangle)_{0}$. In chapter VII, translational polarizations occur and with them, consideration of $\sum_{v}^{(1)} \langle \lambda n000 | \lambda n'000 | 0 \rangle$ is necessitated.

Finally, it should be mentioned that the algebraic method employed in this thesis for the evaluation of the translational factors is, of course, not the only approach which can be taken. Less crude algebraic models, semi-
classical WKB methods, or exact quantum scattering techniques could all be applied to obtain better estimates for the collision parameters. Indeed, Shizgal\textsuperscript{29} has shown that the modified Born approximation tends to underestimate the cross section and has investigated various other techniques for evaluating the translational factors.\textsuperscript{31}
(h) Summary

This concludes a review of kinetic theory as it is applied to the study of the Senftleben-Beenakker effects. Obviously, the treatment is very involved when the details are to be understood. But from this study, a great deal has been learned about the kinetic behaviour of gas systems when internal states play an important role. The aim of the rest of this thesis is to present the topics of pressure broadening and coherence transients to the same depth of understanding. In particular, the treatment of collisions is generalized, see chapters IV and VII. The moment method is also applied, in chapters V, VI and VII, to describe the system motions. Thus, the study of the Senftleben-Beenakker effects has greatly influenced the method of treatment of pressure broadening and coherence transient phenomena, as presented in this thesis. Indeed, the use of a unified notation and parallel development puts the subjects of transport properties and spectroscopic phenomena of gases on the same footing for, it is hoped, a more complete understanding of both.
"Have you guessed the riddle yet?" the Hatter said, turning to Alice again.
"No, I give it up," Alice replied. "What's the answer?"
"I haven't the slightest idea," said the Hatter. "Nor I," said the March Hare.
(a) Introduction

The approach outlined in chapter II had three unsatisfactory aspects - the absence of a well defined collision matrix, no obvious generalization to include degenerate (magnetic) quantum numbers, and no satisfactory discussion of possible translational effects. Fortunately, the approach to S-B effects outlined in chapter III has considered precisely these three aspects in great detail. Thus a synthesis of chapters II and III seems appropriate to produce a kinetic theory treatment of pressure broadening and coherence transients. Chapters IV, V, and VI apply to methods of chapter III to the first two aspects. The final chapter outlines a kinetic theory discussion of the translational effects.

The format of chapter IV parallels that of chapters II and III. Namely, the appropriate equation of motion is first obtained and a useful choice of basis is defined. With these basis elements, the most general moment equations are then derived. A thorough discussion of a general collision matrix element is then presented including a distorted wave Born approximation to the exact form and a modified Born approximation for the translational factor. Some comments on the relationship of these collisional considerations to the work of others then complete this chapter.
(b) General Equation of Motion - The Waldmann Snider Form

As in chapter III, the starting point is the generalized Boltzmann equation of Snider and Sanctuary. In principle, the collision superoperator $\mathcal{J}$ can couple any frequency component $|E><E'|$ of the density operator for the pair of colliding molecules to any other frequency component $|E''><E'''|$. As a consequence of the definition of $\mathcal{J}$ given in appendix A, this frequency coupling can be written as

\begin{equation}
\text{Tr}\left\{ \left( |E''><E'''| \right)^\dagger \mathcal{J} |E><E'| \right\} = <E''|t|E><E'| \delta_{E'E''} - \delta_{EE''}<E'|t^+|E''>
- <E''|G(t)|E><E'|t^+|E''> - <E''|t|E><E'|G(t^+)|E''>
= <E''|t|E><E'| \delta_{E'E''} - \delta_{EE''}<E'|t^+|E''>
- <E''|t|E><E'|t^+|E''> \left\{ \frac{1}{E-E''+i\epsilon} + \frac{1}{E''-E'+i\epsilon} \right\}
\end{equation}

(Here "Tr" denotes the trace over the states of the pair of colliding molecules.) Thus frequency couplings require off-the-energy shell $t$ matrix elements. On-the-energy-shell $t$ matrix elements (denoted by $t_d$) are associated with completed collisions while off-the-energy-shell $t$ matrix elements are associated with duration of collision events. A useful approximation is to ignore the off-energy-shell
matrix elements in eqn. (4.1). This leads to a completed collision (impact) approximation to \( \mathcal{J} \). This approximation is denoted as \( \mathcal{J}_H \), for it was Hess\(^3\) who first pointed out that frequency conserving collisions are expressible in terms of on-the-energy-shell t matrix elements only,

\[
(4.2) \quad \text{Tr}\{(|E''><E'|)\mathcal{J}_H|E><E'|}\}
\]

\[
= \delta_{E,E''} \delta_{E',E''} \{<E''|t_d|E> - <E'|t_d^+|E''> + 2\pi i <E''|t_d|E><E'|t_d^+|E''>\}
\]

The approximation \( \mathcal{J} \rightarrow \mathcal{J}_H \) actually decouples (collisionally) the different frequency components of the density operator. Thus the widths of isolated lines, corresponding to the relaxation of a particular frequency component, are expressible exactly in terms of \( \mathcal{J}_H \) while the overlapping of spectral lines requires the full expression (4.1). The discussions presented in this thesis are restricted to pressure broadening and coherence transients of isolated lines, so that \( \mathcal{J}_H \) is the appropriate collision superoperator.

With the replacement of \( \mathcal{J} \) by \( \mathcal{J}_H \), the equation of motion for the one particle density operator becomes

\[
(4.3) \quad \frac{\partial \rho}{\partial t} = \mathcal{L} \rho + \text{tr}_2 \mathcal{J}_H \rho \rho_2.
\]
Proceeding with the manipulations of the translational states as outlined in chapter III, the Boltzmann equation for the Wigner distribution function is given as

\[
\frac{\partial f}{\partial t} + \frac{p}{m} \cdot \frac{\partial}{\partial r} f = -i\hbar \mathcal{L} f - f^{(0)}_{tr} \mathcal{R}(\phi)
\]

where \( \mathcal{R} \) is a linearized localized collision operator of Waldmann-Snider form, namely

\[
\mathcal{R}(\phi) \equiv -(2\pi)^4 \hbar^2 \left[ \frac{e^{-w^2}}{(2\pi mkT)^{3/2}} \right] \ln \text{tr}_2 \int dp_2 dp' \sim \delta(p + p_2 - p' + p'_2) \\
\langle \phi \rangle_{p_2} \langle \mu g | t_2 | \mu g' \rangle \left\{ \frac{f^{(0)} tr}{n} - \frac{f^{(0)}_2}{n} \phi_2(w_2) \right\}
\]

\[
\delta(p + p_2 - p' + p'_2) + (2\pi i)^{-1} \left[ \langle \mu g | t_2 | \mu g \rangle \right]
\]

\[
\left\{ \frac{f^{(0)} tr}{n} - \frac{f^{(0)}_2}{n} \phi_2(w_2) \right\} \langle \phi \rangle_{p_2} \langle \mu g | t_2 | \mu g \rangle
\]

The actual form of the linearization employed in equation (4.4) is discussed in more detail momentarily. In equation (4.5), it is implicitly implied that \( \mathcal{R} \) collisionally couples one particle internal state frequency components \( \omega \) and \( \omega' \) only if \( \omega = \omega' \) -- alternately, if \( \omega \) and \( \omega' \) differ greatly in frequency, then their corresponding frequency
components are not coupled, collisionally. Note that translational degrees of freedom are classified as zero frequency because of position localization. Further, when $\phi$ is restricted to zero frequency components, equation (4.5) is equivalent to the linearized Waldmann-Snider collision operator. Thus equation (4.4) represents a collisionally decoupled set of equations - one for each frequency component, and in particular, the zero frequency equation is the linearized Waldmann-Snider equation employed in the description of Senftleben-Beenakker effects. Tip has also reached these conclusions via a different approach and obtained equation (4.4) as the long time limit of the generalized Boltzmann equation.

The specific form of linearization used in this chapter differs from that of the previous chapter. In equation (3.9), the equilibrium distribution function represents a local equilibrium state and $\phi$ describes the deviation from this state. No problems of commutation between $f^{(o)}$ and $\phi$ arise because $\phi$ is always diagonal in energy. For this and subsequent chapters, the alternate linearization

\[ f = f^{(o)} + f^{(1)} = f^{(o)} + f^{(o)} \text{tr} \phi \]

is chosen. Here $f^{(o)}$ is the absolute Maxwellian while $\phi$ is no longer restricted to being diagonal in energy. This "non-diagonality" would lead to commutation problems if a
form analogous to (3.9) were chosen (i.e., if $f^{(1)} = f^{(o)} \phi$) as discussed by Snider. The form (4.6), on the other hand, completely avoids this problem. Instead, slightly more complicated collision matrix elements, (with additional internal state Boltzmann factors), are obtained, as discussed further in section (d). Also, the form (4.6) leads to collisional expressions which can most easily be related to those of other workers in pressure broadening phenomena.

The general result (4.4) is now modified to obtain an equation suitable for the description of pressure broadening and coherence transient phenomena. To this end, the Liouville superoperator, describing the motion of the system under the influence of a time dependent electric field, is specified as

$$(4.7) \quad \mathcal{A} = \mathcal{A}_0 + \mathcal{A} \cdot [-2\mathcal{E}_0 \cos(\omega t - k \cdot r),A],$$

where $A$ is an arbitrary one molecule operator. The flow term $\frac{P}{m} \cdot \frac{\partial}{\partial x}$ is neglected in the pressure broadening limit. (The effects of the flow term are discussed in chapter VII.) As a result, the Boltzmann equation becomes

$$(4.8) \quad \frac{\partial f}{\partial t} = -i\hbar \mathcal{L}_0 \cdot f - i\hbar [-2\mathcal{E}_0 \cos(\omega t - k \cdot r),f] - f^{(o)} \mathcal{R}(\phi).$$

This is equivalent to equation (2.4), but with a well defined collision operator. Again, the transformation to
a "rotating frame" is useful to approximately eliminate the explicit time dependence in the interaction. In this frame the truncated equation is

\[ \frac{\partial \hat{f}}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}_o - S, \hat{f} \right] - \frac{i}{\hbar} \left[ -\mu \cdot \hat{E}_o, \hat{f} \right] - f^{(0)}_{tr} \mathcal{R}(\phi). \]

The collision operator is unaffected by this transformation because \( \mathcal{R} \) preserves (internal state) frequency.
The question of an appropriate basis is now tackled. Consideration of two properties of $\mathcal{R}$ - namely frequency conservation and rotational invariance - leads almost immediately to a basis of the form

$$[j_i v_i < j_f v_f]^q \equiv i^q \sum_{m_i, m_f} (2q+1)^{1/2} (-1)^{j_i - m_i}^m \left| j_i m_i v_i < j_f m_f v_f \right|$$

$$\left( \begin{array}{c} j_i \\ q \\ j_f \end{array} \right) \left( \begin{array}{c} -m_i \\ v \\ m_f \end{array} \right) \left| j_i m_i v_i < j_f m_f v_f \right|$$

$$= e^{(q)^v (*)} q [j_i v_i < j_f v_f]^q$$

These tensor operators form an irreducible representation of the rotation group $SO(3)$, and are simultaneously eigenfunctions of the field-free internal state Liouville operator $\mathcal{H}_o = \{ \mathcal{J}_o \}$ with frequency $\omega_j = \frac{j}{(2j+1)} (\epsilon_{j_i, v_i}^q - \epsilon_{j_f, v_f}^q)$. Operators of this type were first introduced by Hess and Kohler, and can be considered as an extension of the $\mathcal{J}_j v v$ operators considered in the last chapter to off-diagonality in "j". Indeed, the relation

$$[j v_i < j v_f]^q = p_{j v_i v_f} \mathcal{J}_j v v (2j+1)^{1/2}$$

is easily verified by a comparison of (4.10) with (3.24). As such, the basis (4.10) can be considered as a synthesis
of the basis (2.15) of chapter II and the basis (3.24) of chapter III. The properties of the \([j_v, j_v']\) are discussed further in Appendix B.

The moment equations for this rather abstract (or at least very "quantum mechanical") basis are now discussed. Involved is the inner product

\[
(4.12) \quad \langle\langle A|B\rangle\rangle \equiv \text{tr} \int d\mathcal{W} \frac{e^{-\mathcal{W}^2}}{\sqrt{2\pi mkT}^{3/2}} A(\mathcal{W})^\dagger B(\mathcal{W})^\dagger \text{tr}\{A^\dagger B\}
\]

when both \(A, B\) are independent of the velocity. This inner product reflects the form of linearization chosen, equation (4.6). The moment equations, in their most general form are written as

\[
(4.13) \quad i\hbar \frac{d}{dt} \langle [j_v, j_v'] \rangle(q)
\]

\[
\equiv i\hbar \frac{d}{dt} \text{tr}\{[j_v, j_v'] \}^\dagger(q)f
\]

\[
= -\hbar \Delta \omega_{j_v j_v'} \langle [j_v, j_v'] \rangle(q)
\]

\[
- \sum_{j\neq j'} \langle [j_v, j_v'] \rangle^\dagger(q) |R| (\langle j_v' > j_v' \rangle)^\dagger >>
\]

\[
(\cdot)^q (\langle [j_v, j_v'] \rangle(q) - \langle [j_v, j_v'] \rangle(q))_{eq}
\]
where the identification

\[(4.14) \quad [\mathcal{H}_o - s, [jv < j'v'] (q) ] = \mathcal{H}_o \delta_{jv, j'v'} [jv < j'v'] (q) = \mathcal{H}_o jv - \omega \delta_{jv, j'v'} [jv < j'v'] (q) \]

has been used, assuming the internal state energies are independent of the magnetic indices. In equation (4.13), a completely general form of the external field-system interaction has been employed,

\[(4.15) \quad \mathcal{H}_{int} = \sum_{q_1, q_2} (q_1) \nu_1 (q_1) M (q_1, \nu_1) \mathcal{U}_{\nu_1} (q_1) \]

where \(M (q_1, \nu_1)\) is the operator property and \(\mathcal{U}_{\nu_1} (q_1)\) is the...
external field property. With the form (4.15), it is seen that the collision independent part of (4.13) is the generalization of the precession equations of Fano to include off diagonal in "j" couplings. That is, while Fano describes polarizations \[ j_{v_i} < j_{v_f} \] \( ^{(q)} \) within each "j" shell, (caused by the presence of external state fields) equation (4.13) allows non-diagonal in "j" coherences \[ j_{i_{v_i}} < j_{f_{v_f}} \] \( ^{(q)} \).

These arise because of resonance interaction (in the rotating frame).

Equation (4.13) represents the fundamental result of this chapter. It bears little resemblance to equations (2.18) or (2.19) of chapter II. However, with the specific form of the radiation-system interaction given as

\[
\mathcal{H}_{\text{int}} = -y \cdot \mathbf{E}_0
\]

connection to chapter II can be made. Chapter V is devoted to just this task. The remaining portion of this chapter deals with the collisional part of equation (4.13).
The evaluation of the general collision matrix element 
$$<[j_i^i v_i^i]<j_f^f v_f^f]^\xi(q)\mid R \mid j_i^i v_i^i><j_f^f v_f^f]^\xi(q)$$
is now discussed.

Explicitly, a combination of (4.12) and (4.5) yields

\begin{equation}
\begin{aligned}
\langle[j_i^i v_i^i]<j_f^f v_f^f]^\xi(q)\mid R \mid j_i^i v_i^i><j_f^f v_f^f]^\xi(q)\rangle \\
= -(2\pi)^4 \hbar^2 n \text{tr}_{1,2} \int dp dp_z \langle[j_i^i v_i^i]<j_f^f v_f^f]^\xi(q)\rangle^+ + \int dp dp_z' \langle \mu_g \mid t_d \mid \mu_g' \rangle \{ f^{(0)} \text{tr}_{\xi^2}^{(0)} [j_i^i v_i^i]<j_f^f v_f^f]^\xi(q) \\
+ \frac{f^{(0)} \text{tr}_{\xi^2}^{(0)} [j_i^i v_i^i]<j_f^f v_f^f]^\xi(q)}{n^2} \} + \frac{f^{(0)} \text{tr}_{\xi^2}^{(0)} [j_i^i v_i^i]<j_f^f v_f^f]^\xi(q)}{n^2} \} \\
\langle \mu_g' \mid t^\dagger \delta(E-E') \mid \mu_g \rangle \delta(p+p_2-p'-p_2')
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
+ (2\pi)^{-1} \int dp \langle \mu_g \mid t_d \mid \mu_g \rangle \{ f^{(0)} \text{tr}_{\xi^2}^{(0)} [j_i^i v_i^i]<j_f^f v_f^f]^\xi(q) \\
+ \frac{f^{(0)} \text{tr}_{\xi^2}^{(0)} [j_i^i v_i^i]<j_f^f v_f^f]^\xi(q)}{n^2} \} \\
- \{ f^{(0)} \text{tr}_{\xi^2}^{(0)} [j_i^i v_i^i]<j_f^f v_f^f]^\xi(q) + \frac{f^{(0)} \text{tr}_{\xi^2}^{(0)} [j_i^i v_i^i]<j_f^f v_f^f]^\xi(q)}{n^2} \} \\
\langle \mu_g \mid t^\dagger \mid \mu_g \rangle \}
\end{aligned}
\end{equation}

where $[j_i^i v_i^i]<j_f^f v_f^f]^\xi(q)$ denotes a coherence associated with molecule 2. This form represents a generalization of equation (3.25) in the sense that operators that are off-diagonal in
"j" are considered. In another sense, however, it is less complicated since no velocity polarizations are present. Indeed, the remainder of this chapter emphasizes the similarities in the collisional aspects of both problems. Thus, while considering completely different phenomena here additional insight into the methods of the last chapter may be gained.

The remarks made in chapter III concerning the invariance properties of the collision superoperator are equally valid here, since both ultimately result from the properties of \( J \). In particular, \( R \) preserves parity, is rotationally invariant, yet can connect operators of different time reversal symmetry. The matrix elements (4.17) reflect these properties. Two useful identities can be established almost immediately - namely,

\[(4.18) \quad \langle[j_i v_i] | R | j_f v_f \rangle_T(q) \]

\[
= (-1)^{j_i + j_f} \langle[j_f v_f] | R | j_i v_i \rangle_T(q) 
\]

and

\[(4.19) \quad \langle[j_i v_i] | R | j_f v_f \rangle_T(q) \]

\[
= \begin{cases} 
\frac{p_{j_i}}{(2j_i+1)} & \frac{p_{j_f}}{(2j_f+1)} \\
\frac{p_{j_i}^*}{(2j_i+1)} & \frac{p_{j_f}^*}{(2j_f+1)} 
\end{cases} \langle[j_f v_f] | R | j_i v_i \rangle_T(q) 
\]

\[
[j_i v_i] | R | j_f v_f \rangle_T(q) 
\]
Here $A_T$ is the "time reversed" operator

$$ (4.20) \quad A_T = \Theta A $$

The first result, equation (4.18), follows from $(\mathcal{J}_H A)^\dagger = -\mathcal{J}_H^\dagger A$ (see appendix A) and the adjoint properties of the bases (4.10), as discussed in appendix III. Equation (4.19) is a consequence of the identification of the superoperator adjoint of $\mathcal{J}_H$, as the time reversed superoperator for $\mathcal{J}_H$ - in other words

$$ (4.21) \quad \mathcal{J}_H^\dagger = \Theta^{-1} \mathcal{J}_H \Theta $$

see appendix A. When equation (4.19) is restricted to the "diagonal in j" case, it becomes

$$ (4.22) \quad [[j_i v_i^< j_f v_f^>]^{\{q\}} | R | [j_i v_i^< j_f v_f^>]^{\{q\}} ] = \frac{P_{j_i}}{(2j+1)} / \frac{P_{j_i'}}{(2j+1)} [[j_i v_i^< j_f v_f^>]^{\{q\}} | R | [j_i v_i^< j_f v_f^>]^{\{q\}} ] $$

The extra Boltzmann factors in this equation are a direct consequence of the form of linearization chosen in this chapter, equation (4.6). With the method of linearization chosen in chapter III, these extraneous factors disappear so that the matrix elements defined in the last chapter are more symmetrical than the ones dealt with here.

Following the practice employed in the study of Senftleben-Beenakker effects, matrix elements of $R$ are expressed as
kinetic theory cross sections

\[ (4.23) \]
\[ \mathcal{G} ([j_i v_i \rangle \langle j_f v_f] (q) | [j'_i v'_i \rangle \langle j'_f v'_f] (q')) \]
\[ = n^{-1} \left( \frac{\pi u}{8kT} \right)^\frac{3}{2} \langle [j_i v_i \rangle \langle j_f v_f] (q) | \mathcal{R} | [j'_i v'_i \rangle \langle j'_f v'_f] (q) \rangle \]
\[ = \delta_{qq'} E(q) \mathcal{G} ([j_i v_i \rangle \langle j_f v_f] (q) | [j'_i v'_i \rangle \langle j'_f v'_f] (q))_o . \]

It is the rotational invariance of \( \mathcal{R} \) that implies that the tensor cross section \( \mathcal{G} \) can be expressed in terms of one scalar cross section \( \mathcal{G}_o \). The last line of equation (4.23) is to be compared with equation (3.55) of the previous chapter. This shows that the application of the principles of rotational invariance in the present chapter is much simpler than in chapter III. In particular, there is only one scalar cross section for each tensor cross section.

From (4.17) and (4.23), the scalar cross section is given as

\[ (4.24) \]
\[ \mathcal{G} ([j_i v_i \rangle \langle j_f v_f] (q) | [j'_i v'_i \rangle \langle j'_f v'_f] (q))_o \]
\[ = (-1) (2\pi)^4 \frac{h}{\pi u} \left( \frac{\pi u}{8kT} \right)^\frac{3}{2} (2q+1)^{-\frac{1}{2}} E(q) (\cdot) 2q tr_1 \left( 2 \frac{1}{\pi^{3/2}} \right) d\gamma \]
\[ ([j_i v_i \rangle \langle j_f v_f] (q))_o^\dagger \]
To obtain equation (4.24), the transformation

\[ j = \frac{1}{\sqrt{2}} (W + W_2) \quad \gamma = \frac{1}{\sqrt{2}} (W_2 - W) \]
\[
(2\pi mkT)^{-3} \int dpdp_2 dp_1^* \delta (p+p_2-p_1^*) = \int d(\mu g') d^3 y
\]
\[
\frac{1}{\pi^{3/2}} \int d^3 y \exp[ - \frac{y^2}{2}] = 1
\]
to relative and centre of mass variables has been employed. The (trivial) centre of mass integration has also been performed. Indeed, the ease with which the centre of mass integration can be carried out represents a second simplifying feature obtained by neglecting the presence of velocity polarizations.

In the language of the last chapter, \(I^{(k)}_{psp's'; 2n' n''} + \delta_{n0} \delta_{n'0} \delta_{n''0} \)

It is convenient, at this stage, to divide the collision section into two parts; namely

(4.26)

\[
\sum[[j^i_1 v^i_1,j^f_1 v^f_1]^{(q)}][j^i_1 v^i_1,j^f_1 v^f_1]^{(q)}_0
\]
\[
= \sum'[[j^i_1 v^i_1,j^f_1 v^f_1]^{(q)}][j^i_1 v^i_1,j^f_1 v^f_1]^{(q)}_0
\]
\[
+ \sum''[[j^i_1 v^i_1,j^f_1 v^f_1]^{(q)}][j^i_1 v^i_1,j^f_1 v^f_1]^{(q)}_0
\]
\[
\exp\left[-\frac{E_{j^1_1 v^1_1}}{kT}\right]
\]
\[
= \sum_{j_2j_2'} \frac{1}{Q} \sum'[[j^i_1 v^i_1,j^f_1 v^f_1]^{(q)}_p j_2 v_2]
\]
\[
+ \sum_{j_2j_1'} \frac{1}{Q} \sum''[[j^i_1 v^i_1,j^f_1 v^f_1]^{(q)}_p j_2 v_2]
\]
\[ \rho_{j_1'v_1'}[j_1v_1><j_f'v_f'](q)]^0. \]

This division is based on whether the internal state coherences \([j_1v_1><j_fv_f](q)\) and \([j_1'v_1'><j_f'v_f'](q)\) refer to the same molecule \((\mathcal{E}')\) or to different molecules \((\mathcal{E}'')\). Explicitly, these cross sections have the form

\[(4.27) \quad \mathcal{G}'([j_1v_1><j_fv_f](q) \rho_{j_2v_2}[j_1v_1><j_fv_f'](q) \rho_{j_2'v_2'})^0 \]

\[
= (-1)(2\pi)^4h^2\left(\frac{\hbar}{8kT}\right)^{1/2}(2q+1)^{-1}E(q)(\cdot)2q^{tr_{1,2}}\frac{1}{2^{3/2}f} \]

\[
d\gamma([j_1v_1><j_fv_f](q))^+ \rho_{j_2v_2} \]

\[
x \int d(\mu g') \exp(-\gamma'[2\mu g'|t|\mu g'][j_1v_1><j_fv_f'](q) \rho_{j_2'v_2'} \]

\[
- [j_1v_1><j_fv_f'](q) \rho_{j_2'v_2'}<\mu g'|t^+|\mu g>] \]

and
These equations are analogous to equations (3.59) and (3.60), respectively.

Rotational invariance of the transition operator itself, as expressed by equation (3.64) for the translational-internal coupling scheme, allows a representation of the scalar cross sections (4.27) and (4.28) entirely in terms of reduced (invariant) quantities. The eventual analogs of (3.65) are found to be

\begin{align*}
(4.29) \quad & \mathcal{G}'(j_i v_i < j_f v_f) (q) [j_i v_i < j_f v_f] (q) \bigg|_{0} \\
& \mathcal{G}'(j_i v_i < j_f v_f) (q) \bigg|_{0} \\
& = (2\pi)^{-3/2} (2q+1)^{-1} E(q) \mathcal{G}'(j_i v_i < j_f v_f) (q) \bigg|_{0} \\
& \times \left[ \int d(\mu g') \exp -\gamma^2 \langle \mu g | t | \mu g' \rangle \rho_{j_i v_i} \langle j_i v_i < j_f v_f \rangle (q) \right] \\
& \times \left[ \int d(\mu g') \exp -\gamma^2 \langle \mu g | t | \mu g' \rangle \rho_{j_f v_f} \langle j_i v_i < j_f v_f \rangle (q) \right]
\end{align*}
\[
(-1)^j i_{j_f} (-i)^j_{j_f} \frac{1}{(kT)^2} \sum_{j_2, v_2} \int E' \frac{dE'}{\text{tr} E'} \exp \left[ \frac{-E^'}{kT} \right] \exp \left[ \frac{-E_{j_2} \delta}{Q} \right] \]

\[
\frac{\pi \hbar^2}{(\mu g')^2} \sum_{j_2, v_2} \int dE \text{tr} \delta \left( E_{f'} v_{f'} + E_{j_2} v_{j_2} + E_{f} - E' \right) \exp \left[ \frac{-E_{j_2} v_{j_2}}{kT} \right] \exp \left[ \frac{-E_f v_f}{kT} \right] \exp \left[ \frac{-E_{f'} v_{f'}}{kT} \right] \exp \left[ \frac{-E_{f'} v_{f'}}{kT} \right] \exp \left[ \frac{-E_{f'} v_{f'}}{kT} \right]
\]

\[
\sum_{\lambda_1 \lambda_2 \lambda} \left[ (2j_1^i + 1)(2j_f^i + 1) \right] \beta (2j_2^i + 1)(2\lambda + 1)(-1)^{q + j_f^i + j_1^i + j_f^i + j_1^i} \]

\[
T(j_1^i v_i^i j_2^i v_2^i \lambda'; \lambda_1 \lambda_2 \lambda; j_1^i v_i^i j_2^i v_2^i \lambda) + T^*(j_1^i v_i^i j_2^i v_2^i \lambda'; \lambda_1 \lambda_2 \lambda; j_f^i v_f^i j_2^i v_2^i \lambda)
\]

\[
\frac{1}{(kT)^2} \sum_{j_2, v_2} \int E \frac{dE}{\text{tr} E} \exp \left[ \frac{-E^'}{kT} \right] \exp \left[ \frac{-E_{j_2} v_{j_2}}{kT} \right] \exp \left[ \frac{-E_f v_f}{kT} \right] \exp \left[ \frac{-E_{f'} v_{f'}}{kT} \right] \exp \left[ \frac{-E_{f'} v_{f'}}{kT} \right] \exp \left[ \frac{-E_{f'} v_{f'}}{kT} \right]
\]

\[
\delta(j_1^i f_1 \mid j_1^i f_1) \left[ T(j_1^i v_i^i j_2^i v_2^i \lambda; 000; j_1^i v_i^i j_2^i v_2^i \lambda) \delta(v_f \mid v_f^i) \right] + T^*(j_f^i v_f^i j_2^i v_2^i \lambda; 000; j_f^i v_f^i j_2^i v_2^i \lambda) \delta(v_i \mid v_i^i) \]

and

(4.30)

\[
\left[ [j_1^i v_i^i \mid v_f^i] (q) \mid [j_1^i v_i^i \mid v_f^i] (q) \right]_0
\]
\[
= (-1)^{j_1} i^* j_f^f (-i)^{j_1} i^f j_f^f \frac{1}{(kT)^2} \sum_{j_1, j_f^f} f E_{tr}^i dE_{tr}^j \exp\left[ \frac{-E_{tr}^i}{kT} \right] \exp\left[ \frac{-E_{tr}^f}{kT} \right]
\]

\[
\frac{\pi \hbar^2}{(\mu g^i)^2} \sum_{j_2, j_2^f} f dE_{tr}^j \delta(E_{tr}^j + E_{tr}^f + E_{tr}^j - j_1^{i^f} + j_1^{i^f} - E_{tr}^f - E_{tr}^j)
\]

\[
\sum_{\lambda_1, \lambda_2} \sum_{\lambda \lambda' \lambda''} [(2j_1^i + 1)(2j_2^i + 1)]^{\frac{3}{2}} (2j_1^f + 1)(2j_2^f + 1)
\]

\[
(1 + \lambda_1 + \lambda_2 + \lambda_1 + \lambda_2 + q) - j_2 + j_1^{i^f} + j_1^{i^f}
\]

\[
\{ q \lambda_2 \lambda_2' \} \{ q \lambda_1 \lambda_1' \} \{ \lambda_2 \lambda_2' q \}
\]

\[
[(2 \lambda_1 + 1)(2 \lambda_2 + 1)(2 \lambda_1' + 1)(2 \lambda_2' + 1)]^{\frac{1}{2}}
\]

\[
T(j_1^{i^f} j_1^{i^f} j_1^{i^f} \lambda; \lambda_1 \lambda_2 \lambda; j_1^{i^f} j_1^{i^f} j_2^{i^f} \lambda)
\]

\[
T^*(j_1^{i^f} j_1^{i^f} j_1^{i^f} \lambda'; \lambda_1 \lambda_2 \lambda; j_1^{i^f} j_1^{i^f} j_2^{i^f} \lambda)
\]

\[
+ (-1)^{j_1} i^* j_f^f (2q + 1) - \frac{1}{(kT)^2} \sum_{\lambda} f E_{tr}^i dE_{tr}^j \exp\left[ \frac{-E_{tr}^i}{kT} \right] \exp\left[ \frac{-E_{tr}^f}{kT} \right]
\]

\[
\exp\left[ \frac{-E_{tr}^i}{kT} \right]
\]
\[
\frac{\pi \hbar^2}{(\mu g')^2} (2\lambda' + 1) [(2j_i + 1)(2j_f + 1)]^{1/2} (-1)^{q + j_f + j'_f}
\]

\[
T(j_i v_i j'_i v'_i \lambda'; q q 0; j_f v_f j'_f v'_f \lambda')
\]

\[
+ \frac{j_i + j'_f (-1)^{j_i + j'_f}}{(2q + 1)^{1/2}} \frac{1}{(kT)^2} \sum \int_{\lambda'} E_{tr}^i dE_{tr} \exp\left[ \frac{-E_{tr}}{kT} \right] \exp\left[ \frac{-E_{tr}}{kT} \right]
\]

\[
\frac{\pi \hbar^2}{(\mu g')^2} (2\lambda' + 1) [(2j_i + 1)(2j_f + 1)]^{1/2} (-1)^{q + j_f + j'_f}
\]

\[
T(j_f v_f j'_i v'_i \lambda'; q q 0; j_i v_i j'_i v'_f \lambda')
\]

In equations (4.29) and (4.30), the identifications (3.68) and (3.69) have been employed. In addition, the definition (4.26) includes all the Boltzmann factors. As such, the forms (4.29) and (4.30) clearly illustrate the unequal Boltzmann averaging of the initial and final states - a direct consequence of the form of linearization (4.6). This is contrasted with the symmetrical averaging of initial and final states employed in equations (3.65) and (3.66). The greater rotational simplicity of the forms (4.29) and (4.30), due to the absence of velocity polarizations, is also readily apparent.

The results (4.29) and (4.30) are exact and represent the starting point for the approximate calculations employed in the next section. But first, other forms of these exact relations are obtained in order to compare with quantities
calculated by other researchers. As mentioned in chapter III, these additional forms can represent preferred starting points for alternate approximation schemes, used to evaluate the generalized cross sections.

The transformation (3.67) can be applied to obtain an S matrix representation for the cross sections, still within a translational-internal coupling scheme. Indeed, the results (4.31)

\[
\sum'([j_1 v_i < j_f v_f)](q) | [j_1' v_i' > j_f' v_f'](q) = \frac{\pi \hbar^2}{(mg')^2} \sum_{j_2 v_2} \int dE_{tr} dE_{tr} \exp\left[\frac{-E_{tr}^*}{kT}\right] \exp\left[\frac{-E_{tr}^*}{kT}\right] \delta(E_{tr} + E_{tr}^* - E_{tr}^* - E_{tr}^*)
\]

\[
\sum_{\lambda_1 \lambda_2 \lambda \lambda'} \frac{\pi \hbar^2}{(mg')^2} \sum_{j_2 v_2} \int dE_{tr} dE_{tr} \delta(E_{tr} + E_{tr}^* + E_{tr}^* - E_{tr}^* - E_{tr}^* - E_{tr}^*)
\]

\[
\times [\delta(j_1 v_i | j_1 v_i') \delta(j_f v_f | j_f v_f') \delta(j_2 v_2 \lambda | j_2 v_2 \lambda') \delta(\lambda_1 \lambda_2 \lambda | 000)]
\]

- \( S(j_1 v_i j_1' v_i' \lambda'; \lambda_1 \lambda_2 \lambda'; j_2 v_2 j_2' v_2' \lambda) \)
\[ S^* \left( \mathbf{j}_f \mathbf{v}_f \mathbf{j}_2 \mathbf{v}_2 \lambda \right) ; \mathcal{L} \not\perp \mathcal{L} ; \mathbf{j}_f \mathbf{v}_f \mathbf{j}_2 \mathbf{v}_2 \lambda \) \]

and

(4.32)

\[
\sum'' \left( [j_i^i v_i^i < j_f^f v_f^f] (q) | [j_i^i v_i^i < j_f^f v_f^f] (q) \right)_0
\]

\[ = \frac{\mathbf{j}_i^i + \mathbf{j}_f^f}{(-i)} \frac{1}{(kT)^2} \sum_{j_1^1 v_1^1} \int \text{d}E_{\text{tr}} \text{d}E_{\text{tr}}' \exp \left[ -\frac{E_{\text{tr}}'}{kT} \right] \exp \left[ -\frac{E_{\text{tr}}}{kT} \right] \]

\[ + \frac{\pi \hbar^2}{(\mu g')^2} \sum_{j_2 v_2} \int \text{d}E_{\text{tr}} \delta (E_{\mathbf{j}_f^f \mathbf{v}_f^f} + \mathbf{E}_{\mathbf{j}_2^2 \mathbf{v}_2^2} + \mathbf{E}_{\text{tr}} - \mathbf{E}_{\mathbf{j}_1^1 \mathbf{v}_1^1} - \mathbf{E}_{\mathbf{j}_f^f \mathbf{v}_f^f} - \mathbf{E}_{\text{tr}}') \]

\[ \sum_{\mathcal{L}_1 \not\perp \mathcal{L}_2 \not\perp \mathcal{L}^i \not\perp \mathcal{L}_1^i} \sum_{\lambda \lambda'} \left[ (2j_1^1 + 1)(2j_1^1 + 1) \right] \frac{1}{2} (2j_1^1 + 1)(2\lambda + 1) \]

\[ \left[ (2 \mathcal{L} + 1)(2 \mathcal{L} + 1)(2 \mathcal{L}_1^i + 1)(2 \mathcal{L}_2^i + 1) \right] \frac{1}{2} \]

\[ (-1)^{j_2^2 + j_1^1 + j_f^f + q} \]

\[ \times \left( \delta(\mathcal{L} \not\perp \mathcal{L}_1 \not\perp \mathcal{L}_2 \not\perp \mathcal{L} | 000000) \delta(\lambda | \lambda') \delta(j_i^i v_i^i | j_i^i v_i^i) \delta(j_f^f v_f^f | j_f^f v_f^f) \right) \]
-S(j_1 v_1 j_2 v_2; \Lambda_1 \Lambda_2 \Lambda; j_1' v_1' j_2' v_2')

S^*(j_1 v_1 j_2 v_2; \Lambda_1 \Lambda_2 \Lambda; j_f v_f j_f v_f)

are almost immediate. These equations are the analogs of (3.71) and (3.72), respectively, and have been previously reported.\(^2\)

A total angular momentum (total \(J\)) coupling scheme has been quite popular in pressure broadening studies, and represents an alternate method of coupling the angular momentum quantities involved in (3.63) to form a scalar (reduced) matrix element. In the notation of Curtiss and coworkers\(^8\),

\[ (4.33) \]

\[ <j_{1 m_1 v_1} j_{2 m_2 v_2} \rho \sigma | t | j_{1'} m_{1'} v_{1'} j_{2'} m_{2'} v_{2'} \rho' \sigma' > = (2\pi \mu)^{-1} (pp')^{-1/2} (-i)^{j_1+j_2+j_1'+j_2'+1} (2J+1) \]

\[ \sum_{jj'JJ} [(2j+1)(2j+1)]^{1/2} (2J+1) \]

\[ \mathcal{A} \]

\[ T^J(j_1 v_1 j_2 v_2 j_{12} v_{12} \rho \sigma | j_1 v_1 j_2 v_2 j_{12} v_{12} \rho \sigma) \]

where \( \mathcal{A} \) is the Yutsis coupling diagram shown in figure 6. Again, note the reversed order of indices employed on opposite sides of the equal sign. A combination of (4.33) with the
Figure 6: Coupling diagram $A$
three equations (4.26) through (4.28), and the subsequent
definition of a reduced S matrix for this coupling scheme,

\begin{equation}
S_J^J(j_1^1v_1^1j_2^1v_2^1j_\lambda'^1j_1^1v_1^1j_2^1v_2^1j_\lambda)
\end{equation}

\[= \delta(j_1^1v_1^1j_2^1v_2^1j_\lambda'^1j_1^1v_1^1j_2^1v_2^1j_\lambda) - T_J^J(j_1^1v_1^1j_2^1v_2^1j_\lambda'^1j_1^1v_1^1j_2^1v_2^1j_\lambda),\]

leads eventually to the invariant expressions

\begin{equation}
\mathcal{I}'(\{j_1^1v_1^1<j_f^1v_f^1\}(q)|\{j_1^1v_1^1<j_f^1v_f^1\}(q))_0
\end{equation}

\[= (-1)^{i_1^1+j_f^1}(-i)^{i_1^1+j_f^1} \frac{1}{(kT)^2} \sum_{j_2^1v_2^1} \int E_{tr}^1 dE_{tr}^1 \exp\left[-\frac{E_{tr}^1}{kT}\right] \exp\left[-\frac{E_{tr}^1}{kT}\right] \frac{-E_{tr}^1}{Q}
\]

\[\frac{\pi\hbar^2}{(\mu g')^2} \sum_{j_2^1v_2^1} \int dE_{tr} \delta(E_{tr}^1 - E_{tr}^1 + E_{tr}^1 + E_{tr}^1 - E_{tr}^1) \exp\left[-\frac{E_{tr}^1}{kT}\right] \exp\left[-\frac{E_{tr}^1}{kT}\right]
\]

\[\sum_{\lambda'jj'jj'}[(2j_2^1+1)(2j_2^1+1)(2j_2^1+1)(2j_2^1+1)]^{1/2}(2j_2^1+1)(2j_2^1+1)
\]

\[
\begin{align*}
\{j_2^1j_2^1j_f^1j_f^1\} & \quad \{j_2^1j_2^1j_f^1j_f^1\} & \quad \{j_2^1j_2^1j_f^1j_f^1\} & \quad \{j_2^1j_2^1j_f^1j_f^1\} & \quad \{j_2^1j_2^1j_f^1j_f^1\} & \quad \{j_2^1j_2^1j_f^1j_f^1\}
\end{align*}
\]
\[
(-1)^j_j^i + f_j^i j_{\frac{1}{2}}^i + j_{\frac{1}{2}}^i f_j^i \quad (-1)^j_j^i + j_{\frac{1}{2}}^i \quad (-1)^j^i - j^i + j^- j +\lambda - \lambda'
\]

\[
[S^J (j_i^i v_1^i j_2^i v_2^i j^i \lambda' \mid j_i^i v_1^i j_2^i v_2^i j^i \lambda)]
\]

\[
S_j^* (j_f^i v_1^i j_2^i v_2^i j^i \lambda' \mid j_f^i v_1^i j_2^i v_2^i j^i \lambda)
\]

\[
- \delta(j_i^i v_1^i j_2^i v_2^i j^i \lambda f v_1^i j_2^i v_2^i j^i \lambda' j_f^i v_1^i j_f^i j^i ')]
\]

and

\[
\left< \left[ j_i^i v_1^i < j_f^i v_f^i \right] \right> (q) \left[ j_i^i v_1^i > j_f^i v_f^i \right] (q)
\]

\[
= (-1)^j_j^i + f_j^i (-1)^j_j^i + f_j^i \frac{1}{(kT)^2} \sum_{j_i^i v_1^i} f E_{tr} dE_{tr} \exp\left[ \frac{-E_{tr}}{kT} \right] \exp\left[ \frac{-E_{f v_1^i}}{kT} \right]
\]

\[
\frac{\pi \hbar^2}{(\mu g')^2} \sum_{j_2^i v_2^i} f dE_{tr} \delta(E_{f v_f^i} + E_{j_2^i v_2^i} + E_{tr} - E_{j_i^i v_1^i} - E_{j_f^i v_f^i} - E_{tr})
\]

\[
\sum_{\lambda \lambda'} [2j^i + 1] (2j_2^i + 1) (2j_f^i + 1) (2j^i + 1) \delta(2J + 1) (2\tilde{J} + 1)
\]

\[
\{ q j_i^i f_j^i \} \quad \{ q j_i^i j_f^i j_j^i \} \quad \{ j_\lambda j_\tilde{\lambda} \} \quad \{ j_\lambda j_\tilde{\lambda} \}
\]

\[
(-1)^j_i j_f^i \quad (-1)^j^i j_{\frac{1}{2}}^i \quad (-1)^j - j + \lambda' - \lambda
\]
Equations (4.35) and (4.36) are exactly equivalent to (4.31) and (4.32). They can also be obtained directly from the first set by the transformation

\[ S^J (j_1^i v_1^j j_2^i v_2^j j' \lambda ') | j_1^i v_1^j j_2^i v_2^j j \lambda ) \]

\[ S^J (j_1^i v_1^j j_2^i v_2^j j' \lambda ') | j_1^i v_1^j j_2^i v_2^j j \lambda ) \]

\[ - \delta (\lambda j j | \lambda ' j' j') \delta (j_1^i v_1^j j_2^i v_2^j j_1^i v_1^j j_2^i v_2^j j') \]

the inverse of which is given in reference (8), equation (79). Actually, at least for the case of no velocity polarizations, this second method of obtaining equations (4.35) and (4.36) is much more cumbersome than the first and indeed has been mentioned only to emphasize that the transformation is known and that the methods employed here are self-consistent. The
results (4.35) and (4.36) are also presented in reference (2). Some additional comments regarding these two equations are given in the last section of this chapter.
The exact collision expressions of the last section, in the forms (4.29) and (4.30), are now evaluated approximately, using the method employed in the previous chapter. This method allows an approximate separation of internal state and translational motions which, in turn, produces a useful physical interpretation of the various collisional effects. Indeed, the categorization is especially useful in visualizing the roles of the translational states - their secondary nature in the relaxation of pure internal state polarizations (as discussed in this chapter) versus their more active role in the relaxation velocity polarizations (as detailed in chapter VII). Thus the approach used here has the advantage of further applicability to translational relaxation and the present treatment of the translational motions should be contrasted with the comments given in the final chapter.

The linear in T terms in equations (4.29) and (4.30) are first transformed using the optical theorem, equation (3.86). As this transformation is exact, the resulting equations are also exact and these are collected as four effective cross sections corresponding to four separate collisional processes. Explicitly, these are

\[(4.38)\]

\[\sum \left( [j_i v_i] < j_f v_f ]^{(q)} \right) [j_i v_i] < j_f v_f ]^{(q)} \]
\[
\begin{align*}
&= (-1)^{j_f j_f} (-1)^{j_i j_i} \frac{1}{(kT)^2} \sum_{j_2 v_2} \int \frac{dE}{E_{tr}} \delta(E_{tr} - E_{tr}^*) \exp\left[ \frac{-E_{tr}}{kT} \right] \exp\left[ \frac{-E_{tr}^*}{kT} \right] \\
&= \frac{\pi \hbar^2}{(\mu g')^2} \sum_{j_2 v_2} \int \frac{dE}{E_{tr}} \delta(E_{tr} - E_{tr}^*) \delta(E_{tr} - E_{tr}^*) \exp\left[ \frac{-E_{tr}}{kT} \right] \exp\left[ \frac{-E_{tr}^*}{kT} \right]
\end{align*}
\]

\[
\sum_{1 \leq 2} \frac{1}{(2j_i^1 + 1)(2j_f^1 + 1)} \frac{1}{(2j_2^1 + 1)(2\lambda_i^1 + 1)} (-1)^{q + j_i^1 + j_f^1} \\
\{ j_i^1 j_i^1 \leq 1 \} \{ j_f^1 j_f^1 \leq q \}
\]

\[
T(j_i^1 v_i^1 j_f^1 v_f^1 \lambda_i^1; \leq 1 \leq 2 \; ; j_i^1 v_i^1 j_f^1 v_f^1 \lambda)
\]

\[
T^*(j_i^1 v_i^1 j_f^1 v_f^1 \lambda_i^1; \leq 1 \leq 2 \; ; j_f^1 v_f^1 j_f^1 v_f^1 \lambda)
\]

and

(4.39)

\[
\mathcal{E}^*(q) = \frac{1}{(kT)^2} \sum_{j_2 v_2} \sum_{j v} \int \frac{dE}{E_{tr}} \delta(E_{tr} - E_{tr}^*) \exp\left[ \frac{-E_{tr}}{kT} \right] \exp\left[ \frac{-E_{tr}^*}{kT} \right]
\]

\[
= \frac{\pi \hbar^2}{(\mu g')^2} \frac{1}{(2\delta(j_j j_f j_i j_f) \int \frac{dE}{E_{tr}} \delta(E_{tr} - E_{tr}^*) \delta(j_i^1 v_i^1 j_f^1 v_f^1)} (2j_2^1 + 1)(2\lambda^1 + 1)
\]
\[ x \{ T^*(j_1^i v_1^i j_2^i v_2^i \lambda'; \lambda_1 \lambda_2 \lambda; j_1 v_1 j_2 v_2 \lambda) + T(j_1^i v_1^i j_2^i v_2^i \lambda'; \lambda_1 \lambda_2 \lambda; j_1 v_1 j_2 v_2 \lambda) \}
\]

\[ \delta(v_f^i v_f^i) \]

\[ + \frac{1}{(kT)^2} \sum \frac{E'_f \tr dE'_f \exp[-\frac{E'_f \tr}{kT}] \exp[-\frac{E'_f}{kT}]}{(\mu g')^2} \frac{\hbar^2}{(2j_2^i + 1)(2\lambda^i + 1)} \delta(j_1 f^i j_1 f^i) \]

\[ x \{ \delta(v_f^i v_f^i) T_h(j_1^i v_1^i j_1^i v_2^i \lambda'; 000; j_1^i v_1^i j_1^i v_2^i \lambda') + \delta(v_i^i v_i^i) T^*(j_1^i v_1^i j_1^i v_2^i \lambda'; 000; j_1^i v_1^i j_1^i v_2^i \lambda') \}
\]

from equation (4.29), and

\[ (4.40) \]

\[ \sum \{ [j_1 v_1^i \rangle \langle j_f v_f^i] (q) \} [j_1 v_1^i \rangle \langle j_f v_f^i] (q) \}
\]

\[ = (-1)^{j_1^i + j_f^i + j_i^i} \frac{1}{(kT)^2} \sum \frac{E'_f \tr dE'_f \exp[-\frac{E'_f \tr}{kT}] \exp[-\frac{E'_f}{kT}]}{(\mu g')^2} \frac{\hbar^2}{2} \sum \frac{\delta(E_f v_f^i + E_f v_f^i)}{2} \delta(E_f v_f^i + E_f v_f^i - E_f v_f^i - E_f v_f^i - E_f v_f^i - E_f v_f^i) \]
\[ \sum_{\mathcal{J}_1 \leq \mathcal{J}_2} \sum_{\lambda \lambda'} [2(j_{11}^j + 1)(2j_{22}^j + 1)]^{1/2} (2j_{11}^j + 1)(2\lambda + 1) \]

\[ (-1)^{j_{11}^j + 1 + j_{22}^j + 1} \sum_{\mathcal{J}_1 \leq \mathcal{J}_2} [2(j_{11}^j + 1)(2j_{22}^j + 1)]^{1/2} \]

\[ \{j_2, j_{1'}_f, j_{1'}_i\} \quad \{j_1, j_{1'}, j_{1''} f\} \quad \{j_1, j_{1'}_f, j_{1'}_i, j_{1''} i\} \]

\[ [2(j_{11}^j + 1)(2j_{22}^j + 1)]^{1/2} \]

\[ T(j_{1'}_1 j_{22}^i j_{1'}_f ; \mathcal{J}_1 \leq \mathcal{J}_2 ; j_{1'}_1 j_{22}^i j_{22}^2 \) \]

\[ T^*(j_{1'}_1 j_{22}^i j_{1'}_f ; \mathcal{J}_1 \leq \mathcal{J}_2 ; j_{1'}_f j_{22}^i j_{22}^2 \) \]

and

\[ (4.41) \]

\[ \sum_{\mathcal{J}_1 \leq \mathcal{J}_2} [\{j_1 v_1 > j_{1'} v_{1'}\}(q)] [\{j_1 v_1 > j_{1'} v_{1'}\}(q)]_o \]

\[ = i^{j_{1}^j + j_{1}^f} \frac{1}{(kT)^2} \sum_{\lambda' \lambda} \frac{\int E_{tr} dE_{tr} \exp[-E_{tr}^i/kT] \exp[-E_{tr}^f/kT]}{Q} \]

\[ \frac{\pi \hbar^2}{(\mu g')^2} \int dE_{tr} \delta(E_{tr}^i - E_{tr}^f + x)(2\lambda' + 1) [2j_{11}^j + 1]^{1/2} \]

\[ [(2j_{11}^j + 1)(2j_{22}^j + 1)]^{1/2} \]
\[
\left( \sum \limits_{\lambda_1 \lambda_2} (-1)^{j_1 + j_2 + j_i + j_f} \right) (-1)^{q + j_f + j_i} \left( \sum \limits_{\lambda_1' \lambda_2'} (-1)^{j_1' + j_2' + j_i' + j_f'} \right) (-1)^{q' + j_f' + j_i'} \left( \sum \limits_{\lambda_1'' \lambda_2''} \right) \left( \sum \limits_{\lambda_1'\lambda_2'} \right) \left( \sum \limits_{\lambda_1''\lambda_2''} \right) \]

\[
\left[ (2 \lambda_1 + 1) (2 \lambda_2 + 1) (2 \lambda_1' + 1) (2 \lambda_2' + 1) \right]^{1/2}
\]

\[
\{ j_1 \ j_f \ j_1' \} \quad \{ j_2 \ j_f' \ j_2' \} \quad \{ \lambda_1' \lambda_1'' \lambda_2' \lambda_2'' \}
\]

\[
T(j_f v_f j_i'^{v_i'} \lambda'; \lambda_1 \lambda_2 \lambda_2' \lambda_1' \lambda_2' \lambda_2' \lambda_2' \lambda_2')
\]

\[
T^*(j_i v_i j_f'^{v_i'} \lambda'; \lambda_1 \lambda_2 \lambda_2' \lambda_1' \lambda_2' \lambda_2' \lambda_2' \lambda_2')
\]

\[
\begin{align*}
\mathbb{S} \{ \exp \left[ \frac{-E_{j_i v_i}}{kT} \right] + \exp \left[ \frac{-E_{j_f v_f}}{kT} \right] \}
\end{align*}
\]

\[
\sum \limits_{\lambda} \int \mathcal{E}_{tr}^t \mathcal{E}_{tr}^t \exp \left[ \frac{-E_{tr}^t}{kT} \right] \left( \frac{\pi \hbar^2}{(\mu g')} \right)^2 (2\lambda' + 1)
\]

\[
\times \left[ \exp \left[ \frac{-E_{j_i v_i}}{kT} \right] \right] \left[ (2j_i + 1)(2j_i + 1) \right]^{1/2} (-1)^{q + j_f' + j_i'}
\]

\[
T_h(j_i v_i j_f'^{v_i'} \lambda'; q q_0 ; j_f v_f j_i'^{v_i'} \lambda')
\]

\[
+ \exp \left[ \frac{-E_{j_f v_f}}{kT} \right] \left[ (2j_i + 1)(2j_i + 1) \right]^{1/2} (-1)^{q + j_f' + j_i'}
\]

\[
\]
from equation (4.30). In equations (4.39) and (4.41), $T_h$ is defined by equation (3.87).

Ignoring for the moment the linear in $T_h$ (shift) contributions, it is seen that the generalized cross section $\sigma_0$ is a sum of four collisional contributions

$$\sigma_0 = \sigma'+0 + \sigma'-0 + \sigma''+0 + \sigma''-0,$$

each of which consists of a rotationally invariant, energy dependent cross section (i.e. quadratic in $T$) that has been Boltzmann averaged over both the relative translational energy and the energy states of the second molecule. The particular collision process which each of these effective cross sections considers, is found by analyzing the arguments of the various reduced transition operators. For example, in a "diagonal" ($j_i v_i = j_i' v_i'$, $j_f v_f = j_f' v_f'$) cross section, $\sigma'+0$ describes collisional events where the state of the molecule of interest is not changed (phase shifting collisions) while $\sigma'-0$ allows for inelastic contributions to the relaxation. Finally, $\sigma''+0$ and $\sigma''-0$ consider "transfer processes", where polarizations are paired from one molecule to another by collision, and their consequent effect on relaxation. These latter collision events are usually ignored. Indeed, the sum of the first two effective cross sections, $\sigma'+0$ and $\sigma'-0$, can be viewed as the rotationally corrected counterparts to equations (2.24) or (2.27) of chapter II. These are also the only cross sections that arise in foreign gas broadening.
The distorted wave Born approximations to these four effective cross sections can readily be obtained. Substitution of equation (3.84), and equation (3.87) where necessary, leads directly to

\[ \sum' + ([j_i v_i] <j_f v_f] (q) [j_i v_i] <j_f v_f] (q))_o \]

\[ = (-1) \sum_{j_2 \nu_2} \exp \left[ -\frac{J_2 v_2^2}{kT} \right] \sum_{j_f \nu_f} (-1)^{q+j_1+j_f} \{ j_1 j_1 L_1 \} \]

\[ \frac{<j_1 v_i||\mathcal{Q}_1 (L_1)||j_1 v_i>} {<j_1 v_i||\mathcal{Q}_1 (L_1)||j_1 v_i> (2 L_1+1)} \]

\[ \frac{|<j_2 v_2||\mathcal{Q}_2 (L_2)||j_2 v_2>|^2 \exp\{-\Delta/2\}}{(2 L_2+1)} \]

\[ \sum_p (00 L_1 L_2)|00 L_1 L_2|E_{j_f v_f} + E_{j_2 v_2} - E_{j_i v_i} - E_{j_i v_i} \]

and

\[ \sum' - ([j_i v_i] <j_f v_f] (q) [j_i v_i] <j_f v_f] (q))_o \]
The terms linear in $T_\text{h}$ vanish identically. Analogous expression are found for $\mathcal{G}$, namely

\begin{equation}
\mathcal{G}'' + ([j_i v_i < j_f v_f]^{(q)} | [j_i v_i | < j_f v_f]^{(q)})_o
\end{equation}

\begin{equation}
= (-1) \sum \exp\left[ \frac{-E_{j_i v_i}}{kT} \right] \sum \delta(j_{i_f} j_{i_f} | j_{i_f} j_{i_f}) L_1 L_2 L
\end{equation}

\begin{equation}
\frac{|<j_i v_i | \mathcal{Q}_2 (L_2) | j_f v_f>|^2 \exp[-\Delta/2] (2L+1)^{-1/2}}{(2L_2+1)}
\end{equation}

\begin{equation}
\sum_{p}^{(1)} (00 ) L_1 L_2 | 00 ) L_1 L_2 | E_{j_f} + E_{j_i v_i} - E_{j_f v_f} - E_{j_i v_i}^{(1)} o
\end{equation}

\begin{equation}
x \frac{1}{2!} \frac{<j_i v_i | \mathcal{Q}_1 (L_1) | j_i v_i> | <j_i v_i | \mathcal{Q}_1 (L_1) | j_i v_i> * \delta(v_f | v_f)}{(2j_{i_f} + 1)(2L_1 + 1)}
\end{equation}

\begin{equation}
+ \frac{<j_i v_i | \mathcal{Q}_1 (L_1) | j_f v_f> | <j_i v_i | \mathcal{Q}_1 (L_1) | j_i v_i> * \delta(v_i | v_i)}{(2j_{i_f} + 1)(2L_1 + 1)}
\end{equation}
\begin{align*}
&\langle 1^+ \ 2^+ \ 1^+ \ 2 \rangle \\
&\{ j_2 j_f^+ j_2 \} \quad \{ q \ \zeta_1 j_2 \} \quad \{ q \ \zeta_1 j_2 \} \quad \{ q \ \zeta_1 j_2 \}
\end{align*}

\begin{align*}
x \langle j_1^+ v_1^+ | \mathcal{O}_1^{(1)} | j_1^+ v_1^+ \rangle^* & \langle j_1^+ v_1^+ | \mathcal{O}_1^{(1)} | j_f v_f^+ \rangle \\
&<j_1^+ v_1^+ | \mathcal{O}_2^{(1)} | j_2 v_2^+ \rangle^* \langle j_f^+ v_f^+ | \mathcal{O}_2^{(1)} | j_2 v_2^+ \rangle
\end{align*}

\begin{align*}
&(2 \zeta + 1)^{1/2} \exp[-\Delta/2] \sum_0^{(1)} (00 \ \zeta_1 \ \zeta_2 | 00 \ \zeta_1 \ \zeta_2 | E_{j_f} v_f^+ + E_{j_2} v_2^+) \\
&- E_{j_1} v_1^+ - E_{j_f} v_f^+
\end{align*}

and

\begin{align*}
&\sum'' - (\langle j_1^+ v_1^+ | j_f v_f^+ \rangle (q) | [j_1^+ v_1^+ | j_f v_f^+ ](q) )_0 \\
&= \frac{1}{2} \left( \exp\left[ \frac{-E_{j_1} v_1^+}{kT} \right] + \exp\left[ \frac{-E_{j_f} v_f^+}{kT} \right] \right) \sum_0 \sum_{j_1^+ j_f^+ \zeta_1 \zeta_2} (-1)^{j_1^+ j_f^+ \zeta_1 \zeta_2} \\
&\{ j_1^+ j_f^+ j_1 \} \quad \{ j_f^+ j_1^+ j_2 \} \quad \{ j_2^+ j_1^+ j_2 \}
\end{align*}

\begin{align*}
&(2 \zeta + 1)^{-1/2} \exp[-\Delta/2] \end{align*}
\[ \langle j_1 v_1 \rvert \mathcal{J}_{1}^{(1)} \lvert j_f v_f \rangle \langle j_i v_i \rvert \mathcal{J}_{1}^{(1)} \rvert j_1 v_1 \rangle \]

\[ \langle j_2 v_2 \rvert \mathcal{J}_{2}^{(2)} \lvert j_i v_i \rangle \langle j_f v_f \rvert \mathcal{J}_{2}^{(2)} \rvert j_2 v_2 \rangle \]

\[ \mathcal{E}_{P}^{(1)}(00 \Lambda 1 \Lambda 2 \mid 00 \Lambda 1 \Lambda 2) E_{j_1 v_1}^{y} + E_{j_2 v_2}^{y} - E_{j_i v_i}^{y} - E_{j_f v_f}^{y} \times \]

\[ \times \frac{1}{2 \pi i} (-1)^{q+j_1^i+j_f^i} \langle j_i v_i \rvert \mathcal{J}_{1}^{(q)} \rvert j_f v_f \rangle \langle j_i v_i \rvert \mathcal{J}_{2}^{(q)} \rvert j_i v_i \rangle \]

\[ \exp \left[ \frac{-E_{j_i v_i}}{kT} \right] - \exp \left[ \frac{-E_{j_f v_f}}{kT} \right] \times \mathcal{E}_{h}^{(1)}(0000)_{qq} \]

In this instance, the contribution from the shift does not automatically vanish. Equations (4.42) through (4.45) are analogous to equations (3.88), (3.89), (3.94) and (3.95) of the last chapter.

The translational integrals \( \mathcal{E}_{P}^{(1)} \) and \( \mathcal{E}_{h}^{(1)} \) are defined by equations (3.91) and (3.93), respectively. These translational factors are now approximated. As in the previous chapter, the chosen method of evaluation is the modified Born approximation. Since this, in itself, is a "high temperature" approximation, the terms involving \( \mathcal{E}_{h}^{(1)} \) are small in the limit \( \frac{E_{j_i v_i} - E_{j_f v_f}}{kT} \ll 1 \), see equation (4.45), and in consequence this translational integral will not be considered further. Thus, within this approximation, all matrix elements of \( \mathcal{R} \) are real and relaxation of any internal state effects is described in terms of only one translational
\[ \sum_p^{(1)} (00 \angle_1 \angle_2 | 00 \angle_1 \angle_2 | x) \]. Its evaluation has been described in chapter III, with the final result being equation (3.109).
In concluding chapter IV, a few qualitative remarks are presented relating the collisional treatment employed in this thesis to approaches taken by other workers. A more quantitative comparison between alternate methods of evaluating the effective cross sections would prove extremely useful, but this is not the aim of this thesis. Indeed, such a detailed investigation can be considered only as a consequence of the present work, in which a single framework is developed to encompass various gas-phase relaxation effects.

Comparison with the effective cross sections of transport phenomena and Senftleben-Beenakker effects has already been given. As previously noted, the only change is in the chosen method of linearization, which results in different Boltzmann factors. Further connections are developed in chapter VII where the effects of velocity relaxation on lineshapes are considered. The translational-internal coupling scheme is employed throughout, as the one most natural for a DWBA method of evaluation.

Gordon, Klemperer, and Steinfeld\textsuperscript{10} have defined an effective cross section in terms of reduced $S$ matrix elements in a total $J$ coupling scheme that is analogous to the $\text{G}'$ expression, equation (4.35), derived in this chapter. An actual derivation of the GKS expression only seems to have appeared in print much later, as part of a paper by Fitz and Marcus.\textsuperscript{11} The relationship between the GKS expression and $\text{G}'$ is established in reference (2) - the transfer
cross section $\sigma$" vanishes for foreign gas broadening. With the GKS expression as a starting point, many approximate methods of evaluation have been studied, including entirely quantum mechanical calculations and also semi-classical calculations. The review article by Rabitz\textsuperscript{12} gives some references to this work. The approximate scheme employed in this thesis may give a cruder estimate of these purely internal state cross sections than those methods just mentioned, but has the advantage of being directly applicable to the study of translational relaxation effects as well (see chapter VII).

The approximate method first employed by Anderson,\textsuperscript{13} and later extended by Tsao and Curnutte,\textsuperscript{14} and Fiutak and Van Krancadonk is mentioned because of its widespread acceptance and popularity. It is one example of a semi-classical approach for calculating generalized cross sections - these are usually viewed (see Gordon et al.\textsuperscript{10}) as obtainable from the fully quantum expression for $\sigma'$ in the total J coupling scheme by formally allowing the orbital angular momenta to approach infinity. We suggest that the Anderson semi-classical formulation, in particular, is more compactly viewed as resulting from the same limiting procedure applied to the translational - internal coupling scheme representation for $\sigma'$. Indeed the parallel development of the two approximate schemes (Anderson's method and the present work) is quite striking. Both represent a perturbation approach and result in products of internal
state factors with translational factors. The translational factors are evaluated algebraically in each case, with very crude assumptions applied to the translational motion. The main differences in the two methods are the actual form of the perturbation and the precise treatment of the translational states. The parallelism remains, however, and because the developments are so analogous, a step-by-step comparison seems feasible, and could lead to a more complete understanding of both treatments.

Pickett has recently produced a relaxation matrix which is similar to the \( \hat{e} \) of this thesis, and discusses the merits of both the total \( J \) and translational-internal coupling schemes. An alternate basis for his relaxation matrix is also presented, which is not rotationally invariant. This basis is useful, however, when strong external static electric or magnetic fields are present, and may be viewed as a generalization of the basis (3.31) to the "off-diagonal in \( j \)" case. The present work has not considered such a basis although the comments made in chapter III regarding the basis (3.31) must also be considered relevant to the spectroscopic case - in particular, it was found necessary to ruthlessly approximate the "\( m \)" dependence of the relaxation matrix in this basis, before any tractable treatment could be devised. Pickett treats the translational degrees of freedom classically and does not consider the possibility of any translational relaxation effects. He has produced a relaxation matrix to describe the decay
of the microwave transient effects - one of the goals of the present work as well. But in contrast to Pickett's qualitative remarks, this latter aspect is treated in mathematical detail in the next two chapters of this thesis.

An excellent paper by Lin and Marcus can be viewed as a more complete development of Pickett's approach. Again, a relaxation matrix is derived which is analogous to \( G \) in a total \( J \) coupling scheme, while no attempt is made to include translational relaxation effects. Equations of motion, complete with collisional shifts, are detailed to describe transient behaviour, and the effects of static fields are also discussed. Much of the paper is restricted to diamagnetic diatomics (or linear polyatomics). A semi-classical treatment for calculating the appropriate relaxation rates for OCS is presented in a subsequent publication. The work of Lin and Marcus represents a point of view alternate to the kinetic theory approach of this thesis.

Finally, the approach of Turner and Snider should be mentioned. These workers are in the process of developing methods of approximating cross sections from an operator viewpoint. This idea is radically different from any of those mentioned above, but fills a logical gap in the general treatment of gas phase relaxation processes. Indeed, as emphasized by Fano, pressure broadening studies are fundamentally concerned with the production and relaxation of operator quantities (coherences) - effects more general than populations. The effective cross sections are
interpretable as appropriate averages over operator differential cross sections.\textsuperscript{2,22} (The density operator viewpoint is necessarily employed throughout this thesis, as well.) Yet all of the methods mentioned in this section are concerned with approximating $S$ or $T$ matrix elements, rather than the cross sections themselves. It is felt that the approach of Turner and Snider gives a more natural description of the physical processes involved, and may lead to new approximate methods of evaluating cross sections which are unattainable from the more traditional point of view.
"Consider your verdict," the King said to the jury.
"Not yet, not yet!" the Rabbit hastily interrupted.
"There's a great deal to come before that!"
(a) Introduction

This chapter applies the two level approximation to the more general considerations presented in chapter IV. The approximate moment equations for specific molecular types—diamagnetic diatomics and linear polyatomics, symmetric top molecules, and inverting symmetric tops—are investigated within the context of this approximation. In particular, the modifications of the simple (two state) theory outlined in chapter II due to a rigorous consideration of the magnetic sublevels are demonstrated. The diamagnetic diatomic and linear polyatomic (DDLP) case is treated in considerable detail in sections (b) and (c). The remaining two sections treat the symmetric top and inverting symmetric top situations in a more concise manner, emphasizing the similarities and differences with DDLP case.

The vectorial (actually, the tensorial) aspects of the problem are emphasized in the method of presentation, since this represents the underlying difference between the two state and two level points of view. This tensorial approach has the further advantage of more clearly demonstrating the connections with the methods employed in the study of the Senftleben-Beenakker effects.

A theory dealing with electric dipole induced transitions between rotational levels or sublevels must, of necessity, be concerned with the electric dipole moment operator \( \mu \), the rotational angular momentum operator \( J \).
and the relation between them. The operator $J$ is always diagonal in "j" quantum numbers. For diamagnetic diatomics and linear polyatomics, $\mu \cdot J = 0$ (see figure 7a) and consequently the electric dipole moment operator contains no diagonal in "j" matrix elements. For symmetric top molecules, the vectors $J$ and $\mu$ are not necessarily orthogonal (see figure 7b, where the quantum number $k$ describes the projection of $J$ on $\mu$), and hence the electric dipole operator can contain a diagonal in "j" part. Finally in an inverting symmetric top like NH$_3$, that part of $\mu$ which is diagonal in "$j_f|k|$" can be further subdivided into inversion motions (see figure 7c) - and $\mu$ is entirely off-diagonal in the inversion quantum number.

These qualitative remarks must be kept in mind when specifying the two level system to be considered. Indeed, the general expression for the electric dipole moment operator is

\begin{equation}
\mu = \sum_{ij} v_{ij} E_{v_i}^* c_{ji} v_{v_f} [j_i v_i < j_f v_f]^{(1)}
\end{equation}

while the two level expressions for the dipole moment operator in each of the three cases of figure 7 are truncations of this expansion. Explicitly, these are given as

\begin{equation}
\mu = c_+ [j < j-1]^{(1)} + c_- [j-1 < j]^{(1)}
\end{equation}
(a) \( (2j+1)\)-fold degenerate \( \mathcal{Y}^{(0)}(j) \rightarrow \mathcal{Y}^{(2j)}(j) \)

(b) \( (2j-1)\)-fold degenerate \( \mathcal{Y}^{(0)}(j) \rightarrow \mathcal{Y}^{(2j-2)}(j) \)

(c) \( (2j+1)\)-fold degenerate \( \mathcal{Y}^{(0)}(j) \rightarrow \mathcal{Y}^{(2j)}(j) \)

Figure 7: Rotational characteristics of (a) diamagnetic diatomics and linear polyatomics, (b) symmetric tops, and (c) inverting symmetric tops.
\[ (5.2b) \quad \mu = C_+ [j_k < j_{-1}k]^{(1)} + C_- [j_{-1}k < j_k]^{(1)} \]

\[ + C_j [j_k < j_{-1}k]^{(1)} + C_{j-1} [j_{-1}k < j_{-1}k]^{(1)} \]

\[ (5.2c) \quad \mu = C_+ [j_1 k^+ < j_1 k^-]^{(1)} + C_- [j_1 k^- < j_1 k^+]^{(1)} \]

where the precise expressions for the scalar coefficients are not of concern at this moment. In the truncations employed in equations (5.2), there is the implicit assumption that the other internal state degrees of freedom (describing electronic and vibrational motions) can be removed from direct consideration. Since the spacing between these states is much larger than that of the rotational states, the dropping of these terms is consistent with the ideas of phase randomization as outlined in chapter III.

Two level approximations to other operators of physical interest, such as \( \Delta N \) and \( \mu \), can also be expressed in terms of the abstract basis \( [j_iv_i < j_f v_f]^{(q)} \), for each of the three physical situations of figure 7. This will be done in the appropriate sections which follow. In these sections, however, the emphasis is still on the more abstract basis operators \( [j_iv_i < j_f v_f]^{(q)} \), as it is this description which is the easiest to manipulate and to generalize.
Consider the two levels \( j \) and \( j-1 \) in figure (7a).

The unperturbed \( j \) level is \((2j+1)\) fold degenerate (that is, there are \( 2j+1 \) possible "\( m_j \)" values) while the \( j-1 \) level is \((2j-1)\) fold degenerate. The total dimensionality of the two level "state space" is therefore \( 4j \) while the dimensionality in the operator space is the square of this, \( 16j^2 \). Thus the operator space is completely spanned by \( 16j^2 \) independent operators. Note that the tensor operator \( [j'\times j]^{(q)} \) has \( 2q+1 \) independent operators \( [j'\times j]^{(q)} \) for \( q = 0, \pm 1, \ldots \). In particular, the operators \( [j \times j]^{(0)}, [j \times j]^{(1)}, \ldots [j \times j]^{(2j)} \) can be formed for each level \( j \), producing \( (2j+1)^2 \) independent operators. Similarly the \( j-1 \) level can be described in terms of \( (2j-1)^2 \) operators of the form \( [j-1 \times j-1]^{(0)}, [j-1 \times j-1]^{(1)}, \ldots [j-1 \times j-1]^{(2j-2)} \).

The remaining \( 16j^2 - (2j+1)^2 - (2j-1)^2 = 2(4j^2 - 1) \) operators are formed with the off diagonal pairs \( [j \times j-1]^{(q)}, [j-1 \times j]^{(q)} \) running from \( [j \times j-1]^{(1)}, \ldots [j \times j-1]^{(2j-1)} \). As an example of these considerations, [see also chapter VI] the \( j=1 \) case of figure 7a is spanned by the operator basis \( [0 \times 0]^{(0)}, [j \times j]^{(0)}, [1 \times 1]^{(1)}, [1 \times 1]^{(2)} \) plus \( [1 \times 0]^{(1)}, [0 \times 1]^{(1)} \).

It is easily verified that this list contains 16 independent operators, as it should.

Associated with this basis of the operator space for the two level system, there are rate equations for the four types of tensor operators \( [j \times j]^{(q)}, [j-1 \times j-1]^{(q)} \),
These equations are obtained by specializing equations (4.13) and (4.16) to the two level situation. These results are

\[(5.3) \quad \frac{\partial}{\partial t} \langle[j] < j] (q) = \]

\[-i\hbar \langle[j] < j] (q) |R| \langle[j] < j] (q) > \circ \langle[j] < j] (q) > \]

\[-\langle[j] < j] (q) >_{eq} - i\hbar \langle[j] < j] (q) |R| \langle[j-1] < j-1] (q) > \circ \]

\langle[j-1] < j-1] (q) > - \langle[j-1] < j-1] (q) >_{eq} \]

\[-\sum_{q_2} \frac{1}{2} (2q_2+1) \frac{1}{2} (2q_2+1) \frac{1}{2} \langle j| \mu | j-1 > \]

\[V(1+q_2) \langle[-1] < j] (q_2) > \frac{-1}{q_2+q_2+1} \]

\[+\sum_{q_2} \frac{1}{2} (2q_2+1) \frac{1}{2} (2q_2+1) \frac{1}{2} \langle j-1| \mu | j > \]

\[V(q_2+q_2+1) <[j] < j-1] (q_2) > \circ (-1)^{q_2+q_2+1} \]

and
\[ (5.4) \quad \frac{\partial}{\partial t} [\langle j-1\rangle\langle j-1\rangle]^{(q)} = \]

\[ -\frac{i}{\hbar} [\langle j-1\rangle\langle j-1\rangle]^{(q)} |R| [\langle j-1\rangle\langle j-1\rangle]^{(q)} \Rightarrow_0 \]

\[ (\langle j-1\rangle\langle j-1\rangle]^{(q)} - (\langle j-1\rangle\langle j-1\rangle]^{(q)} \Rightarrow_{eq} \]

\[ -\frac{i}{\hbar} [\langle j-1\rangle\langle j-1\rangle]^{(q)} |R| [\langle j\rangle\langle j\rangle]^{(q)} \Rightarrow_0 (\langle j\rangle\langle j\rangle]^{(q)} - \]

\[ [\langle j\rangle\langle j\rangle]^{(q)} \Rightarrow_{eq} - \sum_{q_2} i^{q+q_2} (2q+1)^{1/2} (2q_2+1)^{1/2} \]

\[ <j-1||\mu||j>^* \{ \begin{array}{c} q_2^1 \ q_2^2 \\ j \ j-1 \ j-1 \end{array} \} v(q_2q_2) (\cdot)^{1+q_2} \Rightarrow_0 \]

\[ [\langle j\rangle\langle j-1\rangle]^{(q_2)} (-1)^{q+q_2+1} + \sum_{q_2} i^{q+q_2} (2q+1)^{1/2} \]

\[ (2q_2+1)^{1/2} <j||\mu||j-1>^* \{ \begin{array}{c} q_1^1 \ q_2^2 \\ j \ j-1 \ j-1 \end{array} \} v(q_1q_2) (\cdot)^{1+q_2} \]

\[ [\langle j-1\rangle\langle j\rangle]^{(q_2)} \Rightarrow_0 (-1)^{q+q_2+1} \]

for the "diagonal" tensor operators while
\[
(5.5) \quad i\hbar \frac{\partial}{\partial t} \langle \langle j|j-1 \rangle \rangle (q) = -\hbar \Delta \omega \langle \langle j|j-1 \rangle \rangle (q) \\
- \hbar \langle \langle j|j-1 \rangle \rangle (q) \mathcal{R} \langle \langle j|j-1 \rangle \rangle (q) * \langle \langle j|j-1 \rangle \rangle (q) \\
+ \sum_{q_2} i^{q+q_2} (2q+1)^{1/2} (2q_2+1)^{1/2} \langle \langle j||j-1 \rangle * \{ q \ 1 \ q \}_{j-1 \ j-1 \ j} \\
(V(qq_2))(\cdot)^{q+q_2+1} \mathcal{E}_o \langle \langle j-1|j-1 \rangle (q_2) \rangle (-1)^{q+q_2+1} \\
= \sum_{q_2} i^{q+q_2} (2q+1)^{1/2} (2q_2+1)^{1/2} \langle \langle j||j-1 \rangle * \{ q \ q_2 \ 1 \}_{j \ j-1 \ j} \\
V(qlq_2)(\cdot)^{q_2+1} \langle \langle j|j \rangle (q_2) \rangle \mathcal{E}_o (-1)^{q+q_2+1}
\]

and

\[
(5.6) \quad i\hbar \frac{\partial}{\partial t} \langle \langle j-1|j \rangle \rangle (q) = +\hbar \Delta \omega \langle \langle j-1|j \rangle \rangle (q) \\
- \hbar \langle \langle j-1|j \rangle \rangle (q) \mathcal{R} \langle \langle j-1|j \rangle \rangle (q) * \langle \langle j-1|j \rangle \rangle (q) \\
+ \sum_{q_2} i^{q+q_2} (2q+1)^{1/2} (2q_2+1)^{1/2} \langle \langle j||j \rangle * \{ q \ q_2 \ 1 \}_{j \ j-1 \ j} \\
(V(qq_2))(\cdot)^{q+q_2+1} \mathcal{E}_o \langle \langle j|j \rangle (q_2) \rangle (-1)^{q+q_2+1} \\
= \sum_{q_2} i^{q+q_2} (2q+1)^{1/2} (2q_2+1)^{1/2} \langle \langle j-1||j \rangle * \{ q \ q_2 \}_{j-1 \ j-1 \ j} \\
V(qlq_2)(\cdot)^{q_2+1} \langle \langle j-1|j-1 \rangle (q_2) \rangle \mathcal{E}_o (-1)^{q+q_2+1}
\]
represent the moment equations for the "off diagonal" parts. The above equations are the **exact** generalization of equation (2.19) for rotational transitions in diamagnetic diatomics or linear polyatomics. These equations describe the evolution of the **two level** (but 4j states, because of the magnetic sublevels) system compared to the **two state** system described in chapter II. For an arbitrary j, they are still too complicated and some further approximation must be contemplated. (The j=1 case is at least tractable and will be discussed in chapter VI.)

The equations for the first four moments \([j]<j\rangle^{(0)}, [j-1]<j-1\rangle^{(0)}, [j]<j-1\rangle^{(1)}\) and \([j-1]<j\rangle^{(1)}\) can be obtained directly from the above equations using the properties of the 3-j tensors \(V(qlq_2)\) (see appendix B) and the expressions for the 6-j symbols. Indeed,

\[
\begin{align*}
\frac{\partial}{\partial t} \langle [j]<j]\rangle^{(0)} &= -i\hbar \langle [j]<j]\rangle^{(0)} \mathcal{R} \langle [j]<j]\rangle^{(0)} \\
- \langle [j]<j]\rangle^{(0)} - \langle [j]<j]\rangle^{(0)}_{eq} &= -i\hbar \langle [j]<j]\rangle^{(0)} \mathcal{R} \langle [j-1]<j-1]\rangle^{(0)}_{eq} \langle [j-1]<j-1]\rangle^{(0)} \\
- \langle [j-1]<j-1]\rangle^{(0)}_{eq} &= - \frac{\mu_j^{1/2}}{(2j+1)^{1/2}} i V(011)(\cdot)^2 \\
\Ep \langle [j-1]<j]\rangle^{(1)} &= + \frac{\mu_j^{1/2}}{(2j-1)^{1/2}} i V(011)(\cdot)^2 \langle [j]<j-1]\rangle^{(1)}_{Ep}
\end{align*}
\]

and
\[
\begin{align*}
(5.8) \quad i\hbar \frac{\partial}{\partial t} \langle j-1\rangle < j-1 \rangle^{(0)} & = \\
& - i\hbar \langle j-1\rangle < j-1 \rangle^{(0)} | R | \langle j-1\rangle < j-1 \rangle^{(0)} \rangle_o \\
& \langle [j-1]\rangle < j-1 \rangle^{(0)} \rangle - \langle [j-1]\rangle < j-1 \rangle^{(0)} \rangle \rangle_{eq} \\
& - i\hbar \langle j\rangle < j \rangle^{(0)} | R | [j] < j \rangle^{(0)} \rangle_o \\
& \langle [j]\rangle < j \rangle^{(0)} \rangle - \langle [j]\rangle < j \rangle^{(0)} \rangle \rangle_{eq} - \frac{\mu_j^{1/2}}{(2j-1)^{1/2}} i V(011)(\cdot)^2 \\
& E_o \langle [j]\rangle < j-1 \rangle^{(1)} \rangle + \frac{\mu_j^{1/2}}{(2j+1)^{1/2}} i V(011)(\cdot)^2 \langle [j-1]\rangle < j \rangle^{(1)} \rangle \rangle_{E_o}
\end{align*}
\]

are the moment equations for the two diagonal polarizations
while the lowest moments which are off diagonal in "j" are
given as

\[
(5.9) \quad i\hbar \frac{\partial}{\partial t} \langle j\rangle < j-1 \rangle^{(1)} \rangle = -i\hbar \Delta \omega \langle j\rangle < j-1 \rangle^{(1)} \rangle \\
& - i\hbar \langle [j]\rangle < j-1 \rangle^{(1)} \rangle | R | [j] < j-1 \rangle^{(1)} \rangle \rangle_o \langle [j]\rangle < j-1 \rangle^{(1)} \rangle \\
& + \frac{i\mu_j^{1/2}}{(2j-1)^{1/2}} V(101) \cdot E_o \langle [j-1]\rangle < j-1 \rangle^{(0)} \rangle - \frac{i\mu_j^{1/2}}{(2j+1)^{1/2}} \\
& V(110)(\cdot) \langle [j]\rangle < j \rangle^{(0)} \rangle E_o - \left[ \frac{3(j-1)}{2j(2j-1)} \right]^{1/2} \mu_j^{1/2} V(111) \\
& (\cdot)^2 E_o \langle [j-1]\rangle < j-1 \rangle^{(1)} \rangle + \left[ \frac{3(j+1)}{2j(2j+1)} \right]^{1/2} \mu_j^{1/2} V(111)(\cdot)^2
\]
\[ <[j]<j]^{(1)}_{\tilde{E}_o} - i \frac{(2j-3)(j-1)}{(2j+1)2j(2j-1)}^{1/2} \mu_j^{1/2} V(121)(\cdot)^3 \]

\[ E_o \cdot <[j-1]<j-1]^{(2)}_{\tilde{E}_o} + i \frac{(2j+3)(j+1)}{(2j+1)2j(2j-1)}^{1/2} \mu_j^{1/2} \]

\[ V(112)(\cdot)^3 <[j]<j]^{(2)}_{\tilde{E}_o} \]

and

\[ (5.10) \quad i \hbar \frac{\partial}{\partial t} <[j-1]<j]^{(1)}_{\tilde{E}_o} = \hbar \Delta \omega <[j-1]<j]^{(1)}_{\tilde{E}_o} \]

\[ - i \hbar <[j-1]<j]^{(1)}_{\tilde{E}_o} [\mathcal{H}] [j-1]<j]^{(1)}_{\tilde{E}_o}]^{*} <[j-1]<j]^{(1)}_{\tilde{E}_o} \]

\[ + \frac{i\mu_j^{1/2}}{(2j+1)^{1/2}} V(101)(\cdot) E_o <[j]<j]^{(0)}_{\tilde{E}_o} - \frac{i\mu_j^{1/2}}{(2j-1)^{1/2}} \]

\[ V(110)(\cdot) <[j-1]<j-1]^{(0)}_{\tilde{E}_o} E_o - \frac{3(j+1)}{2j(2j+1)} \mu_j^{1/2} \]

\[ V(111)(\cdot)^2 E_o <[j]<j]^{(1)}_{\tilde{E}_o} + \frac{3(j-1)}{2j(2j-1)}^{1/2} \mu_j^{1/2} V(111)(\cdot)^2 \]

\[ <[j-1]<j-1]^{(1)}_{\tilde{E}_o} - i \frac{(2j+3)(j+1)}{(2j+1)2j(2j-1)}^{1/2} \mu_j^{1/2} \]

\[ V(121)(\cdot)^3 E_o <[j]<j]^{(2)}_{\tilde{E}_o} + i \frac{(2j-3)(j-1)}{(2j+1)(2j)(2j-1)}^{1/2} \mu_j^{1/2} \]

\[ V(112)(\cdot)^3 <[j-1]<j-1]^{(2)}_{\tilde{E}_o} \]
In equations (5.7) through (5.10), the relation

\[ (5.11) \quad <j||\mu||j-1> = \mu<j||\hat{r}||j-1> = \mu j^{1/2} \]

has been used which is valid for diamagnetic diatomics and linear polyatomics.

The first thing to notice about equations (5.7) through (5.10) is that they are not a closed set. That is, they involve the additional four moments \([j]<j\rangle^{(1)}, [j]<j\rangle^{(2)}, [j-1]<j-1\rangle^{(1)}\) and \([j-1]<j-1\rangle^{(2)}\). The equations of motion for these latter four moments can also be obtained from the general forms (5.3) and (5.4) but further unknown moments will be introduced at this stage as well. Indeed, the exact closure of the system of equations will not be complete until all of the moments which span the space (having a total of \(16j^2\) independent components) are introduced. Except for the simplest case \(j=1\), treated in chapter VI, the number of moments in the exact problem rapidly rises to unmanageable proportions as the quantum number \(j\) increases. Thus, some approximate scheme must be employed.

Traditional approximate methods are equivalent, in the notation of this section, to neglecting the effect of the operators \([j]<j\rangle^{(1)}, [j]<j\rangle^{(2)}, [j-1]<j-1\rangle^{(1)}\) and \([j-1]<j-1\rangle^{(2)}\) in the set of equations (5.7) through (5.10). This is discussed further in the next section. However, there appears to be no rigorous justification for this rather ad-hoc procedure for closing the system of equations.
Rather, it seems that they are neglected because no physical interpretation has been made for these effects. The present work indicates that, contrary to this opinion, these effects can be well characterized (both mathematically and physically) and should be included for a better description (and understanding) of the two level problem.

The most obvious method of describing the effect of the four operators $[j><j]^{(1)}$, $[j><j]^{(2)}$, $[j-1><j-1]^{(1)}$, and $[j-1><j-1]^{(2)}$ in an approximate manner is to extend the ad-hoc procedure one step further. Namely, include the equations of motion for these four level polarizations and truncate the system of equations at this point. Thus from the general two level equations (5.3) and (5.4), the truncated equations

\begin{equation}
\frac{i}{\hbar} \frac{\partial}{\partial t} [j><j]^{(1)} = -i \hbar [j><j]^{(1)} [\mathcal{H} [j><j]^{(1)}]_0
\end{equation}

\begin{equation}
[j><j]^{(1)} = -i \hbar [j><j]^{(1)} [\mathcal{H} [j-1><j-1]^{(1)}]_0
\end{equation}

\begin{equation}
[j-1><j-1]^{(1)} + \frac{3(j+1)}{2j(2j+1)} \mu_j^{1/2} v(111)(\cdot)^2 \varepsilon_0
\end{equation}

\begin{equation}
[j-1><j]^{(1)} = -\frac{3(j-1)}{(2j(2j+1))} \mu_j^{1/2} v(111)(\cdot)^2
\end{equation}

\begin{equation}
[j><j-1]^{(1)} \varepsilon_0
\end{equation}

and
\begin{align}
(5.13) \quad & i \hbar \frac{\partial}{\partial t} <[j] \langle j]^{(2)} > = - i \hbar <[j] \langle j]^{(2)} | \mathcal{R} | [j] \langle j]^{(2)} >_0 \\
</[j] \langle j]^{(2)} > - i \hbar <[j] \langle j]^{(2)} | \mathcal{R} | [j-1] \langle j-1]^{(2)} >_0 \\
</[j-1] \langle j-1]^{(2)} > + i [\frac{(2j+3)(j+1)}{(2j+1)2j(2j-1)}]^{1/2} \mu j^{1/2} v(211) \\
(\cdot)^2 E_o <[j-1] \langle j]^{(1)} > - i [\frac{(2j+3)(j+1)}{(2j+1)2j(2j-1)}]^{1/2} \mu j^{1/2} v(211) (\cdot)^2 <[j] \langle j-1]^{(1)} >_E_o
\end{align}

describes the possible polarizations of the upper level while

\begin{align}
(5.14) \quad & i \hbar \frac{\partial}{\partial t} <[j-1] \langle j-1]^{(1)} > = \\
- iv <[j-1] \langle j-1]^{(1)} | \mathcal{R} | [j-1] \langle j-1]^{(1)} >_0 <[j-1] \langle j-1]^{(1)} > \\
- i \hbar <[j-1] \langle j-1]^{(1)} | \mathcal{R} | [j] \langle j]^{(1)} >_0 <[j] \langle j]^{(1)} > \\
+ [\frac{3(j-1)}{2j(2j-1)}]^{1/2} \mu j^{1/2} v(111) (\cdot)^2 E_o <[j] \langle j-1]^{(1)} > \\
- [\frac{3(j-1)}{2j(2j-1)}]^{1/2} \mu j^{1/2} v(111) (\cdot)^2 <[j-1] \langle j]^{(1)} >_E_o
\end{align}

and
\[(5.15) \quad i \hbar \frac{\partial}{\partial t} <j-1|j-1|^2> = \]

\[-i\hbar <j-1|j-1|^2 \mathcal{R} <j-1|j-1|^2><j-1|j-1|^2> - i\hbar <j-1|j-1|^2 \mathcal{R} |j><j|^2><j><j|^2> + i \left[ \frac{(2j-3)(j-1)}{(2j+1)2j(2j-1)} \right]^{1/2} \mu_j^{1/2} \cdot v(211)(\cdot)^2 E_0 <j><j-1|^1> - i \left[ \frac{(2j-3)(j-1)}{(2j+1)2j(2j-1)} \right]^{1/2} \mu_j^{1/2} \cdot v(211)(\cdot)^2 <j-1|j|^1>E_0 \]

give the analogous motions associated with the lower level. Equations (5.7) through (5.10), and (5.12) through (5.15), form a closed set of equations describing the response of a two level system to an applied radiation field.

There is something to be said for closing the equation at this point. Indeed, the exact equations point out that at high incident power (large \(E_o\)) the population difference (described in terms of \([j]<j|^0\) and \([j-1]<j-1|^0\)) is changed from its equilibrium value and simultaneously, polarizations within the two rotational levels are produced. Inclusion of the above four moments would, at least approximately, take these effects into account. These effects should definitely be produced (and experimentally observable!) under steady state irradiation at high incident power. Also, the moments which are ignored by this latter ad hoc procedure, namely \([j]<j-1|^2\), \([j]<j-1|^3\), \([j-1]<j|^2\), \([j-1]<j|^3\),
begin to lose physical significance for the electric dipole problem.

One further approximate scheme has been investigated—called the large "j" approximation. That is, does the degree of coupling of these higher moments change as the pair of rotational levels considered reach higher (more classical) values of "j"? One might expect so, on physical grounds, since larger values of "j" mean a much larger range of possible "m_j" values and possible a more even distribution (i.e. no \[j\rangle\langle j\rangle^{(q)}, \[j-1\rangle\langle j-1\rangle^{(q)}\) polarizations) over these values. Unfortunately, this does not seem to be the case as a short consideration of (5.9), (5.10) or (5.14) shows. Indeed, as the large "j" limit is taken in these equations, the coupling does change slightly but ultimately comes to a "j" independent value. Thus there is no possibility that this coupling vanishes for sufficiently high "j" values. Analogous results hold for the higher moment equations for \[j\rangle\langle j\rangle^{(1)}, \[j\rangle\langle j\rangle^{(2)}, \[j-1\rangle\langle j-1\rangle^{(1)},\] and \[j-1\rangle\langle j-1\rangle^{(2)}\) as well—the coupling to additional moments becomes "j" independent at sufficiently high "j". Again, these equations are not closed, even in the large "j" limit, as the additional moments \[j\rangle\langle j-1\rangle^{(2)}, \[j\rangle\langle j-1\rangle^{(3)}, \[j-1\rangle\langle j\rangle^{(2)}\) and \[j-1\rangle\langle j\rangle^{(3)}\) still come into play. Thus at this time, there seems no real hope of satisfactorily closing the system of equations until all of the \(16j^2\) moments are included. The remaining sections of this
are therefore based on the extended ad-hoc method of approximately representing the motion of the system.
The ad hoc methods described in the last section are, in reality, moment methods applied to the spectroscopic problem. Indeed, an expansion of the distribution function $f(\mathbf{v}t)$ in the form

$$f(\mathbf{v}t) = \frac{e^{-W^2}}{(2\pi m kT)^{3/2}} \left\{ [j][j](0) [j][j](0) + [j][j](1) + 3[j][j](1) + 5[j][j](2) + [j-1][j-1](0) [j-1][j-1](0) + [j-1][j-1](1) + 3[j-1][j-1](1) + 5[j-1][j-1](2) + [j][j-1](1) + 3([j][j-1](1)^+) + [j-1][j](1) + 3([j-1][j](1)^+) \right\}$$

and subsequent substitution into equation (4.13) leads to the coupled set of moment equations (5.7) through (5.10), plus (5.12) through (5.15). The identities

$$([j][j-1](1)^+) = -[j-1][j](1)$$

$$<[j][j'][q][j'][j'''][q'''][q''']>< = \delta_{qq'} E(q) \delta_{jj''} \delta_{jj''}$$
which are discussed in appendix B, are also useful in these manipulations. If instead, a further truncation of the distribution function \( f(v_t) \) in the form

\[
(5.18) \quad f(v_t) = \frac{e^{-\frac{W^2}{kT}}}{(2\pi mkT)^{3/2}} \left\{ [j\rangle \langle j]\langle (o) \right\} \langle [j\rangle \langle j]\langle (o) \rangle \\
+ [j\rangle \langle j - 1]\langle (o) \right\} \langle [j\rangle \langle j - 1]\langle (o) \rangle \\
+ [j\rangle \langle j - 1]\langle (1) \right\} \cdot 3\langle ([j\rangle \langle j - 1]\langle (1) \rangle \right\}^\dagger \\
+ [j\rangle \langle j]\langle (1) \right\} \cdot 3\langle ([j\rangle \langle j]\langle (1) \rangle \right\}^\dagger 
\]

is substituted into (4.13), an abbreviated version of the coupled set of moment equations (5.7) through (5.10) result. Namely, the terms involving the moments of \([j\rangle \langle j]\langle (1)\), \([j\rangle \langle j - 1]\langle (1)\), \([j\rangle \langle j]\langle (2)\), and \([j\rangle \langle j - 1]\langle (2)\) are no longer present. For both expansions (5.16) and (5.18), the appropriate equilibrium distribution function is of the form

\[
(5.19) \quad f(v) = \frac{e^{-\frac{W^2}{kT}}}{(2\pi mkT)^{3/2}} \frac{e^{-\mathcal{H}_0/kT}}{Q} = \frac{e^{-\frac{W^2}{kT}}}{(2\pi mkT)^{3/2}} \\
\left\{ [j\rangle \langle j]\langle (o) \right\} \langle [j\rangle \langle j]\langle (o) \rangle \right\} \text{eq} \\
+ [j\rangle \langle j - 1]\langle (0) \right\} \langle [j\rangle \langle j - 1]\langle (0) \rangle \right\} \text{eq} 
\]
The expansions of the distribution function (5.16) or (5.18) in terms of the basis (4.10) is analogous to the expansion of the distribution function in the study of the Senftleben-Beenakker effects using the basis (3.24). In both cases, explicit details of internal state level structure are emphasized. These basis types are especially useful for any detailed collisional calculations (see chapters III and IV) and are mandatory whenever the free motion aspects are sufficiently complicated.

In the study of Senftleben-Beenakker effects, an alternate representation of internal state motions (see equation [3.27]) was found useful in interpreting results for cases in which the internal state motions were not too complicated. In particular, the discussion of the shear viscosity coefficient for \( \text{N}_2 \) given in section III-(d), employed this description. This basis type emphasized the molecular observables, for example the rotational angular momentum operator for the molecule \( J \). As such, a basis of this type allows an alternate, more physical (or at least, more classical) interpretation of the internal state motions. The range of applicability is however more limited.

Similar comments hold for the spectroscopic problem. The discussion of a two level system with the explicit neglect of the more complicated internal state motions involving \( [j><j-1]^{(2)}, [j-1><j]^{(2)}, [j><j-1]^{(3)} \) and \( [j-1><j]^{(3)} \) again allows the possibility of a more classical
"picture" of the phenomena. This is achieved through the operator transformation

\[ \Psi = -\frac{i\mu}{3^{1/2}} [\langle j|<j-1 \rangle^{(1)} + \langle j-1|<j \rangle^{(1)}] \]

\[ \Psi = \frac{\mu^{1/2}}{3^{1/2}} [\langle j|<j-1 \rangle^{(1)} - \langle j-1|<j \rangle^{(1)}] \]

\[ j = (2j+1)^{1/2} \langle j|<j \rangle^{(0)} + (2j-1)^{1/2} \langle j-1|<j-1 \rangle^{(0)} \]

\[ \Delta N = \frac{4j^2 - 1}{2j} \left\{ \frac{\langle j-1|<j-1 \rangle^{(0)}}{(2j-1)^{1/2}} - \frac{\langle j|<j \rangle^{(0)}}{(2j+1)^{1/2}} \right\} \]

\[ \gamma_{j}^{(1)} \langle j\rangle P_{j} = (2j+1)^{1/2} \langle j|<j \rangle^{(1)} \]

\[ \gamma_{j}^{(1)} \langle j\rangle P_{j-1} = (2j-1)^{1/2} \langle j-1|<j-1 \rangle^{(1)} \]

\[ \gamma_{j}^{(2)} \langle j\rangle P_{j} = (2j+1)^{1/2} \langle j|<j \rangle^{(2)} \]

\[ \gamma_{j}^{(2)} \langle j\rangle P_{j-1} = (2j-1)^{1/2} \langle j-1|<j-1 \rangle^{(2)} \]

which can be thought of as a generalization of (2.6) to the two level case. These operators are hermitian and mutually orthogonal in the inner product (4.12), that is,

\[ \langle j|\Delta N\rangle = 0, \quad \langle j|\Psi\rangle = 0 \text{ etc.} \]

and have the normalizations
Note that all normalizations have the same asymptotic behaviour in "j", namely being linear in j for large j. This is convenient if one is interested in attempting a large "j" approximation.

The distribution function \( f(\nu t) \) can alternately be expanded in this basis. The result

\[
\begin{align*}
5.22 \quad f(\nu t) &= \frac{e^{-W^2}}{(2\pi mkT)^{3/2}} \left\{ \frac{1}{4j} \langle 1 \rangle + \frac{\Delta N \Delta N >}{4j^2 - 1} \cdot \frac{2j + 1}{2j^2} \right. \\
&\quad + \frac{\bar{W} \cdot 3 \langle \bar{W} \rangle}{2j^2} + \frac{\langle y^{(1)} (J) P_j \rangle \cdot \langle y^{(1)} (J) P_j \rangle}{(2j + 1)} \\
&\left. + \frac{\langle y^{(1)} (J) P_{j-1} \rangle \cdot \langle y^{(1)} (J) P_{j-1} \rangle}{(2j - 1)} + \frac{\langle y^{(2)} (J) P_j \rangle \cdot \langle y^{(2)} (J) P_j \rangle}{(2j + 1)} \right. \\
&\quad + \frac{\langle y^{(2)} (J) P_{j-1} \rangle \cdot \langle y^{(2)} (J) P_{j-1} \rangle}{(2j - 1)}
\end{align*}
\]
is equivalent to equation (5.16) and indeed can be obtained from (5.16) using equations (5.20) and (5.21). A further truncated moment expansion for \( f(vt) \) which is equivalent to equation (5.18) takes the form

\[
(5.23) \quad f(vt) = \frac{e^{-W^2}}{(2\pi mkT)^{3/2}} \left\{ 1 \frac{<1>}{4j} + \frac{\langle \Delta N \Delta N \rangle}{(4j^2 - 1)} + \frac{\mu \cdot 3 <\mu>}{2\mu^2 j} \right. \\
+ \frac{3 <\mu>}{2\mu^2 j} \right\}.
\]

The equilibrium distribution function \( f^{(o)}(v) \) has the moment expansion

\[
(5.24) \quad f^{(o)} = \frac{e^{-W^2}}{(2\pi mkT)^{3/2}} \left\{ 1 \frac{<1> \text{ eq}}{4j} \\
+ \frac{\Delta N \Delta N}{(4j^2 - 1)} \right\}
\]

and represents the appropriate equilibrium form for either (5.22) or (5.23). In terms of the physical quantities (5.20), the moment equations take the form

\[
(5.25) \quad \frac{3}{\delta t} <1> = - \frac{<\langle 1 | R | \Delta N \rangle \theta >}{(4j^2 - 1)} (\langle \Delta N \rangle - \langle \Delta N \rangle \text{ eq}) \\
- \frac{<\langle 1 | R | 1 \rangle \theta >}{4j} (\langle 1 \rangle - \langle 1 \rangle \text{ eq})
\]
\[
\frac{\partial}{\partial t} \langle \Delta N \rangle = - \frac{2}{\hbar} 3^{1/2} V(011)(\cdot)^2 E_0 \langle \mu \rangle - \frac{\langle \Delta N \mid \mathcal{R} \mid \Delta N \rangle}{4j} (\langle \Delta N \rangle - \langle \Delta N \rangle_{\text{eq}})
\]

\[
\frac{\partial}{\partial t} \langle \mu \rangle = +\Delta \omega \langle \mu \rangle + \frac{2}{\hbar} \frac{(j-1)^{1/2}}{2j} \frac{\mu^2 j}{(2j-1)} V(111)(\cdot)^2 E_0 \langle \gamma^{(1)}(j) \rangle_{j-1} \]

\[
+ \frac{2}{\hbar} \frac{(j+1)}{2j} \frac{\mu^2 j}{(2j+1)} V(111)(\cdot)^2 E_0 \langle \gamma^{(1)}(j) \rangle_{j} \]

\[- \frac{3\langle \mu \mid \mathcal{R} \mid \mu \rangle}{2\mu^2 j} \langle \mu \rangle \]

\[
\frac{\partial}{\partial t} \langle \mu \rangle = - \Delta \omega \langle \mu \rangle + \frac{2}{3^{1/2}} \frac{\mu^2 j}{4j^2-1} V(101) E_0 \langle \Delta N \rangle
\]

\[
- \frac{2}{\hbar} \frac{(2j-3)(j-1)}{6j(2j+1)} \frac{\mu^2 j}{(2j-1)} V(121)(\cdot)^3 E_0 \langle \gamma^{(2)}(j) \rangle_{j-1} \]

\[
+ \frac{2}{\hbar} \frac{(2j+3)(j+1)}{6j(2j-1)} \frac{\mu^2 j}{(2j+1)} V(121)(\cdot)^3 E_0 \langle \gamma^{(2)}(j) \rangle_{j} \]

\[- \frac{3\langle \mu \mid \mathcal{R} \mid \mu \rangle}{2\mu^2 j} \langle \mu \rangle \]
for the first four moments, neglecting any collisional shifts.

The remaining four moment equations are

\[ \frac{\partial}{\partial t} <y^{(1)}_{j}>_P = \frac{3}{\hbar} \left( \frac{j+1}{2j} \right)^{1/2} \cdot V(111) \cdot (\cdot)^2 \cdot E_0 \cdot <y> \]

\[ \frac{\partial}{\partial t} <y^{(1)}_{j}>_j = \frac{3}{\hbar} \left( \frac{j-1}{2j} \right)^{1/2} \cdot V(111) \cdot (\cdot)^2 \cdot E_0 \cdot <y> \]
Within the context of the two level approximation as discussed in the previous section, equation (5.25) are exact while equations (5.26) are approximate (truncated) versions. If, instead, the abbreviated form (5.23) is chosen for \( f(vt) \), then equations (5.25) without the terms involving 
\[ \langle \langle (J)_{\pm} P_{j-1} | \mathcal{R} | (J)_{\pm} P_{j} \rangle \rangle \langle (J)_{\pm} P_{j} \rangle \] 
are necessary to describe the diagonal in "j" polarizations of the pair of levels, as a close examination of the free motion terms in (5.25) and (5.26) indicates. These quantities
are again more "molecular" in nature, rather than explicitly internal level dependent properties.

The collisional effects couple the various moments in alternate ways. It is possible to derive the identities

\[
\langle\Delta N | R | \Delta N \rangle_o = \left(\frac{4j^2-1}{2j}\right)^{1/2} \left[ \langle j\rangle \langle j\rangle (o) | R | [j-1]\langle j-1\rangle (o) \rangle_o \right]
\]

\[
- \left\langle \langle j\rangle \langle j\rangle (o) | R | [j-1]\langle j-1\rangle (o) \rangle_o \right\rangle
\]

\[
+ \left\langle \langle j\rangle \langle j\rangle (o) | R | [j]\langle j\rangle (o) \rangle_o \right\rangle
\]

\[
+ \left\langle \langle j\rangle \langle j\rangle (o) | R | [j]\langle j\rangle (o) \rangle_o \right\rangle (2j+1)
\]

\[
\langle 1 | R | 1 \rangle_o = (2j+1) \left[ \langle j\rangle \langle j\rangle (o) | R | [j]\langle j\rangle (o) \rangle_o \right]
\]

\[
+ (4j^2-1)^{1/2} \left[ \langle j\rangle \langle j\rangle (o) | R | [j-1]\langle j-1\rangle (o) \rangle_o \right]
\]

\[
+ (4j^2-1)^{1/2} \left[ \langle j-1\rangle \langle j-1\rangle (o) | R | [j]\langle j\rangle (o) \rangle_o \right]
\]

\[
+ (2j-1) \left[ \langle j-1\rangle \langle j-1\rangle (o) | R | [j-1]\langle j-1\rangle (o) \rangle_o \right]
\]
\[
\langle 1 | R | \Delta N \rangle_o = \left( \frac{4j^2-1}{2j} \right) \left( \frac{2j+1}{2j-1} \right)^{1/2} \langle [j-1]^{(0)} | R | [j]^{(1)} \rangle_o \]

\[
- \langle [j]^{(0)} | R | [j]^{(0)} \rangle_o
\]

\[
+ \langle [j-1]^{(0)} | R | [j-1]^{(0)} \rangle_o
\]

\[
- \left( \frac{2j+1}{2j-1} \right)^{1/2} \langle [j-1]^{(0)} | R | [j]^{(0)} \rangle_o
\]

\[
\langle \Delta N | R | 1 \rangle_o = \left( \frac{4j^2-1}{2j} \right) \left( \frac{2j+1}{2j-1} \right)^{1/2} \langle [j-1]^{(0)} | R | [j]^{(0)} \rangle_o
\]

\[
+ \langle [j-1]^{(0)} | R | [j-1]^{(0)} \rangle_o
\]

\[
- \langle [j]^{(0)} | R | [j]^{(0)} \rangle_o
\]

\[
- \left( \frac{2j+1}{2j-1} \right)^{1/2} \langle [j]^{(0)} | R | [j-1]^{(0)} \rangle_o
\]

and

\[
\langle u | R | \dot{u} \rangle_o = \langle \dot{u} | R | u \rangle_o
\]

\[
= \frac{\mu}{3} \langle [j]^{(1)} | R | [j-1]^{(1)} \rangle_o
\]

\[
+ \langle [j-1]^{(1)} | R | [j]^{(1)} \rangle_o
\]

The properties of rotational invariance, parity, and frequency conservation have been used to achieve these identifications,
as discussed in chapter IV. To simplify the description further, some of these collisional terms must be approximated—it is usual\(^3\) to set \(\langle\Delta N | \mathcal{R} | 1 \rangle \) and \(\langle 1 | \mathcal{R} | \Delta N \rangle \) equal to zero on the basis that the rate of scattering out of the upper level approximately equals the rate of scattering out of the lower level. This approximation has the effect of completely decoupling the motion of \(\langle l \rangle \) from the other equations. Finally, in equations (5.26), the collisional identifications

\[
\langle y^{(1)} \rangle_{P_j} |\mathcal{R}| y^{(1)}_{P_j} \rangle_o = (2j+1) \langle [j]<j]^{(1)} |\mathcal{R}| [j]<j]^{(1)} \rangle_o
\]

\[
\langle y^{(1)} \rangle_{P_{j-1}} |\mathcal{R}| y^{(1)}_{P_{j-1}} \rangle_o = (4j^2 - 1)^{1/2}
\]

\[
\langle [j]<j]^{(1)} |\mathcal{R}| [j-1]<j-1]^{(1)} \rangle_o
\]

\[
\langle y^{(1)} \rangle_{P_{j-1}} |\mathcal{R}| y^{(1)}_{P_{j-1}} \rangle_o = (4j^2 - 1)^{1/2}
\]

\[
\langle [j-1]<j-1]^{(1)} |\mathcal{R}| [j]<j]^{(1)} \rangle_o
\]

\[
\langle y^{(1)} \rangle_{P_{j-1}} |\mathcal{R}| y^{(1)}_{P_{j-1}} \rangle_o = (2j-1)
\]

\[
\langle [j-1]<j-1]^{(1)} |\mathcal{R}| [j-1]<j-1]^{(1)} \rangle_o
\]

plus similar results for \(y^{(2)}(j)\) have been used. In the large "\(j\)" limit where only the moments of \(\Delta^{(1)}\) and \(\Delta^{(2)}\) are present due to the free motion, it is convenient to
approximate the collisional effects by employing reasoning analogous to that used to decouple $\langle 1 \rangle$. In this limit then, an appropriate system of moment equations useful in describing the behaviour of a two level system is

\begin{equation}
\frac{\partial}{\partial t} \Delta \langle N \rangle = - \frac{2}{\hbar} 3^{1/2} V(011)(\cdot)^2 E_o \cdot \langle \mu \rangle - \frac{1}{T_1} (\Delta \langle N \rangle - \Delta \langle N \rangle_{eq})
\end{equation}

\begin{equation}
\frac{\partial}{\partial t} \langle \mu \rangle = +\Delta \omega \langle \mu \rangle + \frac{\mu^2}{2^{1/2} \hbar} V(111)(\cdot)^2 E_o \langle \Delta^{(1)} \rangle - \frac{1}{T_2} \langle \mu \rangle
\end{equation}

\begin{equation}
\frac{\partial}{\partial t} \langle \Delta^{(1)} \rangle = - \Delta \omega \langle \mu \rangle + \frac{\mu^2}{3^{1/2} \hbar} V(101) \cdot E_o \langle \Delta \langle N \rangle \rangle + \frac{\mu^2}{6^{1/2} \hbar} V(121)(\cdot)^3 E_o \langle \Delta^{(2)} \rangle
\end{equation}

\begin{equation}
\frac{\partial}{\partial t} \langle \Delta^{(2)} \rangle = \frac{1}{T_2} \langle \mu \rangle
\end{equation}

\begin{equation}
\frac{\partial}{\partial t} \langle \Delta^{(1)} \rangle = + \frac{3}{2^{1/2} \hbar} V(111)(\cdot)^2 E_o \langle \mu \rangle - \frac{1}{T_1^{(1)}} \langle \Delta^{(1)} \rangle
\end{equation}

\begin{equation}
\frac{\partial}{\partial t} \langle \Delta^{(2)} \rangle = - \frac{3^{1/2}}{2^{1/2} \hbar} V(211)(\cdot)^2 E_o \langle \mu \rangle - \frac{1}{T_1^{(2)}} \langle \Delta^{(2)} \rangle
\end{equation}

In equation (5.30), the definitions
\[ \frac{1}{T_1} = \frac{\langle \Delta N | R | \Delta N \rangle}{4j} \]

\[ \frac{1}{T_2} = \frac{3\langle \mu | R | \mu \rangle}{2\mu^2 j} = \frac{3\langle \hat{\mu} | R | \hat{\mu} \rangle}{2\mu^2 j} \]

\[ \frac{1}{T_1^{(1)}} = \frac{\langle \Delta^{(1)} | R | \Delta^{(1)} \rangle}{4j} \]

\[ \frac{1}{T_1^{(2)}} = \frac{\langle \Delta^{(2)} | R | \Delta^{(2)} \rangle}{4j} \]

have been employed.

The description to this point has emphasized the vector and tensor nature of the quantities under consideration - something which is especially useful when treating the collisional aspects of the problem. Further, this tensorial character plays an important role whenever additional static electric or magnetic fields are present. (Actually, as studies of Senftleben-Beenakker effects have shown, the treatment presented here is more applicable to the "weak" static field case. A description of the high static field effects on pressure broadening and coherence transients, on the other hand, should require an expansion of the distribution function in terms of an alternate basis set, representing an appropriate generalization of the basis \(3.31\). For
the present purpose, however, it is sufficient to illustrate how these equations describe the response of a two level system to a linearly polarized radiation field. Indeed, for this general class of experiments, each tensor quantity in (5.30) has, at most, only one component that is affected by the radiation. Thus the tensor equations (5.30) can be reduced to a coupled set of scalar equations, as is now shown.

The restriction to linearly polarized light implies that the electric field vector $E_\circ$ can be written as

$$E_\circ = e^{(1)}_\circ E_0$$

where $e^{(1)}_\circ$ is one component of the spherical basis tensors $e^{(q)}_v$ defined in appendix B. When equation (5.32) is substituted into (5.30), decoupled sets of equations result. In particular, the set containing $<\Delta N>$, of interest here, is evaluated using the relevant 3-j symbols

$$\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
1 L 0 \\
0 0 0
\end{array}
\end{array}
\end{array} = \frac{(1)}{3^{1/2}}$$

$$\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
1 L 1 \\
0 0 0
\end{array}
\end{array}
\end{array} = 0$$

$$\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
1 L 2 \\
0 0 0
\end{array}
\end{array}
\end{array} = (15)^{-1/2}$$

and is written explicitly as
\[ \frac{\partial}{\partial t} \langle \Delta N \rangle = + \frac{2}{\hbar} E_0^o \langle \mu \rangle^o - \frac{1}{T_1} \langle \Delta N \rangle_{eq} \]

\[ \frac{\partial \langle \mu \rangle^o}{\partial t} = + \Delta \omega \langle \dot{\mu} \rangle^o - \frac{1}{T_2} \langle \mu \rangle^o \]

\[ \frac{\partial \langle \dot{\mu} \rangle^o}{\partial t} = - \Delta \omega \langle \dot{\mu} \rangle^o + \frac{\mu^2}{3 \hbar} E_0^o \langle \Delta N \rangle - \frac{\mu^2}{3(10)^{1/2}} \frac{1}{\hbar} E_0^o \langle \Delta^{(2)} \rangle^o \]

\[ - \frac{1}{T_2} \langle \dot{\mu} \rangle^o \]

\[ \frac{\partial \langle \Delta^{(2)} \rangle^o}{\partial t} = - \frac{1}{(10)^{1/2}} \frac{1}{T_1} \left( \begin{array}{c} \frac{1}{2} \langle \mu \rangle^o \end{array} \right) - \frac{1}{T_1} \langle \Delta^{(2)} \rangle^o \]

The set of equations (5.34) is termed "the scalar equivalent" of equations (5.30) for linearly polarized light. Note that no component of \( \langle \Delta^{(1)} \rangle \) is affected by the radiation in this set of equations. The other sets of equations do not involve \( \langle \Delta N \rangle \) and consequently require other methods of excitation before they can be observed. These are not considered in this thesis.

In order to make connection with the work of McGurk et al., four additional transformations must be performed. The first involves the transformation of basis tensors \( e^{(q) o} \rightarrow [z]^{(q)} \) as discussed in appendix B. Indeed, with the choice of basis tensors employed up to this point, the quantities \( E_0^o \),
\(<\mu>^0\) and \(<\mu>^\circ\) are complex. The \([z]^{(q)}\) basis rectifies this inconvenience, and the exact relationships are

\[(5.35)\quad E_\circ = E_\circ^0 e_\circ^0 (1) = -iE_\circ^0 \hat{z} = E_z \hat{z} \]

\[\mu = \mu^0 e_\circ^0 (1) = -i\mu^0 \hat{z} = \mu_z \hat{z} \]

\[\mu^* = \mu^0 e_\circ^0 (1) = -i\mu^0 \hat{z} = \mu_z \hat{z} \]

\[\Delta^{(2)} = \Delta^{(2)} e_\circ^0 (2) = -\Delta^{(2)} e_\circ^0 (2) = \Delta^{(2)} \frac{\mu_z^2}{z^2} \]

Finally, the normalization of McGurk et al. is employed for the dipole moment and its conjugate, namely

\[(5.36)\quad p_r = \frac{1}{2} \mu_z \]

\[p_i = -\frac{1}{2} \mu_z \]

Applying (5.35) and (5.36) to the set of equations (5.34) gives the generalization of the two state problem to the two level case.
This completes the discussion of the two level approximation for the diamagnetic diatomic or linear polyatomic type of molecule, presented from a moment method approach. In succeeding sections, a similar description of the two level approximation for symmetric tops and inverting symmetric top molecules is given. The actual presentation is shorter, and an attempt is made to point out the differences in the various descriptions.
(d) Resonant Transitions in Symmetric Top Molecules

The electric dipole interaction of rotational levels of symmetric top molecules with radiation can be divided into two parts. This division corresponds to the separation of the electric dipole moment itself into diagonal and off-diagonal terms in the rotational quantum number. In particular, for two rotational levels "j" and "j-1" the electric dipole operator can be written as equation (5.26) and electromagnetic radiation can cause reorientation within the "j" level, reorientation within "j-1" level, or transitions between these two levels. The first two "reorientation" effects occur when light of very low (approximately zero) frequency is used to perturb the gaseous system of symmetric top molecules and comes under the general heading of Debye relaxation. A kinetic theory approach to this problem has been given by Tip and McCourt. Transitions between two rotational levels can occur when light that is approximately resonant with the energy difference of the two rotational levels under consideration. This "resonant" transition process is now discussed in detail.

As shown in figure (7b), the two level system under consideration is diagonal in "k" quantum number, since the projection of J on y is unaltered by electric dipole transitions, and consists of the two rotational levels "j" and "j-1". Thus the dimensionality of the operator space is again $16j^2$ and is spanned by the four types of operators $[jk\rangle\langle jk]_q$, $[j-1k\rangle\langle j-1k]_q$, $[jk\rangle\langle j-1k]_q$, and $[j-1k\rangle\langle jk]_q$. 
Before proceeding to the equations of motion for a selected number of these operators, a few comments on the system-radiation interaction Hamiltonian should be made. The original time-dependent interaction is of the form

\begin{equation}
\mathcal{H}_{\text{int}} = -2\mu \cdot E_0 \cos(\omega t - k \cdot r)
\end{equation}

\begin{equation}
= -2\mu_\parallel \cdot E_0 \cos(\omega t - k \cdot r) - 2\mu_\perp \cdot E_0 \cos(\omega t - k \cdot r)
\end{equation}

where the electric dipole moment operator has been split up into a part \(\mu_\parallel\) which is parallel to the angular momentum operator \(\mathbf{J}\) and a part which is perpendicular to \(\mathbf{J}\). As discussed in the introduction, this is equivalent, in the two level approximation (see also equation (5.26)), to

\begin{equation}
\mu_\parallel = \frac{-i}{3^{1/2}} \left\{ <jk|\mu|jk>[jk]<jk|^{(1)} \\
+ <j-1k|\mu|j-1k>[j-1k]<j-1k|^{(1)} \right\}
\end{equation}

and

\begin{equation}
\mu_\perp = \frac{-i}{3^{1/2}} \left\{ <jk|\mu|j-1k>[jk]<j-1k|^{(1)} \\
+ <j-1k|\mu|jk>[j-1k]<jk|^{(1)} \right\}
\end{equation}

where, for symmetric tops,
\begin{align*}
(5.41) \quad & <j\|\mu\|j'k'> = \mu \delta_{kk'} i^{j+j'+1} [(2j+1)(2j'+1)]^{1/2} \\
& (-1)^k \begin{pmatrix} j & j' \\ -k & 0 & k \\ \end{pmatrix}
\end{align*}

Then, as discussed in chapter II, the rotating wave approximation causes the diagonal part of $\mu$ to be dropped. The effective time-independent interaction in the rotating frame is therefore given as

\begin{align*}
(5.42) \quad & \mathcal{H}_{\text{int}} = -\mu \mathbf{E}_o \\
\end{align*}

With equation (5.41) as the interaction Hamiltonian, the general equations of motion can be found from (4.13), and include

\begin{align*}
(5.43) \quad & i\hbar \frac{\partial}{\partial t} <jk|\langle jk|^{(o)} = -i\hbar <\langle jk|\langle jk|^{(o)} |\mathcal{R}| |jk|\langle jk|^{(o)} >_o \\
& \langle \langle jk|\langle jk|^{(o)} - \langle \langle jk|\langle jk|^{(o)} >_{\text{eq}} \\
& \quad - i\hbar <\langle jk|\langle jk|^{(o)} |\mathcal{R}| |j-1k|\langle j-1k|^{(o)} >_o \\
& \langle \langle j-1k|\langle j-1k|^{(o)} - \langle \langle j-1k|\langle j-1k|^{(o)} >_{\text{eq}} - \frac{<jk|\mu|j-1k>^*}{(2j+1)^{1/2}} i \\
& \quad - \frac{<j-1k|\mu|jk>^*}{(2j-1)^{1/2}} i \\
V(011)(\cdot)^2 \mathbf{E}_o <[j-1k]<jk|^{(1)} > + \frac{<j-1k|\mu|jk>^*}{(2j-1)^{1/2}} i \\
& \quad - \frac{<j-1k|\mu|jk>^*}{(2j+1)^{1/2}} i \\
V(011)(\cdot)^2 <[jk]<j-1k|^{(1)} > \mathbf{E}_o
\end{align*}
and

\[ (5.44) \quad i\hbar \frac{\partial}{\partial t} \langle j-lk|j-lk\rangle^{(o)} = \]

\[ -i\hbar \langle j-lk|j-lk\rangle^{(o)} |R\rangle \langle j-lk|j-lk\rangle^{(o)} >_o \]

\[ \langle j-lk|j-lk\rangle^{(o)} > - \langle j-lk|j-lk\rangle^{(o)} >_{eq} \]

\[ -i\hbar \langle j-lk|j-lk\rangle^{(o)} |R\rangle \langle jk|jk\rangle^{(o)} >_o \]

\[ \langle jk|jk\rangle^{(o)} > - \langle jk|jk\rangle^{(o)} >_{eq} - \frac{\langle j-lk||u||jk\rangle^{*} i}{(2j-1)^{1/2}} \]

\[ V(011)(\cdot)^2 E_o \langle jk|j-lk\rangle^{(1)} > + \frac{\langle jk||u||j-lk\rangle^{*} i}{(2j+1)^{1/2}} \]

\[ V(011)(\cdot)^2 \langle j-lk|jk\rangle^{(1)} > \]

for the lowest order diagonal polarizations while

\[ (5.45) \quad i\hbar \frac{\partial}{\partial t} \langle jk|j-lk\rangle^{(1)} > = \]

\[ -i\hbar \langle jk|j-lk\rangle^{(1)} |R\rangle \langle jk|j-lk\rangle^{(1)} >_{o}^{*} \]

\[ \langle jk|j-lk\rangle^{(1)} > - \hbar \Delta \omega \langle jk|j-lk\rangle^{(1)} > \]

\[ + \frac{i\langle jk||u||j-lk\rangle^{*}}{(2j-1)^{1/2}} V(101)(\cdot) E_o \langle j-lk|j-lk\rangle^{(o)} > \]

\[ - \frac{i\langle j-lk||u||jk\rangle^{*}}{(2j-1)^{1/2}} V(110)(\cdot) \langle jk|jk\rangle^{(o)} >_{o} \]
\[ \begin{align*}
\left[ \frac{3(j-1)}{2j(2j-1)} \right]^{1/2} & <jk||j-k>* V(111)(*)^2 E_o <[j-1k]<j-1k]^{(1)} > \\
+ \left[ \frac{3(j+1)}{2j(2j+1)} \right]^{1/2} & <jk||j-k>* V(111)(*)^2 <[jk]<jk]^{(2)} > E_o \\
i \left[ \frac{(2j-3)(j-1)}{(2j+1)2j(2j-1)} \right]^{1/2} & <jk||j-k>* V(121)(*)^3 E_o <[j-1k]<j-k]^{(2)} > \\
<[j-1k]<j-k]^{(2)} > + i \left[ \frac{(2j+3)(j+1)}{(2j+1)2j(2j-1)} \right]^{1/2} & <jk||j-k>* V(112)(*)^3 E_o <[jk]<jk]^{(2)} > \\
\end{align*} \]

and

\[ \begin{align*}
(5.46) \quad \hbar \frac{\partial}{\partial \tau} & <[j-1k]<jk]^{(1)} > = \Delta \omega <[j-1k]<jk]^{(1)} > \\
-i \hbar & <[j-1]<k]^{(1)} \left[ R \right] [j-1]<k]^{(1)} >^* <[j-1k]<jk]^{(1)} > \\
+ \frac{i}{(2j+1)^{1/2}} & <j-1k||j-k>* V(101)(*) E_o <[jk]<jk]^{(0)} > \\
- \frac{i}{(2j-1)^{1/2}} & <j-1k||j-k>* V(110)(*) E_o <[j-1k]<j-1k]^{(0)} > \\
- \left[ \frac{3(j+1)}{2j(2j+1)} \right]^{1/2} & <j-1k||j-k>* V(111)(*)^2 E_o <[jk]<jk]^{(1)} > \\
+ \left[ \frac{3(j-1)}{2j(2j-1)} \right]^{1/2} & <j-1k||j-k>* V(111)(*)^2 <[j-1k]<j-1k]^{(1)} > E_o \\
i \left[ \frac{(2j+3)(j+1)}{(2j+1)2j(2j-1)} \right]^{1/2} & <j-1k||j-k>* V(121)(*)^3 E_o <[jk]<jk]^{(2)} > \\
+ i \left[ \frac{(2j-3)(j-1)}{(2j-1)(2j(2j-1))} \right]^{1/2} & <j-1k||j-k>* V(112)(*)^3 <[j-1k]<j-1k]^{(2)} > E_o \\
\end{align*} \]
represent the lowest order off-diagonal effects. The results (5.43) through (5.46) are completely analogous to the DDLP case, equations (5.7) to (5.10), in the rotating frame except that the reduced matrix element of $\mu$ used in this section is given by equation (5.40).

Again, the equations are not closed. The possible approximate schemes for closing these equations, given in connection with the DDLP case, can also be applied here. This is not done explicitly, however, since it follows directly from the previous section's work. Rather, further considerations are confined to the above non-closed set of four moment equations, in order to most concisely present the similarities and differences between the symmetric top and the previously treated cases.

Indeed, the above set of equations, (5.43) through (5.45), gives one representation of the problem. An alternate representation can be found in terms of a second, perhaps more "physical", basis. The transformation is given as:

\begin{equation}
1 = (2j+1)^{1/2} [jk]<jk>(o) + (2j-1)^{1/2} [j-lk]<j-lk>(o)
\end{equation}

\begin{equation}
\Delta N = \frac{4j^2 - 1}{2j} \left\{ \frac{[j-lk]<j-lk>(1)}{(2j-1)^{1/2}} - \frac{[jk]<jk>(o)}{(2j+1)^{1/2}} \right\}
\end{equation}

\begin{equation}
\mu_\perp = \frac{-i<j-k||u||j-lk>}{3^{1/2}} [jk]<j-lk>(1)
\end{equation}

\begin{equation}
\frac{-i}{3^{1/2}} <j-lk||u||jk>[j-lk]<jk>(1)
\end{equation}
\[
\hat{u}_1 = \frac{\langle jk|u||j-1k\rangle}{3^{1/2}} [j<k]^{(1)} - \frac{\langle j-1k|u||jk\rangle}{3^{1/2}} [j-1<k']^{(1)}
\]

\[
y^{(1)}_{Pjk} = (2j+1)^{1/2} [jk]<jk]^{(1)}
\]

\[
y^{(2)}_{Pjk} = (2j+1)^{1/2} [jk]<jk]^{(2)}
\]

\[
y^{(1)}_{Pj-1k} = (2j-1)^{1/2} [j-1k]<j-1k]^{(1)}
\]

\[
y^{(2)}_{Pj-1k} = (2j-1)^{1/2} [j-1k]<j-1k]^{(2)}
\]

In this second basis, the four moment equations (5.43) through (5.46) become

\[(5.48) \quad \frac{\partial <1>/\partial t = - \frac{\langle 1|\mathcal{R}|\Delta N\rangle_0}{4j} (\Delta N - <\Delta N>_eq + \langle 1\rangle - <1>_eq)}{(4j^2-1)}
\]

\[- \frac{\Delta <1>_1}{4j} (\Delta N - <\Delta N>_eq)
\]

\[\frac{\partial \Delta N}{\partial t} = - \frac{2}{5} \Delta^{1/2} \mathcal{V}(011)(\cdot)^2 \varepsilon_0 \frac{\langle \Delta N|\mathcal{R}|1\rangle_0}{4j} (\langle 1\rangle - <\Delta N>_eq) \]

\[- \frac{\Delta <\Delta N|\mathcal{R}|\Delta N\rangle_0}{4j^2-1} (\Delta N - <\Delta N>_eq) \]

\[- \frac{\Delta <\Delta N|\mathcal{R}|\Delta N\rangle_0}{4j^2-1} (\Delta N - <\Delta N>_eq) \]

\[- \frac{\Delta <\Delta N|\mathcal{R}|\Delta N\rangle_0}{4j^2-1} (\Delta N - <\Delta N>_eq) \]
\[
\frac{\partial \langle \mu \rangle}{\partial t} = \Delta \omega \langle \mu \rangle + \frac{2}{\hbar} (\frac{j-1}{2j})^{1/2} \frac{|\langle jk \parallel m \parallel j-1k \rangle|^2}{(2j-1)} V(111)(\parallel)^2
\]

\[
E_0 \langle \gamma_{j}^{(1)}(J)P_{j-1} \rangle + \frac{2}{\hbar} (\frac{j+1}{2j})^{1/2} \frac{|\langle jk \parallel m \parallel j-1k \rangle|^2}{(2j+1)}
\]

\[
V(111)(\parallel)^2 E_0 \langle \gamma_{j}^{(1)}(J)P_{j} \rangle - 3 \frac{\langle \mu \rangle \langle \mu \rangle^{*}}{\langle jk \parallel m \parallel j-1k \rangle|}^2
\]

\[
\frac{\partial \langle \mu \rangle}{\partial t} = - \Delta \omega \langle \mu \rangle + \frac{2}{3} \frac{j^{1/2}}{\hbar} (\frac{2j}{4j^2-1}) \frac{|\langle jk \parallel m \parallel j-1k \rangle|^2}{(2j-1)} V(101)(\parallel)
\]

\[
E_0 \langle \Delta N \rangle = \frac{2}{\hbar} \frac{(2j-3)(j-1)}{6j(2j+1)} \frac{1}{(2j-1)} \frac{|\langle jk \parallel m \parallel j-1k \rangle|^2}{(2j-1)}
\]

\[
V(121)(\parallel)^3 E_0 \langle \gamma_{j}^{(2)}(J)P_{j-1} \rangle + \frac{2}{\hbar} \frac{(2j+3)(j+1)}{6j(2j-1)} \frac{1}{(2j+1)} \frac{|\langle jk \parallel m \parallel j-1k \rangle|^2}{(2j+1)} V(121)(\parallel)^3 E_0 \langle \gamma_{j}^{(2)}(J)P_{j} \rangle
\]

\[
- 3 \frac{\langle \mu \rangle \langle \mu \rangle^{*}}{\langle jk \parallel m \parallel j-1k \rangle|}^2 \langle \mu \rangle
\]

Equation (5.48) is obviously the analog of equation (5.25).

In order to compare the symmetric top case with the two state system of chapter II and the DDLP case, a closer look at equations (5.48) is in order. As discussed in section (c), only one component of \( \mu \) (and \( \hat{\mu} \)) is excited by linearly polarized light. This allows the vector nature of the problem to be eliminated. In particular, equation (5.48) states that the polarizations \( \gamma_{j}^{(1)}(J)P_{j} \rightarrow k \) and
\( \mathcal{Y}^{(1)}_{\text{P} j-lk} \) completely decouple from the rest of the equations and so are unaffected by the application of the (linearly polarized) resonant radiation. This is not so surprising in itself, since the same effect was found in the DDLP case. (Indeed, because the rotating wave approximation effectively drops the \( y_{\mu} \) term from the interaction, see equation (5.42), the symmetric top and DDLP problems become very similar in most respects.) However, recalling equation (5.39) which effectively describes \( y_{\mu} \) in terms of the two operators \( \mathcal{Y}^{(1)}_{\text{Z} j} \) and \( \mathcal{Y}^{(1)}_{\text{P} j-lk} \), or more explicitly

\[
\mathcal{Y}^{(1)}_{\text{P} j-k} = \mathcal{Y}^{(1)}_{\text{Z} j} \quad \text{or more explicitly}
\]

\[
(5.49) \quad \mathcal{Y}^{(1)}_{\text{P} j-k} = \frac{-i}{3^{1/2}} \left( \frac{\langle jk | \mathbf{u} | jk \rangle}{(2j+1)^{1/2}} \right) \mathcal{Y}^{(1)}_{\text{Z} j} + \frac{\langle j-lk | \mathbf{u} | j-lk \rangle}{(2j-1)^{1/2}}
\]

Equations (5.48) state that \( y_{\mu} \) is unaffected by the radiation no matter how intense the source! This latter result is in direct contradiction with the two state problem, see equation (2.22), since in that case the diagonal parts of the dipole moment operator depend on the populations. The populations, of course, do change at high incident power when saturation sets in. Because of this association, the two state model should be employed with caution - even to problems for which the model is supposedly applicable. No inconsistencies of this type arise in the DDLP case since the dipole moment operator is completely off-diagonal in the "j" quantum number.
(e) Inverting Symmetric Tops and the Inversion Spectrum of NH$_3$

This section looks at a third possible relationship between $U$ and $J$, and a third type of two level system. The case under study here is a very common one in microwave spectroscopy - the inversion spectrum of ammonia.$^6,^7$

The inverting motion of the ammonia molecule is attributable to the quantum mechanical tunnelling effect wherein the nitrogen atom has the ability to tunnel through the plane of the three hydrogens and thus can exist on either side of the plane in successive instants of time. The small potential barrier slows down this (essentially vibrational) motion to the extent that it falls in the microwave region of the spectrum. In most symmetric tops like CH$_3$F or CF$_3$H, on the other hand, the potential barrier to this motion is so high that the molecules exist in one form or the other for an infinitely long time. The free motion eigenstates for the inverting molecules can then be considered as linear combinations of the free motion eigenstates of the non-inverting molecules. In particular, the identifications

$$\begin{align*}
(jk|m+\rangle &= \frac{1}{\sqrt{2}} \left[ (jk|m\rangle - (-1)^j |j-k|m\rangle \right]^{-} \\
(jk|m-\rangle &= \frac{1}{\sqrt{2}} \left[ (jk|m\rangle + (-1)^j |j-k|m\rangle \right]^{-}
\end{align*}$$

(5.50)
can be established. Equations (5.50) states that, because of the inverting motion, only the magnitude of $k$ (the projection of $J$ onto $\mathbf{p}$) remains as a good quantum number.

From equations (5.41) and (5.50), the reduced matrix element for this case is given as

\begin{equation}
(5.51) \quad \langle j | k | + | \mu | j | k | - \rangle = \mu i (-1)^{\frac{j}{2}} (2j+1)(-1)^k \left( \begin{array}{ccc}
\text{ } & j & l \\
- & | k | & 0 & | k | \\
\end{array} \right)
\end{equation}

\[= i \mu |k| \left( \frac{(2j+1)}{j(j+1)} \right)^{1/2}\]

where $\mu = <+|\mu|->$, and consideration is restricted to a single "$j$" manifold (i.e. pure inversion spectra). Finally, it is noted that because of parity, $\mathcal{I}$ is completely off-diagonal in the inversion quantum number.

The two level system to be treated in this section is therefore that shown in figure (7c). In this instance the dimensionality of the operator space is $(4j=2)^2$ and is spanned by the four types of basis operators

$[j|k|+><j|k|+]^{(q)}$, $[j|k|+><j|k|+]'^{(q)}$, $[j|k|-><j|k|-]'^{(q)}$

and $[j|k|-><j|k|-]'^{(q)}$ for every value of $q=0,...,2j$.

Again the equations of motion for all of these operators can be determined from the general equations (4.13). In particular, equations for $[j|k|+><j|k|+]^{(0)}$, $[j|k|-><j|k|-]'^{(0)}$, $[j|k|+><j|k|-]'^{(1)}$, and $[j|k|-><j|k|-]'^{(1)}$ can be established and are given as
\begin{align}
\text{(5.52) } & \quad i\hbar \frac{\partial}{\partial t} \langle [j|k|+]<j|k|+]^{(0)} \rangle = \\
& \quad -i\hbar \langle [j|k|+]<j|k|+]^{(0)} \rangle \left\langle \mathcal{R} \{ [j|k|+]<j|k|+]^{(0)} \} \right\rangle_0 \\
& \quad \langle [j|k|+]<j|k|+]^{(0)} \rangle - \langle [j|k|+]<j|k|+]^{(0)} \rangle_{eq} \\
& \quad -i\hbar \langle [j|k|+]<j|k|+]^{(0)} \rangle \left\langle \mathcal{R} \{ [j|k|-]<j|k|-]^{(0)} \} \right\rangle_0 \\
& \quad \langle [j|k|-]<j|k|-]^{(0)} \rangle - \langle [j|k|-]<j|k|-]^{(0)} \rangle_{eq} \\
& \quad + \frac{i}{(2j+1)^{1/2}} \langle [j|k|-]<j|k|-]^{(q)} \rangle - \frac{i}{(2j+1)^{1/2}} \langle [j|k|-]u \rangle [j|k|-]^{*} \\
& \quad \mathcal{V}(011)(\cdot) \langle [j|k|+]<j|k|-]^{(1)} \rangle_{eq} \\
\text{and} \\
\text{(5.55) } & \quad i\hbar \frac{\partial}{\partial t} \langle [j|k|-]<j|k|+]^{(0)} \rangle = \\
& \quad -i\hbar \langle [j|k|-]<j|k|-]^{(0)} \rangle \left\langle \mathcal{R} \{ [j|k|-]<j|k|-]^{(0)} \} \right\rangle_0 \\
& \quad \langle [j|k|-]<j|k|-]^{(0)} \rangle - \langle [j|k|-]<j|k|-]^{(0)} \rangle_{eq} \\
& \quad -i\hbar \langle [j|k|-]<j|k|-]^{(0)} \rangle \left\langle \mathcal{R} \{ [j|k|+]^{(0)} \} \right\rangle_0 \\
& \quad \langle [j|k|+]<j|k|+]^{(0)} \rangle - \langle [j|k|+]<j|k|+]^{(0)} \rangle_{eq}
\end{align}
\[+ \frac{i}{(2j+1)^{1/2}} \langle j|k|\mu|j|k|\rangle \mathbf{V}(011)(\cdot)\mathbf{E}_o\]

\[\langle [j|k|+]\langle j|k|-[1] \rangle - \frac{i}{(2j+1)^{1/2}} \langle j|k|\mu|j|k|-\rangle \mathbf{V}(011)(\cdot)\mathbf{E}_o\]

\[\mathbf{V}(011)(\cdot)^2 \langle [j|k|-]\langle j|k|+]\rangle_{1} \mathbf{E}_o\]

for the moments of rank "0" while

\[5.54 \quad \frac{\hbar}{3} \frac{3}{\partial t} \langle [j|k|+]\langle j|k|-\rangle_{1}\rangle =\]

\[-i\hbar \langle [j|k|+]\langle j|k|-\rangle_{1} \rangle \mathbf{R} \langle [j|k|+]\langle j|k|-\rangle_{1} \rangle_{o} \]

\[\langle [j|k|+]\langle j|k|-\rangle_{1} \rangle - \hbar \Delta \omega \langle [j|k|+]\langle j|k|-\rangle_{1} \rangle_{o} \]

\[+ \frac{i}{(2j+1)^{1/2}} \langle j|k|\mu|j|k|-\rangle \mathbf{V}(101)(\cdot) \mathbf{E}_o\]

\[\langle [j|k|-]\langle j|k|-\rangle \rangle_{1} \mathbf{V}(110)(\cdot) \mathbf{E}_o + \frac{1}{(2j+1)^{1/2}} \left[ \frac{3}{2j(j+1)} \right]^{1/2} \]

\[\langle j|k|\mu|j|k|-\rangle \mathbf{V}(111)(\cdot)^2 \mathbf{E}_o \langle [j|k|-]\langle j|k|-\rangle_{1} \rangle \]

\[- \frac{1}{(2j+1)^{1/2}} \left[ \frac{3}{2j(j+1)} \right]^{1/2} \langle j|k|\mu|j|k|-\rangle \mathbf{V}(111)(\cdot)^2 \]

\[\langle [j|k|+]\langle j|k|+] \rangle_{1} \mathbf{E}_o + \frac{i}{(2j+1)^{1/2}} \left[ \frac{(2j+3)(2j-1)}{2j(j+1)} \right]^{1/2} \]

\[\langle j|k|\mu|j|k|-\rangle \mathbf{V}(121)(\cdot)^3 \mathbf{E}_o \langle [j|k|-]\langle j|k|-\rangle_{2} \rangle \]
\[-\frac{i\hbar}{(2j+1)^{1/2}} \left( \frac{(2j+3)(2j-1)}{2j(j+1)} \right)^{1/2} <j|k|->\|y||j|k|->* \quad V(112) \]

\[(\cdot)^3 <[j|k|-><j|k|+]^{(2)}> \quad E_o \]

and

\[(5.55) \quad \frac{i\hbar}{\hbar} <[j|k|-><j|k|+([1])] = \]

\[-i\hbar <[j|k|-><j|k|+([1])] \quad \mathcal{R} [j|k|-><j|k|+([1])] >_o \]

\[<[j|k|-><j|k|+([1])] > + \hbar \Delta \omega <[j|k|-><j|k|+([1])] > \]

\[+ \frac{i}{(2j+1)^{1/2}} <j|k|->\|y||j|k|->* \quad V(101) (\cdot) \quad E_o \]

\[<[j|k|+><j|k|+]^{(0)}> - \frac{i}{(2j+1)^{1/2}} <j|k|+\|y||j|k|->* \]

\[V(110) (\cdot) <[j|k|-><j|k|-([0])] > E_o + \frac{1}{(2j+1)^{1/2}} \left[ \frac{3}{2j(j+1)} \right]^{1/2} \]

\[<[j|k|->\|y||j|k|->* \quad V(111) (\cdot)^2 E_o <[j|k|+><j|k|+]^{(1)}> \]

\[- \frac{1}{(2j+1)^{1/2}} \left[ \frac{3}{2j(j+1)} \right]^{1/2} <j|k|+\|y||j|k|->* \quad V(111) (\cdot)^2 \]

\[<[j|k|-><j|k|-([1])] > + \frac{i}{(2j+1)^{1/2}} \left[ \frac{(2j+3)(2j-1)}{2j(j+1)} \right]^{1/2} \]

\[<[j|k|->\|y||j|k|->* \quad V(121) (\cdot)^3 E_o <[j|k|+><j|k|-([2])] > \]

\[- \frac{i}{(2j+1)^{1/2}} \left[ \frac{(2j+3)(2j-1)}{2j(j+1)} \right]^{1/2} <j|k|+\|y||j|k|->* \]
\[ v(112)(\cdot)^3 <[j|k|-><j|k|-(2)>_E >_0 \]

are the equations for the next two moments of interest.

The set of equations (5.52) through (5.55) are obviously analogous to the sets (5.7) to (5.10) and (5.43) through (5.46) obtained in the previous sections. The remarks made there are also pertinent to this case. In particular, a transformation of operators

\[ (5.56) \quad l = (2j+1)^{1/2} \{ [j|k|-><j|k|-]^{(0)} + [j|k|+><j|k|+]^{(0)} \} \]

\[ \Delta N = (2j+1)^{1/2} \{ [j|k|-><j|k|-]^{(0)} - [j|k|+><j|k|+]^{(0)} \} \]

\[ \mu = |k| \left( \frac{(2j+1)}{3j(j+1)} \right)^{1/2} \left\{ \mu [j|k|><j|k|]^{(1)} + \mu [j|k|-><j|k|+]^{(1)} \right\} \]

\[ \bar{\mu} = |k| \left( \frac{(2j+1)}{3j(j+1)} \right)^{1/2} i \left\{ \mu [j|k|><j|k|-]^{(1)} - \mu [j|k|-><j|k|+]^{(1)} \right\} \]

e tc.

can be made to recast the above set of equations into an alternate form, although this is not done here explicitly.

Before leaving the discussion of the ammonia inversion spectra, attention is drawn to a feature peculiar to this
The inversion transition in NH$_3$ is unique in the sense that motions involved in the electric dipole transition between the states $|+\rangle$ and $|->$ is completely separate from the rotational effects due to the presence of magnetic sub-levels. All other cases discussed in this chapter involve electric dipole transitions between rotational levels and as a consequence the two effects are intimately mixed. The separation of effects in the ammonia problem allows the four types of operators $[j|k|+><j|k|+]^{(q)}$, $[j|k|+><j|k|-]^{(q)}$, $[j|k|-><j|k|+]^{(q)}$ and $[j|k|-><j|k|-]^{(q)}$ to be compactly represented as a matrix of operators

$$Y^{(q)}_{(J^P_{j|k|})}^{(2j+1)} = \left( \begin{array}{cc} |+><+| & |+><-| \\ |-><+| & |-><-| \end{array} \right)$$

for each value of $q=0,1,\ldots,2j$. Here $\otimes$ denotes a direct product. Then all possible effects for this two level system are described in terms of a direct product of possible rotational effects with possible two state effects. In particular, the set of equations (5.52) to (5.55) show that the particular operators

$$Y^{(o)}_{(J^P_{j|k|})}^{(2j+1)} = \left( \begin{array}{c} |+><+| \\ |-><+| \end{array} \right), \quad Y^{(o)}_{(J^P_{j|k|})}^{(2j+1)} = \left( \begin{array}{c} |+><-| \\ |-><+| \end{array} \right), \quad Y^{(1)}_{(J^P_{j|k|})}^{(2j+1)} = \left( \begin{array}{c} |-><-| \\ |+><+| \end{array} \right),$$

and $Y^{(o)}_{(J|k|)}^{(2j+1)}$ are of direct concern in the two level problem but other operators such as
\[ \psi^{(1)}_{(2j+1)} | \psi^{+,-} \rangle \otimes | \psi^{+,-} \rangle \text{ and } \psi^{(2)}_{(2j+1)} | \psi^{+,-} \rangle \otimes | \psi^{+,-} \rangle \text{ are not affected by linearly polarized radiation. From this point of view, one might say that the two state approximation of chapter II incorrectly considers that the four operators } \\
\begin{equation}
(5.58) \psi^{(0)}_{(2j+1)} | \psi^{+,-} \rangle \otimes 
\begin{pmatrix}
|+++\rangle \\
|+-+\rangle \\
|++--\rangle
\end{pmatrix}
\end{equation}
\]
describe the evolution of the system. The direct product approach for the description of \( \psi \) might also prove useful in separating the effects of reorienting versus phase changing collisions in expressions for \( \frac{1}{T^2} \).
(f) Summary

This chapter has shown that a rigorous approach to the two level problem requires consideration of orientational polarizations of each of the levels at high incident powers, in addition to the overall population change (saturation effects) of the pair of levels. This is a general conclusion, valid for each of the three molecular systems discussed, and some experimental manifestations of these orientational phenomena should be observable, if looked for. Liu and Marcus\textsuperscript{3} appear to be the only other workers who have recognized that additional effects are possible due to the presence of magnetic degeneracy, although their preliminary estimates seem to indicate that such effects are small. The present chapter has gone further by identifying the exact nature of these added effects and indeed, has shown that they are analogous to internal state polarizations found in the study of Senftleben-Beenakker effects.

In the next chapter, further consideration is given to these orientational polarizations in the particular case of the j=0—j=1 transitions of DDLP molecules, where an "exact" treatment is possible. Estimates of relaxation times indicate, for this case at least, that these effects are significant.
CHAPTER VI

The \( j=0 \leftrightarrow j=1 \) Case for DDLP

"I don't see," said the Caterpillar.
"I'm afraid I can't put it more clearly," Alice replied very politely, "for I can't understand it myself, to begin with."
(a) Introduction

In contrast to the three cases treated in the last chapter, the \( j=0 \leftrightarrow j=1 \) microwave transition for diatomics and linear polyatomics represents a situation for which no approximate decoupling scheme is necessary because of the small dimensionality of the problem within the two level approximation. That is, a complete description of this system can be given in terms of the moments \([0]<0>^{(0)}, [1]<1>^{(0)}, [1]<1>^{(1)}, [1]<1>^{(2)}, [1]<0>^{(0)}, \) and \([0]<1>^{(1)}\).

(Technically, a simplifying assumption regarding the collisional motion of \([0]<0>^{(0)} + \frac{1}{3}[1]<1>^{(0)}\) is actually employed in this chapter, see equation (6.18)). The \( j=0 \leftrightarrow j=1 \) problem is treated in some detail with an emphasis placed on the physical interpretation of the various phenomena involved and in particular, how the reorientation effects are included in the response of the system. A thorough understanding of this example should also provide a greater appreciation of the general two level problem. Finally, the format of this chapter parallels that of chapter II to a large extent, in order that the two level and two state approaches can be most easily contrasted.

The contents of this chapter are as follows. First, the vector and scalar forms of the equations of motion are presented as a particular case of the results of the last chapter, although an alternate method is employed for their derivation. The general remarks of chapter IV on collisions
are specialized to allow a DNBA calculation of the relaxation rates involved, for several forms of the intermolecular potential. Steady state and transient solutions to the two level equations of motion are then established, in order to compare the results with the simpler two state theory of chapter II. A discussion of the physical interpretations allowed by the two level model completes this chapter.
The general situation for rotational transitions \( j-1 \rightarrow j \) in diamagnetic diatomics and linear polyatomics has been presented in chapter V, sections (b) and (c). There the dimensionality of the operator space was shown to be \( 16j^2 \).

Obviously, the simplest case to be treated is \( j=1 \), wherein the tensor operators \([0><0]^{(0)}\), \([1><1]^{(0)}\), \([1><1]^{(1)}\), \([1><1]^{(2)}\), \([1><0]^{(1)}\) and \([0><1]^{(1)}\) are sufficient to span the complete space. The equations of motion for these operators are then special cases of equations (5.7) through (5.10), plus equations (5.12) through (5.15). In fact, the treatment and comments employed in sections (b) and (c) are again applicable, including the transformation (5.20) from one basis set of operators to a second set and the ensuing moment equations for these operators. (Obviously, however, the large "\( j \)" limit discussed in chapter V has no relevance here.) But rather than pursuing this approach, an alternate, more concise derivation of the appropriate moment equations is given in this section. By so doing, the vector nature of the problem is emphasized further. The equations obtained by either method are identical.

Within the context of a two level \((j=0 \leftrightarrow j=1)\) approximation, the distribution function \( f \) is expanded in a complete orthogonal set of operators as
\[
(f) = \frac{e^{-\frac{W^2}{2(2\pi m \kappa T)^{3/2}}}}{(2\pi m \kappa T)^{3/2}} \left\{ \frac{1<1>}{4} + \frac{\Delta N<\Delta N>}{3} + \frac{\mu \cdot 3<\mu>}{2\mu^2} + \frac{\gamma^\prime_1(J) \cdot \gamma^\prime_1(J)}{3} + \frac{\gamma^\prime_2(J) \cdot \gamma^\prime_2(J)}{3} \right\}
\]

where

\[
(6.2) \quad l = p_o + p_1
\]

\[
\Delta N = \frac{3}{2}(p_o - \frac{1}{3}p_1)
\]

\[
\mu = p_o \mu p_o + p_1 \mu p_1
\]

\[
\tilde{\mu} = i(p_i \mu p_o - p_o \mu p_1)
\]

\[
\gamma^{(1)}(J) = \gamma^{(1)}(J)p_1
\]

\[
\gamma^{(2)}(J) = \gamma^{(2)}(J)p_1
\]

and
\[<<1|1>> = 4\]
\[<<\Delta N|\Delta N>> = 3\]
\[<<\mu|\mu>> = 2\mu^2\]
\[<<\mu|\mu>> = 2\mu^2\]
\[<<y^{(1)}(j) \cdot y^{(1)}(j)>> = 9\]
\[<<y^{(2)}(j) : y^{(2)}(j)>> = 15\]

Here \(P_0\) and \(P_1\) are the projection operators for the \(j=0\) and \(j=1\) levels, respectively. The equilibrium distribution function is given in this basis as

\[(6.4) \quad f^{(o)} = \frac{e^{-\frac{W^2}{2(2\pi m^p T)^{3/2}}}}{\{1<<1>_{eq} + \Delta N<<\Delta N>_{eq}\}}\]

As described by equation (4.9), the distribution function satisfies, in the rotating frame, an equation of the form

\[(6.5) \quad i\hbar \frac{\partial f}{\partial t} = [\mathcal{H}_{eff}, f] - i\hbar f^{(o)}_{tr}[((f^{(o)}_{tr})^{-1}(f-f^{(o)}))\]

where, for this molecular system,
In order to obtain the moment equations from (6.1) and (6.5), various commutators must be evaluated. In particular, it is trivial to show that

\begin{equation}
[P_{\mu}, R_{\mu}] = -i\mu
\end{equation}

\begin{equation}
[P_{\mu}, R_{\mu}] = i\mu
\end{equation}

\begin{equation}
[P_{\mu}A] = 0 \quad \text{for } A \neq \mu, \bar{\mu}
\end{equation}

\begin{equation}
[\mu, \Delta N] = -2i\mu
\end{equation}

\begin{equation}
[\mu, 1] = 0
\end{equation}

The remaining commutators require a more detailed analysis.

For this purpose, the useful identity

\begin{equation}
P_{j} \bar{P}_{j} P_{j} = \sum_{q=0,1,2} (-i)^q (2q+1)^{1/2} \bar{v}(11q)(\cdot)
\end{equation}

The symbol $v$ is defined as

\begin{equation}
v^{(q)}_{(j)}_{(j')} = \frac{1}{(2j+1)(2j'+1)} \begin{pmatrix}
1 & 1 & 1 \\
0 & 0 & 0 \\
q & q & q
\end{pmatrix}
\end{equation}
plays an important role. Equation (6.8) can then be specialized to give

\begin{equation}
(6.9) \quad \mathbf{P}_{Q \sim 1 \sim o} \mathbf{P}_{o \sim 1 \sim o} = \frac{\mu^2}{3^{1/2}} \mathbf{V}(110) \mathbf{P}_o
\end{equation}

\begin{equation}
\mathbf{P}_{1 \sim o \sim 1 \sim o} = \frac{\mu^2}{3^{1/2}} \mathbf{V}(110) \frac{P_1}{3} + \mu^2 i \mathbf{V}(111)(\cdot) \frac{\gamma^{(1)}_3(J)P_1}{3}
\end{equation}

\begin{equation}
- \mu^2 \frac{(5/3)^{1/2}}{3} \mathbf{V}(112)(\cdot) \frac{2}{3} \gamma^{(2)}_3(J)P_1
\end{equation}

From equation (6.9), the two commutators

\begin{equation}
(6.10) \quad [\mathbf{H}, \mathbf{H}] = i[\mathbf{P}_{o \sim 1 \sim o} \mathbf{P}_{o \sim 1 \sim o} - \mathbf{P}_{1 \sim o \sim 1 \sim o} + (\mathbf{P}_{1 \sim o \sim 1 \sim o})^t]
\end{equation}

\begin{equation}
= \frac{4\mu^2 i}{v^3} \mathbf{V}(110) \frac{\Delta N}{3} + 2i\mu^2 (\frac{5}{3})^{1/2} \mathbf{V}(112)(\cdot) \frac{2}{3} \gamma^{(2)}_3(J)
\end{equation}

\begin{equation}
[\mathbf{H}, \mathbf{H}] = \mathbf{P}_{o \sim 1 \sim o} \mathbf{P}_{o \sim 1 \sim o} - (\mathbf{P}_{o \sim 1 \sim o})^t + \mathbf{P}_{1 \sim o \sim 1 \sim o}
\end{equation}

\begin{equation}
- \mathbf{P}_{1 \sim o \sim 1 \sim o}^t
\end{equation}

\begin{equation}
= 2\mu^2 i \mathbf{V}(111) \gamma^{(1)}_3(J)
\end{equation}
follow directly. To evaluate the remaining two commutators, the coefficients $\alpha_q$ and $\beta_q$ in

\[(6.11) \quad [\mu, \gamma^{(q)}(\tilde{\gamma})] = \alpha_q V(lq1)(\cdot)\mu + \beta_q V(lq1) \cdot \tilde{\mu} \quad \text{for } q=1,2\]

must be established. Equation (6.9) can be used to this end, as well. Indeed, $\alpha_q$ is evaluated from equation (6.11) by multiplying by $\tilde{\mu}$ and taking the trace

\[(6.12) \quad \text{tr} \{\tilde{\mu} [\mu, \gamma^{(q)}(\tilde{\gamma})] \} = \text{tr} \{[\mu, \tilde{\mu}] \gamma^{(q)}(\tilde{\gamma}) \} = \alpha_q V(lq1) \cdot \text{tr} \{\mu \tilde{\mu}\}\]

which implies

\[(6.13) \quad \alpha_q = 3i\delta_{q,1}.\]

Analogously, $\mu$ times equation (6.11) and subsequent tracing yields

\[(6.14) \quad \text{tr} \{\mu [\mu, \gamma^{(q)}(\tilde{\gamma})] \} = \text{tr} \{[\mu, \mu] \gamma^{(q)}(\tilde{\gamma}) \} = \beta_q V(lq1) \cdot \text{tr} \{\mu \mu\}\]
and the eventual identification

\[ (6.15) \quad \beta_q = -i/15 \delta_{q,2} \]

results. The orthogonality and normalizations (equation (6.3)) of the various operators were also used in arriving at equations (6.13) and (6.15). The remaining commutators of interest are therefore

\[ (6.16) \quad [\mu, \mathcal{U}^{(1)}(J)] = 3i \, V(111) \cdot \mu \]

\[ [\mu, \mathcal{U}^{(2)}(J)] = -\sqrt{15} \, V(121) \cdot \mu \]

The moment equations are now readily obtained by substitution of the form (6.1) into equation (6.5) using the commutation relations (6.7), (6.10) and (6.16). The result is a set of five coupled equations

\[ (6.17) \quad \frac{\partial}{\partial t} \langle AN \rangle + \frac{2}{\hbar \omega_0} \langle \dot{\mu} \rangle + \frac{\langle \langle AN | R | AN \rangle \rangle_0}{4} (\langle AN \rangle - \langle AN \rangle_{eq}) = 0 \]

\[ \frac{\partial}{\partial t} \langle \mathcal{U}^{(2)}(J) \rangle + \frac{\sqrt{15}}{\hbar} \, E_0 \cdot V(121) \cdot \langle \dot{\mu} \rangle + \frac{\langle \langle \mathcal{U}^{(2)}(J) | R | \mathcal{U}^{(2)}(J) \rangle \rangle_0}{3} \]

\[ \langle \mathcal{U}^{(2)}(J) \rangle = 0 \]
Here, the sixth moment equation involving \( \langle 1 \rangle \) has been decoupled and ignored, by employing the collisional approximation

\[
\langle 1 \rangle = 0
\]

Equations (6.17) are the counterparts to equations (5.30) obtained in the last chapter. In particular, the same types of effects that were noted in the last chapter occur here as well—only the relative magnitudes of the couplings have changed, since they are actually "j" dependent.

The methods presented here can also be generalized to provide an alternate, more direct derivation of the moment equations obtained in the last chapter. The identity (6.8) is particularly useful in this regard. However, dimensional
considerations and the use of the basis $\langle j' \mid j \rangle^{(q)}$ allow a more complete view of the general problem, especially in regards to what information is lost by a truncated expansion and in the treatment of the collision aspects. In summary then, both derivations have their own merits and so both have been presented in this thesis.

The scalar forms of equation (6.17) for linearly polarized incident radiation follow from the comments presented in chapter V, section (c). Indeed, employing equations (5.33), (5.35) and (5.36), the scalar equations of interest become

\begin{equation}
\frac{\partial}{\partial t} \frac{\hbar \Delta N}{4} - E_z p_i + \frac{1}{T_1} (\langle \hbar \Delta N \rangle - \langle \hbar \Delta N \rangle_{eq}) = 0
\end{equation}

\begin{equation}
\frac{\partial}{\partial t} \frac{\hbar Y_{2z}^{(2)} (J)}{2} - E_z p_i + \frac{1}{T_p} \frac{\hbar Y_{2z}^{(2)} (J)}{2} = 0
\end{equation}

\begin{equation}
\frac{\partial}{\partial t} r + \Delta \omega p_i + \frac{1}{T_2} r = 0
\end{equation}

\begin{equation}
\frac{\partial}{\partial t} r - \Delta \omega p_i + \frac{8 \mu^2}{9 \hbar^2} E_z \langle \hbar \Delta N \rangle + \frac{2 \mu^2}{9 \hbar^2} E_z \langle \hbar Y_{2z}^{(2)} (J) \rangle
\end{equation}

\begin{equation}
+ \frac{1}{T_2} p_i = 0
\end{equation}

where the relaxation rates have been identified as
Equations (6.19) and (6.20) are the fundamental equations governing the \( j=0 \leftrightarrow j=1 \) transition in diamagnetic diatomics and linear polyatomics. In addition to the three expectation values usually employed in the description of the two state system (see chapter II), a fourth scalar moment has appeared which can be directly traced to the consideration of the magnetic states of the upper level. These equations represent the simplest example of the difference between the two state and two level approaches. The collisional aspects will be explored further in section (c) while subsequent sections will deal with various solutions of these equations.
(c) Collision Integrals

This section illustrates how the DWBA expressions, derived in chapter IV for a general internal state collisional integral, can be specialized to the evaluation of the collision integrals of interest here, equations (6.20). In so doing, estimates of these collision integrals are obtained for several assumed forms of the intermolecular potentials.

The starting point is equations (4.42) and (4.43) of chapter IV which, for DDLP can be rewritten as

\[
\begin{align*}
\left< j_i \left| j'_f \right| (q) \right| \left< j'_i \left| j'_f \right| (q) \right> &= \frac{\exp\left(- \frac{1}{2} (e - e_{j'_f} - e_{j'_i}) \right) (-1)^{q+\lambda_1+j_f+j_i}}{(2\lambda_1+1)^{1/2}} I_{\lambda_2}^{j_i j_i \lambda_1} \\
\exp\left(- \frac{1}{2} (e - e_{j'_f} - e_{j'_i}) \right) \frac{1}{2} \frac{\left< j_i \left| \Omega_1^{(\lambda_1)} \right| j'_i \right| \left< j'_i \left| \Omega_1^{(\lambda_1)} \right| j'_f \right>}{(2j_i+1)(2\lambda_1+1)} + \delta(j_i j_f | j'_i j'_f) \sum_j \\
\exp\left(- \frac{1}{2} (e - e_{j'_f} - e_{j'_i}) \right) \frac{1}{2} \frac{\left< j_i \left| \Omega_1^{(\lambda_1)} \right| j'_i \right| \left< j'_i \left| \Omega_1^{(\lambda_1)} \right| j'_f \right>}{(2j_i+1)(2\lambda_1+1)} + \delta(j_i j_f | j'_i j'_f) \sum_j [\exp\left(- \frac{1}{2} (e - e_{j'_f} - e_{j'_i}) \right)] \\
\frac{1}{2} \frac{\left< j_i \left| \Omega_1^{(\lambda_1)} \right| j'_f \right|^2}{(2j'_f+1)(2\lambda_1+1)}
\end{align*}
\]
Here $\mathcal{G}_P^{(1)}$ is an integral involving only the translational motion, see equation (3.109), while $I'_{\mathcal{L}_{2}}$ is the associated sum over the internal states of the collision partner, namely

\[
I'_{\mathcal{L}_{2}} \equiv \sum_{j_2 j'_2} \frac{\exp[-\frac{1}{2}e_{j_2}] \exp[-\frac{1}{2}e_{j'_2}]}{\Omega} \frac{|\langle j_2 | \mathcal{O}_{\mathcal{L}_{2}}^{(1)} | j'_2 \rangle|^2}{(2\mathcal{L}_{2}+1)}.
\]

For the special case of populations, (6.21) reduces to

\[
\mathcal{G}([j<j^0] [j'<j'])_{o/\mathcal{G}_P^{(1)} (2\mathcal{L}+1)^{-1/2}} I'_{\mathcal{L}_{2}}
\]

\[
= \delta_{jj'} \sum_{j} \exp[-\frac{1}{2}(e_{j} - e_{j'})] \frac{|\langle j| \mathcal{O}_{1}^{(L1)} | j' \rangle|^2}{(2j'+1)(2\mathcal{L}_{1}+1)}
\]

\[
- \exp[-\frac{1}{2}(e_{j} - e_{j'})] \frac{|\langle j| \mathcal{O}_{1}^{(L1)} | j' \rangle|^2}{(2j+1)^{1/2}(2j'+1)^{1/2}(2\mathcal{L}_{1}+1)}
\]

which shows that only inelastic effects contribute. In the above expressions, the form of the reduced matrix element for DDLP, namely,

\[
\langle j'| \mathcal{O}' \mathcal{L}' \rangle |j'' \rangle = i^{j'+L'+j''} [2j'+1](2\mathcal{L}'+1)(2j''+1)]^{1/2}
\]

\[
\begin{pmatrix}
  j' & L' & j'' \\
  0 & 0 & 0
\end{pmatrix}
\]

is to be employed. A combination of these equations with the equations (5.28) yields
\begin{align*}
(6.25) \quad \frac{1}{T_1} &= n \left( \frac{8kT}{\pi \hbar} \right)^{1/2} \sum_\mathcal{L} (\frac{1}{2L+1})^{-1/2} \frac{4j^2-1}{4j} \\
&= \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \frac{4j}{2j-1} \begin{pmatrix} j^{-1} & 1 & j \end{pmatrix}^2 \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \frac{4j}{2j+1} \begin{pmatrix} j^{-1} & 1 & j \end{pmatrix}^2 \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \frac{2j+1}{2j-1} \begin{pmatrix} j^{-1} & 1 & j \end{pmatrix}^2 \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \frac{2j+1}{2j+1} \begin{pmatrix} j^{-1} & 1 & j \end{pmatrix}^2 \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \frac{2j+1}{2j+1} \begin{pmatrix} j^{-1} & 1 & j \end{pmatrix}^2 \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \frac{2j+1}{2j+1} \begin{pmatrix} j^{-1} & 1 & j \end{pmatrix}^2
\end{align*}

\begin{align*}
(6.26) \quad \frac{1}{T_2} &= \frac{n}{2} \left( \frac{8kT}{\pi \hbar} \right)^{1/2} \sum_\mathcal{L} (\frac{1}{2L+1})^{1/2} \frac{1}{4j} \\
&= \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \left[ \frac{(2j+1)(2j+1+1)(2j-1)(2j-L-1)}{2j} \right]^{1/2} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \left( \frac{1}{2j+1} + \sum_{j \neq j} \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \right) \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \left( \frac{1}{2j+1} + \sum_{j \neq j} \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \right) \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \left( \frac{1}{2j+1} + \sum_{j \neq j} \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \right) \\
&+ \sum_{j \neq j, j-1} \begin{pmatrix} j & 1 & j^{-1} \end{pmatrix}^2 \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \left( \frac{1}{2j+1} + \sum_{j \neq j} \exp\left[ -\frac{1}{2}(\varepsilon_j - \varepsilon_{j-1}) \right] \right)
\end{align*}
\[(6.27) \quad \frac{1}{T_p} = n \left( \frac{\hbar k T}{\pi \mu} \right)^{1/2} \sum_p \left( \begin{array}{c} 1 \\ j' \\ j'' \end{array} \right) (2j' + 1)^{-1/2} I'_{j'} \left( \begin{array}{ccc} j' & j & j'' \\ 0 & 0 & 0 \end{array} \right)^2 \]

\[\frac{(4j' + 3) 2j(j+1)(j+2) - 3[2j(j+1) - \zeta \zeta_1 \zeta_1 + 1]}{2j(j+1)(2j+3)} \]

\[+ \sum_{j \neq j'} \exp\left\{ -\frac{1}{2} (\varepsilon_j - \varepsilon_{j'}) \right\} (2j' + 1)^{j' \zeta_1 \zeta_1} \left( \begin{array}{ccc} j' & j & j'' \\ 0 & 0 & 0 \end{array} \right)^2 \].

The explicit formulas for the 6-j symbols in equation (6.21),

\[(6.28) \quad \left\{ \begin{array}{c} \zeta_1 \\ j \end{array} \right\} = \frac{(-1)^{\zeta_1}}{(2j-1) 2j(2j+1)} \]

\[\left( (2j+\zeta_1)(2j+\zeta_1+1)(2j-\zeta_1)(2j-\zeta_1-1) \right)^{1/2} \]

\[\left\{ \begin{array}{c} \zeta_1 \\ j \end{array} \right\} = (-1)^{\zeta_1} \]

\[2\left[ 3[2j(j+1) - \zeta \zeta_1 \zeta_1 + 1](2j(j+1) - \zeta \zeta_1 \zeta_1 + 1) - 4j^2(j+1)^2 \right] \]

\[\left( (2j-1) 2j(2j+1)(2j+2)(2j+3) \right)^{1/2} \]

have been used in arriving at the above formulae. For the

j=1 case of interest for this chapter, the forms for the

relaxation rates \( \frac{1}{T_1}, \frac{1}{T_2} \) and \( \frac{1}{T_p} \) simplify to
\[ (6.29) \quad \frac{1}{T_1} = \frac{3n}{4} \left( \frac{8kT}{\pi \mu} \right)^{1/2} \sum_p (2\ell + 1)^{-1/2} \{ \begin{array}{ccc} 1 & 0 & 2 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] + \frac{4}{3} \{ \begin{array}{ccc} 0 & \ell_1 & 1 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] \]

\[ \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] + \sum_{\ell \neq 0, 1} \{ \begin{array}{ccc} \ell & 0 & 1 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] \]

\[ (2\ell + 1) + \{ \begin{array}{ccc} \ell & 0 & 1 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] \frac{2\ell + 1}{3} \} \]

\[ (6.30) \quad \frac{1}{T_2} = \frac{n}{2} \left( \frac{8kT}{\pi \mu} \right)^{1/2} \sum_p (2\ell + 1)^{-1/2} \{ \begin{array}{ccc} 1 & 0 & 2 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] + \sum_{\ell \neq 0, 1} \{ \begin{array}{ccc} \ell & 0 & 1 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] \]

\[ \sum_{\ell \neq 0, 1} \{ \begin{array}{ccc} \ell & 0 & 1 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] \frac{2\ell + 1}{3} \} \]

and

\[ (6.31) \quad \frac{1}{T_p} = \frac{n}{2} \left( \frac{8kT}{\pi \mu} \right)^{1/2} \sum_p (2\ell + 1)^{-1/2} \{ \begin{array}{ccc} 1 & 0 & 2 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] + \sum_{\ell \neq 0, 1} \{ \begin{array}{ccc} \ell & 0 & 1 \\ 0 & 0 & 0 \end{array} \} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] \frac{2\ell + 1}{3} \} \]

\[ (\ell_1^4 + 2\ell_1^3 - 5\ell_1^2 - 6\ell_1 - 20) + \sum_{\ell \neq 0, 1} \exp\left[ -\frac{1}{2} (\varepsilon - \varepsilon_0) \right] (2\ell + 1) \{ \begin{array}{ccc} \ell & 0 & 1 \\ 0 & 0 & 0 \end{array} \} \]
Equations (6.29), (6.30) and (6.31) are the DWBA expressions for the relaxation rates of interest in this chapter. The 3-j symbols determine which rotational levels are collisionally coupled. As these equations indicate, if only one anisotropic potential $\langle J_1 J_2 J \rangle$, dominates all three rates are proportional to the same translational and perturber molecule factors, namely $\sum_p (2\ell+1)^{-1/2}$ and $I_1^\ell$, respectively. The three rates differ only because of the explicit expressions for the internal state factors of the "first" molecule.

The above three equations are now evaluated for four different multiple potentials - the dipole-dipole ($J_1 = J_2 = 1, J = 2$); the dipole-quadrupole ($J_1 = 1, J_2 = 2, J = 3$); the quadrupole-dipole ($J_1 = 2, J_2 = 1, J = 3$); and the quadrupole-quadrupole ($J_1 = 2, J_2 = 2, J = 4$). The summations and integrations involved are performed explicitly with the aid of one additional approximation - the high temperature approximation. For the "first molecule" parts of equations (6.29), (6.30) and (6.31), this amounts to neglecting the differences in Boltzmann weights. For the "perturber" molecule expression, $I_1^\ell$, the high temperature approximation again allows the differences in Boltzmann factors to be neglected. Indeed, from equations (6.22) and (6.24), the high temperature approximation for any multiple $J_2$ gives
where $B$ is the rotational constant. Finally, as discussed in chapter IV, the neglect of energy inelasticity (as suggested by a high temperature approximation) coupled with the assumption that the only vectorial dependence of the transition operator matrix element is associated with the direction of the momentum transfer vector, yields a modified Born approximation to the translational collision integral, equation (3.109). For a multipole form of interaction potential, the coefficients $b_{\ell_1\ell_2\ell}$ are given as

$$b_{\ell_1\ell_2\ell} = (-1)^{\ell_2} \left[ \frac{(2\ell_1+1)!}{(2\ell_1+1)! (2\ell_2+1)!} \right]^{1/2} \frac{M_{\ell_1} M_{\ell_2}}{(2\ell+1)^{1/2}}$$
where $M_1$ and $M_2$ are the multipole moments and $\mu$ is the reduced mass. A combination of (3.109) and (6.33) gives the modified Born approximation for the translational integrals

\[ (6.34) \sum_p^{(1)} (00211|00211|0) = 5^{1/2} \frac{2\pi^3 \mu}{\hbar^2 kT} \frac{D^2 Q^2}{3d^2} \]

\[ \sum_p^{(1)} (00312|00312|0) = 7^{1/2} \frac{2\pi^3 \mu}{\hbar^2 kT} \frac{D^2 Q^2}{6d^4} \]

\[ \sum_p^{(1)} (00321|00321|0) = 7^{1/2} \frac{2\pi^3 \mu}{\hbar^2 kT} \frac{Q^2 D^2}{6d^4} \]

\[ \sum_p^{(1)} (00422|00422|0) = 9^{1/2} \frac{2\pi^3 \mu}{\hbar^2 kT} \frac{Q^2 Q^2}{30d^6} \]

where $D$ is the dipole moment and $Q$ is the quadrupole moment.

Substitution of the high temperature approximations (6.32) and (6.34) into equations (6.29) through (6.31) gives estimates of the three relaxation rates for the first few multipole interactions. Indeed, in terms of the convenient quantity

\[ (6.35) \Lambda \equiv n \left( \frac{8kT}{\pi \mu} \right)^{1/2} \frac{2\pi^3 \mu}{h^2 kT} \]

the relaxation rates are
assuming the dipole-dipole potential dominates, while

\[ \frac{1}{T_1} \text{DD} = \frac{\Lambda}{2} \frac{D^2 D^2}{d^2} \]
\[ \frac{1}{T_2} \text{DD} = \frac{\Lambda}{3} \frac{D^2 D^2}{d^2} \]
\[ \frac{1}{T_p} \text{DD} = \frac{\Lambda}{3} \frac{D^2 D^2}{d^2} \]

when the dipole-quadrupole interaction is assumed. Similarly, a quadrupole-dipole interaction leads to relaxation rates

\[ \frac{1}{T_1} \text{DQ} = \frac{\Lambda}{4} \frac{D^2 Q^2}{d^4} \]
\[ \frac{1}{T_2} \text{DQ} = \frac{\Lambda}{6} \frac{D^2 Q^2}{d^4} \]
\[ \frac{1}{T_p} \text{DQ} = \frac{\Lambda}{6} \frac{D^2 Q^2}{d^4} \]

\[ \frac{1}{T_1} \text{QD} = \frac{3\Lambda}{20} \frac{Q^2 D^2}{d^4} \]
\[ \frac{1}{T_2} \text{QD} = \frac{\Lambda}{6} \frac{Q^2 D^2}{d^4} \]
\[ \frac{1}{T_p} \text{QD} = \frac{\Lambda}{6} \frac{Q^2 D^2}{d^4} \]
and a quadrupole-quadrupole interaction yields

\[(6.39) \quad \frac{1}{T_1} \Omega = \frac{21A}{100} \frac{\sigma^2 \gamma^2}{d^6}\]

\[(\frac{1}{T_2} \Omega) = \frac{7A}{30} \frac{\sigma^2 \gamma^2}{d^6}\]

\[(\frac{1}{T_p} \Omega) = \frac{7A}{30} \frac{\sigma^2 \gamma^2}{d^6}\]

for the three relaxation rates.

The above calculations demonstrate two points. First, the general DWBA results derived in chapter IV are specialized to obtain expressions for the desired internal state relaxation rates by manipulating only the internal state factors. Any of the relaxation rates introduced in chapter V can also be studied in this manner. Secondly, it is shown that for the \(j=0\) to \(j=1\) case at least, the three relaxation rates are of similar sizes, \(\frac{1}{T_1} \sim \frac{1}{T_2} \sim \frac{1}{T_p}\). In particular, the ratio \(\frac{T_2}{T_1} = 1.5\) has been established in the first two equations, (6.36) and (6.37). Here, \(\ell_1 = 1\) and the 3-j symbol describing the elastic contributions to \(\frac{1}{T_2}\), \(\frac{1}{T_1}\), vanishes identically. The ordering \(\frac{1}{T_1} > \frac{1}{T_2}\) has also been found by Liu and Marcus in those cases when elastic (and reorientation) contributions to \(\frac{1}{T_2}\) are small. Conversely, the ratio \(\frac{T_2}{T_1} = 0.9\) has been found for the remaining two cases [see equations (6.38) and (6.39)] where \(\ell_1 = 2\). In this instance, the elastic
contributions \[
\begin{pmatrix}
1 & 1 \\
0 & 0
\end{pmatrix}
\] are effective in increasing the \( \frac{1}{T_2} \) relaxation rate. This latter ordering, \( \frac{1}{T_1} \leq \frac{1}{T_2} \), is reminiscent of the one usually assumed in qualitative discussions, see equation (2.30). Indeed, the qualitative argument is also based on the importance of elastic collisions in determining the size of \( \frac{1}{T_2} \).

A "generalized strong collision model", in which

\[
(6.40) \quad \frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{T_p} = \frac{1}{T}
\]

provides a useful "idealized" situation in which the transient response of a two level system can be presented in closed form - see section (e). The calculations of the present section indicate that such a model is reasonable.
(d) Steady State Absorption and the General Transient Experiment

The equations of motion (6.19) describe the evolution of a two level system in the rotating frame. In this section, some comments on the solutions to these equations are given which require no assumptions on the relative sizes of $T_1$, $T_2$ and $T_p$. This section generalizes the discussions given in section (e) of chapter II to the two level case.

As discussed in chapter II, the traditional steady state absorption experiment corresponds to setting all time derivatives equal to zero in the equations of motion when written in the rotating frame. Thus equations (6.19) become

\begin{align*}
(6.41) \quad & -E P_I + \frac{1}{T_1} \frac{\hbar \Delta N}{4} = \frac{1}{T_1} \frac{\hbar \Delta N}{4} \text{ eq} \\
& -E P_I + \frac{1}{T_p} \frac{\hbar \gamma_{z}^{(2)} (J) }{2} = 0 \\
& \Delta \omega P_I + \frac{1}{T_2} p_I r = 0 \\
& \Delta \omega P_r + E Z \frac{8 \mu^2}{9 \hbar^2} \frac{\hbar \Delta N}{4} + E Z \frac{2 \mu^2}{9 \hbar^2} \frac{\hbar \gamma_{z}^{(2)} (J) }{2} + \frac{p_I}{T_2} = 0
\end{align*}

This set of four simultaneous equations in four unknowns is easily solved to give
Equations (2.33) are obtained from equations (6.42) in the limit $\frac{1}{T_p} >> \frac{1}{T_1}, \frac{1}{T_2}$ (i.e. when the relaxation to equal populations in the three magnetic states of the $j=1$ level is very much faster than the relaxation of the population difference between the $j=0$ and $j=1$ levels and the relaxation
of the coherences between the $j=0$ and $j=1$ levels. Also, in the low input power case where $\frac{2\mu^2}{\hbar^2} E^2 < 1$, equations (6.42) show that there is no saturation, \( <\frac{\hbar\Delta N}{4} > = <\frac{\hbar\Delta N}{4} >_{\text{eq}} \), and there is no polarization of the $j=1$ level, 
\( \frac{\hbar^2}{2} \langle 2^2 (j) \rangle \rightarrow 0 \). Finally, the observed absorption, which is proportional to $P_1$ (see equation (2.49)), "looks" the same as the two state description for any input power. This is seen from equation (6.42) by defining $T_1^{\text{off}} = T_1 + \frac{1}{4} T_p$ in the expression for $P_1$.

A general discussion of the transient solutions admitted by equations (6.19) is now given. Section (e) presents more detailed remarks on transient absorption and transient emission experiments. For ease of manipulation, the results are described in terms of the following quantities,

\begin{align*}
\alpha &= \frac{1}{k E} T_1 \\
\beta &= \frac{1}{k E} T_2 \\
M &= \frac{k}{4} <\Delta N> \\
Y &= \frac{1}{k E} T_p \\
M_0 &= \frac{k}{4} <\Delta N>_{\text{eq}} \\
\delta &= \frac{\Delta \omega}{k E} \\
Y &= \frac{k}{2} \gamma^2 \langle 2^2 (j) \rangle \\
\end{align*}

The resulting equations are now of the form

\begin{align*}
(6.43) \quad k &= 2^{1/2} \frac{2\mu}{3\hbar} \\
\alpha &= \frac{1}{k E} T_1 \\
\beta &= \frac{1}{k E} T_2 \\
M &= \frac{k}{4} <\Delta N> \\
Y &= \frac{1}{k E} T_p \\
M_0 &= \frac{k}{4} <\Delta N>_{\text{eq}} \\
\delta &= \frac{\Delta \omega}{k E} \\
Y &= \frac{k}{2} \gamma^2 \langle 2^2 (j) \rangle \\
\end{align*}
\[
\begin{align*}
\text{(6.44)} & \quad \frac{d}{d\tau} p + \beta p + \delta p_i = 0 \\
& \quad \frac{d}{d\tau} p_i + \beta p - \delta p + M + \frac{1}{4} Y = 0 \\
& \quad \frac{dM}{d\tau} + \alpha M - p_i = \alpha M_o \\
& \quad \frac{dY}{d\tau} + \gamma Y - p_i = 0
\end{align*}
\]

Written in this manner, equations (6.44) are seen to be a generalization of the form treated by Torrey\(^2\) and by McGurk et al.\(^3\) in their appendix A1.

The Laplace transform of a function \(f(\tau)\) is defined as
\[
\text{(6.45)} \quad f(u) = \int_0^\infty f(\tau) e^{-u\tau} d\tau
\]
and when applied to equations (6.44) yields the matrix equation
\[
\begin{pmatrix}
u + \beta & \delta & 0 & 0 \\
-\delta & u + \beta & 1 & \frac{1}{4} \\
0 & -1 & u + \alpha & 0 \\
0 & -1 & 0 & u + \gamma
\end{pmatrix}
\begin{pmatrix}
u - p_r \\
u - p_i \\
u - M \\
u - Y
\end{pmatrix} =
\begin{pmatrix}
u - p_r \\
u - p_i \\
u - M \\
u - Y
\end{pmatrix}
\begin{pmatrix}
\alpha M_o \\
\gamma Y_o \\
m_o u + \alpha \\
t_o
\end{pmatrix}
\]
Here \( r_o, i_o, m_o, \) and \( y_o \) are the initial values of \( P_r/M_o, P_i/M_o, M/M_o, \) and \( Y/M_o, \) respectively. The determinant of coefficients \( \Delta(u) \) in equation (6.46) is evaluated as

\[
\Delta(u) = (u+\beta)^2(u+\alpha)(u+\gamma) + (u+\beta)(u+\gamma) + \frac{1}{4}(u+\beta)(u+\alpha) + \delta^2(u+\gamma)(u+\alpha).
\]

From Cramer's rule, the solutions to equations (6.46) can then be written in the form

\[
f(u) = \frac{M_0 g(u)}{\Delta(u)}
\]

where \( f(u) \) is any one of \( P_r, P_i, M, \) and \( Y \) and \( g(u) \) is a quartic form in \( u \) which is different for each of the four quantities.

If, as proven below, it is found that the equation

\[
\Delta(u) = 0
\]

has at least two real negative roots \(-a\) and \(-b\), then the quartic form equation (6.47) can be factored as

\[
\Delta(u) = (u+a)(u+b)[(u+c)^2 + \Omega^2]
\]

and equation (6.49) can be expanded in partial fractions to give
Here, there is a different set of coefficients \( \Lambda, B, C, D \) and \( E \) for each of the four quantities \( \bar{P}_1, \bar{P}_1, \bar{M} \) and \( \bar{Y} \). The inverse Laplace transform of equation (6.51) is

\[
(6.52) \quad f(T) = A e^{-\alpha T} + B e^{-\beta T} + C e^{-\gamma T} \cos \Omega T + \frac{D}{\Omega} e^{-\gamma T} \sin \Omega T.
\]

This represents the general form of the time dependent solutions to the two level problem. Equation (6.52) is the counterpart of equation (2.34), which describes the two state case. When \( T \) relaxation is very fast, the factor \( u + \gamma \) dominates equation (6.47) and the approximate result

\[
(6.53) \quad \Delta(u) = (u + \gamma) \left[ (u + \beta)^2 (u + \alpha) + (u + \beta) + \delta^2 (u + \alpha) \right]
\]

\[
= (u + \gamma) \text{[equation (2.35)]}
\]

is obtained. Equation (6.53) thus illustrates how the two state case can be recovered from the two level description.

Before closing this section, it must be established that the quartic equation (6.49) always possesses two real negative roots. This is necessary in order to have decay to an equilibrium state. (For the two state system of chapter II, the cubic equation (2.35) must be shown to have one negative real root in order to describe decay to
equilibrium and this is trivially proven.) For the quartic form, it is not so trivial to show that $\Delta(u)<0$ for some values of $u<0$, and must be accomplished in several steps.

First, because all of the coefficients in equation (6.47) are positive, this represents a quartic form which opens upward. Secondly since $\frac{d\Delta(u)}{du}$ is a cubic form, also with all positive coefficients, then the cubic equation

$$\frac{d\Delta(u)}{du} = 0$$

has no positive real roots and thus all maxima and minima of $\Delta(u)$ must occur for $u<0$. In other words, $\Delta(u)$ is monotonically increasing for $u \geq 0$.

To proceed further, all possible relationships between the relaxation rates $\alpha$, $\beta$, and $\gamma$ must be considered. For the case of all relaxation times equal $\alpha=\beta=\gamma=s$,

$$\Delta(u) = (u+s)^2[(u+s)^2 + \delta^2 + s/4]$$

and equation (6.49) has two equal negative real roots. For the case $\alpha=\beta = s \neq \gamma$, equation (6.47) takes the form

$$\Delta(u) = (u+s)[(u+s)^2(u+\gamma) + (u+\gamma) + \frac{1}{4}(u+s) + \delta^2(u+\gamma)].$$

The remaining cubic portion of (6.56) must have at least one negative real root, so that again equation (6.49) has two negative real (but unequal) roots. For the cases
\( \alpha = \gamma = s \neq \beta \) and \( \beta = \gamma = s \neq \alpha \), similar reasoning again shows that (6.49) has two unequal negative real roots.

For the remaining situations where the relaxation rates are unequal, a different approach is taken. Consider the situation for which \( \alpha < \beta < \gamma \) or \( \gamma < \beta < \alpha \). Then, the evaluation

\[
(6.57) \quad \Delta(u) \big|_{u = -\beta} = \delta^2 (\gamma - \beta) (\alpha - \beta) < 0
\]

shows that \( \Delta(u) \) is negative and hence the quartic form must have crossed the \( \Delta(u) = 0 \) axis. This implies at least two real negative roots of equation (6.49). If the relationships \( \beta < \alpha < \gamma \) or \( \gamma < \alpha < \beta \) occur, then \( \Delta(u) \) evaluated at \( u = -\alpha \), is again negative. Finally, the evaluation of \( \Delta(u) \) at \( u = -\gamma \) establishes that \( \Delta(u) \) is negative at this point if \( \alpha < \gamma < \beta \) or \( \beta < \gamma < \alpha \). Thus, for all possible relationships between the relaxation rates, equation (6.49) possesses at least two negative real roots. A variety of shapes for the \( \Delta(u) \) versus \( u \) plots are still possible, as exemplified by figure 8.

The comments presented in this section are not actually confined to the \( j=0 \) to \( j=1 \) transition in DDLP molecules but are equally valid whenever the two level system can be approximately described by four coupled scalar equations - see for example, equations (5.34). In such situations, the relative size of the coupling of the orientational moment may be expected to differ numerically from the value \( 1/4 \) used in this chapter, but this has no effect on the general form of the solutions.
Figure 8: Some possible shapes for $\Delta(u)$ versus $u$ curves.
Transient absorption and transient emission experiments, as discussed in sections (g) and (h) of chapter II, are now reexamined within the context of the two level system. The treatment given here is more concise than that of chapter II, and emphasizes the modifications in the system motion due to the presence of a fourth scalar moment.

As in chapter II, some additional assumptions on the relative sizes of the parameters involved is required in order to present the transient absorption experiment in closed form. Contrary to the situation discussed in chapter II, however, an "on-resonance" assumption (i.e. \( \Delta \omega = 0 \)) produces no useful simplification. The other case treated in section (g) of chapter II does have a worthwhile generalization - the generalized strong collision model, equation (6.40) - which allows the two level transient absorption experiment to be solved in closed form. This hypothesis of a generalized strong collision model has been made at least plausible by the calculations presented in section (c) of this chapter.

Employing equation (6.40) and assuming that the system is initially at equilibrium, equations (6.46) are rewritten as
where \( s = (kE_0 T_1)^{-1} \). The determinant (6.47) in this notation takes the factorized form

\[
(6.59) \quad \Delta(u) = (u+s)^2 \left( (u+s)^2 + \delta^2 + 5/4 \right).
\]

As mentioned in section (e), the solutions to equation (6.58) have the general form (6.48) and, in particular, \( \vec{P}_i \) is evaluated as

\[
(6.60) \quad \vec{P}_i = -\frac{M_o}{u} \frac{u+s}{(u+s)^2 + \delta^2 + 5/4} = \frac{C(u+s) + D}{(u+s)^2 + \delta^2 + 5/4} + \frac{E}{u}
\]

where the coefficients \( C, D \) and \( E \) in the partial fraction expansion satisfy the system of three equations
The solutions of equations (6.61) are

\[
(6.62) \quad C = -E = \frac{-M_o s}{s^2 + \delta^2 + 5/4}
\]

\[
D = \frac{-M_o (\delta^2 + 5/4)}{s^2 + \delta^2 + 5/4}
\]

and the inverse Laplace transform of equation (6.60) can then be performed to yield

\[
(6.63) \quad P_i(T) = \frac{-M_o s}{s^2 + \delta^2 + 5/4} [1 - e^{-sT} \cos((\delta^2 + 5/4)^{1/2}T)]
\]

\[
- e^{-sT} (\delta^2 + 5/4)^{1/2} \frac{M_o}{s^2 + \delta^2 + 5/4} \sin((\delta^2 + 5/4)^{1/2}T)
\]

Equation (6.63) is a particular example of the general time dependent solution (6.52) and the remaining moments \( P_x(T) \), \( M(T) \), and \( Y(T) \) can be evaluated in a similar manner. For example
\[ Y(T) = \frac{M_0}{\delta^2 + 5/4 + s^2} \left( e^{-sT} \cos[(\delta^2 + 5/4)^{1/2}T] - 1 \right) \]

\[ + \frac{se^{-sT}}{(\delta^2 + 5/4)^{1/2}} \sin[(\delta^2 + 5/4)^{1/2}T] \]

describes the transient behaviour of the orientational polarization during absorption.

Using the transformations (6.43), equations (6.63) and (6.64) are rewritten in the original notation as

\[ P_i(t) = \frac{-k^2 E_i <\Delta N>}{4 \pi^2 + \Omega^2} \left[ \frac{1}{T^2} + \Omega^2 \right] \left[ T e^{-t/T} \cos \Omega t \right] \]

\[ + \Omega e^{-t/T} \sin \Omega t \]

\[ \frac{k^2 (E_z)^2 <\Delta N>}{4 \pi^2 + \Omega^2} \left[ e^{-t/T} \cos \Omega t \right] \]

\[ + \frac{1}{T} e^{-t/T} \frac{\sin \Omega t}{\Omega} \]

where

\[ \Omega^2 = \Delta \omega^2 + 5/4 k^2 (E_z)^2 \]

There are two points to notice about equations (6.65). First, the transient solutions decay to the previously established steady state values (see equations (6.42)) as
t→∞. Secondly, the observed transient absorption, as detected via equation (2.49), is of the same form as that given in the two state case, see equation (2.54). Only the precise definition of the frequency of oscillation \( \Omega \), as given by equation (6.66) has been changed because of presence of the fourth moment.

The transient emission experiment requires no additional approximation, such as the generalized strong collision model, to allow the solution to be presented in closed form. If the exciting radiation is turned off at time \( t=0 \), then from equations (6.19), the behaviour of the system for times \( t>0 \) is governed by the set of equations

\[
\begin{align*}
\frac{d}{dt} \langle \Delta N \rangle &= \frac{1}{T_1} \left( \langle \Delta N \rangle - \langle \Delta N \rangle_{\text{eq}} \right) = 0 \\
\frac{d}{dt} \left( \frac{\hbar \mathcal{U}^{(2)}_2(J)}{2} \right) &= \frac{1}{T_p} \left( \frac{\hbar \mathcal{U}^{(2)}_2(J)}{2} \right) = 0 \\
\frac{d}{dt} p_r &= \Delta \omega p_i + \frac{1}{T_2} p_r = 0 \\
\frac{d}{dt} p_i &= -\Delta \omega p_r + \frac{1}{T_2} p_i = 0
\end{align*}
\]

Assuming an appropriate set of initial conditions \( \langle \Delta N \rangle(0) \), \( \mathcal{U}^{(2)}_2(J)(0) \), \( p_r(0) \), and \( p_i(0) \), the solutions to equations (6.67) are immediately established as
\[ P_r(t) = e^{-t/T_2} \{ P_r(0) \cos \Delta \omega t - P_i(0) \sin \Delta \omega t \} \]

\[ P_i(t) = e^{-t/T_2} \{ P_i(0) \cos \Delta \omega t + P_r(0) \sin \Delta \omega t \} \]

\[ <\Delta N>(t) = <\Delta N>_{eq} + (<\Delta N>(0) - <\Delta N>_{eq}) e^{-t/T_1} \]

\[ <\gamma_z^2(J)> (t) = <\gamma_z^2(J)> (0) e^{-t/T_p} \]

The steady state values, equations (6.42), represent one such set of appropriate initial conditions. However, independent of the choice of initial conditions, equations (6.68) demonstrate that \(<\Delta N>\) and \(<\gamma_z^2(J)>\) decouple during the transient emission process.

This concludes the discussion of the transient behaviour of a two level system. Although additional transient experiments can be performed (see chapter II), the examples presented in this section are sufficient to illustrate the manner in which a two level description of the phenomena can be obtained.
(f) Summary of the Two Level Point of View

The two level point of view is now summarized by emphasizing the physical interpretation of the phenomena which the present treatment allows. Here, the "exact" two level system (j=0 to j=1) transition in DDLp) is considered explicitly, although similar arguments can be applied to the general two level systems discussed in chapter V.

Consider the j=1, m=0 state of the upper level. This is the only one of the three magnetic states that is affected by the linearly polarized radiation. In the absence of collisions, then, a description of the upper level in terms of the basis operators |lm><lm'| would seem the most appropriate because only one of these operators is affected by the radiation. Thus the two level problem is reduced to the two state problem - but only in the absence of collisions. Collisional coupling between the degenerate magnetic states requires that the states j=1, m=±1 also be considered. The precise manner in which these magnetic states enter the problem follows from the assumed rotational invariance of the collision superoperator. Indeed, the basis operators |lm><lm'| must be decomposed into rotationally irreducible parts, yielding an alternate description of the j=1 level. In particular,

\[ (6.69) \quad |10><10| = \frac{\mathcal{Q}^{1}}{3} - \frac{\mathcal{Y}^{(2)}_{1} (J)}{2} \frac{\mathcal{Q}^{1}}{3} \]
which is a special case of the inverse to equation (3.24). Equation (6.69) shows that when radiation interacts with the \( j=1, m=0 \) state, two effects are produced. First, the overall population of the \( j=1 \) level is altered. Second, the population of the \( m=0 \) state relative to the \( m=\pm 1 \) states is selectively changed, producing a polarization of the \( j=1 \) level, described by \( \gamma_z^{(2)}(J)\bar{\Omega} \). These two effects have independent collisional relaxation rates.

In order to rationalize why it is a \( \gamma_z^{(2)}(J) \) polarization that must be formed instead of a \( \gamma_z^{(1)}(J) \) or some other polarization, a pictorial argument can be established as an alternative to the more mathematical derivations presented earlier. These physical pictures have the further advantage of demonstrating the interrelationship between the scalar and vectorial (or tensorial) descriptions, as well as emphasizing the differences between the microscopic and macroscopic motions of the system.

As illustrated in figure 9, the application of linearly polarized microwave radiation, with its polarization vector oscillating in the \( z \) direction, produces a macroscopic oscillation of the gaseous system, also in the \( z \) direction. In terms of the individual molecules, however, this macroscopic oscillation is equivalent to rotations around an arbitrary axis in the \( x-y \) plane, with equal numbers of molecules rotating in the positive and negative directions. Indeed, the rotational motion is necessary to produce the macroscopic oscillation in a collection of
Rotational motions produced by linearly polarized radiation.

Figure 9: Rotational motions produced by linearly polarized radiation.
rigid rotors because the positive and negative ends of the molecular dipole don't tunnel through each other, in general. Since there are no components of this macroscopically oscillating dipole in the x or y directions, it is required that equal numbers of molecules must be rotating in the positive and negative sense.

The effects of these motions on the orientation of $\mathbf{J}$ can be easily understood. Remembering that $\mathbf{J}$ is perpendicular to $\mathbf{y}$ for each individual molecule, the induced rotational motion therefore produces an alignment of $\mathbf{J}$ vectors in the x-y plane, at the expense of $\mathbf{J}$ vectors in the z direction. This alignment of individual $\mathbf{J}$ vectors is expressed macroscopically as one component of the polarization tensor $\mathbf{J}^{(2)}(\mathbf{J})$.

Finally, granted the existence of this orientational polarization whenever a sufficiently intense microwave source is applied, what is the best way to detect its presence? Considerations in this chapter of both steady state and transient solutions indicate that the effect of the fourth moment on $P_4(t)$ - and hence, on the observed absorption - is not dramatic. Indeed, in each instance, the general shape of the solution remains unaltered and only the exact magnitude of the parameters is changed. We feel that a more direct measurement of the orientational effect is preferred in order to unambiguously establish its existence, experimentally. To this end, a new experiment is suggested which is a combination of intense
microwave (cw) irradiation and optical, depolarized Rayleigh (DPR) light scattering. The intense microwave radiation polarizes the medium while the existence of a DPR spectrum indicates the presence of a $\gamma^{(2)}(J)$ polarization. Here, the line width of the DPR spectrum is proportional to the relaxation rate $\frac{1}{T_P}$. Experimentally, the setup should be somewhat analogous to that used for microwave-optical double resonance measurements - see also figure 10.
Figure 10: A combination microwave absorption-optical light scattering experiment.
"It's too late to correct it," said the Red Queen: "when you've once said a thing, that fixes it, and you must take the consequences."
(a) Introduction

This final chapter discusses the influence of molecular velocities on pressure broadening. Indeed, chapter VII can be considered as a generalization of the two state model of chapter II to include translational motion (in terms of \( W \)) in a manner analogous to the way in which the two state model was generalized in chapters IV, V and VI to account for rotational motion (in terms of \( J \)). The resulting model of the molecule allows for a complete description of the molecular motions - oscillation (\( u, \dot{u} \)), rotation (\( J \)), and translation (\( W \)). Further, this chapter justifies the neglect of translational effects in earlier chapters, by indicating under what conditions this is reasonable. Relationships between Seftleben-Beenakker effects and those of pressure broadening are most readily established within the context of the present chapter, since in each case, both internal state and translational motions are of concern. In particular, the present treatment of collisions is very similar to that in chapter III. Finally, as established by the present point of view, certain areas where additional work is required are indicated.
The effect of a distribution of molecular velocities on the shape of a spectral line was mentioned in chapter I. In particular, it was pointed out that if the Doppler shift of the natural oscillation frequency of the molecules was included, then in the absence of collisions, the resulting line shape expression is Gaussian with a characteristic width $\Delta \omega_0$.

Further, if collisions are assumed to affect only the internal states of the molecules, then a Voigt profile is obtained - a convolution of the Gaussian with a Lorentz lineshape for the pure internal state effects. To this point then, this thesis has not yet discussed the possibility of "velocity changing" collisions and their effect on lineshapes.

Dicke\textsuperscript{1} was the first to describe the effects of "velocity changing" collisions on the pure Gaussian profile and he found that the lineshape narrows - this is known as "Dicke narrowing". The effects of both "velocity changing" and "internal state changing" collisions has been considered by Galentry\textsuperscript{2} and resulted in a more involved pressure dependence of the lineshape, although the solution is still represented as a convolution of translational and internal state factors. Nelkin and Ghatak\textsuperscript{3} used a method involving a kinetic equation to obtain Dicke's results while, in an excellent paper by Rautian and Sobelman,\textsuperscript{4} a kinetic equation formulation of Galantry's "combined problem" was firmly established. In addition, by pointing out that a
single collision event can lead to both velocity changes and internal state changes, they showed that a general lineshape is not expressible as a convolution of translational and internal state factors. Similar conclusions were obtained independently by Gersten and Foley.

The preceding treatment are all of a classical and phenomenological nature, especially in their handling of the internal state parts. A description of these (no-saturation) lineshapes, obtained from a more fundamental starting point, is presented in a series of papers by a group of researchers from JILA. Indeed, beginning with a completely quantum mechanical treatment of both radiation and matter, Smith et al. obtained a quantum mechanical kinetic equation capable of describing the combined effects of Doppler and pressure broadening. They then simplified this result in a second paper by employing a classical path approximation for the translational motions. In so doing, the formal expressions are presented in such a way that the physical processes which influence Doppler and pressure broadening are separated (but not uncorrelated). The possible correlation effects are explained in a separate paper, using a "one interacting level" approximation which is appropriate to a discussion of optical transitions. In fact, because these authors are completely concerned with the explanation of optical lineshapes, some discretion should be employed in directly applying their work to the corresponding microwave case.
Berman has independently derived a very similar quantum mechanical kinetic equation. In addition to the application of this equation to the study of spectral lineshapes, this author (and coworkers) have employed it in the explanation of velocity modifications to coherence transient effects. Again, however, the work of Berman is directed towards optical transitions.

However, it is the work of Hess that most closely resembles the method of approach emphasized throughout this thesis. A paper describing velocity corrections to DPR spectra was later extended, in a comprehensive paper, to more general spectral line shapes. In this latter work, the complete transition (as the gas density increases) from the Doppler broadened region to the pressure broadened region is established. This also allowed connections to be made between the previously mentioned work on line-shapes and the kinetic theory methods which are most appropriate to the study of microwave phenomena.

In the following sections, a kinetic theory approach to velocity effects in microwave pressure broadening and coherence transients is presented within the general framework established in this thesis. This includes some considerations on the evaluation of the appropriate relaxation expressions. Specific observations relating this work to that of earlier workers are given where appropriate.
A Kinetic Equation which includes Velocity Effects

This short section presents a kinetic equation appropriate to the discussion of the effects of velocity on spectroscopic phenomena. Its derivation points out the assumptions and approximations inherent in the present treatment, and allows a comparison with the kinetic equations (3.15) and (4.9) used in the descriptions of Senftleben-Beenakker effects and purely internal state spectroscopic effects, respectively. Connections with the kinetic equations cited in the previous section can also be more readily established.

As in chapters III and IV, the starting point is the generalized Boltzmann equation of Snider and Sanctuary, equation (3.1) - see also appendix A. For convenience, it is rewritten here as

\[
\frac{i\hbar}{\partial t} \rho = \mathcal{L}_{tr}\rho + \mathcal{L}_o\rho + \mathcal{L}_1\rho + \text{tr}_2 \mathcal{J} \rho \rho_2
\]

where

\[
\mathcal{L}_{tr}\rho = [\frac{E_0^2}{2m},\rho] ; \quad \mathcal{L}_o\rho = [\mathcal{H}_o,\rho];
\]

\[
\mathcal{L}_1\rho = [-2\mu \cdot E_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r}),\rho],
\]

and the collision superoperator \( \mathcal{J} \) is defined by equation (A.18). A representation of equation (7.1) in terms of the Wigner
distribution is again preferred, in order to make the
handling of the translational degrees of freedom more
meaningful. Indeed, employing the equivalent forms of the
Wigner distribution function

\[
(7.3) \quad f(\varepsilon pt) = \frac{1}{h^3} \int e^{i g \cdot \varepsilon / \hbar} \rho_{p+1/2q} |p - 1/2q > d\eta
\]

\[
= \frac{1}{h^3} \int e^{-i n \cdot p / \hbar} <p + 1/2q |\rho |p - 1/2q > d\eta ;
\]
equations (7.2) in this new representation are given by

\[
(7.4) \quad \frac{1}{h^3} \int e^{i g \cdot \varepsilon / \hbar} \rho_{p+1/2q} \int tr \rho |p - 1/2q > d\eta = -i \frac{p}{m} \frac{\partial}{\partial \varepsilon} f(\varepsilon pt)
\]

\[
\frac{1}{h^3} \int e^{i q \cdot r / p} \rho_{p+1/2q} \int tr \rho |p - 1/2q > d\eta = \int_0 f(\varepsilon pt)
\]

and

\[
(7.5) \quad \frac{1}{h^3} \int e^{-i n \cdot p / \hbar} \rho_{p+1/2q} \int tr \rho |p - 1/2q > d\eta = -2\mu \cdot E_o \cos(\omega t - k \cdot \varepsilon),
\]

\[
\frac{1}{h^3} \int e^{-i n \cdot p / \hbar} \rho_{p+1/2q} \int tr \rho |p - 1/2q > | \cos \frac{k \cdot n}{2} d\eta
\]

\[
+ [-2\mu \cdot E_o \sin(\omega t - k \cdot \varepsilon), \frac{1}{h^3} \int e^{-i n \cdot p / \hbar} <p + 1/2q |\rho |p - 1/2q > \sin \frac{k \cdot n}{2} d\eta].
\]
Finally, the transformed collision operator has the same form as equation (3.4), except in this instance, the Wigner distribution functions on which it acts are no longer restricted to being diagonal in internal state energies.

The transformations represented by equations (7.4), (7.5) and (3.4) are exact - no information about the quantum nature of the translational degrees of freedom has been lost. It is sufficient for the present purpose, however, to consider that the distribution functions are only slowly varying functions of position. In this instance, equation (7.5) can be approximately evaluated as

\[
\frac{1}{\hbar} \int e^{-i n \cdot \mathbf{A}} <\sum_{k=0}^{n} |\psi_{n}|^2 \rho_{\sum_{k=0}^{n}|\psi_{n}|^2} \, d\eta
\]

\[
= \{-2 \mathbf{v} \cdot \mathbf{E}_0 \cos(\omega t - k \cdot x), f(\mathbf{x} t)\}
\]

\[
+ \frac{i \hbar}{2} \left( \frac{\partial \mathcal{H}_1}{\partial \mathbf{x}} \cdot \frac{\partial}{\partial \mathbf{p}} f(\mathbf{x} t) \right)_+ \, \mathbf{V}
\]

where \([A,B]_+\) is the anti-commutator of A and B, and the identifications

\[
\cos \frac{k \cdot n}{2} \sim 1 \quad \sin \frac{k \cdot n}{2} \sim \frac{k \cdot n}{2}
\]

\[
\frac{\partial \mathcal{H}_1}{\partial \mathbf{x}} = \frac{\partial}{\partial \mathbf{x}} \{-2 \mathbf{v} \cdot \mathbf{E}_0 \cos(\omega t - k \cdot x)\}
\]

\[
= k \{-2 \mathbf{v} \cdot \mathbf{E}_0 \sin(\omega t - k \cdot x)\}
\]
have also been employed. Further, as discussed in chapter III, this assumption of slowly-varying position dependence allows the collision term to be simplified as well. Indeed, the localized collision operator $J_o(r_{pt})$ is the result, where $J_o(r_{pt})$ has the same form as equation (3.8), assuming that internal state frequencies are conserved. Thus, with the above treatment of the translational degrees of freedom, the kinetic equation (7.1) is rewritten as

$$(7.8) \quad \frac{\partial f}{\partial t} + \frac{P}{m} \cdot \frac{\partial}{\partial r} f - \frac{1}{2} \left( \frac{\partial f}{\partial r} \cdot \frac{\partial f}{\partial P} \right) + U$$

$$= -i\hbar \left( -2\mu \cdot E_0 \cos(\omega t - k \cdot r) + J_o(r_{pt}) \right)$$

Finally, the linearized version of equation (7.8) is obtained, using the specific linearization, equation (4.6). In particular, the anticommutator terms in equation (7.8) is smaller than the other oscillatory term by a factor of

$$(7.9) \quad k \cdot \frac{P}{mk_BT} = \left( \frac{\omega}{k_BT} \right) \left( \frac{\nu}{c} \right) \ll 1$$

and so is not considered further. (Smith et al. have employed similar reasoning to approximate the flow term in their kinetic equation.) The linearized localized collision superoperator $\mathcal{R}$, defined by equation (4.17), is again of the Waldmann-Snider form. The linearized version of equation (7.8) is then
As with all equations used to describe the interaction of an oscillating field with a system of molecules, equation (7.10) contains a time dependent Hamiltonian. It is desirable to approximately eliminate this time dependence by a transformation to a rotating frame with a subsequent neglect of the highly oscillatory terms (the rotating wave approximation). In the present case, the transformation used in chapter IV in terms of the internal state operator $S$ can again be employed. This operator has no effect on the collision term as long as $A$ is local and preserves frequency. The rotating wave approximation to equation (7.10) is

\[
\frac{\partial \tilde{f}}{\partial t} + \frac{E}{m} \cdot \frac{\partial}{\partial \tilde{x}} \tilde{f} = \frac{i}{\hbar} \left[ S \left( 1 - \frac{\hat{p}}{m} \frac{\hat{k}}{c} \right) - H_0, \tilde{f} \right] + \frac{i}{\hbar} [\hat{\mu} \cdot \hat{E}_0, \tilde{f}] - f^{(0)}_{tr} \mathcal{R} \left[ f^{(0)}_{tr} - 1 \left( \tilde{f} - f^{(0)}_{tr} \right) \right]
\]

In equation (7.11), it is usual to neglect the effect of the term in the rotating frame - this is consistent with the idea of a slowly varying position dependence.

Equation (7.11) is the appropriate kinetic equation to be used for a description of the modifications of
microwave experiments due to velocity effects, both of the steady state and transient variety. Similar versions of this equation have been obtained in different contexts, as discussed in the previous section. Many of these authors prefer to split the collision operator $\mathcal{R}$ into "velocity changing" and "phase changing parts" - namely,

$$
(7.12) \quad \mathcal{R}[\phi] = \mathcal{R}_{\text{vc}}[\phi] + \mathcal{R}_{\text{pc}}[\phi]
$$

where

$$
(7.13) \quad \mathcal{R}_{\text{vc}}[\phi] \equiv -(2\pi)^{4} \hbar^{2} \left[ \frac{e^{-W^{2}}}{(2\pi mkT)^{3/2}} \right]^{-1} n \text{tr} \int d\mathbf{p} \int d\mathbf{p}' \delta(p+p_{2}'-p_{2}) \langle \mu_{g} | t | \mu_{g}' \rangle
$$

$$
\{ \frac{f(o)^{\prime}}{n} \text{tr} \frac{f(o)^{\prime}}{n} [\phi(\mathbf{W}') - \phi(\mathbf{W})] + \frac{f(o)^{\prime}}{n} \text{tr} \frac{f(o)^{\prime}}{n} [\phi_{2}(\mathbf{W}') - \phi_{2}(\mathbf{W})] \langle \mu_{g}' | \delta(\mathbf{E}-\mathbf{E}') t^{+} | \mu_{g} \rangle
$$

and
(7.14) $\mathcal{R}_{pc}[(\theta)] \equiv -(2\pi)^4 \hbar^2 \left[ \frac{e^{-\mu^2}}{(2\pi m k T)^{3/2}} \right] n \text{ tr}_2 \int d\rho_2$

\[ \left[ \int d\rho_1^p d\rho_2^p \delta(p+p_2-p'-p_2') \langle \mu g | t | \mu g' \rangle \right] \]

\[
\{ \frac{f(o)}{n} \text{ tr} \frac{f(o)'}{n} \phi(\bar{\omega}) + \frac{f(o)}{n} \frac{f(o)'}{n} \phi_2(\bar{\omega}_2) \}
\]

\[
\langle \mu g' | \delta(E-E') t^+ | \mu g \rangle + (2\pi i)^{-1} \langle \mu g | t | \mu g \rangle 
\]

\[
\{ \frac{f(o)}{n} \text{ tr} \frac{f(o)'}{n} \phi(\bar{\omega}) + \frac{f(o)}{n} \frac{f(o)'}{n} \phi_2(\bar{\omega}_2) \}
\]

\[
-\{ \frac{f(o)}{n} \text{ tr} \frac{f(o)'}{n} \phi(\bar{\omega}) + \frac{f(o)}{n} \frac{f(o)'}{n} \phi_2(\bar{\omega}_2) \}
\]

\[
\langle \mu g | t^+ | \mu g \rangle \}
\] .

In particular, it is seen that $\mathcal{R}_{pc}$ is the appropriate collision operator for pure internal state collision effects (see chapter IV) since $\mathcal{R}_{vc} = 0$ when $\phi$ is independent of the velocity. Moreover, because of the optical theorem, $\mathcal{R}_{pc}$ vanishes when $\phi$ is independent of internal states. This division of $\mathcal{R}$ is in many ways similar to the division employed by Chen et al.\textsuperscript{17} in their evaluation of collision matrix elements obtained in the study of Senftleben-Beenakker effects.

The succeeding sections explore the implications of equation (7.11).
(c) The Moment Method Applied to a Discussion of Velocity Effects

The moment method has been applied in chapter III to the discussion of Senftleben-Beenakker effects, and in chapters V and VI to the solution of the two level problem. In the present section, this method is applied to equation (7.11) in order to determine the effects of the Doppler shift on spectroscopic phenomena.

For the purpose of illustration, it is sufficient to consider as representative of the internal state motions, the j=0 to j=1 two level system for the DDLP case. This system was considered in chapter VI in the absence of any velocity effects. Alternate choices of two level systems are possible, see chapter V, but the basic description remains unchanged.

The simplest ansatz which allows velocity modifications to be included requires \( \tilde{f} \) to have the form

\[
\tilde{f}(pt) = \frac{e^{-W^{2}}}{(2 \pi m k T)^{3/2}} \left\{ \frac{1}{4} \langle 1 \rangle + \frac{\Delta N \langle \Delta N \rangle}{3} + \frac{3 \mu \cdot \langle \dot{\mu} \rangle}{2 \mu^2} \right. \\
+ \frac{3 \mu \cdot \langle \mu \rangle}{2 \mu^2} \left. + \frac{Y^{(1)}(j) \cdot \langle \dot{Y}^{(1)}(j) \rangle}{3} + \frac{Y^{(2)}(j) \cdot \langle \dot{Y}^{(2)}(j) \rangle}{3} \right. \\
+ \frac{3}{2 \mu^2} \langle L^{10} \mu \rangle + \frac{3}{2 \mu^2} \langle L^{10} \mu \rangle \langle L^{10} \mu \rangle \}
\]

where (see also equation (3.18))
Equation (7.15) can be compared directly with equation (6.1) which represents the description of the two level system in the absence of velocity effects. Indeed, equation (5.24) is the relevant equilibrium distribution function for both situations.

The appropriate moment equations are found by substituting equation (7.15) into the kinetic equation (7.11). (As mentioned earlier, the $\frac{\partial}{\partial \bar{r}}$ term in the rotating frame has been dropped.) The results are

\begin{align}
\frac{d}{dt} \langle \mu \rangle &= -\Delta \omega \langle \zeta \rangle + k \frac{B}{m} \frac{T}{1/2} k \cdot \langle L^{10} \dot{\zeta} \rangle \\
&- \frac{2}{3} \frac{\mu^2}{\hbar} E_0 \cdot V(111) \cdot \langle \mathcal{C}^{(1)} (J) \rangle + \frac{1}{T} \langle \mu \rangle = 0
\end{align}

\begin{align}
\frac{d}{dt} \langle \dot{\mu} \rangle + \Delta \omega \langle \zeta \rangle &= -k \frac{B}{m} \frac{T}{1/2} k \cdot \langle L^{10} \mu \rangle \\
&- \frac{4}{9} \frac{\mu^2}{\hbar} E_0 \langle \Delta N \rangle - \frac{2}{3} \frac{\mu^2}{\hbar} (\frac{5}{3})^{1/2} \frac{E_0}{\zeta} \cdot V(112) \cdot \langle \mathcal{C}^{(2)} (J) \rangle \\
&+ \frac{1}{T} \langle \rho \rangle = 0
\end{align}
\[ \frac{d\langle \Delta N \rangle}{dt} + \frac{2}{\hbar} E_0 \cdot \langle \dot{\mathbf{r}} \rangle + \frac{1}{T_1} (\langle \Delta N \rangle - \langle \Delta N \rangle_{eq}) = 0 \]

\[ \frac{d\langle J^1 (J) \rangle}{dt} - \frac{3}{\hbar} E_0 \cdot \mathbf{v} (111) \cdot \langle \dot{\mathbf{r}} \rangle + \frac{1}{T_p} \langle J^1 (J) \rangle = 0 \]

\[ \frac{d\langle J^2 (J) \rangle}{dt} + \frac{(15)^{1/2}}{\hbar} E_0 \cdot \mathbf{v} (121) \cdot \langle \dot{\mathbf{r}} \rangle + \frac{1}{T_p} \langle J^2 (J) \rangle = 0 \]

\[ \frac{d\langle L^{10} \mu \rangle}{dt} - \Delta \omega \langle L^{10} \dot{\mu} \rangle + \frac{1}{\hbar} \langle \mathcal{B} \rangle^{1/2} \langle \dot{\mu} \rangle + \frac{1}{T_f} \langle L^{10} \mu \rangle = 0 \]

\[ \frac{d\langle L^{10} \dot{\mu} \rangle}{dt} + \Delta \omega \langle L^{10} \mu \rangle - \frac{1}{\hbar} \langle \mathcal{B} \rangle^{1/2} \langle \dot{\mu} \rangle + \frac{1}{T_f} \langle L^{10} \dot{\mu} \rangle = 0 \]

In equations (7.17), it is assumed that \( \langle \Delta N | R | 1 \rangle \rangle = 0 \), which implies that \( | 1 \rangle \) is decoupled from the other moments.

The relaxation times are defined as

(7.18) \[ \frac{1}{T_1} = \frac{\langle \Delta N | R | \Delta N \rangle_{eq}}{4}, \quad \frac{1}{T_p} = \frac{\langle J^1 (J) | R | J^1 (J) \rangle_{eq}}{3} \]

\[ \frac{1}{T_p} = \frac{\langle J^2 (J) | R | J^2 (J) \rangle_{eq}}{3} \]

\[ \frac{1}{T_2} = 3 \frac{\langle \mu | R | \mu \rangle_{eq}}{2\mu^2} = 3 \frac{\langle \dot{\mu} | R | \dot{\mu} \rangle_{eq}}{2\mu^2} \]

\[ \frac{1}{T_f} = 3 \frac{\langle L^{10} \mu | R | L^{10} \mu \rangle_{eq}}{2\mu^2} = 3 \frac{\langle L^{10} \dot{\mu} | R | L^{10} \dot{\mu} \rangle_{eq}}{2\mu^2} \]
Equations (7.17) are the generalization of equations (6.17) to include velocity effects. Notice that oscillations $\mu, \nu$; rotations $\gamma^{(1)}(J), \gamma^{(2)}(J)$, and translations $L^{10}_\nu, L^{10}_\nu$ are all contained in this picture. In particular, the origin of the velocity effects has been clearly indicated - they represent a flux of oscillating dipoles $\mu, \nu$ in the direction of propagation $k$ of the incident light beam.

More complex velocity polarizations can also occur. These include those moments that have been neglected by the ansatz (7.15); for example $<L^{10}_\Delta N>, <L^{01}_\mu>, <L^{01}_\nu>, <L^{20}_\mu>, \text{and} <L^{20}_\nu>$. These higher order corrections to the velocity description become significant at lower densities when they are produced at a rate no longer insignificant compared to their relaxation times. (The appropriate order parameter is the radiation wavelength divided by the mean free path.) Also, because it is the Doppler shift of the oscillation which basically gives rise to these velocity polarizations, it is expected that the polarizations $<L^{PS}_\mu>, <L^{PS}_\nu>$ will occur one order of magnitude sooner than the corresponding polarization $<L^{PS}_\Delta N>$. For example, in deriving equation (7.17), it is consistent to consider the polarizations $<L^{10}_\mu>$ and $<L^{10}_\nu>$ while ignoring the effects of $<L^{10}_\Delta N>$.

With the above description of the velocity effects, the kinetic theory treatments of Senftleben-Beenakker effects and the spectroscopic experiments are seen to have much in common. In the first case, velocity polarizations
of the gas sample are created by the presence of velocity or temperature gradients. In the second case, it is the oscillating microwave field which establishes these fluxes. In both cases, the descriptions of the actual velocity polarizations present become more complicated as the number of gaseous molecules in the cell is decreased. The comparisons in the internal state motions produced by each kind of experiment have been emphasized in previous chapters, while the similarities in the treatments of collisional expressions is established in the next section.

Various solutions to equation (7.17) can be envisaged, corresponding to different microwave experiments, which illustrate the effects of the velocity polarization. For example, a no-saturation, steady state experiment leads to a Lorentzian lineshape with a modified width
\[
\frac{1}{T_2} + \frac{k_B T}{m} T_f, \text{ assuming } \frac{1}{T_f} \gg \Delta \omega. \quad (\text{Hess}^{14} \text{ has also found this effect when considering velocity modifications to DPR lineshapes by a moment method approach.}) \] However, since little experimental work has been done on velocity modifications to microwave experiments (especially transient experiments), explicit solutions to equation (7.17) are not pursued here. The lack of experimental observations probably stems from the fact that under normal gas pressure conditions, velocity effects play a minor role in the microwave region of the electromagnetic spectrum. (This is not the case in the optical regions.) These facts also imply, however, that the description of velocity effects in the
microwave region should be much simpler than in the optical regions. In the language of the present section, the microwave case should be described sufficiently accurately by the moments $L^{10}$ and $L^{10}$, while the optical regions generally require that additional velocity polarizations such as $L^{10}$$\Delta N$ and $L^{20}$ etc., be taken into account. Thus, the microwave region has the advantage of offering a definite velocity polarization to be measured.
Collisional Description of Velocity Effects

The previous section has discussed an equivalence between transport properties and spectroscopic phenomena. In the present section, this equivalence is extended to the step by step treatment of the collisional aspects. Indeed, the collisional expressions obtained in chapters III and IV are shown to be special cases of the general results presented here.

Employing the natural basis set

\[ \text{Equation (7.19)} \]

\[ \text{Apqst} \left( j_{i_1} v_{i_1} | j_{f_1} v_{f_1} \right) \equiv L_p^S(W) [j_{i_1} v_{i_1} \rangle \langle j_{f_1} v_{f_1} ](q) \]

and the inner product (4.12), matrix elements of \( R \) are equivalently expressed as generalized collision cross sections

\[ \text{Equation (7.20)} \]

\[ \sum (\text{Apqst} \left( j_{i_1} v_{i_1} | j_{f_1} v_{f_1} \right) | p'q's' \left[ j_{i_1} v_{i_1} \right] \langle j_{f_1} v_{f_1} ])^2 \]

\[ \equiv n^{-1} \left( \frac{n \mu}{8 k T} \right)^{1/2} \langle \langle \text{Apqst} \left( j_{i_1} v_{i_1} | j_{f_1} v_{f_1} \right) | \text{Apqst} \left( j_{i_1} v_{i_1} | j_{f_1} v_{f_1} \right) \rangle \rangle . \]

Equations (7.19) and (7.20) are generalizations of equations (3.54) and (3.55) to include "off-diagonal in \( j \)" situations.

As discussed in chapter III, the rotational invariance property of \( R \) allows the tensor cross section to be expressed in terms of a set \( \text{E}(-|-)_k \) of scalar cross sections, according to

\[ \text{Equation (7.21)} \]

\[ \sum (\text{Apqst} \left( j_{i_1} v_{i_1} | j_{f_1} v_{f_1} \right) | p'q's' \left[ j_{i_1} v_{i_1} \right] \langle j_{f_1} v_{f_1} ])^2 \]
The integration over the centre of mass momentum is then formally performed by the transformation $I^{(k)}_{\kappa n^{k}n';psp's'}$, so that the scalar cross sections of equation (7.21) are expressible in terms of relative velocity cross sections $\mathcal{G}_k'$ and $\mathcal{G}_k''$. Explicitly, this transformation to relative velocity cross sections is

$$(7.22) \sum (pq^s[j_{i}v_{i}|j_{f}v_{f}] |p'q's'[j_{i}v_{i}'|j_{f}v_{f}'])_k$$

$$= (2k+1) \sum_{\kappa n^{k}n'} \left\{ \frac{\Omega(kq'p')}{\Omega(kpp')} \right\}^{1/2} I^{(k)}_{\kappa n^{k}n';psp's'}$$

$$\{ [\mathcal{G}'(\kappa qn[j_{i}v_{i}|j_{f}v_{f}] |q'n'[j_{i}v_{i}'|j_{f}v_{f}'])_k$$

$$+ (-1)^{q'} \sum (\kappa qn[j_{i}v_{i}'|j_{f}v_{f}'] |q'n'[j_{i}v_{i}'|j_{f}v_{f}'])_k \}.$$ 

Equations (7.21) and (7.22) are generalizations of equations (3.55) and (3.58) of chapter III. Here, the relative velocity scalar cross section $\mathcal{G}_k'$ is given explicitly as

$$(7.23) \sum (\kappa qn[j_{i}v_{i}|j_{f}v_{f}] |q'n'[j_{i}v_{i}'|j_{f}v_{f}'])_k$$

$$= (-1)^{q'-q+\kappa +q'} j_{i}^{+}j_{f}^{-}j_{i}^{-}j_{f}^{+} (-1)^{k} \Omega(kq')^{-1/2} \Omega(kpp')^{-1/2}$$
\[
\frac{1}{(kT)^2} \sum_{j_1 v_1, j_2 v_2} \int \exp\left[-\frac{E_1^t}{kT}\right] \exp\left[-\frac{E_2^t}{kT}\right] \frac{\hbar^2}{(\mu g')^2} \int \exp\left[\sum_{\gamma} n_\gamma (\gamma) \bar{\alpha} n'_{\gamma'} (\gamma')\right] \\
\delta(E_1^t + E_2^t - E_1^t - E_2^t) \\
\sum_{\lambda, \lambda', \lambda''} \langle(2\lambda + 1)(2\lambda' + 1)(2q + 1)(2q' + 1)\rangle^2 \langle(2\lambda + 1)(2\lambda' + 1)(2\lambda' + 1)(2\lambda'' + 1)\rangle^2 \\
\langle(2j_1 + 1)(2j_2 + 1)(2j_1 + 1)(2j_2 + 1)(2j_1 + 1)(2j_2 + 1)\rangle^2 \\
\sum_{\lambda_1 \lambda_2 \lambda'} \langle(2\lambda_1 + 1)(2\lambda_2 + 1)(2\lambda' + 1)(2\lambda_1 + 1)(2\lambda_2 + 1)\rangle^2 \\
T(j_1^t v_1, j_2^t v_2; j_1^t v_1, j_2^t v_2) \\
T^*(j_1^t v_1^t, j_2^t v_2; j_1^t v_1, j_2^t v_2) \\
((-1)^{\lambda' + \lambda''} j_1^t + j_2^t) \\
\left(\begin{array}{ccc}
\lambda' \lambda'' \lambda' \\
0 0 0
\end{array}\right) \left(\begin{array}{ccc}
0 0 0
\end{array}\right) \left(\begin{array}{ccc}
\lambda' \lambda'' \lambda' \\
\lambda_1 \lambda_2 \lambda_1
\end{array}\right) \\
\left(\begin{array}{ccc}
\lambda' \lambda'' \lambda' \\
\lambda_1 \lambda_2 \lambda_1
\end{array}\right) \left(\begin{array}{ccc}
\lambda' \lambda'' \lambda' \\
\lambda_1 \lambda_2 \lambda_1
\end{array}\right) \\
\frac{(-1)^{k + k'}}{(kT)^2} \int \exp\left[-\frac{E_1^t}{kT}\right] \exp\left[-\frac{E_2^t}{kT}\right] \frac{\hbar^2}{(\mu g')^2} \int \exp\left[\sum_{\gamma} n_\gamma (\gamma) \bar{\alpha} n'_{\gamma'} (\gamma')\right] \\
\Omega(kqq')^{-\frac{1}{2}} \Omega(kq'q')^{-\frac{1}{2}} \Omega(q + q')^{-\frac{1}{2}} (2j_1 + 1)(2j_2 + 1)(2j_1 + 1)(2j_2 + 1)^{-\frac{1}{2}} \\
\left(\begin{array}{ccc}
\lambda' \lambda'' \lambda' \\
0 0 0
\end{array}\right) \left(\begin{array}{ccc}
0 0 0
\end{array}\right) \left(\begin{array}{ccc}
\lambda' \lambda'' \lambda' \\
\lambda_1 \lambda_2 \lambda_1
\end{array}\right) \\
\left(\begin{array}{ccc}
\lambda' \lambda'' \lambda' \\
\lambda_1 \lambda_2 \lambda_1
\end{array}\right) \left(\begin{array}{ccc}
\lambda' \lambda'' \lambda' \\
\lambda_1 \lambda_2 \lambda_1
\end{array}\right) \\
\frac{(-1)^{k + k'}}{(kT)^2} \int \exp\left[-\frac{E_1^t}{kT}\right] \exp\left[-\frac{E_2^t}{kT}\right] \frac{\hbar^2}{(\mu g')^2} \int \exp\left[\sum_{\gamma} n_\gamma (\gamma) \bar{\alpha} n'_{\gamma'} (\gamma')\right] \\
\Omega(kqq')^{-\frac{1}{2}} \Omega(kq'q')^{-\frac{1}{2}} \Omega(q + q')^{-\frac{1}{2}} (2j_1 + 1)(2j_2 + 1)(2j_1 + 1)(2j_2 + 1)^{-\frac{1}{2}}
\[
\sum_{\lambda' \lambda''} \left[ (2\lambda + 1)(2\lambda' + 1)(2q + 1)(2q' + 1) \right]^{\frac{1}{2}} \left( \begin{array}{ccc}
\lambda & \lambda' & k \\
0 & 0 & 0
\end{array} \right) \left[ (2\lambda + 1)(2\lambda' + 1) \right]^{\frac{1}{2}}
\]

\[
\left[ (2j_i^1 + 1)(2\lambda'' + 1) \right]^{\frac{1}{2}} \delta(j_f^1 v_f^1 | j_i^1 v_i^1) \left( \begin{array}{ccc}
j_i^1 + j_i^1 & j_i^1 + \lambda
\end{array} \right) (-1)^{j_i^1 + \lambda}
\]

\[
T(j_i^1 v_i^1 j_2^1 v_2^1; k0k; j_i^1 v_i^1 j_2^1 v_2^1) \{ q_i^1, q_i^1, k \} \}
\]

\[
\left[ (2j_i^1 + 1)(2\lambda + 1) \right]^{\frac{1}{2}} \delta(j_i^1 v_i^1 | j_i^1 v_i^1) \left( \begin{array}{ccc}
j_i^1 + j_i^1 & j_i^1 + \lambda
\end{array} \right) (-1)^{j_i^1 + \lambda'}
\]

\[
T^*(j_f^1 v_f^1 j_2^1 v_2^1; k0k; j_f^1 v_f^1 j_2^1 v_2^1) \{ q_f^1, q_f^1, k \} \} (-1)^{k + q + q'}
\]

while \( \sum''_k \) is analogously expressed as

\[
(7.24) \quad \sum''_k \langle \Delta q_n [j_i^1 v_i^1 | j_f^1 v_f^1] | \lambda' q'n' [j_i^1 v_i^1 | j_f^1 v_f^1] \rangle
\]

\[
= (-1)^{i q' + q' + j_f^1} \Omega(kq')^{-\frac{1}{2}} \Omega(kq'')^{-\frac{1}{2}} \frac{1}{(kT)^2} \sum_{j_2^1 v_2^1} \int E_{tr}^i dE_{tr}^i
\]

\[
\exp\left[ \frac{-E_{tr}^i}{kT} \right] \exp\left[ \frac{-E_{tr}^i}{kT} \right] \frac{v^2}{Q} \int dE_{tr} \mathcal{R} n(\gamma) \mathcal{R} n' \lambda' \gamma')
\]

\[
\delta(E_{tr}^i + E_{tr}^i - E_{tr}^i, j_2^1 v_2^1, E_{tr}^i - E_{tr}^i - E_{tr}^i)
\]

\[
\sum_{\lambda' \lambda''} \left[ (2\lambda + 1)(2\lambda' + 1)(2q + 1)(2q' + 1) \right]^{\frac{1}{2}} \left[ (2j_i^1 + 1)(2j_i^1 + 1) \right]^{\frac{1}{2}} \left( \begin{array}{ccc}
(2j_i^1 + 1)(2j_i^1 + 1) & (2j_i^1 + 1)(2j_i^1 + 1)
\end{array} \right)
\]

\[
[ (2\lambda + 1)(2\lambda' + 1)]^{\frac{1}{2}} (2\lambda' + 1)(2\lambda'' + 1)
\]
\[ \sum \left[ (2 \Lambda_1 + 1) (2 \Lambda_2 + 1)(2 \Lambda_1^' + 1)(2 \Lambda_2^' + 1)(2 \Lambda_1^'' + 1)(2 \Lambda_2^'' + 1) \right]^{1/2} \]

\[ T(j_1^1 v_1^1; j_1^1 v_1^1; j_1^j v_2^j) \]

\[ T^*(j_1^1 v_1^1; j_1^1 v_1^1; j_1^j v_2^j) \]

\[ (-1)^{-1} \Lambda_2^+ \Lambda_1^' \Lambda_1^'' q^r \]

\[ + (-1)^{k+q_1+q_1'} 1_{q+q_1'+q_1''} \Omega(k_qq) \]

\[ \exp \left[ \frac{-E_{tr}}{kT} \right] \exp \left[ \frac{-E_{j_1^1 v_1^1}}{kT} \right] \frac{n^2}{(\mu_g')^2} \bar{A}_{n^1 \Lambda} \bar{A}_{n^1 \Lambda}^{-1} \delta j_1^1 j_1^j \delta v_1^1 v_2^j \delta v_1^1 v_1^1 \]

\[ \sum \left[ (2 \Lambda_1 + 1)(2 \Lambda_1^' + 1)(2 \Lambda_1^'' + 1) \right]^{1/2} \]

\[ [\delta j_2^j \delta v_2^j \delta j_1^j \delta v_1^1] \left[ (2j_1^j + 1)(2j_1^j + 1)(2 \Lambda_1^'' + 1) \right]^{1/2} \]
The derivations of these expressions are not given here but can be obtained by straightforward generalizations of the methods used to obtain equations (3.65) and (3.66). (These methods are outlined in chapter III, section (e), and presented in greater detail by Hunter and Snider.\textsuperscript{18}) The S matrix versions of (7.23) and (7.24) have been quoted previously\textsuperscript{19} and are obtainable from these equations by employing the definition (3.67). Finally, for the case of no velocity polarizations $\varepsilon=\lambda'=n=n'=k=0$, equations (7.23) and (7.24) reduce to equations (4.35) and (4.36), respectively.

Equations (7.23) and (7.24) are exact and express rotationally invariant generalized cross sections in terms of rotationally invariant $T$ (or $S$) matrix elements in the translational-internal coupling scheme. This representation is particularly appropriate to situations in which the anisotropic part of the intermolecular potential is assumed small. With this assumption, the reduced transition operator $T(\cdots |j_1|j_2| \cdots)$ is conveniently expressed as equation (3.84), and a distorted wave Born approximation to the generalized cross sections $\sum'_{k}$ and $\sum''_{k}$ can be established. For convenience of writing, these are expressed as sums, $\sum'_{k} = \sum_{+}'+\sum_{-}'$ and $\sum''_{k} = \sum_{+}''+\sum_{-}''$ according to (7.25)
\[
\sum_{\lambda_1 \lambda_2 \lambda_1'^{'}} (-1)^{\lambda_1} \lambda_1 + \lambda_2 \lambda_1' + \lambda_2 (-1)^{j_1 + j_1' + j_1^f + j_1'^f} \left\{ \begin{array}{ccc}
\lambda_1 & \lambda_1' & k \\
j_1 & j_1 & q \\
j_1^f & j_1^f & j_1^f q'
\end{array} \right\} \left\{ \begin{array}{ccc}
\lambda_2 & \lambda_1' & k \\
j_2 & j_1 & q \\
j_2^f & j_1^f & j_1^f q'
\end{array} \right\}
\]

\[
\langle j_1 v_1 \mid \mathcal{O}_1 \mid j_1 v_1' \rangle \langle j_1 v_1 \mid \mathcal{O}_1 \mid j_1 v_1' \rangle^*
\]

\[
\langle j_2 v_2 \mid \mathcal{O}_2 \mid j_2 v_2' \rangle \langle j_2 v_2 \mid \mathcal{O}_2 \mid j_2 v_2' \rangle^* \quad (2\lambda_2 + 1)^{-1} \exp[-\Delta/2]
\]

\[
(\mathcal{E}_V^{(1)} - \mathcal{E}_p^{(1)}) \langle \lambda n \lambda_1 \lambda_2 \mid \lambda' n' \lambda_1' \lambda_2' \rangle \langle j_1 v_1 \mid f_{v_f} \rangle \langle j_1 v_1' \mid f_{v_f} \rangle \langle j_2 v_2 \mid f_{v_f} \rangle \langle j_2 v_2' \mid f_{v_f} \rangle \exp[-\Delta/2]
\]

\[
(7.26)
\]

\[
\sum_{\lambda_1 \lambda_2 \lambda_1'^{'}} (-1)^{\lambda_1} \lambda_1 + \lambda_2 \lambda_1' + \lambda_2 (-1)^{j_1 + j_1' + j_1^f + j_1'^f} \left\{ \begin{array}{ccc}
\lambda_1 & \lambda_1' & k \\
j_1 & j_1 & q \\
j_1^f & j_1^f & j_1^f q'
\end{array} \right\} \left\{ \begin{array}{ccc}
\lambda_2 & \lambda_1' & k \\
j_2 & j_1 & q \\
j_2^f & j_1^f & j_1^f q'
\end{array} \right\}
\]

\[
\langle j_1 v_1 \mid \mathcal{O}_1 \mid j_1 v_1' \rangle \langle j_1 v_1 \mid \mathcal{O}_1 \mid j_1 v_1' \rangle^* \exp[-\Delta/2]
\]

\[
\langle j_2 v_2 \mid \mathcal{O}_2 \mid j_2 v_2' \rangle \langle j_2 v_2 \mid \mathcal{O}_2 \mid j_2 v_2' \rangle^* \quad (2\lambda_2 + 1)^{-1} \exp[-\Delta/2]
\]

\[
= i^{q+q'} \sum_{\lambda_1 \lambda_2 \lambda_1'^{'}} (-1)^{\lambda_1} \lambda_1 + \lambda_2 \lambda_1' + \lambda_2 (-1)^{j_1 + j_1' + j_1^f + j_1'^f} \left\{ \begin{array}{ccc}
\lambda_1 & \lambda_1' & k \\
j_1 & j_1 & q \\
j_1^f & j_1^f & j_1^f q'
\end{array} \right\} \left\{ \begin{array}{ccc}
\lambda_2 & \lambda_1' & k \\
j_2 & j_1 & q \\
j_2^f & j_1^f & j_1^f q'
\end{array} \right\}
\]

\[
\langle j_1 v_1 \mid \mathcal{O}_1 \mid j_1 v_1' \rangle \langle j_1 v_1 \mid \mathcal{O}_1 \mid j_1 v_1' \rangle^* \quad (2\lambda_2 + 1)^{-1} \exp[-\Delta/2]
\]

\[
(7.26)
\]

\[
\sum_{\lambda_1 \lambda_2 \lambda_1'^{'}} (-1)^{\lambda_1} \lambda_1 + \lambda_2 \lambda_1' + \lambda_2 (-1)^{j_1 + j_1' + j_1^f + j_1'^f} \left\{ \begin{array}{ccc}
\lambda_1 & \lambda_1' & k \\
j_1 & j_1 & q \\
j_1^f & j_1^f & j_1^f q'
\end{array} \right\} \left\{ \begin{array}{ccc}
\lambda_2 & \lambda_1' & k \\
j_2 & j_1 & q \\
j_2^f & j_1^f & j_1^f q'
\end{array} \right\}
\]

\[
\langle j_1 v_1 \mid \mathcal{O}_1 \mid j_1 v_1' \rangle \langle j_1 v_1 \mid \mathcal{O}_1 \mid j_1 v_1' \rangle^* \exp[-\Delta/2]
\]
\[ \sum_{p} (1) \left( \sum_{l_{1}l_{2}l_{1}'l_{2}'} \mathcal{O}_{1} \mathcal{O}_{1}' \right) |E_{1} v_{1} + E_{2} v_{2} - E_{1} v_{1}' - E_{2} v_{2}'\rangle \kappa \]

\[ + (-1)^{k+q+q'} \left( \sum_{j_{1}'v_{1}} \delta(j_{1}'v_{1}|j_{1}v_{1}') \right) \left( \sum_{j_{f}v_{f}} \delta(j_{f}v_{f}|j_{f}v_{f}') \right) \]

\[ \langle j_{f}v_{f}' | \mathcal{J}_{1} | j_{1}'v_{1}' \rangle \langle j_{1}v_{1} | \mathcal{J}_{1}' | j_{f}v_{f} \rangle \exp[-\Delta/2] \]

\[ \sum_{p} (1) \left( \sum_{l_{1}l_{2}l_{1}'l_{2}'} \mathcal{O}_{1} \mathcal{O}_{1}' \right) |E_{1} v_{1} + E_{2} v_{2} - E_{1} v_{1}' - E_{2} v_{2}'\rangle \kappa \]

\[ + \frac{(-1)^{q+q'}}{2\pi i} \sum_{j_{2}v_{2}} \exp\left[ -\frac{E_{j_{2}v_{2}}}{kT} \right] \Omega(kq')^{-\frac{1}{2}} [(2q+1)(2q'+1)]^{\frac{k}{2}}(2j_{2}+1)(2k+1)^{-3/2} \]

\[ (-1)^{j_{1}+j_{f}} \sum_{h} (\sum_{\xi} \mathcal{O}_{h}^{(k)} \mathcal{O}_{h}^{(k)'}) \delta(j_{1}v_{1}|j_{1}v_{1}') \]

\[ \times \langle j_{f}v_{f}' | \mathcal{J}_{1} | j_{1}v_{1}' \rangle \delta(j_{f}v_{f}|j_{f}v_{f}') \]

\[ - (-1)^{k+q+q'} \langle j_{1}v_{1} | \mathcal{J}_{1} | j_{1}v_{1}' \rangle \delta(j_{f}v_{f}|j_{f}v_{f}') \]

\[ \text{(7.27)} \]

\[ \sum_{\epsilon} (\sum_{\xi} \mathcal{J}_{1} \mathcal{J}_{1}') |\epsilon \rangle q' n' |j_{1}'v_{1}'|j_{f}'v_{f}'\rangle \kappa \]

\[ = i^{q'-q} \Omega(kq')^{-\frac{1}{2}} \sum_{j_{2}v_{2}} \exp\left[ -\frac{E_{j_{1}v_{1}'}}{kT} \right] [(2q+1)(2q'+1)]^{\frac{k}{2}} (-1)^{j_{1}+j_{f}} \]

\[ \sum_{\epsilon} (\sum_{\xi} \mathcal{J}_{1} \mathcal{J}_{1}') |\epsilon \rangle q' n' |j_{1}'v_{1}'|j_{f}'v_{f}'\rangle \kappa \]

\[ = i^{q'-q} \Omega(kq')^{-\frac{1}{2}} \sum_{j_{2}v_{2}} \exp\left[ -\frac{E_{j_{1}v_{1}'}}{kT} \right] [(2q+1)(2q'+1)]^{\frac{k}{2}} (-1)^{j_{1}+j_{f}} \]

\[ \sum_{\epsilon} (\sum_{\xi} \mathcal{J}_{1} \mathcal{J}_{1}') |\epsilon \rangle q' n' |j_{1}'v_{1}'|j_{f}'v_{f}'\rangle \kappa \]
\[
\langle j_1^v_1 | \mathcal{O}_1 (\mathcal{L}_1) | j_1^v_1 \rangle \langle j_2^v_2 | \mathcal{O}_2 (\mathcal{L}_2) | j_1^v_1 \rangle \\
\langle j_1^v_1 | \mathcal{O}_1 (\mathcal{L}_1') | j_f^v_f \rangle \langle j_2^v_2 | \mathcal{O}_2 (\mathcal{L}_2') | j_f^v_f \rangle \exp[-\Delta/2] \\
(\sum_{\mathcal{P}}^{(1)} - \sum_{\mathcal{P}}^{(1)}) (\mathcal{Qn} \mathcal{L}_1 \mathcal{L}_2 | \mathcal{E} Q \mathcal{L}_1 \mathcal{L}_2 | E_{j_f^v_f} + E_{j_2^v_2} - E_{j_1^v_1} - E_{j_1^v_1}) k
\]

and

(7.28)
\[
\sum_{\mathcal{P}}^{(1)} (-\mathcal{Qn} [j_1^v_1 | j_f^v_f] | \mathcal{Q}' Q [j_1^v_1 | j_f^v_f]) k
\]

= \text{i} ^{q \times q'} \Omega (k q q') ^{-\frac{1}{2}} \sum_{j_2^v_2} \exp \left[ \frac{-E_{j_1^v_1}}{k T} \right] (-1)^{j_1 + j_f} \left[ (2q+1)(2q'+1) \right] ^{\frac{1}{2}}
\]

\[
\sum_{j_1^v_1} \sum_{j_2^v_2} \frac{1}{2} \left\{ L_1 L_1' q \right\} \left\{ L_2 L_2' q \right\} \sum_{j_f^v_f} \left\{ \mathcal{L}_1 \mathcal{L}_2 \mathcal{L} \right\} \left\{ \mathcal{L}_1 \mathcal{L}_2 \mathcal{L}' \right\}
\]

\[
\langle j_1^v_1 | \mathcal{O}_1 (\mathcal{L}_1) | j_1^v_1 \rangle \langle j_2^v_2 | \mathcal{O}_2 (\mathcal{L}_2) | j_1^v_1 \rangle \exp[-\Delta/2] \\
\langle j_1^v_1 | \mathcal{O}_1 (\mathcal{L}_1') | j_1^v_1 \rangle \langle j_2^v_2 | \mathcal{O}_2 (\mathcal{L}_2') | j_1^v_1 \rangle
\]

x \left[ \delta(j_2^v_2 | j_1^v_1') \delta(j_1^v_1' | j_f^v_f) \right]

\[
(\sum_{\mathcal{P}}^{(1)} (-\mathcal{Qn} \mathcal{L}_1 \mathcal{L}_2 | \mathcal{Q}' Q \mathcal{L}_1 \mathcal{L}_2 | E_{j_1^v_1} + E_{j_2^v_2} - E_{j_1^v_1} - E_{j_1^v_1}) k
\]

+ \delta(j_2^v_2 | j_1^v_1') \delta(j_1^v_1' | j_1^v_1)
These DWBA expressions reduce to equations (4.42) through (4.45) for the case of no velocity polarizations ($\xi = \nu = \xi' = \nu' = k = 0$), and to equations (3.88), (3.89), (3.94) and (3.95) when only "diagonal in $j$" polarizations are considered. (In this latter case, care must be taken to observe the different linearization (3.9) employed in chapter III, which leads to different Boltzmann weights in these expressions, and the definition (4.11), which gives different (2j+1)$^k_2$ degeneracy factors.)

Equations (7.25) through (7.28) involve the translational integrals $\mathbb{G}^{(1)}_V$, $\mathbb{G}^{(1)}_P$ and $\mathbb{G}^{(2)}_h$ which still must be evaluated. In analogy with the approach taken in chapter III, section (g) and chapter IV, section (e), these integrals are estimated by a (high temperature) modified Born approximation and only for a specific example - the relaxation of the dipole moment flux described by $\langle \langle L^{10} \nu | \mathcal{R} | L^{10} \nu \rangle \rangle$. Other collisional rates such as $\langle \langle L^{10} \Delta N | \mathcal{R} | L^{10} \Delta N \rangle \rangle$ and $\langle \langle L^{20} \nu | \mathcal{R} | L^{20} \nu \rangle \rangle$, which arise when making (low density) corrections to the description provided in the last section, can be evaluated similarly.
First, the contribution of \( \sum_{h}^{(k)} \) vanishes for \( k=0 \) in the high temperature approximation. For terms involving \( \sum_{V}^{(1)} \), it is assumed that the spherical parts of the potential dominate so that only \( \sum_{V}^{(1)}(\ell n 000|\ell n 000|x)_{0} \) is of importance. In particular then, the relationship

\[
(7.29) \quad \int_{V}^{(1)}(10 000|10 000|0)_{0} = \frac{4}{3} (\frac{2\pi \mu}{kT})^{3/2} \Omega^{(1,1)}
\]

can be established (see chapter III, equation (3.101) or reference (17)) when energetically inelastic collisions can be neglected. Here the \( \Omega^{(\ell, s)} \) integrals are those of Chapman and Cowling\(^{21} \) while, in particular, \( \Omega^{(1,1)} \) is related to the diffusion constant. The transformation back from the relative velocity description to the description in terms of the velocities of the two colliding molecules, as required by equation (7.22), is given in this case by

\[
(7.30) \quad I^{(0)}(10 10; \ell n \ell n) = \delta_{\ell,1} \delta_{n,0}.
\]

Further, because of the spherical potential is the identity operator for internal states, contributions from \( \mathcal{C}' \) ultimately produce an internal state factor \( \langle \psi(\cdot) \psi \rangle \), while contributions from \( \mathcal{C}'' \) vanish identically because \( \text{tr}_{1,2}\{\psi(\cdot)\psi(\cdot)\psi(\cdot)\} = 0 \).

Next, for terms involving \( \sum_{P}^{(1)} \), a modified Born approximation to this collision integral is employed, namely

\[
(7.31) \quad \sum_{P}^{(1)}(\ell n \ell 1 \ell 2|\ell n \ell 1 \ell 2|0)_{0} = (2 \ell +1)^{3/2} \frac{\pi^{3/2}}{2} \int_{0}^{\infty} \int_{Y} R_{n\ell}(Y) R_{n\ell}(Y) dy dY \]

\[
= (2 \ell +1)^{3/2} \frac{\pi^{3/2}}{2} \int_{0}^{\infty} \sum_{A} A_{\ell 1 \ell 2}^{2} dY dY.
\]
as discussed by Snider. In the absence of velocity polarizations, \( \ell = n = 0 \) and equation (7.31) becomes equation (3.109). When velocity polarizations are present - of interest here - it is useful to further assume that the differential cross section \( |\mathcal{A}_{\ell_1 \ell_2}|^2 \) is independent of the velocity so that equation (7.31) is approximately

\[
(7.32) \quad \sum_{\mathcal{P}}^{(1)}(\ell n \ell_1 \ell_2 | \ell n \ell_1 \ell_2 | 0)_{0} = \omega_{nn} \sum_{\mathcal{P}}^{(1)}(00 \ell_1 \ell_2 | 00 \ell_1 \ell_2 | 0)_{0}.
\]

The weight factor

\[
(7.33) \quad \omega_{nn} = 2 \int \gamma^3 d\gamma \exp \left[ -\gamma^2 \right] \Re n_\ell(\gamma) \Re n_\ell(\gamma)
\]

is the only part of equation (7.32) that depends on the presence of the velocity polarizations. Indeed, the transformation (7.22) affects only equation (7.33). Further, as discussed by Chen et al, the approximate effect of this transformation is to average \( \omega_{nn} \) to unity in contributions from \( \mathcal{B}' \) and to cause contributions from \( \mathcal{B}'' \) to vanish. This has the interesting consequence that equations (7.25) and (7.26) reduce to equations (4.42) and (4.43). (To see this, consider equations (7.25) and (7.26) for \( k = 0 \), \( \sum_{\mathcal{P}}^{(1)} \) contributions ignored, and \( \sum_{\mathcal{P}}^{(1)} \) given by equations (7.32).)

Thus, the relaxation of the "composite polarization" \( L^{10}(W) \) can be approximately split into two parts - the first representing the relaxation of \( L^{10}(W) \) under the influence of the spherical potential and the second giving the pure internal state relaxation of \( W \). Explicitly,
where the prime indicates that only \( L \) type contributions are considered.

Consistent with the DWBA approach, the term \( \frac{1}{T_f} \) is expected to be smaller than the spherical part, \( 16n \Omega^{(1,1)} \). The division exhibited by equation (7.34) into "velocity changing" and "phase changing" parts is reminiscent of the division of the collision superoperator itself, equation (7.12).

In the treatment of collisions presented in this thesis, a hierarchy of approximations has been described. This can be interrupted at any stage if more exact expressions are desired. However, if this hierarchy is followed to its most approximate end, a simple physical "picture" of the relaxation process results. Consider the arbitrary velocity and internal state polarizations \( \xi^\mu_L \) and \( \xi^\nu_q \), respectively. Then the relaxation of such a "composite polarizations can be expressed as

\[
\langle \xi q^n | \xi q^n \rangle_0 = F \langle \xi n000 | \xi n000 \rangle_0 + G \langle \xi n000 | \xi n000 \rangle_0
\]

where \( F, G \) are calculable factors and \( (\angle \angle_1 \angle_2) \) represents the dominant anisotropic potential. Equation (7.34), which describes the relaxation of
the composite polarization \( L_{10}^{(W)} \), is an example of this structure. The term involving \( \mathcal{F}_{p}^{(1)} \) does not contribute to pure velocity relaxation \((q=0)\) - for example, see equation (3.105) describing the relaxation of \( L_{20}^{(W)} \). On the other hand, the \( \mathcal{F}_{v}^{(1)} \) part of equation (7.35) vanishes if only internal state relaxation processes are of interest. In the spectroscopic case, the operators \( \mathcal{D}(q) \) are generally "off-diagonal in j" while in Senftleben-Beenakker studies, \( \mathcal{D}(q) \) is restricted to "diagonal in j" forms. The relaxation of \( \mu \), specified by \( \frac{1}{\tau_{2}} \), is an example of the first type and the relaxation of \( \gamma^{(2)}(J) \), described in chapter III by \( \tau_{\text{int}}^{-1} \), is an example of the second type of pure internal state decay.

In both spectroscopic and S-B experiments, the production terms \( \mathcal{S}(\& q n|\ell' q' n')_{k}, k \neq 0 \), are expected to be small. However, while in the former they can be safely neglected, in the latter they are fundamental to a proper description of the phenomena and can not be ignored. Thus in chapter III, a production term, \( \psi \), was a necessary part of the formalism.

This completes the description of the collisional aspects of velocity effects on spectroscopic phenomena and their relationship to Senftleben-Beenakker studies.
(e) Model Methods applied to Velocity Effects.

The moment method has been employed throughout this thesis to solve the various equations of motion and obtain a description of the motions of the gas system. In fact, however, this description is of limited validity and applies only in the "continuum region" where the density of gas molecules is sufficiently high. In this region, the gas molecules collide often enough to allow any non-equilibrium character to be described in terms of average polarizations of the gas. As the density is lowered, the number of polarizations necessary to give a good description of the gas motions increases to unmanageable proportions. This reflects the physical situation where collisions are so infrequent that each molecule has its individual velocity characteristics. To effectively describe the motions of the gas in this density region, an alternate approach must be taken. The model method is such an alternate approach.

The model method retains the exact free streaming parts of the equation of motion but employs an approximate (model) collision operator which possess many qualitative and average properties of the true collision operator. This method was originally applied to the classical linearized Boltzmann equation and later extended to linearized quantum Boltzmann equations, both the Wang-Chang Uhlenbeck and the Waldmann-Snider versions.
Indeed, model methods applied to this last equation would allow the description of Senftleben-Beenakker effects in the continuum region (chapter III, section (d)), to be extended to the rarefied gas (or Knudsen) regime.

The present section applies the model method to the steady state, non saturation lineshape problem. As such, the modelling of the linearized collision operator, equation (7.12), of the Waldmann-Snider form is considered. This should be sufficient to introduce the method to the discussion of spectroscopic phenomena. This section may be considered as a "justification" of the previously presented moment method approach to spectroscopic phenomena, in the sense that the moment method represents the high density (continuum) limit of the model method.

The restriction to non-saturation, steady state effects, introduces a great simplification into the description. Indeed, as far as the internal states are concerned, there are only two operators, \( \mu \) and \( \nu \), which are perturbed from equilibrium. Equivalently, the two operators

\[
\mu_+ \equiv \mu + i\nu
\]

\[
\mu_- \equiv \mu - i\nu = (\mu_+)^\dagger
\]

can be used, and are used here, to describe the internal state non equilibrium character. Thus, the distribution
function appropriate to this problem is written as

\[(7.37) \quad f(v) = \frac{e^{-\frac{w^2}{(2\pi mkT)^{3/2}}} \left\{ e^{-\frac{H_0}{kT}} + \phi(v) \right\}}{\Omega},\]

where the perturbation, \(\phi(v)\), has the form

\[(7.38) \quad \phi(v) = \phi_+(v) + \phi_-(v)\]

Here, \(\phi_+(v)\) and \(\phi_-(v)\) are those parts of \(\phi(v)\) which are proportional to \(\mu_+\) and \(\mu_-\), respectively. More precisely, these relationships are

\[(7.39) \quad \phi_+(v) = \mu_+ \cdot \mathcal{A}_+(v) \cdot \frac{3\mu_+ \cdot \langle \phi_+ \rangle^+}{\langle \mu_+ | \mu_+ \rangle}\]
\[\quad \phi_-(v) = \mu_- \cdot \mathcal{A}_-(v) \cdot \frac{3\mu_- \cdot \langle \phi_- \rangle^+}{\langle \mu_- | \mu_- \rangle}\]

where the last forms represent the high density limits. Indeed, this section specifies the manner in which the limits (7.39) occur.

Employing equations (7.37) and (7.38) in equation (7.11), the equations of motion for \(\phi_+(v)\) and \(\phi_-(v)\) are

\[(7.40) \quad -i(\Delta \omega - k \cdot v) \phi_+ + \mathcal{R} [\phi_+] = i\kappa^2 \frac{\hbar \Delta N}{4} \left\{ \frac{3\mu_+ \cdot E_0}{\langle \mu_+ | \mu_+ \rangle} \right\} \]
respectively. These equations are collisional uncoupled on the assumption that collisions conserve frequency. As (7.40) and (7.41) are complex conjugates of each other, it is sufficient to study just one of the pair. The remainder of this section will consider the solution of (7.14) for various models of the collision superoperator .

In the past, two models have been traditionally employed,

\[(7.42) \quad \mathcal{R}[\phi_] = \frac{1}{\tau_a} \phi_\]

and

\[(7.43) \quad \mathcal{R}[\phi_] = \frac{1}{\tau_a} \frac{3\mu_- \cdot \phi_+}{\langle \mu_- | \cdot \mu_+ \rangle} + \frac{1}{\tau_b} (\phi_- - \frac{3\mu_- \cdot \phi_+}{\langle \mu_- | \cdot \mu_+ \rangle} )\]

In order to make proper connection with the high density limits, the identifications
are made, where the last equalities follow, ignoring collisional shifts. However, these "traditional" methods ignore an important invariance property of $R$, namely conservation of parity.

$$R[\phi] = R_e[\phi^e] + R_o[\phi^o]$$

where $\phi^e$ and $\phi^o$ are the even and odd (in velocity) parts of $\phi$, respectively. Equation (7.45) implies that (7.42) and (7.43) are special cases of the more general modellings

$$R[\phi^-] = \frac{1}{T_a} \phi^- + \frac{1}{T_b} \phi^-$$

and

$$R[\phi^-] = \frac{1}{T_a} \frac{3\mu_- \langle y^+ \rangle}{\langle y_- \cdot y_- \rangle} + \frac{1}{T_c} (\phi^e - 3\mu_- \langle y^+ \rangle) + \frac{1}{T_b} \phi^-$$

In equation (7.47), the identification
\[ (7.48) \quad \frac{1}{\tau_c} = \frac{15 < l^{20}_{\nu} \mid \mathcal{R} \mid l^{20}_{\nu} >}{< l^{20}_{\nu} \mid \dagger l^{20}_{\nu} >} \]

\[ = \frac{15 < l^{20}_{\nu} \mid \mathcal{R} \mid l^{20}_{\nu} >}{< l^{20}_{\nu} \mid \dagger l^{20}_{\nu} >} \]

again follows from the high density limit. Thus, in order to treat all relevant cases, equation (7.41) is solved using the model (7.47), and then special cases of this model are considered.

With \( \mathcal{R} \) expressed as equation (7.47), the perturbation \( \phi_- \) is divided into

\[ (7.49) \quad \phi_- = \frac{3\mu_- \cdot <\mu_+>}{<\mu_- \cdot \mu_->} + \phi^0 - \frac{3\mu_- \cdot <\mu_+>}{<\mu_- \cdot \mu_->} \]

and the coupled set of integral equations

\[ (7.50) \quad (i\Delta \omega + \frac{1}{\tau_a}) \frac{3\mu_- \cdot <\mu_+>}{<\mu_- \cdot \mu_->} = \frac{i\int dp e^{-p^2}}{(2\pi mkT)^{3/2}} \mathbf{k} \cdot \mathbf{v} \phi^0 \]

\[ - i\kappa^2 \frac{3\mu_- \cdot \mathcal{E}}{4 \text{ eq} <\mu_- \cdot \mu_->} \]

\[ (i\Delta \omega + \frac{1}{\tau_b}) \phi^0 = i\kappa \mathbf{v} \left[ \frac{3\mu_- \cdot <\mu_+>}{<\mu_- \cdot \mu_->} + \left( \phi^e - \frac{3\mu_- \cdot <\mu_+>}{<\mu_- \cdot \mu_->} \right) \right] \]
are obtained from equation (7.41). The solution of this set of equations allows the moment \( \langle \mu_+ \rangle \) to be expressed as

\[
(7.51) \quad \langle \mu_+ \rangle \equiv \text{tr} / \frac{dp e^{-W^2}}{(2\pi mkT)^{3/2}} (\mu_-) + \phi - \frac{i \Delta \omega + 1}{\tau_b} \]

\[
1 - \left( \frac{1}{\tau_c} - \frac{1}{\tau_a} \right) \int \frac{dp e^{-W^2}}{(2\pi mkT)^{3/2}} \frac{(i \Delta \omega + 1)}{[(i \Delta \omega + 1/\tau_b)(i \Delta \omega + 1/\tau_c) + (k \cdot \nu)^2]}.
\]

Of course, the expression for the absorption coefficient is proportional to \( \langle \mu \rangle \), which can be obtained from \( \langle \mu_+ \rangle \) by the relation

\[
(7.52) \quad \langle \mu \rangle = \frac{\langle \mu_+ \rangle - \langle \mu_- \rangle}{2}
\]

\[
= \Im \langle \mu_+ \rangle.
\]

Equation (7.51) gives a three relaxation parameter description of a microwave absorption lineshape, valid over a wide range of gas density. In particular, it gives the
Doppler lineshape at the low density extreme and a Lorenztian lineshape at the high density limit. Equation (7.51) represents the most complete description given in this thesis of the manner in which the transition from the Doppler broadened regime to the pressure broadened regime is achieved.

The simpler collision model equations (7.42), (7.43) and (7.46), lead to special cases of the result (7.51). In particular, the Voigt profile is obtained with a one relaxation time model, \((\tau_c = \tau_b = \tau_a)\),

\[
\langle \mu_+ \rangle = -i\kappa^2 \frac{\hbar \Delta N}{4} \text{eq } E_0 \int \frac{dp \ e^{-W^2}}{(2\pi mkT)^{3/2}} \left( i\Delta \omega + \frac{1}{\tau_a} \right) \frac{(i\Delta \omega + \frac{1}{\tau_b})}{[(i\Delta \omega + \frac{1}{\tau_a})^2 + (k \cdot \chi)^2]}. \tag{7.53}
\]

If the model, equation (7.43), is employed \((\tau_c = \tau_b)\), the resulting expression

\[
\langle \mu_+ \rangle = \frac{-i\kappa^2 \frac{\hbar \Delta N}{4} \text{eq } E_0 \int \frac{dp \ e^{-W^2}}{(2\pi mkT)^{3/2}} \left( i\Delta \omega + \frac{1}{\tau_a} \right) \frac{(i\Delta \omega + \frac{1}{\tau_b})}{[(i\Delta \omega + \frac{1}{\tau_a})^2 + (k \cdot \chi)^2]}}{1 - \left( \frac{1}{\tau_a} - \frac{1}{\tau_b} \right) \int \frac{dp \ e^{-W^2}}{(2\pi mkT)^{3/2}} \left( i\Delta \omega + \frac{1}{\tau_b} \right) \frac{(i\Delta \omega + \frac{1}{\tau_b})}{[(i\Delta \omega + \frac{1}{\tau_b})^2 + (k \cdot \chi)^2]}}. \tag{7.54}
\]
produces a lineshape that has also been discussed previous­ly.\textsuperscript{4,15} Finally, if $T_c = T_a$, the model (7.46) gives

\begin{equation}
\langle U \rangle = -i k^2 \frac{\kappa N}{4} \text{eq} \frac{E_0}{\pi m T} \frac{d \rho e^{-\omega^2}}{2} (2\pi m k T)^{3/2}
\end{equation}

\begin{equation}
\frac{(i \Delta \omega + \frac{1}{\tau_b})}{[(i \Delta \omega + \frac{1}{\tau_a})(i \Delta \omega + \frac{1}{\tau_b}) + (k \cdot y)^2]}
\end{equation}

Equation (7.55) results from emphasizing parity conservation. Its associated lineshape has not been considered previously.

Equation (7.53) yields a linewidth that increases monotonically with pressure, even at very low gas densities. This is in contradiction with usual experimental observa­tion. Equations (7.54) and (7.55) allow for more general pressure dependences of the lineshape. Of the two, the form (7.55) gives a simpler description. More careful experimental measurements on the pressure dependence of lineshapes are required in order to ascertain which form will give a more faithful representation of the observed behaviour.

The more general problem of describing the effects of velocity on saturated lineshapes and coherence transient experiments in the microwave region, have yet to be attempted from a model method approach. The result, of course, would be a description valid over a whole range of
gas densities and such that equations (7.17) are obtained as the high density limits. A treatment of these types of effects for the optical region has been given by Berman et al. but we feel that further consideration is necessary before their simple model can be applied to the microwave case.
(f) Thesis Conclusion

This thesis has presented the subjects of pressure broadening and coherence transient effects in the microwave region of the spectrum from a kinetic theory point of view. The various free motion aspects of the molecular motions—oscillations, rotations, and translations—have all been treated in a uniform manner. In particular, the concept of a two level system has been developed in order to analyze the rotational motions in a consistent fashion. The collisional effects on these motions have also been discussed in detail—the exact forms of the relevant matrix elements of the collision superoperator $\mathcal{R}$ have been specified and these have been approximately evaluated within the context of a distorted wave Born approximation.

The vector (and tensor) nature of the motions have been emphasized throughout the thesis. This gives a clearer understanding of the physical motions that are involved, indicates additional effects which should be observable experimentally, and allows the smallest number of independent collision matrix elements to be specified (through use of the rotational invariance properties of $\mathcal{R}$).

The methods employed in this thesis parallel those used to describe the Senftleben-Beenakker effects. Indeed, connections with the theory of the S-B effects have been stressed throughout (especially in the collisional treatments). This "unified point of view" should contribute to
a more complete understanding of both spectroscopic and transport phenomena. As an example of this, consider the rotational polarizations \( y^{(q)}(j\rho^j vv') \) which have been used extensively in the explanation of Senftleben-Beenakker effects. The work of this thesis has shown how these polarizations also arise in pressure broadening and coherence transient effects.

As a further indication of the usefulness of such a unified approach, experiments involving the effects of oscillating fields on transport phenomena\(^{28}\) should be pointed out. These experiments represent modifications of the usual Senftleben-Beenakker effects since oscillating fields are used in place of, or in conjunction with, the static electric or magnetic fields. As the frequency of the applied field is swept through the natural oscillation frequencies of the molecules, resonances occur - just as in the normal spectroscopic experiments discussed in this thesis. The effects of these resonances on the transport properties of the gas are then observed. The application of the theory presented in this thesis to the (quantum mechanical) description of these phenomena, represents a natural extension of the present work.
Chapter I


3. H. Kuhn, Phil. Mag. 18, 987 (1934).


Chapter II


Chapter III


31. B. Shizgal, to be published.

Chapter IV

Chapter V


Chapter VI


Chapter VII


9. see P. R. Berman, Phys. Rev. A5, 927 (1972), and references therein.


27. G. Tonti and R. C. Desai, to be published.


Appendix A


Appendix B

APPENDIX A

The Generalized Boltzmann Equation of Snider and Sanctuary

The starting point is the $N$-molecule Liouville equation

$$i\hbar\frac{\partial \rho^{(N)}}{\partial t} = \mathcal{L}^{(N)}\rho^{(N)} = \mathcal{H}^{(N)}\rho^{(N)} - \rho^{(N)}\mathcal{H}^{(N)}, \quad (A.1)$$

where the Hamiltonian $\mathcal{H}^{(N)}$ is assumed to be a sum of one- and two-molecule terms

$$\mathcal{H}^{(N)} = \sum_i \mathcal{H}_i + \sum_{i<j} V_{ij}, \quad (A.2)$$

and the $N$-molecule density $\rho^{(N)}$ is normalized as

$$\text{tr}_n \rho^{(N)} = N! \quad (A.3)$$

Equations for the reduced density operators

$$\rho^{(N)} = \text{tr}_{(N-n)} \rho^{(N)}/(N-n)! \quad (A.4)$$

can be derived from equation (A.1) by taking the appropriate traces. In particular, the first two equations in this quantum BBGKY hierarchy are

$$i\hbar\frac{\partial \rho^{(1)}}{\partial t} = \mathcal{L}_1 \rho^{(1)} + \text{tr}_2 \mathcal{V}_{12} \rho^{(2)}, \quad (A.5)$$

and
where

\( (A.7) \quad \mathcal{V}_{12} = \mathcal{V}_{12} \) \quad \text{and} \quad \mathcal{V}_{12} \)

\( (A.8) \quad \mathcal{L}_{12}^{(2)} = \mathcal{K}_{12} + \mathcal{V}_{12} \equiv \mathcal{L}_1 + \mathcal{L}_2 + \mathcal{V}_{12} \)

This set of equations is not closed and some approximation scheme (usually by truncation) must be developed to close it.

The truncation scheme described here is within the "philosophy" of the Boltzmann equation. Namely, (i) only binary collisions are important and these are assumed to occur on a time scale short compared to the time between collisions \( \tau_f \); and (ii) the pair density operator factors before a collision. Thus, assumption (i) allows the term involving \( \rho_{123}^{(3)} \) to be neglected in equation (A.6), while assumption (ii) implies that the pair density operator satisfies the asymptotic condition.

\( (A.9) \quad \text{tr-lim} \left[ \rho_{12}^{(2)}(t_o) - \rho_{1}^{(1)}(t_o) \rho_{2}^{(1)}(t_o) \right] \rightarrow 0. \)
Here "∞" is a time long compared to the duration of a collision but short compared to the time between collisions. Equation (A.6), with the $\rho_{123}^{(3)}$ term neglected, and equation (A.8), leads to the definition of the Moller superoperator $\Omega$ as

\[(A.10) \quad \rho^{(2)}(t) = \Omega \rho^{(2)}(t) \rho^{(1)}(t)\]

\[= \operatorname{tr} \lim_{t \to -\infty} e^{-i\hbar \mathcal{L}^{(2)}_0 t} e^{i\hbar \mathcal{K}_0 t} \rho^{(2)}(t) \rho^{(1)}(t).\]

Further, if the Moller wave operator $\Omega$ exists, it has been proven\(^2\) that

\[(A.11) \quad \Omega \mathcal{L} = \mathcal{L} \Omega^+\]

Substitution of equation (A.10) into equation (A.5), results in the generalized quantum Boltzmann equation\(^1\)

\[(A.12) \quad i\hbar \frac{\partial}{\partial t} \rho_1 = \mathcal{L}_1 \rho_1 + \operatorname{tr}_2 \mathcal{J}_{12} \rho_1 \rho_2\]

where the superscript notation has been dropped and where the transition superoperator $\mathcal{J}$ is defined as

\[(A.13) \quad \mathcal{J} = \mathcal{V} \Omega\]

Equation (A.12) is the superoperator analog of the transition
that appears in the usual formal theory of scattering. Indeed, substitution of (A.11) and (A.14) into (A.13) gives the identification

\[(A.15) \quad \mathcal{J}A = tA\Omega^+ - \Omega A t^+\]

A form for \(\mathcal{J}\) alternate to equation (A.15) is obtained by employing the Lippmann-Schwanger integral equation for \(\Omega\). Most precisely, this integral equation is written as

\[(A.16) \quad \Omega = 1 + G[V\Omega] = 1 + G[t]\]

where \(G\) is a "Green's function superoperator"

\[(A.17) \quad G[t] = \lim_{\varepsilon \to 0^+} (-\mathcal{H} + i\varepsilon)^{-1} [t]\]

Equations (A.15) and (A.16) can then be combined to give

\[(A.18) \quad \mathcal{J}A = tA - At^+ - tAG[t^+] - G[t]At^+\]

The expressions for \(\mathcal{J}\), equations (A.15) or (A.18), generally involve "off-the-energy-shell" transition operators
t. In many applications, however, it is conventional to assume that only "on-the-energy-shell" transition operators \( t_d \) are important. In this case, equation (A.17) is approximated as

\[(A.19) \quad \mathcal{J}_A = \mathcal{J}_{H \Lambda} = t_d \Lambda - \Lambda t_d^* + 2\pi i t_d \delta(H) t^*\]

Here, \( \mathcal{J}_H \) is a "frequency conserving" transition superoperator. In addition to this property of "frequency conservation," \( \mathcal{J}_H \) possesses an important symmetry property under time reversal - namely

\[(A.20) \quad \Theta \mathcal{J}_H \Theta^{-1} = \mathcal{J}_{H^\neq}\]

where "\( \neq \)" represents the superoperator adjoint and \( \Theta \) is the time-reversal superoperator

\[(A.21) \quad \Theta A = \theta A \theta^{-1},\]

here expressed in terms of the (antilinear) time reversal operator \( \theta \). This property of \( \mathcal{J}_H \) under time reversal follows directly from the behaviour of \( t_d \) under time reversal. Indeed, with (A.14), (A.16), and \( t_d \) restricted to the energy \( E \), \( t_d \) can be conveniently expressed as
\( t_d(E) = V + \text{st-lim}_{\epsilon \to 0^+} V(E - \mathcal{H}^{(2)} + i\epsilon)^{-1} V \)

so that under time reversal,

\( t_d(E) = 0 t_d(E) \theta^{-1} \)

\[ = V + \text{st-lim}_{\epsilon \to 0^+} V[E - \mathcal{H}^{(2)} - i\epsilon]^{-1} V \]

\[ = t_d^+(E). \]

This follows from the hermitian properties of \( V \) and \( \mathcal{H}^{(2)} \).

A combination of equations (A.23) and (A.19) then establishes equation (A.20).
APPENDIX B

Irreducible Tensors of SO(3)

A spherical basis for the 2q+1 dimensional space of symmetric traceless rank q tensors is e(q)V. These are chosen to satisfy the group operations

\[ (B.1) \quad J_z^{(q)} e^{(q)V} = \nu e^{(q)V} \]

\[ J_+^{(q)} e^{(q)V} = (q(q+1) - \nu(\nu+1))^{1/2} e^{(q)V+1} \]

where \( J_z^{(q)} \), \( J_x^{(q)} = \frac{1}{2}(J_+^{(q)} + J_-^{(q)}) \), and \( J_y = -\frac{i}{2}(J_+ - J_-) \) are the infinitesimal rotation operators of the group acting on rank q tensors. Explicitly, \( J_z^{(q)} \) is given by

\[ (B.2) \quad J_z^{(q)} = -i \sum_{n=1}^{q} \begin{pmatrix} 1 \otimes \cdots \otimes 1 \otimes 0 \end{pmatrix} \cdot e \otimes 1 \cdots \otimes 1, (n^{th} \text{ position}) \]

where \( e \) is the third rank completely antisymmetric tensor.

To complete the specification of the basis \( e^{(q)V} \), it is necessary only to specify \( e^{(q)o} \) as

\[ (B.3) \quad e^{(q)o} = i q \left[ \frac{(2q)!}{2^q q!} \right]^{1/2} \hat{\nu}^q \]

Then the remaining \( e^{(q)V}, \nu \neq 0 \) are obtained from (B.3) by employing the raising or lowering operators \( J_\pm^{(q)} \). Thus, for q=1, the spherical basis tensors are
The associated covariant basis $e^{(q)}_\nu$ is defined so that

$$e^{(q)}_\nu = (-1)^{q-\nu} e^{(q)-\nu} = (e^{(q)}_\nu)^*$$

The natural projection operator $E^{(q)}$ is then represented as

$$E^{(q)} = \sum_{\nu} e^{(q)}_\nu e^{(q)}_\nu = \sum_{\nu} (-1)^{q-\nu} e^{(q)}_\nu e^{(q)-\nu}$$

With this definition of the spherical basis tensors, the spherical components of any symmetric traceless tensor can be easily obtained. In particular, the tensor $[j_i^i j_f^f]^{(q)}$ has been considered in the main body of the thesis. The spherical components of this tensor are

$$[j_i^i j_f^f]^{(q)} \equiv e^{(q)}_\nu (\cdot)^q [j_i^i j_f^f]^{(q)}$$

$$= i^q \sum_{m_i m_f} (2q+1)^{1/2} (-1)^{j_i-m_i} j_i^q j_f^f ([j_i^i j_f^f]^{(q)})$$
The inverse of equation (B.7) is

\[(B.8) \quad |j_{i} m_{i} v_{i} < j_{f} m_{f} v_{f}| = \sum (-1)^{q}(2q+1)(-1)^{j_{i} - m_{i}} \\
\times (-1)^{q} (2q+1)(-1)^{-m_{i} v_{i} m_{f}} \]

which shows that the basis \([j_{i} v_{i} < j_{f} v_{f}] (q)\) is complete.

Furthermore, these operators possess the adjoint property

\[(B.9) \quad ([j_{i} v_{i} < j_{f} v_{f}] (q) )^{\dagger} = (-1)^{j_{i} - j_{f}} [j_{f} v_{f} < j_{i} v_{i}] (q)\]

and are orthogonal in the sense that

\[(B.10) \quad \text{tr}\{([j_{i} v_{i} < j_{f} v_{f}] (q) )^{\dagger} [j_{i'} v_{i'} < j_{f'} v_{f'}] (q') v'\} = \delta_{i j_{i}} \delta_{j_{f} j_{f'}} \delta_{v_{i} v_{i'}} \delta_{v_{f} v_{f'}} q_{q'} \delta_{v v'} \delta(j_{i} j_{f} q)\]

In particular, when restricted to being "diagonal in j" the operator identification

\[(B.11) \quad [j_{i} v_{i} < j_{f} v_{f}] (q) = \frac{\mathcal{Y}^{(q)}(j) \rho^{j}(v_{i} v_{f})}{(2j+1)^{1/2}}\]

is useful. Finally, the reduced matrix element
(B.12) \[ <j_f \nu_f|\sum_{j_f \nu_f} <j_i \nu_i|(q)\sqrt{\langle j_f \nu_f|j_i \nu_i\rangle (q)}> = iq(2q+1)^{1/2} \]

is established from equation (B.7).

Also using the spherical basis tensors \( e^{(q)} \nu \), it is seen that the components of the 3\( -j \) tensors \( V(q q_1 q_2) \) are exactly the 3\( j \) symbols

\[
V(q q_1 q_2) = e^{(q)} \nu_2 e^{(q_1)} \nu_1 e^{(q)} \nu_1 (q) v^{(q+q_1+q_2)}
\]

Indeed, the choice of phase for the \( e^{(q)} \nu \), as indicated by equation (B.3), is made precisely so that the components of the 3\( -j \) tensors are real. For other purposes, it is sometimes convenient to choose basis tensors which are real. That is, instead of (B.3), the basis tensors

(B.14) \[ z = -i e^{(1)} 0 \]

\[ [\hat{z}]^{(2)} = w^{(2)} (\frac{2}{3})^{1/2} e^{(2)} 0 \] etc.

could be alternately employed.